

# Integrated Science Assessment for Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter- Ecological Criteria



# **Integrated Science Assessment for Oxides of Nitrogen, Oxides of Sulfur, and Particulate Matter— Ecological Criteria**

**(Final)**

Center for Public Health and Environmental Assessment  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, NC

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# CONTENTS

<b>AUTHORS, CONTRIBUTORS, AND REVIEWERS</b>	<b>xxxii</b>
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<b>CLEAN AIR SCIENTIFIC ADVISORY COMMITTEE</b>	<b>xxxvii</b>
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Chair of the Charter Clean Air Scientific Advisory Committee	xxxvii
Charter Clean Air Scientific Advisory Committee Members	xxxvii
Chair, Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter—Ecological Criteria Review Panel	xxxvii
Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter—Ecological Criteria Review Panel Members	xxxvii

<b>ACRONYMS AND ABBREVIATIONS</b>	<b>xxxix</b>
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<b>PREFACE</b>	<b>xlix</b>
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Legislative Requirements for the Review of the National Ambient Air Quality Standards	xlix
Overview and History of the Reviews of the Secondary National Ambient Air Quality Standards for Nitrogen Dioxide, Sulfur Dioxide, and Particulate Matter	i
Nitrogen Dioxide Secondary National Ambient Air Quality Standards	i
Sulfur Dioxide Secondary National Ambient Air Quality Standards	li
Particulate Matter Secondary National Ambient Air Quality Standards	lv
Combined Review of the Oxides of Nitrogen and Oxides of Sulfur National Ambient Air Quality Standards	lviii

<b>EXECUTIVE SUMMARY</b>	<b>1</b>
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ES.1	Purpose and Scope of the Integrated Science Assessment	1
	Figure ES-1 Roadmap of the Integrated Science Assessment (ISA) linking atmospheric concentrations and deposition, soil and aquatic biogeochemistry, and biological effects.	4
ES.2	Emissions, Ambient Air Concentrations, and Deposition	4
	Figure ES-2 Wet plus dry deposition of (A) oxidized nitrogen, (B) reduced nitrogen, (C) total nitrogen, and (D) total sulfur over the 3-year periods 2000–2002 and 2016–2018.	6
ES.3	Ecological Effects	7
	Table ES-1 Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO <sub>x</sub> /SO <sub>x</sub> Integrated Science Assessment (ISA) or the 2009 ISA for Particulate Matter (PM), for other effects of PM, and the current draft ISA.	8
	Figure ES-3 Causal relationships between the criteria pollutants and ecological effects.	12
ES.4	Direct Phytotoxic Effects of Gas-Phase Oxides of Nitrogen (NO <sub>y</sub> ) and Oxides of Sulfur (SO <sub>x</sub> )	13
ES.5	Ecological Effects of Nitrogen and Sulfur Deposition	13
	ES.5.1 Acidification of Terrestrial and Freshwater Ecosystems	13
	ES.5.2 Nitrogen Enrichment/Eutrophication of Terrestrial, Wetland, and Aquatic Ecosystems	15
	Figure ES-4 Summary of critical loads for nitrogen in the U.S. for shrubs and herbaceous plants (yellow), trees (blue), lichens (green), and mycorrhizae (gray). Values expressed by major U.S. ecoregions.	17
	ES.5.3 Sulfur (S) Enrichment of Wetland and Freshwater Ecosystems	19

ES.5.4	Ecological Effects of Particulate Matter Other Than Those Associated with Nitrogen and Sulfur Deposition	20
ES.6	Ecosystem Services	20
ES.7	Integrating across Ecosystems	21
	Figure ES-5 Causal relationships between the criteria pollutants and ecological effects organized under ecosystem type.	22

## **INTEGRATED SYNTHESIS** \_\_\_\_\_ **1**

IS.1	Introduction to This Integrated Science Assessment (ISA)	1
	IS.1.1 Purpose	1
	IS.1.2 Process and Development	4
	Figure IS-1 Workflow for collecting relevant literature for the 2017 Integrated Science Assessment for Oxides of Nitrogen, Oxides of Sulfur, and Particulate Matter—Ecological Criteria.	5
IS.2	Connections, Concepts, and Changes	7
	IS.2.1 Connections	7
	Figure IS-2 Overview of atmospheric chemistry, deposition, and ecological effects of emissions of oxides of nitrogen, oxides of sulfur, and reduced nitrogen.	8
	IS.2.2 Concepts	8
	Figure IS-3 An example of the matrix of information considered in defining and calculating critical loads (see discussion in text). Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits could be used.	13
	IS.2.3 Changes: New Evidence and Causal Determinations	20
	Table IS-1 Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO <sub>x</sub> /SO <sub>x</sub> Integrated Science Assessment (ISA) or the 2009 Particulate Matter (PM) ISA, for other effects of PM, and the current draft ISA.	22
	Figure IS-4 Causal relationships between the criteria pollutants and ecological effects.	25
IS.3	Emissions and Atmospheric Chemistry	27
	IS.3.1 Sources and Atmospheric Transformations	28
	IS.3.2 Measurement and Modeling Techniques	29
	IS.3.3 Spatial and Temporal Variability in Deposition	29
	Figure IS-5 Wet plus dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	31
	Figure IS-6 Wet plus dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	32
	Figure IS-7 Wet plus dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	33
	Figure IS-8 Wet plus dry deposition of total sulfur over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	35
	Figure IS-9 Total acidifying deposition of total oxidized nitrogen, reduced nitrogen, and oxidized sulfur expressed as H <sup>+</sup> equivalents per hectare per year over the contiguous U.S. 2016–2018.	36
IS.4	Gas-Phase Direct Phytotoxic Effects	36
	IS.4.1 Sulfur Dioxide	37
	IS.4.2 Nitrogen Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate	38
	IS.4.3 Nitric Acid	38
IS.5	Terrestrial Ecosystem Nitrogen Enrichment and Acidification	39
	IS.5.1 Soil Biogeochemistry	40

	Table IS-2	Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.	41
IS.5.2		Biological Effects of Terrestrial Nitrogen Enrichment	46
	Figure IS-10	Summary of critical loads for nitrogen in the U.S. for shrubs and herbaceous plants (yellow), trees (blue), lichens (green), and mycorrhizae (gray).	56
IS.5.3		Biological Effects of Acidification	57
	Figure IS-11	Forest ecosystem critical loads for soil acidity related to base cation soil indicators.	60
IS.6		Freshwater Ecosystem Nitrogen Enrichment and Acidification	61
IS.6.1		Freshwater Biogeochemistry	62
	Table IS-3	Summary of key aquatic geochemical processes and indicators associated with eutrophication and acidification.	64
IS.6.2		Biological Effects of Freshwater Nitrogen Enrichment	69
IS.6.3		Biological Effects of Freshwater Acidification	73
	Figure IS-12	Surface water critical loads for acidity in the U.S. 10th percentile aggregation for 36-km <sup>2</sup> grids with sulfur (S) and nitrogen (N).	77
IS.7		Estuarine and Near-Coastal Ecosystem Nitrogen Enrichment	79
IS.7.1		Estuary and Near-Coastal Biogeochemistry	79
IS.7.2		Biological Effects of Nitrogen Enrichment	82
IS.7.3		National-Scale Sensitivity and Critical Loads	86
IS.8		Wetland Ecosystem Nitrogen Enrichment and Acidification	88
IS.8.1		Wetland Biogeochemistry	88
IS.8.2		Biological Effects of Wetland Nitrogen Enrichment/Eutrophication	89
IS.9		Freshwater and Wetland Ecosystem Sulfur Enrichment	93
IS.9.1		Biogeochemistry	93
IS.9.2		Biological Effects of Sulfur Enrichment	94
IS.9.3		National-Scale Sensitivity and Critical Loads	97
IS.10		Ecological Effects of Particulate Matter Other Than Nitrogen (N) and Sulfur (S) Deposition	98
IS.11		Recovery of Ecosystems from Nitrogen (N) and Sulfur (S) Deposition in the U.S.	100
	IS.11.1	Overarching Concepts of Ecological Recovery from Acidification	100
	IS.11.2	Acidification Recovery in the U.S.	101
	IS.11.3	Nitrogen (N) Driven Nutrient Enrichment Recovery in the U.S.	103
IS.12		Climate Modification of Ecosystem Response to Nitrogen (N) and Sulfur (S) Deposition	103
IS.13		Ecosystem Services	104
IS.14		Key Scientific Uncertainties	106
	IS.14.1	Atmospheric Science	107
	IS.14.2	Ecological Effects	110
	IS.14.3	Aquatic Acidification Index	116
<b>APPENDIX 1 QUALITY ASSURANCE AND INTRODUCTION TO APPENDICES</b>			<b>1-1</b>
<b>APPENDIX 2 SOURCE TO DEPOSITION</b>			<b>2-1</b>
2.1		Introduction	2-1
2.2		Sources of Nitrogen and Sulfur Compounds and Particulate Matter to the Atmosphere	2-5
	2.2.1	National Emissions by Source	2-6
		Table 2-1 Emissions of NO <sub>x</sub> (nitric oxide + nitrogen dioxide), sulfur dioxide, and ammonia by source category for 2017 (Teragrams N, S/yr).	2-7
	2.2.2	Methods of Estimating Emissions	2-8
		Figure 2-1 Modeling system used to compute 2014 Fertilizer Application Emissions.	2-11
		Figure 2-2 Process to produce specific location and practice specific daily emission factors for livestock waste.	2-13

2.2.3	Evaluation and Uncertainty	2-13
2.3	Atmospheric Chemistry of Nitrogen and Sulfur Species and Particulate Matter (PM)	2-16
2.3.1	Nitrogen Oxides	2-16
	Figure 2-3 Schematic diagram showing pathways for reactive nitrogen species in ambient air.	2-18
	Table 2-2 Henry's law coefficients for selected reactive nitrogen species at 25°C in water.	2-19
2.3.2	Sulfur Oxides	2-21
	Figure 2-4 Rate of conversion of sulfur (IV) to sulfur (VI) by different oxidation paths as a function of pH.	2-22
2.3.3	Acid Neutralization by Ammonia	2-23
2.3.4	Organic Nitrogen and Sulfur	2-25
2.3.5	Organic Acids	2-26
2.3.6	Particulate Matter (PM)	2-27
	Figure 2-5 Contributions of organic carbon (OC), elemental carbon (EC), sulfate, nitrate, sea salt, and crustal components to PM <sub>2.5</sub> at selected sites (A) 2003–2005 (B) 2013–2015.	2-28
2.4	Concentration and Deposition Measurements	2-29
2.4.1	Monitoring Networks	2-29
	Table 2-3 Summary of monitoring networks used by Schwede and Lear (2014a).	2-31
2.4.2	NO <sub>2</sub> , NO <sub>x</sub> , and NO <sub>y</sub>	2-33
2.4.3	Ammonia	2-35
2.4.4	Sulfur Dioxide	2-38
	Table 2-4 Sources of uncertainty for individual Ozone Monitoring Instrument measurements in the study of Nowlan et al. (2014).	2-39
2.4.5	Filter-Based Concentration Measurements	2-39
	Figure 2-6 Clean Air Status and Trends Network filter pack.	2-40
	Figure 2-7 Comparison between weekly average measurements of sulfur dioxide using the Clean Air Status and Trends Network filter pack and the trace ultraviolet pulsed fluorescence monitor in 2014.	2-42
2.4.6	Deposition Measurements	2-43
2.5	Modeling Chemistry, Transport, and Deposition	2-46
2.5.1	Advances in Chemistry-Transport Model (CTM) Modeling	2-46
2.5.2	Modeling Deposition	2-48
	Figure 2-8 Schematic diagram showing mechanisms for transferring pollutants from the atmosphere to the surface.	2-49
	Table 2-5 Average dry deposition velocities (cm/s) for several gases over land surfaces.	2-50
	Table 2-6 Deposition velocity (cm/s) for sulfur dioxide averaged over different land use types for summer and winter.	2-50
	Figure 2-9 Modeled and measured deposition velocities over grass (left figure) and coniferous forest canopies (right figure) for particles of density 1 gm/cm <sup>3</sup> depositing under similar friction velocity ( $u^*$ ) ( $35 < u^* < 56$ cm/s).	2-52
	Figure 2-10 Schematic of the interactions involved in the exchange of nitrogen oxides between the atmosphere and the forest canopy as identified by Min et al. (2014).	2-55
	Figure 2-11 Scatterplots showing transference ratios for oxidized nitrogen and sulfur oxides comparing the Community Multiscale Air Quality model to the Comprehensive Air Quality Model with Extensions in (a) and (c) and comparing 2005 to 2014 in (b) and (d).	2-60
2.5.3	Model Evaluation and Uncertainty	2-61

	Table 2-7	Reported comparisons of chemical transport models and observations of nitrogen and sulfur wet deposition _____	2-62
2.6	Geographic Distribution of Concentration and Deposition _____		2-62
2.6.1	pH and H <sup>+</sup> Equivalents _____		2-65
	Figure 2-12	(Left) pH of rainwater, 1989–1991; (Right) pH of rainwater, 2016–2018. _____	2-66
	Figure 2-13	Difference in wet deposition of nitrate, ammonium, and sulfate expressed as hydrogen ion equivalents (eq/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. _____	2-67
2.6.2	Total Nitrogen _____		2-68
	Figure 2-14	Total (wet + dry) deposition of nitrogen (kg N/ha/yr) over the contiguous U.S. 2016–2018. _____	2-69
	Figure 2-15	(A) Percentage of total nitrogen deposition as reduced inorganic nitrogen over the contiguous U.S. 2016–2018. (B) Percentage of total nitrogen deposition as oxidized nitrogen over the contiguous U.S. 2016–2018. _____	2-70
	Figure 2-16	Trends in U.S. total deposition flux of total nitrogen, oxidized nitrogen, reduced nitrogen, and major nitrogen species 2000–2017. _____	2-71
	Figure 2-17	Three-year average percentage of total nitrogen deposition by species (i.e., those species that are not measured in the networks) simulated by the Community Multiscale Air Quality modeling system for 2016–2018. _____	2-72
	Figure 2-18	Wet deposition of ammonium + nitrate (kg N/ha/yr) over the contiguous U.S. in two, 3-year periods, 2016 to 2018 and 1989 to 1991. Also shown are active National Trends Network sites in either period. _____	2-73
2.6.3	Oxidized Nitrogen _____		2-74
	Figure 2-19	Geographic distribution of annual U.S. NO <sub>x</sub> emissions in 2017. _____	2-75
	Figure 2-20	Distribution of annual average total oxidized nitrogen species concentrations for 2011 simulated by Community Multiscale Air Quality modeling system. _____	2-76
	Figure 2-21	Seasonal average surface nitrogen dioxide mixing ratios in parts per billion for winter (upper panel) and summer (lower panel) derived by the Ozone Monitoring Instrument/GEOS-Chem model for 2009–2011. The Ozone Monitoring Instrument has an overpass at approximately 1:30 p.m. local standard time. _____	2-77
	Figure 2-22	Three-year average (2016–2018) surface concentrations of nitric acid based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots). _____	2-79
	Figure 2-23	Three-year average (2016–2018) surface concentrations of particulate nitrate based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots). _____	2-80
	Figure 2-24	Trends in particulate nitrate concentration 1990–2017: (A) average eastern U.S. concentration based on 34 sites; (B) average western concentration based 16 sites. _____	2-81
	Figure 2-25	Total oxidized nitrogen deposition over the contiguous U.S. 2016–2018. _____	2-82
	Figure 2-26	(Left) nitrate wet deposition, 1989–1991; (Right) nitrate wet deposition, 2016–2018. _____	2-83
	Figure 2-27	Difference in wet deposition of nitrate (kg N/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. The range of positive values is smaller than that for negative values. _____	2-84
	Figure 2-28	Trends in oxidized nitrogen emissions and deposition 2000–2017: (A) total national emissions; (B) national average total deposition flux. _____	2-85
2.6.4	Reduced Nitrogen _____		2-85

	Figure 2-29	Geographic distribution of annual U.S. ammonia (NH <sub>3</sub> ) emissions in 2017. _____	2-86
	Figure 2-30	Average (2017) surface concentration of ammonia obtained by the Ambient Ammonia Monitoring Network at select Clean Air Status and Trends Network sites. Concentrations of ammonia (µg/m <sup>3</sup> ) can be converted to mixing ratios (parts per billion) to rough approximation at normal temperature and pressure by multiplying by 1.4. _____	2-87
	Figure 2-31	Three-year average (2016–2018) surface concentrations of particulate ammonium (µg/m <sup>3</sup> ) based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots). _____	2-88
	Figure 2-32	Total reduced inorganic nitrogen deposition over the contiguous U.S. 2016–2018. _____	2-89
	Figure 2-33	(Left) ammonium wet deposition, 1989–1991; (Right) ammonium wet deposition, 2016–2018. _____	2-90
	Figure 2-34	Difference in wet deposition of ammonium (kg N/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. _____	2-91
	Figure 2-35	Trends in reduced nitrogen emissions and deposition 2000–2017: (A) total national NH <sub>3</sub> emissions; (B) national average reduced nitrogen deposition flux. _____	2-92
2.6.5	Sulfur Oxides	_____	2-92
	Figure 2-36	Geographic distribution of annual U.S. sulfur dioxide (SO <sub>2</sub> ) emissions by county from the 2017 National Emissions Inventory. _____	2-93
	Figure 2-37	Trends in total national sulfur dioxide emissions. _____	2-93
	Figure 2-38	Three-year average (2016–2018) surface concentrations of sulfur dioxide obtained by fusion of monitoring data obtained at Clean Air Status and Trends Network sites (black dots) and Community Multiscale Air Quality model system results. Concentrations (µg/m <sup>3</sup> ) can be converted to mixing ratios (parts per billion) at normal temperature and pressure) to rough approximation by multiplying by 0.37. _____	2-95
	Figure 2-39	Three-year average (2016–2018) surface concentrations of particulate sulfate based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots). _____	2-96
	Figure 2-40	Trends in oxides of sulfur oxides concentrations 1990–2017: (A) average eastern U.S. SO <sub>2</sub> concentration based on 34 sites; (B) average western U.S. SO <sub>2</sub> concentration based on 16 sites; (C) average eastern U.S. sulfate concentration based on 34 sites; (D) average western U.S. sulfate concentration based on 16 sites. _____	2-97
	Figure 2-41	Total deposition of sulfur (kg S/ha/yr) over the contiguous U.S. 2016–2018. _____	2-98
	Figure 2-42	Percentage of deposition of total sulfur as dry deposition over the contiguous U.S. 2016–2018. _____	2-99
	Figure 2-43	(Left) sulfate wet deposition, 1989–1991; (Right) sulfate wet deposition, 2016–2018. _____	2-100
	Figure 2-44	Difference in wet deposition of sulfate (kg S/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. The range of positive values is much smaller than for negative values. _____	2-100
	Figure 2-45	Trends in average sulfur deposition flux for 34 monitoring sites in the eastern U.S. 1989–2017. _____	2-101
2.6.6	Particulate Matter (PM)	_____	2-101
	Figure 2-46	Three-year average concentrations of particulate matter smaller than 2.5 µm diameter (PM <sub>2.5</sub> ) 2013–2015. _____	2-102

	Figure 2-47	National monthly average concentrations of particulate matter smaller than 2.5 $\mu\text{m}$ diameter ( $\text{PM}_{2.5}$ ; top) and sulfate in $\text{PM}_{2.5}$ (bottom) from 2000–2016 (concentrations in $\mu\text{g}/\text{m}^3$ ). _____	2-103
	Figure 2-48	98th percentile concentrations for $\text{PM}_{10-2.5}$ between 2013–2015. ____	2-104
2.6.7	Distributions of Dry Deposition of Nitrogen Dioxide and Sulfur Dioxide Derived Using Satellite-Based Measurements and Chemistry Transport Models _____		2-104
	Figure 2-49	Top panel: modeled deposition velocities for nitrogen dioxide and sulfur dioxide for 2005 to 2007; middle panel satellite-model estimates of annual mean dry deposition fluxes of nitrogen dioxide and sulfur dioxide; bottom panel: uncertainties in estimates. _____	2-106
2.6.8	Background Concentrations and Deposition _____		2-107
	Figure 2-50	Contributions to oxidized and reduced nitrogen deposition from U.S.: anthropogenic (top), foreign anthropogenic (middle), and natural sources (bottom). _____	2-108
2.7	Supplemental Material on Changes in Deposition since 2000 _____		2-112
	Figure 2-51	Wet plus dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-114
	Figure 2-52	Wet deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-115
	Figure 2-53	Dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-116
	Figure 2-54	Percent of total nitrogen as dry deposition over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-117
	Figure 2-55	Wet plus dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-118
	Figure 2-56	Percent of total nitrogen as oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-119
	Figure 2-57	Dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-120
	Figure 2-58	Percent of total nitrogen dry deposited as oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-121
	Figure 2-59	Combined dry deposition of nitric acid and particulate nitrate over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-122
	Figure 2-60	Dry deposition of nitric acid over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-123
	Figure 2-61	Dry deposition of particulate nitrate over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-124
	Figure 2-62	Dry deposition of modeled (unmeasured) nitrogen species over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-125
	Figure 2-63	Percent of total nitrogen as modeled (unmeasured) species over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-126
	Figure 2-64	Wet plus dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-127
	Figure 2-65	Percent of total nitrogen deposition by reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-128
	Figure 2-66	Dry deposition of ammonia over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-129
	Figure 2-67	Dry deposition of particulate ammonium over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-130
	Figure 2-68	Dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-131
	Figure 2-69	Percent of total nitrogen deposition by dry reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018. _____	2-132

Figure 2-70	Wet plus dry deposition of total sulfur over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-133
Figure 2-71	Wet deposition of total sulfur over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-134
Figure 2-72	Dry deposition of total sulfur over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-135
Figure 2-73	Percent of total sulfur deposition by dry deposition over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-136
Figure 2-74	Dry deposition of sulfur dioxide over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-137
Figure 2-75	Dry deposition of particulate sulfate over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.	2-138

### **APPENDIX 3 DIRECT PHYTOTOXIC EFFECTS OF GASEOUS OXIDIZED NITROGEN AND SULFUR ON VEGETATION** **3-1**

3.1	Introduction	3-1	
	Figure 3-1	The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial) leaf surface. Carbon dioxide, oxides of sulfur, oxides of nitrogen, and ozone gases generally enter by diffusion through the guard cells (or stomata) on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).	3-3
3.2	Direct Phytotoxic Effects of Sulfur Dioxide on Vegetation	3-3	
	Figure 3-2	Map of maximum 3-hour daily max average sulfur dioxide concentration reported at Air Quality System monitoring sites for 2016.	3-5
3.3	Direct Phytotoxic Effects of Nitric Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate	3-7	
	Figure 3-3	Map of U.S. annual average nitrogen dioxide concentrations for 2013.	3-8
3.4	Direct Phytotoxic Effects of Nitric Acid	3-13	
3.5	Direct Phytotoxic Effects of Reduced Nitrogen Gases	3-15	
3.6	Summary	3-16	
	3.6.1	Sulfur Dioxide	3-16
	3.6.2	Nitrogen Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate	3-17
	3.6.3	Nitric Acid	3-17

### **APPENDIX 4 SOIL BIOGEOCHEMISTRY** **4-1**

4.1	Introduction	4-1	
4.2	Nitrogen and Sulfur Sources to Soil	4-2	
	Figure 4-1	Dominant sources of nitrogen across the U.S. at 8-digit hydrologic unit codes.	4-3
	Figure 4-2	Percentage of nitrogen input from nitrogen deposition at 8-digit hydrologic unit codes.	4-3
4.3	Soil Pools and Processes	4-4	
	Table 4-1	Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.	4-6
4.3.1	Nitrogen Pathways and Pools	4-6	
	Table 4-2	Pathways and pools.	4-8
4.3.2	Nitrogen Accumulation, Saturation, and Leaching	4-11	
	Figure 4-3	A conceptual framework for the responses of the ecosystem nitrogen (N) cycle to nitrogen (N) addition.	4-12
	Figure 4-4	A hypothetical model to account for the effects of nitrogen supply on plant nitrogen uptake and belowground carbon	

	allocation, microbial production of inorganic nitrogen, and nitrogen leaching. _____	4-15
	Table 4-3 Nitrogen accumulation, saturation, and leaching. _____	4-16
4.3.3	Sulfate Accumulation, Adsorption, and Leaching _____	4-22
	Table 4-4 Sulfate adsorption, accumulation, and leaching. _____	4-24
4.3.4	Base Cation Leaching and Exchange _____	4-27
	Table 4-5 Base cation leaching and exchange. _____	4-30
4.3.5	Aluminum Mobilization _____	4-35
	Table 4-6 Aluminum mobilization. _____	4-37
4.3.6	Nitrification and Denitrification _____	4-39
	Table 4-7 Nitrification and denitrification. _____	4-41
	Figure 4-5 Effects of nitrogen addition on biogenic nitrous oxide emission. _____	4-46
	Figure 4-6 The weighted response ratio for the responses to nitrogen addition for fluxes and pools related to the ecosystem nitrogen cycle in agricultural (open bars) and nonagricultural (closed bars) ecosystems. _____	4-47
4.3.7	Decomposition _____	4-47
	Table 4-8 Decomposition. _____	4-49
4.3.8	Nitrogen Mineralization _____	4-56
	Table 4-9 Nitrogen mineralization. _____	4-58
	Figure 4-7 Effects of nitrogen inputs on soil carbon, carbon:nitrogen ratio, and minimum nitrogen in forest floors (panels A–C) and mineral soils (panels D–F). _____	4-60
4.3.9	Dissolved Organic Carbon Leaching _____	4-61
	Table 4-10 Terrestrial dissolved organic carbon (DOC) leaching. _____	4-62
	Figure 4-8 Conceptual diagram of positive (solid arrows) and negative (dashed arrows) fluxes in nitrogen pools (squares) and carbon pools (ovals) and the biological processes (no border) that are affected by experimental nitrogen deposition. _____	4-67
4.3.10	Belowground Carbon Pools _____	4-67
	Figure 4-9 Estimation of the changes in carbon budget of terrestrial ecosystem under nitrogen addition. _____	4-69
	Table 4-11 Belowground carbon pools. _____	4-70
4.3.11	New Biogeochemical Indicators _____	4-72
	Table 4-12 New biogeochemistry indicators. _____	4-73
4.3.12	Differential Effects of Reduced and Oxidized Nitrogen _____	4-74
	Table 4-13 The effects of different forms of inorganic nitrogen on biogeochemical processes and indicators according to meta-analyses. See Table 6-1 for the effects of different forms of inorganic nitrogen on biological endpoints. _____	4-75
4.4	Soil Monitoring and Databases _____	4-76
	Table 4-14 Biogeochemistry monitoring and databases. _____	4-77
4.5	Models _____	4-80
4.5.1	Updates to Key Previously Identified Models _____	4-81
	Table 4-15 Photosynthesis and Evapotranspiration—Biogeochemical (PnET-BGC) and DayCent. _____	4-87
4.5.2	New Models (Published since 2008) _____	4-89
4.5.3	Comparative Analyses _____	4-91
	Table 4-16 Overview of properties of four dynamic soil chemistry models as characterized in Bonten et al. (2015). _____	4-93
	Table 4-17 Model comparison. _____	4-95
4.6	National-Scale Sensitivity _____	4-98
4.6.1	Acidification Recovery _____	4-98
	Table 4-18 Recovery. _____	4-100
4.6.2	Critical Loads _____	4-103

	Figure 4-10	Forest ecosystem critical loads for soil acidity related to base cation soil indicators. _____	4-104
	Figure 4-11	Map of critical loads for nitrate leaching by ecoregion in the U.S. _____	4-106
4.7	Modification of Terrestrial Soil Response to Nitrogen (N) _____		4-106
	4.7.1	Disturbance and Stand Age Effects on Nitrogen Retention _____	4-107
	4.7.2	Nitrogen and Phosphorus Interactions _____	4-107
	4.7.3	Climate Modification of Acidification Effects on Soil _____	4-108
	4.7.4	Climate Modification of Nitrogen-Driven Eutrophication in Soil _____	4-109
	Figure 4-12	The potential mechanisms that regulate the responses of carbon dioxide (CO <sub>2</sub> ), methane (CH <sub>4</sub> ), and nitrous oxide (N <sub>2</sub> O) production and consumption to elevated nitrogen (N). _____	4-112
4.8	Summary _____		4-113
	4.8.1	Sources _____	4-113
	4.8.2	Soil Processes and Indicators _____	4-113
	Table 4-19	Summary of key soil geochemical processes and indicators associated with eutrophication and acidification. _____	4-116
	4.8.3	Monitoring _____	4-119
	4.8.4	Models _____	4-120
	4.8.5	National-Scale Sensitivity _____	4-122
	4.8.6	Climate Modification of Soil Response to Nitrogen Addition _____	4-123
<b>APPENDIX 5 BIOLOGICAL EFFECTS OF TERRESTRIAL ACIDIFICATION _____</b>			<b>5-1</b>
5.1	Introduction _____		5-1
	Figure 5-1	Diagram based on Fenn et al. (2006) showing indicators of forest physiological function, growth, and structure that are linked to biogeochemical cycles through processes that control rates of calcium supply. Calcium affects plant physiological processes that influence growth rates and the capacity of plants to resist environmental stresses, such as extremes of temperature, drought, insects, and diseases. Therefore, acidifying deposition, which can deplete soil calcium or interfere with calcium uptake through mobilization of soil aluminum, can affect forest health. _____	5-3
	Table 5-1	Relationships between soil chemistry indicators and biological endpoints that have been evaluated in the literature since the 2008 Integrated Science Assessment. _____	5-4
5.2	Effects on Terrestrial Organisms and Ecosystems _____		5-6
	5.2.1	Trees and Forests _____	5-6
	Table 5-2	Summary of calcium addition studies in North America. _____	5-9
	Figure 5-2	Relationship between the proportion of seedlings that were sugar maple and soil base saturation in the upper B-horizon. _____	5-13
	5.2.2	Forest Understory and Grassland Species _____	5-20
	5.2.3	Lichens _____	5-21
	5.2.4	Soil Biota _____	5-22
	5.2.5	Fauna _____	5-24
5.3	Characteristics, Distribution, and Extent of Sensitive Ecosystems _____		5-26
5.4	Application of Terrestrial Acidification Models _____		5-27
5.5	Levels of Deposition at Which Effects Are Manifested _____		5-27
	5.5.1	Impacts of Elevated Nitrogen and Sulfur Deposition _____	5-28
	Table 5-3	Impacts of acidifying nitrogen and sulfur deposition. _____	5-31
	5.5.2	Impacts of Ambient Deposition _____	5-36
	Table 5-4	Results of Spearman's rank correlation analysis comparing growth versus critical load exceedance by species for the forested plots in the northeastern U.S. [from Duarte et al. (2013)]. Modeled sulfur and nitrogen deposition on the plots	

		ranged from 242 to 1,154 eq/ha/yr and 256 to 920 eq/ha/yr, respectively. Correlations shown here are significant at $\alpha = 0.05$ .	5-37
	Table 5-5	Results of Spearman's rank correlation analyses comparing tree vigor, crown density and dieback, and canopy transparency versus critical load exceedance by species for the forested plots in the northeastern U.S. [from Duarte et al. (2013)]. Modeled sulfur and nitrogen deposition on the plots ranged from 242 to 1,154 eq/ha/yr and 256 to 920 eq/ha/yr, respectively. Correlations shown here are significant at $\alpha = 0.05$ .	5-38
	5.5.3	Critical Loads and Exceedances	5-40
5.6		Climate Modification of Ecosystem Response	5-46
5.7		Summary	5-48
	5.7.1	Physiology and Growth	5-48
	5.7.2	Biodiversity	5-50
	5.7.3	National-Scale Sensitivity and Critical Loads	5-50
	Table 5-6	Mode of action for acidifying nitrogen and sulfur deposition.	5-52

<b>APPENDIX 6 TERRESTRIAL ECOSYSTEMS: NITROGEN ENRICHMENT EFFECTS ON ECOLOGICAL PROCESSES</b>		<b>6-1</b>	
6.1	Introduction	6-1	
6.2	Linking Nitrogen Deposition to Changes in Physiology, Growth, and Productivity in Terrestrial Ecosystems	6-2	
	6.2.1	Introduction	6-2
	6.2.2	Mechanisms Operating across Terrestrial Ecosystems	6-3
	Figure 6-1	Effects of nitrogen additions on plant growth and net primary productivity.	6-8
	Figure 6-2	Effects of added nitrogen on ecosystem carbon pools and fluxes.	6-9
	Table 6-1	The effects of different forms of inorganic nitrogen on biological endpoints according to meta-analyses. See Table 4-13 for the effects of different forms of inorganic nitrogen on biogeochemical processes and indicators.	6-14
	6.2.3	Forests	6-17
	Table 6-2	Growth, productivity, and carbon cycle responses of ectomycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.	6-21
	Table 6-3	Growth, productivity, and carbon cycle responses of arbuscular mycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.	6-31
	Table 6-4	Abundance and carbon cycle responses of forest soil microorganisms and soil invertebrates to nitrogen added in experimental treatments.	6-33
	Table 6-5	Growth and physiology responses of forest epiphytic lichens to nitrogen added via atmospheric deposition or experimental treatments.	6-41
	Figure 6-3	Studies reporting the response of forest (A) aboveground biomass carbon sequestration and (B) ecosystem carbon sequestration to nitrogen deposition or long-term nitrogen additions.	6-47
	6.2.4	Arctic and Alpine Tundra and Grasslands	6-48
	Table 6-6	Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.	6-50
	Table 6-7	Alpine and Arctic tundra lichen growth and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.	6-68

	Table 6-8	Growth and biodiversity responses of ericoid mycorrhizal fungi to nitrogen added in experimental treatments. _____	6-72
	Table 6-9	Alpine and Arctic tundra microbial biomass responses to experimental nitrogen additions. _____	6-73
6.2.5	Grasslands	_____	6-75
	Table 6-10	Grassland microbial biomass responses to experimental nitrogen additions. _____	6-81
6.2.6	Arid and Semiarid Ecosystems	_____	6-83
	Table 6-11	Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments. _____	6-86
	Table 6-12	Arid and semiarid microbial biomass responses to experimental nitrogen additions. _____	6-96
6.3	Relationships between Nitrogen Deposition and Terrestrial Species Composition, Species Richness, and Biodiversity	_____	6-98
6.3.1	Introduction	_____	6-98
6.3.2	Mechanisms Operating across Terrestrial Ecosystems	_____	6-99
6.3.3	Forests	_____	6-103
	Table 6-13	Forest plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments. _____	6-106
	Table 6-14	Forest microbial biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments. _____	6-113
	Table 6-15	Ectomycorrhizal biodiversity responses to nitrogen added via atmospheric deposition or experimental N additions. _____	6-117
	Table 6-16	Arbuscular mycorrhizal responses to nitrogen added via atmospheric deposition or experimental treatments. _____	6-122
	Table 6-17	Arthropod and other invertebrate responses to experimental nitrogen additions. _____	6-126
6.3.4	Alpine and Arctic Tundra	_____	6-130
	Table 6-18	Alpine and Arctic tundra plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments. ____	6-132
	Table 6-19	Alpine and Arctic tundra microbial diversity responses to nitrogen added via experimental treatments. _____	6-137
6.3.5	Grasslands	_____	6-139
	Table 6-20	Grassland microbial diversity responses to nitrogen added via experimental treatments. _____	6-146
6.3.6	Arid and Semiarid Ecosystems	_____	6-148
	Table 6-21	Arid and semiarid ecosystem plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments. _____	6-150
	Table 6-22	Arid and semiarid ecosystem microbial diversity responses to nitrogen added via experimental treatments. _____	6-157
6.3.7	Lichens	_____	6-158
	Table 6-23	Lichen biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments. _____	6-159
6.3.8	Most Sensitive Ecosystems	_____	6-162
6.4	Climate Modification of Ecosystem Nitrogen Response	_____	6-163
6.5	Critical Loads	_____	6-165
	Figure 6-4	Comparison of European and U.S. empirical critical loads for nitrogen from Pardo et al. (2011a). _____	6-168
6.5.1	Mycorrhizal Fungi	_____	6-168
	Figure 6-5	Map of critical loads for mycorrhizal fungi by ecoregion in the U.S. _____	6-170
	Table 6-24	Mycorrhizal critical loads. _____	6-171
6.5.2	Lichens and Bryophytes	_____	6-171
	Figure 6-6	Map of critical loads for lichens by ecoregion in the U.S. _____	6-173

	Table 6-25	Lichen critical loads. _____	6-174
6.5.3	Herbaceous and Shrub Species _____		6-176
	Table 6-26	Herbaceous and shrub critical loads. _____	6-178
	Figure 6-7	Map of critical loads for herbaceous plants and shrubs by ecoregion in the U.S. _____	6-181
	Figure 6-8	Nitrogen deposition (gray scale) and critical loads for nitrogen deposition based on total graminoid plus forb species richness (colored symbols). _____	6-182
6.5.4	Trees _____		6-184
	Table 6-27	Tree critical loads. _____	6-184
	Figure 6-9	Map of critical loads for forest ecosystems by ecoregion in the U.S. _____	6-185
6.5.5	Critical Loads Exceedance Studies _____		6-186
6.6	Summary _____		6-188
6.6.1	Physiology, Growth, and Productivity Summary _____		6-188
6.6.2	Biodiversity Summary _____		6-190
6.6.3	Critical Loads Summary _____		6-193
	Table 6-28	Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information. _____	6-194

## **APPENDIX 7 AQUATIC BIOGEOCHEMISTRY \_\_\_\_\_ 7-1**

7.1	Biogeochemistry of Nitrogen and Sulfur in Freshwater Systems _____		7-1
	Table 7-1	Summary of key freshwater indicators of eutrophication and acidification. _____	7-4
7.1.1	Nitrogen and Sulfur Sources _____		7-4
	Table 7-2	Summary of recent studies quantifying nitrogen deposition contribution to total nitrogen loading in freshwater systems. _____	7-7
7.1.2	Ecosystem Processes, Effects, and Indicators _____		7-10
	Figure 7-1	Nitrogen cycle in freshwater ecosystem. _____	7-11
	Figure 7-2	Quarterly measured concentrations of a range of water chemistry variables at Blue Lough from 1990 to 2014. _____	7-16
	Figure 7-3	Dissolved organic carbon (DOC) concentrations from 1993 to 2013 for Bracey Pond (a), Salmon Pond (b), Jellison Pond (c), Second Pond (d), Little Long Pond (e), and Tilden Pond (f) in Maine. _____	7-30
7.1.3	Freshwater Monitoring and Databases _____		7-33
	Table 7-3	Monitoring and resurvey results of aquatic acidification and/or chemical recovery since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	7-35
7.1.4	Models _____		7-42
	Table 7-4	Recent process-based model estimates of surface water acidification and chemical recovery in the U.S. _____	7-44
7.1.5	National-Scale Sensitivity and Response _____		7-45
	Table 7-5	Model projections of surface water sulfate and associated acid neutralizing capacity, shown as changes between dates, for Adirondack and Shenandoah streams. _____	7-47
7.1.6	Water Quality Criteria _____		7-57
	Table 7-6	Numeric nutrient water quality criteria for rivers/streams by state (all values in mg/L). _____	7-59
	Table 7-7	U.S. EPA aggregate Level III ecoregion nutrient criteria (all values in mg/L; U.S. EPA ecoregional nutrient criteria documents for rivers and streams). _____	7-63
	Figure 7-4	Total nitrogen criterion values by ecoregion. _____	7-64
	Figure 7-5	Chlorophyll a criterion values by ecoregion. _____	7-64

7.1.7	Freshwater Biogeochemistry Summary	7-65
7.2	Biogeochemistry of Nitrogen in Estuarine and Near-Coastal Systems	7-68
	Table 7-8 Summary of key indicators of nitrogen enrichment in estuaries.	7-70
7.2.1	Nitrogen Sources	7-70
	Figure 7-6 Chemical nitrogen cascade in the Chesapeake Bay watershed (metric tons/year).	7-72
	Table 7-9 Summary of studies quantifying atmospheric nitrogen contribution to total nitrogen in coastal areas via watersheds and/or direct deposition to estuary surface waters.	7-73
7.2.2	The Estuary Environment	7-77
	Figure 7-7 Schematic diagram illustrating sources, transformations, and fate of nitrogen along the estuary-to-ocean continuum. Surface, subsurface, and atmospheric pathways of externally supplied or new nitrogen inputs attributable to anthropogenic activities are shown as internal nitrogen cycling. The combined anthropogenic nitrogen inputs are shown as a thick arrow (upstream), which decreases in thickness downstream as a portion of the nitrogen inputs settles to the bottom sediments and is buried and/or denitrified. Nitrogen (N <sub>2</sub> ) fixation is a biologically mediated new nitrogen input. The linkage of anthropogenically enhanced nitrogen inputs to accelerated primary production or eutrophication and its trophic and biogeochemical fate are also shown.	7-78
7.2.3	Dissolved Oxygen and Hypoxia	7-78
7.2.4	Estuarine and Near-Coastal pH	7-79
	Figure 7-8 A conceptual model for a large river plume eutrophication and subsurface water hypoxia and acidification.	7-80
7.2.5	Nitrogen in Surface Waters	7-82
7.2.6	Nitrogen Cycling	7-83
	Figure 7-9 New complexities in nitrogen cycling have been detailed since the 2008 ISA as shown in this illustration of the sedimentary N cycle in the Lower St. Lawrence estuary.	7-84
7.2.7	Monitoring Data	7-95
	Figure 7-10 Percentage of area in each coastal region scoring good, fair, and poor based on the Water Quality Index for the NCCA 2010.	7-96
7.2.8	Modeling Estuaries and Near-Coastal Areas	7-99
7.2.9	National-Scale Sensitivity	7-104
7.2.10	Water Quality Criteria for Estuaries	7-105
	Figure 7-11 State progress toward developing numeric nutrient criteria for estuaries <a href="https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality">https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality</a> .	7-106
7.2.11	Estuary and Near-Coastal Biogeochemistry Summary	7-107
<b>APPENDIX 8 BIOLOGICAL EFFECTS OF FRESHWATER ACIDIFICATION</b>		
8.1	Introduction	8-1
8.2	Chronic versus Episodic Acidification	8-3
8.3	Aquatic Organisms Impacted by Acidifying Deposition	8-5
	8.3.1 Plankton	8-5
	8.3.2 Periphyton	8-9
	8.3.3 Benthic Invertebrates	8-10
	Figure 8-1 Total macroinvertebrate species (community) richness as a function of median pH in 36 streams sampled in the western Adirondack Mountains of New York, 2003–2005; the four standard (New York State) impact categories for species richness are defined.	8-12

	Table 8-1	Thresholds of biological response to changes in water acidity for benthic invertebrates published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	8-13
8.3.4	Bacteria, Macrophytes, and Bryophytes _____		8-14
8.3.5	Amphibians _____		8-15
8.3.6	Fish _____		8-16
	Figure 8-2	Relationship between (a) inorganic monomeric aluminum and gill aluminum for parr and smolt, and (b) acid neutralizing capacity and gill aluminum. _____	8-20
	Figure 8-3	Critical aquatic pH ranges for fish species. _____	8-22
	Table 8-2	pH thresholds in fish published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	8-24
	Figure 8-4	Number of fish species per lake verses acidity status, expressed as acid neutralizing capacity, for Adirondack lakes. _____	8-25
	Table 8-3	Expected ecological effects and concern levels in freshwater ecosystems at various levels of acid neutralizing capacity. _____	8-27
	Table 8-4	Threshold values of aluminum for various fish species and associated effects. _____	8-29
	Figure 8-5	Relationship between (a) pH, (b) cationic aluminum, (c) acid neutralizing capacity, and (d) gill aluminum as compared with accumulated mortality of Atlantic salmon smolt. _____	8-33
8.3.7	Fish-Eating Birds _____		8-34
8.3.8	Aquatic Assemblages _____		8-34
	Figure 8-6	Species richness of biotic groups in 30 Adirondack study lakes relative to midsummer epilimnetic pH during sample years. _____	8-36
	Figure 8-7	Structure of diatom assemblage in 20 streams across a pH gradient of 4.5–8.5. (a) Species richness ( $\log_{10}$ -transformed numbers of diatom species per stream), (b) total abundance of diatoms ( $\log_{10}$ -transformed numbers of individuals per $m^2$ ), (c) chlorophyll a concentration (mg chlorophyll a per $m^2$ ), as a measure of algal biomass. _____	8-37
	Figure 8-8	Macroinvertebrate community composition in 20 streams across a pH gradient. Taxon richness (total number of primary consumer taxa; left panel) and benthic density [number of individuals $\log_{10}(x + 1)$ -transformed; right panel] plotted against stream pH, all primary consumers (a, b), shredders (excluding Leuctridae and Nemouridae) (c, d), herbivore-detritivores (Leuctridae and Nemouridae) (e, f), collectors (g, h) and grazers (i, j). _____	8-38
8.4	Documentation of Biological Recovery _____		8-39
8.4.1	Phytoplankton Recovery _____		8-42
	Table 8-5	Paleolimnological responses to changing lake chemistry published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	8-43
8.4.2	Zooplankton Recovery _____		8-44
	Figure 8-9	(A) Midsummer sulfate concentration in the epilimnion of Brooktrout Lake ( $\circ$ ) and in annual wet deposition ( $\bullet$ ) at local National Atmospheric Deposition Program/National Trends Network Station NY52 from 1984–2012. (B) Midsummer epilimnetic concentrations of inorganic monomeric aluminum ( $\square$ ) and [hydrogen ion] ( $\blacksquare$ ) in Brooktrout Lake from 1984–2012. (C) Midsummer phytoplankton ( $\Delta$ ) and total plankton (phytoplankton, rotifers, crustaceans) ( $\blacktriangle$ ) species richness in Brooktrout Lake from 1984–2012. _____	8-46

	Table 8-6	Midsummer values and productivity analytes in the epilimnion of Brooktrout Lake in the Adirondack Park from the 1980s through 2010–2012. _____	8-47
8.4.3		Benthic Invertebrate Recovery _____	8-50
8.4.4		Fish and Amphibian Recovery _____	8-53
8.4.5		Bird Recovery _____	8-55
8.4.6		Mitigation _____	8-56
8.5		Levels of Deposition at Which Effects Are Manifested _____	8-58
8.5.1		Most Sensitive and Most Affected Ecosystems and Regions _____	8-58
	Figure 8-10	Map of landscape sensitivity to acidic deposition for the northeastern and mid-Atlantic U.S. Stippled areas were not considered. _____	8-59
8.5.2		Extent and Distribution of Sensitive Ecosystems/Regions _____	8-60
	Figure 8-11.	Surface water Acid Neutralizing Capacity (ANC) map, based on data compiled by Sullivan (2017) _____	8-62
	Figure 8-12	(a) Minimum critical loads of surface water acidity for nitrogen and sulfur. Grids represent the minimum calculated critical load from all data within the 36 × 36-km grid cell (b) Mean critical loads of surface water acidity. Grids represent the average calculated critical load from all data within the 36 × 36-km grid cell. The critical chemical criterion used was an acid neutralizing capacity 50 µeq/L. _____	8-63
8.5.3		Climate Modification of Ecosystem Response to Nitrogen and Sulfur _____	8-64
8.5.4		Critical Loads _____	8-64
	Table 8-7	Recent empirical critical loads to protect against aquatic acidification in U.S. ecosystems. _____	8-67
	Table 8-8	Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification. _____	8-68
	Figure 8-13	Target loads for sulfur deposition in the Adirondack Park to protect lake acid neutralizing capacity to 50 µeq/L in the year 2010 (left map) and their exceedance (right map). _____	8-74
	Figure 8-14.	Modeled target loads and median measured Acid Neutralizing Capacity (ANC) in the period 1993 to 1996 from 30 Great Smoky Mountain National Park (GRSM) streams to achieve an ANC of 20 µeq/L by the year 2150. _____	8-77
	Figure 8-15.	Exceedance level of current NO <sub>3</sub> <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> atmospheric deposition for 387 stream sites in the GRSM. Exceedances were calculated for the years 2050 and 2150 using two targets for modeled stream ANC recovery of 20 µmolc/L and 20 µmolc/L less than the simulated preindustrial ANC. _____	8-78
8.6		Aquatic Acidification Summary and Causal Determinations _____	8-80
	Table 8-9	Ecological indicators for aquatic acidification. _____	8-82
8.6.1		Phytoplankton _____	8-82
8.6.2		Zooplankton _____	8-83
8.6.3		Benthic Invertebrates _____	8-83
8.6.4		Fish 8-84 _____	
8.6.5		Thresholds of Response _____	8-85
	Table 8-10	Results of recent biological effects studies in surface waters indicative of thresholds of biological response to changes in water acidity. _____	8-86
8.6.6		Biological Recovery _____	8-86
8.6.7		Most Sensitive and Most Affected Regions _____	8-87
8.6.8		Critical Loads _____	8-88

**APPENDIX 9 BIOLOGICAL EFFECTS OF FRESHWATER NITROGEN ENRICHMENT \_\_\_\_\_ 9-1**

9.1		Introduction to Nitrogen Enrichment and Eutrophication in Freshwater Systems _____	9-1
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	Figure 9-1	Conceptual model of the influence of atmospheric nitrogen deposition on freshwater nutrient enrichment. _____	9-2
9.1.1	Deposition to Freshwater Systems _____		9-5
	Table 9-1	Summary of studies using diatoms as biological indicators of nitrogen enrichment evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	9-9
	Figure 9-2	Phytoplankton responses to nitrogen and/or phosphorus enrichment for Rocky Mountain lakes receiving low or high atmospheric nitrogen deposition, given as the ratio of final chlorophyll concentration in the enriched treatment (+phosphorus, +nitrogen, or +nitrogen + phosphorus) to the chlorophyll concentration in the unenriched control. _____	9-12
9.2	Biological Indicators _____		9-15
	9.2.1	Diatoms _____	9-16
	9.2.2	Ratios of Nitrogen and Phosphorus _____	9-17
	9.2.3	Phytoplankton Biomass Nitrogen (N) to Phosphorus (P) Limitation Shift _____	9-18
	9.2.4	Periphyton/Microbial Biomass _____	9-18
	9.2.5	Chlorophyll <i>a</i> _____	9-20
	Table 9-2	Summary of additional evidence for nitrogen limitation on productivity of freshwater ecosystems that has been evaluated since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	9-24
	9.2.6	Potential Biological Indicators _____	9-27
9.3	Community Composition, Species Richness, and Diversity _____		9-29
	9.3.1	Archaea and Bacterial Diversity _____	9-30
	9.3.2	Phytoplankton Diversity _____	9-30
	Table 9-3	Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	9-31
	9.3.3	Benthic Algal Diversity _____	9-39
	9.3.4	Zooplankton Diversity _____	9-40
	9.3.5	Macroinvertebrate Diversity _____	9-41
	9.3.6	Macrophyte Diversity _____	9-42
	9.3.7	Amphibian Diversity _____	9-43
	9.3.8	Fish Diversity _____	9-43
9.4	Animal Behavior and Disease _____		9-43
	9.4.1	Behavior _____	9-43
	9.4.2	Disease _____	9-44
9.5	Summary of Thresholds, Levels of Deposition at Which Effects Are Manifested, and Critical Loads _____		9-44
	Table 9-4	Summary of critical loads for nitrogen eutrophication for surface water in the U.S. [adapted from Pardo et al. (2011c) with newer studies added]. _____	9-45
	Table 9-5	Summary of mean lake nitrate (NO <sub>3</sub> <sup>-</sup> ) concentrations, inorganic nitrogen deposition amounts, and nutrient enrichment inflection points where lake NO <sub>3</sub> <sup>-</sup> concentrations reflect increased nitrogen deposition. [from Baron et al. (2011b)]. _____	9-48
9.6	Summary and Causal Determination _____		9-48

## **APPENDIX 10 BIOLOGICAL EFFECTS OF NITROGEN ENRICHMENT IN ESTUARIES AND NEAR-COASTAL SYSTEMS \_\_\_\_\_ 10-1**

10.1	Introduction _____		10-1
	Figure 10-1	Eutrophication can occur when the availability of nutrients increases above normal levels. _____	10-3

	Figure 10-2	Overall eutrophication condition on a national scale. _____	10-5
10.1.1		Nitrogen Sources to Estuaries and Coasts _____	10-5
10.1.2		Trends in Atmospheric Deposition of Nitrogen _____	10-6
10.1.3		Nitrogen Limitation _____	10-6
10.1.4		Characteristics of Coastal Systems Sensitive to Eutrophication _____	10-8
10.2		Indicators of Nutrient Enrichment _____	10-11
	Table 10-1	Indicators of Estuarine Eutrophication. _____	10-12
	Figure 10-3	Biological indicator responses to nutrient enrichment. _____	10-13
10.2.1		Chlorophyll a _____	10-13
	Table 10-2	Chlorophyll a thresholds used in methods to evaluate the status of phytoplankton in U.S. coastal and estuarine water bodies. _____	10-14
10.2.2		Harmful/Nuisance/Toxic Algal Blooms _____	10-16
	Table 10-3	Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria. _____	10-20
10.2.3		Macroalgal Abundance _____	10-25
10.2.4		Dissolved Oxygen _____	10-26
	Figure 10-4	The range of ecological impacts exhibited as dissolved oxygen levels drop from saturation to anoxia. _____	10-27
	Figure 10-5	Coastal eutrophic and hypoxic areas of North America and the Caribbean. _____	10-29
10.2.5		Submerged Aquatic Vegetation _____	10-32
	Table 10-4	Nitrogen loading thresholds from multiple watershed sources versus eelgrass loss. _____	10-34
	Figure 10-6	Extent of submerged aquatic vegetation in the Chesapeake Bay 1978–2016. _____	10-36
10.2.6		Indices of Estuarine Condition _____	10-37
10.3		Effects on Biodiversity _____	10-39
10.3.1		Paleontological Diversity _____	10-39
10.3.2		Phytoplankton Diversity _____	10-40
10.3.3		Diversity of Phytoplankton Under Different Forms of Nitrogen (Reduced vs. Oxidized) _____	10-41
	Figure 10-7	Summary conceptual schematic illustrating the effect of changes in the proportion of $\text{NH}_4^+$ and $\text{NO}_3^-$ in the loads of N provided to a natural system. When $\text{NH}_4^+$ is the dominant form, and when waters are warmer, flagellates, cyanobacteria, and chlorophytes among other classes may proliferate, leading to overall productivity dominated by the small size class of algae (e.g., $<5\ \mu\text{m}$ ). In contrast, when $\text{NO}_3^-$ is the dominant form provided, especially under cooler water conditions, diatoms more likely dominate, and their overall production will be more likely dominated by cells of a larger size class (e.g., $>5\ \mu\text{m}$ ). Moreover, chlorophyll a yield and total production may be higher than under the $\text{NH}_4^+$ enrichment condition. _____	10-43
10.3.4		Diversity of Bacteria, Archaea, and Microzooplankton _____	10-44
10.3.5		Benthic Diversity _____	10-45
10.3.6		Fish Diversity _____	10-46
10.3.7		Trophic Interactions _____	10-46
10.3.8		Models Linking Indicators to Nitrogen Enrichment _____	10-47
	Figure 10-8	Forecasting curves for effects on total nitrogen loadings on (A) chlorophyll and (B) dissolved oxygen (mean and 95% confidence interval) for selected estuaries demonstrating the full range of sensitivity to relative total nitrogen loading. _____	10-49
10.4		Animal Behavior and Disease _____	10-50
10.4.1		Behavior _____	10-50

	Figure 10-9	The pathway of effects of eutrophication on different reproductive behaviors and selection forces in <i>Gasterosteus aculeatus</i> .	10-51
10.4.2	Disease		10-52
10.5	Nitrogen Enrichment and Acidification Effects on Calcifying Organisms		10-53
	Figure 10-10	Pathway from nitrogen loading to biological effects of nutrient-enhanced coastal acidification. Both microbial respiration of organic matter and increasing atmospheric carbon dioxide lower pH of coastal waters.	10-55
10.6	Summary of Thresholds and Levels of Deposition at Which Effects Are Manifested		10-58
10.7	Summary and Causality Determination		10-59
<b>APPENDIX 11 NITROGEN ENRICHMENT EFFECTS IN WETLANDS</b>			<b>11-1</b>
11.1	Introduction		11-1
	Table 11-1	Wetland classification used in the Integrated Science Assessment.	11-2
11.2	Regional Sensitivity		11-4
	Figure 11-1	Estimated extent of wetlands stressed by nonnative plants as determined by Nonnative Plant Stressor Indicator, at a national or regional level.	11-5
11.2.1	Climate Modification of Ecosystem Response to Nitrogen		11-6
11.3	Soil Biogeochemistry		11-6
	11.3.1	Nitrogen Pools and Processes	11-7
		Table 11-2	New studies on nitrogen addition effects on nitrogen cycling in wetlands. 11-13
	11.3.2	Soil Carbon Cycling	11-19
		Table 11-3	Loading effects upon belowground carbon cycling. 11-25
		Table 11-4	Nitrogen loading effects upon methane emissions. 11-34
11.4	Production and Aboveground Biomass		11-36
	11.4.1	Salt Marsh	11-36
	11.4.2	Mangrove	11-38
	11.4.3	Freshwater Tidal Marsh	11-38
	11.4.4	Intermittent Wetland	11-39
	11.4.5	Bog and Fen	11-39
	11.4.6	Summary Table	11-41
		Table 11-5	Nitrogen loading effects upon production and biomass. 11-41
11.5	Plant Stoichiometry and Physiology		11-48
	11.5.1	Salt Marsh	11-49
	11.5.2	Mangrove	11-49
	11.5.3	Freshwater Marsh	11-50
	11.5.4	Riparian Wetland	11-51
	11.5.5	Bog and Fen	11-51
	11.5.6	Summary Table	11-56
		Table 11-6	Nitrogen loading effects upon plant stoichiometry and physiology. 11-56
11.6	Plant Architecture		11-68
	11.6.1	Salt Marsh	11-68
	11.6.2	Mangrove	11-69
	11.6.3	Freshwater Tidal Marsh	11-69
	11.6.4	Riparian Wetland	11-70
	11.6.5	Summary Table	11-70
		Table 11-7	Nitrogen loading effects upon architecture. 11-70
11.7	Demography		11-72
	11.7.1	Mangrove	11-73

11.7.2	Riparian Wetland	11-73
11.7.3	Summary Table	11-74
	Table 11-8 Nitrogen loading effects upon demography.	11-74
11.8	Biodiversity/Community	11-74
11.8.1	Plants	11-75
	Table 11-9 Nitrogen loading effects upon plant biodiversity and communities.	11-79
11.8.2	Consumers	11-84
11.9	Critical Loads	11-85
11.9.1	Freshwater Wetland	11-85
11.9.2	Coastal Wetlands	11-85
11.9.3	Comparison to Critical Loads from Europe	11-86
11.10	Summary	11-87
11.10.1	Causality across Wetland Types	11-88
	Figure 11-2 Summary of the levels of nitrogen addition where a change to nitrogen cycling is observed.	11-89
	Figure 11-3 Summary of new literature of nitrogen load effects on belowground and aboveground carbon cycling.	11-91
	Figure 11-4 Summary of the level of nitrogen load that caused a change in the response variables of plant stoichiometry and physiology in wetlands.	11-93
	Figure 11-5 Summary of nitrogen addition studies on wetland biodiversity.	11-95
11.10.2	Coastal versus Freshwater Wetlands	11-96
	Figure 11-6 Summary of field nitrogen addition studies for coastal wetlands (blue borders) versus critical load (black border).	11-97
	Figure 11-7 Summary of nitrogen load studies for freshwater wetlands as well as current critical loads.	11-98

## **APPENDIX 12 NONACIDIFYING SULFUR ENRICHMENT EFFECTS** 12-1

12.1	Introduction	12-2
	Figure 12-1 Effects of sulfur oxide deposition on chemical (blue boxes), biological (green boxes), and atmospheric (yellow boxes) indicators of ecosystem change, as documented by the previous Integrated Science Assessment and more recent research.	12-4
12.2	Ecosystem Effects of Altered Sulfur Cycling	12-4
12.2.1	The Sulfur Cycle	12-4
	Figure 12-2 Sulfur cycle in terrestrial, forested ecosystems.	12-5
12.2.2	Deposition and Sulfur Stores	12-9
	Table 12-1 New study on sulfur (S) deposition effects on sulfur (S) cycling.	12-10
12.2.3	Sulfide Toxicity	12-10
	Table 12-2 Quantitative effects of sulfide on wetland and aquatic plant species.	12-11
	Figure 12-3 Schematic from Minnesota Pollution Control Agency that illustrates the mitigating effect of iron on the toxicity of sulfide and the stimulatory effect that organic carbon has on sulfide production.	12-15
12.2.4	Internal Eutrophication	12-16
	Figure 12-4 Mechanisms of linked sulfur, iron, and phosphorus cycling in wetland waters and soils.	12-17
12.2.5	Sulfur Effects on Methane Emissions	12-18
	Table 12-3 New studies on nonacidifying sulfur effects on methane emissions.	12-20
12.3	Interactions between Sulfur Deposition and Mercury	12-22

	Figure 12-5.	Sulfate, dissolved organic carbon, and inorganic mercury are all important determinants of the rate and amount of methyl mercury produced by sulfate-reducing prokaryotes. _____	12-23
12.3.1	Mercury Cycle and the Importance of Methylation _____		12-24
	Figure 12-6	Cycling of mercury (Hg) and methylmercury (MeHg) in ecosystems. _____	12-24
12.3.2	Biology of Sulfate-Reducing Prokaryotes _____		12-26
	Table 12-4	New studies on the biology of sulfate-reducing prokaryotes. _____	12-27
	Figure 12-7	The effect of different environmental factors on the relationship between sulfate and mercury methylation. Methylmercury (MeHg) accumulation is minimal at low and high sulfate concentrations, with an optimum near 100 $\mu$ M sulfate (blue line). High dissolved organic matter (DOM) will increase the magnitude of MeHg production across the range of sulfate concentrations (red line). Sulfide produced by methylators will inhibit further methylation if it accumulates in the aqueous environment where methylation occurs, shifting the MeHg optimum left (purple line). However if ecosystem chemistry (iron [Fe], reoxidation of sulfide, organic matter [OM]) allows for rapid sequestration of sulfide to large particles and sediments, the relaxation of the negative feedback of sulfide to sulfur-reducing prokaryotes (SRPs) will shift the MeHg optimum right (green line). _____	12-35
12.3.3	Environmental Drivers of Mercury Methylation Potential _____		12-36
	Table 12-5	Environmental factors that affect mercury (Hg) methylation. _____	12-36
	Figure 12-8	The relationship between surface water sulfate and total mercury or methylmercury fraction in river/leaf litter mesocosms. _	12-40
	Table 12-6	New mesocosm or incubation studies on sulfur addition effects on methylmercury. _____	12-41
	Figure 12-9	Total methylmercury mass in water at Little Rock Lake, WI, annually (a), and in relationship to annual mercury (b) or sulfur (c) deposition. _____	12-46
12.3.4	Mercury Methylation in Sulfur Addition Field Studies _____		12-53
	Table 12-7	New studies on mercury methylation in sulfur-amended ecosystems. _____	12-54
	Table 12-8	New studies on mercury (Hg) and sulfur (S) cycling in the Everglades Water Conservation Areas (WCA). _____	12-61
	Figure 12-10	The relationship between surface water sulfate and methylmercury concentrations in the Florida Everglades. _____	12-63
12.3.5	Drivers of Mercury Methylation under Ambient Conditions _____		12-66
	Table 12-9	New studies on correlations between sulfur (S) and methylmercury (MeHg) in ecosystems. _____	12-68
	Figure 12-11	Concentrations of soil sulfur (S), elevated by sulfur oxides (SO <sub>x</sub> ) deposition, correlate with rice grain (methylmercury [MeHg]) and rice grain %MeHg in rice paddies near industrial emitters in China. _____	12-74
	Figure 12-12	Interactions between mercury (Hg) and sulfur (S) cycles. _____	12-74
	Table 12-10	New studies on deposition of sulfur (S) and mercury (Hg) and their effect on methylmercury (MeHg). _____	12-75
	Table 12-11	New studies of Interactions between organic matter and sulfur (S) in Controlling methylmercury (MeHg). _____	12-78
12.4	Sulfur Impacts on Mercury in Wildlife _____		12-80
	Figure 12-13	Bioconcentration and biomagnification result in methylmercury concentrations about 1 million times higher in predator fish than in stream water. _____	12-81
	Table 12-12	New studies on sulfur (S) impacts upon mercury (Hg) in wildlife. _	12-82

	Figure 12-14	Tissue mercury concentrations as a function of surface water sulfate concentrations (n = 2,360 surface water samples) in the Everglades Protection Area. _____	12-86
12.5	Extent and Distribution of Sensitive Ecosystems _____		12-87
	Figure 12-15	Fish mercury concentrations across the U.S. _____	12-88
12.6	Critical Loads _____		12-89
12.7	Summary of Nonacidifying Sulfur Effects _____		12-89
	Table 12-13	Summary of quantitative effects of nonacidifying sulfur enrichment. _____	12-90
12.7.1	Terrestrial Sulfur Cycling _____		12-92
12.7.2	Aquatic Sulfur Cycling _____		12-93
12.7.3	Sulfide Toxicity _____		12-93
	Figure 12-16	Thresholds of sulfate or sulfide concentrations in water, which cause biological and chemical effects in ecosystems. _____	12-94
12.7.4	Internal Eutrophication _____		12-95
12.7.5	Effects on Methane Production _____		12-95
12.7.6	The Role of Microbes in Mercury Methylation _____		12-95
	Figure 12-17	Linear relationships between sulfate and methylmercury concentrations in published studies. _____	12-97
12.7.7	Impacts of Sulfur upon Mercury Cycling _____		12-98
	Figure 12-18	Thresholds of sulfate addition or deposition from published studies which affect chemical or biological changes in ecosystems. _____	12-99
12.7.8	Sensitive Ecosystems _____		12-100
12.7.9	Mercury Effects on Animal Species _____		12-100
12.8	Supplemental Materials: Mercury Cycling _____		12-102
12.8.1	Transfer of Mercury from the Atmosphere to Terrestrial Ecosystems _____		12-102
12.8.2	Transfer of Mercury from Terrestrial to Aquatic Ecosystems _____		12-103
12.8.3	Transfer of Mercury from Atmosphere to Aquatic Ecosystems _____		12-104
12.8.4	Methylmercury Cycling _____		12-104
12.8.5	Transfer of Methylmercury from Terrestrial to Aquatic Ecosystems _____		12-104
12.8.6	Transfer of Methylmercury from Wetlands to Aquatic Ecosystems _____		12-105
12.8.7	Methylmercury Cycling in Aquatic Ecosystems—Lake Onondaga, NY _____		12-105
	Figure 12-19	Mercury and methylmercury mass balance cycle in Lake Onondaga in 1992. The quantities of mercury in each flux are indicated in parentheses by (kg total Hg/yr, kg MeHg/yr). _____	12-106
12.8.8	Methylmercury in Sediments and Water Column—Lakes _____		12-107
12.8.9	Methylmercury in Sediments and Water Column—Wetlands _____		12-108
12.8.10	Methylmercury in Sediments and Water Column—Estuarine and Marine Ecosystems _____		12-109

**APPENDIX 13 CLIMATE MODIFICATION OF ECOSYSTEM RESPONSE TO NITROGEN AND SULFUR \_\_\_\_\_ 13-1**

13.1	Climate Modification of Soil Acidification and Nitrogen Enrichment _____		13-2
13.1.1	Nitrogen Transport and Transformation _____		13-2
	Figure 13-1	Summary of key interactions between nitrogen, anthropogenic-driven climate change, and hydrology. _____	13-3
	Table 13-1	Summary on climate modification sulfur and nitrogen cycling in Appendix 4 and Appendix 6 in addition to those in Appendix 13. ____	13-6
13.1.2	Nitrogen, Climate, and Carbon Cycling _____		13-7
	Figure 13-2	The effects of increased nitrogen, temperature, and precipitation on terrestrial carbon pools (left panel) and fluxes (right panel) from published meta-analyses. _____	13-9

	Table 13-2	Summary on climate modification of nitrogen (N) effects on carbon (C) cycling in Appendix 4 and Appendix 6 in addition to those in Appendix 13. _____	13-11
13.1.3	Climate and Acidification _____		13-12
	Table 13-3	Summary on climate modification of acidification in Appendix 4 and Appendix 5 in addition to those in Appendix 13. _____	13-15
13.1.4	Nitrogen, Climate, and Biodiversity _____		13-16
	Table 13-4	Summary on climate modification of nitrogen (N) effects on biodiversity in Appendix 6 in addition to those in Appendix 13. _____	13-19
13.2	Estuaries _____		13-20
13.3	Wetlands _____		13-21

## **APPENDIX 14 ECOSYSTEM SERVICES \_\_\_\_\_ 14-1**

14.1	Introduction _____		14-1
14.2	Ecosystem Services Frameworks _____		14-2
14.3	United States Applications _____		14-4
	14.3.1 Acidification _____		14-5
	Table 14-1	Ecosystem services research related to ecosystem acidification. _____	14-7
	14.3.2 Eutrophication _____		14-8
	Figure 14-1	Economic nitrogen cascade in the Chesapeake Bay Watershed. _____	14-11
	Table 14-2	Potential damage costs of nitrogen (N) (\$/kg N; 2008 or as reported) to air, land, and water resources in the conterminous U.S. in the early 2000s as synthesized by Sobota et al. (2015). Low, median, and high costs derive from the specific damage cost reference. Negative values indicate an economic benefit. _____	14-12
	Figure 14-2	Map of ecosystem services altered by nitrogen critical load exceedance. _____	14-15
	Table 14-3	Numbers of chains, Final Ecosystem Goods and Services (FEGS), and beneficiaries (bens) associated with each initial biological indicator (Clark et al., 2017). _____	14-16
	Table 14-4	Ecosystem services research related to nitrogen-driven eutrophication. _____	14-17
	14.3.3 Nitrogen and Climate Modification _____		14-18
	Table 14-5	Summary of recent literature examining economic impacts of ocean acidification on U.S. fisheries. _____	14-19
14.4	European and Canadian Applications _____		14-20
	Figure 14-3	Benefits and costs associated with the 25% decline in nitrogen deposition in the U.K. since 1990. _____	14-21
14.5	Global Perspective _____		14-21
14.6	Summary _____		14-22
14.7	Supplemental Materials: Ecosystem Services Profiles of Select Species _____		14-24
	14.7.1 Balsam Fir _____		14-24
	14.7.2 Eel Grass _____		14-25
	14.7.3 Green Turtle _____		14-27
	14.7.4 White Ash _____		14-28
	14.7.5 Lace Lichen _____		14-30

## **APPENDIX 15 OTHER ECOLOGICAL EFFECTS OF PARTICULATE MATTER \_\_\_\_\_ 15-1**

15.1	Introduction _____		15-1
15.2	Direct Effects of Particulate Matter on Radiative Flux _____		15-2
15.3	Particulate Matter Deposition to Ecosystems _____		15-3
	15.3.1 Metals _____		15-3
	15.3.2 Organics _____		15-4
15.4	Effects of Particulate Matter on Vegetation _____		15-5

15.4.1	Vegetative Surfaces _____	15-5
15.4.2	Foliar Uptake of Particulate Matter _____	15-7
15.4.3	Particulate Matter Impacts on Gas Exchange Processes _____	15-8
15.4.4	Plant Physiology _____	15-8
15.4.5	Uptake of Particulate Matter by Plants from Soils _____	15-9
15.4.6	Effects on Plant Growth and Reproduction _____	15-10
15.5	Effects of Particulate Matter on the Soil Environment _____	15-11
15.5.1	Bioavailability in Soils _____	15-11
15.5.2	Soil Nutrient Cycling _____	15-12
15.5.3	Soil Community Effects _____	15-14
15.5.4	Soil Microbe Interactions with Plant Uptake of Particulate Matter _____	15-17
15.5.5	Effects of Particulate Matter on Physical Properties of Soils _____	15-18
15.6	Effects of Particulate Matter on Fauna _____	15-19
15.6.1	Laboratory Bioassays _____	15-19
15.6.2	Wildlife as Biomonitors of Particulate Matter _____	15-21
15.6.3	Biomagnification _____	15-22
15.7	Effects of Particulate Matter on Ecological Communities and Ecosystems _____	15-23
15.7.1	Gradient Effects near Smelters _____	15-24
15.7.2	Urban Environments _____	15-25
15.7.3	Aquatic Ecosystems _____	15-25
15.7.4	Experimental Microecosystems _____	15-26
15.8	Summary of Ecological Effects of Particulate Matter _____	15-26

**APPENDIX 16 CASE STUDIES \_\_\_\_\_ 16-1**

	Figure 16-1	Critical loads (CL) exceedance in Class I areas. _____	16-1
16.1	Northeastern U.S. Case Study: Acadia National Park, Hubbard Brook Experimental Forest, and Bear Brook Watershed _____		16-2
16.1.1	Background _____		16-2
	Figure 16-2	Locations of northeastern U.S. case study areas and nearby human population centers. _____	16-3
	Table 16-1	Selected characteristics of northeastern case study areas. _____	16-3
	Figure 16-3	Site map of Hubbard Brook Experimental Forest in the White Mountains of New Hampshire. _____	16-5
	Table 16-2	Land use/land cover for northeastern case study areas. _____	16-7
	Figure 16-4	Land cover in the Northeast case study region. _____	16-8
	Table 16-3	Literature cited by Northeast U.S. case study area. _____	16-8
	Table 16-4	Key recent research literature focused on the case study region. _____	16-12
16.1.2	Deposition _____		16-13
	Figure 16-5	Total nitrogen deposition (A) and percentage of oxidized nitrogen deposition (B) for the Northeast case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. _____	16-14
	Figure 16-6	Total sulfur deposition (A) for the Northeast case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. Time series of wet deposition (B) from the National Atmospheric Deposition Program/National Trends Network in the Hubbard Brook Experimental Forest, NH. _____	16-15
16.1.3	Critical Loads and Other Dose-Response Relationships _____		16-16
	Table 16-5	Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the northeastern U.S. _____	16-17
	Table 16-6	Empirical critical loads for nitrogen in Acadia National Park, by receptor, from Pardo et al. (2011c). _____	16-20

	Figure 16-7	Annual stream calcium and magnesium export (paired bars), and cumulative excess export in West Bear Brook compared with East Bear Brook (line), over the study period 1989–2000 at the Bear Brook Watershed experiment. _____	16-22
	Table 16-7	Critical loads of nutrient nitrogen for the Northern Forests ecoregion. _____	16-23
	Figure 16-8	Conceptual diagram showing the direct and indirect effects of changes in temperature and precipitation on biogeochemical processes in forests and on the services forests provide. Also shown are feedbacks that further influence climatological effects. _____	16-25
	Table 16-8	Aquatic empirical research on the response of nitrogen and sulfur deposition for the northeastern U.S. _____	16-26
	Table 16-9	Critical and target load and exceedance modeling studies in the northeastern U.S. _____	16-30
	Table 16-10	Empirical and modeled nitrogen critical loads applicable to the northeastern U.S. _____	16-32
16.1.4	Long-Term Ecological Monitoring _____		16-33
	Table 16-11	Summary table of observed terrestrial and aquatic acidification long-term trends in Hubbard Brook Experimental Forest and Bear Brook Watershed. _____	16-34
	Table 16-12	Example surface water acidification chemistry studies in the Northeast case study region. _____	16-37
	Table 16-13	Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions. _____	16-40
16.1.5	Recovery _____		16-45
16.2	Adirondack Case Study: Adirondack Region of New York _____		16-46
	16.2.1 Background _____		16-46
	Figure 16-9	Map of Adirondack park land cover. _____	16-48
	16.2.2 Deposition _____		16-49
	Figure 16-10	Total nitrogen deposition (A) and percentage of oxidized nitrogen deposition (B) for the Adirondack case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. _____	16-50
	Figure 16-11	Total sulfur deposition (A) for the Adirondack case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. Time series of wet deposition (B) from the National Atmospheric Deposition Program/National Trends Network Whiteface Mountain, NY. _____	16-51
16.2.3	Critical Loads and Other Dose-Response Relationships _____		16-52
	Table 16-14	Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the Adirondack Mountains. _____	16-52
	Figure 16-12	Number of fish species per lake and acidity status, expressed as acid neutralizing capacity, for Adirondack lakes. _____	16-56
	Figure 16-13	Total macroinvertebrate species (community) richness as a function of median pH in 36 streams sampled in the western Adirondack Mountains of New York, 2003–2005; the four standard (New York State) impact categories for species richness are defined. _____	16-58
	Figure 16-14	Species richness of biotic groups in 30 Adirondack study lakes relative to midsummer epilimnetic pH during sample years. _____	16-59
	Table 16-15	Aquatic empirical research on the response of nitrogen and sulfur deposition for the Adirondacks. _____	16-60
	Table 16-16	Critical and target load and exceedance modeling studies in Adirondack Mountains. _____	16-62

16.2.4	Long-Term Monitoring		16-63
	Figure 16-15	(A) Midsummer sulfate concentration in the epilimnion of Brooktrout Lake (○) and in annual wet deposition (●) at local National Atmospheric Deposition Program/National Trends Network Station NY52 from 1984–2012. (B) Midsummer epilimnetic concentrations of inorganic monomeric aluminum (□) and hydrogen ion (■) in Brooktrout Lake from 1984–2012. (C) Midsummer phytoplankton (Δ) and total plankton (phytoplankton, rotifers, crustaceans) (▲) species richness in Brooktrout Lake from 1984–2012.	16-68
16.3	Southeastern Appalachia Case Study		16-69
16.3.1	Background		16-69
	Table 16-17	Species in the Southeast case study region that are listed as threatened or endangered or as a species of concern.	16-72
	Figure 16-16	Great Smoky Mountains National Park and nearby Class I wilderness areas, with emphasis on water sampling locations within GSMNP and critical loads for watersheds described in Appendix 16.2.3.2.	16-77
	Figure 16-17	Land cover in the southern Appalachian Mountains case study region.	16-78
16.3.2	Deposition		16-78
	Figure 16-18	Deposition over Great Smoky Mountain National Park.	16-79
	Figure 16-19	Trends in wet deposition of nitrogen and sulfur in Great Smoky Mountain National Park, 1990–2014.	16-80
	Figure 16-20	Total nitrogen deposition on left, total sulfur deposition on right, for the 3-year average, 2011–2013 in Great Smoky Mountain National Park.	16-81
	Figure 16-21	Modeled sulfur and nitrogen deposition to the Great Smoky Mountain National Park for the year 2000.	16-82
	Figure 16-22.	Annual-averaged monthly footprint of reactive N deposition in Great Smoky Mountain National Park (10.4 kg N/ha/yr), and pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model.	16-83
16.3.3	Critical Loads and Other Dose-Response Relationships		16-83
16.3.4	Characterization and Long-Term Monitoring		16-86
	Table 16-18	Example soil, terrestrial biota, and surface water acidification characterization and long-term monitoring studies in the southern Appalachian Mountains region.	16-87
16.4	Tampa Bay Case Study		16-90
16.4.1	Background		16-90
	Figure 16-23	Tampa Bay mainstem segments and watershed. Also shown are the National Atmospheric Deposition (NADP) National Trends Network wet deposition monitoring site FL41 at Verna wellfield in Sarasota County and the NADP Atmospheric Integrated Research Monitoring Network site FL18 in Hillsborough County.	16-92
	Figure 16-24	Tampa Bay overview map highlighting watershed development and land use.	16-95
16.4.2	Deposition		16-96
	Figure 16-25	Annual wet deposition of ammonium, nitrate, sulfate, and acidity at the National Atmospheric Deposition National Trends Network monitoring site closest to the Tampa Bay case study area.	16-96
	Figure 16-26	Estimated annual loads of total nitrogen from various sources to Tampa Bay summarized from 1976 to 2011.	16-97
	Figure 16-27	(A) Wet and dry nitrogen deposition in Tampa Bay and the surrounding area. (B) Percentage of oxidized nitrogen deposition in Tampa Bay and the surrounding area.	16-99

16.4.3	Long-Term Ecological Monitoring	16-99
	Figure 16-28 Submerged aquatic vegetation cover loss in Tampa Bay.	16-101
	Figure 16-29 Comparison of observed chlorophyll <i>a</i> and that predicted from the total nitrogen load—chlorophyll <i>a</i> relationships for all four mainstem Tampa Bay segments, for 1986–1998 and 1999–2007.	16-102
	Figure 16-30 Total seagrass coverage in Tampa Bay circa 1950 through 2014.	16-104
	Figure 16-31 Trend in hydrologically normalized total nitrogen load to Tampa Bay relative to population increases in the Tampa Bay metropolitan area.	16-105
16.4.4	Nitrogen Management	16-106
	Table 16-19 Numeric nutrient criteria for chlorophyll <i>a</i> for the four mainstem segments of Tampa Bay adopted by the Florida Department of Environmental Protection.	16-106
	Table 16-20 Numeric nutrient criteria for total nitrogen for the four mainstem segments of Tampa Bay.	16-107
16.5	Rocky Mountain National Park Case Study	16-109
16.5.1	Background	16-109
	Figure 16-32 Rocky Mountain National Park ecosystems.	16-110
	Figure 16-33 Rocky Mountain National Park land coverage using the land cover classifications as mapped by the National Land Cover Dataset. Percentage of cover is shown for the four dominant cover types.	16-113
	Figure 16-34 Rocky Mountain National Park hydrologic unit code 12 watersheds.	16-114
16.5.2	Deposition	16-115
	Figure 16-35 Total atmospheric nitrogen and sulfur deposition in the Rocky Mountain National Park region based on TDEP calculations averaged from 2011–2013 (see Appendix 2) and long-term trends in wet atmospheric deposition from the Beaver Meadows National Atmospheric Deposition Program Monitoring site within Rocky Mountain National Park.	16-116
	Figure 16-36 Percentage of atmospheric nitrogen deposited in oxidized forms and through wet deposition in the Rocky Mountain National Park region based on TDEP calculations averaged from 2011–2013 (see Appendix 2).	16-117
	Figure 16-37 Rocky Mountain National Park nitrogen cycle.	16-118
	Figure 16-38 National Park from November 2008 to November 2009, including organic nitrogen and particulate organic nitrogen.	16-119
	Figure 16-39 Annual-averaged monthly footprint of reactive N deposition in Rocky Mountain National Park (4.0 kg N/ha/yr), and pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model.	16-120
16.5.3	Critical Loads and Other Dose-Response Relationships	16-120
	Table 16-21 Terrestrial empirical critical loads of nutrient nitrogen for the Northwestern Forested Mountains ecoregion.	16-121
	Table 16-22 Montane forest and alpine ecosystem critical loads for nitrogen deposition research published since the critical load assessment by Pardo et al. (2011c).	16-124
	Table 16-23 Hindcast absolute and percentage changes in species abundance between 1900 and 2010 in response to historical reconstructions of nitrogen deposition (Sullivan et al., 2005) and historical climate change (IPCC, 2007b).	16-127
	Table 16-24 Critical loads for nitrogen for eutrophication for surface water (high-elevation lakes) in the Rocky Mountains.	16-129

	Table 16-25	Lake water nitrate concentrations in nitrogen deposition studies observing phytoplankton responses. _____	16-130
	Table 16-26	Paleolimnological biological responses in Rocky Mountain lakes exposed to anthropogenic nitrogen deposition. _____	16-131
	Table 16-27	Critical loads of nitrogen or sulfur for surface water acidification Rocky Mountain National Park and other high-elevation lakes in the Rocky Mountains. _____	16-133
	Figure 16-40	The continuum of ecological sensitivity to nitrogen deposition. ____	16-135
	Figure 16-41	Critical load thresholds for current and possible future biogeochemical and biological effects of nitrogen deposition. ____	16-136
16.5.4	Highlights of Additional Research Literature and Federal Reports since January 2008 _____		16-136
	Table 16-28	Summary of freshwater eutrophication studies in the Rocky Mountains since 2008. _____	16-138
16.5.5	Rocky Mountain National Park Initiative _____		16-139
	Figure 16-42	Rocky Mountain National Park Initiative glidepath and current wet nitrogen deposition at Loch Vale in Rocky Mountain National Park. _____	16-141
	Figure 16-43	Rocky Mountain National Park Initiative accomplishment timeline. _____	16-142
16.5.6	Interactions between Nitrogen Deposition, Precipitation, and Large-Scale Ecological Disturbances _____		16-142
16.6	Southern and Central California _____		16-144
	16.6.1 Background _____		16-144
	Figure 16-44	Map of the distribution of vegetation types and land cover in California. _____	16-145
	Table 16-29	Land coverages of Sequoia, Kings Canyons, and Joshua Tree national parks. _____	16-148
	Figure 16-45	Southern and central California case study region showing locations of human population centers. _____	16-149
	16.6.2 Deposition _____		16-150
	Figure 16-46	Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. A and B show the 3-year average total deposition of nitrogen and sulfur for 2011–2013 _____	16-151
	Figure 16-47	Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. A shows the partitioning between oxidized and reduced nitrogen; B and C show the 3-year average total percentage of wet deposition of nitrogen and sulfur for 2011–2013. _____	16-152
	Figure 16-48	Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. The 25-year time series for wet deposition of nitrate, ammonium, sulfate, and hydrogen ion obtained from the National Atmospheric Deposition Program/National Trends Network monitoring site CA67. _____	16-153
	Figure 16-49	Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons national parks and surrounding region in California. A and B show the 3-year average total deposition of nitrogen and sulfur for 2011–2013. _____	16-154
	Figure 16-50	Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons national parks and surrounding region in California. A shows the partitioning between oxidized and reduced nitrogen, indicated as the fraction of total nitrogen which is oxidized; B and C show the 3-year average total percentage of wet deposition of nitrogen and sulfur for 2011–2013. _____	16-155

Figure 16-51	Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons and in Yosemite national parks and surrounding regions in California. A and B show the 25-year time series for wet deposition of nitrate, ammonium, sulfate, and hydrogen obtained from the National Atmospheric Deposition Program/National Trends Network monitoring sites CA99 and CA75. _____	16-156
Figure 16-52	Annual-averaged monthly footprint of reactive N deposition in Joshua Tree National Park (3.2 kg N/ha/yr) and Sequoia National Park (5.7 kg N/ha/yr). Also shown for each park is a pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model. _____	16-158
16.6.3	Critical Loads and Other Dose-Response Relationships _____	16-158
Figure 16-53	Composite critical load exceedance maps for all seven vegetation types included in the study of Fenn et al. (2010) showing the combined exceedance areas and the level of exceedance (kg N/ha/yr). _____	16-161
Table 16-30	Summary of recent empirical dose-response and critical load studies focused on the southern/central California case study area and published since Pardo et al. (2011c). _____	16-162
Table 16-31	Terrestrial critical and target load and exceedance modeling studies in southern/central California. _____	16-165
Table 16-32	Example surface water acidification studies in Sequoia and Kings Canyons National Parks and other Sequoia and Kings Canyons National Parks—relevant areas in the southern/central California case study region. _____	16-168
16.6.4	Highlights of Additional Research Literature and Federal Reports since January 2008 _____	16-173
Table 16-33	Key recent research literature focused on the case study region. _____	16-173
16.6.5	Summary _____	16-175
Figure 16-54	Continuum of critical loads in southern/central California case study area and relevant surrounding region. _____	16-176

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# ACRONYMS AND ABBREVIATIONS

Acronym/Abbreviation	Meaning	Acronym/Abbreviation	Meaning
ACCENT	Atmospheric Composition Change: the European Network of excellence	Ba	barium
AIRMoN	Atmospheric Integrated Research Monitoring Network	BBW	Bear Brook Watershed
AIRS	Atmospheric Infrared Sounder (instrument)	BBWM	Bear Brook Watershed, Maine
Al	aluminum	Bc or BC	base cation
Al <sup>3+</sup>	aluminum ion	BCE	exchangeable base cations
Ali	inorganic aluminum	BCS	base-cation surplus
Al <sup>2+</sup>	aluminum ion	BCw	base cation weathering
Al <sub>o</sub>	organic aluminum	BGC	Biogeochemical (model)
Al(OH) <sub>3</sub>	aluminum hydroxide	B-IBI	benthic index of biological integrity
ALSC	Adirondack Lake Survey Corporation	BMPs	best management practices
ALTM	Adirondack Long Term Monitoring	BNF	biological nitrogen fertilization
AMD	acid mine drainage	Br	bromine
ANC	acid neutralizing capacity	Br <sup>-</sup>	bromide ion
ANPP	aboveground net primary production	Br <sub>2</sub>	molecular bromine
AOD	aerosol optical depth	BrCl	bromine chloride
AOSR	Athabasca oil sands region	BrO	bromine monoxide
AQCD	Air Quality Criteria Document	BUV	Backscatter Ultraviolet Spectrometer
AQEG	Air Quality Expert Group	BUVD	Beneficial Use Values Database
AQI	Air Quality Index	C	carbon; concentration
AQS	Air Quality System (database)	<sup>12</sup> C	carbon-12, stable isotope of carbon
Ar	argon	<sup>13</sup> C	carbon-13, stable isotope of carbon
ARS	Agricultural Research Service	C <sub>a</sub>	ambient air concentration
As	arsenic	Ca	calcium
ASI	Acid Stress Index	Ca <sup>2+</sup>	calcium ion
asl	above sea level	CAA	Clean Air Act
ATMOS	Atmospheric Trace Molecule Spectroscopy	CAAA	Amendments to the Clean Air Act
ATTILA	type of Lagrangian model	CAAAC	Clean Air Act Advisory Committee
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments	CaCl <sub>2</sub>	calcium chloride
AVIRIS	Airborne Visible and Infrared Imaging Spectrometer	CaCO <sub>3</sub>	calcium carbonate
		CALIPSO	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (satellite)
		Ca(NO <sub>3</sub> ) <sub>2</sub>	calcium nitrate

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
Ca(OH) <sub>2</sub>	calcium hydroxide	CINO <sub>2</sub>	nitryl chloride
CAPMoN	Canadian Air and Precipitation Monitoring Network	CMAQ	Community Multiscale Air Quality (modeling system)
CaSO <sub>4</sub> ·2H <sub>2</sub> O	gypsum	CMSA	consolidated metropolitan statistical area
CASTNet	Clean Air Status and Trends Network	CO	carbon monoxide
CB4	Carbon Bond 4 (model)	CO <sub>2</sub>	carbon dioxide
Cd	cadmium	CO <sub>3</sub> <sup>-</sup>	carbonate
CEC	cation exchange capacity	CONUS	contiguous U.S.
CENTURY	model that simulates carbon, nitrogen, phosphorus, sulfur, and water dynamics in the soil-plant system at monthly intervals over time scales of centuries and millennia	CPUE	catch per unit effort
CFCs	chlorinated fluorocarbons	CRREL	U.S. Army Cold Regions Research and Engineering Laboratory
CG	cloud-to-ground (lightning flash)	CS	Consumer surplus
Chl <i>a</i>	chlorophyll <i>a</i>	CS <sub>2</sub>	carbon disulfide
CH <sub>4</sub>	methane	CSS	coastal sage scrub (ecosystem)
C <sub>2</sub> H <sub>4</sub>	ethene	CTM	chemical transport model
C <sub>2</sub> H <sub>6</sub>	ethane	Cu	copper
C <sub>3</sub> H <sub>8</sub>	isoprene	CV	contingent valuation
CH <sub>3</sub> CHO	acetaldehyde	CVM	contingent valuation method
CH <sub>3</sub> C(O)	acetyl radical	Δ, δ	delta, difference; change
CH <sub>3</sub> C(O)OO	acetyl peroxy radical	DayCent	model for daily biogeochemistry for forest, grassland, cropland, and savanna systems
CH <sub>2</sub> I <sub>2</sub>	diiodomethane	DayCent-Chem	combination of DayCent-Chem and PHREEQC models
CH <sub>2</sub> O	formaldehyde	DC	dichotomous choice
CH <sub>3</sub> OOH	methyl hydroperoxide	DDRP	Direct Delayed Response Project
CH <sub>3</sub> -S-CH <sub>3</sub>	dimethylsulfide, DMS	DDT	Damage Delay Time
CH <sub>3</sub> -S-H	methyl mercaptan	DECOMP	decomposition model based on soil-plant system dynamics
(CH <sub>3</sub> ) <sub>2</sub> SO	dimethyl sulfoxide, DMSO	DEP	Department of Environmental Protection
CH <sub>3</sub> SO <sub>3</sub> H	methanesulfonic acid	DIC	dissolved inorganic carbon
CH <sub>3</sub> -S-S-CH <sub>3</sub>	dimethyl disulfide, DMDS	DIN	dissolved inorganic nitrogen
C <sub>i</sub>	interstitial air concentration	DMDS	dimethyl disulfide, CH <sub>3</sub> -S-S-CH <sub>3</sub>
CL	critical load	DMS	dimethyl sulfide, CH <sub>3</sub> -S-CH <sub>3</sub>
Cl	chlorine	DMSO	dimethylsulfoxide
Cl <sup>-</sup>	chloride ion	DNDC	Denitrification-Decomposition (model)
Cl <sub>2</sub>	molecular chlorine	DO	dissolved oxygen
CLaMS	type of Lagrangian model		
CloudSat	NASA Earth observation satellite		

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
DOC	dissolved organic carbon	FLEXPART	type of Lagrangian model
DON	dissolved organic nitrogen	ForSAFE	three-component model using nitrogen, carbon cycling, and soil chemistry
EBB	East Bear Brook	FRM	Federal Reference Method
EC	elemental carbon	FTIR	Fourier Transform Infrared Spectroscopy
EEAs	Essential Ecological Attributes	FW2	black carbon soot
ELA	Experimental Lakes Area	F <sub>x</sub>	flux
ELS	Eastern Lakes Survey	$\gamma\text{N}_2\text{O}_5$	uptake coefficient for N <sub>2</sub> O <sub>5</sub> on particles
EMAP	Environmental Monitoring and Assessment Program	GAW	Global Atmospheric Watch (program)
EMEFS	Eulerian Model Evaluation Field Study	GCE	Goddard Cumulus Ensemble (model)
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe	GDP	gross domestic product
EMF	ectomycorrhizal fungi	GEOS	Goddard Earth Observing System
EOS	Earth Observation System	GEOS-Chem	Goddard Earth Observing System (with global chemistry transport model)
U.S. EPA	U.S. Environmental Protection Agency	GEOS-IDAS	Goddard Earth Observing System Data Assimilation System
eq	equivalents	GFED	Global Fire Emissions Database
ER	ecosystem respiration	GHG	greenhouse gas
EPT	Ephemeroptera-Plecoptera-Tricoptera (index)	GOES	Geostationary Operational Environmental Satellites
ERP	Episodic Response Project	GOME	Global Ozone Monitoring Experiment
ESA	European Space Agency	GPP	gross primary productivity
EVRI	Environmental Valuation Reference Inventory	g <sub>s</sub>	stomatal conductance
<i>F</i>	flux	GtC	gigaton carbon
F <sup>-</sup>	fluoride ion	Gton	gigaton
FAB	First-order Acidity Balance model	GWP	global warming potential
FACE	free-air CO <sub>2</sub> enrichment (studies)	H	hydrogen; hydrogen atom
Fe	iron	<sup>2</sup> H	hydrogen-2, deuterium, stable isotope of hydrogen
FePO <sub>4</sub>	iron phosphate	H <sup>+</sup>	proton, hydrogen ion; relative acidity
FeS	iron sulfide	ha	hectare
F-factor	fraction of the change in mineral acid anions that is neutralized by base cation release	HAPs	hazardous air pollutants
FHM	Forest Health Monitoring	HBEF	Hubbard Brook Experimental Forest
FIA	Forest Inventory and Analysis (program)		
FISH	Fish in Sensitive Habitats (project)		

Acronym/Abbreviation	Meaning	Acronym/Abbreviation	Meaning
HBES	Hubbard Brook Ecosystem Study	INO <sub>3</sub>	iodine nitrate
HBN	Hydrologic Benchmark Network	INTEX-NA	Intercontinental Chemical Transport Experiment—North America
HC	hydrocarbon	IO	iodine oxide
HCHO	formaldehyde	IPCC	Intergovernmental Panel on Climate Change
HCl	hydrochloric acid	IPCC-AR4	Intergovernmental Panel on Climate Change 4th Assessment Report
HCO <sub>3</sub> <sup>-</sup>	bicarbonate	IPCC-TAR	Intergovernmental Panel on Climate Change 3rd Assessment Report
Hg	mercury	IQR	interquartile range
HNO <sub>2</sub> , HONO	nitrous acid	IR	infrared
HNO <sub>3</sub> , HOONO	nitric acid	ISA	Integrated Science Assessment
HNO <sub>4</sub>	pernitric acid	<i>J</i>	flux from a leaf, deposition flux (g/cm/second)
HO <sub>2</sub>	hydroperoxyl radical	<i>JK</i>	Joyce Kilmer
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide	JPL	Jet Propulsion Laboratory
HO <sub>2</sub> NO <sub>2</sub>	peroxynitric acid	JRGCE	Jasper Ridge Global Climate Change Experiment
HOBr	hypobromous acid	K	potassium
HOCl	hypochlorous acid	K <sup>+</sup>	potassium ion
HOX	hypohalous acid	<i>K<sub>a</sub></i>	dissociation constant
HP	hedonic pricing	<i>K<sub>b</sub></i>	dissociation constant
HSO <sub>3</sub> <sup>-</sup>	bisulfate ion	<i>K<sub>H</sub></i>	Henry's Law constant in M/atm (M•atm <sup>-1</sup> )
HSO <sub>4</sub> <sup>-</sup>	sulfuric acid ion	kmol	kilomole
H <sub>2</sub> S	hydrogen sulfide	KNO <sub>3</sub>	potassium nitrate
H <sub>2</sub> SO <sub>3</sub>	sulfurous acid	K <sub>w</sub>	ion product of water
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid	LAF	Lake Acidification and Fisheries
HUC-8s	8-digit Hydrologic Unit Codes	LAR	leaf-area ratio
hν	energy of photon with frequency ν	LB	laboratory bioassay
I	iodine	LC <sub>0.01</sub>	lethal concentration at which 0.01% of exposed animals die
I <sub>2</sub>	molecular iodine	LD <sub>33</sub>	lethal dose at which 33% of exposed animals die
IA	Integrated Assessment	LDH	lactic acid dehydrogenase
IADN	Integrated Atmospheric Monitoring Deposition Network	LG	Linville Gorge
IC	intracloud (lightning flash)	LIDAR	Light Detection and Ranging (remote sensing system)
ILWAS	Integrated Lake-Watershed Acidification Study	LIF	laser-induced fluorescence
IPC	International Cooperative Programme		
IEc	Industrial Economicsym		
IIASA	International Institute for Applied Systems Analysis		
IMPROVE	Interagency Monitoring of Protected Visual Environments		

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
LIMS	Limb Infrared Monitor of the Stratosphere	MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
LMCO	Lacasse-like multicopper oxidase	MOZART	Model for Ozone and Related Chemical Tracers
LOD	limit of detection	MPAN	peroxymethacrylic nitrate
LP	long-path	MPCA	Minnesota Pollution Control Agency
LRTAP	Long Range Transport of Air Pollution	MSA	metropolitan statistical area
LTER	Long-Term Ecological Research (program)	Mt	million, or mega tons
LTM	Long-Term Monitoring (project)	N	nitrogen
M	air molecule	N, n	number of observations
MA	Millennium Ecosystem Assessment	<sup>14</sup> N	nitrogen-14, stable isotope of nitrogen
MAGIC	Model of Acidification of Groundwater in Catchments (model)	<sup>15</sup> N	nitrogen-15, stable isotope of nitrogen
MAHA	Mid-Atlantic Highlands Assessment of streams	N <sub>2</sub>	molecular nitrogen; nonreactive nitrogen
MAQSIP	Multiscale Air Quality Simulation Platform (model)	N14C	plant soil N and C cycling model
MAT	moist acidic tundra	NA	not available; insufficient data
MAX-DOAS	multiple axis differential optical absorption spectroscopy	Na	sodium
MBC	microbial biomass carbon	Na <sup>+</sup>	sodium ion
MBL	marine boundary layer	NAAQS	National Ambient Air Quality Standards
MDN	Mercury Deposition Network	NaCl	sodium chloride
MeHg	Methylmercury	NADP	National Atmospheric Deposition Program
MEM	model ensemble mean	Na <sub>2</sub> MoO <sub>4</sub>	sodium molybdate
µeq	Microequivalent	NAMS	National Air Monitoring Stations
Mg	Magnesium	NANI	Net anthropogenic nitrogen inputs
Mg <sup>2+</sup>	magnesium ion	NAPAP	National Acid Precipitation Assessment Program
MIMS	membrane inlet mass spectrometry	NASQAN	National Stream Quality Accounting Network
MM5	National Center for Atmospheric Research/Penn State Mesoscale Model, version 5	NARSTO	program formerly known as North American Regional Strategy for Atmospheric Ozone
Mn	Manganese	NAS	National Academy of Sciences
MOBILE6	Highway Vehicle Emission Factor Model	NASA	National Aeronautics and Space Administration
MODIS	Moderate Resolution Imaging Spectroradiometer	Na <sub>2</sub> SO <sub>4</sub>	sodium sulfate
MOPITT	Measurement of Pollution in the Troposphere (satellite instrument)	NASQAN	National Stream Quality Accounting Network

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
NATTS	National Air Toxics Trends (network)	NOAA	U.S. National Oceanic and Atmospheric Administration
NAWQA	National Water Quality Assessment (program)	NOAA-ARL	U.S. National Oceanic and Atmospheric Administration Air Resources Laboratory
NCore	National Core Monitoring Network	NOAEL	no-observed-adverse-effect level
N-dep	nitrogen deposition	NOEC	no-observed-effect concentration
NEE	net ecosystem exchange	NO <sub>x</sub>	sum of NO and NO <sub>2</sub>
NEG/ECP	New England Governors and Eastern Canadian Premiers	NO <sub>y</sub>	sum of NO <sub>x</sub> and NO <sub>z</sub> ; odd nitrogen species; total oxidized nitrogen
NEI	National Emissions Inventory	NO <sub>z</sub>	sum of all inorganic and organic reaction products of NO <sub>x</sub> (HONO, HNO <sub>3</sub> , HNO <sub>4</sub> , organic nitrates, particulate nitrate, nitro-PAHs, etc.)
NEON	National Ecological Observatory Network	NPOESS	National Polar-orbiting Operational Environmental Satellite System
NEP	net ecosystem productivity	NPP	net primary production
N-fert	nitrogen-fertilization	NPS	National Park Service
N-fix	nitrogen-fixing vegetation	Nr	reactive nitrogen
NFI	net factor income	NRC	National Research Council
NH <sub>3</sub>	ammonia	NS or n.s.	nonsignificant
NH <sub>2</sub>	amino (chemical group)	NSF	National Science Foundation
NH <sub>4</sub> <sup>+</sup>	ammonium ion	NSS	National Stream Survey
NH <sub>4</sub> Cl	ammonium chloride	Nss	nonsea salt
NH <sub>4</sub> NO <sub>3</sub>	ammonium nitrate	NSTC	National Science and Technology Council
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	ammonium sulfate	NSWS	National Surface Water Survey
NH <sub>x</sub>	category label for NH <sub>3</sub> plus NH <sub>4</sub> <sup>+</sup>	NTN	National Trends Network
NH <sub>y</sub>	total reduced nitrogen	NuCM	nutrient cycling model
Ni	nickel	O <sub>2</sub>	molecular oxygen
NILU	Norwegian Institute for Air Research	O <sub>3</sub>	ozone
NITREX	Nitrogen saturation Experiments	<sup>16</sup> O	oxygen-16, stable isotope of oxygen
nitro-PAH	nitro-polycyclic aromatic hydrocarbon	<sup>18</sup> O	oxygen-18, stable isotope of oxygen
NLCD	National Land Cover Data	<sup>19</sup> O	oxygen-19, radioactive isotope of oxygen
N <sub>min</sub>	nitrogen mineralization	OC	organic carbon
NMOC	nonmethane organic compound	O-CN	terrestrial biosphere model
NO	nitric oxide	OCO	Orbiting Carbon Observatory
NO <sub>2</sub>	nitrogen dioxide	OCS	carbonyl sulfide
NO <sub>2</sub> <sup>-</sup>	nitrite		
NO <sub>3</sub> <sup>-</sup>	nitrate		
N <sub>2</sub> O	nitrous oxide		
N <sub>2</sub> O <sub>5</sub>	dinitrogen pentoxide		

Acronym/Abbreviation	Meaning	Acronym/Abbreviation	Meaning
O( <sup>1</sup> D)	electronically excited oxygen atom	PM <sub>10-2.5</sub>	particulate matter with aerodynamic diameter between 10 and 2.5 μm
OH	hydroxyl radical	PM-CAMx	Comprehensive Air Quality Model with extensions and with particulate matter chemistry
OM	organic matter	PnET	Photosynthesis and EvapoTranspiration (model)
OMI	Ozone Monitoring Instrument	PnET-BGC	Photosynthesis and EvapoTranspiration-Biogeochemical (model)
O( <sup>3</sup> P)	ground-state oxygen atom	PnET-CN	Photosynthesis and EvapoTranspiration model of C, water, and N balances
P	phosphorus	PnET-N-DNDC	Photosynthesis and EvapoTranspiration-Denitrification-Decomposition (model)
P, p	probability value	pNO <sub>3</sub> <sup>-</sup>	particulate nitrate
P <sub>1</sub>	1st percentile	P(O <sub>3</sub> )	production of O <sub>3</sub>
P <sub>5</sub>	5th percentile	PO <sub>4</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>	phosphate
P <sub>95</sub>	95th percentile	POPs	persistent organic pollutants
P <sub>99</sub>	99th percentile	ppb	parts per billion
PAHs	polycyclic aromatic hydrocarbons	PPN	peroxypropionyl nitrate
PAMS	Photochemical Assessment Monitoring Stations	ppt	parts per trillion
PAN	peroxyacetyl nitrate	PRB	policy relevant background
PANs	peroxyacyl nitrates	PRE-STORM	Preliminary Regional Experiment for STORM
PARASOL	Polarization and Anisotropy of Reflectances for Atmospheric Sciences coupled with Observations from a Lidar (satellite instrument)	PROFILE	model using soil mineralogy as input
Pb	lead	PS	producer surplus
PBL	planetary boundary layer	pSO <sub>4</sub> <sup>2-</sup>	particulate sulfate
PC	payment card	P(SO <sub>4</sub> <sup>2-</sup> )	production of sulfate
PCBs	polychlorinated biphenyl compounds	Q	flow rate; discharge
pH	relative acidity	Q <sub>10</sub>	temperature coefficient
P(HNO <sub>3</sub> )	production of nitric acid	QAPP	Quality Assurance Project Plan
PHREEQC	model for soil and water geochemical equilibrium	R	generic organic group attached to a molecule
PIRLA	Paleoecological Investigation of Recent Lake Acidification (projects)	R <sup>2</sup>	coefficient of determination
pK <sub>a</sub>	dissociation constant	r <sup>2</sup>	correlation coefficient
PM	particulate matter	R <sub>a</sub>	aerodynamic resistance
PM <sub>2.5</sub>	particulate matter with aerodynamic diameter of #2.5 μm	R <sub>aboveground</sub>	aboveground respiration
PM <sub>10</sub>	particulate matter with aerodynamic diameter #10 μm	R <sub>autotrophic</sub>	soil autotrophic respiration
		R <sub>b</sub>	boundary layer resistance

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
<i>R<sub>c</sub></i>	internal resistance	SAO	Smithsonian Astrophysical Observatory
RADM	Regional Acid Deposition Model	SAPRAC	Statewide Air Pollution Research Center
RAMS	Regional Atmospheric Modeling System	SBC	sum of base cation concentrations
RAPS	Regional Air Pollution Study	SBUV	Solar Backscatter Ultraviolet Spectrometer
RCOO-s	strongly acidic organic anions	SC	safe concentration
RC(O)OO	organic peroxy radical	SCAQS	Southern California Air Quality Study
RDT	Recovery Delay Time	SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Cartography
REMAP	Regional Environmental Monitoring and Assessment Program	Se	selenium; standard error
RH	relative humidity	SEARCH	Southeastern Aerosol Research and Characterization Study (monitoring program)
RLTM	Regional Long-Term Monitoring	Si	silicon
<i>R<sub>microbial</sub></i>	microbial respiration	SIP	State Implementation Plan
RMCC	Research and Monitoring Coordinating Committee	SJAQS	San Joaquin Valley Air Quality Study
RMSE	root mean squared error	SLA	specific leaf area
RO <sub>2</sub>	organic peroxy; organic peroxy	SLAMS	State and Local Air Monitoring Stations
RONO <sub>2</sub>	organic nitrate	SMART	Simulation Model for Acidification's Regional Trends (model)
RO <sub>2</sub> NO <sub>2</sub>	peroxynitrate	SMB	Simple Mass Balance (model)
ROS	rain on snow	SMBE	steady-state mass-balance equations
RP	revealed preferences	SO	sulfur monoxide
RR <sub>x</sub>	lognormal-transformed response ratio	SO <sub>2</sub>	sulfur dioxide
RR	response ratio	SO <sub>3</sub>	sulfur trioxide
<i>R<sub>soil</sub></i>	total soil respiration	SO <sub>3</sub> <sup>2-</sup>	sulfite
RuBisCO	ribulose-1,5-bisphosphate carboxylase/oxygenase	SO <sub>4</sub> <sup>2-</sup>	sulfate ion
s	second	S <sub>2</sub> O	disulfur monoxide
S	sulfur	SOM	soil organic matter
<sup>32</sup> S	sulfur-32, stable isotope of sulfur	SONEX	Subsonics Assessment Ozone and Nitrogen Oxides Experiment
<sup>34</sup> S	sulfur-34, stable isotope of sulfur	SOS	Southern Oxidant Study
<sup>35</sup> S	sulfur-35, radioactive isotope of sulfur	SOS/T	State of Science/Technology (report)
SAA	sum of mineral acid anion concentrations	SO <sub>x</sub>	sulfur oxides
SAFE	Soil Acidification in Forest Ecosystems (model)		
SAMAB	Southern Appalachian Man and the Biosphere (program)		
SAMI	Southern Appalachian Mountains Initiative		

<b>Acronym/Abbreviation</b>	<b>Meaning</b>	<b>Acronym/Abbreviation</b>	<b>Meaning</b>
SP	stated preferences	TOR	tropospheric ozone residual
SPARROW	SPATIally Referenced Regressions on Watershed Attributes (model)	TP	total phosphorus
SR	Shining Rock	TRACE-P	Transport and Chemical Evolution over the Pacific
Sr	strontium	TSI	timber-stand improvement
<sup>86</sup> Sr	strontium-86, stable isotope of strontium	TSS	total suspended solids
<sup>87</sup> Sr	strontium-87, stable isotope of strontium	T <sub>water</sub>	water temperature
SRB	sulfate-reducing bacteria	UAN	urea and ammonium nitrate fertilizer
SRP	soluble reactive phosphorus	UMD-CTM	University of Maryland Chemical Transport Model
SSWC	Steady State Water Chemistry (model)	UNECE	United Nations Economic Commission for Europe
STA	Soil Texture Approximations (model)	USDA	U.S. Department of Agriculture
STE	stratospheric-tropospheric exchange	USFS	U.S. Forest Service
STN	Speciation Trends Network	USGS	U.S. Geological Survey
SUM06	seasonal sum of all hourly average concentrations $\geq 0.06$ ppm	UV	ultraviolet
SVOC	semivolatile organic compound	UV-A	ultraviolet radiation of wavelengths from 320 to 400 nm
SWAS	Shenandoah Watershed Study	UV-B	ultraviolet radiation of wavelengths from 280 to 320 nm
T, $\tau$	tau, atmospheric lifetime	v <sub>a</sub>	deposition rate, deposition velocity (cm/s)
T	time; duration of exposure	VOC	volatile organic compound
TAF	Tracking and Analysis Framework (model)	VSD	Very Simple Dynamic (soil acidification model)
T <sub>air</sub>	air temperature	VTSSS	Virginia Trout Stream Sensitivity Study
TAMM	Timber Assessment Market Model	WARMS	Waterfowl Acidification Response Modeling System
TAR	Third Assessment Report	WATERSN	Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen
TC	total carbon; travel cost	WBB	West Bear Brook
TCM	travel cost method	WEBB	Water, Energy, and Biogeochemical Budgets
TDLAS	Tunable Diode Laser Absorption Spectrometer	WFPS	water-filled pore space
Tg	teragram	WGE	Working Group on Effects
TIME	Temporally Integrated Monitoring of Ecosystems (program)	WLS	Western Lakes Survey
TN	total nitrogen	WMO	World Meteorological Organization
TOC	total organic carbon	WMP	Watershed Manipulation Project
TOMS	Total Ozone Mapping Spectrometer	WSA	Wadeable Stream Assessment (survey)

<b>Acronym/Abbreviation</b>	<b>Meaning</b>
wt %	percent by weight
WTA	willingness-to-accept
WTP	willingness-to-pay
XNO <sub>3</sub>	nitrate halogen-X salt
XO	halogen-X oxide
yr	year
Zn	zinc
ZnO	zinc oxide

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# PREFACE

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## Legislative Requirements for the Review of the National Ambient Air Quality Standards

Two sections of the Clean Air Act (CAA) govern the establishment, review, and revision of the National Ambient Air Quality Standards (NAAQS). Section 108 [42 U.S. Code (U.S.C.) 7408] directs the Administrator to identify and list certain air pollutants and then to issue air quality criteria for those pollutants. The Administrator is to list those air pollutants that in their “judgment, cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare,” “the presence of which in the ambient air results from numerous or diverse mobile or stationary sources,” and “for which ... [the Administrator] plans to issue air quality criteria ...” [42 U.S.C. 7408(a)(1); ]. Air quality criteria are intended to “accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare, which may be expected from the presence of [a] pollutant in the ambient air ...” [42 U.S.C. 7408(b)]. Section 109 [42 U.S.C. 7409; [CAA, 1990b](#)] directs the Administrator to propose and promulgate “primary” and “secondary” NAAQS for pollutants for which air quality criteria are issued. Section 109(b)(1) defines a primary standard as one “the attainment and maintenance of which in the judgment of the Administrator, based on such criteria and allowing an adequate margin of safety, are requisite to protect the public health.”<sup>1</sup> A secondary standard, as defined in Section 109(b)(2), must “specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator, based on such criteria, is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of [the] air pollutant in the ambient air.”<sup>2</sup>

In setting standards that are “requisite” to protect public health and welfare as provided in Section 109(b), the U.S. EPA’s task is to establish standards that are neither more nor less stringent than necessary for these purposes. In so doing, the U.S. EPA may not consider the costs of implementing the standards.<sup>3</sup> Likewise, “[a]ttainability and technological

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<sup>1</sup> The legislative history of Section 109 indicates that a primary standard is to be set at “... the maximum permissible ambient air level ... which will protect the health of any [sensitive] group of the population,” and that for this purpose “reference should be made to a representative sample of persons comprising the sensitive group rather than to a single person in such a group” S. Rep. No. 91:1196, 91st Cong., 2d Sess. 10 (1970).

<sup>2</sup> Section 302(h) of the Act [42 U.S.C. 7602(h)] provides that all language referring to effects on welfare includes, but is not limited to, “effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being ...” ([CAA, 2005](#)).

<sup>3</sup> See generally, *Whitman v. American Trucking Associations*, 531 U.S. 457, 465–472, 475–476 (2001).

feasibility are not relevant considerations in the promulgation of national ambient air quality standards.”<sup>1</sup>

Section 109(d)(1) requires that “not later than December 31, 1980, and at 5-year intervals thereafter, the Administrator shall complete a thorough review of the criteria published under Section 108 and the national ambient air quality standards ... and shall make such revisions in such criteria and standards and promulgate such new standards as may be appropriate ....” Section 109(d)(2) requires that an independent scientific review committee “shall complete a review of the criteria ... and the national primary and secondary ambient air quality standards ... and shall recommend to the Administrator any new ... standards and revisions of existing criteria and standards as may be appropriate ....” Since the early 1980s, this independent review function has been performed by the Clean Air Scientific Advisory Committee (CASAC).<sup>2</sup>

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## **Overview and History of the Reviews of the Secondary National Ambient Air Quality Standards for Nitrogen Dioxide, Sulfur Dioxide, and Particulate Matter**

NAAQS are defined by four basic elements: indicator, averaging time, level, and form. The indicator defines the pollutant to be measured in the ambient air for the purpose of determining compliance with the standard. The averaging time defines the time period over which air quality measurements are to be obtained and averaged or cumulated, considering evidence of effects associated with various time periods of exposure. The level of a standard defines the air quality concentration used (i.e., an ambient concentration of the indicator pollutant) in determining whether the standard is achieved. The form of the standard defines the air quality statistic that is compared to the level of the standard in determining whether an area attains the standard. The Administrator considers these four elements collectively in evaluating the protection to public health provided by the primary NAAQS.

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### **Nitrogen Dioxide Secondary National Ambient Air Quality Standards**

The first air quality criteria and standards for oxides of nitrogen were issued in 1971 [[U.S. EPA, 1971](#)], 36 FR 8186]. Both the primary and secondary standards were set at 0.053 parts per million (ppm), as an annual arithmetic mean (36 FR 8186). In 1982, the U.S. EPA published Air Quality Criteria for Oxides of Nitrogen ([U.S. EPA, 1982a](#)),

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<sup>1</sup> See *American Petroleum Institute v. Costle*, 665 F. 2d at 1185.

<sup>2</sup> Lists of chartered CASAC members and of members of the CASAC Panels are available at: <http://yosemite.epa.gov/sab/sabproduct.nsf/WebCASAC/CommitteesandMembership?OpenDocument>.

which updated the scientific criteria upon which the initial standards were based. On February 23, 1984, the U.S. EPA proposed to retain these standards (49 FR 6866). After taking into account public comments, the U.S. EPA published the final decision to retain the existing standards on June 19, 1985 (50 FR 25532).

In November 1991, the U.S. EPA initiated another review and released an updated draft air quality criteria document (AQCD) for review and comment by CASAC and the public (56 FR 59285). The final AQCD was released later in 1993 ([U.S. EPA, 1993](#)). Staff of the Office of Air Quality Planning and Standards (OAQPS) prepared a draft Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised air quality criteria document and identified the critical elements to be considered in the review of the NO<sub>2</sub> NAAQS. The Staff Paper was reviewed by the CASAC and the public in December 1994, and in September 1995, the U.S. EPA finalized the Staff Paper ([U.S. EPA, 1995b](#)). On October 2, 1995, the Administrator announced her proposed decision not to revise either the primary or secondary NAAQS for NO<sub>2</sub> based on the information available in this review (60 FR 52874; October 11, 1995). After consideration of public comments, the Administrator made a final determination that revisions to neither the primary nor the secondary NAAQS for NO<sub>2</sub> were appropriate at that time (61 FR 52852; October 8, 1996).

The most recent review of the secondary NAAQS standards for oxides of nitrogen was performed jointly with a review of the secondary NAAQS for oxides of sulfur beginning in 2005 (described below).

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## **Sulfur Dioxide Secondary National Ambient Air Quality Standards**

Based on the 1969 sulfur oxides criteria document ([HEW, 1969](#)), the U.S. EPA promulgated the initial primary and secondary NAAQS for SO<sub>2</sub> on April 30, 1971 (36 FR 8186). The secondary standards were 0.02 ppm as an annual arithmetic mean and 0.5 ppm as a maximum 3-hour, not to be exceeded more than once per year. These secondary standards were established on the basis of vegetation effects evidence described in the 1970 criteria document. Based on additional data available in 1973, revisions were made to Chapter 5 “Effects of Sulfur Oxide in the Atmosphere on Vegetation” of the *Air Quality Criteria for Sulfur Oxides* ([U.S. EPA, 1973](#)), which led the U.S. EPA to propose (38 FR 11355) and then finalize a revocation of the annual mean secondary standard (38 FR 25678). At that time, the U.S. EPA additionally considered welfare effects related to effects on materials, visibility, soils, and water. However, the U.S. EPA concluded that either protection from such effects was afforded by the primary

standard or that sufficient data were not then available to develop criteria for standards based on these effects (38 FR 25680).

In 1980, the U.S. EPA released a combined AQCD for sulfur oxides and particulate matter for CASAC review. Following its review of a draft revised criteria document in August 1980, the CASAC concluded that acidic deposition was a topic of extreme scientific complexity, noting that a fundamental problem of addressing acid deposition in a criteria document is that acidic deposition is produced by several pollutants, including oxides of sulfur, oxides of nitrogen, and the fine particulate fraction of suspended particles [(U.S. EPA, 1982b), pp. 125–126]. Following CASAC closure on the criteria document in December 1981, the U.S. EPA released a final AQCD (U.S. EPA, 1982b), and the OAQPS prepared a Staff Paper that was released in November 1982 (U.S. EPA, 1982c). The issue of acidic deposition was not, however, assessed directly in the OAQPS Staff Paper because the U.S. EPA followed the guidance given by CASAC.

In response to CASAC recommendations for a separate comprehensive discussion of acidic deposition as part of the criteria documents, the U.S. EPA subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (U.S. EPA, 1984a, b) and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* [(Bennett et al., 1985); 53 FR 14935–14936]. Although these documents were not considered criteria documents and had not undergone CASAC review, they represented the most comprehensive summary of relevant scientific information completed by the U.S. EPA at that point (58 FR 21355).

At about the same time in 1980 as the CASAC recommendation for a comprehensive assessment of acidic deposition, Congress created the National Acid Precipitation Assessment Program (NAPAP). During the 10-year course of this program, a series of reports were issued and a final report was issued in 1990 (NAPAP, 1991).

On April 26, 1988, the U.S. EPA proposed not to revise the existing primary and secondary standards. This proposal regarding the secondary SO<sub>2</sub> NAAQS was due to the Administrator's conclusions that (1) based upon the then-current scientific understanding of the acidic deposition problem, it would be premature and unwise to prescribe any regulatory control program at that time and (2) when the fundamental scientific uncertainties had been reduced through ongoing research efforts, the U.S. EPA would draft and support an appropriate set of control measures (53 FR 14926). Subsequent to proposal, Congress took up consideration of acidic deposition.

On November 15, 1990, Amendments to the CAA were passed by Congress and signed into law by the President. In Title IV of these Amendments, Congress included a

statement of findings that had led them to take this action, including that: “(1) the presence of acidic compounds and their precursors in the atmosphere and in deposition from the atmosphere represents a threat to natural resources, ecosystems, materials, visibility, and public health; (2) the problem of acid deposition is of national and international significance; and that (3) current and future generations of Americans will be adversely affected by delaying measures to remedy the problem...” The goal of Title IV was to reduce emissions of SO<sub>2</sub> by 10 million tons and oxides of nitrogen emissions by 2 million tons from 1980 emission levels in order to achieve reductions over broad geographic regions/areas. In envisioning that further action might be necessary in the long term, Congress included Section 404 of the 1990 Amendments. This section requires the U.S. EPA to conduct a study on the feasibility and effectiveness of an acid deposition standard or standards to protect “sensitive and critically sensitive aquatic and terrestrial resources” and at the conclusion of the study, submit a report to Congress. Five years later, the U.S. EPA submitted to Congress its report titled *Acid Deposition Standard Feasibility Study: Report to Congress* ([U.S. EPA, 1995a](#)) in fulfillment of this requirement. The Report to Congress concluded that establishing acid deposition standards for sulfur and nitrogen deposition might at some point in the future be technically feasible although appropriate deposition loads for these acidifying chemicals could not be defined with reasonable certainty at that time.

The 1990 Amendments also added new language to sections of the CAA that pertain to the scope or application of the secondary NAAQS designed to protect the public welfare. Section 108 (g) specified that “the Administrator may assess the risks to ecosystems from exposure to criteria air pollutants (as identified by the Administrator in the Administrator’s sole discretion).” The definition of public welfare in Section 302 (h) was expanded to state that the welfare effects identified should be protected from adverse effects associated with criteria air pollutants “...whether caused by transformation, conversion, or combination with other air pollutants.”

In response to these legislative initiatives, the U.S. EPA and other federal agencies continued research on the causes and effects of acidic deposition and related welfare effects of SO<sub>2</sub> and implemented an enhanced monitoring program to track progress (58 FR 21357). In 1993, the U.S. EPA announced a decision not to revise the secondary standard, concluding that revision to address acidic deposition and related SO<sub>2</sub> welfare effects was not appropriate at that time (58 FR 21351). In reaching this decision, the U.S. EPA took into account the significant reductions in SO<sub>2</sub> emissions, ambient SO<sub>2</sub> concentrations and ultimately deposition expected to result from implementation of the Title IV program, which was expected to significantly decrease the acidification of water bodies and damage to forest ecosystems and to permit much of the existing damage to be reversed with time (58 FR 21357). While recognizing that further action might be needed

to address acidic deposition in the longer term, the U.S. EPA judged it prudent to await the results of the studies and research programs then underway, including those assessing the comparative merits of secondary standards, acidic deposition standards, and other approaches to control of acidic deposition and related effects, and then to determine whether additional control measures should be adopted or recommended to Congress (58 FR 21358).

In 2000, the U.S. EPA announced receipt of two items related to acidic deposition and the NAAQS (65 FR 48699). The first was a petition submitted to the U.S. EPA in 1999 by representatives of seven northeastern states for the promulgation of revised secondary NAAQS for the criteria pollutants associated with the formation of acid rain (including NO<sub>2</sub>, SO<sub>2</sub>, and fine particulate matter [PM<sub>2.5</sub>]). The petition states that the language in Section 302(h) of the CAA “clearly references the transformation of pollutants resulting in the inevitable formation of sulfate and nitrate aerosols and/or their ultimate environmental impacts as wet and dry deposition, clearly signaling Congressional intent that the welfare damage occasioned by sulfur and nitrogen oxides be addressed through the secondary standard provisions of Section 109 of the Act.” The petition further stated that “recent federal studies, including the NAPAP Biennial Report to Congress: An Integrated Assessment, document the continued—and increasing—damage being inflicted by acid deposition to the lakes and forests of New York, New England, and other parts of our nation, demonstrating that the Title IV program had proven insufficient.” The petition also listed other adverse welfare effects associated with the transformation of these criteria pollutants, including visibility impairment, eutrophication of coastal estuaries, global warming, tropospheric ozone, and stratospheric ozone depletion.

The second item was a related request from the U.S. Department of Interior (DOI) that the U.S. EPA address many of the same adverse environmental effects associated with the same types of air pollutants and with ozone that the DOI asserted were occurring in national parks and wilderness areas (65 FR 48699). Included among the effects of concern identified in the request were acidification of streams, surface waters and/or soils, eutrophication of coastal waters, visibility impairment, and foliar injury from ozone (65 FR 48701). The U.S. EPA requested comment on the issues raised by these requests, stating that it would consider any relevant comments and information submitted, along with the information provided by the petitioners and DOI, before making any decision concerning a response to these requests for rulemaking, which if commenced would include opportunity for public review and comment (65 FR 48701).

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## Particulate Matter Secondary National Ambient Air Quality Standards

The U.S. EPA first established NAAQS for particulate matter (PM) in 1971 (36 FR 8186, April 30, 1971) based on the original AQCD ([NAPCA, 1969](#)). The AQCD assessed the evidence for a variety of PM-associated welfare effects, including visibility impairment and materials damage (e.g., soiling, corrosion). Based on evidence for such effects, the secondary standards were set at 150  $\mu\text{g}/\text{m}^3$  for the 24-hour average not to be exceeded more than once per year and 60  $\mu\text{g}/\text{m}^3$  for the annual geometric mean. The federal reference method (FRM) specified for determining attainment of the original standards was the high-volume sampler, which collects PM up to a nominal size of 25 to 45 micrometers ( $\mu\text{m}$ ; referred to as total suspended particulates or TSP).

In October 1979 (44 FR 56730; October 2, 1979), the U.S. EPA announced the first periodic review of the air quality criteria and NAAQS for PM. Revised primary and secondary standards were promulgated in 1987 (52 FR 24634; July 1, 1987). In the 1987 decision, the U.S. EPA changed the indicator for particles from TSP to  $\text{PM}_{10}$  to focus on the subset of inhalable particles small enough to penetrate to the thoracic region of the respiratory tract (including the tracheobronchial and alveolar regions) referred to as thoracic particles.<sup>1</sup> The level of the 24-hour standards (primary and secondary) was set at 150  $\mu\text{g}/\text{m}^3$ , and the form was one expected exceedance per year, on average, over 3 years. The level of the annual standards (primary and secondary) was set at 50  $\mu\text{g}/\text{m}^3$ , and the form was annual arithmetic mean averaged over 3 years.

In April 1994, the U.S. EPA announced its plans for the second periodic review of the air quality criteria and NAAQS for PM, and in 1997, the U.S. EPA promulgated revisions to the NAAQS (62 FR 38652, July 18, 1997). In the 1997 decision, the U.S. EPA determined that the fine and coarse fractions of  $\text{PM}_{10}$  should be considered separately. This determination was based on evidence that serious health effects were associated with short- and long-term exposures to fine particles in areas that met the existing  $\text{PM}_{10}$  standards. The U.S. EPA added new standards using  $\text{PM}_{2.5}$  as the indicator for fine particles (with  $\text{PM}_{2.5}$  referring to particles with a nominal mean aerodynamic diameter less than or equal to 2.5  $\mu\text{m}$ ). These new standards were as follows: (1) an annual standard with a level of 15.0  $\mu\text{g}/\text{m}^3$  based on the 3-year average of annual arithmetic mean  $\text{PM}_{2.5}$  concentrations from single or multiple community-oriented monitors and (2) a 24-hour standard with a level of 65  $\mu\text{g}/\text{m}^3$  based on the 3-year average of the 98th percentile of 24-hour  $\text{PM}_{2.5}$  concentrations at each monitor within an area. Also, the

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<sup>1</sup>  $\text{PM}_{10}$  refers to particles with a nominal mean aerodynamic diameter less than or equal to 10  $\mu\text{m}$ . More specifically, 10  $\mu\text{m}$  is the aerodynamic diameter for which the efficiency of particle collection is 50%. Larger particles are not excluded altogether but are collected with substantially decreasing efficiency while smaller particles are collected with increasing efficiency.

U.S. EPA established a new reference method for the measurement of PM<sub>2.5</sub> in the ambient air and adopted rules for determining attainment of the new standards. To continue to address the coarse fraction of PM<sub>10</sub> (referred to as thoracic coarse particles or PM<sub>10-2.5</sub>; generally including particles with a nominal mean aerodynamic diameter greater than 2.5 µm and less than or equal to 10 µm), the U.S. EPA retained the annual PM<sub>10</sub> standard and revised the form of the 24-hour PM<sub>10</sub> standard to be based on the 99th percentile of 24-hour PM<sub>10</sub> concentrations at each monitor in an area. The U.S. EPA revised the secondary standards by setting them equal in all respects to the primary standards.

Following promulgation of the 1997 PM NAAQS, petitions for review were filed by a large number of parties, addressing a broad range of issues. In May 1999, the U.S. Court of Appeals for the District of Columbia Circuit (D.C. Circuit) upheld the U.S. EPA's decision to establish fine particle standards, holding that "the growing empirical evidence demonstrating a relationship between fine particle pollution and adverse health effects amply justifies establishment of new fine particle standards." *American Trucking Associations v. EPA*, 175 F. 3d 1027, 1055–56 (D.C. Cir., 1999). The D.C. Circuit also found "ample support" for the U.S. EPA's decision to regulate coarse particle pollution, but vacated the 1997 PM<sub>10</sub> standards, concluding that the U.S. EPA had not provided a reasonable explanation justifying use of PM<sub>10</sub> as an indicator for coarse particles (175 F. 3d at 1054–55). Pursuant to the D.C. Circuit's decision, the U.S. EPA removed the vacated 1997 PM<sub>10</sub> standards, and the pre-existing 1987 PM<sub>10</sub> standards remained in place (65 FR 80776, December 22, 2000). The D.C. Circuit also upheld the U.S. EPA's determination not to establish more stringent secondary standards for fine particles to address effects on visibility (175 F. 3d at 1027).

The D.C. Circuit also addressed more general issues related to the NAAQS, including issues related to the consideration of costs in setting NAAQS and the U.S. EPA's approach to establishing the levels of NAAQS. Regarding the cost issue, the court reaffirmed prior rulings holding that in setting NAAQS the U.S. EPA is "not permitted to consider the cost of implementing those standards" (Id. at 1040–41). Regarding the levels of NAAQS, the court held that the U.S. EPA's approach to establishing the level of the standards in 1997 (i.e., both for PM and for the ozone NAAQS promulgated on the same day) effected "an unconstitutional delegation of legislative authority" (Id. at 1034–40). Although the court stated that "the factors U.S. EPA uses in determining the degree of public health concern associated with different levels of ozone and PM are reasonable," it remanded the rule to the U.S. EPA, stating that when the U.S. EPA considers these factors for potential nonthreshold pollutants "what U.S. EPA lacks is any determinate criterion for drawing lines" to determine where the standards should be set.

The D.C. Circuit's holding on the cost and constitutional issues were appealed to the U.S. Supreme Court. In February 2001, the Supreme Court issued a unanimous decision upholding the U.S. EPA's position on both the cost and constitutional issues. *Whitman v. American Trucking Associations*, 531 U.S. 457, 464, 475–76. On the constitutional issue, the Court held that the statutory requirement that NAAQS be “requisite” to protect public health with an adequate margin of safety sufficiently guided the U.S. EPA's discretion, affirming the U.S. EPA's approach of setting standards that are neither more nor less stringent than necessary.<sup>1</sup>

In October 1997, the U.S. EPA published its plans for the third periodic review of the air quality criteria and NAAQS for PM (62 FR 55201; October 23, 1997). On September 21, 2006, the U.S. EPA announced its final decisions to revise the primary and secondary NAAQS for PM to provide increased protection of public health and welfare, respectively (71 FR 61144; October 17, 2006). With regard to the primary and secondary standards for fine particles, the U.S. EPA revised the level of the 24-hour PM<sub>2.5</sub> standards to 35 µg/m<sup>3</sup>, retained the level of the annual PM<sub>2.5</sub> standards at 15.0 µg/m<sup>3</sup>, and revised the form of the annual PM<sub>2.5</sub> standards by narrowing the constraints on the optional use of spatial averaging. With regard to the primary and secondary standards for PM<sub>10</sub>, the U.S. EPA retained the 24-hour standards, with levels at 150 µg/m<sup>3</sup>, and revoked the annual standards.<sup>2</sup> The Administrator judged that the available evidence generally did not suggest a link between long-term exposure to existing ambient levels of coarse particles and health or welfare effects. In addition, a new reference method was added for the measurement of PM<sub>10-2.5</sub> in the ambient air, in order to provide a basis for approving federal equivalent methods (FEMs) and to promote the gathering of scientific data to support future reviews of the PM NAAQS.

Several parties filed petitions for review following promulgation of the revised PM NAAQS in 2006. These petitions addressed the following issues: (1) selecting the level of the primary annual PM<sub>2.5</sub> standard; (2) retaining PM<sub>10</sub> as the indicator of a standard for

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<sup>1</sup> The Supreme Court remanded the case to the Court of Appeals for resolution of any remaining issues that had not been addressed in that court's earlier rulings (Id. at 475–76). In a March 2002 decision, the Court of Appeals rejected all remaining challenges to the standards, holding that the U.S. EPA's PM<sub>2.5</sub> standards were reasonably supported by the administrative record and were not “arbitrary and capricious” *American Trucking Associations v. EPA*, 283 F. 3d 355, 369–72 (D.C. Cir. 2002).

<sup>2</sup> In the 2006 proposal, the U.S. EPA proposed to revise the 24-hour PM<sub>10</sub> standard in part by establishing a new PM<sub>10-2.5</sub> indicator for thoracic coarse particles (i.e., particles generally between 2.5 and 10 µm in diameter). The U.S. EPA proposed to include any ambient mix of PM<sub>10-2.5</sub> that was dominated by resuspended dust from high density traffic on paved roads and by PM from industrial and construction sources. The U.S. EPA proposed to exclude any ambient mix of PM<sub>10-2.5</sub> that was dominated by rural windblown dust and soils and by PM generated from agricultural and mining sources. In the final decision, the existing PM<sub>10</sub> standard was retained, in part due to an “inability...to effectively and precisely identify which ambient mixes are included in the [PM<sub>10-2.5</sub>] indicator and which are not” (71 FR 61197; October 17, 2006).

thoracic coarse particles, retaining the level and form of the 24-hour PM<sub>10</sub> standard, and revoking the PM<sub>10</sub> annual standard; and (3) setting the secondary PM<sub>2.5</sub> standards identical to the primary standards. On February 24, 2009, the U.S. Court of Appeals for the District of Columbia Circuit issued its opinion in the case *American Farm Bureau Federation v. EPA*, 559 F. 3d 512 (D.C. Cir. 2009). The court remanded the primary annual PM<sub>2.5</sub> NAAQS to the U.S. EPA because the U.S. EPA failed to adequately explain why the standards provided the requisite protection from both short- and long-term exposures to fine particles, including protection for at-risk populations (*American Farm Bureau Federation v. EPA*, 559 F. 3d 512, 520–27; D.C. Cir. 2009). With regard to the standards for PM<sub>10</sub>, the court upheld the U.S. EPA’s decisions to retain the 24-hour PM<sub>10</sub> standard to provide protection from thoracic coarse particle exposures and to revoke the annual PM<sub>10</sub> standard (*American Farm Bureau Federation*, 559 F. 2d at 533–38). With regard to the secondary PM<sub>2.5</sub> standards, the court remanded the standards to the U.S. EPA because the Agency failed to adequately explain why setting the secondary PM standards identical to the primary standards provided the required protection for public welfare, including protection from visibility impairment (*American Farm Bureau Federation*, 559 F. 2d at 528–32). The U.S. EPA responded to the court’s remands as part of the next review of the PM NAAQS, which was initiated in 2007.

In June 2007, the U.S. EPA initiated the fourth periodic review of the air quality criteria and the PM NAAQS by issuing a call for information in the *Federal Register* (72 FR 35462; June 28, 2007). In December 2012, the U.S. EPA announced its final decisions with regard to the secondary PM standards, the U.S. EPA retained the 24-hour and annual PM<sub>2.5</sub> standards and the 24-hour PM<sub>10</sub> standard to address visibility and nonvisibility welfare effects. On judicial review, the revised standards were upheld in all respects (*NAM v EPA*, 750 F.3d 921; D.C. Cir. 2014).

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### **Combined Review of the Oxides of Nitrogen and Oxides of Sulfur National Ambient Air Quality Standards**

In 2005, the U.S. EPA initiated a joint review of the air quality criteria for oxides of nitrogen and sulfur and the secondary NAAQS for NO<sub>2</sub> and SO<sub>2</sub>. In so doing, the U.S. EPA assessed the scientific information, associated risks, and standards relevant to protecting the public welfare from adverse effects associated jointly with oxides of nitrogen and sulfur. Although the U.S. EPA has historically adopted separate secondary standards for oxides of nitrogen and oxides of sulfur, the U.S. EPA conducted a joint review of these standards because oxides of nitrogen and sulfur and their associated transformation products are linked from an atmospheric chemistry perspective, as well as from an environmental effects perspective. The joint review was also responsive to the

National Research Council (NRC) recommendation for the U.S. EPA to consider multiple pollutants, as appropriate, in forming the scientific basis for the NAAQS ([NRC, 2004](#)).

The review was initiated on December 13, 2005 with a call for information (70 FR 73236) for the development of a revised ISA. A draft Integrated Review Plan (IRP) was released in October 2007, reviewed by CASAC; the final IRP was released in December 2007 ([U.S. EPA, 2007](#)). The first and second drafts of the ISA were released in December 2007 and August 2008 (73 FR 10243), respectively, for CASAC and public review. The final ISA ([U.S. EPA, 2008a](#)) was released in December 2008 (73 FR 75716).

Based on the scientific information in the ISA, the U.S. EPA developed a Risk and Exposure Assessment (REA) to further assess the national impact of the effects documented in the ISA. The Draft Scope and Methods Plan for Risk/Exposure Assessment: Secondary NAAQS Review for Oxides of Nitrogen and Oxides of Sulfur outlining the scope and design of the future REA was released in March 2008 (73 FR 10243). A first and second draft of the REA were released (August 2008 and June 2009) for CASAC review and public comment. The final REA ([U.S. EPA, 2009c](#)) was released in September 2009. Drawing on the information in the final REA and ISA, a first draft, second draft, and final Policy Assessment (PA) were released in March 2010, September 2010, and January 2011, respectively ([U.S. EPA, 2011a](#)).

On August 1, 2011, based on consideration of the scientific information and quantitative assessments, the U.S. EPA published a proposal to (1) retain the existing NO<sub>2</sub> and SO<sub>2</sub> secondary standards, (2) add secondary standards identical to the NO<sub>2</sub> and SO<sub>2</sub> primary 1-hour standards, and (3) not set a new multipollutant secondary standard in this review. After consideration of public comments on the proposed standards and on design of a new field pilot program to gather and analyze additional relevant data, the Administrator signed a final decision in this rulemaking on March 20, 2012. The Administrator's decision was that, while the current secondary standards were inadequate to protect against adverse effects from deposition of oxides of nitrogen and sulfur, it was not appropriate under Section 109(b) to set any new secondary standards at this time due to the limitations in the available data and uncertainty as to the amount of protection the metric developed in the review would provide against acidification effects across the country (77 FR 20281). In addition, the Administrator decided that it was appropriate to retain the current NO<sub>2</sub> and SO<sub>2</sub> secondary standards to address direct effects of gaseous NO<sub>2</sub> and SO<sub>2</sub> on vegetation. Thus, taken together, the Administrator decided to retain and not revise the current NO<sub>2</sub> and SO<sub>2</sub> secondary standards: an NO<sub>2</sub> standard set at a level of 0.053 ppm as an annual arithmetic average, and an SO<sub>2</sub> standard set at a level of 0.5 ppm as a 3-hour average, not to be exceeded more than once per year (77 FR 20281).

The U.S. EPA's decision to not set a secondary NAAQS for oxides of nitrogen and sulfur even though the Administrator had concluded that the existing standards are not adequate to protect against the adverse impacts of aquatic acidification on sensitive ecosystems was challenged by the Center for Biological Diversity and other environmental groups. The petitioners argued that having decided that the existing standards were not adequate to protect against adverse public welfare effects such as damage to sensitive ecosystems, the Administrator was required to identify the requisite level of protection for the public welfare and to issue a NAAQS to achieve and maintain that level of protection. The D.C. Circuit disagreed, finding that the U.S. EPA acted appropriately in not setting a secondary standard given the U.S. EPA's conclusions that "the available information was insufficient to permit a reasoned judgment about whether any proposed standard would be 'requisite to protect the public welfare ...'" (*Center for Biological Diversity, et al. v. EPA*, 749 F.3d 1079, 1087; 2014). In reaching this decision, the court noted that the U.S. EPA had "explained in great detail" the profound uncertainties associated with setting a secondary NAAQS to protect against aquatic acidification.

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# EXECUTIVE SUMMARY

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## ES.1 Purpose and Scope of the Integrated Science Assessment

This *Integrated Science Assessment (ISA) for Oxides of Nitrogen, Oxides of Sulfur, and Particulate Matter—Ecological Criteria* is a comprehensive evaluation and synthesis of the most policy-relevant science aimed at characterizing the ecological effects caused by these criteria pollutants.<sup>1</sup> These criteria pollutants are reviewed here together because they all contribute to nitrogen (N) and sulfur (S) deposition, which causes substantial ecological effects. In this document, the term “oxides of nitrogen” refers to total oxidized N ( $\text{NO}_Y$ ), including nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) and all other gaseous and particulate oxidized N containing compounds formed from NO and  $\text{NO}_2$ .<sup>2</sup> Total sulfur oxides ( $\text{SO}_X$ ) includes gaseous chemical species (e.g., sulfur dioxide [ $\text{SO}_2$ ], sulfur monoxide [SO], disulfur monoxide [ $\text{S}_2\text{O}$ ], and sulfur trioxide [ $\text{SO}_3$ ]) as well as particulate species, such as ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ] ([U.S. EPA, 2011a](#)). Particulate species include  $\text{SO}_X$  species like sulfites ( $\text{SO}_3^{2-}$ ) and sulfates ( $\text{SO}_4^{2-}$ ), but among these two species usually only  $\text{SO}_4^{2-}$  make a major contribution to particulate mass. Throughout this document  $\text{SO}_X$  is defined as the sum of  $\text{SO}_2$  and particulate sulfate ( $\text{SO}_4^{2-}$ ), which together represent virtually all of the  $\text{SO}_X$  mass in the atmosphere.<sup>3</sup> Particulate matter (PM) is composed of some or all of the following components: nitrate ( $\text{NO}_3^-$ ),  $\text{SO}_4^{2-}$ , ammonium ( $\text{NH}_4^+$ ), metals, minerals (dust), and organic and elemental carbon.

This ISA serves as the scientific foundation for the review of the ecological effects associated with the secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for  $\text{NO}_Y$ ,  $\text{SO}_X$ , and PM. The health effects of these criteria pollutants are considered in separate assessments for  $\text{NO}_Y$  ([U.S. EPA, 2016f](#)),  $\text{SO}_X$  ([U.S. EPA, 2016e](#)), and PM ([U.S. EPA, 2019](#)).<sup>4</sup> The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and

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<sup>1</sup> The general process for developing an ISA, including the framework for evaluating weight of evidence and drawing scientific conclusions and causal judgments, is described in a companion document, *Preamble to the Integrated Science Assessments* ([U.S. EPA, 2015e](#)), [www.epa.gov/isa](http://www.epa.gov/isa).

<sup>2</sup> This ISA reserves the abbreviation  $\text{NO}_X$  strictly as the sum of NO and  $\text{NO}_2$ —consistent with its use in the atmospheric science community—and uses the term “oxides of nitrogen” to refer to the broader list of oxidized nitrogen species. Oxides of nitrogen refers to  $\text{NO}_Y$  as the total oxidized nitrogen in both gaseous and particulate forms. The major gaseous and particulate constituents of  $\text{NO}_Y$  include nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ ), nitric acid ( $\text{HNO}_3$ ), peroxyacetyl nitrate (PAN), nitrous acid (HONO), organic nitrates, and particulate nitrate ( $\text{NO}_3^-$ ). This ISA uses the definitions adopted by the atmospheric sciences community.

<sup>3</sup> The same definition of  $\text{SO}_X$  used in the 2011  $\text{NO}_X\text{SO}_X$  Policy Assessment ([U.S. EPA, 2011a](#)).

<sup>4</sup> In this ISA, the blue electronic links can be used to navigate to cited materials as well as appendices, sections, tables, figures, and studies from this ISA.

climate, as well as effects on man-made materials, economic values, and personal comfort and well-being.

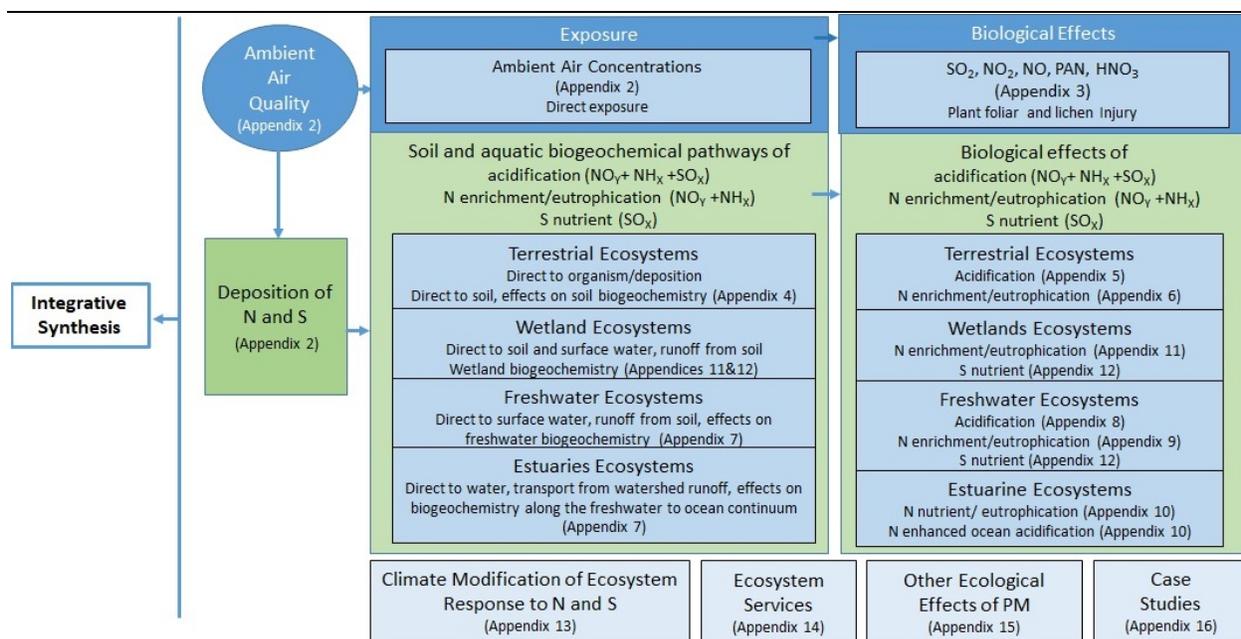
The current secondary NAAQS for NO<sub>Y</sub> and SO<sub>X</sub> were set to protect against direct damage to vegetation by NO<sub>2</sub> or SO<sub>2</sub>. The secondary NAAQS for NO<sub>2</sub> is identical to the primary standard set in 1971: an annual average not to exceed 0.053 ppm N dioxide. The secondary NAAQS for SO<sub>2</sub>, set in 1973, is a 3-hour average of 0.5 ppm SO<sub>2</sub>, not to be exceeded more than once per year. The current secondary standards for PM are intended to address PM-related visibility and nonvisibility welfare effects. These standards are a 3-year annual mean PM<sub>2.5</sub> concentration of 15 µg/m<sup>3</sup>, with the 24-hour average PM<sub>2.5</sub> and PM<sub>10</sub> set at concentrations of 35 µg/m<sup>3</sup> and 150 µg/m<sup>3</sup>, respectively.

This ISA updates the 2008 *ISA for Oxides of Nitrogen and Oxides of Sulfur—Ecological Criteria* [hereafter referred to as 2008 ISA ([U.S. EPA, 2008a](#))], as well as the ecological portion of the 2009 *ISA for Particulate Matter* ([U.S. EPA, 2009a](#)) with studies and reports published from January 2008 through May 2017. There are some studies included that were published more recently than the May 2017 literature cutoff date; these studies were added based on recommendations from the Clean Air Scientific Advisory Committee (CASAC). The U.S. EPA conducted in-depth searches to identify peer-reviewed literature on relevant topics. Subject-matter experts and the public were also able to recommend studies and reports during a kick-off workshop held by the U.S. EPA in March 2014 for NO<sub>Y</sub> and SO<sub>X</sub> and in June 2016 for PM. CASAC recommended the inclusion of additional studies during the review of the first draft. To fully describe the state of available science, the U.S. EPA also carried over the most relevant studies from previous assessments to include in this ISA.

This ISA determines whether NO<sub>Y</sub>, SO<sub>X</sub>, and PM concentrations in the air or deposition from the air cause ecological effects. The ecological effects of deposition are grouped into three main categories: (1) acidification (caused by gaseous NO<sub>Y</sub>, SO<sub>X</sub>, and particulate NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), (2) N enrichment/N driven eutrophication (caused by gaseous NO<sub>Y</sub> and particulate NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>), and (3) S enrichment (caused by SO<sub>X</sub> and particulate forms of SO<sub>4</sub><sup>2-</sup>). Ecological effects are further subdivided into terrestrial, wetland, freshwater, and estuarine/near-coastal ecosystems. These ecosystems and effects are linked by the connectivity of terrestrial and aquatic habitats through biogeochemical pathways of N and S.

A schematic of the document organization is given by [Figure ES-1](#). The [Integrated Synthesis](#) (IS) brings together key information on specific subject matter found in the appendices. [Appendix 1](#) is an introduction to the purpose and organization of the material covered in [Appendix 2–Appendix 16](#). [Appendix 2](#) characterizes the sources and atmospheric processes involving NO<sub>Y</sub>, SO<sub>X</sub>, and PM, as well as trends in ambient

concentrations and deposition. [Appendix 3](#) describes direct effects of gas-phase NO<sub>y</sub> and SO<sub>x</sub> on plants and lichens. [Appendix 4](#) describes N and S deposition effects on terrestrial biogeochemistry, and [Appendix 5](#) and [Appendix 6](#) describe the biological effects of terrestrial acidification and terrestrial N enrichment, respectively. [Appendix 7](#) describes N and S deposition effects on aquatic biogeochemistry. [Appendix 8](#) through [Appendix 10](#) characterize the biological effects of freshwater acidification, freshwater N enrichment, and marine eutrophication, respectively. [Appendix 11](#) describes the effects of N deposition on wetlands. [Appendix 12](#) describes the wetland and freshwater effects of S enrichment. [Appendix 13](#) discusses the climate modification of ecosystem response to N and S deposition, and [Appendix 14](#) presents information on N and S deposition effects on ecosystem services. Information on the ecological effects of forms of PM beyond those related to N or S deposition is presented in [Appendix 15](#) (the nonecological welfare effects associated with PM, such as visibility, climate, and material effects, are considered as part of a separate review of PM [81 FR 87933, December 6, 2016]). [Appendix 16](#) includes six locations in the U.S. selected as case study areas that are candidates for additional analysis of risk and exposure. These candidate sites were selected because they have abundant data on ecological effects.



HNO<sub>3</sub> = nitric acid; N = nitrogen; NH<sub>x</sub> = reduced nitrogen; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; NO<sub>y</sub> = nitrogen oxides; PAN = peroxyacetyl nitrate; PM = particulate matter; S = sulfur; SO<sub>2</sub> = sulfur dioxide; SO<sub>x</sub> = sulfur oxides.

**Figure ES-1 Roadmap of the Integrated Science Assessment (ISA) linking atmospheric concentrations and deposition, soil and aquatic biogeochemistry, and biological effects.**

## ES.2 Emissions, Ambient Air Concentrations, and Deposition

The atmospheric chemistry from emission to deposition discussed in this ISA<sup>1</sup> is for the criteria pollutants NO<sub>y</sub>, SO<sub>x</sub>, and PM. NO<sub>y</sub> and SO<sub>x</sub> cause ecological effects in the gas phase and/or after N and S deposition to surfaces. Particulate matter (PM) effects discussed in this document focus on N and S containing species, which together usually make up a large fraction of the PM<sub>2.5</sub> mass in most areas of the U.S. NH<sub>x</sub> (NH<sub>x</sub> = NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) includes both gas-phase NH<sub>3</sub> and the PM component NH<sub>4</sub><sup>+</sup>. NH<sub>3</sub> is estimated to account for 19–63% of total observed inorganic N deposition, depending on region ([Appendix 2.1](#)). Therefore, NH<sub>3</sub> is discussed in this ISA along with NO<sub>y</sub> and relevant PM components to better understand and compare their contributions to both wet and dry N deposition.

<sup>1</sup> The term concentration is used throughout the ISA to denote either a mass per unit volume or a volume per unit volume (mixing ratio). The use of concentration to denote abundance expressed as mixing ratio is firmly entrenched in the literature; therefore, it is retained here.

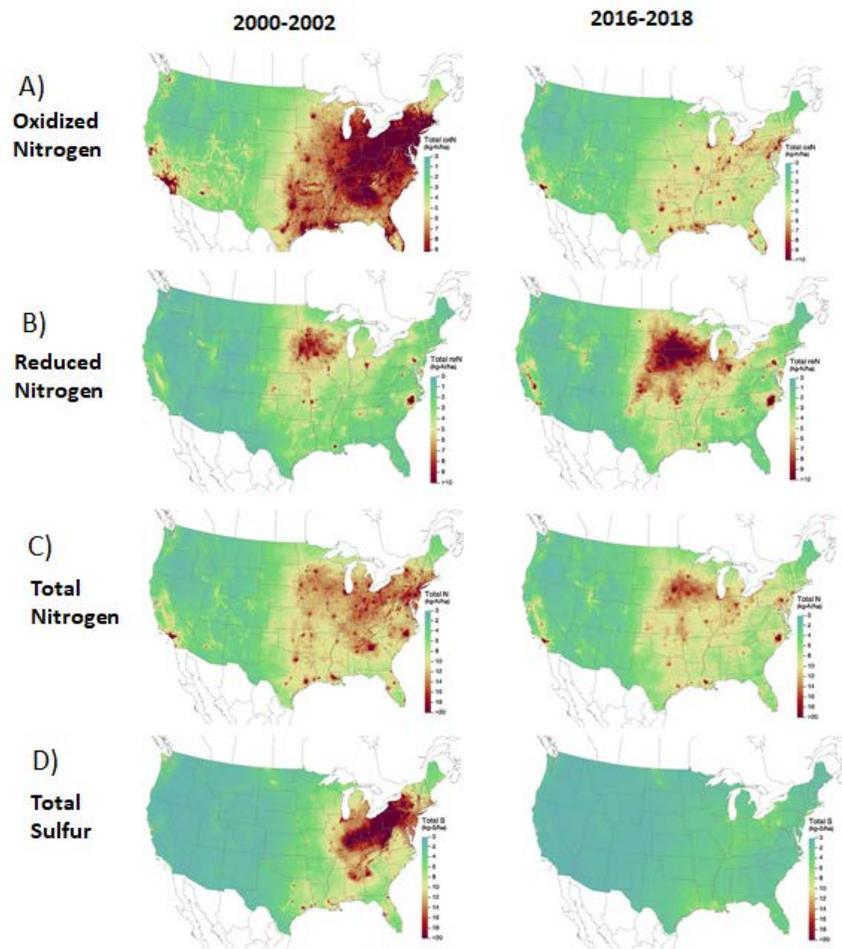
Both gaseous and particulate forms of  $\text{NO}_y$ ,  $\text{SO}_x$ , and  $\text{NH}_x$  contribute to atmospheric wet and dry deposition. The major components of PM in the U.S. are  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , organic matter, elemental C, crustal material, and sea salt. Of these,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  usually have a strong influence on acid deposition, and  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , and in some cases organic N (organic nitrates and reduced organic N), contribute substantially to N deposition and eutrophication.

The sources and precursors to gaseous and particulate forms of  $\text{NO}_y$ ,  $\text{SO}_x$ , and  $\text{NH}_x$  vary. The main contributors to acidifying precipitation are formed from precursor emissions of the gases  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  ([Appendix 2.2](#)). Electricity-generating units (EGUs) are the source of about half of national gaseous emissions of  $\text{SO}_2$ , mainly from coal-fired power plants. Notably,  $\text{SO}_2$  emissions from EGUs have been decreasing.  $\text{NO}_x$  emissions have a wider distribution of sources, with substantial contributions from highway and off-highway vehicles, lightning, and EGUs. Fertilizer application and animal waste are the main national-scale sources of  $\text{NH}_3$ , with animal waste contributing the most. Primary  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  emissions are dominated by dust and combustion products of fires, but much of the  $\text{PM}_{2.5}$  mass in the U.S. is produced by reaction of gas-phase precursors to form secondary  $\text{PM}_{2.5}$ . In this process, particulate  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  are primarily derived from the gaseous precursors  $\text{NH}_3$ ,  $\text{NO}_x$ , and  $\text{SO}_2$  ([Appendix 2.3](#)). Formation of particulate N and S is described in the 2019 *ISA for Particulate Matter* ([U.S. EPA, 2019](#)). An understanding of the sources, chemistry, and atmospheric processes for these gas-phase and PM species is necessary to understand acidifying and N deposition.

Since the passage of the Clean Air Act Amendments in 1990, the emissions of  $\text{NO}_x$  and  $\text{SO}_2$  have declined dramatically. Total emissions of  $\text{SO}_2$  decreased by 89% from 1990 to 2017, resulting in a decrease in  $\text{SO}_2$  concentrations of 89% in the eastern U.S. and 45% in the western U.S. Emissions of  $\text{NO}_x$  in the U.S. declined by 61% between 1990 and 2017, while nationwide annual average 98th percentile  $\text{NO}_2$  concentrations decreased by 53% from 1990 to 2017. These reductions have in turn led to decreases in  $\text{PM}_{2.5}$  concentrations because of declines in the amount of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  produced, and a decrease in the fraction of  $\text{PM}_{2.5}$  accounted for by  $\text{SO}_4^{2-}$ . Between 1989 and 2017, average particulate  $\text{SO}_4^{2-}$  concentration decreased by 75% in the eastern U.S. and 35% in the western U.S., and average particulate  $\text{NO}_3^-$  concentration decreased by 51% in the eastern U.S. and 37% in the western U.S.

Averaged across the contiguous U.S., deposition of total N (oxidized + reduced N, in kg N/ha/yr) has changed only slightly since 2000 ([Appendix 2.6.2](#)). [Figure ES-2](#) shows that between 2000 and 2018 large decreases in oxidized nitrogen ([Figure ES-2A](#)) have combined with large increases in reduced nitrogen deposition ([Figure ES-2B](#)) to produce a small decrease in total nitrogen deposition ([Figure ES-2C](#)). There is large spatial

variability in N deposition over the contiguous U.S. (Figure ES-2C). According to National Atmospheric Deposition Program Total Deposition Committee's (TDEP's) estimates for 2016–2018 (Appendix 2.6.2), much of the eastern U.S. is estimated to receive at least 10 kg N/ha/yr dry + wet deposition, with some areas receiving more than 15 kg N/ha/yr. Figure ES-2 A through C shows that between 2000 and 2018, large decreases in oxidized nitrogen deposition occurred.



Ha = hectare; kg = kilogram; N = nitrogen; OxN = oxidized nitrogen; ReN = reduced nitrogen; S = sulfur.

Source: We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure ES-2** Wet plus dry deposition of (A) oxidized nitrogen, (B) reduced nitrogen, (C) total nitrogen, and (D) total sulfur over the 3-year periods 2000–2002 and 2016–2018.

For S, wet deposition tends to dominate over dry deposition in large areas of the contiguous U.S. However, in some regions, mostly in the west, dry deposition of mainly SO<sub>2</sub> is greater than wet deposition. Anthropogenic emissions of S and subsequent deposition have declined markedly since the 1990s, with the most pronounced declines in the eastern U.S., as shown in [Figure ES-2D](#). Currently, the highest values of total (wet + dry) SO<sub>x</sub> deposition in the U.S. are in parts of the Ohio Valley region where they range between 15 and 20 kg S/ha/yr.

Both N and S deposition contribute to acidification of ecosystems. The acidity of rainwater has decreased, as indicated by the increase of rainwater pH across the U.S. since 1990, coincident with decreases in the wet deposition of nitrate and sulfate. However, widespread areas are still affected by acidifying precipitation, mainly in the eastern U.S. (see [Appendix 2.6.1](#)). Total acidifying deposition (wet + dry N + S, expressed as H<sup>+</sup> equivalents) fluxes for 2016 to 2018 ranged from a few tenths of H<sup>+</sup> keq/ha/yr over much of the western U.S. to over 1.5 H<sup>+</sup> keq/ha/yr in parts of the Midwest and the Mid-Atlantic regions, and in other isolated hotspots surrounding areas of concentrated industrial or agricultural activity ([Figure IS-6](#)). Estimated deposition fluxes greater than 1.5 keq/ha/yr covered a much smaller portion of the U.S. in 2016–2018 than in 2000–2002.

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### **ES.3 Ecological Effects**

In this ISA, information on ecological effects from controlled exposure, field addition, ambient deposition, and toxicological studies, among others, are integrated to form conclusions about the causal nature of relationships between NO<sub>y</sub>, SO<sub>x</sub>, and PM and ecological effects. Studies on the ecological effects are considered in relation to a range of ambient concentration and deposition loads that are within two orders of magnitude from current conditions [Preamble ([U.S. EPA, 2015e](#)), Section 5c]. A consistent and transparent framework [Preamble ([U.S. EPA, 2015e](#)), Table II] is applied to classify the ecological effect evidence according to a five-level hierarchy:

1. Causal relationship
2. Likely to be a causal relationship
3. Suggestive of, but not sufficient to infer, a causal relationship
4. Inadequate to infer a causal relationship
5. Not likely to be a causal relationship

The conclusions presented in [Table ES-1](#) are based on recent findings integrated with information from the 2008 ISA ([U.S. EPA, 2008a](#)). The conclusions of [Table ES-1](#) are based on careful consideration of errors and uncertainty in the supporting studies. We

also consider the coherence of findings integrated across studies of underlying geochemical and biological mechanisms. There are 18 causality statements in this ISA ([Table ES-1](#)). Fourteen are causal relationships repeated from the 2008 ISA or modified from the 2008 ISA to include specific endpoints. For these causality statements, new research strengthens the evidence base and is consistent with the 2008 ISA. There is one likely causal relationship repeated from the 2009 *ISA for Particulate Matter*. Three causal relationships are new endpoint categories not evaluated in the 2008 ISA. Although NO<sub>y</sub> and SO<sub>x</sub> can cause phytotoxic injury, current monitored concentrations of gas-phase NO<sub>y</sub> and SO<sub>x</sub> are not high enough to injure vegetation. For all other identified causal relationships identified in this ISA, the evidence indicates a causal association from current levels of S and/or N deposition.

**Table ES-1 Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 ISA for Particulate Matter (PM), for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current Draft ISA
<b>Gas-phase direct phytotoxic effects</b>		
Gas-phase SO <sub>2</sub> and injury to vegetation <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.1</a>	Causal relationship	Causal relationship
Gas-phase NO, NO <sub>2</sub> , and PAN and injury to vegetation <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.2</a>	Causal relationship	Causal relationship
Gas-phase HNO <sub>3</sub> and injury to vegetation <sup>a</sup> <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.3</a>	Causal relationship	Causal relationship
<b>N and acidifying deposition to terrestrial ecosystems</b>		
N and S deposition and alteration of soil biogeochemistry in terrestrial ecosystems <sup>b</sup> <a href="#">Section IS.5.1</a> and <a href="#">Appendix 4.1</a>	Causal relationship	Causal relationship
N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems <sup>c</sup> <a href="#">Section IS.5.2</a> and <a href="#">Appendix 6.6.1</a>	Not included	Causal relationship
N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems <sup>c</sup> <a href="#">Section IS.5.2</a> and <a href="#">Appendix 6.6.2</a>	Causal relationship	Causal relationship

**Table ES-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 ISA for Particulate Matter (PM), for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current Draft ISA
Acidifying N and S deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems <sup>d</sup> <a href="#">Section IS.5.3</a> and <a href="#">Appendix 5.7.1</a>	Not included	Causal relationship
Acidifying N and S deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems <sup>d</sup> <a href="#">Section IS.5.3</a> and <a href="#">Appendix 5.7.2</a>	Causal relationship	Causal relationship
<b>N and acidifying deposition to freshwater ecosystems</b>		
N and S deposition and alteration of freshwater biogeochemistry <sup>e</sup> <a href="#">Section IS.6.1</a> and <a href="#">Appendix 7.1.7</a>	Causal relationship	Causal relationship
Acidifying N and S deposition and changes in biota, including physiological impairment and alteration of species richness, community composition, and biodiversity in freshwater ecosystems <sup>f</sup> <a href="#">Section IS.6.3</a> and <a href="#">Appendix 8.6</a>	Causal relationship	Causal relationship
N deposition and changes in biota, including altered growth and productivity, species richness, community composition, and biodiversity due to N enrichment in freshwater ecosystems <sup>g</sup> <a href="#">Section IS.6.2</a> and <a href="#">Appendix 9.6</a>	Causal relationship	Causal relationship
<b>N deposition to estuarine ecosystems</b>		
N deposition and alteration of biogeochemistry in estuarine and near-coastal marine systems <a href="#">Section IS.7.1</a> and <a href="#">Appendix 7.2.10</a>	Causal relationship	Causal relationship
N deposition and changes in biota, including altered growth, total primary production, total algal community biomass, species richness, community composition, and biodiversity due to N enrichment in estuarine environments <sup>h</sup> <a href="#">Section IS.7.2</a> and <a href="#">Appendix 10.7</a>	Causal relationship	Causal relationship
<b>N deposition to wetland ecosystems</b>		
N deposition and the alteration of biogeochemical cycling in wetlands <a href="#">Section IS.8.1</a> and <a href="#">Appendix 11.10</a>	Causal relationship	Causal relationship

**Table ES-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 ISA for Particulate Matter (PM), for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current Draft ISA
N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands <a href="#">Section IS.8.2</a> and <a href="#">Appendix 11.10</a>	Causal relationship	Causal relationship
<b>S deposition to wetland and freshwater ecosystems</b>		
S deposition and the alteration of mercury methylation in surface water, sediment, and soils in wetland and freshwater ecosystems <sup>i</sup> <a href="#">Section IS.9.1</a> and <a href="#">Appendix 12.7</a>	Causal relationship	Causal relationship
S deposition and changes in biota due to sulfide phytotoxicity, including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems <a href="#">Section IS.9.2</a> and <a href="#">Appendix 12.7</a>	Not included	Causal relationship
	2009 PM ISA	Current Draft ISA
<b>Other ecological effects of PM</b>		
PM and a variety of effects on individual organisms and ecosystems <a href="#">Section IS.10</a> and <a href="#">Appendix 15.8</a>	Likely to be a causal relationship	Likely to be a causal relationship

C = carbon; Hg = mercury; HNO<sub>3</sub> = nitric acid; ISA = Integrated Science Assessment; N = nitrogen; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; PAN = peroxyacetyl nitrate; S = sulfur; SO<sub>2</sub> = sulfur dioxide.

<sup>a</sup>The 2008 ISA causality statements for gas-phase HNO<sub>3</sub> was phrased as “changes in vegetation.”

<sup>b</sup>The 2008 ISA included two causality statements for terrestrial biogeochemistry phrased as “relationship between acidifying deposition and changes in biogeochemistry” and “relationship between N deposition and the alteration of biogeochemical cycling of N.”

<sup>c</sup>The 2008 ISA causality statement for biological effects of N enrichment in terrestrial ecosystems was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity.”

<sup>d</sup>The 2008 ISA causality statement for biological effects of acidifying deposition in terrestrial ecosystems was phrased as “relationship between acidifying deposition and changes in terrestrial biota.”

<sup>e</sup>The 2008 ISA included three causality statements for freshwater biogeochemistry phrased as “relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems,” “relationship between N deposition and the alteration of biogeochemical cycling of N,” and “relationship between N deposition and the alteration of biogeochemical cycling of C.”

<sup>f</sup>The 2008 ISA causality statement for biological effects of acidifying deposition in freshwater ecosystems was phrased as “relationship between acidifying deposition and changes in aquatic biota.”

<sup>g</sup>The 2008 ISA causality statement for biological effects of N deposition in freshwater ecosystems was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity in freshwater aquatic ecosystems.”

<sup>h</sup>The 2008 ISA causality statement for biological effects of N deposition to estuaries was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity in estuarine ecosystems.”

<sup>i</sup>The 2008 ISA causality statement for biological effects of S deposition effects on ecosystems was phrased as “relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors is within adequate range for methylation.”

[Figure ES-3](#) presents a visualization of the causality statements integrated into a single diagram. There is not a one-to-one correspondence between the number of causality statements, of which there are 18, and the cells indicated to have causal relationships in the diagram because some causal statements include effects across more than one level of biological organization. The main findings are that gaseous  $\text{NO}_y$  and  $\text{SO}_x$  cause phytotoxic effects, while N and S deposition cause alteration in (1) biogeochemical components of soil and water chemistry and (2) multiple levels of biological organization ranging from physiological processes to shifts in biodiversity and ecological function.

NOx SOx PM Integrated Science Assessment for Ecological Effects*														
Indicator			Gases ‡	Nitrogen Deposition				Sulfur Deposition				Nitrogen and Sulfur Deposition		
Class of Pollutant Effect			Direct Phytotoxic	N-enrichment/Eutrophication				Sulfide Toxicity		Mercury Methylation		Acidification		
Ecosystem			Terrestrial	Terrestrial	Wetland	Fresh Water	Estuary	Wetland	Fresh Water	Wetland	Fresh Water	Terrestrial	Fresh Water	
Scale of Ecological Response	Ecosystem	Productivity	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Not evaluated in causal framework	
		Community	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Causal	
	Population	Individual	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Causal	Not evaluated in causal framework	
		Individual	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	
	Geochemistry	Soil or sediment chemistry	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal	Causal	Causal	Not evaluated in causal framework				
		Surface water chemistry	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal

**Causality framework**

Causal
Likely causal
Suggestive
Inadequate
Not likely
Not evaluated in causal framework

\* A causal relationship is likely to exist between deposition of PM and a variety of effects on individual organisms and ecosystems, based on information from the previous review and limited new findings in this review

‡ Includes: NO, NO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and PAN

**Figure ES-3 Causal relationships between the criteria pollutants and ecological effects.**

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## **ES.4 Direct Phytotoxic Effects of Gas-Phase Oxides of Nitrogen (NO<sub>Y</sub>) and Oxides of Sulfur (SO<sub>X</sub>)**

The current NO<sub>2</sub> and SO<sub>2</sub> secondary NAAQS are set to protect against direct damage to vegetation by exposure to gas-phase oxides of NO<sub>Y</sub> and SO<sub>X</sub>. NH<sub>3</sub> can also have direct phytotoxic effects, but reduced N gases such as NH<sub>3</sub> are not criteria air pollutants. Research continues to support causal relationships between SO<sub>2</sub>, NO<sub>2</sub>, NO, peroxyacetyl nitrate (PAN), HNO<sub>3</sub>, and injury to vegetation (e.g., visible foliar injury, damage to photosynthesis, decline of growth and abundance; ([Table IS-1](#), [Section IS.4](#), [Appendix 3](#)), but research that tests plant response to the lower exposure levels representative of current atmospheric NO<sub>Y</sub> and SO<sub>X</sub> concentrations is limited. Consequently, few studies are available to help determine whether current monitored concentrations of gas-phase NO<sub>Y</sub> and SO<sub>X</sub> are high enough to injure vegetation. It is also known that these can be gases taken up by plants and alter the N cycle in some ecosystems.

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## **ES.5 Ecological Effects of Nitrogen and Sulfur Deposition**

It is clear from the body of evidence that NO<sub>Y</sub>, SO<sub>X</sub>, and PM contribute to total N and S deposition. In turn, N and S deposition cause alteration of the biogeochemistry and the physiology of organisms, resulting in harmful declines in biodiversity in terrestrial, freshwater, wetland, and estuarine ecosystems in the U.S. Decreases in biodiversity mean that some species become relatively less abundant and may be locally extirpated. In addition to the loss of unique living species, the decline in total biodiversity can be harmful because biodiversity is an important determinant of the stability of ecosystems and their ability to provide socially valuable ecosystem services (see more on biodiversity in [Section IS.2.2.4](#)).

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### **ES.5.1 Acidification of Terrestrial and Freshwater Ecosystems**

Several decades of research have documented that N and S deposition cause freshwater and terrestrial ecosystem acidification in the U.S. New evidence strengthens the causal relationships for ecosystem acidification determined in the 2008 ISA ([Table IS-1](#)).

Many of the terrestrial and freshwater ecosystems most sensitive to acidification in the U.S. are found in the Northeast and Southeast. In the West, freshwater and terrestrial ecosystems acidified from deposition are now limited in extent and occur mostly in high-elevation sites. Watershed sensitivity to acid inputs depends on characteristics such as underlying geology ([Appendix 4](#) and [Appendix 7](#)) and the sensitivity of species in the local biological community ([Appendix 5](#) and [Appendix 8](#)). Regional heterogeneity of deposition levels that cause ecological effects are in part due to historic exposure and

climate. In the East, especially the southern Appalachian Mountains, and the Northeast, the effects of acidifying deposition have been studied for several decades.

Acidified aquatic habitats have a lower number of species (species richness) of fishes, macroinvertebrates, and phytoplankton. The effects of acidifying deposition on aquatic ecosystems also include physiological impairment or mortality of sensitive species and shifts in biodiversity of both flora and fauna. Organisms at all trophic levels are affected by acidification, with clear linkages to chemical indicators for effects on algae, zooplankton, benthic invertebrates, and fish. Acid-neutralizing capacity (ANC) is a measure of the buffering capacity of natural waters against acidification. Even though ANC does not directly alter the health of biota, it is a key metric of acidification that relates to pH and aluminum levels. Biological effects are primarily attributable to low pH and high inorganic aluminum concentration. Characterization of ANC and its levels of concern have not changed appreciably with the newly available information since the 2008 ISA. Few or no fish species are found in lakes and streams that have very low ANC (near zero) and low pH (near 5.0), and the number of fish species generally increases with higher ANC and pH ([Appendix 8.3](#)). The fish lost to acidification include culturally and recreationally important species.

Acidified terrestrial habitats are characterized by the detrimental physiological effects seen on vegetation, including inhibited growth and decreased plant health. Acidifying deposition can decrease membrane stability and freezing tolerance in young red spruce needles. For many species, calcium (Ca) depletion from the soil and aluminum mobilization cause decreased root uptake of Ca and disrupt fine root physiological functions. Reduced availability of (base) cations in the soil can also make trees more vulnerable to other stresses, such as damage from insects and other pathogens. Within the eastern U.S., the physiological effects of acidifying deposition have been well documented for the several culturally and commercially important tree species with known ecosystem services, particularly sugar maple (*Acer saccharum*) and red spruce (*Picea rubens*). Consistent and coherent evidence available before and since the 2008 ISA suggests acidifying deposition among these species can decrease foliar cold tolerance, increase rates of crown dieback, decrease tree growth, suppress seedling regeneration, and increase mortality rates. ([Section IS.5.3](#); [Appendix 5](#)). Since the 2008 ISA, studies from the northeastern U.S. have shown that Ca addition can alleviate many of these effects, demonstrating that acidification effects can be ameliorated in the short term by soil amendments, suggesting the potential for recovery. However, Ca additions have been studied in only a few areas. Acidifying deposition has also been linked to changes in forest understory plant community composition in the northeastern U.S., grass and forb biodiversity in eight ecoregions across the U.S., and decreased grassland plant species richness in Europe.

Examples of improvement in acidification have been documented in some aquatic ecosystems in the regions most affected. Along with those improvements in acidification, chemical recovery has been observed in the Northeast, as seen by trends in water quality indicators ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , pH, ANC, inorganic monomeric Al, MeHg) towards inferred preindustrial values or, in the case of inorganic Al and MeHg, below water quality threshold values protective of biota and human health. Chemical recovery has not been observed in studies of the southern Appalachians. In a few examples in the Northeast, chemical recovery co-occurs with the movement of biological indicators toward recovery. However, biological recovery has been highly variable among ecosystems and taxonomic groups. Biological recovery lags behind, sometimes by decades, chemical recovery. In addition, the biological recovery trajectory may exhibit hysteresis, in which a system does not follow the same path from acidification to recovery. Most biological communities studied to date where signs of reversal are found have not returned to preacidification conditions and are unlikely to do so, given the extirpation of some species, fundamental alterations in function and structure, decade-long depletion of base cations, and changes in other interacting influences such as climate and land use.

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## **ES.5.2 Nitrogen Enrichment/Eutrophication of Terrestrial, Wetland, and Aquatic Ecosystems**

Terrestrial, wetland, freshwater, and estuarine ecosystems in the U.S. are affected by N enrichment/eutrophication caused by N deposition. N enrichment/eutrophication refers to N nutrient-driven changes in growth, physiology, and biodiversity. These effects have been consistently documented across the U.S. for hundreds of species. New evidence strengthens the causal relationships for ecosystem N enrichment/eutrophication determined in the 2008 ISA ([Table IS-1](#)).

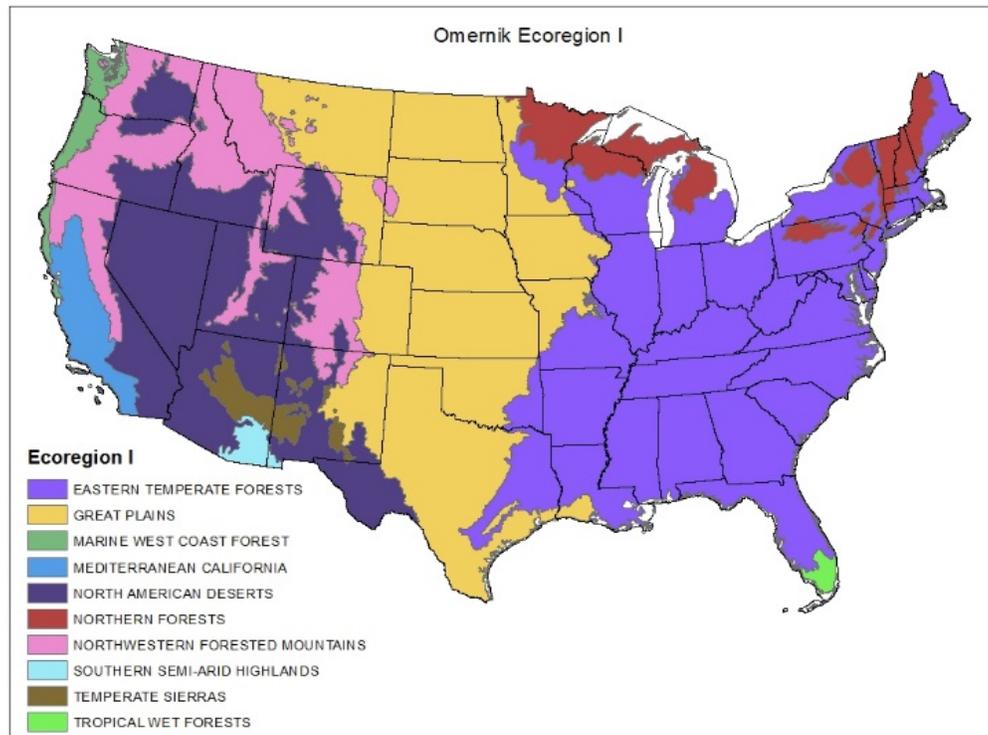
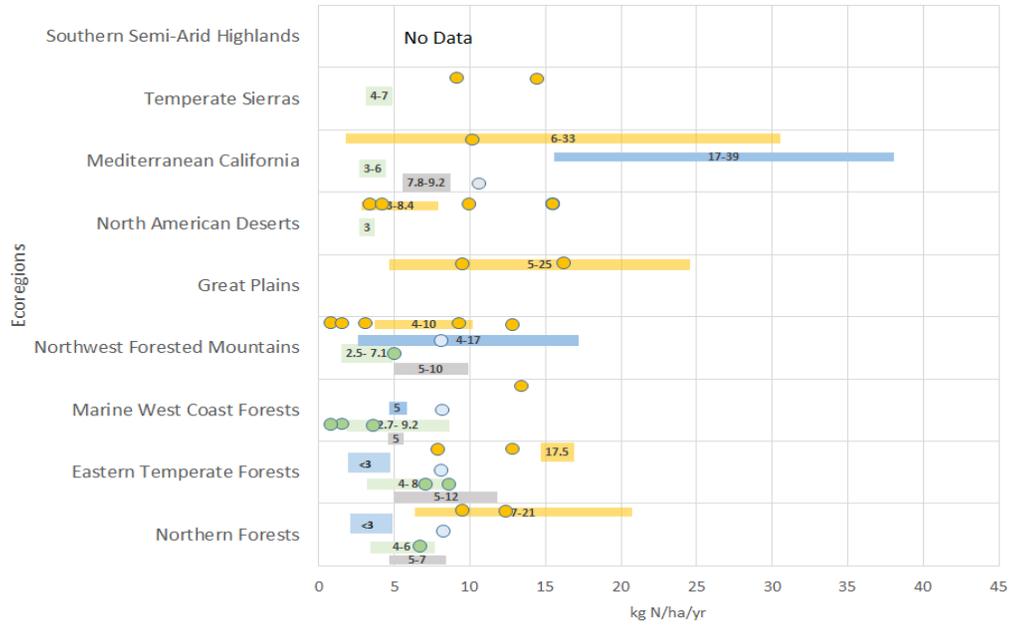
The 2008 ISA documented that the N enrichment effect in sensitive terrestrial and wetland ecosystems starts with the accumulation of N in the soil. This increases the availability of N, a nutrient that increases the growth of some species of soil microbes and vascular plants at the expense of other species, which may decrease biodiversity. Since the 2008 ISA, the largest increase in ecological evidence is for terrestrial N driven enrichment/eutrophication effects ([Section IS.5.1](#), [Section IS.5.2](#); [Appendix 4](#), and [Appendix 6](#)).

This new research confirms the causal relationship between N deposition and ecological effects documented in the 2008 ISA and improves our understanding of the mechanistic links that inform causal determinations between N deposition, biogeochemistry, and biota in terrestrial ecosystems ([Table IS-1](#)). A new causal determination has been added to reflect more specific categories of effects to include physiology, growth, and ecosystem productivity. Further, there is now stronger empirical evidence from across most regions

of the U.S. to quantify critical loads (CLs) for N deposition. The figure below provides estimates of CLs across broad ecoregions and shows the ranges for different functional groups within these systems ([Figure ES-4](#)). Under the CLs, significant harmful effects from N deposition do not occur according to present knowledge, while at or above CLs, N deposition can cause a myriad of ecological effects, including decreased tree growth and increased mortality, and declines in grasses/forbs, lichens, and mycorrhizal fungi.

Since the 2008 ISA, studies have strengthened evidence of species-specific effects of N deposition on tree growth and mortality in the U.S. Although overall tree growth has generally been enhanced by N deposition over the last several decades, there is wide variation among species in growth and mortality responses. Moreover, within some individual species, N deposition can increase growth and/or survival at low levels, while decrease growth and/or survival at higher levels. Species with varying responses have also been shown to co-occur in places in the U.S., suggesting overstory tree community composition shifts with N deposition.

Since the 2008 ISA, studies have also strengthened the findings of N effects on decreasing lichen and mycorrhizal fungi biodiversity and provided additional CL estimates. In terrestrial ecosystems, new evidence provides support that epiphytic lichens (an algal- and/or cyanobacteria-fungal symbiont) and mycorrhizae (a plant-fungal symbiosis at the tips of plant roots) are the organisms most sensitive to atmospheric N deposition and acidifying deposition. Although lichens typically are only a small portion of terrestrial biomass, these changes in lichen communities are meaningful because lichens provide food and habitat for insects, birds, and mammals; contribute to nutrient and hydrologic cycling; have many traditional human uses; and have considerable potential for pharmaceutical use. Changes in the community composition of mycorrhizal fungi and declines in mycorrhizal abundance have been observed in the U.S. These fungi are important for supplying nutrients and water to plants, influencing soil C sequestration, and producing fruiting bodies (mushrooms) used by humans and wildlife.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

The rectangles indicate the range of CLs designated by [Pardo et al. \(2011a\)](#); the circles indicate new papers that have specified CLs; data from [Table 6-28](#).

**Figure ES-4 Summary of critical loads for nitrogen in the U.S. for shrubs and herbaceous plants (yellow), trees (blue), lichens (green), and mycorrhizae (gray). Values expressed by major U.S. ecoregions.**

For wetland ecosystems, the 2008 ISA documented that wetlands receiving a larger fraction of their total water budget in the form of precipitation are more sensitive to the effects of N deposition. For example, bogs and fens (55–100% of hydrological input from rainfall) are more sensitive to N deposition than coastal wetlands (10–20% as rainfall). Since the 2008 ISA, CLs for U.S. coastal and freshwater wetlands have been established. The CL for freshwater wetlands is based on C cycling, as well as biodiversity represented by the morphology and population dynamics of the purple pitcher plant (*Sarracenia purpurea*). The CL for coastal wetlands is based on several different ecological endpoints, including plant community composition, microbial activity, and biogeochemistry.

The 2008 ISA documented that the process of N eutrophication is similar in freshwater and estuarine ecosystems and typically begins with a nutrient-stimulated algal bloom that is followed by anoxic conditions. The lack of oxygen in the water due to the respiration and decomposition of the algae affects higher trophic species. The contribution of N deposition to total N loading varies among freshwater lakes and stream ecosystems. Atmospheric deposition is the main source of new N inputs to most headwater stream, high-elevation lake, and low-order stream watersheds far from the influence of other N sources like agricultural runoff and wastewater effluent. N deposition was known at the time of the 2008 ISA to alter biogeochemical processes, nutrient ratios, and concentrations in recipient freshwater ecosystems. New CLs published since the 2008 ISA support previous observations of increased productivity of phytoplankton and algae, species changes, and reductions in diversity in atmospherically N enriched lakes and streams. The productivity of many freshwater ecosystems is N limited. Thus, even small amounts of N can shift nutrient ratios and affect the trophic status of lakes and streams. As reported in the 2008 ISA and newer studies, a shift from N limitation to either colimitation by N and P or limitation by P has been observed in some alpine lakes in the U.S. and other countries, with these shifts correlated with elevated N deposition.

Estuaries support a large biodiversity of flora and fauna and play a role in nutrient cycling. At the time of the 2008 ISA, N was recognized as the major cause of harm to the majority of estuaries in the U.S. Elevated N inputs to coastal areas can alter key processes that influence N and C cycling in near-coastal environments. Data evaluating sources of N to estuaries, from the 2008 ISA and newer studies reviewed in this ISA, indicate that N from atmospheric sources ranges from <10% to approximately 70% of total estuary N inputs; the atmospheric input for most estuaries is between 15 to 40% of total N inputs. N from atmospheric and other sources contributes to increased primary productivity, leading to eutrophication. In some coastal areas eutrophication from N loading may affect carbonate chemistry under certain circumstances, potentially contributing to acidifying conditions along with atmospheric anthropogenic CO<sub>2</sub> inputs and other factors. Since

2008, new paleontological studies, observational studies, and experiments have further characterized the effects of N on phytoplankton growth and community dynamics, macroinvertebrate response, and other indices of biodiversity in streams, rivers, lakes and estuaries. For this ISA, new information is consistent with the 2008 ISA, and the causal determinations for N enrichment in aquatic systems have been updated to reflect more specific categories of effects, including measures of productivity and altered growth of biota ([Table ES-1](#)).

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### **ES.5.3 Sulfur (S) Enrichment of Wetland and Freshwater Ecosystems**

SO<sub>x</sub> deposition increases SO<sub>4</sub><sup>2-</sup> concentration in surface waters. New evidence supports links between aqueous S concentrations in freshwater ecosystems and both mercury (Hg) methylation and sulfide toxicity ([Table ES-1](#)); however, quantitatively linking these outcomes to atmospheric deposition remains a challenge.

Increasing SO<sub>4</sub><sup>2-</sup> concentration in surface waters can stimulate the microbial transformation of inorganic Hg into methylmercury (MeHg; [Appendix 12](#)). MeHg is the most persistent and toxic form of Hg affecting animals in the natural environment. Indicators of S deposition effects upon Hg methylation include increases in MeHg concentrations or fraction of total Hg in water, sediments, and peat, as well as increases in MeHg concentrations in periphyton, submerged aquatic plants, invertebrates, and fish. New evidence confirms the relationship between aqueous concentrations of SO<sub>4</sub><sup>2-</sup> and MeHg and broadens our understanding of where methylation occurs from the wetlands and lakes reported in the 2008 ISA to include rivers, reservoirs, streams, and saturated forest soils. Hg methylation occurs at anoxic-oxic boundaries in peat moss and periphyton, as well as in wetland, lake, estuarine, and marine sediments. There are published quantitative relationships between surface water SO<sub>4</sub><sup>2-</sup> concentrations and MeHg concentrations, MeHg and total Hg in water, and Hg load in larval mosquitoes and fish. There is also evidence that decreasing S deposition loads over time (observational studies of SO<sub>x</sub> deposition, experimental studies of simulated SO<sub>x</sub> wet deposition) result in lower concentrations of MeHg in water, invertebrates, and fish.

There is new evidence since the 2008 ISA to infer a causal relationship between S deposition and sulfide phytotoxicity, which alters growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems ([Appendix 12](#)). This new causal statement reflects new research on sulfide phytotoxicity in North American wetlands, as the 2008 ISA described sulfide phytotoxicity only in European ecosystems. Current levels of S deposition cause sulfide toxicity in wetland and aquatic plants. Indicators of sulfide phytotoxicity caused by S deposition include increases in water or sediment sulfide concentrations. Sulfide

negatively effects growth, competitive ability, and persistence in several wetland species, including the economically important species of wild rice and the keystone sawgrass species in the Everglades marshes. To date, no published studies have established regional sensitivities to sulfide phytotoxicity, although studies have observed its effects in New York, Minnesota, and Florida freshwater marshes. There are no S deposition-based critical loads for Hg methylation or sulfide phytotoxicity, although researchers have proposed water quality values to protect biota against these effects in several ecosystems ([Appendix 12](#)).

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#### **ES.5.4 Ecological Effects of Particulate Matter Other Than Those Associated with Nitrogen and Sulfur Deposition**

There is a likely causal relationship between PM and ecological effects on biota other than those associated with N and S deposition ([Table ES-1](#); [Appendix 15](#)). Since publication of the 2009 PM ISA, new literature has built upon the existing knowledge of ecological effects associated with PM components, especially metals and organics. In some instances, new techniques have enabled further characterization of the mechanisms of PM on soil processes, vegetation, and effects on fauna. New studies provide additional evidence for community-level responses to PM deposition, especially in soil microbial communities. However, uncertainties remain due to the difficulty in quantifying relationships between ambient concentrations of PM and ecosystem response.

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#### **ES.6 Ecosystem Services**

“Ecosystem services” refers to the concept that ecosystems provide benefits to people, directly or indirectly ([Costanza et al., 2017](#)) and produce socially valuable goods and services deserving of protection, restoration, and enhancement.

The ecosystem services literature has expanded since the 2008 ISA to include studies that better characterize ecosystem service valuation and quantification related to acidification and N enrichment/eutrophication.

Several new studies have paired biogeochemical modeling and benefit transfer equations informed by willingness-to-pay surveys to estimate the monetary damage done to ecosystems and the services they provide in the Adirondacks and Shenandoah regions due to ecosystem acidification ([Appendix 14](#)). Despite this progress, for many regions and specific services, poorly quantified relationships between deposition, ecological effects, and services are the greatest challenge in developing specific data on the economic benefits of emission reductions.

In the 2008 ISA, there were no publications that had specifically evaluated the effects of N deposition on ecosystem services associated with N driven enrichment/eutrophication. Since the 2008 ISA, several comprehensive studies have been published on the ecosystem services related to excessive N in U.S. water bodies. These include an evaluation of services affected by multiple N inputs (including N deposition) to the Chesapeake Bay, a synthesis of the cost-benefits on N loading across the nation, an estimation of the social cost of nitrogen when applied as fertilizer, and an analysis of how N lost from its intended area of application (e.g., agricultural fields) affects ecosystem services of adjacent ecosystems. Most notably, new work identifies over 1,000 links between N deposition and human beneficiaries.

Considering the full body of literature on ecosystem services related to N and S, the following conclusions are offered: (1) there is evidence that N and S emissions/deposition have a range of effects on U.S. ecosystem services and their social value; (2) some economic studies demonstrate such effects in broad terms, but it remains methodologically difficult to derive economic costs and benefits associated with specific regulatory decisions/standards; and (3) numerous, but still inadequately quantified, relationships are now documented between N and S air pollution and changes in final ecosystem goods and services.

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## **ES.7 Integrating across Ecosystems**

Overall, new evidence since the 2008 ISA increases the weight of evidence for ecological effects, confirming concepts previously identified and improving quantification of dose-response (or deposition-ecological indicator) relationships, particularly for N and S deposition. The ecological effects are described by the causality determinations in [Figure ES-5](#), which reorganizes the information in [Figure ES-3](#) to show a visualization of the effects of NO<sub>y</sub>, SO<sub>x</sub>, and PM by ecosystem type (e.g., terrestrial, wetland, freshwater, and estuarine). With this organization, the multiple effects occurring in each ecosystem due to various pollution combinations of NO<sub>y</sub>, SO<sub>x</sub>, and PM are emphasized. Between two and four different classes of pollutant effects may occur in each ecosystem type in the U.S. For more information on key messages, see the expanded discussion in the [Integrated Synthesis](#); detailed information on specific ecosystem types and specific classes of pollutant effects included in the ISA may be found in the appendices.

Ecosystem			Terrestrial			Wetland			Fresh Water			Estuary	
Class of Pollutant Effect			Direct Phytotoxic	Acidification	N-enrichment/Eutrophication	N-enrichment/Eutrophication	Sulfide Toxicity	Mercury Methylation	Acidification	N-enrichment/Eutrophication	Sulfide Toxicity	Mercury Methylation	N-enrichment/Eutrophication
Indicator			Gases ‡	N+S dep	N dep	N dep	S dep	S dep	N+S dep	N dep	S dep	S dep	N dep
Scale of Ecological Response	Ecosystem	Productivity	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal
	Community	Biodiversity	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Causal	Causal	Causal	Not evaluated in causal framework	Causal
	Population	Individual	Growth rate	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal
	Individual	Physiological alteration, stress or injury	Causal	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Causal	Not evaluated in causal framework	Causal	Not evaluated in causal framework	Not evaluated in causal framework
	Geochemistry	Soil or sediment chemistry	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Not evaluated in causal framework
		Surface water chemistry	Not evaluated in causal framework	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Not evaluated in causal framework	Causal	Causal	Causal	Not evaluated in causal framework	Causal	Causal

**Causality framework**

Causal	Likely causal	Suggestive	Inadequate	Not likely	Not evaluated in causal framework
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‡ Includes: NO, NO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and PAN

**Figure ES-5 Causal relationships between the criteria pollutants and ecological effects organized under ecosystem type.**

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# INTEGRATED SYNTHESIS

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## IS.1 Introduction to This Integrated Science Assessment (ISA)

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### IS.1.1 Purpose

The Integrated Science Assessment (ISA) is a comprehensive evaluation and synthesis of the policy-relevant science. Policy-relevant science is that which is “useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of [a] pollutant in the ambient air,” as described in Section 108 of the Clean Air Act ([CAA, 1990a](#)).<sup>1</sup> This ISA communicates critical science judgments on the ecological criteria for oxides of nitrogen, oxides of sulfur, and particulate matter (PM). Accordingly, this ISA is the scientific foundation for the review of the ecological effects of the current secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen, oxides of sulfur, and particulate matter. The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort and well-being. The nonecological welfare effects associated with particulate matter, such as climate and visibility, are considered part of a separate, ongoing review of PM that is outlined in the *Integrated Review Plan (IRP) for the National Ambient Air Quality Standards for Particulate Matter* ([U.S. EPA, 2016d](#)). The human health effects are evaluated in separate assessments conducted as part of the review of the primary (human health-based) NAAQS for oxides of nitrogen ([U.S. EPA, 2016f](#)), oxides of sulfur ([U.S. EPA, 2016e](#)), and as noted above, particulate matter ([U.S. EPA, 2019](#)).

Oxides of nitrogen, oxides of sulfur, and particulate matter are reviewed here together because they are interrelated through complex chemical and physical atmospheric processes and because they all contribute to nitrogen (N) and sulfur (S) deposition, which in turn contributes to well-documented ecological effects. In this document, the term “oxides of nitrogen” refers to all forms of oxidized nitrogen (NO<sub>y</sub>) compounds, including

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<sup>1</sup> The general process for developing an ISA, including the framework for evaluating weight of evidence and drawing scientific conclusions and causal judgments, is described in a companion document, *Preamble to the Integrated Science Assessments* ([U.S. EPA, 2015e](#)).

NO, NO<sub>2</sub>, and all other oxidized N containing compounds formed from NO and NO<sub>2</sub>.<sup>1</sup> Oxides of sulfur<sup>2</sup> are defined here to include sulfur monoxide (SO), sulfur dioxide (SO<sub>2</sub>), sulfur trioxide (SO<sub>3</sub>), disulfur monoxide (S<sub>2</sub>O), and sulfate (SO<sub>4</sub><sup>2-</sup>). However, SO, SO<sub>3</sub>, and S<sub>2</sub>O are present at much lower ambient levels than SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> and are therefore not discussed further. Particulate matter is composed of some or all of the following components: nitrate (NO<sub>3</sub><sup>-</sup>), SO<sub>4</sub><sup>2-</sup>, ammonium (NH<sub>4</sub><sup>+</sup>), metals, minerals (dust), and organic and elemental carbon (C).

This ISA updates the 2008 *Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria* [hereafter referred to as the 2008 ISA ([U.S. EPA, 2008a](#))], as well as the ecological portion of the *Integrated Science Assessment for Particulate Matter* ([U.S. EPA, 2009a](#)), with studies and reports published from January 2008 through May 2017. Thus, this ISA updates the state of the science that was available for the 2008 ISA, which informed decisions on the secondary oxides of nitrogen and oxides of sulfur NAAQS in the review completed on March 20, 2012. In the final rulemaking, the Administrator’s decision was that, while the current secondary standards were inadequate to protect against adverse effects from deposition of oxides of nitrogen and oxides of sulfur, it was not appropriate under Section 109(b) to set any new secondary standards at this time due to the limitations in the available data and uncertainty as to the amount of protection the metric (Aquatic Acidification Index—see [Section IS.2.2.6](#)) developed in the Policy Assessment ([U.S. EPA, 2011a](#)) would provide against acidification effects across the country (77 FR 20281). In addition, the Administrator decided that it was appropriate to retain the current nitrogen dioxide (NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) secondary standards to address direct effects of gaseous NO<sub>2</sub> and SO<sub>2</sub> on vegetation. Thus, taken together, the Administrator decided to retain and not revise the current NO<sub>2</sub> and SO<sub>2</sub> secondary standards: an NO<sub>2</sub> standard set at a level of 0.053 ppm, as an annual arithmetic average, and an SO<sub>2</sub> standard set at a level of 0.5 ppm, as a 3-hour average, not to be exceeded more than once per year (77 FR 20281). The current secondary standards for PM are intended to address PM-related welfare effects, including visibility impairment, ecological effects, and effects on materials and climate. These standards are a 3-year annual mean PM<sub>2.5</sub> concentration of 15 µg/m<sup>3</sup>, with the 24-hour average PM<sub>2.5</sub> and PM<sub>10</sub> set at concentrations of 35 µg/m<sup>3</sup> and 150 µg/m<sup>3</sup>, respectively.

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<sup>1</sup> This ISA reserves the abbreviation NO<sub>x</sub> strictly as the sum of NO and NO<sub>2</sub>—consistent with that used in the atmospheric science community—and uses the term “oxides of nitrogen” to refer to the broader list of oxidized nitrogen species. Oxides of nitrogen refers to NO<sub>y</sub> as the total oxidized nitrogen in both gaseous and particulate forms. The major gaseous and particulate constituents of NO<sub>y</sub> include nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), peroxyacetyl nitrate (PAN), nitrous acid (HONO), organic nitrates, and particulate nitrate (NO<sub>3</sub>). This ISA uses the definitions adopted by the atmospheric sciences community.

<sup>2</sup> Oxides of sulfur refers to the criteria pollutant category.

This new review of the secondary oxides of nitrogen, oxides of sulfur, and particulate matter NAAQS is guided by several policy-relevant questions that were identified in *The Integrated Review Plan for the Secondary National Ambient Air Quality Standard for Nitrogen Oxides, Sulfur Oxides, and Particulate Matter* [hereafter referred to as the 2017 IRP ([U.S. EPA, 2017c](#))].

To address these questions, this ISA aims to characterize the evidence available in the peer-reviewed literature for ecological effects associated with:

- the major gaseous and particulate constituents of total oxidized N ( $\text{NO}_Y$ ), which include NO,  $\text{NO}_2$ ,  $\text{HNO}_3$ , PAN, HONO, organic nitrates, and  $\text{NO}_3^-$ ;
- the major gaseous and particulate constituents of  $\text{SO}_X$ , which include  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ ; and
- PM composed of some or all of the following components: particulate  $\text{NO}_3^-$ , particulate  $\text{SO}_4^{2-}$ , ammonium ( $\text{NH}_4^+$ ), metals, minerals (dust), and organic and elemental carbon (C).

The assessment activities include:

- Identifying policy-relevant literature.
- Evaluating strength, limitations, and consistency of findings.
- Integrating findings across scientific disciplines and across related ecological outcomes.
- Considering important uncertainties identified in the interpretation of the scientific evidence.
- Assessing policy-relevant issues related to quantifying ecological risks, such as ambient air concentrations, deposition, durations, and patterns associated with ecological effects; the relationship between ambient air concentrations, deposition, and ecological response and the existence of thresholds below which effects do not occur; and species and populations potentially at increased risk of ecological effects.

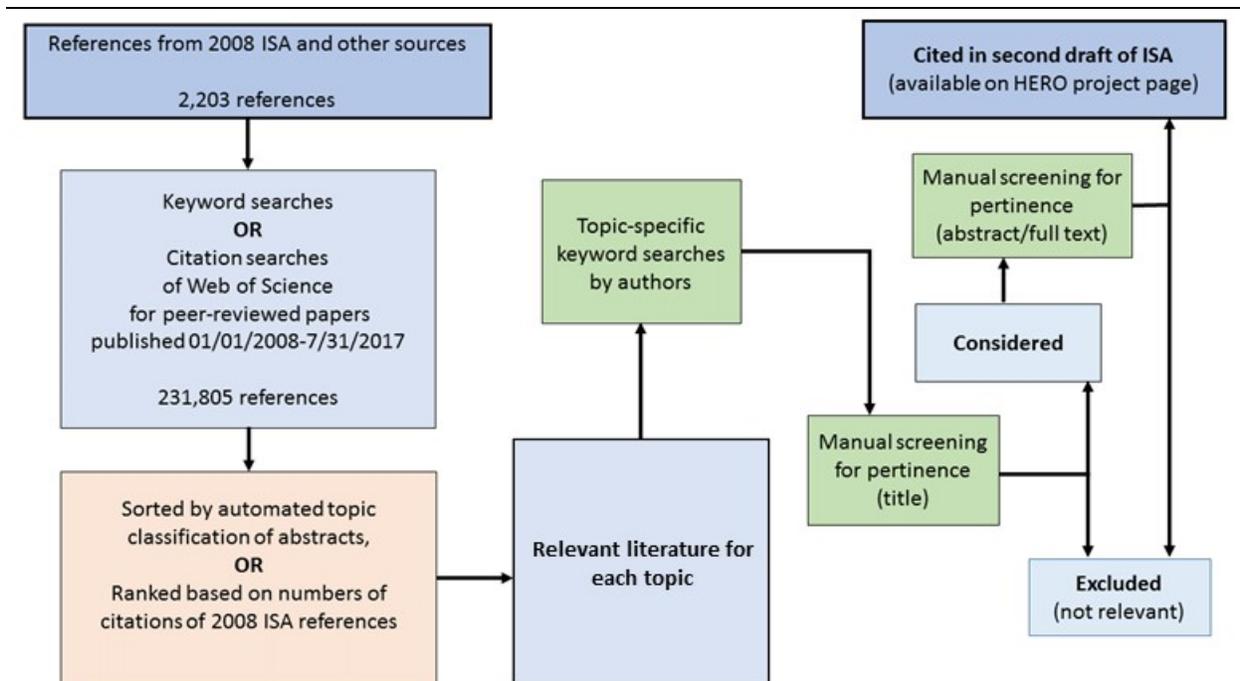
New analyses with the goal of quantifying risk, such as new model runs, Critical Loads (CLs) exceedance maps, and quantified uncertainties regarding modeled scenarios are not conducted in the ISA. These types of analyses, if pursued, require the selection of chemical or biological limits that define CLs and represent adversity. These analyses would also require choosing a time period over which to average deposition. Such scope-of-analysis decisions are more appropriate for the Risk and Exposure Assessment, as described in the 2017 IRP ([U.S. EPA, 2017c](#)). The information summarized in this ISA will serve as the scientific foundation of the Risk and Exposure and Policy Assessments during the current review of the secondary oxides of nitrogen, oxides of sulfur, and particulate matter NAAQS.

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## IS.1.2 Process and Development

The U.S. EPA uses a structured and transparent process to evaluate scientific information and determine the causality of relationships between air pollution and ecological effects [see Preamble ([U.S. EPA, 2015e](#))]. The ISA development includes approaches for literature searches, criteria for selecting and evaluating relevant studies, and a framework for evaluating the weight of evidence and forming causal determinations. As part of this process, the ISA is reviewed by the public and by the Clean Air Scientific Advisory Committee (CASAC), which is a formal independent panel of scientific experts. This ISA informs the review of the secondary oxides of nitrogen, oxides of sulfur, and particulate matter NAAQS and therefore integrates and synthesizes information characterizing NO<sub>y</sub>, SO<sub>x</sub>, and PM air concentrations. It also examines deposition of these substances and their ecological effects. Relevant studies include those examining atmospheric chemistry, spatial and temporal trends, and deposition, as well as U.S. EPA analyses of air quality and emissions data. Relevant ecological research includes geochemistry, microbiology, physiology, toxicology, population biology, and community ecology. The research includes experimental laboratory and field additions of the pollutants, as well as gradient studies.

The U.S. EPA conducted literature searches to identify relevant peer-reviewed studies published since the previous ISA (i.e., from January 2008 through May 2017; [Figure IS-1](#)).



HERO = Health and Environmental Research Online; ISA = Integrated Science Assessment.

**Figure IS-1 Workflow for collecting relevant literature for the 2017 Integrated Science Assessment for Oxides of Nitrogen, Oxides of Sulfur, and Particulate Matter—Ecological Criteria.**

Multiple search methods were used in the Web of Science database [Preamble ([U.S. EPA, 2015e](#)), [Appendix 2](#)], including searches by keyword and by citations of 2008 ISA references. Subject-matter experts and the public were also permitted to recommend studies and reports during kick-off workshops held by the U.S. EPA in March 2014 for oxides of nitrogen and oxides of sulfur and in February 2015 for particulate matter. The new references were sorted by automated methods into topic areas based on wording in the publication’s abstract or numbers of citations of 2008 ISA references, and the resultant relevant literature was reviewed by the ISA authors. Studies were screened first based on the title and then by the abstract; studies that did not address a relevant research topic based on this screening were excluded. The U.S. EPA also identified studies from previous assessments as definitive works on particular topics to include in this ISA. The HERO project page for this ISA ([https://heronet.epa.gov/heronet/index.cfm/project/page/project\\_id/2965](https://heronet.epa.gov/heronet/index.cfm/project/page/project_id/2965)) contains the references that are cited in the ISA and electronic links to bibliographic information and abstracts.

*The Preamble to the Integrated Science Assessments* ([U.S. EPA, 2015e](#)) describes the general framework for evaluating scientific information, including criteria for assessing study quality and developing scientific conclusions. For ecological studies, emphasis is placed on studies that characterize quantitative relationships between criteria pollutants and ecological effects that occur at concentration and deposition levels relevant to current ambient levels in the U.S. However, experimental studies with higher exposure concentrations are included if they contribute to an understanding of mechanisms.

This ISA draws conclusions about relationships between NO<sub>y</sub>, SO<sub>x</sub>, and PM and ecological effects by integrating information across scientific disciplines and related ecological outcomes and synthesizing evidence from previous and recent studies. Determinations are made about causation, not just association, and are based on judgments of consistency, coherence, and scientific plausibility of observed effects, as well as related uncertainties. The ISA uses a formal causal framework [Table II of the Preamble ([U.S. EPA, 2015e](#))], which is based largely on the aspects for causality proposed by Sir Austin Bradford Hill to classify the weight of evidence according to the five-level hierarchy summarized below.

- Causal relationship
- Likely to be a causal relationship
- Suggestive of, but not sufficient to infer, a causal relationship
- Inadequate to infer the presence or absence of a causal relationship
- Not likely to be a causal relationship

APPENDIX 7 This ISA includes the [Preface](#) (legislative requirements and history of the secondary oxides of nitrogen, oxides of sulfur, and particulate matter NAAQS), an [Executive Summary](#), an [Integrated Synthesis](#), and 16 appendices. The general process for developing an ISA is described in a companion document, *Preamble to the Integrated Science Assessments* ([U.S. EPA, 2015e](#)). The [Integrated Synthesis](#) summarizes the scientific evidence that best informs policy-relevant questions that frame this review. [Appendix 1](#) is an introduction to the appendices. [Appendix 2](#) characterizes the sources, atmospheric processes, and the trends in ambient concentrations and deposition of NO<sub>y</sub>, SO<sub>x</sub>, and PM. [Appendix 3](#) describes direct effects of NO<sub>y</sub> and SO<sub>x</sub> gases on plants and lichens. [Appendix 4–Appendix 6](#) describe N and S deposition effects on terrestrial biogeochemistry and the terrestrial biological effects of terrestrial acidification and N enrichment. [Appendix 7](#) describes the effects of N and S deposition on aquatic biogeochemistry. [Appendix 8–Appendix 10](#) characterize the biological effects of freshwater acidification, freshwater N enrichment, and N enrichment in estuaries and near-coastal systems. [Appendix 11](#) describes the effects of N deposition on wetlands, and [Appendix 12](#) characterizes the ecological effects of S as a nutrient. [Appendix 13](#) presents

information on climate modification of ecosystem response to N and S, and [Appendix 14](#) discusses ecosystem services. [Appendix 15](#) is a review of the ecological effects of forms of PM that are not related to N or S deposition. Finally, [Appendix 16](#) presents case studies for six locations in the U.S. (southern/central California, northeastern U.S., Rocky Mountain National Park, southeastern Appalachia, Tampa Bay, and the Adirondacks) where data are sufficient to well characterize the ecological effects of N and S deposition. These sites would therefore make good candidates for further study to better understand the linkages across various effects and ecosystems and to better assess risk and exposure.

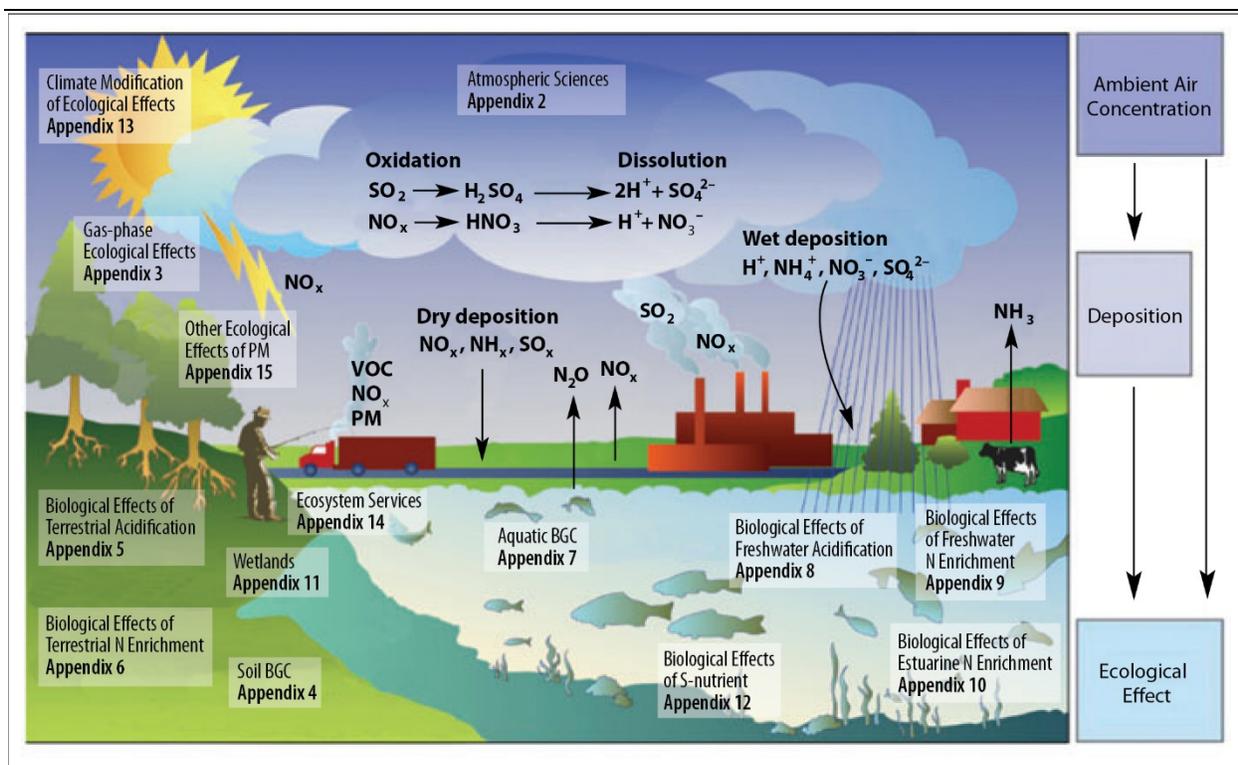
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## **IS.2 Connections, Concepts, and Changes**

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### **IS.2.1 Connections**

Although scientific material in this ISA is divided into separate appendices for atmospheric science and the multiple ecological effects, the strong links between the atmosphere and terrestrial and aquatic ecosystems are acknowledged ([Figure IS-2](#)). Emissions of NO<sub>y</sub>, SO<sub>x</sub>, and PM contribute to an accumulation of N and S in the environment that creates a multitude of effects on terrestrial, wetland, and aquatic ecosystems. Nitrogen is a vital component of all biological systems, serving as an essential element to molecules such as amino acids and nucleic acids, which are among the biochemical building blocks of life. As an organizing concept to understand the effects of N within the environment, the sequence of transfers, transformations, and environmental effects has been described as the “N cascade” ([Galloway and Cowling, 2002](#)). The concept of cascading effects also applies to S, which is also an essential macronutrient. Specifics of biogeochemical cycling and biological effects of N are discussed in [Section IS.5](#) and for S are discussed in [Section IS.9](#).



Ca<sup>2+</sup> = calcium ion; GHG = greenhouse gas; H<sup>+</sup> = hydrogen ion; H<sub>2</sub>SO<sub>4</sub> = sulfuric acid; HNO<sub>3</sub> = nitric acid; Mg<sup>2+</sup> = magnesium ion; N<sub>2</sub>O = nitrous oxide; N = nitrogen; NH<sub>3</sub> = ammonia; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>x</sub> = NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup> + reduced organic nitrogen compounds; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; NO<sub>3</sub><sup>-</sup> = nitrate; NO<sub>x</sub> = NO + NO<sub>2</sub>; PAN = peroxyacetyl nitrate; PM = particulate matter; SO<sub>2</sub> = sulfur dioxide; SO<sub>4</sub><sup>2-</sup> = sulfate; SO<sub>x</sub> = SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>; VOC = volatile organic compounds.

The sum of reactive oxidized nitrogen species is referred to as NO<sub>y</sub> (NO<sub>y</sub> = NO + NO<sub>2</sub> + HNO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO + NO<sub>3</sub><sup>-</sup> + N<sub>2</sub>O PAN + other organic nitrates).

Although not explicitly indicated, wet and dry deposition of PM components (e.g., metals, minerals, and secondary organic aerosols) also occur and contribute to ecological effects.

Source: Modified from [U.S. EPA \(2008a\)](#).

**Figure IS-2 Overview of atmospheric chemistry, deposition, and ecological effects of emissions of oxides of nitrogen, oxides of sulfur, and reduced nitrogen.**

## IS.2.2 Concepts

This ISA draws on many methodological approaches and disciplines within the larger scientific fields of ecology and atmospheric sciences. The studies discussed herein are best understood in the context of some general concepts within these fields, such as ecosystem scale, structure, and function ([Section IS.2.2.1](#)); deposition and source apportionment to ecosystems ([Section IS.2.2.2](#)); critical loads ([Section IS.2.2.3](#)); biodiversity ([Section IS.2.2.4](#)); the effects of reduced versus oxidized forms of N

([Section IS.2.2.5](#)); and the metric developed in the previous secondary NAAQS review, the Aquatic Acidification Index (AAI; [Section IS.2.2.6](#)). The topics discussed in this “Concepts” section do not have separate sections dedicated to them in the [Integrated Synthesis](#). The topics of ecosystem recovery, ecosystem services, and uncertainty, while conceptual in nature, are not discussed here because they are the focus of more detailed discussions in [Section IS.11](#), [Section IS.13](#), and [Section IS.14](#), respectively.

Ecosystem structure comprises both biodiversity and geography. Biodiversity encompasses many quantitative measures of the abundance and distribution of organisms within a defined geographical area (for a more explicit definition, see [Section IS.2.2.1](#) and [Section IS.2.2.4](#)). Ecosystem function refers to processes that control fluxes and pools of matter and energy in the ecosystem ([Section IS.2.2.1](#)). The loss of biodiversity is a key consequence of the air pollutants discussed in this ISA. The importance of preserving biodiversity and ecosystem function contributes to the sustainability of ecosystem services that benefit human welfare and society in general ([Section IS.2.2.4](#) and [Appendix 14](#)).

In human health assessments, dose-response relationships are used to identify quantitative relationships between chemical exposure (dose) and health outcomes (response), with emphasis on identifying thresholds, or the lowest doses at which negative health outcomes are observed. In ecology, CLs provide a similar quantitative relationship between chemical dose (e.g., deposition) and specific, quantitative changes in ecological properties or processes ([Section IS.2.2.3](#)). For CLs to be used in evaluating the effects of deposition upon ecosystems that receive N or S from multiple sources, those other sources must be considered in comparison to deposition level ([Section IS.2.2.2](#)), as well as the heterogeneous sensitivities of organisms and ecosystems to different chemical forms of deposition ([Section IS.2.2.5](#)).

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### **IS.2.2.1 Ecosystem Scale, Structure, and Function**

For this assessment, an ecosystem is defined as the interactive system formed from all living organisms (biota) and their abiotic (chemical and physical) environment within a given area ([IPCC, 2007a](#)). Ecosystem spatial boundaries are somewhat arbitrary, depending on the focus of interest or study. Thus, the spatial extent of an ecosystem may range from very small, well-circumscribed systems such as a small pond, to biomes at the continental scale, or the entire globe ([U.S. EPA, 2008a](#)). Ecosystem spatial scale does not always correlate with complexity. A small pond may be a complex system with multiple trophic levels ranging from phytoplankton to invertebrates to several feeding guilds of fish. A large lake, on the other hand, may be a very simple ecosystem, such as the Great

Salt Lake in Utah that covers approximately 1,700 square miles but contains only bacteria, algae, diatoms, and two invertebrate species ([U.S. EPA, 2013b](#)). All ecosystems, regardless of size or complexity, have multiple interactions between biota and abiotic factors. Ecosystems include both structural (geography and biodiversity [e.g., soil type and food web trophic levels]) and functional (flow of energy and matter [e.g., decomposition, nitrification]) attributes. Ecosystem changes are often considered undesirable if important structural or functional components of the ecosystems are altered following pollutant exposure ([U.S. EPA, 2013b](#), [1998a](#)).

Biotic or abiotic structure may define an ecosystem. Abiotic structure includes climatic and edaphic components. Biotic structure includes species abundance, richness, distribution, evenness, and composition, measured at the population, species, community, ecosystem, or global scale. A species (for eukaryotic organisms) is defined by a common morphology, genetic history, geographic range of origin, and ability to interbreed and produce fertile offspring. A population consists of interbreeding groups of individuals of the same species that occupy a defined geographic space. Interacting populations of different species occupying a common spatial area form a community ([Barnthouse et al., 2008](#)). Community composition may also define an ecosystem type, such as a pine forest or a tall grass prairie. Pollutants can affect the ecosystem structure at any of these levels of biological organization ([Suter et al., 2005](#)).

Individual plants or animals may exhibit changes in metabolism, enzyme activities, hormone function, or may suffer gross lesions, tumors, deformities, or other pathologies. However, only some organism-level endpoints affected by pollution, such as growth, survival, and reproductive output, have been definitively linked to effects at the population level and above ([U.S. EPA, 2013b](#)). Population-level effects of pollutants include changes over time in abundance or density (number of individuals in a defined area), age or sex structure, and production or sustainable rates of harvest ([Barnthouse et al., 2008](#)). Community-level attributes affected by pollutants include species richness, species abundance, composition, evenness, dominance of one species over another, or size (area) of the community ([U.S. EPA, 2013b](#)). Pollutants may affect communities in ways that are not observable in organisms or populations ([Bartell, 2007](#)), including (1) effects resulting from interactions between species, such as altered predation rates or competitive advantage; (2) indirect effects, such as reducing or removing one species from the assemblage and allowing another to emerge ([Petraitis and Latham, 1999](#)); and (3) alterations in trophic structure.

Alternatively, ecosystems may be defined on a functional basis. “Function” refers to the suite of processes and interactions among the ecosystem components that involve energy or matter. Examples include water dynamics and the flux of trace gases such as rates of

photosynthesis, decomposition, nitrification, or carbon cycling. Pollutants may affect biotic structure indirectly. For example, a pollutant may first alter abiotic conditions (e.g., soil chemistry), which in turn influences biotic structure and function ([Bartell, 2007](#)).

Some ecosystems, and some aspects of particular ecosystems, are less vulnerable to long-term consequences of pollutant exposure. Other ecosystems may be profoundly altered if a single attribute is affected by pollution. Thus, spatial and temporal definitions of ecosystem structure and function become essential factors in defining affected ecosystem services and in determining CLs for certain pollutants, either as single pollutants or in combination with other stressors.

The main causal determinations of this ISA ([Section IS.2.3](#)) are that N and S deposition affect ecosystem structure, with effects ranging from biogeochemical alterations in soil and water chemistry to multiple levels of biological organization, including species-level alterations of physiological processes and shifts in biodiversity and ecological function.

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#### **IS.2.2.2 Deposition and Source Contribution of Nitrogen (N) and Sulfur (S) to Ecosystems**

Deposition of N and S results from a variety of human activities and atmospheric processes. Emissions from stationary, mobile, and agricultural sources undergo atmospheric transformation ([Section IS.3.1](#)) to form products that are eventually deposited out of the air onto the land or waterscape ([Section IS.3.3](#)). The contribution of atmospheric deposition to total loading for N and S varies within and among terrestrial, wetland, freshwater, and estuarine ecosystems.

In the 2008 ISA, atmospheric deposition was identified as the main source of anthropogenic N to unmanaged terrestrial ecosystems. This conclusion has been confirmed by new studies on N sources to lands and waterways ([Appendix 4.2](#)). Across all watersheds, atmospheric N deposition is the second largest overall human-mediated N source; agriculture is the largest, and the largest N source to 33% of watersheds. Current deposition levels in the U.S. are discussed in [Appendix 2](#) and [Section IS.3.3](#). No new information has been published on nonatmospheric sources of S in terrestrial ecosystems ([Appendix 4.2](#)); S inputs from the atmosphere are discussed in [Appendix 2](#) and [Section IS.3.3](#).

In the 2008 ISA, atmospheric deposition was also identified as the main source of N to some freshwater ecosystems, including headwater streams, high-elevation lakes, lower order streams in undisturbed areas, and freshwater wetlands (e.g., bogs and fens). Evidence for the influence of N deposition on water chemistry has been further supported

by new studies that quantify the contribution of N deposition to total N loading in freshwater lakes and streams, and which quantify atmospheric contributions during storm events ([Table 7-1](#)). As shown in these studies, deposition can represent a substantial portion of total N loading to surface waters. However, other nonpoint and point sources of N dominate N inputs to high-order streams.

In fresh surface waters and wetlands, S that contributes to enrichment induces acidifying effects. Sources of S include weathering of minerals in sediments and rocks, leaching from terrestrial S cycling, internal cycling, and direct atmospheric deposition. The 2008 ISA showed that drought can release S stored in wetlands or lake sediments because bound sulfide ( $S^{2-}$ ) is exposed to atmospheric oxygen and oxidized to  $SO_4^{2-}$ . Increases in waterborne  $SO_4^{2-}$  concentration through various concurrent processes has been observed as a result of drought in whole-lake observational research (93% increase in Little Rock Lake, WI, from 1.5 to 2.9 mg/L), and in response to variation in water levels from climate change-induced droughts in modelling using Model of Acidification of Groundwater in Catchments (MAGIC). New evidence confirms that fluctuating water levels in wetlands increase  $SO_4^{2-}$  concentration in pulses following water level recovery.

The importance of atmospheric deposition as a cause of estuarine eutrophication is determined by the relative contribution of the atmospheric versus nonatmospheric sources of N input. Sources of N in coastal areas may include direct deposition to the water surface, coastal upwelling from oceanic waters, and transport from watersheds. Freshwater inflows to estuaries often transport N from agriculture, urban, wastewater, and atmospheric deposition sources. Atmospheric deposition constitutes less than half of the total N supply in most, but not all, estuaries ([Table 7-9](#)). Both point sources and nonpoint sources (including runoff, as well as atmospheric deposition) have been identified as targets for mitigation of N loading in coastal areas. Seawater contains high concentrations of  $SO_4^{2-}$ , so atmospheric inputs of S are unlikely to contribute substantially to biogeochemical or biological effects in coastal areas.

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### IS.2.2.3 Critical Loads Concept and General Approaches

The following section provides a discussion of important concepts regarding Critical Loads (CLs). The definition of a CL is, “a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge” ([Nilsson and Grennfelt, 1988](#)). This definition is intended as background material to support a better understanding of the CL calculations presented throughout the ISA. The main concepts presented here include CLs as an organizing principle, CL heterogeneity across the

landscape, more than one CL for a given location, the pros and cons of methods used to calculate CLs (e.g., empirical, steady state, and dynamic), and a comparison of CLs versus target loads. Uncertainty in calculating CLs is discussed in [Section IS.13](#).

Throughout this ISA, the CL concept is used as an organizing principle to relate atmospheric deposition to ecological endpoints that indicate impairment. The development of a quantitative CL estimate requires a number of steps. An illustrative example of the eight general steps is shown in [Figure IS-3](#).

1) Disturbance	Acidification				Eutrophication	
2) Receptor	Forest		Lake		Grassland	Lake
3) Biological indicator	Sugar Maple	Norway Spruce	Brook trout	Fish species richness	Species diversity	Primary productivity
4) Critical biological response	Failure to reproduce	Seedling death	Presence absence	Species loss	Species loss	Excess productivity
5) Chemical indicator	Soil % Base Saturation	Soil Ca/Al ratio	Lakewater ANC	Lakewater ANC	Soil C/N ratio	Lakewater NO <sub>3</sub>
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO <sub>4</sub> , NO <sub>3</sub> , NH <sub>4</sub>	SO <sub>4</sub> , NO <sub>3</sub> , NH <sub>4</sub>	SO <sub>4</sub> , NO <sub>3</sub> , NH <sub>4</sub>	SO <sub>4</sub> , NO <sub>3</sub> , NH <sub>4</sub>	NO <sub>3</sub> , NH <sub>4</sub>	NO <sub>3</sub> , NH <sub>4</sub>
8) Critical pollutant load	???	???	???	???	???	???

Al = aluminum; ANC = acid-neutralizing capacity; C = carbon; Ca = calcium; L = liter; µeq = microequivalents; N = nitrogen; NH<sub>4</sub> = ammonium; NO<sub>3</sub> = nitrate; SO<sub>4</sub> = sulfate.

Source: [U.S. EPA \(2008a\)](#).

**Figure IS-3** An example of the matrix of information considered in defining and calculating critical loads (see discussion in text). Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits could be used.

It is important to recognize that there is no single “definitive” CL for an ecological effect. CL estimates reflect the current state of knowledge and the selected limits, indicators, and responses. Changes in scientific understanding may include, for example, new dose-response relationships, better resource maps and inventories, larger survey data sets, continuing time-series monitoring, and improved numerical models.

Calculating multiple CLs for a given pollutant at a single location is not uncommon because of the nested sequence of disturbances, receptors, and biological indicators considered for a given pollutant. Multiple CL values may also arise from an inability to agree on a single definition of “harm.” Calculation of CLs for multiple definitions of “harm” may be deemed useful in subsequent discussions of the analysis and in the decision-making steps that may follow CL calculation.

The heterogeneity of natural environments can affect responsiveness of ecosystems to deposition load. For example, the high spatial variability of soils almost guarantees that for any reasonably sized soil-based “receptor” that might be defined in a CL analysis, there will be a continuum of CL values for any indicator chosen. Although the range of this continuum of values might be narrow, there is nevertheless an a priori expectation in any CL analysis that multiple values (or a range of values) will result from the analysis. Given the heterogeneity of ecosystems affected by N and S deposition, published CL values for locations in the U.S. vary depending on both biological and physical factors.

The three approaches to developing CLs (i.e., empirical observation, steady-state modeling, and dynamic modeling) each have strengths and limitations. It is suggested that the combined approach of calculating CLs from biogeochemical simulation models in conjunction with empirical analyses is the most effective way to characterize the effects of deposition to a given environment ([Fenn et al., 2015](#)). For all three types of models, spatial boundaries of where to apply a CL are important. For example, a CL may apply to a watershed, ecoregion, or species range, depending on how the CL is defined.

An important advantage of empirical CLs is that they are based on measured (vs. modeled) changes in ecological variables in response to inputs. Consequently, the links between deposition and the measured response variable are direct; full process-level knowledge is not required. Empirical CLs are important for validating CL values determined with models ([Fenn et al., 2015](#)).

[Fenn et al. \(2015\)](#) discussed that the advantages of models, “are that ecosystem responses to alternative scenarios can be tested. These might include changes in atmospheric deposition, disturbance or climatic conditions, and responses to silvicultural treatments, grazing, fire, and other disturbances. Simulation modeling allows temporal aspects of ecosystem response in relation to CLs and CL exceedances to be evaluated, including evaluation of historical and future conditions.”

Two key ways that steady-state and dynamic models differ in their modeling of CLs is by how they assume ecosystem equilibrium and by the amount of input data they need for parameterization.

Steady-state models assume that the ecosystem is in equilibrium with the CL of deposition; therefore, the long-term sustainable deposition, that is the CL, is indicated. This is the relevant information needed to provide protection from deposition in perpetuity as the system comes into equilibrium with the pollutant CL. In the U.S., few (if any) ecosystems qualify as steady-state systems. Therefore, the assumption of equilibrium in the steady-state model is often false. The steady-state models give no information concerning the time to achieve the equilibrium or what may happen to the receptor along the path to equilibrium. The recovery of an ecosystem based on a CL from a steady-state model may take several hundred years. In other words, the assumption that attainment of a deposition value below the steady-state CL will result in biological recovery within a specified time period may not be valid. Dynamic models calculate time-dependent CLs and, therefore, do not assume an ecosystem that is in equilibrium. The time-dependent calculation is relevant information to provide protection from damage by the pollutant within a specific time frame. Generally, the shorter the time frame selected, the lower the CL.

Data requirements for steady-state models tend to be much lower than for dynamic models. Therefore, the data required to conduct dynamic modeling are not available for as many places as the data required to conduct steady-state modeling. The few national-scale modeling efforts for both terrestrial and aquatic acidification are both done with steady-state models for this reason.

The results of all three CL approaches are difficult to extrapolate across geographic space. Spatially, variation in biological and biogeochemical processes imposed by climate, geology, biota, and other environmental factors may alter the deposition-response relationship. Empirical CLs may only be applied with confidence to sites with highly similar biotic and environmental conditions ([Pardo et al., 2011a](#)). This is particularly problematic in areas where deposition has received sparse research attention—as is sometimes the case for CLs of N deposition related to N driven eutrophication ([Appendix 6.4](#)). Models may be run at different locations, but the data needed to parameterize them is not always available.

CLs are different from target loads. [Fenn et al. \(2011b\)](#) defined the “target load” as follows: “The acceptable pollution load that is agreed upon by policy makers or land managers. The target load is set below the CL to provide a reasonable margin of safety, but could be set higher than the CL at least temporarily.” Target loads are selected based on the level of ecosystem protection desired, economic considerations, and stakeholder input at a given location.

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#### IS.2.2.4 The Importance of Biodiversity

There are causal relationships between additions of N and/or S to an ecosystem and biodiversity loss in terrestrial, freshwater, wetland, and estuarine ecosystems in the U.S. ([Table IS-1](#)). What does it mean to lose biodiversity? Biodiversity loss not only means the extirpation of unique living species, it represents the potential loss of ecosystem function and ecosystem services, as shown by several decades of research in a wide variety of natural systems ([Hooper et al., 2012](#); [Balvanera et al., 2006](#); [Tilman, 2000](#)). Numerous studies demonstrate that the number and diversity of organisms in a system control the abundance of habitat for other species, the biogeochemical cycling of nutrients and carbon, and the efficiency at which biotic systems are able to transform limited resources into biomass ([Cardinale et al., 2011](#)). Among plant communities, higher biodiversity leads to higher overall plant productivity and greater retention of soil nutrients ([Reich et al., 2012](#); [Tilman, 2000](#)). In multitrophic systems, higher prey diversity leads to both higher predator growth rates and a smaller impact of predation on prey abundance ([Duffy et al., 2007](#)). Positive impacts of biodiversity on ecosystem services have been documented in forests ([Gamfeldt et al., 2013](#); [Zhang et al., 2012b](#)), grasslands ([Tilman et al., 2012](#)), arid and semiarid ecosystems ([Maestre et al., 2012](#)), and marine systems ([Gamfeldt et al., 2015](#); [Worm et al., 2006](#)) and include effects such as greater carbon storage, fruit production, wood production, and nutrient cycling. In marine ecosystems, biodiversity loss has been linked to increased rates of exponential decreases in water quality through metrics such as higher numbers of beach closures and harmful algal blooms [HABs; [Worm et al. \(2006\)](#)]. Notably, HABs are linked to increased disease prevalence among humans, domestic animals/pets, and aquatic organisms ([Johnson et al., 2010](#)). In addition to the relationship between HABs and disease, there is now empirical evidence from many ecosystems of a broader link between declines in biodiversity and increased transmission and severity of disease ([Johnson et al., 2015b](#)) caused by plant, wildlife, and human pathogens. As a whole, these decades of research have produced an overwhelming body of evidence indicating that the loss of biodiversity risks a deterioration of the ecosystem goods and services on which humanity depends on ([Gamfeldt et al., 2015](#); [Cardinale et al., 2012](#)).

One of the most important consensus observations in biodiversity research is that ecosystem processes are more stable (have less temporal variability) at higher levels of diversity ([Cardinale et al., 2012](#); [McCann, 2000](#); [Naeem and Li, 1997](#); [Tilman and Downing, 1994](#)). This stability occurs because species respond differently to environmental variation. In diverse communities, it is more likely that declines in the growth of one species caused by an environmental change will provide more resources for competing species ([Cardinale et al., 2012](#); [Tilman, 2000](#)). This property was predicted by economists and is similar to how more diversified investment portfolios provide

enhanced stability under fluctuating market conditions ([Doak et al., 1998](#); [Tilman et al., 1998](#)). Notably, there is also consensus that the impact of biodiversity on ecosystem processes is nonlinear, wherein declines in ecosystem processes accelerate as the number of species in a system declines ([Cardinale et al., 2012](#)). Accelerating ecosystem service declines in response to species loss may be because different ecosystem functions require the presence of different sets of species ([Isbell et al., 2015](#); [Reich et al., 2012](#); [Zavaleta et al., 2010](#)). The increased stability of diverse ecosystems makes these systems less vulnerable to environmental change or collapse caused by external forces such as drought or human disturbance ([Isbell et al., 2015](#); [Tilman et al., 2012](#); [Isbell et al., 2011](#); [Worm et al., 2006](#)). For example, coastal systems with higher species diversity had lower rates of fishery collapse and extinction for commercially important fish and invertebrate species, and large marine ecosystems with higher fish diversity recovered more quickly from collapse ([Worm et al., 2006](#)). Thus, there is strong evidence that high biodiversity helps sustain ecosystem services and makes these ecosystem services more resilient to environmental change.

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### IS.2.2.5 Reduced versus Oxidized Nitrogen Effects across Ecosystems

Individual biochemical and geochemical processes involve specific chemical forms of N, suggesting that there may be consequences in many ecosystems from the ongoing trend of decreasing  $\text{NO}_y$  deposition and increasing  $\text{NH}_x$  deposition in many parts of the U.S. ([Section IS.3](#)). The largest body of evidence that the effects of reduced versus oxidized N may have different consequences for ecological structure and function is for estuaries where the form of N delivered to some coastal areas of the U.S. is shifting from primarily  $\text{NO}_3^-$  to an increase in reduced forms of N. Although unlikely to be attributed solely to atmospheric sources due to the large contribution of N from wastewater, agriculture, and other sources, inputs of ammonia ( $\text{NH}_3$ ) and  $\text{NH}_4^+$  selectively favor specific phytoplankton functional groups (e.g., cyanobacteria, dinoflagellates) including harmful species ([Figure 10-7](#)). Shifts in phytoplankton community composition to species that respond strongly to reduced N have been observed in some coastal regions ([Appendix 10.3.2](#)). Growth of some species of phytoplankton ([Appendix 10.2.2](#)) and macroalgae (seaweed; [Appendix 10.2.3](#)) appear to be related to the form of N. There is also increasing evidence in freshwater systems for the importance of N in harmful algal blooms (HABs), and several studies have shown that the form of N influences freshwater algal species composition ([Appendix 9.2.6.1](#)). In terrestrial systems, oxidation-reduction status of inorganic N seems to have little influence on the biological responses to N deposition ([Appendix 4.3.12](#)).

Because some soil biogeochemical processes involve specific chemical forms of N (e.g., denitrification, ammonium toxicity), there is the potential that biological responses to N deposition (or N addition) could depend on whether the dominant form of deposited N is oxidized ( $\text{NO}_y$ ) or reduced ( $\text{NH}_x$ ). Different responses to individual forms of N have been observed for some soil biogeochemical processes ([Table 4-13](#)) and terrestrial biological responses ([Table 6-1](#)). Moreover, a number of individual studies have observed differential effects of  $\text{NH}_4^+$  versus  $\text{NO}_3^-$  additions on plant community diversity [e.g., [Kleijn et al. \(2008\)](#); [Dias et al. \(2014\)](#)]. In general, however, meta-analyses in the literature have tended to find no difference in the effects of individual forms of N on terrestrial biological endpoints like plant productivity or microbial biomass ([Table 6-1](#)). This result suggests that terrestrial community diversity is also generally not differentially affected by the form of N, possibly because plant uptake of N is mediated by soil biogeochemical cycles that often rapidly transform N between oxidized and reduced forms.

Evidence of wetland responses to different chemical forms of N come primarily from N addition experiments conducted outside of the U.S. In European bogs and fens, both forms of N addition decreased ecosystem N retention, but oxidized N addition caused dissolved organic nitrogen (DON) leaching, while reduced N caused dissolved inorganic nitrogen (DIN) leaching as well as cation leaching ([Appendix 11.3.1.6](#)). Reduced N caused greater physiological stress or injury than equivalent loads of oxidized N in moss species ([Appendix 11.4.5](#) and [Appendix 11.5.5](#)).

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### IS.2.2.6 Aquatic Acidification Index (AAI)

The 2017 IRP ([U.S. EPA, 2017c](#)) described the Aquatic Acidification Index (AAI) to be a novel approach for a multipollutant standard intended to address deposition-related effects. Scientifically, the AAI represented an advancement in ecological methodology to (1) calculate CLs for aquatic acidification on a national scale, when previously CLs had been calculated on the spatial scale of a watershed and (2) provide a uniform level of ecological protection at the national scale. These advancements were accomplished by first aggregating CLs calculated for the same chemical limit within a defined spatial region. Next, the distribution of the “population” of CL values was evaluated, and the percentage of water bodies to protect was selected as a potential method to evaluate different conservation targets. The AAI also presented novel advancements in atmospheric sciences, including (1) using transference ratios to relate atmospheric concentrations of criteria pollutants to deposition levels and (2) allowing quantification of criteria pollutants ( $\text{NO}_y$  and  $\text{SO}_x$ ) and noncriteria pollutant (e.g.,  $\text{NH}_x$ ) contributions to total acidifying deposition. As a scientific publication, the AAI is documented in [Scheffe](#)

[et al. \(2014\)](#). The AAI was originally developed in the 2011 NO<sub>x</sub>SO<sub>x</sub> Policy Assessment ([U.S. EPA, 2011a](#)), and the equation is described with terms that traditionally define a NAAQS [the indicator,<sup>1</sup> averaging time,<sup>2</sup> form,<sup>3</sup> and level<sup>4</sup>—further described in the 2017 IRP ([U.S. EPA, 2017c](#))].

Key scientific aspects of the AAI equation, as the form of a potential standard, are described in the following excerpt from 2017 IRP ([U.S. EPA, 2017c](#)):

“The AAI, as described in the PA ([U.S. EPA, 2011a](#)), was constructed from steady-state ecosystem modeling, and included atmospheric transference ratios and deposition of reduced forms of nitrogen (ammonia gas and ammonium ion, expressed as NH<sub>x</sub>). These nonoxidized forms of nitrogen were included since ecosystems respond to total nitrogen deposition, whether from oxidized or reduced forms. More specifically, the AAI equation was defined in terms of four ecological and atmospheric factors and the ambient air indicators NO<sub>Y</sub> and SO<sub>X</sub>:

$$AAI = F1 - F2 - F3[NO_Y] - F4[SO_X]$$

**Equation IS-1**

where  $F1^5$  represents the ecosystems natural ability to provide acid-neutralizing capacity (e.g., geology, plant uptake of nitrogen deposition) and other processes;  $F2^6$  represents acidifying deposition associated with reduced forms of nitrogen, NH<sub>x</sub>; and  $F3^7$  and  $F4^8$  are the

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<sup>1</sup> The “indicator” of a standard defines the chemical species or mixture that is measured in determining whether an area attains the standard.

<sup>2</sup> The “averaging time” defines the time period over which ambient measurements are averaged (e.g., 1-hour, 8-hour, 24-hour, annual).

<sup>3</sup> The “form” of a standard defines the air quality statistic that is compared to the level of the standard in determining whether an area attains the standard.

<sup>4</sup> The “level” defines the allowable concentration of the criteria pollutant in the ambient air.

<sup>5</sup>  $F1$  is defined as:  $ANC_{lim} + CL_r/Q_r$ , with  $ANC_{lim}$  representing a target ANC level. With regard to  $CL_r$ , the PA developed distributions of calculated critical loads for a specific ecoregion; in setting an AAI-based standard, a percentile would need to be specified to reference the value of  $CL_r$  to be used in the AAI equation [[U.S. EPA \(2011a\)](#), p. 7–37]. The PA described the percentile as an aspect of the form for the standard [[U.S. EPA \(2011a\)](#), Section 7.7].

<sup>6</sup>  $F2$  is defined as:  $NH_x/Q_r$ , where  $NH_x$  is the deposition divided by  $Q_r$  [[U.S. EPA \(2011a\)](#), p. 7–37].

<sup>7</sup>  $F3$  is defined as:  $TNO_Y/Q_r$ , where  $TNO_Y$  is the transference ratio that converts deposition of NO<sub>Y</sub> to ambient air concentrations of NO<sub>Y</sub> [[U.S. EPA \(2011a\)](#), p. 7–37].

<sup>8</sup>  $F4$  is defined as:  $TSO_X/Q_r$ , where  $TSO_X$  is the transference ratio that converts deposition of SO<sub>X</sub> to ambient air concentrations of SO<sub>X</sub> [[U.S. EPA, 2011a](#)], p. 7–37].

transference ratios that convert concentrations of  $\text{NO}_Y$  and  $\text{SO}_X$  to related deposition of nitrogen and sulfur [[U.S. EPA \(2011a\)](#), Section 7.7].”

Several other key scientific considerations are included in the AAI that were discussed in the 2011  $\text{NO}_X\text{SO}_X$  Policy Assessment ([U.S. EPA, 2011a](#)).

- Spatial heterogeneity of factors in the AAI equation: The value of factors in the AAI equation vary across the U.S. Factors could be calculated for a spatial boundary based on an ecologically similar landscape (e.g., Omernick ecoregion).
- Temporal heterogeneity: There is a relatively high degree of interannual variability expected in the AAI because it is so strongly influenced by the amount and pattern of precipitation that occurs within a region from year to year; therefore, averaging calculated annual AAI values over 3 to 5 years would provide reasonable stability.
- Level: With regard to a level for the AAI, the 2011  $\text{NO}_X\text{SO}_X$  Policy Assessment ([U.S. EPA, 2011a](#)) concluded that consideration should be given to a level within the range of 20 to 75  $\mu\text{eq/L}$ , noting that a target Acid Neutralizing Capacity (ANC) value of 20  $\mu\text{eq/L}$  would be a reasonable lower end of this range, so as to protect against chronic acidification-related adverse impacts on fish populations which have been characterized as severe at ANC values below this level.

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### IS.2.3 Changes: New Evidence and Causal Determinations

Since the 2008 ISA, several conceptual changes have occurred in our understanding of the atmospheric sciences and ecological effects of  $\text{NO}_X$ ,  $\text{SO}_X$  and PM. They include our understanding of the sources of N deposition and in the relationship between atmospheric concentration and deposition ([Section IS.3](#) and [Appendix 2](#)). Models of N deposition rely on accurate emissions data. Since the 2008 ISA, deposition of oxidized nitrogen has been decreasing but deposition of reduced nitrogen has been increasing. As a result, the uncertainty in total reactive N emissions ( $\text{NO}_X + \text{NH}_X$ ) has increased because emissions estimates that have the lowest levels of uncertainty are from stationary and mobile sources, which contribute more to  $\text{NO}_X$  than  $\text{NH}_X$  emissions, and higher levels of uncertainty are associated with agricultural emissions, which contribute more to  $\text{NH}_X$  than  $\text{NO}_X$  emissions.

A better understanding of the relationship between atmospheric concentration and deposition has resulted from advances in understanding bidirectional exchange of  $\text{NH}_3$  and  $\text{NO}_Y$  chemistry within canopies. These advances have led to the first efforts to provide a detailed characterization of N and S deposition on a national scale, by using both measured and modeled values to provide estimates of total sulfur and nitrogen deposition across the U.S.

New evidence since the 2008 ISA increases the weight of evidence for ecological effects, confirming concepts previously identified and improving quantification of dose (deposition)–response relationships, particularly for N deposition. The ecological effects are described by the causality determinations. There are 18 causality statements in this ISA ([Table IS-1](#)). Fourteen are causal relationships repeated from the 2008 ISA or modified from the 2008 ISA to include specific endpoints. One is a likely causal relationship repeated from the 2009 PM ISA. Three are new endpoint categories not evaluated in the 2008 ISA. [Table IS-3](#) shows that N and S deposition cause alteration of (1) biogeochemical components of soil and water chemistry and (2) multiple levels of biological organization ranging from physiological processes to shifts in biodiversity and ecological function ([Figure IS-4](#)).

The current NO<sub>2</sub> and SO<sub>2</sub> secondary NAAQS are set to protect against direct damage to vegetation by exposure to gas-phase oxides of nitrogen and oxides of sulfur. Research continues to support causal relationships between SO<sub>2</sub>, NO<sub>2</sub>, NO, peroxyacetyl nitrate (PAN), HNO<sub>3</sub>, and injury to vegetation ([Table IS-1](#)), but research that tests plant response to the lower exposure levels that represent current atmospheric NO<sub>Y</sub> and SO<sub>X</sub> concentrations is limited. Therefore, little evidence is available to help determine whether current monitored concentrations of gas-phase NO<sub>Y</sub> and SO<sub>X</sub> are high enough to injure vegetation.

It is clear that the criteria pollutants NO<sub>Y</sub>, SO<sub>X</sub>, and PM, in addition to the noncriteria pollutant NH<sub>3</sub>, contribute to total N and S deposition, which alters the biogeochemistry and the physiology of organisms, resulting in harmful declines in biodiversity. Decreases in biodiversity mean that some species become relatively less abundant and may be locally extirpated. The current period in Earth's history is the Anthropocene. In addition to a spike in soil radiocarbon from nuclear bomb testing ([Turney et al., 2018](#)), a defining attribute of the Anthropocene is global, human-driven mass extinctions of many species. The biodiversity loss reported in this assessment contributes to the Anthropocene loss of biodiversity ([Rockstrom et al., 2009](#)). In addition to the loss of unique living species, the decline in total biodiversity is harmful because biodiversity is an important determinant of the stability of ecosystems and the ability of ecosystems to provide services to humanity (see more on biodiversity in [Section IS.2.2.4](#)).

**Table IS-1 Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 Particulate Matter (PM) ISA, for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current ISA
<b>Gas-phase direct phytotoxic effects</b>		
Gas-phase SO <sub>2</sub> and injury to vegetation <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.1</a>	Causal relationship	Causal relationship
Gas-phase NO, NO <sub>2</sub> , and PAN and injury to vegetation <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.2</a>	Causal relationship	Causal relationship
Gas-phase HNO <sub>3</sub> and injury to vegetation <sup>a</sup> <a href="#">Section IS.3</a> and <a href="#">Appendix 3.6.3</a>	Causal relationship	Causal relationship
<b>N and acidifying deposition to terrestrial ecosystems</b>		
N and S deposition and alteration of soil biogeochemistry in terrestrial ecosystems <sup>b</sup> <a href="#">Section IS.5.1</a> and <a href="#">Appendix 4.1</a>	Causal relationship	Causal relationship
N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems <sup>c</sup> <a href="#">Section IS.5.2</a> and <a href="#">Appendix 6.6.1</a>	Not included	Causal relationship
N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems <sup>c</sup> <a href="#">Section IS.5.2</a> and <a href="#">Appendix 6.6.2</a>	Causal relationship	Causal relationship
Acidifying N and S deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems <sup>d</sup> <a href="#">Section IS.5.3</a> and <a href="#">Appendix 5.7.1</a>	Not included	Causal relationship
Acidifying N and S deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems <sup>d</sup> <a href="#">Section IS.5.3</a> and <a href="#">Appendix 5.7.2</a>	Causal relationship	Causal relationship
<b>N and acidifying deposition to freshwater ecosystems</b>		
N and S deposition and alteration of freshwater biogeochemistry <sup>e</sup> <a href="#">Section IS.6.1</a> and <a href="#">Appendix 7.1.7</a>	Causal relationship	Causal relationship

**Table IS-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 Particulate Matter (PM) ISA, for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current ISA
Acidifying N and S deposition and changes in biota, including physiological impairment and alteration of species richness, community composition, and biodiversity in freshwater ecosystems <sup>f</sup> <a href="#">Section IS.6.3</a> and <a href="#">Appendix 8.6</a>	Causal relationship	Causal relationship
N deposition and changes in biota, including altered growth and productivity, species richness, community composition, and biodiversity due to N enrichment in freshwater ecosystems <sup>g</sup> <a href="#">Section IS.6.2</a> and <a href="#">Appendix 9.6</a>	Causal relationship	Causal relationship
<b>N deposition to estuarine ecosystems</b>		
N deposition and alteration of biogeochemistry in estuarine and near-coastal marine systems <a href="#">Section IS.7.1</a> and <a href="#">Appendix 7.2.10</a>	Causal relationship	Causal relationship
N deposition and changes in biota, including altered growth, total primary production, total algal community biomass, species richness, community composition, and biodiversity due to N enrichment in estuarine environments <sup>h</sup> <a href="#">Section IS.7.2</a> and <a href="#">Appendix 10.7</a>	Causal relationship	Causal relationship
<b>N deposition to wetland ecosystems</b>		
N deposition and the alteration of biogeochemical cycling in wetlands <a href="#">Section IS.8.1</a> and <a href="#">Appendix 11.10</a>	Causal relationship	Causal relationship
N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands <a href="#">Section IS.8.2</a> and <a href="#">Appendix 11.10</a>	Causal relationship	Causal relationship
<b>S deposition to wetland and freshwater ecosystems</b>		
S deposition and the alteration of mercury methylation in surface water, sediment, and soils in wetland and freshwater ecosystems <sup>i</sup> <a href="#">Section IS.9.1</a> and <a href="#">Appendix 12.7</a>	Causal relationship	Causal relationship

**Table IS-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO<sub>x</sub>/SO<sub>x</sub> Integrated Science Assessment (ISA) or the 2009 Particulate Matter (PM) ISA, for other effects of PM, and the current draft ISA.**

Effect Category	Causal Determination	
	2008 NO <sub>x</sub> /SO <sub>x</sub> ISA	Current ISA
S deposition and changes in biota due to sulfide phytotoxicity, including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems <a href="#">Section IS.9.2</a> and <a href="#">Appendix 12.7</a>	Not included	Causal relationship
	2009 PM ISA	Current Draft ISA
<b>Other ecological effects of PM (course and fine particles, without regard to chemical speciation)</b>		
PM and a variety of effects on individual organisms and ecosystems <a href="#">Section IS.10</a> and <a href="#">Appendix 15.7</a>	Likely to be a causal relationship	Likely to be a causal relationship

C = carbon; Hg = mercury; HNO<sub>3</sub> = nitric acid; ISA = Integrated Science Assessment; N = nitrogen; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; PAN = peroxyacetyl nitrate; S = sulfur; SO<sub>2</sub> = sulfur dioxide.

<sup>a</sup>The 2008 ISA causality statements for gas-phase HNO<sub>3</sub> was phrased as “changes in vegetation.”

<sup>b</sup>The 2008 ISA included two causality statements for terrestrial biogeochemistry which were phrased as “relationship between acidifying deposition and changes in biogeochemistry” and “relationship between N deposition and the alteration of biogeochemical cycling of N.”

<sup>c</sup>The 2008 ISA causality statement for biological effects of N enrichment in terrestrial ecosystems was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity.”

<sup>d</sup>The 2008 ISA causality statement for biological effects of acidifying deposition in terrestrial ecosystems was phrased as “relationship between acidifying deposition and changes in terrestrial biota.”

<sup>e</sup>The 2008 ISA included three causality statements for freshwater biogeochemistry phrased as “relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems,” “relationship between N deposition and the alteration of biogeochemical cycling of N,” and “relationship between N deposition and the alteration of biogeochemical cycling of C.”

<sup>f</sup>The 2008 ISA causality statement for biological effects of acidifying deposition in freshwater ecosystems was phrased as, “relationship between acidifying deposition and changes in aquatic biota.”

<sup>g</sup>The 2008 ISA causality statement for biological effects of N deposition in freshwater ecosystems was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity in freshwater aquatic ecosystems.”

<sup>h</sup>The 2008 ISA causality statement for biological effects of N deposition to estuaries was phrased as “relationship between N deposition and the alteration of species richness, species composition, and biodiversity in estuarine ecosystems.”

<sup>i</sup>The 2008 ISA causality statement for biological effects of S deposition effects on ecosystems was phrased as “relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors is within adequate range for methylation.”

NOx SOx PM Integrated Science Assessment for Ecological Effects*													
Indicator		Gases †	Nitrogen Deposition				Sulfur Deposition				Nitrogen and Sulfur Deposition		
Class of Pollutant Effect		Direct Phytotoxic	N-enrichment/Eutrophication				Sulfide Toxicity		Mercury Methylation		Acidification		
Ecosystem		Terrestrial	Terrestrial	Wetland	Fresh Water	Estuary	Wetland	Fresh Water	Wetland	Fresh Water	Terrestrial	Fresh Water	
Scale of Ecological Response	Ecosystem	Productivity	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Not evaluated in causal framework	
	Community	Biodiversity	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	
	Population	Individual	Growth rate	Not evaluated in causal framework	Causal	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Not evaluated in causal framework	
	Individual		Physiological alteration, stress or injury	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal
	Geochemistry	Soil or sediment chemistry	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal	Causal	Causal	Not evaluated in causal framework			
		Surface water chemistry	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Causal	Not evaluated in causal framework	Not evaluated in causal framework	Causal	Causal	Not evaluated in causal framework	Causal

**Causality framework**

Causal
Likely causal
Suggestive
Inadequate
Not likely
Not evaluated in causal framework

\* A causal relationship is likely to exist between deposition of PM and a variety of effects on individual organisms and ecosystems, based on information from the previous review and limited new findings in this review

† Includes: NO, NO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and PAN

**Figure IS-4 Causal relationships between the criteria pollutants and ecological effects.**

Since the 2008 ISA, there is more evidence to support the direct effects of gaseous SO<sub>x</sub> and NO<sub>y</sub> on vegetation. This causality determination is uniquely modified by the observation that there is little or no evidence that such effects are continuing at current, lower levels of exposure now occurring in the U.S.

Since the 2008 ISA, the largest increase in ecological evidence is for terrestrial N driven eutrophication effects ([Section IS.5.1](#), [Section IS.5.2](#), [Appendix 4](#), and [Appendix 6](#)). This new research confirms the causal relationship between N deposition and ecological effects documented in the 2008 ISA. Further, this new research improves our understanding of the mechanistic links that inform causal determinations between N additions via atmospheric deposition, biogeochemistry, and biota in terrestrial ecosystems ([Table IS-1](#)). There is now stronger empirical evidence from across most regions of the U.S. to quantify the levels of N deposition (empirical CLs) that cause biodiversity declines of lichens and grasses/forbs. There is new evidence to quantify empirical CLs across much of the U.S. for nitrate leaching, tree survivorship, and mycorrhizal biodiversity. Many of the N deposition effects are due to historical and continuing N deposition.

New research confirms that N + S deposition causes terrestrial ecosystem acidification, as documented in the 2008 ISA ([Table IS-1](#)). New evidence to characterize terrestrial acidification (soil biogeochemistry changes and biological effects) across large regions of the U.S. is available; in particular, new modeling work has improved calculation of CLs for soil acidification ([Section IS.5.3](#); [Appendix 4](#) and [Appendix 5](#)). Many of the acidification effects are due to historical and continuing N and S deposition ([Section IS.11](#)).

New evidence for freshwater acidification CLs builds on several decades of research documenting freshwater acidification effects on aquatic biota in the U.S. and confirms the causal relationships determined in the 2008 ISA ([Table IS-1](#)). Many of the acidification effects are due to historical and continuing N and S deposition ([Section IS.11](#)).

The sources of N driven eutrophication of fresh waters, estuaries, and wetlands include atmospheric N deposition and N from agricultural and other wastewaters. New research has helped show how these respective sources contribute to total loading. In freshwater ecosystems where atmospheric deposition is the primary source of N, such as in high alpine watersheds, new CLs since the 2008 ISA support previous observations of increased algal productivity, species changes, and reductions in diversity. New evidence also supports clear links between aqueous S concentrations in aquatic systems and both mercury methylation and sulfide toxicity; however, quantitatively linking these outcomes to atmospheric deposition remains a challenge.

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## IS.3 Emissions and Atmospheric Chemistry

The atmospheric chemistry from emission to deposition discussed in this ISA is for the criteria pollutants  $\text{NO}_Y$ ,  $\text{SO}_X$ , and PM. In addition to gas-phase indicators like  $\text{SO}_2$  and  $\text{NO}_2$  used to monitor criteria pollutant trends, deposition of total N, total S, and total N + S that accounts for a wider range of species is also a main focus.

A wide variety of N containing compounds (oxidized + reduced, and organic + inorganic) contribute to wet and dry N deposition ([Appendix 2.1](#)).  $\text{NH}_X$  ( $\text{NH}_X = \text{NH}_3 + \text{NH}_4^+$ ) includes both the PM component  $\text{NH}_4^+$  and gas-phase  $\text{NH}_3$ . The contribution of  $\text{NH}_3$  to total observed inorganic N deposition may range from 19% in northwestern U.S. locations to 63% in locations in the southwestern U.S. and is generally greater in the summer than in the winter. Therefore,  $\text{NH}_3$  is discussed in the ISA along with  $\text{NO}_Y$  and relevant PM components to better understand and compare their contributions to both wet and dry N deposition. In addition, PM impacts discussed in this document are also mainly focused on N and S containing species, which together usually make up a large fraction of  $\text{PM}_{2.5}$  mass in most areas of the U.S. and have greater and better understood ecological impacts than other PM components.

Gaseous, particulate, and dissolved forms of  $\text{NO}_Y$ ,  $\text{SO}_X$ , and  $\text{NH}_X$  all contribute to atmospheric wet and dry deposition. The major components of particulate matter in the U.S. are  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , particulate organic matter, elemental carbon, crustal material, and sea salt. While organic matter usually accounts for a large fraction of  $\text{PM}_{2.5}$ , only a small portion can be identified at a molecular level. As a result, there is little information on organic PM impacts, except for individual compounds that make minor contributions to mass. Assessment of ecological impacts of major PM species is largely limited to  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ . Of these,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are also components of total oxides of sulfur and nitrogen, respectively.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  usually have a strong influence on acid deposition.  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , and in some cases organic nitrogen (organic nitrates and reduced organic N), make a substantial contribution to N deposition.

Since the 2008 ISA, there have been several new developments including:

- Expansion of ambient monitoring networks to include  $\text{NH}_3$  and  $\text{NO}_Y$  at selected sites, and comparisons of monitoring methods with research grade instruments ([Appendix 2.4](#));
- Adoption of new methods, such as data-model fusion, to integrate deposition information across the U.S. ([Appendix 2.5](#));
- Incorporation of bidirectional exchange into models of dry deposition ([Appendix 2.5.2](#)); and

- Improvements in techniques using satellite-based measurements and chemical transport model simulations to estimate emissions, concentrations, and dry deposition of NO<sub>2</sub>, SO<sub>2</sub>, and NH<sub>3</sub> ([Appendix 2.6](#)).

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### IS.3.1 Sources and Atmospheric Transformations

Both gaseous and particulate forms of N and S contribute to atmospheric deposition. The main contributors to acidifying precipitation are H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and NH<sub>4</sub><sup>+</sup>, which are formed from precursor emissions of SO<sub>2</sub>, NO<sub>x</sub> (NO + NO<sub>2</sub>), and NH<sub>3</sub> ([Appendix 2.2](#)). Gaseous emissions of NH<sub>3</sub> are dominated by agricultural fertilizer application and animal waste from intensive animal feeding operations, with important local contributions from motor vehicles and episodic contributions from wildland and agricultural fires. Roughly half of SO<sub>2</sub> emissions are from by electricity-generating units (EGUs), mainly coal-fired power plants. Notably, SO<sub>2</sub> emissions from EGUs have been decreasing. NO<sub>x</sub> emissions have a wider distribution of sources, with substantial contributions from highway and off-highway vehicles, lightning, and EGUs. Primary PM<sub>2.5</sub> and PM<sub>10</sub> emissions are dominated by dust and fires, but much of the PM<sub>2.5</sub> mass in the U.S. is produced by reactions that form secondary PM<sub>2.5</sub> from gas phase precursor N and S species. Because of these processes, a sharp decrease in SO<sub>2</sub> emissions and smaller, but substantial decreases in NO<sub>x</sub> emissions have occurred since the passage of the Clean Air Act Amendments in 1990. Emissions of NO<sub>x</sub> in the U.S. declined 61% between 1990 and 2017 ([U.S. EPA, 2020a](#)), while nationwide annual average 98th percentile NO<sub>2</sub> concentrations decreased by 53% from 1990 to 2017 ([U.S. EPA, 2016f](#)). Total emissions of SO<sub>2</sub> decreased by 89% from 1990 to 2017 ([U.S. EPA, 2020a](#)), resulting in a decrease in SO<sub>2</sub> concentrations of 89% in the eastern U.S. and 45% in the western U.S. ([Appendix 2.6.5](#)). National annual NH<sub>3</sub> emissions have fluctuated as a result of changes in both emissions and methods of estimating emissions. However, no clear trend is evident for national NH<sub>3</sub> emissions, with estimates for 1990 and 2017 differing by less than 1% ([U.S. EPA, 2020a](#)). National NH<sub>3</sub> monitoring is too recent for evaluating long-term concentration trends, although more limited studies of NH<sub>3</sub> emissions, concentrations and deposition each suggest slight increases may have occurred ([Appendix 2.6.4](#)).

Major components of particulate N and S include NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, which are primarily derived from gaseous precursors NH<sub>3</sub>, NO<sub>x</sub>, and SO<sub>2</sub> ([Appendix 2.3](#)). Together, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> make up a large fraction of PM<sub>2.5</sub> mass in most areas of the U.S. Formation of particulate N and S is described in the 2019 *ISA for Particulate Matter* ([U.S. EPA, 2019](#)). An understanding of the sources, chemistry, and atmospheric processes for these gas-phase and PM species provides a background for understanding acidifying and N deposition.

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### IS.3.2 Measurement and Modeling Techniques

Monitoring networks across the U.S. measure  $\text{NO}_Y$ ,  $\text{SO}_X$ , and  $\text{NH}_X$  species involved in deposition ([Appendix 2.4.1](#)). The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) has monitored precipitation chemistry for several decades at many U.S. sites. The Clean Air Status and Trends Network (CASTNET) has monitored concentrations of inorganic gas and particulate-phase N and S species since 1990. Monitoring of  $\text{NH}_3$  ([Appendix 2.5.3](#)) in the Ammonia Monitoring Network (AMoN), part of the NADP network, was initiated at a subset of CASTNET sites in 2007.  $\text{NH}_3$  was also measured as a part of the Southern Aerosol Characterization (SEARCH) network from 2004 until its termination in 2016. The Interagency Monitoring of Protected Visual Environments (IMPROVE) network and the Chemical Speciation Network (CSN) measure PM and PM components, including  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , although these data are not routinely used to estimate deposition rates ([Appendix 2.4.1](#)).

Atmospheric N deposition rates are calculated from measurements and models. Direct measurement of  $\text{NO}_2$  concentration has limited utility for quantifying  $\text{NO}_Y$  deposition rates in areas with less urban influence. Because  $\text{NO}_Y$  is composed of diverse chemical species with a wide range of deposition velocities and physical properties, concentrations of unmeasured component species of  $\text{NO}_Y$  in general and of all  $\text{NO}_Y$  species in data-sparse regions must be provided by regional models. For  $\text{NO}_2$  and  $\text{NH}_3$  this can be done in conjunction with satellite-based remote sensing data ([Appendix 2.4.2](#)).

Estimates of dry deposition ([Appendix 2.5.2](#)) over the contiguous U.S. are inferred by atmospheric models, used with monitoring network data. When combined with accurate estimates of historical trends in emissions and meteorology, these models are able to capture the historical long-term changes in  $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , but are subject to uncertainties in their treatment of turbulence, surface interactions, and in particular, seasonal variability in  $\text{NO}_3^-$  deposition, mainly because of uncertainties in  $\text{NH}_3$  emissions. Consequently, dry deposition rates (and ratios of wet-to-dry deposition) continue to be uncertain.

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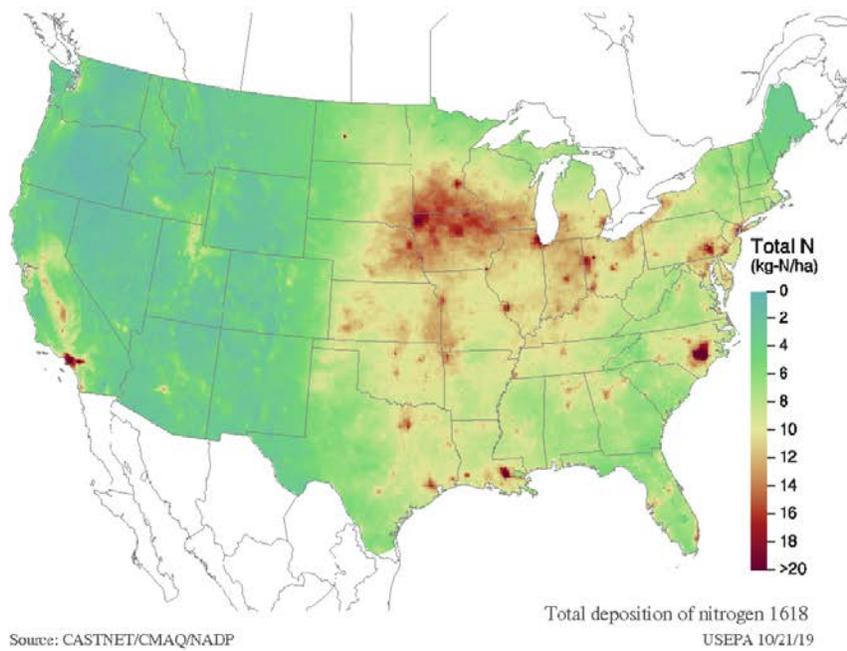
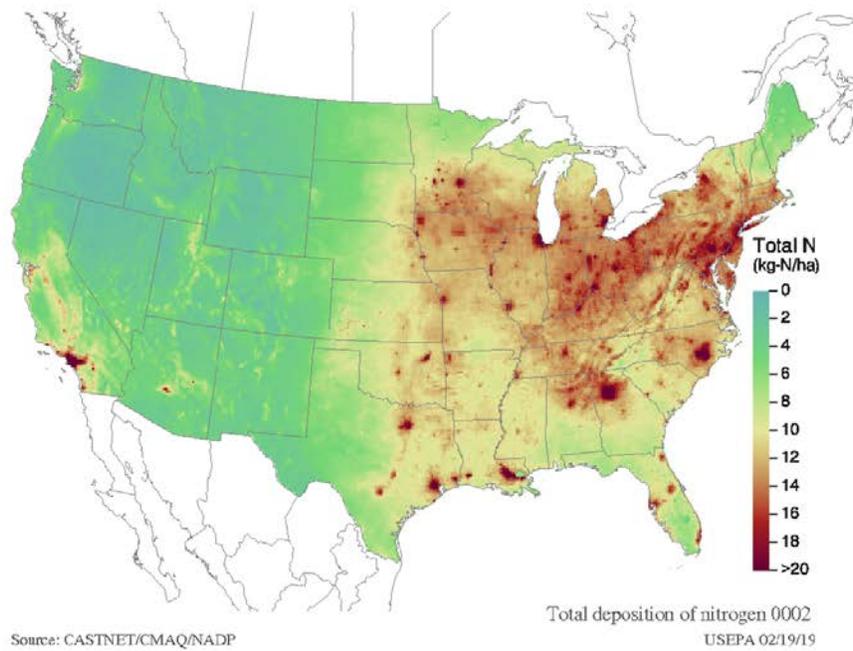
### IS.3.3 Spatial and Temporal Variability in Deposition

Overall deposition of total N (oxidized + reduced N) has decreased slightly over the past since 2000 ([Appendix 2.6.2](#)). This is because although  $\text{NO}_Y$  deposition has declined considerably in the contiguous U.S., deposition of  $\text{NH}_X$  has increased. The large spatial variability in N deposition and changes in geographic distribution of 3-year average N deposition between 2000–2002 and 2016–2018 are evident in the maps ([Figure IS-5](#)) of

3-year average annual dry + wet deposition of  $\text{NO}_Y$  and  $\text{NH}_X$  over the contiguous U.S. estimated using the TDEP (Total Deposition) modeling approach ([Appendix 2.6](#)), which combines output from the Community Multiscale Air Quality (CMAQ) system with wet deposition from the NADP/NTN ([Schwede and Lear, 2014b](#)) and air concentrations from CASTNET.

According to TDEP estimates for 2016–2018 ([Appendix 2.6](#)), much of the eastern contiguous U.S. is estimated to receive at least 10 kg N/ha/yr dry + wet deposition, with some areas receiving more than 15 kg N/ha/yr. Estimates for the spatial extent of the areas receiving at least 10 kg N/ha/yr of deposition and the overall amount of N deposited could be low because reduced organic N species are not routinely monitored.

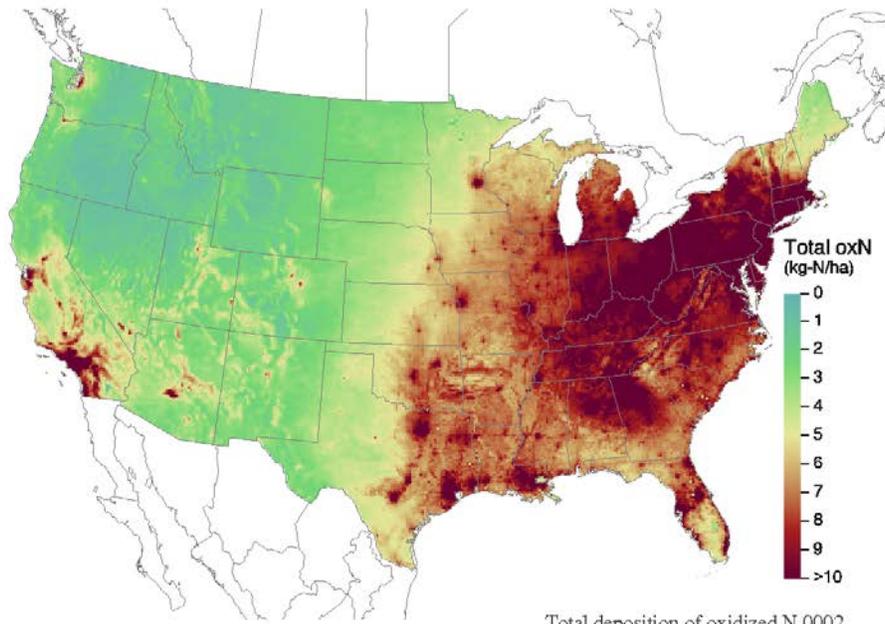
In general, wet deposition of reduced N exceeds that of oxidized N across the contiguous U.S. According to estimates based on CASTNET and NADP data and CMAQ modeling results ([Figure 2-16](#)), deposition of N nationwide occurs mainly by dry deposition of  $\text{HNO}_3$  and  $\text{NH}_3$  (with  $\text{NH}_3$  dominant) and wet deposition of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (with  $\text{NH}_4^+$  dominant). Hybrid satellite/modeling and CMAQ results indicate that dry deposition of  $\text{NO}_2$  is also a nontrivial source of deposited N in many areas ([Appendix 2.6.6](#)). Over the past 30 years, NADP/NTN data show that wet deposition of inorganic N (oxidized + reduced) decreased in areas such as the Northeast but remained constant or increased in areas such as the central U.S. (see [Figure 2-18](#) in [Appendix 2.6](#)). Wet deposition of total inorganic N has remained fairly constant over the past 30 years, despite declines in  $\text{NO}_X$  emissions, indicating that most of the increases in N wet deposition seen today is of reduced inorganic N. Data for total (wet + dry) deposition are available for a shorter time series than wet deposition, but show a similar increase in the share of reduced N relative to oxidized N. [Figure IS-6](#) shows reductions in TDEP 3-year average oxidized N deposition over the contiguous U.S. between 2000–2002 and 2016–2018, while [Figure IS-8](#) shows the decrease in reduced N deposition compared between the same periods.



Ha = hectare; kg = kilogram; N = nitrogen.

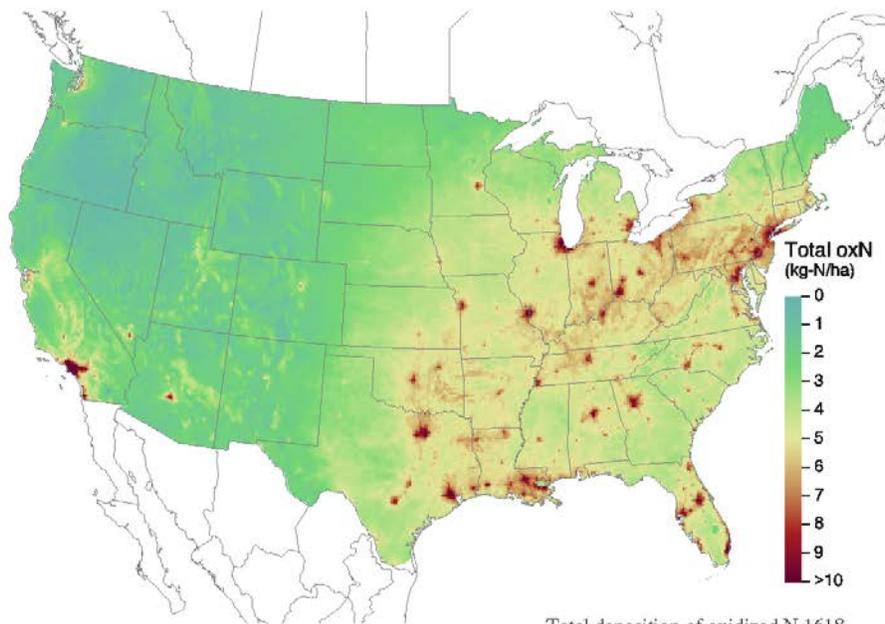
Source: CASTNET/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure IS-5 Wet plus dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

USEPA 09/12/18



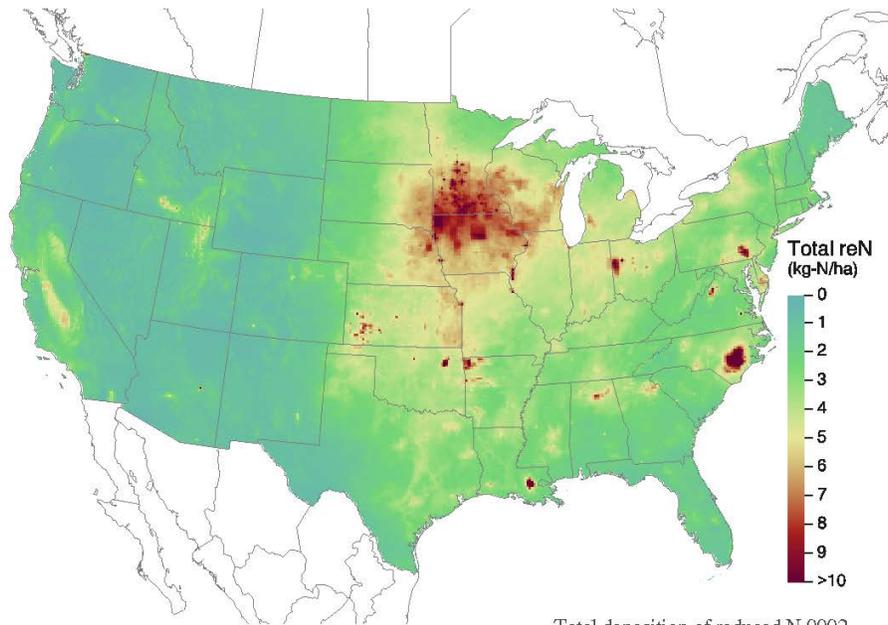
Source: CASTNET/CMAQ/NADP

USEPA 10/21/19

OxN = oxidized nitrogen.

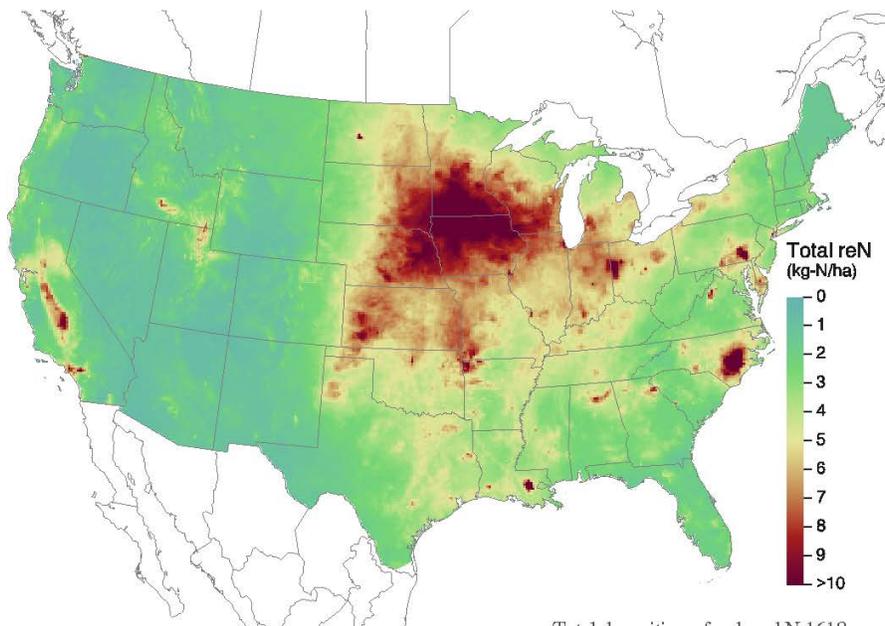
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition (NADP) Program for their role in making the TDep data and maps available.

**Figure IS-6 Wet plus dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Total deposition of reduced N 0002  
USEPA 09/12/18



Source: CASTNET/CMAQ/NADP

Total deposition of reduced N 1618  
USEPA 10/21/19

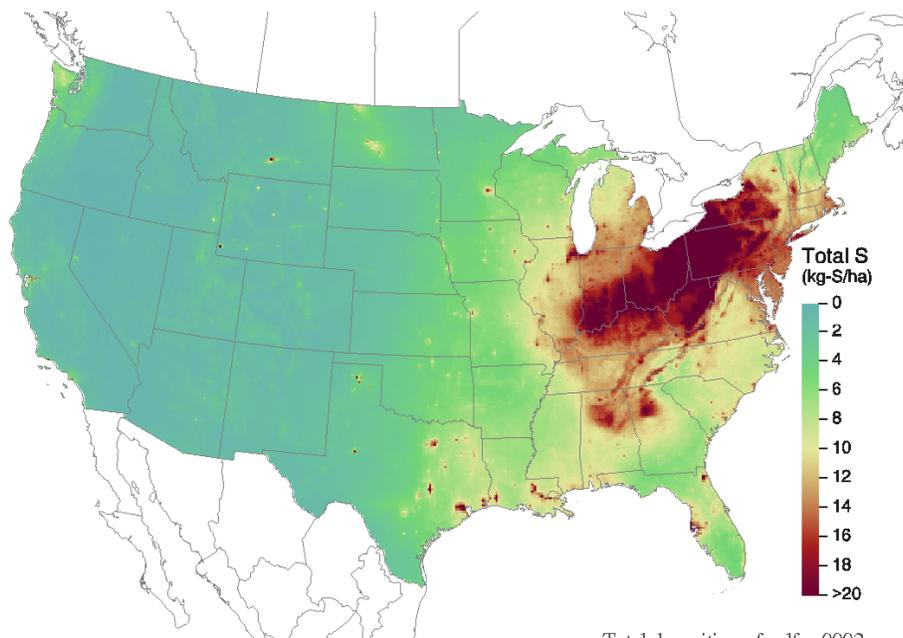
reN = reduced nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure IS-7 Wet plus dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**

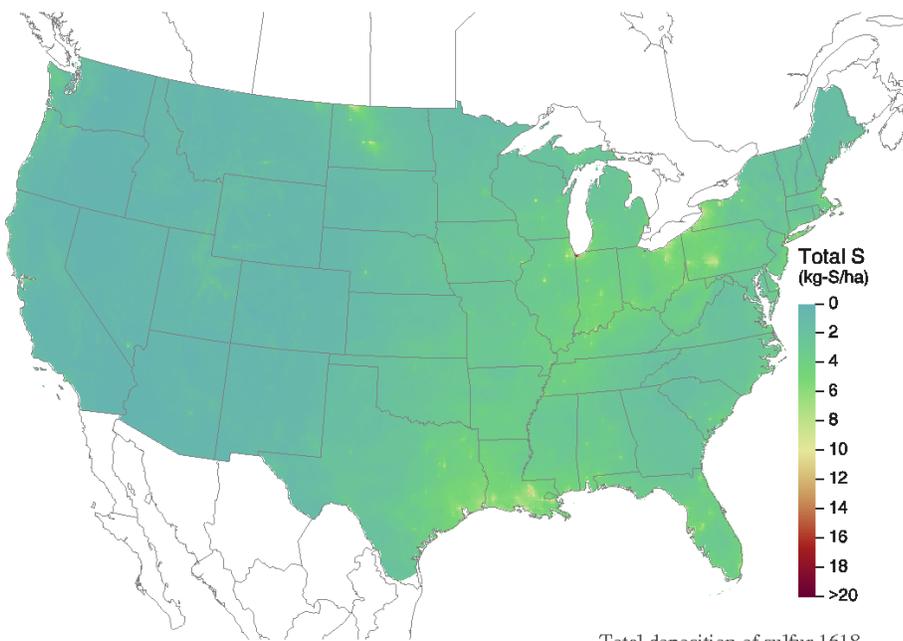
For S deposition, wet deposition tends to dominate over dry deposition in large areas of the contiguous U.S. However, in some regions mainly in the West, dry deposition of mainly SO<sub>2</sub> makes a greater contribution than wet deposition. Anthropogenic emissions of S and subsequent deposition have declined markedly since the 1990s, with the most pronounced declines in the eastern U.S. Currently, some of the highest values of total (wet + dry) SO<sub>x</sub> deposition in the U.S. are in parts of the Ohio Valley region ([Figure 2-41](#)). However, [Figure IS-8](#) shows that TDEP 3-year average total S deposition has decreased substantially between 2000–2002 and 2016–2018, especially in this region.

Both N and S deposition contribute to acidification of ecosystems. The pH of rainwater has increased markedly across the U.S. since 1990, coincident with decreases in the wet deposition of nitrate and SO<sub>4</sub><sup>2-</sup>. However, there are still widespread areas affected by acidifying precipitation, mainly in the eastern U.S. (see [Appendix 2.6](#)). Total acidifying deposition (wet + dry N + S, expressed as H<sup>+</sup> equivalents) fluxes for 2016 to 2018 ranged from a few tenths of H<sup>+</sup> keq/ha/yr over much of the western U.S. to over 1.5 H<sup>+</sup> keq/ha/yr in parts of the Midwest and the Mid-Atlantic regions, and in other isolated hotspots surrounding areas of concentrated industrial or agricultural activity ([Figure IS-9](#)).



Source: CASTNET/CMAQ/NADP

Total deposition of sulfur 0002  
USEPA 09/12/18



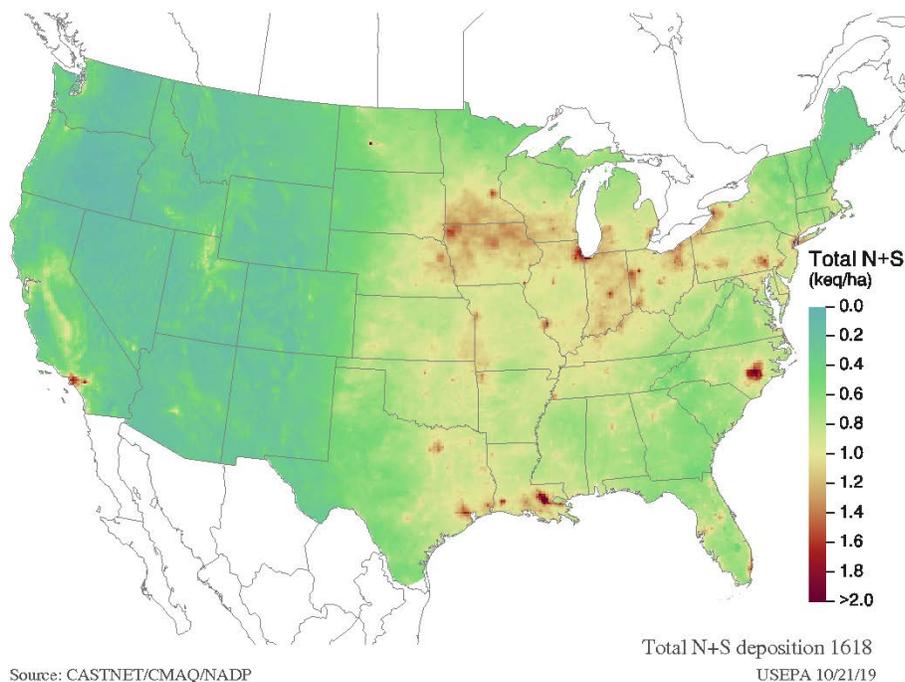
Source: CASTNET/CMAQ/NADP

Total deposition of sulfur 1618  
USEPA 10/21/19

S = sulfur.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure IS-8 Wet plus dry deposition of total sulfur over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



eq. = equivalents; H<sup>+</sup> = hydrogen ion; ha = hectare; N = nitrogen; S = sulfur; yr = year.

Source: NADP. Note: We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure IS-9 Total acidifying deposition of total oxidized nitrogen, reduced nitrogen, and oxidized sulfur expressed as H<sup>+</sup> equivalents per hectare per year over the contiguous U.S. 2016–2018.**

Dry deposition rates are a strong function of surface characteristics, which modify the structure of surface layer turbulence and the resistance to uptake by vegetation ([Appendix 2.5.2](#)). As a result, spatially aggregated estimates of dry deposition fluxes are subject to uncertainty, in addition to uncertainties that are inherent in the measurement of species concentrations and in the inference of dry fluxes (see [Section IS.13](#)). Wet fluxes are not directly influenced by surface characteristics (although orography affects transport and precipitation) but are subject to smaller uncertainties in the measurement of rainfall and chemistry.

## IS.4 Gas-Phase Direct Phytotoxic Effects

New evidence supports the causal determinations made in the 2008 ISA regarding gas-phase effects on vegetation, and there are no new causal statements for gas-phase

effects. As in the 2008 ISA, the current ISA concludes that there are causal relationships between SO<sub>2</sub>, NO<sub>2</sub>, NO, PAN, HNO<sub>3</sub>, and injury to vegetation. This determination is based on consistent, coherent, and biologically plausible evidence ([Appendix 3.2](#), [Appendix 3.3](#), and [Appendix 3.4; Table IS-1](#)). The clearest evidence for these conclusions comes from studies available at the time of the 2008 ISA, but there have been some additional studies since then. Most evidence on the direct effects of gaseous NO<sub>y</sub> and SO<sub>x</sub> comes from controlled exposure studies across many species of vegetation. Most controlled exposure studies over the past several decades have used concentrations of gas-phase NO<sub>y</sub> and SO<sub>x</sub> above current ambient conditions observed in the U.S. Relevant information is lacking on exposures and effects reflecting the more recent lower pollutant conditions. Therefore, there is little evidence available to inform whether current monitored concentrations of gas-phase NO<sub>y</sub> and SO<sub>x</sub> are high enough to injure vegetation.

NH<sub>3</sub> can also have direct phytotoxic effects if the uptake exceeds the ability of a plant to detoxify and assimilate it. However, reduced N gases such as NH<sub>3</sub> are not criteria air pollutants or oxides of N and, therefore, are not the focus of this review of the gas-phase effects. Direct damage from NH<sub>3</sub> to foliage can occur on higher plants and effect bryophytes and lichens. Declines in shrubs and lichens and changes in peat bogs have been reported with NH<sub>3</sub> exposure. Besides being potentially phytotoxic to vegetation, NH<sub>3</sub> exposure can lead to more N inputs into plants and ecosystems through foliage uptake. Ammonia deposition that leads to N enrichment is an important consideration when evaluating total N deposition. These N nutrient effects to vegetation are discussed in [Appendix 6](#).

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#### IS.4.1 Sulfur Dioxide

In the 2008 ISA, evidence was sufficient to infer a causal relationship between exposure to SO<sub>2</sub> and injury to vegetation. The current secondary standard for SO<sub>2</sub> is a 3-hour average of 0.50 ppm, which is designed to protect against acute foliar injury in vegetation. There has been limited research on acute foliar injury since the 1982 PM-SO<sub>x</sub> Air Quality Criteria Document (AQCD), and there is no clear evidence of acute foliar injury below the level of the current standard. The limited new research since 2008 adds more evidence that SO<sub>2</sub> can have acute negative effects on vegetation but does not change conclusions from the 2008 ISA regarding the causal relationship between SO<sub>2</sub> exposure and vegetation damage or the SO<sub>2</sub> levels producing these effects (see [Appendix 3.1](#)). Consistent with the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between gas-phase SO<sub>2</sub> and injury to vegetation.**

Increased SO<sub>2</sub> exposure concentrations and longer exposure times are associated with decreases in plant growth and yield. The 1982 PM-SO<sub>x</sub> AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. However, very few studies of the effects of SO<sub>2</sub> on the growth of vegetation in the U.S. have been conducted since 1982. Recent studies from eastern Europe indicate recovery of tree growth in response to decreases in SO<sub>2</sub> concentrations since the 1980s and that annual SO<sub>2</sub> concentrations of 4 ppb decreased silver fir (*Abies alba*) growth. In West Virginia, the growth of eastern red cedar (*Juniperus virginiana*) trees increased with declines in SO<sub>2</sub> emissions since the 1980s.

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#### IS.4.2 Nitrogen Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate

In the 2008 ISA, evidence was sufficient to infer a causal relationship between exposure to NO, NO<sub>2</sub>, and PAN and injury to vegetation. It is well known that in sufficient concentrations, NO, NO<sub>2</sub>, and PAN can have phytotoxic effects on plants by decreasing photosynthesis and inducing visible foliar injury. However, the 1993 Oxides of Nitrogen AQCD concluded that concentrations of NO, NO<sub>2</sub>, and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation ([U.S. EPA, 1993](#)), and very little new research has been performed at concentrations currently observed in the U.S. (see [Appendix 3.3](#)). It is also known that these gases alter the N cycle in some ecosystems, and nutrient effects of N are discussed in [Section IS.5](#). Thus, consistent with the previous 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between gas-phase NO, NO<sub>2</sub>, and PAN and injury to vegetation.**

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#### IS.4.3 Nitric Acid

In the 2008 ISA, evidence was sufficient to infer a causal relationship between exposure to HNO<sub>3</sub> and changes to vegetation. The 2008 ISA reported experimental exposure to HNO<sub>3</sub> resulted in damage to the leaf cuticle of pine and oak seedlings, which may predispose those plants to other stressors such as drought, pathogens, and other air pollutants. Since the 2008 ISA, [Padgett et al. \(2009b\)](#) investigated dry deposition of HNO<sub>3</sub> on the foliage in a fumigation study and confirmed the earlier research. Nitric acid can also add to N nutrient enrichment of ecosystems and is discussed in [Section IS.5](#). The 2008 ISA also reported several lines of evidence that past and current HNO<sub>3</sub> concentrations may be contributing to the decline in lichen species in the Los Angeles basin. Subsequent studies conducted in the Los Angeles basin since the 2008 ISA provide further evidence of the impacts (see [Appendix 3.4](#)). These new studies continue to

support the causal findings of the 2008 ISA, such that **the body of evidence is sufficient to infer a causal relationship between gas-phase HNO<sub>3</sub> and changes to vegetation.**

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## IS.5 Terrestrial Ecosystem Nitrogen Enrichment and Acidification

For terrestrial ecosystems, new evidence reinforces causal findings from the 2008 ISA and provides the basis for two new causal statements that reflect a more comprehensive understanding of how N and acidifying deposition alter terrestrial ecosystem biota ([Table IS-1](#)). In general, N deposition may cause soil N enrichment and stimulate the growth of opportunistic species. However, in sensitive soils, deposition of N and/or S can cause soil acidification, which may decrease growth and cause mortality among sensitive plant species. Atmospheric deposition of N and S alter the species composition of terrestrial systems by one of four mechanisms: (1) nutrient enrichment (eutrophication; [Appendix 4](#) and [Appendix 6](#)), (2) acidification ([Appendix 4](#) and [Appendix 5](#)), (3) direct damage ([Appendix 3](#)), and (4) secondary effects (e.g., wildfire; [Appendix 6](#)). Ecosystems and communities may be simultaneously affected by one or more mechanisms depending on the sensitivity of environmental and biological properties to each mechanism.

Despite the abundance of N in the environment, plants are unable to directly access the large pools of N contained in the atmosphere as N<sub>2</sub> gas and in the soil as large organic molecules. Consequently, the limited availability of reactive N often constrains biological activity in terrestrial ecosystems. N deposition is therefore considered nutrient enrichment because N additions generally stimulate plant growth and productivity (cumulative growth of all vegetation within a community), which has been recognized since the second half of the 19th century. In comparison, the biological effects of acidifying deposition are less common and largely constrained to ecosystems with historically high rates of deposition and that are vulnerable because of factors such as geology and climate. While S is also an essential macronutrient, less S is required for growth than N, and areas affected by acidifying deposition typically receive S at rates that greatly exceed biotic demand. Instead, the impact of acidifying deposition stems from the disruptions to biochemical processes caused by decreased pH and shifts in soil physiochemical processes that decrease the supply of other essential nutrients (e.g., Ca, Mg) and from increased mobilization of toxic forms of Al.

Current knowledge of soil biogeochemistry indicates soil N enrichment and soil acidification occur in sensitive ecosystems across the U.S. at present levels of deposition. Newly published work indicates decreasing SO<sub>2</sub> emissions and S deposition have led to early signs of recovery from acidification in some northeastern watersheds, but areas in the Southeast do not show recovery ([Appendix 4](#)). There are many well-defined soil

indicators related to the biological effects of acidifying (N + S) deposition. New evidence uses these indicators to describe the status of ecosystems, either by empirical observation or models. Soil indicators for acidification are more typically modeled than those for eutrophication effects. There is an abundance of new information on biogeochemical pools and processes, including a new conceptual framework for the N saturation of terrestrial ecosystems.

The enrichment of terrestrial ecosystems by N deposition often increases plant productivity and causes changes in physiology and growth rates that vary among species. This has been observed for herbaceous plants and trees across ecoregions. The changing growth rates transform competitive interactions between species, and consequently, lower species diversity is often observed with increasing N deposition within terrestrial communities. The level of N deposition negatively affecting community composition is often expressed as a Critical Load (CL). There are many new CLs available since the 2008 ISA, including those for lichens, herbaceous plants, and mycorrhizae.

The process of terrestrial acidification has been well understood and documented for decades. Recent research, since the 2008 ISA, has confirmed and strengthened this understanding and provided more quantitative information, especially across regional-scale landscapes. Several studies have evaluated the relationships between soil chemical indicators of acidification and ecosystem biological endpoints (see [Table 5-6](#)), and some biogeochemical models are well established. There have been new advances in the parameterization of acidification models to U.S. soils since the 2008 ISA ([Appendix 4.5](#)) resulting in better certainty of CLs. Biological endpoints included in the evaluations include physiological and community responses of trees and other vegetation (such as lichens), soil biota, and fauna.

The following section summarizes the main effects of N and S deposition on terrestrial ecosystems.

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### **IS.5.1 Soil Biogeochemistry**

In the 2008 ISA, evidence was sufficient to infer causal relationships between (1) acidifying deposition and changes in terrestrial biogeochemistry and (2) between N deposition and terrestrial biogeochemical cycling of N. There is new evidence of how deposition contributes to total loading in ecosystems, as well as new information from addition, gradient, and time-series studies characterizing how deposition affects soil pools and processes. Much of the new work focuses on the effects of N deposition, with relatively little work focusing on S deposition. Soil N enrichment and soil acidification occur in sensitive ecosystems across the U.S. at present levels of deposition. Decreasing

S emissions have led to early signs of recovery from acidification in some northeastern watersheds, but areas in the Southeast do not show recovery (for additional discussion on recovery see [Section IS.11](#)). Deposition rates of total N ( $\text{NO}_Y + \text{NH}_X$ ) are relatively unchanged across much of the contiguous US ([Appendix 2.7](#)). Accordingly, there are no signs of recovery from N enrichment effects. CL determinations have been made at the ecoregion scale for  $\text{NO}_3^-$  leaching. CLs for biological effects are summarized below ([Section IS.5.1.2](#), [Section IS.5.2.2](#), and [Section IS.5.3.3](#)). **The body of evidence is sufficient to infer a causal relationship between N and S deposition and alteration of soil biogeochemistry in terrestrial ecosystems**, which is consistent with the conclusions of the 2008 ISA.

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### IS.5.1.1 Soil Processes and Indicators

Deposition of N or N + S alters soil chemistry, which can have cascading effects on aquatic ecosystems (for effects on aquatic biology and chemistry see [Appendix 7–Appendix 10](#)). Soil acidification is a natural process that can be accelerated by N or S deposition. Deposition in the forms of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  can directly acidify soils; however, deposition of reduced forms of N (e.g.,  $\text{NH}_X$ ) can also cause soil acidification by releasing hydrogen ions ( $\text{H}^+$ ) during the microbial oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . There are a number of soil biogeochemical processes associated with acidification ([Table IS-2](#)). Base cations can counterbalance acid anions. Base cations are added to the soil by weathering and atmospheric deposition and are removed by leaching and biological uptake. Where acidifying deposition rates are high relative to base cation input, deposition can deplete exchangeable base cation pools in soils. There are several useful indicators of soil acidification ([Table IS-2](#)) that have quantitative relationships to biological responses ([Appendix 5](#)).

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**Table IS-2 Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
<b>Process</b>			
N saturation	X	X	New empirical evidence suggests revising the N saturation concept; specifically, it is now observed that $\text{NO}_3^-$ leaching can occur even if the ecosystem N capacity to retain N has not yet been saturated.

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**Table IS-2 (Continued): Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Soil N accumulation	X	X	New meta-analyses across ecosystem types confirm inorganic soil NO <sub>3</sub> <sup>-</sup> concentration increases with N addition. A new gradient study confirms that N concentration increases with N deposition. A new addition study confirms increased soil N accumulation. New studies on Soil N accumulation are summarized in <a href="#">Table 4-3</a> .
NO <sub>3</sub> <sup>-</sup> leaching	X	X	New meta-analyses confirm leaching increases with N additions. Regional-scale gradient analyses: <8 kg N/ha/yr onset of leaching; <1 kg N/ha/yr in European forests; in the NE U.S., 90% retention for sites receiving 7 kg N/ha/yr to 60% retention for sites receiving 11 kg N/ha/yr. New USFS CLs for the onset of leaching: 8–10 kg N/ha/yr in eastern and western U.S., 17 kg N/ha/yr in the Sierra Nevada and San Bernardino Mountains. New studies on Soil N accumulation are summarized in <a href="#">Table 4-3</a> .
S accumulation and adsorption		X	Some soils (notably in many watersheds in the SE U.S.) have the capacity to adsorb substantial quantities of S, with essentially no acidification of drainage water. Nevertheless, S adsorption capacity is finite, and under continual high S deposition loading, the adsorptive capacity of soil will eventually be exceeded. New studies of 27 watersheds in the SE indicate most will begin releasing SO <sub>4</sub> <sup>2-</sup> in the next two decades; NE watersheds show a net loss of S from soils now in response to decreased levels of atmospheric S deposition. New studies on soil S accumulation are summarized in <a href="#">Table 4-4</a> .
SO <sub>4</sub> <sup>2-</sup> leaching		X	Atmospheric S deposition generally increases leaching of SO <sub>4</sub> <sup>2-</sup> to surface waters. The amount of deposition that causes the onset of leaching varies across the landscape. New studies on soil SO <sub>4</sub> <sup>2-</sup> leaching are summarized in <a href="#">Table 4-4</a> .
Base cation leaching and exchange		X	Base cation (Ca, Mg, K, Na) release from soil particles to the soil solution occurs in response to the input of acid anions (SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> ) from deposition. New studies confirm base cation depletion continues to occur in the Rocky Mountains (threshold 28 kg N/ha/yr) and in U.K. grasslands, while in a NE forest, 17 yr of N addition did not cause further depletion. A meta-analysis suggests cation depletion soon after increased deposition of acid anions, but this depletion tapers off with time. New studies on base cation leaching and exchange are summarized in <a href="#">Table 4-5</a> .

**Table IS-2 (Continued): Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Al mobilization		X	The threshold for inorganic Al mobilization from soil is <15–20% soil base saturation. This is an extremely important effect of acidifying deposition because inorganic monomeric Al is toxic to biota ( <a href="#">Appendix 5</a> and <a href="#">Appendix 8</a> ). Inorganic Al is minimally soluble at pH 6.0, but solubility increases steeply at pH below 5.5. New studies on Al in soils are summarized in <a href="#">Table 4-6</a> .
Nitrification	X	X	Nitrification releases 2 mol hydrogen ion (H <sup>+</sup> ) per mol NH <sub>4</sub> <sup>+</sup> converted to NO <sub>3</sub> <sup>-</sup> , acidifying soils. As soil inorganic N accumulates, net nitrification rates often increase, and NO <sub>3</sub> <sup>-</sup> can leach from the ecosystem. New N gradient and meta-analysis studies confirm N addition increases nitrification. New studies on nitrification are summarized in <a href="#">Table 4-6</a> .
Denitrification	X		Denitrification is the microbial reduction of NO <sub>3</sub> <sup>-</sup> to NO <sub>2</sub> <sup>-</sup> , NO, the greenhouse gas N <sub>2</sub> O, and N <sub>2</sub> , which occurs under anaerobic conditions. In Europe, soil switched from a source to a sink after two decades of N deposition exclusion. New meta-analysis confirms N addition increases denitrification rates. New studies on denitrification are summarized in <a href="#">Table 4-6</a> .
DOC leaching	X	X	In recent years, the DOC of many lakes and streams has risen, with the source likely from the soils in the adjacent terrestrial watershed. However, the mechanism causing the observed increase is unclear and may be due to a combination of soil recovery from acidification, changes in climate (e.g., temperature and precipitation), and N deposition among other mechanisms. New studies are summarized in <a href="#">Table 4-10</a> .
Decomposition	X	X	The addition of N can stimulate the breakdown of labile compounds that degrade during the initial stages of decomposition, but added N can suppress the decomposition of more recalcitrant material. There are new addition studies and meta-analyses on mechanisms and response trends. New studies are summarized in <a href="#">Table 4-8</a> .
<b>Indicator</b>			
Soil [N]	X	X	Increases in soil [N] indicate soil N accumulation and the size of the soil N pool that may be assimilated by organisms or mobilized via leaching.
Soil C:N ratio	X	X	Decreasing soil C:N linked to changes in decomposition and increases in nitrification and NO <sub>3</sub> <sup>-</sup> leaching. <20–25 causes increased nitrification and elevated risk of NO <sub>3</sub> <sup>-</sup> leaching in the U.S. and <25–30 for increased NO <sub>3</sub> <sup>-</sup> leaching in Europe.

**Table IS-2 (Continued): Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Soil base saturation		X	Increasing N + S deposition decreases the soil pool of exchangeable base cations. <15–20% exchange ion chemistry is dominated by inorganic Al and may cause injury to vegetation (see <a href="#">Appendix 5</a> ).
Soil Bc:Al ratio		X	Increasing N + S deposition decreases the soil pool of exchangeable base cations, often decreasing the Ca:Al ratio. Ca:Al <1.0 causes physiological stress, decreased growth, and mortality of sensitive plant species (see <a href="#">Appendix 5</a> ).
Fungi-to-bacteria ratio	X		New indicator: increasing N deposition decreases the fungi-to-bacteria ratio and causes a transition from N to C limitation among soil food webs.

Al = aluminum; Al<sup>3+</sup> = aluminum(III); Bc = base cations; C = carbon; Ca = calcium; DOC = dissolved organic carbon; H<sup>+</sup> = hydrogen ion; ha = hectare; K = potassium; kg = kilogram; Mg = magnesium; N = nitrogen; N<sub>2</sub> = molecular (atmospheric) nitrogen; N<sub>2</sub>O = nitrous oxide; Na = sodium; NE = northeastern; NH<sub>4</sub><sup>+</sup> = ammonium; NO = nitric oxide; NO<sub>2</sub><sup>-</sup> = nitrite; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SE = southeastern; SO<sub>4</sub><sup>2-</sup> = sulfate; U.K. = United Kingdom; U.S. = United States; USFS = U.S. Forest Service; yr = year.

Some of the same processes and indicators associated with acidification are also associated with the N enrichment of soils in response to the input of exogenous N ([Appendix 4.3](#)). The 2008 ISA documented that the increase in global reactive N (defined as  $\text{NO}_Y + \text{NH}_X + \text{organic N}$ ) that occurred over the previous century was largely due to three main causes: (1) widespread cultivation of crops that promote conversion of  $\text{N}_2$  gas to organic N through biological N fixation, (2) fossil fuel combustion converting atmospheric  $\text{N}_2$  and fossil N to  $\text{NO}_X$ , and (3) the Haber-Bosch process, which converts nonreactive  $\text{N}_2$  to reactive N to sustain food production and some industrial activities ([Galloway et al., 2003](#); [Galloway and Cowling, 2002](#)).

The 2008 ISA documented that atmospheric deposition of N can increase soil N, the accumulation of which is linked to increased N leaching and decreased retention of N. CLs for the onset of elevated  $\text{NO}_3^-$  leaching are given in [Appendix 4.6.2.2](#).

The 2008 ISA described the conceptual model of N saturation, which occurs when N input rates to terrestrial ecosystems exceed the uptake capacity of the soils and biota and is indicated by the onset of increased soil N leaching. However, more recent work has revised the N saturation model in response to observations in which N leaching resulted from N input rates that are faster than vegetation and soil uptake rates, thus distinguishing capacity N saturation from kinetic N saturation. Budgets from 83 forested watersheds in the northeastern U.S. show that N retention averages 76% of the incoming atmospheric N deposition and decreases from 90% retention at 7 kg N/ha/yr of deposition to 60% retention at 11 kg N/ha/yr of deposition.

The 2008 ISA documented that N enrichment is associated with changes in microbially mediated biogeochemical processes, including nitrification, denitrification, and decomposition ([Appendix 4.3](#)). The addition of N can increase nitrification (the microbial conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ ), which contributes to soil acidification. N deposition to soils can decrease surface soil C:N ratio, which can stimulate nitrification when C:N ratios fall below 20 to 25. The  $\text{NO}_3^-$  created by nitrification may be leached, biologically immobilized, or denitrified. Denitrification is the microbial reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ , NO, the greenhouse gas  $\text{N}_2\text{O}$ , and  $\text{N}_2$ , which occurs under anaerobic conditions. Several syntheses have been published since 2008 evaluating N addition effects on denitrification and nitrification in terrestrial ecosystems. A new meta-analysis shows N addition substantially increases denitrification from many types of ecosystems (e.g., coniferous forest, deciduous forest, tropical forest, wetland, grassland), but not heathlands. Among five chemical forms of N studied,  $\text{NO}_3^-$  addition showed the strongest stimulation of  $\text{N}_2\text{O}$  emission. Using data extracted from 206 peer-reviewed papers, a second meta-analysis observed that the largest changes in the ecosystem N cycle caused by N addition were increased nitrification (+154%),  $\text{N}_2\text{O}$  emissions (+134%), and denitrification (+84%).

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### IS.5.1.2 National-Scale Sensitivity and Critical Loads

As of the 2008 ISA, the regions of the U.S. with abundant acid-sensitive soils had been well delineated. These acid-sensitive ecosystems are generally located in mountainous terrain in the eastern U.S. and are underlain by bedrock resistant to weathering. However, a similar delineation of the areas sensitive to the eutrophication effects of N had not yet been completed. There is strong evidence demonstrating that biogeochemical sensitivity to deposition-driven eutrophication and acidification is the result of historical loading, geologic/soil conditions (e.g., mineral weathering and S adsorption), and/or natural sources of N and S loading to the system.

Since the 2008 ISA, several new publications have advanced our understanding of soil recovery from acidification and CLs. New publications report the results of field observations and modeling studies on soil recovery from acidification, specifically in the northeastern U.S., and the lack of recovery in the southern Appalachian Mountains ([Table 4-18](#)). New ecoregion-scale terrestrial CLs for  $\text{NO}_3^-$  leaching were published in 2011 and have been updated by more recent published work. Finally, [Clark et al. \(2018\)](#) estimated areas exceeding CLs for terrestrial acidification and  $\text{NO}_3^-$  leaching for the contiguous U.S. for 1800 to 2025. For terrestrial acidification, area exceeding the minimum CL peaked at almost 2.8 million  $\text{km}^2$  by 1975 before declining; whereas, for  $\text{NO}_3^-$  leaching, the area exceeding the minimum CL peaked at roughly 3.4 million  $\text{km}^2$  around 1995.

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### IS.5.2 Biological Effects of Terrestrial Nitrogen Enrichment

The enrichment of terrestrial ecosystems by N deposition often increases plant productivity and causes changes in physiology and growth rates that vary among species. This combination of effects can alter the composition and decrease diversity of terrestrial communities by transforming competitive interactions between species and changing the availability of other essential resources, including light, water, and nutrients. Because N deposition can cause both eutrophication and acidification and these processes can occur simultaneously, the relationship between N deposition and community composition has often been derived empirically. Many of the effects of N deposition are similar across ecosystems and life forms because N is an essential macronutrient, but the composition and magnitude of how these effects are expressed within an ecosystem can differ as a result of biotic and abiotic influences. Consequently, as with the 2008 ISA, we have grouped the effects of N deposition on physiology and biodiversity by biome (e.g., forest, tundra, grassland, and arid lands), with further framing by life form (e.g., plants, microorganisms) and functional groups (e.g., trees, herbaceous plants). In comparison,

the broadest CLs created by the scientific community are at the ecoregion level, in which spatial boundaries across the landscape are typically defined based on ecological, climatological, and geological differences.

The 2008 ISA documented consistent evidence that N additions increased plant productivity broadly across a wide range of terrestrial ecosystems. Since 2008, a large body of new research on the biological effects of added N in terrestrial ecosystems has been published from investigations of plant and microbial physiology, long-term ecosystem-scale N addition experiments, regional and continental-scale monitoring studies, and syntheses. These studies have been conducted in ecosystems representing biomes in the U.S., including tundra, grasslands, arid and semiarid lands, and tropical, temperate, and boreal forests. Because of the breadth of this research, there is a strong mechanistic and empirical understanding for many of the biological effects of added N. **This body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.**

The varying effects of N deposition on the growth and physiology of individual species have consequence(s) for biodiversity. In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in terrestrial ecosystems. The 2008 ISA documented consistent evidence of reduced species richness and altered community composition from N addition studies in the U.S. and N deposition gradient studies in Europe for grassland plant diversity, forest understory plants, and forest mycorrhizal fungi. There was also consistent evidence of altered plant and mycorrhizal community composition from N addition studies in arid and semiarid ecosystems, particularly in southern/central California. There was little evidence of changes in forest overstory tree composition. Since the 2008 ISA, new research techniques have been developed to understand community composition, a larger number of communities have been surveyed, and new regional and continental-scale studies have made it possible to isolate the influence of N deposition from other environmental factors. This new research has provided more extensive and mechanistic evidence, and combined with the findings of the 2008 ISA, **this body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.**

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### IS.5.2.1 Physiology and Biodiversity

At the time of the 2008 ISA, terrestrial ecologists had used meta-analyses to broadly quantify the effects that N deposition can have on the growth of terrestrial plants, concluding that N additions stimulate plant productivity by 20–30% in grasslands, forests, tundra, and wetlands, increase aboveground productivity in herbaceous plant communities, alter plant tissue chemistry, decrease biomass of mycorrhizal fungi, and alter litter decomposition ([Appendix 6.6.1](#)). Recent research has provided further coherent and consistent evidence that N additions stimulate plant growth and productivity, but this research is still dominated by studies of temperate ecosystems and aboveground plant responses ([Figure 6-1](#) and [Figure 6-2](#)).

In the 2008 ISA, the positive plant growth response to N deposition was attributed to higher rates of photosynthesis. However, evidence for this is mixed: increases in photosynthesis following N additions have been observed across a variety of plant functional types, but higher rates of photosynthesis have not been consistently observed in response to chronic N additions meant to simulate atmospheric deposition. There is new support for another mechanism that would increase aboveground growth: decreases in the quantity of C allocated by plants to roots and mycorrhizae. There was evidence in the 2008 ISA that N additions increase aboveground biomass more than belowground biomass, raising the shoot-to-root ratio among plants, but evidence is now more consistent and widespread. Plants also invest substantial amounts of C to support mycorrhizal fungi, but there is evidence this investment declines when N is added to terrestrial ecosystems.

Evidence that biodiversity change can be a consequence of N deposition has accumulated since 2008 and includes new information for major taxonomic groups, including herbaceous plants, overstory trees, and two groups of symbionts (lichens and mycorrhizae). Evidence is now more widespread for decreases in lichen species richness as the result of N deposition in the U.S. There are direct observations that N deposition in the U.S. is changing mycorrhizal community composition and altering herbaceous plant species richness across a broad range of ecosystems, including forests, grasslands, arid and semiarid ecosystems, and alpine tundra. In addition, based on variation in mortality and growth rates of co-occurring tree species, there is also indirect evidence that N deposition is altering overstory tree community composition.

A substantial body of research linking changes in biodiversity to shifts in N availability has been developed. Two hypotheses for species loss are (1) the random-loss hypothesis and (2) the functional trait hypothesis. The random-loss hypothesis suggests rare species are most likely to disappear as increased competition for resources, such as light, eliminates less successful individuals; whereas the functional trait hypothesis predicts

that organisms with disadvantageous traits (e.g., shorter plants) will be outcompeted when N is added. Both hypothesized mechanisms can operate simultaneously, and both tie the changes in physiology, growth, and productivity caused by increased N availability to declines in biodiversity.

As noted in [Appendix 4](#), soil microorganisms have important roles in regulating N and C cycling. There are several mechanisms to alter soil microbial biomass and physiology, including changes in soil pH, increases in inorganic N availability, shifts in soil food webs, and changes in the quantity and quality of available C. There were some observations in the 2008 ISA that added N decreases microbial biomass, but there is now more evidence that added N generally negatively or neutrally affects microbial biomass C and microbial biomass N ([Table 6-4](#)).

#### **IS.5.2.1.1 Forests**

Forests occur within every U.S. state, but are most abundant in the eastern U.S., montane and coastal portions of the western U.S., and Alaska. The distribution of forests is bound by water availability, cold temperatures, and land management. In the 2008 ISA, there was consistent evidence that N additions stimulated forest productivity, but these responses varied widely and included both neutral and negative effects of N additions on tree growth. However, there had been no empirical analyses of how atmospheric N deposition altered forest productivity in the U.S. at broad scales. The 2008 ISA lacked information on whether N deposition had any impact on the diversity and composition of forest overstory trees, but it did present evidence for changes in the composition of herbaceous vegetation, epiphytic lichens, and microbial communities. The addition of new research since the 2008 ISA provides coherent evidence that N deposition alters the physiology and growth of overstory trees and provides indirect evidence that N deposition changes the community composition of overstory trees. Further, new research supports N deposition altering the physiology, growth, and community composition of understory plants, lichens, mycorrhizal fungi, soil microorganisms, and arthropods ([Appendix 6.2.3](#) and [Appendix 6.3.3](#)).

As of the 2008 ISA, most long-term N addition experiments were conducted in temperate forests in the northeastern U.S. or in temperate or boreal forests in Europe. In these studies, conifer species were less likely than broadleaf species to exhibit positive growth responses to added N and more frequently exhibited increased mortality and decreased growth. Since the 2008 ISA, new observations from experiments, forest inventory studies, model simulations, and data synthesis efforts have been published, quantifying increases in forest net primary productivity (NPP), net ecosystem productivity (NEP), and ecosystem C storage ([Figure 6-3](#)). Overall, evidence is consistent that N deposition

broadly increases tree growth and forest productivity, including specific evidence indicating that current rates of N deposition in the contiguous U.S. broadly stimulate aboveground forest productivity ([Appendix 6.2.3.1](#)).

Despite these broad effects, it is also clear that with N addition growth and mortality responses vary by tree species. Many of the observations in the 2008 ISA have been reinforced by more recent research, including long-term forest inventory data collected from across the U.S. and Europe. Recent analyses of U.S. forest inventory data by [Horn et al. \(2018\)](#) found that tree species vary in their growth and mortality responses to N deposition ([Appendix 6.2.3.1](#)). Responses of individual tree species ranged from consistently increasing growth with greater N deposition; to increasing growth at lower N deposition but decreasing growth at higher levels; to consistently decreasing growth with greater N deposition. Mortality responses showed a similar pattern between species. Notably, species with varying responses in growth and mortality co-occurred in places in the U.S. Thus, this indirect evidence suggests that changes in tree community composition are occurring due to N deposition ([Appendix 6.3.3.1](#)). These analyses represent an advancement in our understanding from the time of the 2008 ISA.

In comparison, there is direct evidence that N deposition is altering the composition of forest understory plant communities ([Appendix 6.3.3.2](#)). The evidence for altered forest understory plant communities (also known as herbaceous layer or groundcover vegetation) comes from both the 2008 ISA and from the more recent literature. Changes in understory plant communities have been observed in monitoring plots along atmospheric N deposition gradients in the U.S. and in Europe. In Europe, forest understory plant communities have shifted with increasing N toward more nutrient-demanding and shade-tolerant plant species.

Higher rates of aboveground tree growth in response to N deposition might be due to shifts in C allocation away from belowground processes. Changes in C allocation in response to additional N have been accompanied by decreases in the abundance of mycorrhizal fungi and changes in mycorrhizal community composition ([Table 6-2](#), [Table 6-14](#)). Evidence for composition change is particularly abundant in ectomycorrhizal fungal communities ([Table 6-14](#)); there are fewer observations of how arbuscular mycorrhizal fungal communities change in response to N additions ([Table 6-3](#); [Table 6-16](#)). There are also numerous observations of altered total microbial (including bacterial) biomass and community composition. For microbial biomass, most studies identified since 2008 showed either negative or neutral effects of N additions, consistent with the results of syntheses published before the 2008 ISA ([Table 6-4](#)). Changes in soil microbial community composition were identified along an N deposition gradient in Europe and in all three N addition studies ([Table 6-14](#)). The effects of N additions on

individual microbial taxonomic groups (bacteria, archaea, fungi, etc.) have been less consistent ([Table 6-15](#)). Overall, there is evidence that N additions can decrease total microbial biomass and alter microbial communities in forest soils.

Within soil food webs, soil microorganisms have both direct and indirect links to arthropods. Because arthropods feed upon both microorganisms and litter, they can be important regulators of decomposition, nutrient cycling, and forest productivity. Several studies have examined the response of forest arthropod communities to added N, including a group of studies on insect herbivores conducted in southern California ([Table 6-17](#)). There is coherent evidence that N additions can alter forest arthropod communities.

Epiphytic lichens have long been recognized as sensitive to air pollution. Although these organisms often make up a small portion of forest biomass, they have important roles in hydrologic cycling, nutrient cycling, and as sources of food and habitat for other species. New research on lichen community composition identified since the 2008 ISA has further added to the consistent and coherent evidence that lichen communities in the U.S. and Europe are sensitive to current levels of atmospheric N deposition ([Appendix 6.2.6](#); [Table 6-23](#)). In particular, the U.S. Forest Service's Forest Inventory and Analysis Program has ample data on the abundance of lichens throughout the U.S., and shifts in lichen community composition clearly attributable to atmospheric N pollution have been observed in forests throughout the West Coast, in the Rocky Mountains, and in southeastern Alaska. Shifts in epiphytic lichen growth or physiology have been observed along atmospheric N deposition gradients in the highly impacted area of southern California, but also in more remote locations such as Wyoming and southeastern Alaska ([Table 6-5](#)). Experimental N studies have also created more detailed insight into changes in lichen physiology processes.

Overall, there is widespread evidence from forests that N deposition alters the growth and physiology of trees, and indirectly suggests N deposition affects tree community composition. Nitrogen deposition in forests also alter the growth, physiology, and biodiversity of herbaceous plants, lichens, soil microorganisms, and arthropods.

#### **IS.5.2.1.2 Tundra**

Within the U.S., tundra ecosystems are limited to Arctic ecosystems in Alaska and to relatively isolated, high elevation sites. Although these ecosystems tend to be remote, the influence of atmospheric N deposition is distinct and there was evidence in the 2008 ISA indicating that alpine tundra plant communities were sensitive to atmospheric N deposition. Alpine organisms may be more sensitive to N deposition because of the

unique nature of N cycling in these ecosystems, which tend to have limited inorganic N availability. Since the 2008 ISA, numerous studies of tundra physiological, productivity, and community composition responses to added N have been published, providing further evidence that N deposition alters the growth and physiology of alpine plant communities, including vascular plants (herbaceous and woody), bryophytes, and lichens ([Appendix 6.2.4](#)), as well as evidence of altered soil microbial communities ([Table 6-8](#); [Table 6-19](#)).

As in forests, increases in N content in response to additional N are widespread in tundra plant communities ([Table 6-6](#)). Higher tissue N concentrations in response to added N have been observed in multiple studies for vascular plants, bryophytes, and lichens. The 2008 ISA noted that plant growth and biomass responses tended to be species specific. Subsequent studies have confirmed this result ([Table 6-6](#)), showing varying responses to added N among ecosystem types, plant functional groups, and species. Whereas vascular plants tend to show a positive response to added N, both bryophytes and lichens tend to decrease in biomass and cover ([Table 6-5](#); [Table 6-6](#)).

Given the varying effects of N addition on species physiology and growth, the numerous observations of N addition impacts on species richness, species diversity, and community composition among vascular plants, bryophytes, and lichens in alpine and Arctic tundra ecosystems are unsurprising ([Appendix 6.3.4](#); [Table 6-18](#)). Within the U.S., these observations have included effects of N additions on plant community composition in Colorado and Washington. In northern Europe, decreases in plant species richness along atmospheric N deposition gradients have been documented. Overall, this new research has provided further evidence that experimental N additions can alter plant biodiversity in alpine and Arctic tundra ecosystems and has provided new evidence that current rates of atmospheric N deposition in Europe are associated with a loss of plant species richness in these ecosystems.

There are relatively few observations regarding the effect of N additions on total microbial biomass or the biomass response of individual microbial taxonomic groups in tundra ecosystems, and these results have also been largely inconsistent. However, new research has provided evidence that N additions can alter microbial community composition in alpine tundra ecosystems ([Table 6-8](#); [Table 6-19](#)).

### **IS.5.2.1.3 Grasslands**

Grasslands are most prevalent in the central U.S., yet also are widely distributed across the U.S. in areas where woody vegetation is excluded by environmental factors or management. There was widespread evidence at the time of the 2008 ISA that the

growth, physiology, and productivity of grassland plants could be altered by N deposition. In addition, there were multiple lines of evidence in the 2008 ISA that grassland plant, mycorrhizal, and microbial communities were sensitive to N inputs. Combined with subsequent research, the evidence is clear that physiology, growth, and community composition of plants, mycorrhizae, soil microorganisms, and arthropods are sensitive to N inputs in grasslands.

Although NPP can be limited by multiple factors (e.g., water, herbivores, other nutrients) in all ecosystems, limitations other than N tend to be more marked in grasslands than forests, making it harder to understand and predict the effects of increased N availability. However, the general response is similar ([Appendix 6.2.5](#)): N additions stimulate NPP, increase foliar N, and increase allocation to aboveground biomass (increased ratio of shoot:root mass).

Evidence from the U.S. of grassland plant community composition change in the 2008 ISA was based on N addition studies in Mediterranean grasslands in California and northern prairie ecosystems. However, large-scale assessments of biodiversity across observed atmospheric N deposition gradients were restricted to Europe. Recent research provides further evidence that N deposition reduces grassland biodiversity in the U.S. and Europe ([Appendix 6.3.5](#)). Since 2008, there have been direct observations of reduced species richness along atmospheric N deposition gradients for grasslands in the U.S. and Europe. These gradient studies have documented an interaction with soil pH, noting that N deposition causes a greater loss of species richness and a shift in community composition at sites with lower pH. Together, these findings from deposition gradients in the U.S. and Europe provide coherent evidence that N deposition causes shifts in plant community composition and the loss of plant species richness through mechanisms of both acidification and eutrophication. Experimental studies published since 2008 have provided more insight into the mechanisms linking changes in plant and microbial community composition to increased N availability, providing evidence that declines in species richness increase with time and that competition for resources such as water may exacerbate the effects of N addition on diversity.

Overall, the additional studies in grassland ecosystems have confirmed that many of the responses observed in the older N addition studies also occur at present rates of atmospheric N deposition. These changes include losses in forb species richness (which make up the majority of grassland biodiversity), greater growth of grass species (which make up the majority of grassland biomass), changes in reproductive rates, as well as shifts in mycorrhizal ([Table 6-16](#)), soil microbial ([Table 6-20](#)), and arthropod populations. In total, because of the prevalence of N limitation in grasslands and the dominance by fast-growing species that can shift in abundance rapidly (in contrast to

forest trees), grasslands appear especially sensitive to N input rates comparable to N deposition across much of the contiguous U.S.

#### **IS.5.2.1.4 Arid and Semiarid**

Arid and semiarid ecosystems are abundant in areas of the western U.S. where climate or orography create annually or seasonally dry conditions. At the time of the 2008 ISA, a large amount of information was available on how N deposition affected the growth and physiology of plants and microorganisms in arid and semiarid ecosystems, and there was coherent evidence that plant communities in these ecosystems could be altered by the added N. Evidence for these effects was particularly strong in coastal sage scrub (CSS), chaparral, and Mojave Desert ecosystems in southern California. Within the CSS ecosystems, N deposition has been linked to increased mortality in native shrubs, decreased abundance of arbuscular mycorrhizal fungi, higher cover of invasive annual plants, and increased wildfire activity. Similar increases in invasive annual plant cover and fire frequency have also been attributed to N deposition in areas of the Mojave Desert downwind of urban centers in southern California. Research since 2008 has further documented these effects, with consistent evidence that N deposition can affect the physiology, growth, and community composition of plants and soil microorganisms in arid and semiarid systems.

The effects of N deposition on physiological and biogeochemical processes in arid and semiarid ecosystems are even more clearly dependent on moisture availability than in grasslands ([Appendix 6.2.6](#)). In these ecosystems, inorganic N often accumulates in the soil during dry periods, and growth and physiological responses to additional N are only observed when and where sufficient moisture is available. Two additional important effects of aridity include (1) higher soil base saturation and pH that buffer these systems from the acidification effects of N deposition and (2) spatially patchy nutrient availability that develops beneath isolated shrub canopies. One important effect of N deposition on arid and semiarid ecosystems is to decrease the patchiness of nutrient availability, which promotes the growth of invasive annual plants in the spaces between the isolated shrubs. The growth of these annual plants creates a more continuous fuel bed for wildfires, increasing the prevalence of fire, and shifting plant community composition toward more fire-adapted plant species.

Since 2008, increases in aboveground plant biomass or plant cover have been observed in the U.S. in the Mojave and Sonoran Deserts, and in southern California chaparral, and internationally in China and Spain ([Appendix 6.2.6](#)). Given the linkage to fire, it is notable that there have been multiple observations of increased annual plant growth in the Mojave Desert in response to added N.

New research has also provided further evidence that N deposition alters plant communities in arid and semiarid ecosystems, particularly in southern California, but also in other locations ([Appendix 6.3.6](#)). Many of these studies documented changes in plant community composition, with fewer observations of plant species loss or changes in plant diversity. Overall, this body of research has provided consistent and coherent evidence that N deposition is altering the growth, physiology, and community composition of plants in arid and semiarid ecosystems. Relative to plants, there are fewer studies of microbial communities ([Table 6-12](#); [Table 6-22](#)), but these studies provided evidence that N additions can alter the abundance, physiology, and community composition of soil microorganisms in arid and semiarid ecosystems.

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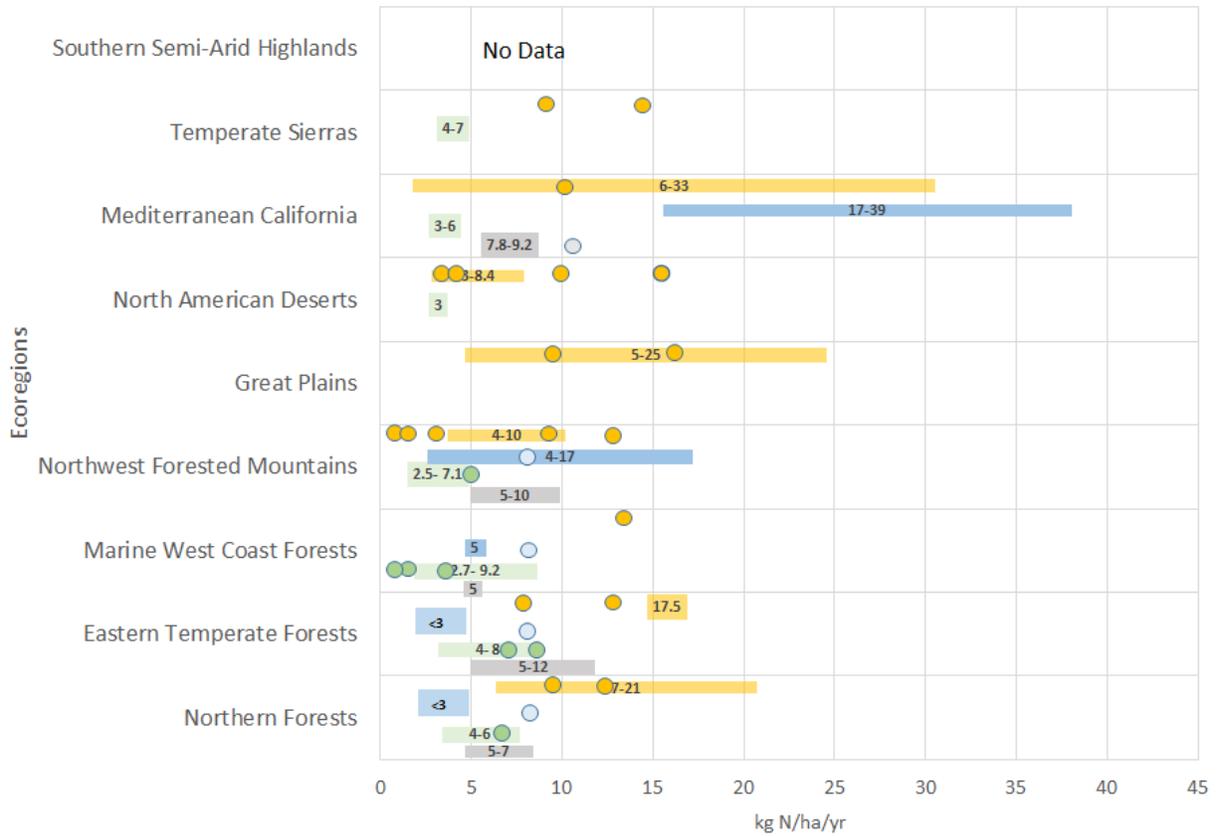
### IS.5.2.2 National-Scale Sensitivity and Critical Loads

At the time of the 2008 ISA, there had been little quantification of the extent and distribution of N sensitivity in terrestrial ecosystems in the U.S. In the 2008 ISA, there was no published U.S. national CL assessment. Since then, substantial work has been done on quantifying N CLs for U.S. ecoregions. The most notable new work is the U.S. Department of Agriculture—Forest Service (USDA-FS) *Assessment of Nitrogen Deposition Effects and Empirical Critical Loads* ([Pardo et al., 2011a](#)). That assessment was organized by Level 1 ecoregions, and where data were available, CL calculations were made for individual ecosystem types (e.g., forests within the Mediterranean California ecoregion) and life forms (i.e., lichens, mycorrhizal fungi). This ISA largely follows that structure, reporting terrestrial N CLs for life forms (e.g., herbaceous plants) within each ecoregion, which is a geographically defined area within a broader biome (e.g., forests) based on distinct physical and biological features (e.g., Northwest Forested Mountains, Eastern Temperate Forests, etc.).

Newer CL studies are presented in tandem with the CLs reported by [Pardo et al. \(2011a\)](#) in [Table 6-28](#) and [Figure IS-10](#). The majority of values for new CLs are within the range of CLs identified by [Pardo et al. \(2011a\)](#). Notably, however, [Simkin et al. \(2016\)](#) identified a new average CL for herbaceous plants in open canopy (7.9 kg N/ha/yr) forests in the Eastern Temperate Forest ecoregion, and new lower CLs were derived for alpine ecosystems in the Northwest Forested Mountains ecoregion. There are also new CLs for herbaceous species in two ecoregions previously lacking a CL for herbaceous plants [[Table 6-28](#), [Simkin et al. \(2016\)](#)].

Recently, [Clark et al. \(2018\)](#) estimated CL exceedance areas for the contiguous U.S. over a more than 200 year period. Overall, this analysis showed that terrestrial N CLs have been exceeded for many decades in areas across the U.S. Exceedance areas peaked in

1995 for changes in lichen communities and plant community composition at 3.47 and 2.87 million km<sup>2</sup>, respectively, before declining marginally by 2006. The minimum forest tree health CL was exceeded in 2.41 million km<sup>2</sup> by 1855 and did not change much over time, primarily because the relatively low CL compared to deposition values in the Eastern Temperate and Northern forest ecoregions.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

The rectangles indicate the range of CLs designated by [Pardo et al. \(2011a\)](#); the circles indicate new papers that have specified CLs; data from [Table 6-28](#).

**Figure IS-10 Summary of critical loads for nitrogen in the U.S. for shrubs and herbaceous plants (yellow), trees (blue), lichens (green), and mycorrhizae (gray).**

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### IS.5.3 Biological Effects of Acidification

Since publication of the 2008 ISA, the overarching understanding of terrestrial acidification has not appreciably changed. Recent research has confirmed and strengthened this understanding that acidification can be caused by acidifying deposition (N + S) and provided more quantitative information, especially across regional-scale landscapes. Several studies have evaluated the relationships between soil chemistry indicators of acidification and ecosystem biological endpoints (see [Table 5-6](#)). Soil chemistry indicators examined in recent literature include exchangeable base cations (Bc), soil pH, exchangeable acidity (H<sup>+</sup> and Al), exchangeable Bc:Al ratio, base saturation, and Al concentrations. The most common indicator used in determining CLs is the soil solution Bc:Al ratio. [Appendix 5.2.1](#) discusses the uncertainty considerations when using this indicator. Biological endpoints included in the evaluations consisted of physiological and community responses of trees and other vegetation, lichens, soil biota, and fauna.

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#### IS.5.3.1 Physiology and Growth

In the 2008 ISA, evidence was sufficient to infer a causal relationship between acidifying deposition and changes in terrestrial biota; the evidence included changes in plant physiology, plant growth, and terrestrial biodiversity. The physiological effects of acidification on terrestrial ecosystems in the U.S. were well characterized at the time of the 2008 ISA and included slower growth and increased mortality among sensitive plant species. Consistent and coherent evidence from multiple species and studies in 2008 showed that the biological effects of acidification on terrestrial ecosystems were generally attributable to physiological impairment caused by Al toxicity and decreased ability of plant roots to take up base cations (Appendix 3.2.2.3 of the 2008 ISA). Much of the new evidence for the negative effects of acidifying deposition comes from Ca addition experiments, in which the addition of Ca has alleviated many of the negative plant physiological and growth effects. Consistent with the findings of the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.**

In the 2008 ISA, acidifying deposition, in combination with other stressors, was found to be a likely contributor to physiological effects that led to the decline of sugar maple (*Acer saccharum*) trees occurring in portions of the eastern U.S. with base-poor soils. Studies since the 2008 ISA support these findings (see [Appendix 5.2.1.1](#)). For example, recent field studies have shown relationships between soil chemical indicator threshold values

and tree responses. Substantial declines in sugar maple regeneration have been found at soil base saturation levels <20%, which is consistent with the range reported in the 2008 ISA.

In new studies, sugar maple grew more rapidly and showed increased regeneration responses with increasing exchangeable base cations, base saturation, and soil pH, however, growth was stunted and regeneration reduced with increasing exchangeable Al. In other studies, the growth, regeneration, and physiological responses of sugar maple to the soil conditions created by acidifying deposition were reversed or ameliorated by Ca additions. Similarly, the 2008 ISA reported that processes associated with soil acidification contributed to physiological stress, high mortality rates, and decreasing growth trends of red spruce (*Picea rubens*) trees. New evidence from Ca addition studies provides further support for these mechanisms (see [Appendix 5.2.1.2](#)). Added Ca reversed or ameliorated many of the physiological responses to acidification.

In the 2008 ISA, there was limited information on the effects of acidification on other tree species. Since the 2008 ISA, research has observed varying physiological sensitivity to soil acidification among eight eastern U.S. tree species. New studies since the 2008 ISA have also added new information about the effects of acidifying deposition on forest understory vegetation, grasslands, lichens, and higher trophic level organisms (snails and salamanders) that support the terrestrial acidification conclusions of the 2008 ISA.

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### IS.5.3.2 Biodiversity

The 2008 ISA noted strong evidence that acidifying deposition could alter terrestrial community composition and cause a loss of terrestrial biodiversity. The physiological and growth effects of acidifying deposition are not uniform across species, resulting in altered species composition and decreased biodiversity whereby sensitive species are replaced by more tolerant species. For example, increasing soil base cation availability was tied to greater sugar maple growth and seedling colonization, whereas American beech (*Fagus grandifolia*) was relatively more dominant on soils with lower base cation availability (see [Appendix 5.2.1.3.1](#)). Measurements of soil acid-base chemistry have been used as a predictor of understory species composition, with 50 understory species associated with high soil base cation status. In another set of studies, soil acid-base chemistry was correlated with soil biodiversity and community composition. For example, addition of Ca resulted in changes in soil bacterial community composition and bacterial community structure that were correlated with soil exchangeable Ca, pH, and P (see [Appendix 5.2.4](#)). Based on research included in the 2008 ISA and these new studies, **the body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and**

## **the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.**

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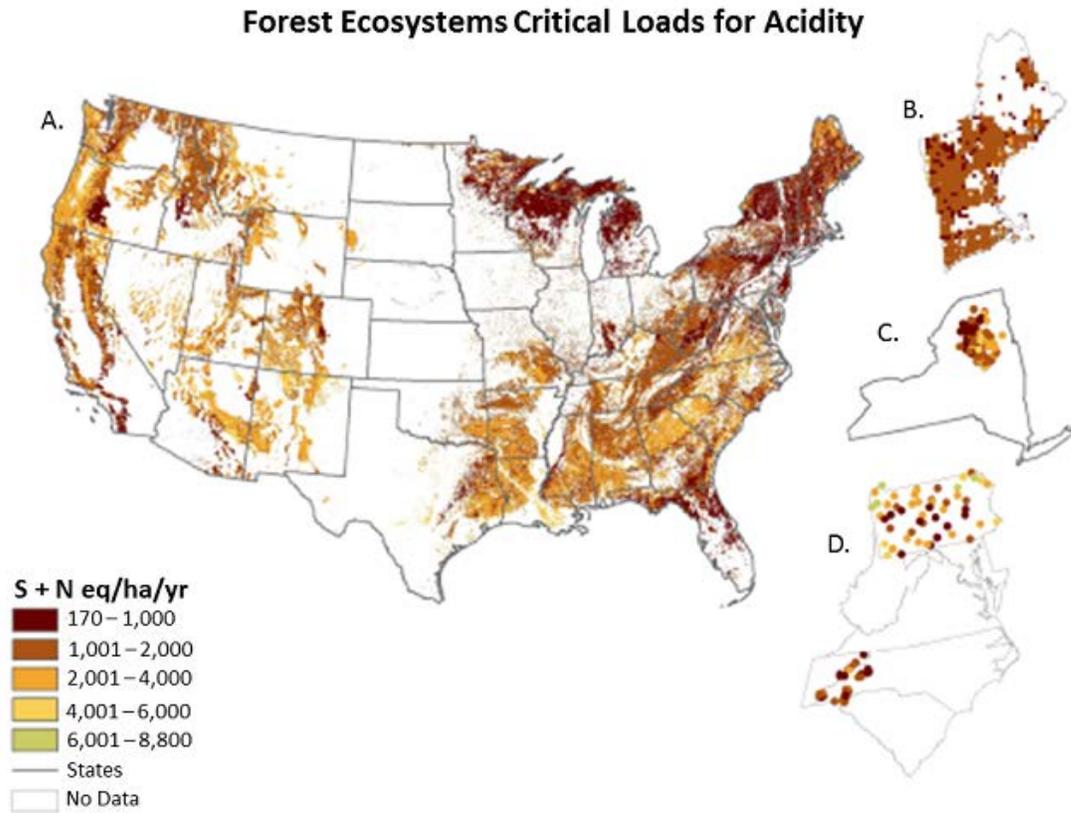
### **IS.5.3.3 National-Scale Sensitivity and Critical Loads**

The sensitivity of soils to acidifying deposition is discussed in detail in [Appendix 4](#). In general, surficial geology is the principal factor governing the sensitivity of terrestrial ecosystems soil to acidification from S and N deposition. Other factors that contribute to the sensitivity of soils to acidifying deposition include topography, soil chemistry, and land use. Several widely accepted models are currently used in the U.S. to assess the terrestrial effects of S and N deposition ([Appendix 4.5](#)). These models are typically used to evaluate acidification effects on biota by assigning a value of a soil parameter that relates to the onset of a harmful biological effect. Since the 2008 ISA, estimates of base cation weathering (BCw), which are input to soil acidification models have improved and are being applied for deriving new CLs in the U.S. Forests of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and mountain tops and ridges forest ecosystems in the southern Appalachians are the regions that are most sensitive to terrestrial acidification from atmospheric deposition (Appendix 3.2.4.2 of the 2008 ISA).

Models used to determine CLs of acidifying deposition included SMB, STA, MAGIC, ForSAFE-VEG, and empirical models. Several models and extrapolation methods to estimate BCw rates were also investigated. The PROFILE model was evaluated as a model to estimate soil BCw rates to support estimates of SMB CLs in the U.S. (see [Appendix 4.5](#)). In general, recently published models used soil solution Bc:Al ranging from 1.0 to 10.0 as an indicator to estimate CLs in North America.

Ecosystem sensitivities to ambient N and S deposition were also characterized by developing CLs and exceedances (see [Appendix 4.6](#); [Figure IS-11](#), and [Appendix 5.5](#)). Calculated CLs for forest plots based on the soil solution Bc:Al of 10.0 in the northeastern U.S. ranged from 11 to 6,540 eq/ha/yr (eq quantifies the supply of available H<sup>+</sup> ions, combining the acidifying effects of N and S deposition), and 15–98% (calculated using maximum and minimum weathering rates) of these plot-level CLs were exceeded by N and S deposition. In this region, correlation analyses showed that the growth of 17 tree species were negatively correlated with CL exceedance. In Pennsylvania, CLs based on the soil solution Bc:Al of 10.0 for hardwood forests ranged from 4 to 10,503 eq/ha/yr and were exceeded by estimated N and S deposition in the year 2002 in 53% of the plots. Several studies found that CL and exceedance determinations could be influenced by BCw rates, soil chemical indicators, N retention, tree species-specific base

cation uptake, and the type and accuracy of deposition estimates (i.e., wet, bulk, total, measured or modeled).



eq = equivalent; ha = hectare; yr = year.

(A) [McNulty et al. \(2007\)](#); CLs are mapped at 1-km<sup>2</sup> grids (center map). For uncertainty, see [Li and McNulty \(2007\)](#). (B) [Duarte et al. \(2013\)](#); CLs are mapped at 4-km<sup>2</sup> grids. (C and D) [Phelan et al. \(2014\)](#); CLs are mapped for each sampling site (Pennsylvania). [McDonnell et al. \(2014b\)](#); [Sullivan et al. \(2011b\)](#); [Sullivan et al. \(2011a\)](#); CLs are mapped as a single point at the center point of the watershed (New York and North Carolina).

Source: <http://nadp.slh.wisc.edu/committees/clad>.

**Figure IS-11 Forest ecosystem critical loads for soil acidity related to base cation soil indicators.**

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## IS.6 Freshwater Ecosystem Nitrogen Enrichment and Acidification

For freshwater systems, new evidence reinforces causal findings from the 2008 ISA ([Table IS-1](#)). It also expands the scope of existing causal findings to include additional biota affected by N enrichment and acidifying deposition and supports quantification of these effects with new CLs (see [Section IS.6.3.2](#)). Freshwater systems include lakes (lentic systems) and rivers and streams (lotic systems). In freshwater ecosystems, N may cause N enrichment/eutrophication. Aquatic eutrophication results in increased productivity of algae and aquatic plants, altered nutrient ratios, and sometimes decreased oxygen levels. Deposition of N, S, or N + S can cause acidification, which affects watershed biogeochemical processes and surface water chemistry. Freshwater N enrichment and acidification take place in sensitive ecosystems across the U.S. at present levels of deposition and may occur simultaneously in some water bodies.

New studies have added to the body of evidence in the 2008 ISA that N nutrient enrichment and acidifying deposition alter freshwater biogeochemistry with subsequent biological effects. There is new information on biogeochemical processes including cycling of N and S. Both N enrichment/eutrophication and acidification can impact physiology, survival, and biodiversity of sensitive aquatic biota. The 2008 ISA and new studies provide examples of lakes and streams that show signs of eutrophication, especially increased algal growth and shifts in algal biodiversity, in response to N addition. The current causal statement for nutrient enrichment effects of N deposition now includes altered algal growth and productivity as well as the endpoints of species richness, community composition, and biodiversity reported in the 2008 ISA ([Table IS-1](#)). For biological effects of aquatic acidification, the current causal statement has been expanded from the 2008 ISA to include the specific endpoints of physiological impairment, alteration of species richness, community composition, and biodiversity ([Table IS-1](#)). New studies also show that despite reductions in acidifying deposition, many aquatic ecosystems across the U.S. are still experiencing changes in ecological structure and functioning at multiple trophic levels. Although there is evidence for chemical recovery in many previously acidified ecosystems, biological recovery has been limited ([Appendix 8.4](#)).

A number of freshwater monitoring efforts have facilitated the analysis of long-term trends in surface water chemistry and ecological response in areas affected by acidifying (N + S) deposition ([Appendix 7.1.3](#)). Many of these studies have been conducted in the U.S., especially in the Northeast and the Appalachian Mountains. Although many of these monitoring programs were in existence at the time of the 2008 ISA and were considered in that analysis, more recent publications reflect the longer period of

monitoring and strengthen previous conclusions. Surface water chemistry data from long-term monitoring by federal, state, and local agencies, as well as university research groups and nonprofits has been combined into several publicly available metadatabases ([Appendix 7.1.3.2](#)) enabling further regional trend analysis. Since the early 2000s, U.S. EPA, together with the states, tribes, and other entities and individuals, have collaborated on a series of statistically representative surveys (National Aquatic Resource Surveys [NARS]) of the nation's waters, including surveys of lakes ([U.S. EPA, 2016h, 2009b](#)), streams ([U.S. EPA, 2016i](#)), wetlands ([U.S. EPA, 2016j](#)), and coastal waters ([U.S. EPA, 2016g](#)). These periodic surveys, which are based on standard sampling and analysis protocols and consistent quality assurance, include chemical and biological indicators of nutrient enrichment and acidification ([Appendix 7.1.3](#)).

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## IS.6.1 Freshwater Biogeochemistry

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N and S deposition and the alteration of biogeochemical cycling of N and C in freshwater ecosystems, and between acidifying deposition and changes in biogeochemistry of fresh waters. As documented in the 2008 ISA and by newer studies, biogeochemical processes and surface water chemistry are influenced by characteristics of the catchment and the receiving waters. A number of studies since 2008 have focused on improving understanding of aquatic acidification and eutrophication processes mediated by N. Many of these studies have focused on pathways of pollutant and other constituent movement within ecosystems, including monitoring studies of various kinds. Chemical indicators of N deposition identified by the 2008 ISA were  $\text{NO}_3^-$  and DIN concentrations in surface waters. Increased N deposition to freshwater systems via runoff or direct atmospheric deposition, especially to N limited and N and phosphorus (P) colimited systems, can alter N cycling ([Appendix 7](#)) and stimulate primary production ([Appendix 9](#)). Data from long-term monitoring, experimental manipulations, and modeling studies provide consistent and coherent evidence for biogeochemical changes associated with acidifying N and S deposition. The strongest evidence for a causal relationship between acidifying deposition and aquatic biogeochemistry comes from studies of changes in surface water chemistry. Surface water chemistry indicators of acidic conditions and acidification effects include concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , inorganic aluminum (Al), calcium (Ca), sum and surplus of base cations, acid-neutralizing capacity (ANC), and surface water pH. New information on biogeochemical cycling of N and S, acidifying deposition effects on biogeochemical processes and changes to chemical indicators of surface water chemistry associated with acidification and N nutrient enrichment is consistent with the conclusions

of the 2008 ISA, and **the body of evidence is sufficient to infer a causal relationship between N and S deposition and the alteration of freshwater biogeochemistry.**

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### IS.6.1.1 Freshwater Processes and Indicators

Key processes and geochemical indicators of freshwater acidification and N enrichment ([Table IS-3](#)) link to biological effects ([Appendix 8](#) and [Appendix 9](#)). Surface water chemistry integrates the sum of soil and water processes that occur upstream within a watershed. Several key biogeochemical processes cause or contribute to surface water eutrophication and acidification, and these processes have been the focus of substantial research over the last three decades. Since the 2008 ISA, experimental studies, isotopic analyses, and monitoring and observational studies have further investigated the cycling of S, N, C, and base cations; these studies substantiate and further quantify earlier findings.

Spatial and temporal patterns of  $\text{NO}_3^-$  in lakes and streams have typically been used as indicators that a freshwater system is receiving excess N which will cause acidification or eutrophication. Qualitatively, northeastern U.S. spatial patterns in surface water  $\text{NO}_3^-$  concentrations suggest an influence by atmospheric N deposition. However, considerable variation in the relationship between stream chemistry and deposition was associated with land use and watershed attributes. It was well known at the time of the 2008 ISA that key processes such as nitrification and denitrification are quantitatively important portions of the N cycle and that they can be influenced by atmospheric inputs. More recent research has further substantiated these earlier findings and provided additional quantitative context ([Appendix 7.1.2.3](#)).

Deposition is a source of S to watersheds that, along with geologic sources of S such as sulfide minerals, contribute  $\text{SO}_4^{2-}$  to surface waters ([Appendix 4](#)). The 2008 ISA found that S deposition alters soil and drainage water chemistry through sustained leaching of  $\text{SO}_4^{2-}$ , associated changes in soil chemistry, and accumulation of S in the soil through adsorption and biological assimilation. Declines in lake  $\text{SO}_4^{2-}$  concentrations have been observed in locations where S deposition has decreased significantly such as in the Adirondack Mountains ([Appendix 7.1.5.1](#)). In addition, internal watershed sources of S, which were earlier believed to be relatively minor in the northeastern U.S., have and will likely continue to become proportionately more important as S deposition continues to decline. Reductions in  $\text{SO}_x$  deposition have not consistently resulted in increases of ANC in surface water.

**Table IS-3 Summary of key aquatic geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
<b>Process</b>			
NO <sub>3</sub> <sup>-</sup> leaching into water bodies	X	X	Leaching from terrestrial ecosystems is an important source of NO <sub>3</sub> <sup>-</sup> in freshwater ecosystems. See NO <sub>3</sub> <sup>-</sup> leaching in <a href="#">Table IS-2</a> .
SO <sub>4</sub> <sup>2-</sup> leaching into water bodies		X	Leaching from terrestrial ecosystems is an important source of SO <sub>4</sub> <sup>2-</sup> in freshwater ecosystems. See SO <sub>4</sub> <sup>2-</sup> leaching in <a href="#">Table IS-2</a> .
Nitrification	X	X	Nitrification is an acidifying process, releasing 2 mol hydrogen ion (H <sup>+</sup> ) per mol NH <sub>4</sub> <sup>+</sup> converted to NO <sub>3</sub> <sup>-</sup> . As the N cycle becomes enriched through cumulative N addition, net nitrification rates often increase, and NO <sub>3</sub> <sup>-</sup> concentrations increase.
Denitrification	X		Denitrification is the microbial process that transforms NO <sub>3</sub> <sup>-</sup> by anaerobically reducing it to NO <sub>2</sub> <sup>-</sup> , NO, N <sub>2</sub> O, and N <sub>2</sub> .
DOC leaching into water bodies	X	X	DOC contributes to acidity of freshwater ecosystems. See DOC leaching in <a href="#">Table IS-2</a> .
<b>Indicator</b>			
Surface water [NO <sub>3</sub> <sup>-</sup> ]	X	X	Increased N deposition (to surface waters or to terrestrial watershed; see <a href="#">Table IS-2</a> ) increases the water NO <sub>3</sub> <sup>-</sup> concentration. High concentrations of NO <sub>3</sub> <sup>-</sup> in lakes and streams, indicative of terrestrial ecosystem N saturation, have been found at a variety of locations throughout the U.S. ( <a href="#">U.S. EPA, 2006c</a> ; <a href="#">Stoddard, 1994</a> ). Comparison of preindustrial estimates to modern measurements suggested elevated concentrations in water bodies as a result of N deposition ( <a href="#">Fenn et al., 2011b</a> ).
Surface water DIN	X		Increased N deposition increases DIN in most freshwater aquatic environments, largely as NO <sub>3</sub> <sup>-</sup> .
Surface water N:P ratios	X		Increased N deposition can alter the ratio of N to P in freshwater systems. Freshwater biota have different nutrient requirements and changes in nutrient ratios may alter species richness, community structure, and biodiversity, especially primary producers.
Surface water [SO <sub>4</sub> <sup>2-</sup> ]		X	Increased S deposition (to surface waters or to terrestrial watershed, see <a href="#">Table IS-2</a> ) increases the water SO <sub>4</sub> <sup>2-</sup> concentration. Comparison of preindustrial estimates to modern measurements suggested elevated concentrations in water bodies are a result of S deposition.

**Table IS-3 (Continued): Summary of key aquatic geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Surface water (base cation)		X	Several studies in the eastern U.S. suggested that base cation concentrations in surface waters increased during the initial phases of acidification into the 1970s. This trend reversed, and base cations have decreased primarily in response to decreasing $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentrations. Many base cations (especially $\text{Ca}^{2+}$ ) are important nutrients for aquatic biota.
Surface water ANC		X	Increased N and S deposition decrease ANC. Surface water ANC correlates with other biologically influential chemical metrics, including pH, inorganic Al concentration, Ca concentration, and organic acidity. ANC <50–100 $\mu\text{eq/L}$ typically poses a risk for species survival, species richness, and biodiversity.
Surface water pH		X	Surface water pH is a common alternative to ANC as an indicator of acidification, but ANC is a better indicator at pH >6.0 and is less sensitive to dissolved $\text{CO}_2$ . N and S deposition are associated with decreasing pH in surface waters.
Surface water Inorganic Al		X	Acidifying N and S deposition increase mobilization of inorganic Al from terrestrial ecosystems into surface water, increasing surface water concentrations. Inorganic Al in surface waters is (1) widely toxic and (2) leaches from terrestrial ecosystems only in response to acidic conditions. Earlier studies demonstrated reduced growth and survival of various species of fish at inorganic Al concentrations between approximately 2 and 7.5 $\mu\text{mol/L}$ . Most recently, 20% mortality of young-of-the-year brook trout was documented in situ during a 30-day period with a median inorganic Al concentration of 2 $\mu\text{mol/L}$ .

Al = aluminum; ANC = acid-neutralizing capacity; Ca = calcium;  $\text{CO}_2$  = carbon dioxide; DIN = dissolved inorganic nitrogen; DOC = dissolved organic carbon;  $\text{H}^+$  = hydrogen ion; ha = hectare; kg = kilogram; L = liter;  $\mu\text{eq}$  = microequivalents;  $\mu\text{mol}$  = micromole; N = nitrogen;  $\text{N}_2$  = molecular (atmospheric) nitrogen;  $\text{N}_2\text{O}$  = nitrous oxide; NE = northeast;  $\text{NH}_4^+$  = ammonium; NO = nitric oxide;  $\text{NO}_2$  = nitrogen oxide;  $\text{NO}_3^-$  = nitrate; P = phosphorus; S = sulfur;  $\text{SO}_4^{2-}$  = sulfate; U.S. = United States; USFS = U.S. Forest Service; yr = year.

#### IS.6.1.1.1 Acidification

The acidifying effects of N and S deposition in U.S. waters have been well characterized for several decades. Traditionally, acidification involves both chronic and episodic processes. [Driscoll et al. \(2001b\)](#) characterized chronically acidic lakes and streams as having ANC of <0  $\mu\text{eq/L}$  throughout the year, while episodic acidification occurs when ANC falls below 0  $\mu\text{eq/L}$  only for hours to weeks. Chronic acidification refers to average conditions and is often measured as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Chronic acidification is no longer prevalent in regions of the U.S. affected by acidic deposition ([Fakhraei et al., 2016](#); [Fakhraei et al., 2014](#)). Episodic acidification is associated with precipitation or snowmelt events when high

volumes of water flow through watersheds. Episodes generally cause changes in the following chemical parameters: ANC, pH, base cations,  $\text{SO}_4^{2-}$  concentration,  $\text{NO}_3^-$  concentration, inorganic Al concentration, organic acid anions, or DOC. New studies show that both N and S contributed to episodic acidification over a 20-year period at Bear Brook, ME (see [Appendix 7.1.5.1.2](#)). It is known that the biota in many streams/lakes are impacted when the ANC is consistently below 50  $\mu\text{eq/L}$ . For example, the U.S. EPA National Lakes Assessment used an ANC threshold of  $>50 \mu\text{eq/L}$  as indicative of nonacidified water bodies ([U.S. EPA, 2009b](#)).

The most widely used measure of surface-water acidification is ANC. As reported in the 2008 ISA and newer studies, ANC is the primary chemical indicator of historic acidification and for predicting the recovery expected from decreasing atmospheric deposition. ANC correlates with the surface water constituents (pH,  $\text{Ca}^{2+}$ , and inorganic Al concentration) that contribute to or ameliorate acidity effects in biota. As reported in the 2008 ISA, lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations ([Appendix 7.1.5.1](#)). Biological indicators of acidification, such as decreased fish species richness, are discussed in [Appendix 8.3](#).

Surface water pH is another indicator of acidification. It also correlates with surface water chemical constituents that have biotic effects (inorganic Al,  $\text{Ca}^{2+}$ , and organic acids). The 2008 ISA included the scientific consensus that low pH can have direct toxic effects on aquatic species ([U.S. EPA, 2008a](#); [Driscoll et al., 2001b](#)). A pH value of 6.0 is the level below which biota are at increased risk from acidification ([Appendix 8.3](#)). The 2008 ISA noted that increasing trends in pH (decreasing acidification) were common in surface waters in the northeastern U.S. through the 1990s and up to 2004. This trend has continued in more recent times at many locations ([Appendix 7.1.2.5](#)). Rates of change have generally been relatively small.

As stated in the 2008 ISA, the concentration of dissolved inorganic monomeric Al in surface waters is an especially useful indicator of acidifying deposition because (1) it is toxic to many aquatic species and (2) it leaches from soils only under acidic conditions including acidifying deposition, acid mine drainage, or from rare geologic deposits. Inorganic Al has well-documented effects on aquatic biota at specific thresholds ([Appendix 8.3](#)) and is often the greatest threat to aquatic biota below pH 5.5. The 2008 ISA noted that concentrations of inorganic Al decreased slightly in some surface waters in the northeastern U.S. in response to decreased levels of acidifying deposition, suggesting chemical recovery in some of these surface waters ([U.S. EPA, 2008a](#)), and

this trend has generally continued ([Appendix 7.1.5](#); see discussion on recovery [Section IS.11](#)).

Assessments of acidifying deposition effects dating from the 1980s and reported in the 2008 ISA showed  $\text{SO}_4^{2-}$  to be the primary acidifying ion in most acid-sensitive waters in the U.S. The 2008 ISA presented temporal data that showed a trend of increasing concentrations of  $\text{SO}_4^{2-}$  in surface waters before the period of peak S emissions in the early 1970s. After the peak,  $\text{SO}_4^{2-}$  surface water concentrations decreased in a widespread trend. The rate of recovery varied by ecosystem, and new studies indicate that as atmospheric S deposition has declined, soils with large stores of historically deposited S (e.g., the Blue Ridge Mountain region) have begun releasing this adsorbed S to drainage water ([Appendix 4](#)), preventing or slowing aquatic recovery.

As stated in the 2008 ISA, the quantitatively most important component of the overall surface water acidification and chemical recovery responses has been the change in base cation supply. Decreases in base cation concentrations in surface waters in the eastern U.S. have been ubiquitous over the past two to three decades and closely tied to trends in  $\text{SO}_4^{2-}$  concentrations in surface waters. Change in base cation supply with surface water acidification was highlighted in [Charles and Christie \(1991\)](#) and in the 2008 ISA. Base cations are added to watershed soils by weathering of minerals and atmospheric deposition, and are removed by uptake into growing vegetation or by leaching. Acidic deposition increased leaching of base cations, because  $\text{SO}_4^{2-}$  anions percolating through the soil tend to carry base cations along with them to maintain the charge balance. In watersheds that received high levels of historical acidic deposition, current exchangeable concentrations of  $\text{Ca}^{2+}$  and other base cations are substantially reduced from likely preindustrial levels, having been depleted by many years of acidic deposition. This base cation depletion in watersheds constrains ANC and pH recovery of surface waters, as described in the 2008 ISA. New studies of base cations, which include experiments, modeling, and gradient studies, have further corroborated these earlier findings.

Changes in DOC concentration or properties can affect the acid-base chemistry of surface waters and perhaps the composition of aquatic biota. In soils and water, DOC constitutes only a portion of dissolved organic matter (DOM), which also includes other constituents such as organic nitrogen, phosphorus, and sulfur. However, the very large majority of studies that include DOC do not explicitly include all of DOM. It has been recognized that surface water DOC concentrations decreased to some extent as a result of acidification, and that these concentrations would likely increase with recovery. However, the strength of this response and the magnitude of DOC changes have exceeded scientific predictions. Recent research on this topic has been diverse and has included experiments, observation, isotope studies, and synthesis and integration work.

Overall, these studies illustrate large increases in DOC with acidification recovery in some aquatic systems. Increases in DOC constrain the extent of ANC and pH recovery, but decrease the toxicity of dissolved Al by converting some of it from inorganic to organic forms ([Lawrence et al., 2013](#)). However, DOC is not an indicator of recovery everywhere; some recovering sites have not shown increasing trends in DOC.

#### **IS.6.1.1.2 Nitrogen Enrichment/Eutrophication**

In aquatic systems, N is a nutrient that stimulates growth of primary producers (algae and/or aquatic plants). Atmospheric deposition of N to freshwater systems can increase the absolute supply of nutrients and alter N and P ratios. The freshwater ecosystems in the U.S. most likely to be sensitive to nutrient enrichment from N deposition are headwater streams, lower order streams, and alpine lakes, which have very low nutrients and productivity and are far from local pollution sources ([U.S. EPA \(2008a\); Appendix 9.1.1.4](#)). These nutrient shifts alter stoichiometric composition of water chemistry, thereby shifting the nutrient status of lakes. Even small inputs of N in low nutrient water bodies can affect biogeochemical processing of N and increase the productivity of photosynthesizing organisms, resulting in a larger pool of fixed carbon (C). Nutrient enrichment leads to changes in aquatic assemblages and biodiversity in freshwater ([Appendix 9](#)) and coastal regions ([Appendix 10](#)).

Indicators of altered N cycling include changes in the concentrations of  $\text{NO}_3^-$  in surface waters. The concentration of  $\text{NO}_3^-$  in water provides an index of the balance between removal and addition of N to terrestrial ecosystems. Studies of several types have been conducted in recent years to elucidate these processes and include experimental studies, isotopic analyses, and monitoring and observational studies. Both water column and sediment N transformations have been further characterized ([Appendix 7.1.2.3](#)). New research suggests that denitrification may, in some situations, play a larger role than was previously recognized in the 2008 ISA in removing oxidized N from the watershed.

As reported in the 2008 ISA and in newer studies, atmospheric N has been positively correlated to total N in lakes along gradients of atmospheric deposition. N deposition in some high-deposition lakes has changed the nutrient status of these lakes from a more-or-less balanced (mainly N deficient) state to more consistently P limited conditions ([Appendix 9.2.4](#)). Since the 2008 ISA, several studies have reported increases in P deposition to water bodies in the U.S., possibly affecting shifts in lake trophic status from P to N limitation or colimitation, as well as prolonging N limitation ([Appendix 9.1.1.2](#)). In higher order streams, N deposition typically mixes with N derived from other nonatmospheric sources, including urban/suburban point and nonpoint

sources, industrial sources, and agricultural sources, with atmospheric sources typically being most pronounced during high flow conditions ([Table 7-2](#)).

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### **IS.6.1.2 Models**

Models used to assess the effects of N and S deposition on U.S. ecosystems were reviewed in the 2008 ISA (Annex A). Several of the models used for terrestrial ecosystems (see [Section IS.5.3.3](#)) such as MAGIC and PnET/BGC are also applicable to aquatic systems. Both models have been widely applied, mainly to relatively small, upland watersheds. Three other models, Spatially Referenced Regressions on Watershed Attributes (SPARROW), Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N), and Surface Water Assessment Tool (SWAT) have been used to evaluate N loading to mixed-use watersheds in larger river systems. Another model that has been applied to the analysis of nutrient enrichment in aquatic systems is AQUATOX, which simulates nutrient dynamics and effects on aquatic biota. Few new freshwater acidification or eutrophication models have been developed and published since 2008. A new national water quality modeling system (Hydrologic and Water Quality System, HAWQS) is under development by Texas A&M University and the USDA for the U.S. EPA's Office of Water (<https://epahawqs.tamu.edu/>). The model is intended to assist resource managers and policy makers in evaluating the effectiveness of water pollution control efforts. Freshwater eutrophication and acidification models are described in greater detail in [Appendix 7.1.4.2](#).

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### **IS.6.1.3 National-Scale Sensitivity**

Sensitivity of lakes, streams, and rivers to biogeochemical changes associated with N and S deposition varies across the U.S. The biogeochemical sensitivity to acidifying deposition will be discussed together with biological sensitivity in [Section IS.6.2.2](#). Sensitivity to N enrichment will be discussed with biological sensitivity in [Section IS.6.3.2](#).

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## **IS.6.2 Biological Effects of Freshwater Nitrogen Enrichment**

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in freshwater ecosystems. The freshwater systems most affected by nutrient enrichment due to atmospheric deposition of N were remote oligotrophic high-elevation

lakes with low N retention capacity. In these ecosystems, N changes the biota, especially by increasing algal growth and shifting algal communities. Freshwater organism responses to N enrichment can be assessed through biological indicators, including chlorophyll *a*, phytoplankton and periphyton (algae attached to a substrate) biomass, diatoms, and trophic status. The current causal statement has been expanded to include effects on algal growth and productivity ([Table IS-1](#)). New evidence since 2008 of N enrichment includes paleolimnology, phytoplankton community dynamics, macroinvertebrate response, and indices of biodiversity. This new evidence is consistent with the conclusions and strengthens the evidence base of the 2008 ISA, and together, **the body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota, including altered growth and productivity, species richness, community composition, and biodiversity due to N enrichment in freshwater ecosystems.**

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### **IS.6.2.1 Physiology and Biodiversity Effects**

Inputs of N to freshwater systems stimulate algal growth, which leads to a cascade of effects on algal community composition and biodiversity. Algal species have differential responses to N loading and shifts in nutrient ratios, so dominant species may change in response to N enrichment. As reported in the 2008 ISA and in newer studies, shifts in nutrient limitation from N limitation to colimitation by N and P, or to P limitation, have been observed in some alpine lakes. New biodiversity studies are summarized in [Table 9-3](#). Since the 2008 ISA, several meta-analyses have reported an increase in P atmospheric deposition to water bodies, highlighting the need to account for how sustained P deposition can modify the effects of anthropogenically emitted N deposition on productivity ([Appendix 9.1.1.4](#)). P addition delays the shift to P limitation (prolonged N limitation) for phytoplankton.

#### **IS.6.2.1.1 Primary Producers**

The body of evidence for biological effects of N enrichment in remote freshwater systems (where atmospheric deposition is the predominant source of N) is greatest for phytoplankton, the base of the freshwater food web. Most studies focused on phytoplankton, although several new studies indicate that both benthic and pelagic primary producers respond to N inputs, and at least some studies have shown that periphyton outcompeted phytoplankton for limiting nutrients ([Appendix 9.3.3](#)). The 2008 ISA and new studies include lake surveys, fertilization experiments, and nutrient bioassays that show a relationship between increased N concentrations in the water

column and increased pelagic and benthic algal productivity (measured by chlorophyll *a* concentration). An increase in lake phytoplankton biomass with increasing N deposition was reported in the Snowy Range in Wyoming and in Europe. New studies in the Colorado Rocky Mountains, where atmospheric deposition ranged from 2 to 7 kg N/ha/yr, found correlations between higher chlorophyll *a* and higher rates of deposition ([Appendix 9.2.1](#)).

The 2008 ISA and newer studies ([Table 9-1](#) and [Appendix 9.3.2](#)) show a general shift in algal dominance from chrysophytes that dominate low N lakes to cyanophytes and chlorophytes in higher N lakes. Two nitrophilous species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, serve as indicators of N enrichment in lakes; however, increased relative abundance of *A. formosa* has also been attributed to lake warming in some regions where N deposition is decreasing ([Appendix 9.3.2](#)). New studies show that glacial meltwater has higher NO<sub>3</sub><sup>-</sup> relative to snow meltwater with different influences on algal community composition in some regions of the U.S. ([Appendix 9.3.2](#)). In a comparison of lakes in the Rockies with different meltwater sources, fossil diatom richness in snowpack-fed lakes was at least double the richness of lakes with both glacial and snow meltwater inputs; however, alterations in phytoplankton community structure were not observed in lakes in the northern Cascade Mountains, WA. Some shifts in algal biodiversity observed in high-elevation waters are attributed to climate change or nutrient effects and climate as costressors ([Appendix 13](#)).

The role of N in freshwater harmful algal bloom formation has been further researched since the 2008 ISA. Additional evidence continues to show that availability and form of N influences algal bloom composition and toxicity, and inputs of inorganic N selectively favor some HAB species, including those that produce microcystin. Microcystin is prevalent in U.S. waters as reported in recent regional and national surveys. The risk of HAB formation is low in high-elevation oligotrophic water bodies where N deposition is the dominant source of N, but transport of atmospheric inputs can exacerbate eutrophic conditions in downstream water bodies. Increased understanding of the role of N as a limiting nutrient in many freshwater systems has led to recommendations to consider both N and P in nutrient-reduction strategies.

Few studies in the U.S. have considered the effects of atmospheric deposition on aquatic macrophytes, although declines in macrophyte occurrence were noted in a new survey of Lake Tahoe that compared the lake's biota with that from a survey conducted in the 1960s ([Caires et al., 2013](#)). Atmospheric N contributions are a substantial portion (approximately 57%) of the total N loading to Lake Tahoe.

### **IS.6.2.1.2 Zooplankton**

Compared to changes in primary producers, biological responses to N deposition at higher trophic levels are not well characterized, but atmospheric N can alter food web interactions (see [Appendix 9.3.4](#)). A few studies in the 2008 ISA and newer studies showed zooplankton responses to N related shifts in phytoplankton biomass potentially altering food web interactions.

### **IS.6.2.1.3 Macroinvertebrates**

Few studies published since the 2008 ISA have linked atmospheric N deposition to taxonomic shifts and declines in invertebrates ([Appendix 9.3.5](#)). These studies do not attribute shifts in the abundance of higher invertebrates to N deposition alone, because their abundance is also determined by additional factors such as climate and the presence of invasive species. New studies provide additional evidence that trophic interactions may moderate algal growth following nutrient loading. In Lake Tahoe, which receives 57% of N inputs from atmospheric sources, endemic invertebrate taxa have declined 80 to 100% since the 1960s due to nutrient inputs and invasive species.

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## **IS.6.2.2 National-Scale Sensitivity and Critical Loads**

New data have not appreciably changed the identification of sensitive lakes and streams in the U.S. since the 2008 ISA. Nutrient enrichment effects from N most likely occur in undisturbed, low-nutrient headwater and lower order streams and lakes at higher elevations in the western U.S. ([Appendix 9.1](#)), including the Snowy Range in Wyoming, the Sierra Nevada, and the Colorado Front Range. A portion of these lakes and streams where effects are observed are in Class I wilderness areas which are afforded special Clean Air Act protections. The responses of high-elevation lakes vary with catchment characteristics ([Appendix 9.1](#)) and N deposition estimates at these high elevation sites are associated with considerable uncertainty, especially dry deposition ([Appendix 2](#)). In these systems, even low inputs of atmospheric N can shift N limitation to colimitation by N and P, or to P limitation ([Appendix 9.2.4](#)), altering algal species composition and productivity.

In the 2008 ISA, diatom assemblage shifts were reported at N deposition rates as low as 1.5 kg N/ha/yr. Additionally, a hindcasting exercise in remote alpine Rocky Mountain National Park lakes associated algal changes between 1850 and 1964 with an increase in wet N deposition of 1.5 kg N/ha/yr. Since the 2008 ISA, empirical and modeled CLs for the U.S. have been estimated based on surface water  $\text{NO}_3^-$  concentration, diatom

community shifts, and phytoplankton biomass nutrient limitation shifts indicative of a shift from N limitation to P limitation. A CL ranging from 3.5 to 6.0 kg N/ha/yr was identified for high-elevation lakes in the eastern U.S. based on the nutrient enrichment inflection point [where  $\text{NO}_3^-$  concentrations increase in response to increasing N deposition; [Baron et al. \(2011b\)](#)]. Another CL of 8.0 kg N/ha/yr for eastern lakes based on the value of N deposition at which significant increases in surface water  $\text{NO}_3^-$  concentrations occur was estimated by [Pardo et al. \(2011c\)](#). In both Grand Teton and Yellowstone National Parks, CLs for total N deposition ranged from  $<1.5 \pm 1.0$  kg N/ha/yr to  $>4.0 \pm 1.0$  kg N/ha/yr ([Nanus et al., 2017](#)). Exceedance estimates were as high as 48% of the Greater Yellowstone area study region, depending on the threshold value of  $\text{NO}_3^-$  concentration in lake water selected as indicative of biological harm. An empirical CL of 4.1 kg N/ha/yr above which phytoplankton biomass P limitation is more likely than N limitation was identified by [Williams et al. \(2017b\)](#) for the western U.S. Modeled CLs ranged from 2.8 to 5.2 kg N/ha/yr.

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### IS.6.3 Biological Effects of Freshwater Acidification

The 2008 ISA found evidence sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota, including strong evidence that acidified aquatic habitats had lower species richness of fishes, macroinvertebrates, and phytoplankton. The effects of acidifying deposition on aquatic ecosystems also include physiological impairment or mortality of sensitive species and shifts in biodiversity of both flora and fauna. Organisms at all trophic levels are affected by acidification, with clear linkages to chemical indicators for effects on algae, benthic invertebrates, and fish ([Table 8-9](#)). Biological effects are primarily attributable to low pH and high inorganic Al concentration. ANC integrates chemical components of acidification ([Table IS-2](#)) but does not directly alter the health of biota.

Effects of acidification on fish species are especially well characterized and many species are harmed. Both in situ and lifestage experiments in fish support thresholds of chemical indicators for biological effects. Most of these effects were documented in a rigorous review of acidification effects on aquatic biota that was included in the 2008 ISA. Overall, the updated research synthesized in this ISA reflects incremental improvements in scientific knowledge of aquatic biological effects and indicators of acidification as compared with knowledge summarized in the 2008 ISA. The fundamental understanding of mechanisms has not changed, and the causal relationships between acidifying deposition and biological effects on aquatic ecosystems are now, and were in 2008, well supported. New studies also show that despite reductions in acidifying deposition, alterations in aquatic biodiversity and ecosystem functioning caused by acidification

persist. Although there is evidence for chemical recovery in many ecosystems, biological recovery has been limited ([Section IS.6.2.2](#)). New research is consistent with the causal determination in the 2008 ISA and has strengthened the evidence base for these effects. The current causal statement has been expanded to include specific endpoints of physiological impairment, as well as effects at higher levels of biological organization ([Table IS-1](#)). **The body of evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biota, including physiological impairment and alteration of species richness, community composition, and biodiversity in freshwater ecosystems.**

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### IS.6.3.1 Physiology and Biodiversity Effects

The deterioration in water quality caused by acidification affects the physiology, survivorship, and biodiversity of many species from several taxonomic groups and at multiple trophic levels. As stated in the 2008 ISA, biological effects are primarily attributable to low pH (or ANC) and high inorganic Al concentrations under chronic or episodic acidic conditions. During acidification episodes, water chemistry may exceed the acid tolerance of resident aquatic biota, with effects that include fish mortalities, changes in species composition, and declines in species richness across multiple taxa. Studies reviewed in the 2008 ISA showed that the earlier aquatic lifestages were particularly sensitive to acidification. New effects thresholds have been identified for aquatic organisms consistent with observations in the 2008 ISA ([Table 8-10](#)). New evidence is congruent with findings in the 2008 ISA that high levels of acidification (to pH values below 5 and ANC lower than the range of 50 to 100 µeq/L) eliminate sensitive species from freshwater streams. This information is reviewed below.

#### IS.6.3.1.1 Primary Producers

Phytoplankton are primary producers at the base of the aquatic food web. These photosynthetic organisms vary in tolerance of acidic conditions and include diatoms, cyanobacteria, dinoflagellates, and other algal groups. The 2008 ISA reported reduced species richness of freshwater plankton in response to acidification-related decreases in pH and increases in inorganic Al. Effects were most prevalent when pH decreased to the 5 to 6 range. Effects on productivity are uncertain. Since the 2008 ISA, several paleolimnological and field studies have further linked phytoplankton community shifts to chemical indicators of acidification ([Appendix 8.3](#)). For example, [Lacoul et al. \(2011\)](#) reviewed information on the effects of acidification and observed that the largest declines in phytoplankton species richness occur over a pH range of 4.7 to 5.6 in Atlantic Canada.

#### **IS.6.3.1.2 Zooplankton**

Zooplankton comprise many groups of freshwater unicellular and multicellular organisms including protozoans, rotifers, cladocerans, and copepods. Zooplankton feed on phytoplankton or other zooplankton. Decreases in ANC and pH and increases in inorganic Al concentration have been shown to contribute to the loss of zooplankton species or abundance in lakes. In the 2008 ISA, thresholds for zooplankton community alteration were between pH 5 and 6. In the Adirondacks, a decrease in pH from 6 to 5 decreased zooplankton richness in lakes, and at ANC <0, zooplankton richness was only 45% of the richness in unacidified lakes. Newer studies support effects in a similar pH range (see [Appendix 8.3.1.2](#)). Zooplankton have also been used as indicators of biological recovery ([Appendix 8.4.2](#)).

#### **IS.6.3.1.3 Benthic Invertebrates**

Acidification has strong impacts on aquatic invertebrates because H<sup>+</sup> and Al are directly toxic to sediment-associated invertebrates like bivalves, worms, gastropods, and insect larvae. In the 2008 ISA and in new studies in [Appendix 8.3.3](#), decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in abundance or extirpation of benthic invertebrate species in streams. Acidification to pH values below 5 eliminates mayflies (Ephemeroptera), a taxa indicative of stream water quality, along with other aquatic organisms. Since the 2008 ISA, a survey of benthic macroinvertebrates by [Baldigo et al. \(2009\)](#) in the Adirondack Mountains indicated that macroinvertebrate communities were intact at a pH above 6.4, with moderate acidification effects at pH 5.1 to 5.7, and severe acidification effects at a pH less than 5.1. Similarly, thresholds of pH 5.2 to 6.1 were identified for sensitive invertebrates from Atlantic Canada ([Appendix 8.3.3](#)).

#### **IS.6.3.1.4 Fish**

The effects of low pH and ANC and of high inorganic Al concentrations have been well characterized in fish for many decades ([Appendix 8.3.6](#)). The 2008 ISA reported that acidification impairs gill function and can cause respiratory and circulatory failure in fish. Sensitivity to pH and inorganic Al varies among fish species, and among lifestages within species, with early lifestages more sensitive to acidification. The most commonly studied species were brown trout (*Salmo trutta*), brook trout (*Salvelinus fontinalis*), and Atlantic salmon (*Salmo salar*). Studies published since the 2008 ISA, especially in Atlantic salmon, add to the existing information on sublethal effects and confirm variation in

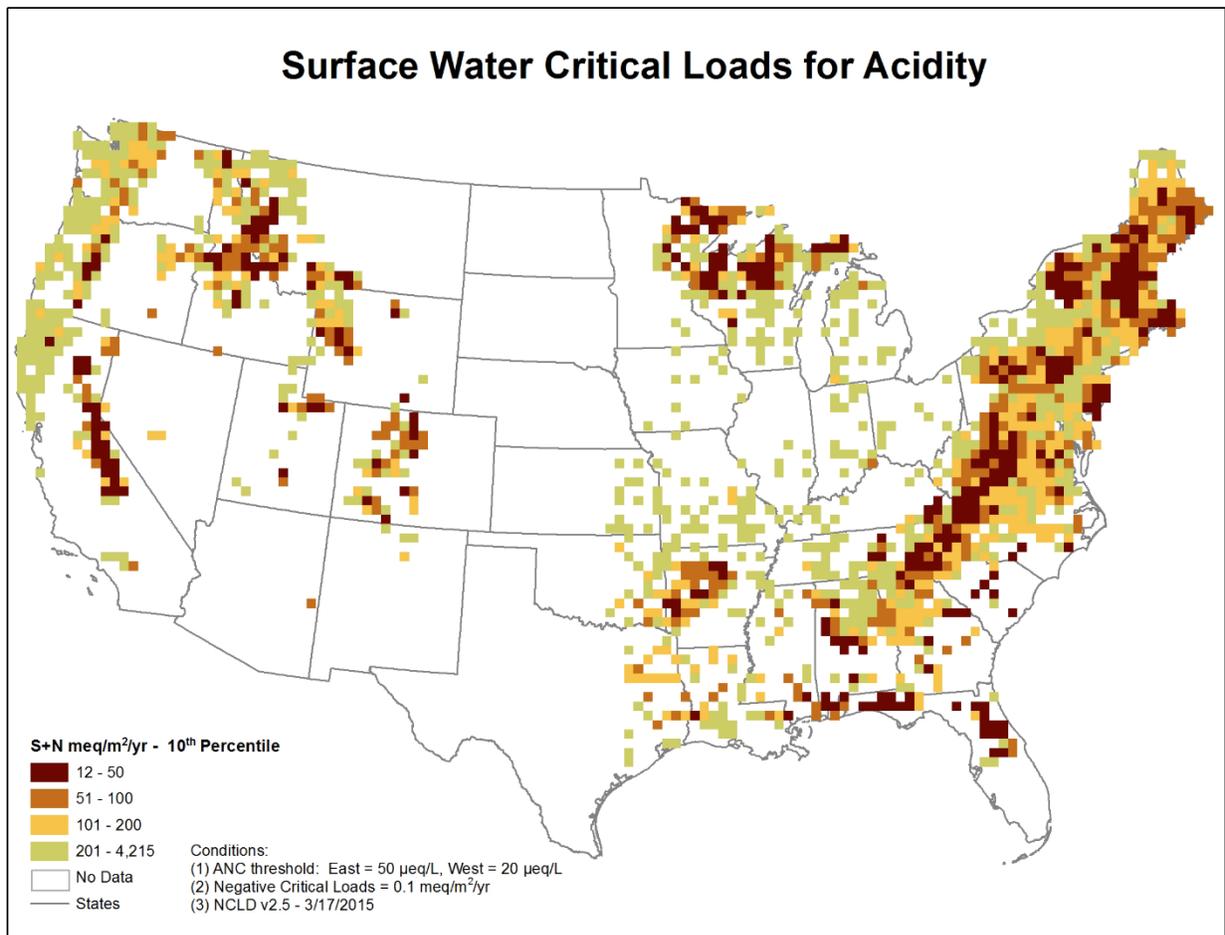
sensitivity among lifestages ([Appendix 8.3.6.1](#)). Since 2008, new studies include acidification effects on migratory activities and behavior. New studies on fish show behavioral effects at pH <6.6 ([Appendix 8.3.6.5](#)).

As summarized in [Baker et al. \(1990a\)](#) and the 2008 ISA, fish populations in acidified streams and lakes of Europe and North America have declined, and some have been eliminated as a result of atmospheric deposition of N and S and the resulting changes in pH, ANC, and inorganic Al concentrations in surface waters. There is often a positive relationship between pH and the number of fish species, particularly between pH 5.0 and 6.5. Additional pH thresholds published since the 2008 ISA ([Table 8-2](#)) support this range, and several new studies consider the role of DOC in controlling pH and subsequent effects on biota. In the 2008 ISA and in new research, few or no fish species are found in lakes and streams that have very low ANC (near zero; [Figure 8-4](#) and [Table 8-3](#)) and low pH (near 5.0). The number of fish species generally increases at higher ANC and pH values. Al is very toxic to fish, and thresholds to elevated concentrations of this metal in acidified waters are summarized in [Table 8-4](#).

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### **IS.6.3.2 National-Scale Sensitivity, Biological Recovery, and Critical Loads**

The extent and distribution of acid-sensitive freshwater ecosystems and sensitive regions in the U.S. were well known at the time of the 2008 ISA. Measured data on lake and stream ANC across the U.S. exhibit clear spatial patterns ([Figure 8-11](#)). Surface waters in the U.S. that are most sensitive to acidification are largely found in the Northeast, southern Appalachian Mountains, Florida, the upper Midwest, and the mountainous West ([Figure IS-12](#)). Levels of acidifying deposition in the West are low in most areas and rare in acidic surface waters, and the extent of chronic surface water acidification to date has been very limited. However, episodic acidification occurs in both the East and West at sensitive locations, and this is partly natural and partly caused by humans. Geographic patterns in acidification sensitivity vary in response to spatial differences in geology, hydrologic flow paths, presence and depth of glacial till, climate, and other factors ([Appendix 8.5.1](#)). In the eastern U.S., acid-sensitive ecosystems are generally located in upland, mountainous terrain underlain by weathering-resistant bedrock. Some of the most in-depth studies of the effects of acid stress on fish were conducted in streams in Shenandoah National Park in Virginia and in lakes in the Adirondack Mountains of New York. Effects on fish have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York, and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina.



ANC = acid-neutralizing capacity; meq = milliequivalent; yr = year.

Source: <http://nadp.slh.wisc.edu/committees/clad>.

**Figure IS-12** Surface water critical loads for acidity in the U.S. 10th percentile aggregation for 36-km<sup>2</sup> grids with sulfur (S) and nitrogen (N).

Biological recovery in acid-affected areas is discussed in [Section IS.11](#). Typically, biological recovery occurs only if chemical recovery ([Appendix 7.1.5.1](#)) is sufficient to allow growth, survival, and reproduction of acid-sensitive plants and animals. Surface water chemistry recovery varies by region, with the strongest evidence for improvement in the Northeast and little or no recovery in central Appalachian streams. Acidification and recovery of fresh waters will also be affected by the physical, chemical, and biological modifications to acid inputs projected to occur with changes in annual mean temperature and magnitude of precipitation ([Appendix 8.5.3](#)). As reported in the 2008 ISA and in new studies, biological recovery is slower than chemical recovery in many

systems (see [Appendix 8.4](#)). The time required for biological recovery is unknown and only partial biological recovery may be possible.

Since the 2008 ISA, considerable CL research has focused on aquatic acidification in the U.S. The CLs for deposition for aquatic acidification are expressed in eq/ha/yr of S, N, or S + N because one or both pollutants can contribute to the observed effects. New empirical CLs include 571 eq N/ha/yr in the Northeast and 286 eq N/ha/yr in the West to prevent episodic acidification in high-elevation lakes ([Table 8-7](#)). Steady-state CLs have been derived at many locations since the 2008 ISA ([Table 8-8](#)). Steady-state CLs of acidifying deposition for lakes in the Adirondack Mountains (1,620 eq/ha/yr) and for the central Appalachian streams (3,700 eq/ha/yr) were calculated to maintain a surface water ANC of 50  $\mu\text{eq/L}$  on an annual basis ([NAPAP, 2011](#)). CL values of less than 500 eq/ha/yr were calculated for one-third of streams in the Blue Ridge ecoregion, to maintain stream ANC at 50  $\mu\text{eq/L}$ . For lakes in Class I and II wilderness areas in the Sierra Nevada, CLs for acidifying deposition in 2008 were estimated at ANC values of 0, 5, 10, and 20  $\mu\text{eq/L}$ , which span the range of minimum ANC values observed in Sierra Nevada lakes. The median CL for granitic watersheds based on a critical ANC limit of 10  $\mu\text{eq/L}$  was 149 eq/ha/yr. Slightly more than one-third of these lakes had estimated rates of acidifying deposition higher than their CL.

In addition to the steady-state and empirical loads described above, CL estimates have been derived from dynamic modeling ([Appendix 8.5.4](#)). For example, there is new work on simulated past and future effects of N and S on stream chemistry in the Appalachians and Adirondack Mountain lakes. In 12 watersheds in the Great Smoky Mountain National Park, target levels of ANC to protect aquatic life were used and ranged from minimal (0  $\mu\text{eq/L}$ ) to considerable protection (50  $\mu\text{eq/L}$ ). For the 12 study streams, target levels of  $\text{NO}_3^- + \text{SO}_4^{2-}$  deposition ranged from 270 to 3,370 eq/ha/yr to reach an ANC of 0  $\mu\text{eq/L}$  by 2050 and 0 to 1,400 eq/ha/yr to reach an ANC of 50  $\mu\text{eq/L}$  by 2050. However, the majority of streams could not achieve the ANC target of 50  $\mu\text{eq/L}$ . Modeling also suggests that complete recovery from acidification may not be possible by the year 2100 at all sites in the southern Blue Ridge region ([Sullivan et al., 2011b](#)) even if S emissions cease entirely. In Shenandoah National Park, MAGIC modeling based on simulations of 14 streams identified a target load of about 188 eq S/ha/yr to achieve an ANC = 50  $\mu\text{eq/L}$  (preindustrial level based on hindcast simulations) in 2100 in sensitive streams. In a dynamic modeling simulation in the Adirondack Mountains, about 30% of the lakes in the region had a target load <500 eq/ha/yr to protect lake ANC to 50  $\mu\text{eq/L}$  ([Sullivan et al., 2012a](#)). Future decreases in  $\text{SO}_4^{2-}$  deposition are suggested to be more effective in that region in increasing Adirondack lake water ANC than equivalent decreases in  $\text{NO}_3^-$  deposition. In another modeling study of 20 Adirondack watersheds, estimates of

preindustrial ANC for the study lakes ranged from 18 to 190  $\mu\text{eq/L}$ , and simulations estimate that lake ANC has decreased by 26 to 100  $\mu\text{eq/L}$  as a legacy of acidification.

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## **IS.7 Estuarine and Near-Coastal Ecosystem Nitrogen Enrichment**

For estuaries (areas where fresh water from rivers meets the salt water of oceans) and near-coastal systems, causality determinations from the 2008 ISA are further supported and strengthened by additional studies ([Table IS-1](#)). Estuaries support a large biodiversity of flora and fauna and play a role in nutrient cycling. N from the atmosphere and other sources contributes to increased primary productivity, leading to eutrophication ([Table 10-1](#)), and N pollution is the major cause of harm to most estuaries in the U.S. ([Appendix 10](#)). Source apportionment data in the 2008 ISA and newer studies indicate that atmospheric contributions to estuarine N are heterogeneous across the U.S., ranging from <10% to approximately 70% of total estuary N inputs ([Table 7-9](#)). In estuaries, increasing nutrient over-enrichment leading to eutrophication is indicated by water quality deterioration, resulting in numerous harmful effects, including areas of low dissolved oxygen (DO) concentration (hypoxic zones), species mortality, and HABs. New studies support the 2008 ISA's causal findings that increased N loading to coastal areas can alter biogeochemical processes and lead to shifts in community composition, reduced biodiversity, and mortality of biota. The current causal statement of biological effects of N enrichment in estuarine ecosystems has been expanded to include total primary production, altered growth, and total algal community biomass ([Table IS-1](#)).

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### **IS.7.1 Estuary and Near-Coastal Biogeochemistry**

In the 2008 ISA, the evidence was sufficient to infer a causal relationship between reactive N deposition and biogeochemical cycling of N and C in estuarine and near-coastal marine systems. Evidence reviewed in the 2008 ISA, along with new studies, indicates elevated N inputs to coastal areas can alter key processes that influence N and C cycling in near-coastal environments. As external organic matter loading to coastal areas has increased in recent decades in many parts of the U.S., the varying rates of different N cycling processes within estuaries themselves can also affect the magnitude of eutrophication experienced as a result of external N enrichment. Nitrogen additions not only cause the total pool of N to be larger but may also perturb N cycling in such a way that the system may exacerbate eutrophication to a greater extent than expected based on N additions alone. Research conducted since the 2008 ISA has shown that many of these N cycling processes are more important in the estuarine environment than previously understood. The removal of N through denitrification is a valuable ecosystem service in

terms of constraining the extent and magnitude of eutrophication. Additional research has established dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  (DNRA) as a more important N reduction pathway in some estuaries. Ammonium produced via DNRA can lead to enhanced productivity and respiration, which may exacerbate hypoxia. Recent studies indicate that DNRA rates are higher in warmer months and can also take up a larger percentage of total N reduction activity when temperatures are higher. The roles of sedimentary microbial processes of denitrification and  $\text{N}_2$  production via anaerobic ammonium oxidation (anammox) have been further characterized. New research has shown that the community of N fixing microorganisms is more diverse in estuarine and coastal waters than previously thought, and that N fixation occurs more widely than previously assumed. Influence of benthic macrofauna on N cycling has received increased research attention in part due to the potential for these organisms to mitigate external N enrichment. Along with atmospheric anthropogenic  $\text{CO}_2$  inputs and other factors, eutrophication from N loading may affect carbonate chemistry in coastal areas, contributing to acidifying conditions in some circumstances such as where there is spatial or temporal decoupling of production and respiration processes. Monitoring of coastal areas shows that excess nutrient inputs continues to be a widespread problem in many parts of the U.S. New research further supports conclusions of the 2008 ISA, and **the body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemistry in estuarine and near-coastal marine systems.**

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### IS.7.1.1 Nitrogen Enrichment

Estuarine biogeochemistry is complicated because it directly controls more than just the N cycle; the response to N loading resulting in eutrophication affects the chemical cycling of metals and DO ([Appendix 7.2.3](#)), redox conditions, pH ([Appendix 7.2.4](#)), and ultimately energy transfer (e.g., food webs from microbes to humans). The response to N loading is also tightly controlled by the availability of organic matter (i.e., C) and its lability and reactivity. External organic matter loading to estuarine and coastal waters appears to be increasing and these excess nutrient inputs are occurring within the context of other stressors such as climate change ([Appendix 7.2.6.12](#)) and rising atmospheric  $\text{CO}_2$ , which further modify coastal biogeochemistry ([Doney, 2010](#)). As reported in the 2008 ISA, estuaries are generally N limited, and have received sufficiently high levels of N input from human activities (including deposition, agricultural runoff, and wastewater) to cause eutrophication. Highly variable environments within estuaries are characterized by a gradient of increasing salinity toward the ocean. As N moves downstream, some fraction is taken up by phytoplankton or removed by microbial denitrification. Key processes that influence N cycling include hypoxia, nitrification, denitrification, and

decomposition. Until recently, it was generally believed that  $\text{NH}_3$  oxidation was accomplished only by Proteobacteria in marine environments. New research has discovered that some archaea can also oxidize  $\text{NH}_3$ . These ammonia-oxidizing archaea are dominant in some estuaries, while ammonia-oxidizing bacteria are more important in others.

In the complex environment of the freshwater-to-ocean continuum, there are many chemical and biological indicators of eutrophic condition. One approach is to measure total nutrient loading and concentrations; however, these data need to be interpreted in the context of the physical and hydrological characteristics that determine ecosystem response. Water quality measures such as pH and DO, along with key biological indicators such as chlorophyll *a*, phytoplankton abundance, HABs, macroalgal abundance, and submerged aquatic vegetation (SAV; rooted vascular plants that do not emerge above the water), can all be used to assess responses to nutrient loading ([Table 10-1](#)). Nitrogen removal from the estuary is also influenced by faunal as well as microbial communities.

Organic particles in coastal regions sink to the sediment-water interface where they accumulate and decompose. Decomposition of these organic particles transforms nutrients and depletes  $\text{O}_2$  in the water. Decreasing DO can create hypoxic (<2 mg/L of dissolved  $\text{O}_2$ ) or anoxic zones inimical to fish and other aerobic life forms. Oxygen depletion largely occurs only in bottom waters under stratified conditions, not throughout the entire water column. This can result in seasonal hypoxia in shallow coastal regions, particularly those that are receiving high inputs of nutrients from coastal rivers. Development of hypoxia is increasingly a concern in estuaries across the U.S. ([Appendix 10.2.4](#)).

Since the 2008 ISA, a number of papers have identified links between nutrient enrichment and effects on estuarine carbonate chemistry, resulting in coastal acidification or basification ([Appendix 7.2.4](#)). Eutrophication and acidification/basification are complex biogeochemical processes that are driven by the same hydrological (stratification) and biological (production/respiration) processes that can result in hypoxia and enhanced organic matter loading. Acidification can occur by direct atmospheric anthropogenic  $\text{CO}_2$  dissolution into the ocean. But under certain conditions N enrichment can contribute to acidifying/basifying conditions, such as in systems with strong thermal stratification or with spatial or temporal decoupling of production and respiration processes. With increasing N inputs to coastal waters,  $\text{CO}_2$  in the water column is produced from degradation of excess organic matter from changing land use, as well as respiration of living algae and seagrasses, which in turn can make the water more acidic.

Estuarine carbonate chemistry is complex, responding to a wide variety of natural, anthropogenic, physical (mixing), chemical and biological drivers.

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### IS.7.1.2 Models

Since the 2008 ISA, several new applications of existing models have quantified eutrophication processes in estuaries and near-coastal marine ecosystems. These have included studies that focused primarily on N cycling or hypoxia. Other models of estuarine eutrophication focus on N load apportionment, or on relationships between N loads and ecological endpoints. Since the 2008 ISA, SPARROW has been used to estimate total N loads within watersheds to determine sources of N to streams and rivers; it has also been applied at regional and national scales. Additional models and tools that include the contribution of N directly from the atmosphere have been applied to U.S. estuaries, including the Watershed N Loading Model (NLM) and the Watershed Deposition Tool (WDT). The latter was developed by the U.S. EPA to map atmospheric deposition estimates to watersheds using wet and dry deposition data from CMAQ ([Schwede et al., 2009](#)). This tool links air and water quality modeling data for use in total maximum daily load (TMDL) determinations and analysis of nonpoint-source impacts. New model applications include studies that focused primarily on endpoints of N cycling, hypoxia, and HABs. Models of coastal eutrophication are described in greater detail in [Appendix 7.2.8](#).

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### IS.7.1.3 National-Scale Sensitivity

Sensitivity of estuaries to biogeochemical changes associated with N enrichment varies across the U.S. The biogeochemical sensitivity of estuaries and near coastal areas will be discussed together with national-scale biological sensitivity to N enrichment in [Section IS.7.3](#).

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## IS.7.2 Biological Effects of Nitrogen Enrichment

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in estuarine ecosystems. The strongest evidence for a causal relationship was from changes in biological indicators of nutrient enrichment (chlorophyll *a*, macroalgal [seaweed] abundance, HABs, DO, and changes in SAV; [Table 10-1](#)). Some indicators, such as chlorophyll *a*, are directly linked to nutrient enrichment and provide evidence of

early ecosystem response; other indicators, such as low DO and decreases in SAV, indicate more advanced eutrophication. Phytoplankton are the base of the coastal food web and increases in primary producer biomass and altered community composition associated with increased N can lead to a cascade of direct and indirect effects at higher trophic levels. At the time of the 2008 ISA, N was recognized as the major cause of harm to the most estuaries in the U.S. Since 2008, new paleontological studies, observational studies, and experiments have further characterized the effects of N on phytoplankton growth and community dynamics, macroinvertebrate response, and other indices of biodiversity. For this ISA, new information is consistent with the 2008 ISA and the causal determination has been updated to reflect more specific categories of effects to include total primary production, altered growth, and total algal community biomass. This new research strengthens the evidence base and is consistent with the 2008 ISA ([Table IS-1](#)) that **the body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota including total primary production, altered growth, total algal community biomass, species richness, community composition, and biodiversity due to N enrichment in estuarine environments.**

Since the 2008 ISA, additional evidence has shown that reduced forms of atmospheric N play an increasingly important role in estuarine and coastal eutrophication and HAB dynamics. New studies emphasize that N inputs interact with physical and hydrologic factors to increase primary productivity and eutrophication in coastal areas. Climate-related changes in temperature, precipitation, and wind patterns, as well as extreme weather events, stronger estuary stratification, increased metabolism and organic production, and rising sea-levels are all expected to modify coastal habitats ([Appendix 10.1.4.1](#)).

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### IS.7.2.1 Primary Producers

Algae are the base of the coastal food web, and the 2008 ISA showed that changes in chemical composition of N inputs can shift the algal community and cascade up the food web. Chlorophyll *a* is a broadly recognized indicator of phytoplankton biomass and is used as a proxy for assessing effects of estuarine nutrient enrichment. It can signal an early stage of water quality degradation related to nutrient loading and is incorporated into water quality monitoring programs and national-scale assessments including U.S. EPA's National Coastal Condition Assessment ([Appendix 7.2.7](#)). Phytoplankton sampling, microcosms studies, and sediment core analysis have shown changes in phytoplankton community structure in estuaries with elevated N inputs ([Appendix 10.3](#)). These shifts at the base of the food web to species that are not as readily grazed (e.g., cyanobacteria, dinoflagellates) have a cascade of effects including poor trophic

transfer and an increase in unconsumed algal biomass, which could stimulate decomposition and O<sub>2</sub> consumption, and thus increase the potential for hypoxia.

There is consistent and coherent evidence that the incidence of HAB outbreaks is increasing in both freshwater and coastal areas, a problem that has been recognized for several decades ([Appendix 10.2.2](#)). Of the 81 estuary systems for which data were available for the National Estuarine Eutrophication Assessment (NEEA), 26 exhibited a moderate or high symptom expression for nuisance or toxic algae ([Bricker et al., 2007](#)). Since the 2008 ISA, HAB conditions and effects of HAB toxins on wildlife have been further characterized ([Appendix 10.2.2](#)). Toxins released during HABs can be harmful to fish and shellfish and may be transferred to higher trophic levels. The form of N affects phytoplankton growth and toxin production of some HAB species. Increasing loads of NH<sub>3</sub><sup>+</sup>/NH<sub>4</sub><sup>+</sup> have been linked to the expansion of HABs and altered phytoplankton community dynamics ([Appendix 10.3.3](#)). Cyanobacteria, and many chlorophytes and dinoflagellates, may be better adapted to NH<sub>4</sub><sup>+</sup>, while diatoms generally thrive in the presence of oxidized forms of N such as NO<sub>3</sub><sup>-</sup> ([Figure 10-7](#)).

Macroalgal (seaweed) growth is also stimulated by increased N inputs, which increase the dominance of faster growing benthic or pelagic macroalgae to the exclusion of other species ([Appendix 10.2.3](#)). Studies published since the 2008 ISA provide further evidence that macroalgae respond to the form of N, with some species showing greater assimilation and growth rates with NH<sub>4</sub><sup>+</sup> than with NO<sub>3</sub><sup>-</sup>. Increased abundance of macroalgae, which block light, and increased epiphyte loads on the surface of SAV may reduce the growth and biomass of SAV. SAV, including the eelgrass *Zostera marina*, are important ecological communities found within some coastal bays and estuaries that are sensitive to elevated nutrient loading, and the loss of this habitat can lead to a cascade of ecological effects because many organisms are dependent upon seagrasses for cover, breeding, and as nursery grounds. Recently, the presence of seagrass beds was linked to decreased bacterial pathogens of humans, fishes, and invertebrates in the water column and lower incidence of disease in adjacent coral reefs ([Appendix 10.2.5](#)). The 2008 ISA reported correlations between increased N loading and declines in SAV abundance, and newer studies have further characterized this relationship. In a survey of southern New England estuaries, reduced eelgrass extent was observed at increased watershed N loading. New studies have characterized the role of invertebrate mesograzers, such as small crustaceans and gastropods, in controlling algal growth, potentially buffering eutrophication effects on seagrass communities ([Appendix 10.3.7](#)). Macroalgae may not be a good indicator of eutrophication in some upwelling-influenced estuaries in the Pacific Northwest because an increase in macroalgal biomass in these systems does not appear to be associated with temporal declines in eelgrass ([Appendix 10.2.3](#)).

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### IS.7.2.2 Bacteria and Archaea

Ammonia-oxidizing prokaryotes carry out nitrification in estuarine waters.

Ammonia-oxidizing archaea have been described relatively recently, and several studies since the 2008 ISA have considered community responses of ammonia-oxidizing bacteria and archaea. Community structure of ammonia-oxidizers is related to nutrient inputs and affected by the form of available N ([Appendix 10.3.4](#)).

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### IS.7.2.3 Invertebrates

In coastal areas with severe seasonal hypoxia, the community of benthic organisms shifts toward shorter life spans and smaller body size ([Appendix 10.2.4](#)). Reduced species density and diversity in the northern Gulf of Mexico are linked to persistent hypoxic events. The form of N present has been shown to affect molluscan taxonomic assemblages ([Appendix 10.3.5](#)). Shifts in algal composition and productivity can affect growth of shellfish that feed on phytoplankton. Shellfish contribute to N and C cycling and can improve water quality, and recent research has explored the use of these organisms for coastal N remediation ([Appendix 7.2.6.11](#)). Harvest of shellfish for human consumption removes nutrients from estuaries.

N enrichment is one of several factors linked to increased disease susceptibility, bleaching, and reduced calcification rate in corals ([Appendix 10.4.2](#)). Several studies have isolated effects of N, which affects corals via pathways that are distinct from P. The threatened status of staghorn coral (*Acropora cervicornis*) and elkhorn coral (*Acropora palmata*) under the U.S. Endangered Species Act has been linked to indirect N pollution effects, specifically low DO, algal blooms that alter habitat, and other non-nutrient stressors ([Hernández et al., 2016](#)). Increasing acidification of coastal waters, which may be exacerbated by elevated N inputs under certain circumstances ([Appendix 7.2.4](#)), is projected to alter marine habitat, have a wide range of effects at the population and community level and affect food web processes. Although the interactions between elevated CO<sub>2</sub>, decreasing pH, and nutrient inputs are complex, calcareous plankton, oysters, clams, sea urchins, and coral that produce calcium carbonate shells may be affected by long-term decreases in pH ([Appendix 10.5](#)).

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### IS.7.2.4 Fish

Fish biodiversity is altered by increased N inputs and resulting changes in biological and chemical indicators ([Appendix 10.3.6](#)). Many fish are unable to persist at DO levels

below 2 mg/L ([Figure 10-4](#)). Recent studies in the southern Gulf of Saint Lawrence have linked SAV loss to declines in fish biodiversity, although organisms did not change positions within food webs. In laboratory conditions, turbidity associated with eutrophication alters fish reproductive behaviors. Hypoxia has also recently been shown to affect reproduction in fish. For example, hypoxia acts as an endocrine disruptor in Atlantic croaker (*Micropogonias undulatus*; [Appendix 10.2.4](#)).

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### IS.7.3 National-Scale Sensitivity and Critical Loads

The NEEA, the most recent comprehensive survey of eutrophic conditions in U.S. estuaries conducted by the National Oceanic and Atmospheric Administration, defined eutrophication susceptibility as the natural tendency of an estuary to retain or flush nutrients ([Bricker et al., 2007](#)). In estuaries that have longer water residence times, nutrients are more likely to lead to eutrophic conditions ([Appendix 10.1.4](#)). As reported in the 2008 ISA and newer studies, nutrient loading accelerates hypoxia, which is more likely in marine waters with limited water exchange, water column stratification, and high production and settling of C to bottom waters. Other factors identified in the 2008 ISA that increase estuary sensitivity to eutrophication include human population, agricultural production, and the size of the estuary relative to its drainage basin. The NEEA reported that the most eutrophic estuaries in the U.S. occur in the mid-Atlantic region, and the estuaries with the lowest degree of eutrophication are in the North Atlantic ([Figure 10-2](#)). Estuaries identified in the 2008 ISA as susceptible to eutrophication include the Chesapeake Bay, Pamlico Estuary in North Carolina, Long Island Sound, as well as along the continental shelf adjacent to the Mississippi and the Atchafalaya River discharges to the Gulf of Mexico. New research at the regional scale includes long-term studies of several coastal systems that are looking at trends in coastal water quality and chemistry. A 23-year study of the Chesapeake Bay concluded that water quality has decreased and chlorophyll *a* levels have increased since 1986, in part due to long-term climate trends (see [Appendix 10.2.5](#)).

Since the 2008 ISA, there is additional information on the extent and severity of eutrophication and hypoxia in sensitive regions. Areas of eutrophication-related hypoxia are found on the U.S. eastern and western coasts and the Gulf of Mexico ([Figure 10-5](#)). The 2008 ISA reported that the largest zone of hypoxic coastal water in the U.S. was the northern Gulf of Mexico on the Louisiana-Texas continental shelf. In the summer of 2017, the hypoxic zone in the Gulf was the largest ever measured at 14,123 km<sup>2</sup> [8,776 mi<sup>2</sup>; [U.S. EPA \(2017f\)](#)]. Atmospheric deposition to watersheds in the Mississippi/Atchafalaya River Basin contributes approximately 16 to 26% of the total N load to the Gulf of Mexico ([Appendix 10.2.4](#)). Long Island Sound also experiences

periods of anoxia. In other U.S. coastal systems, hypoxia incidence is increasing, but DO impacts are relatively limited temporally and spatially. In the Pacific Northwest, coastal upwelling not related to anthropogenic sources can be a large source of nutrient loads, and the advection of this upwelled water can introduce hypoxic water into estuaries.

The NEEA suggested that only a small fraction of the estuary systems evaluated showed moderate to high SAV loss ([Bricker et al., 2007](#)), mostly in the mid-Atlantic region.

While seagrass coverage is improving in some estuaries, such as Tampa Bay (Tampa Bay Case Study, [Appendix 16](#)), many estuaries continue to see declines in seagrass extent. SAV is often at a competitive disadvantage under N enriched conditions because of the fast growth of opportunistic macroalgae that preferentially take up  $\text{NH}_4^+$  and can block light from seagrass beds.

There are thresholds of response identified for some biological and chemical indicators of N enrichment in estuaries ([Appendix 10](#)). The amount of chlorophyll *a* is an indicator of phytoplankton biomass, and thus, a proxy for assessing estuarine nutrient enrichment. In general, 0–5  $\mu\text{g/L}$  chlorophyll *a* is considered a good condition, concentrations between 5 and 20  $\mu\text{g/L}$  are classified as fair condition, and concentrations of >20  $\mu\text{g/L}$  indicate poor conditions ([Table 10-2](#)). A new response threshold of tidal-averaged total N concentration of <0.34 mg/L has been identified for healthy eelgrass in Massachusetts waters. Markedly decreased eelgrass coverage is observed at N loading rates  $\geq 100$  kg N/ha/yr, and levels above 50 kg N/ha/yr are likely to impact SAV habitat extent in shallow New England estuaries ([Table 10-4](#)). [Greaver et al. \(2011\)](#) identified the range of 50–100 kg N/ha/yr total N loading as the empirical CL for loss of eelgrass based on [Latimer and Rego \(2010\)](#). In terms of DO, concentrations of 0 mg/L are anoxic, 0–2 are indicative of hypoxic conditions, and 2–5 mg/L are biologically stressful conditions ([Figure 10-4](#)). Oxygen depletion largely occurs only in bottom waters under stratified conditions, not throughout the entire water column.

The indicators of nutrient enrichment in coastal areas (chlorophyll *a*, HABs, macroalgal abundance, DO, SAV, and benthic diversity) have been incorporated into indices of coastal eutrophication. In the 2008 ISA, the Assessment of Estuarine Tropic Status (ASSETS) categorical Eutrophication Condition index (ECI) developed for the NEEA was used as an assessment framework for coastal U.S. estuaries ([Bricker et al., 2007](#)). Additional indices of estuarine functioning that incorporate biological indicators have since been developed both in the U.S. and internationally ([Appendix 10.2.6](#)).

Comparisons of these frameworks have identified robust methods to measure estuarine response, such as incorporation of annual data, frequency of occurrence, spatial coverage, secondary biological indicators, and a multicategory rating scale.

Since the 2008 ISA, N enrichment has been linked to coral bleaching and reduced calcification rates ([Appendix 10.4.2](#)). Near-coastal coral reefs in the U.S. occur off south Florida, Texas, Hawaii, and U.S. territories in the Caribbean and Pacific.

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## IS.8 Wetland Ecosystem Nitrogen Enrichment and Acidification

New evidence, including new CLs, supports and strengthens the causal findings from the 2008 ISA regarding N enrichment effects in wetlands ([Table IS-1](#)). In freshwater wetlands and coastal wetland ecosystems, deposition of N and S does not tend to cause acidification-related effects at levels currently common in the U.S. However, the 2008 ISA documented that wetlands can be sensitive to N enrichment and eutrophication effects. Newer studies have characterized N effects on biogeochemistry, physiology, biodiversity, national sensitivity, and CLs for freshwater and coastal wetlands; coastal wetlands are typically tolerant of higher N loading than freshwater wetlands.

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### IS.8.1 Wetland Biogeochemistry

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of wetland biogeochemical cycling. Although sources and rates of N inputs vary widely among wetlands, N deposition contributes substantially to total loading in many wetlands. This additional N alters C cycling, N cycling, and the release of nutrients to hydrologically connected surface waters. New research together with the information included in the 2008 ISA shows that **the body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling in wetlands.**

The 2008 ISA reported that N enrichment altered N cycling in wetland ecosystems. Chemical indicators of N deposition in wetlands include  $\text{NO}_3^-$  and  $\text{NH}_4^+$  leaching, DON leaching, N mineralization, denitrification rates, and  $\text{N}_2\text{O}$  emissions. A wetland can act as a source, sink, or transformer of atmospherically deposited N, and these functions vary with season and hydrological conditions. Vegetation type, physiography, local hydrology, and climate all influence source/sink N dynamics in wetlands. A new synthesis of global wetland data showed that a wetland's reactive N removal and water quality improvement is proportional to its reactive N load, and removal efficiency is 26% higher in nontidal than tidal wetlands. Further, a new meta-analysis showed that N enrichment increases wetland  $\text{N}_2\text{O}$  emissions by 207%. New studies have also evaluated the effects of N loading/N addition on other endpoints related to N cycling in peat bog, riparian, mangrove, and salt marsh wetlands (see [Appendix 11.3.1](#)). The endpoints evaluated

include ecosystem N retention, wetland export of N to surface waters, N fixation, N mineralization, denitrification, emission of N<sub>2</sub>O, and bacterial abundance, activity, and composition in wetland soils. The results of North American studies are summarized in [Figure 11-2](#). Across studies, N enrichment decreases the ability of wetlands to retain and store N, which may diminish the wetland ecosystem service of improving water quality.

In the 2008 ISA, evidence from Canadian and European peatlands showed that N deposition had negative effects on *Sphagnum* (moss) bulk density and mixed effects on *Sphagnum* productivity depending on the history of deposition. There is new information on how N deposition alters biogeochemical cycling of C in wetlands. Chemical indicators of N deposition in wetlands include soil organic matter, total soil C or peat C, CO<sub>2</sub> emissions, and CH<sub>4</sub> emissions. Long-term C storage is an important ecosystem service of wetlands for which measures of physical marsh stability can serve as a proxy, and physical indicators of N deposition can include temperature, bulk density, physical resistance, and soil water content. In addition, changes to plant growth rates and productivity indicate altered C cycling in wetlands, and are summarized in [Section IS.8.2](#).

The literature evaluates the effects of N deposition, N loading, or experimental N addition on C cycling in bogs, fens, riparian or intermittent marshes, freshwater tidal marshes, mangroves, and salt marshes (see [Appendix 11.3.2](#)). Significant effects of N loading upon biogeochemical cycling of C in North American wetlands (in which the N addition was 500 kg N/ha/yr or lower) are summarized in [Figure 11-3](#). N enrichment decreases wetland retention of C, as indicated by new studies and a new meta-analysis that show that N enrichment increases methane production in salt marshes. New studies of marshes along the Gulf Coast and East Coast find that N enrichment also decreases the bulk density of salt marshes, making marshes less resilient to physical stresses from tidal or storm flooding, and may accelerate coastal marsh loss.

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## IS.8.2 Biological Effects of Wetland Nitrogen Enrichment/Eutrophication

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in wetlands. New evidence is presented in the following sections regarding the effects of N upon wetland plant physiology, architecture, demography, and biodiversity. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands.**

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### IS.8.2.1 Growth, Productivity, and Physiology

In the 2008 ISA, evidence from Canadian and European bogs and fens showed that N deposition had negative or mixed effects on *Sphagnum* (moss) productivity, depending on history of deposition. In Canadian ombrotrophic peatlands experiencing deposition of 2.7–8.1 kg N/ha/yr, peat accumulation increased with N deposition, but accumulation rates had slowed by 2004, indicating a degree of N saturation. Coastal wetlands responded to N enrichment with increased primary production, which shifted microbial and plant communities and altered pore water chemistry, although many of the studies in coastal wetlands used N enrichment levels more like those of wastewater than atmospheric deposition. New research on N enrichment effects on growth and productivity was conducted in ombrotrophic bogs, intermittent wetlands, freshwater tidal marsh, mangroves, and coastal salt marshes (see [Appendix 11.4](#)). Ecological endpoints evaluated to assess N loading effects on growth and productivity include plant aboveground biomass and productivity, plant belowground biomass of roots and rhizomes, and growth rates, and are summarized along with N effects on C cycling in [Figure 11-3](#). The effects of N additions on plant physiology were not addressed in the 2008 ISA, but information regarding these effects is available for bogs and fens, riparian wetlands, freshwater tidal marshes, mangroves, and salt marshes (see [Appendix 11.5](#)). Ecological endpoints evaluated to assess N loading effects on plant physiology include stoichiometry (i.e., nutrient concentrations and ratios of multiple nutrients in plant tissue), nutrient acquisition efficiency (including insectivory rates in carnivorous plants), nutrient use efficiency, and nutrient reabsorption efficiency. These endpoints are summarized in [Figure 11-4](#).

In general, across types of wetlands, nitrogen loading increases aboveground growth and productivity while decreasing or not affecting belowground growth and productivity. In bogs and fens, N deposition decreases growth of state-listed *Sarracenia purpurea* (purple pitcher plant), and N enrichment increases aboveground productivity of emergent sedges more than of peat-building moss species. These changes cascade up to affect biodiversity in bogs and fens (see below, [Section IS.8.2.2](#)). In freshwater and tidal marshes, N enrichment increases aboveground productivity while decreasing belowground productivity, and this shift from belowground to aboveground plant productivity may account for changes in wetland C storage (see [Section IS.8.1](#)).

Changes to plant physiology and stoichiometry vary by species tolerance to N and N acquisition strategies. In bogs, N enrichment typically causes increased plant tissue N concentrations, decreased N use efficiency, and decreased N resorption efficiency during senescence. After several years of exposure to high rates of N loading, bog plants may experience leaf N saturation and limitation by other nutrients (e.g., P, K, and Ca,

indicated by increasing reabsorption efficiencies), resulting in leaf damage in sensitive species. *S. purpurea* (purple pitcher plant) decreases its dependence upon insectivory for nutrition at N deposition rates of 4.4 kg N/ha/yr. In freshwater marshes, N enrichment also increases plant tissue N concentrations while increasing P limitation and altering resorption efficiencies.

Plant architecture was not addressed in the 2008 ISA, and demography was addressed only for bogs and fens. Aboveground, plant architecture includes branching patterns, as well as the size, shape, and position of leaves and flower organs. New studies find N enrichment affects plant architecture in a salt marsh, in mangroves, in freshwater tidal marshes, and in a riparian wetland ([Appendix 11.6](#)). In terms of plant demography, the 2008 ISA found positive population growth rates for *S. purpurea* at 0 or 1.4 kg N/ha/yr, but population losses at 14 kg N/ha/yr. N deposition above 6.8 kg N/ha/yr increases population extinction risk of *S. purpurea*. New studies show that N addition has species-specific effects on reproduction of West Coast salt marsh plant species and that it increases mortality across the global distribution of mangrove species ([Appendix 11.7](#)).

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### IS.8.2.2 Biodiversity

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in wetlands. Notably, the 2008 ISA cited 4,200 native plant species in U.S. wetlands, 121 of which are federally endangered. Given their relative area, wetlands provide habitat to a disproportionately high number of rare plants. Many wetland species have adapted to N limited conditions, including endangered species in the genera *Isoetes* (3 endangered species) and *Sphagnum* (15 endangered species), as well as insectivorous plants such as pitcher plants (*Sarracenia* spp.) and sundews (*Drosera rotundifolia*).

Coastal wetlands responded to N enrichment with increased primary production, changing microbial and plant communities, and altered pore water chemistry, although many of the studies available in 2008 used high N enrichment levels more similar to N loading from wastewater than from atmospheric deposition. New research since 2008 across environmentally relevant N levels including N deposition gradient studies, experimental N addition studies, and observational studies show that N enrichment altered biodiversity in bogs and fens, intermittent wetlands, freshwater wetlands, freshwater tidal wetlands, and coastal salt marshes (see [Appendix 11.8](#)).

New research from wetland ecosystems strengthens the 2008 causal statement. New research confirms that, as in terrestrial systems, N addition can decrease the abundance and richness of sensitive species while increasing the abundance and richness of tolerant

species. In bogs and fens, N enrichment decreases the survival of insectivorous plants and the cover of mosses, while increasing the cover of shrub species. In freshwater marshes, N enrichment changes plant community composition, increases the abundance of and stresses caused by invasive plant species, promotes the harmful algal species that produce the toxin microcystin, and increases mosquito larvae that are vectors for zoonotic diseases (see [Figure 11-1](#)). In freshwater tidal and coastal marshes, N enrichment changes plant community composition, increases cover of invasive plant species, increases herbivory by invertebrates, and increases herbivory by the invasive mammal *Myocastor coypus* (nutria).

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### IS.8.2.3 National Sensitivity and Critical Loads for Wetlands.

Freshwater and coastal wetlands tend to have different sensitivity to added N. Broadly, wetlands that receive a larger fraction of their total water budget in the form of precipitation are more sensitive to the effects of N deposition. For example, bogs (70–100% of hydrological input from rainfall) are more sensitive to N deposition than fens (55–83% as rainfall), which are more sensitive than coastal wetlands (10–20% as rainfall).

Since the 2008 ISA, an N CL for U.S. coastal wetlands has been established. The CL is based on several different ecological endpoints, including plant community composition, microbial activity, and biogeochemistry (63–400 kg N/ha/yr) and that this CL includes total N loading values not just N deposition. [Figure 11-6](#) shows a comparison of the N CL for coastal wetlands with recent studies of ecological impacts of N (at N levels of 100–250 kg N/ha/yr).

Since the 2008 ISA, two N CLs for U.S. freshwater wetlands have been established. The CL for wetland C cycling, quantified as altered peat accumulation and NPP, is between 2.7 and 13 kg N/ha/yr. The upper end of this CL range is based on measurements of wet deposition only (10 to 13 kg N/ha/yr), and therefore, does not reflect total N loading. There is also a CL to protect biodiversity based on morphology and population dynamics of the purple pitcher plant (*Sarracenia purpurea*) between 6.8–14 kg N/ha/yr. A more recent study across an N deposition gradient suggests that purple pitcher plant populations experience negative effects of N deposition at rates lower than this CL, but the more recent research has not yet been incorporated into the CL framework. A comparison of freshwater wetland CLs to observed ecological impacts of N from recent studies (4.4–500 kg N/ha/yr) is given in [Figure 11-7](#).

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## IS.9 Freshwater and Wetland Ecosystem Sulfur Enrichment

New evidence from wetland and freshwater aquatic ecosystems strengthens and extends the causal findings of the 2008 ISA regarding nonacidifying sulfur effects and provides the basis for a new causal determination ([Table IS-1](#)). New research together with the information included in the 2008 ISA shows that the evidence is sufficient to infer a causal relationship between S deposition and the alteration of Hg methylation in surface water, sediment, and soils in wetland and freshwater ecosystems. **New evidence is sufficient to infer a new causal relationship between S deposition and changes in biota due to sulfide phytotoxicity, including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems.**

SO<sub>x</sub> deposition can have chemical and biological effects other than acidification, particularly in flooded wetland soils and aquatic ecosystems. The 2008 ISA described qualitative relationships between SO<sub>4</sub><sup>2-</sup> deposition and a number of ecological endpoints, including altered S cycling, sulfide phytotoxicity, internal eutrophication of aquatic systems, altered methane emissions, increased mercury (Hg) methylation, and increased Hg loading in animals, particularly fish. [Table 12-11](#) summarizes the chemical concentrations that alter ecological endpoints and the quantitative relationships describing the effects of SO<sub>4</sub><sup>2-</sup> deposition. Recent research supports these relationships between S deposition and ecological endpoints and provides the basis for SO<sub>x</sub> deposition levels, water column SO<sub>4</sub><sup>2-</sup> concentrations, and water column sulfide concentrations protective of plants and animals.

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### IS.9.1 Biogeochemistry

SO<sub>x</sub> deposition alters biogeochemical processes via S enrichment. The processes include S cycling (see [Appendix 12.2.1](#)), P cycling (see [Appendix 12.2.4](#)), C cycling (see [Appendix 12.2.5](#)), and Hg cycling (see [Appendix 12.3](#)). The primary chemical indicator for nonacidifying or enrichment effects of S in wetland and aquatic ecosystems is surface water SO<sub>4</sub><sup>2-</sup> concentration, as it is for acidifying effects. The 2008 ISA reported that chemical reduction of SO<sub>4</sub><sup>2-</sup> was an important indicator of SO<sub>x</sub> effects on water chemistry because the process generates ANC. There are no new studies on ANC generation through SO<sub>4</sub><sup>2-</sup> reduction, although microbial SO<sub>4</sub><sup>2-</sup> reduction remains an active area of research. In aquatic ecosystems for which atmospheric and terrestrial S inputs are similar in magnitude to rates of microbial SO<sub>4</sub><sup>2-</sup> reduction, the products of microbial SO<sub>4</sub><sup>2-</sup> transformation may be more reliable indicators of S enrichment effects

than surface water  $\text{SO}_4^{2-}$  concentrations. These chemical indicators include methylmercury (MeHg), sulfide, and phosphate.

MeHg is the most persistent and toxic form of Hg in the natural environment. It is measured in surface water or aquatic sediments (MeHg concentration or the percentage of MeHg in total Hg) to predict its effects on biota. Several new studies demonstrate significant positive relationships between surface water  $\text{SO}_4^{2-}$  concentrations and water or sediment MeHg concentrations (see [Appendix 12.3.5](#)). Another product of  $\text{SO}_4^{2-}$  reduction, sulfide (measured as surface water or sediment pore water  $\text{S}^{2-}$  concentrations), is also a water quality indicator of deposition effects on biota. In freshwater ecosystems with iron-rich sediments, sulfide may react with iron bound to phosphates in the sediment to release phosphate into the water column, increasing primary productivity recent literature refers to this process as internal eutrophication ([Appendix 12.2.4](#)).

In terms of S enrichment effects on carbon cycling, the 2008 ISA documented the suppression of methane emissions in wetland soils by  $\text{SO}_4^{2-}$  addition in several studies and noted that 15 kg S/ha/yr suppressed methane emissions. Recent research has confirmed that S enrichment increases the abundance or metabolic activity of  $\text{SO}_4^{2-}$ -reducing prokaryotes (SRPs), which under some conditions compete with methanogens by suppressing their activity, and in turn, suppressing methane emissions ([Appendix 12.2.4](#)). However, there are no new studies documenting S deposition effects on methane emissions in U.S. ecosystems.

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## IS.9.2 Biological Effects of Sulfur Enrichment

Nonacidifying S effects upon biota include plant toxicity, changes in plant growth and biodiversity, and increased Hg concentrations in biota. The toxicological effects of Hg accumulation in animals were documented in the 2008 ISA and newer studies.

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### IS.9.2.1 Sulfur Nutrient and Toxicity to Plants

Plants and other organisms require S as an essential nutrient. The deposition of S can affect plant protein synthesis by affecting S availability for S containing amino acids, which in turn will affect N uptake. The 2008 ISA documented the effects of  $\text{SO}_4^{2-}$  toxicity on plant development and reproduction at very high S loads. There is no new evidence of S deposition effects upon plant S nutrition or  $\text{SO}_4^{2-}$  toxicity. The product of microbial  $\text{SO}_4^{2-}$  reduction, sulfide, is an important plant toxin, and the 2008 ISA documented sulfide phytotoxicity in European systems. Together with new research showing sulfide phytotoxicity in North American wetlands, **the body of evidence is**

**sufficient to infer a causal relationship between S deposition and changes in biota due to sulfide phytotoxicity including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems.**

The 2008 ISA showed that sulfide toxicity decreased the biomass of wetland plants and aquatic macrophytes in mesocosms under aquatic S concentrations higher than current U.S. concentrations. In Europe, research showed that a threshold value of  $<48 \text{ mg SO}_4^{2-}/\text{L}$  in surface water would protect the sensitive aquatic species *Stratiotes aloides* and *Potamogeton acutifolius* (not native to contiguous US), as well as to protect *P. zosteriformis* and *Utricularia vulgaris*, which are both native and widely distributed in contiguous US. New research has demonstrated sulfide phytotoxicity effects at current ambient sulfide concentrations in multiple ecosystems within the U.S. ([Appendix 12.2.3](#)). Sulfide decreased total plant cover and cover of dominant species in a New York fen and decreased the growth rate of *Cladium jamaicense* (sawgrass), a keystone species in the Florida Everglades. *Zizania palustris* (wild rice) is an economically and culturally important species sensitive to sulfide, and the Minnesota Pollution Control Agency has developed a model for this species that calculates protective levels of water  $\text{SO}_4^{2-}$  concentrations, given (specific) iron and DOC concentrations in water bodies. A recent review identifies sulfide thresholds between  $0.3\text{--}29.5 \text{ mg S}^{2-}/\text{L}$  for altered growth, productivity, physiology, or increased mortality of 16 freshwater wetland emergent plant and aquatic submerged macrophyte species native to North America (see [Table 12-2](#)).

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### IS.9.2.2 Sulfur Effects on Mercury Methylation

In the 2008 ISA, evidence was sufficient to infer a causal relationship between S deposition and increased methylation of Hg in aquatic environments where the value of other factors is within an adequate range for methylation. In the 2008 ISA, sulfur-reducing bacteria (SRB) were identified as the organisms responsible for Hg methylation. New evidence shows the ability to methylate Hg is more broadly distributed phylogenetically, including both bacteria and archaea, which is why this document refers to  $\text{SO}_4^{2-}$ -reducing mercury methylators as sulfur-reducing prokaryotes (SRPs) rather than SRB ([Appendix 12.3.2](#)). In the 2008 ISA, wetland and lake-bottom sediments were identified as habitat for mercury methylating SRPs. Recent research documents microbial mercury methylation in lakes, in wetland sediments and moss, within periphyton, in marine ecosystems, and within disturbed terrestrial forest soils ([Appendix 12.3.2](#) and [Appendix 12.3.3](#)). Microbial mercury methylation responsive to  $\text{SO}_x$  deposition occurs in freshwater lakes, freshwater wetlands, freshwater reservoirs, and freshwater agricultural areas ([Appendix 12.3.4](#)). Between the 2008 ISA and new research, **the body of evidence**

**is sufficient to infer a causal relationship between S deposition and the alteration of Hg methylation in surface water, sediment, and soils in wetland and freshwater ecosystems.**

Hg methylation is determined in part by surface water  $\text{SO}_4^{2-}$ , because many strains of SRPs possess the recently identified gene pair *hgcAB*, and pair their metabolism of C with both dissimilatory  $\text{SO}_4^{2-}$  reduction and mercury methylation (see [Appendix 12.3.2](#) and [Figure 12-5](#)). Microbial methylation rates are determined by other environmental requirements of SRPs, including seasonality and temperature, pH, salinity, amount of organic matter in the water and sediments, and concentrations of iron and nitrate ([Appendix 12.3.3](#)). New research demonstrates that Hg methylation occurs at current ambient  $\text{SO}_4^{2-}$  concentrations within U.S. water bodies. Multiple lines of evidence support a relationship between  $\text{SO}_4^{2-}$  surface water concentrations and MeHg concentration or production in various freshwater systems. Linear relationships between  $\text{SO}_4^{2-}$  concentrations and MeHg concentrations were observed in sediments of the South River, VA, across peat bogs in Minnesota and Ontario, and across prairie pothole lakes in Saskatchewan ([Figure 12-17](#)). In addition to the studies of lake and wetland sediments reviewed in the 2008 ISA, studies employing lab incubations show that  $\text{SO}_4^{2-}$  increases Hg methylation in samples from Adirondack peat bogs, from South River, VA sediments, from periphyton growing in North American lakes and wetlands, and from leaf packs in Minnesota river water ([Appendix 12.3.3.1](#)). Experimental addition of S to field mesocosms or whole ecosystems has shown that S enrichment as wet S deposition increases MeHg in water, sediment, or biota, in Little Rock Lake, WI; Bog Lake Fen, MN; the Experimental Lakes Area, Ontario; and the bog experiment at Degerö Stormyr, Sweden ([Appendix 12.3.4.1](#)). In observational studies of S and Hg deposition, fish Hg concentrations decline with temporal declines in  $\text{SO}_x$  deposition in Isle Royale (a Class I area). Fish Hg concentrations correlate positively with Hg and S deposition across Texas ecoregions, and a 12-year study found that fish Hg in Voyageurs National Park (a Class I area) declined in lakes with decreasing S deposition only when lake DOC remained constant ([Appendix 12.3.5.1](#)). New research is consistent and coherent with the research presented in the 2008 ISA in demonstrating that sulfur enrichment from  $\text{SO}_x$  deposition stimulates mercury methylation in North American ecosystems. Current research suggests that mercury methylation generally peaks between 10 and 100 mg  $\text{SO}_4^{2-}$ /L in surface water, and quantitative relationships between S and Hg, such as target values or thresholds, are reported in [Table 12-12](#).

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### IS.9.2.3 Sulfur, Mercury, and Animal Species

Mercury is a developmental, neurological, endocrine, and reproductive toxin across animal species. The 2008 ISA documented Hg accumulation in fish, songbirds, four turtle species, insectivorous passerine birds, and the common loon (*Gavia immer*). Recent research also documented Hg accumulation in insectivore songbirds, bats, and fish in agricultural wetlands. The 2008 ISA reported that 23 states had issued fish advisories by 2007 in response to the U.S. EPA's fish tissue criterion of 0.3 µg MeHg/g fish (0.3 ppm), set to protect human health. The 2008 ISA reported on the negative impacts of Hg on the development, morphology, survival, or reproduction in the following fish species: walleye (*Stizostedion vitreum*), grayling (*Thymallus thymallus*), mummichog (*Fundulus heteroclitus*), rainbow trout (*Oncorhynchus mykiss*), fathead minnows (*Pimephales promelas*), and zebrafish (*Danio rerio*). However, a recent report on Hg in streams of the U.S. by the USGS summarizes current research indicating that birds, fish, and fish-eating wildlife experience negative effects of Hg at lower concentrations than the 0.3 ppm criterion set to protect human health on the basis of fish consumption.

The 2008 ISA documented a link between decreased S deposition and decreased fish MeHg concentrations. Recent research in Voyageurs National Park (a Class I Area) supports this finding, and there is supporting evidence from fish surveys of Texas reservoirs across regions with different S deposition loads. There is also supporting evidence from an S addition experiment in a peat bog in the Marcell Experimental Forest in northern Minnesota, where increased S loading increased Hg concentrations in larval *Culex* spp. (mosquitoes), which are an important food source for both aquatic and terrestrial species ([Appendix 12.4](#) and [Figure 12-18](#)). In addition to the studies that consider S deposition, there are recent studies that consider  $\text{SO}_4^{2-}$  concentrations in water in relation to fish Hg concentrations in six lakes in South Dakota, and in the marshes of the Everglades ([Appendix 12.4](#)). In the freshwater marshes of the Everglades, recent work indicates a concentration of 1 mg/L  $\text{SO}_4^{2-}$  to keep water MeHg low ([Appendix 12.3.4.3](#)) and protect fish from elevated Hg burdens in that system ([Figure 12-14](#)).

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### IS.9.3 National-Scale Sensitivity and Critical Loads

The 2008 ISA identified ecosystems in the Northeast as particularly sensitive to Hg methylation in response to S deposition because many watersheds in this region have abundant wetlands and freshwater water bodies with high DOC and low pH. The U.S. EPA national stream surveys found that MeHg in predator fish exceeded the Hg criterion in a quarter of stream miles and half the lakes surveyed. Fish MeHg levels were highest

in streams in watersheds with considerable wetland area, and surveys showed highest fish MeHg concentrations in the southeastern U.S., suggesting that ecosystems sensitive to SO<sub>x</sub> deposition effects on Hg methylation extend beyond the Northeast ([Figure 12-15](#)). Recent studies confirm that Hg methylation is more widespread than was documented at the time of the 2008 ISA. New research conducted in agricultural wetlands in California suggests Hg methylation in these systems may provide a route to animal and human Hg exposure through food, specifically MeHg concentrations in rice seeds.

There are no CLs for S to prevent sulfide phytotoxicity or Hg methylation, although there are SO<sub>4</sub><sup>2-</sup> and sulfide water quality values that represent protective levels against toxic effects of sulfide and Hg to biota (see [Table 12-12](#)). There are European CLs for Hg concentrations in soil and fish tissue targeted to protect human health, drinking water quality, and terrestrial soils, but these CLs are not framed in terms of SO<sub>x</sub>, Hg, or PM deposition (see [Appendix 12.6](#)).

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## IS.10 Ecological Effects of Particulate Matter Other Than Nitrogen (N) and Sulfur (S) Deposition

Since publication of the 2009 PM ISA, new literature builds upon the existing knowledge of ecological effects associated with PM components other than those associated with N and S deposition, especially metals and organics. In some instances, new techniques have enabled further characterization of the mechanisms of PM on soil processes, vegetation, and effects on fauna. New studies provide additional evidence for community-level responses to PM deposition, especially in soil microbial communities. However, uncertainties remain due to the difficulty in quantifying relationships between ambient concentrations of PM and ecosystem response. Overall, **the body of evidence is sufficient to infer a likely causal relationship between deposition of PM and a variety of effects on individual organisms and ecosystems**, based on information from the previous review and new findings in this review. However, the new findings are limited in scope.

PM deposition comprises a heterogeneous mixture of particles differing in origin, size, and chemical composition. Exposure to a given concentration of PM may, depending on the mix of deposited particles, lead to a variety of toxic responses and ecosystem effects. Effects of PM on ecological receptors can be both chemical and physical ([U.S. EPA, 2009a, 2004](#)). As described in the 2009 *Integrated Science Assessment for Particulate Matter* (2009 PM ISA), particulates that elicit direct and indirect effects on ecological receptors vary by size, origin, and chemical composition. Ecological outcomes are attributed more to particle composition than to particle size ([Grantz et al., 2003](#)).

PM-associated metals and organics are linked to responses in biota; however, the heterogeneous nature of PM composition and distribution coupled with the variability inherent in natural environments confound assessment of the ecological effects of particulates. Although most effects are from chemical composition of PM, there are some effects of particle size such as changes to flux of solar radiation and soiling of leaves by large coarse particles in areas near industrial facilities and unpaved roads. Atmospheric deposition of PM from crustal material may be a source of base cations (especially  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ) that can partially ameliorate the effects of acidifying deposition. Base cations are important plant nutrients that in some locations are in short supply ([U.S. EPA, 2009a](#)).

In general, new studies on PM deposition to vegetation support findings in previous PM reviews on altered photosynthesis, transpiration, and reduced growth. Since the 2009 PM ISA, additional characterization of PM effects at the leaf surface has led to a greater understanding of PM foliar uptake. Alterations in leaf fatty acid composition are associated with metals transferred to plant tissues from PM deposition on foliar surfaces ([Appendix 15.4.2](#)).

An important characteristic of fine particles (0.1 to 1.0  $\mu\text{m}$ ) is their ability to affect the flux of solar radiation increases in the diffuse component. A newly available research method links changes in expression of proteins involved in photosynthesis to increases in the diffuse component due to aerosols and PM. Although this method has not been widely applied, it may represent an important way to study mechanistic changes to photosynthesis in response to more diffuse radiation resulting from PM in the air column ([Appendix 15.2](#)).

Several studies published since the 2009 PM ISA show PM chemical constituent effects on soil physical properties and nutrient cycling. Previous findings in the PM ISA of changes to microbial respiration and biomass are further supported by new studies. Microbial communities respond to PM in various ways depending on their tolerance to heavy metals and organics ([Appendix 15.5.3](#)).

In fauna, results from ecotoxicity assays with PM extracts using bacteria, rotifers, nematodes, zebrafish, and earthworms support findings in the 2009 PM ISA that toxicity is not related to the total mass of PM in the extract, but to the chemical components of the PM. In nematodes exposed to PM from air filters, the insulin-signaling pathway was identified as a possible molecular target. Use of wildlife as PM biomonitors has been expanded to new taxa since the last PM review. Several studies in invertebrates and birds report physiological responses to air pollutants, including PM ([Appendix 15.6](#)).

For ecosystem-level effects, a gradient of response with increasing distance from PM source was reported in the 2009 PM ISA. Newly available studies from long-term ecological monitoring sites provide limited evidence for recovery in areas such as those around former smelters due to the continued presence of metals in soils after operations ceased. A novel experimental microecosystem using microbial communities living in terrestrial mosses indicates that PM deposition alters responses of primary producers, decomposers, and predators ([Appendix 15.3](#)).

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## **IS.11 Recovery of Ecosystems from Nitrogen (N) and Sulfur (S) Deposition in the U.S.**

Evidence from across the U.S. of ecosystem recovery from N nutrient enrichment and acidification corresponding to long-term trends in N and S emissions varies. Most studies of recovery focus on ecosystem acidification recovery due to decreases in S emissions and deposition. Overall N emissions and deposition have been increasing or relatively steady, although a few areas have seen some decrease ([Appendix 2.7](#)). Consequently, the amount of new information available and reported here on N enrichment recovery is small.

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### **IS.11.1 Overarching Concepts of Ecological Recovery from Acidification**

Both chemical and biological indicators are used to assess the degree of ecological degradation associated with environmental stressors and document responses in ecosystems where improved conditions allow for recovery. Recovery can be documented by measurement of indicators and projected/modeled recovery trajectories.

Chemical recovery of aquatic and terrestrial ecosystems is characterized by trends in water quality indicators ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , pH, ANC, inorganic monomeric Al, MeHg) towards inferred preindustrial values or, in the case of inorganic Al and MeHg, below water quality threshold values protective of biota and human health. Preindustrial conditions varied across the U.S. depending on climate, geology, and biological communities, and preindustrial chemical indicator values are currently inferred from models, paleolimnology samples, or historical samples. When evaluating ecosystem recovery from acidification, it is important to note that different chemical pools within the soil or water column may recover at different rates with the same decreases in atmospheric deposition. For example, the soil solution Ca:Al ratio,  $\text{SO}_4^{2-}$ , or  $\text{NO}_3^-$  respond more quickly than will total N. Indicators of slowly recovering pools (such as the percentage of base saturation in the soil or soil C to N ratio) will have long response

times with regard to changes in atmospheric deposition. An indicator such as acid-neutralizing capacity (ANC), which is influenced by both fast and slow pools, has an intermediate response time. Chemical indicators such as ANC or pH may not necessarily follow a recovery path that mirrors the reverse of the acidification path due to dynamic relationships among ANC, pH, DOC, and inorganic Al; depletion of soil base cation pools; and/or pH-dependent S adsorption on soils. In addition, the ANC level that reflects recovery of pH or Al<sub>i</sub> may differ between the acidification and recovery phases ([Hesthagen et al., 2008](#)).

Biological recovery may follow chemical recovery of such water and soil quality constituents; however, there may be a lag of decades between the onset of chemical recovery and biological recovery [[U.S. EPA \(2008a\)](#); [Appendix 8](#)]. As observed in some of the early studies on formerly acidified systems, the biological recovery trajectory may exhibit hysteresis, where a system does not follow the same path from acidification to recovery ([Frost et al., 2006](#)). Complete biological recovery would entail a return to the same species make-up, richness, and abundance as existed in the ecosystem in question prior to the advent of human-caused acidic deposition (around the year 1860 in North American ecosystems). In a practical sense, complete biological recovery is probably not attainable at most acidified locations within a reasonable management time frame (perhaps 100 years) because soil reserves of base cations at many locations have been depleted in response to many decades of acidic deposition and because other stressors, in addition to acidic deposition, have also altered ecosystem structure and/or function or will do so in the coming decades. Such stressors include changes in climate, land use, and other perturbations. More commonly, partial biological recovery may be possible. Ecosystems deemed to be on a recovery trajectory are those found to be moving towards a mix of species presence and abundance that approximates the undisturbed state. There is substantial evidence that recovery rates from acidification differ between taxonomic groups [e.g., rotifers vs. crustaceans; [Frost et al. \(2006\)](#); [Malley and Chang \(1994\)](#)]. In general, recovery in freshwater ecosystems is characterized by populations of plankton and benthic invertebrates prior to the recovery of fish populations, although most biological communities studied to date have not returned to preacidification conditions, even after recovery of chemical parameters.

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## IS.11.2 Acidification Recovery in the U.S.

Long-term monitoring has been very important in tracking the ecological response to N and acidifying deposition ([Appendix 7](#) and [Appendix 4.4](#)). Experimental liming studies have also provided some evidence for biological recovery, although these types of studies are limited in the U.S. ([Appendix 4.3.4](#) and [Appendix 8.4.6](#)). The historical focus on

aquatic acidification has resulted in more data to evaluate recovery in aquatic than terrestrial ecosystems ([Appendix 7.1.3](#)). Fewer studies have tracked the potential recovery of terrestrial ecosystems; however, since the early 1990s, increasing evidence indicates that soils in some areas are beginning to recover, yet most sensitive regions continue to acidify in response to deposition ([Appendix 4.6.1](#)). In areas where N and S deposition has decreased, chemical recovery must first create physical and chemical conditions favorable for growth, survival, and reproduction of the pre-1860 assemblage for biological recovery to occur.

The northeastern U.S. and southern Appalachians are two regions of the U.S. where a large body of research has evaluated recovery. In the Northeast, evidence for chemical recovery is primarily from soils ([Appendix 4.6.1](#)) and freshwater lakes and streams ([Appendix 7.1.5.1](#)). In regard to biological recovery ([Appendix 8.4](#)), newer studies have documented some evidence for zooplankton recovery and the successful reintroduction of brook trout in previously acidified Adirondack water bodies or recolonization of previously acidic lakes from refugia ([Appendix 8.6.6](#)). In addition to decreased acidification, a few studies report declines in methylmercury concentrations in biota or water in response to decreasing S, which is suggestive of ecosystem recovery ([Appendix 12.5](#)).

In contrast to the northeastern U.S., there is little evidence for recovery in the southern Appalachian Mountain region ([Appendix 4.6.1](#) and [Appendix 16.3](#)). This area is characterized by an abundance of low-ANC streams situated on acidic, highly weathered soils. Streams in this region are strongly affected by  $\text{SO}_4^{2-}$  adsorption on soils, and long-term monitoring studies suggest that soil base cation depletion has prevented chemical recovery ([Appendix 7.1.5.1.4](#)). Biogeochemistry modeling scenarios suggest that even with large decreases in  $\text{SO}_4^{2-}$  deposition, it may take decades for soil base cation levels to recover in this region.

New studies continue to support findings in the 2008 ISA that biological response to water chemistry recovery varies among taxa and water bodies, and that most biological communities studied have not returned to preacidification conditions, even after recovery of chemical parameters ([Appendix 8.4](#)). Since the 2008 ISA, research has demonstrated that the DOC of many lakes and streams has risen, with the source of the DOM and associated DOC likely to be the soils in the terrestrial watershed ([Table IS-2](#); [Appendix 4.3.9](#) and [Appendix 7.1.2.9](#)). The mechanism causing the observed increase in DOC is unclear; it may be a combination of soil recovery from acidification, changes in climate (e.g., temperature and precipitation), and N deposition, among other mechanisms. DOC interacts like a weak acid; therefore, DOC concentration may affect pH and ANC levels and constrain the extent of recovery from acidification. At the same time, the

acidic properties of DOC make it a host for binding trace metals such as toxic inorganic Al (for additional discussion on inorganic Al and DOM see [Appendix 4.3.5](#)) and decreases the toxicity of dissolved Al to aquatic organisms. Overall, current research indicates DOC increases are inconsistent across surface waters in the U.S., with large increases in DOC with acidification recovery in some locations and no increases in other recovering sites.

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### **IS.11.3 Nitrogen (N) Driven Nutrient Enrichment Recovery in the U.S.**

Most freshwater systems sensitive to nutrient effects of atmospheric deposition of N have shown no evidence for biological recovery, although decreases in  $\text{NO}_3^-$  concentrations consistent with declines in N deposition have been reported in some regions of the U.S., notably the Appalachian, Adirondack, and Rocky Mountains ([Appendix 7.1.5](#)). Some estuaries have shown improvements in biological indicators, such as increases in the extent of SAV, in response to decreases in N inputs from atmospheric deposition and in wastewater and agricultural runoff. For an example, see the Tampa Bay case study ([Appendix 16](#)). In other coastal areas of the U.S., biological indicators of nutrient enrichment have remained relatively unchanged or declined. In the well-studied Chesapeake Bay watershed where extensive restoration efforts have been implemented, water quality and measures of ecological condition have shown little improvement during a 23-year period ([Williams et al., 2010](#)). The one exception to the pattern of no improvement in water quality was an observed increase in the amount of SAV ([Appendix 10.2.5](#)).

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## **IS.12 Climate Modification of Ecosystem Response to Nitrogen (N) and Sulfur (S) Deposition**

Nitrogen and S deposition occur in many ecosystems concurrently experiencing multiple stressors, including human-driven climate change. Climate change effects on U.S. ecosystems were recently summarized in the U.S. National Climate Assessment ([Galloway et al., 2014](#); [Groffman et al., 2014](#)). Each appendix of the ISA evaluating N enrichment or acidification includes a section on how climate modifies the ecosystem response. In the context of this section of the ISA, climate refers to meteorological factors over a 5-year horizon (because NAAQS are reviewed every 5 years) in contrast to long-term climate change, or associated changes to  $\text{CO}_2$  concentrations. Additionally, to serve as a foundation for the discussion, text in [Appendix 13](#) is excerpted from [Greaver et al. \(2016\)](#), a current review of how climate (e.g., temperature and precipitation) modifies ecosystem response to N that focuses on empirical observations.

Anthropogenic emissions of greenhouse gases are likely to cause a global-average temperature increase of 1.5 to 4.0°C and a significant shift in the amount and distribution of precipitation by the end of the 21st century ([Collins et al., 2013](#)). Recent work has focused on the effects of anthropogenic N on the Earth’s radiative forcing ([Pinder et al., 2012](#)) and how temperature and precipitation alter ecological responses to N exposure ([Greaver et al., 2016](#)). Most work is conducted on the effects of climate interactions with N or acidifying deposition (N + S); relatively little work is conducted on how climate modifies ecosystem response to S nutrient-related effects.

Understanding climate effects on ecosystems is a rapidly expanding field with many new empirical studies, meta-analyses, and modeling work published since the 2008 ISA. General patterns of how climate affects some biogeochemical processes are known and how climate alters growth rates and biodiversity of some species have been identified, [Figure 13-1](#) is an example of how processes relevant to N enrichment and acidification may be altered with either wetter or drier conditions. In addition to the excerpt from [Greaver et al. \(2016\)](#), additional studies are summarized for effects of climate on N transport and transformation ([Table 13-1](#)), N and C cycling ([Table 13-2](#)), acidification ([Table 13-3](#)), and biodiversity ([Table 13-4](#)). Our understanding of the effects of climate on ecosystem response to N and S deposition varies; for many ecological endpoints, data are insufficient to quantify either the direction or magnitude of how climate may alter ecosystem response with certainty.

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## IS.13 Ecosystem Services

“Ecosystem services” refers to the concept that ecosystems provide benefits to people, directly or indirectly ([Costanza et al., 2017](#)), and that ecosystems produce socially valuable goods and services deserving of protection, restoration, and enhancement ([Boyd and Banzhaf, 2007](#)). The concept of ecosystem services recognizes that human well-being and survival are not independent of the rest of nature, and that humans are an integral and interdependent part of the biosphere ([Costanza et al., 2017](#)). In some cases, and in line with more conventional economic thinking, ecosystem services analysis can result in attaching monetary values to ecosystem outcomes. However, because ecosystem services are often public goods their benefits can be difficult to monetize. We emphasize that this practical difficulty in no way implies that ecosystem service benefits are small or without value. At a minimum, ecosystem services analysis involves discussion and, ideally, quantification of ecological outcomes understood by households, communities, and businesses. Explicitly linking ecosystem services to social and economic welfare measures has proven difficult because of the broad definition of ecosystem services and the numerous types of services that could be affected. An analysis of ecosystem services

specifically altered by NO<sub>x</sub>, SO<sub>x</sub>, and PM would translate the effects of ambient concentrations and deposition into biological, physical, or monetary metrics that give insight to public welfare effects.

For acidification, the ecosystem service literature since the 2008 ISA includes studies that better characterize ecosystem service valuation by pairing biogeochemical modeling and benefit transfer equations informed by willingness-to-pay surveys, especially for the Adirondacks and Shenandoah regions ([Appendix 14](#)). Aside from valuation studies, there is an improved understanding of the numerous causal pathways by which N and S deposition may affect ecosystem services, supported by studies that relate deposition to final ecosystem services under the FEG-CS ([Bell et al., 2017](#); [Clark et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Rhodes et al., 2017b](#)). However, for many regions and specific services, poorly characterized dose-response between deposition, ecological effect, and services are the greatest challenge in developing specific data on the economic benefits of emission reductions ([NAPAP, 2011](#)).

In the 2008 ISA there were no publications that specifically evaluated the effects of N deposition on ecosystem services associated with N driven eutrophication. Since then several comprehensive studies have been published on the ecosystem services related to N pollution in the U.S. ([Appendix 14](#)). These include an evaluation of services affected by multiple N inputs (including N deposition) to the Chesapeake, a synthesis of the cost-benefits on N loading across the nation, and analysis of the amount of N that leaked out of its intended application area causing effects on adjacent ecosystems and ecosystem services, two calculations of the social cost of nitrogen (Minnesota and the Mississippi Alluvial Valley), and an estimate of the cost to remove N from the White River Basin in Indiana (this work specifically identified the costs of the atmospheric portion of total N loading). The estimate of the total number of ecosystem services affected by N is better quantified by the new studies that use FEG-CS ([Bell et al., 2017](#); [Clark et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Rhodes et al., 2017b](#)). In these analyses, CL exceedances for N related air pollution were used as a model stressor from which a total of 1,104 unique chains linking stressor to beneficiary were identified.

The conclusions considering the full body of literature are that (1) there is evidence that N and S emissions/deposition have a range of effects on U.S. ecosystem services and their social value; (2) there are some economic studies that demonstrate such effects in broad terms; however, it remains methodologically difficult to derive economic costs and benefits associated with specific regulatory decisions/standards; and (3) there is an improved understanding of the numerous causal pathways by which N and S deposition may affect ecosystem services, though most of these causal relationships remain to be quantified.

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## IS.14 Key Scientific Uncertainties

Evaluation of uncertainty is an important part of ecosystem assessment. Uncertainty refers to the absence of information and is a way to describe how certain we are in scientific knowledge. As described by [Curry and Webster \(2011\)](#), the nature of uncertainty can be expressed by the distinction between ontic uncertainty and epistemic uncertainty. Ontic uncertainty is associated with inherent variability or randomness and is an irreducible form of uncertainty. Epistemic uncertainty is associated with imperfections of knowledge, which may be reduced by further research and empirical investigation. [Walker et al. \(2003\)](#) [as summarized in [Curry and Webster \(2011\)](#)] characterized uncertainty as a progression from deterministic understanding to total ignorance:

**“Statistical uncertainty** is the aspect of uncertainty that is described in statistical terms. An example of statistical uncertainty is measurement uncertainty, which can be due to sampling error or inaccuracy or imprecision in measurements.

**“Scenario uncertainty** implies that it is not possible to formulate the probability of occurrence of one particular outcome. A scenario is a plausible but unverifiable description of how the system and/or its driving forces may develop over time. Scenarios may be regarded as a range of discrete possibilities with no a priori allocation of likelihood.

**“Recognized ignorance** refers to fundamental uncertainty in the mechanisms being studied and a weak scientific basis for developing scenarios. Reducible ignorance may be resolved by conducting further research, whereas irreducible ignorance implies that research cannot improve knowledge.”

The understanding and reporting of uncertainty is not consistent across scientific disciplines, and uncertainty may be quantified by various methods. [Csavina et al. \(2017\)](#) provided an overview of terminology and definitions of 41 different terms used to describe uncertainty. Here we provide a summary of some of the key methods that may be used to evaluate the uncertainty of the relationships between NO<sub>x</sub>, SO<sub>x</sub>, and PM pollutants and ecological effects. This summary presents uncertainties associated with several specific concepts, including source emissions measurements, atmospheric deposition estimates, empirical measurements of CLs, models used to estimate CLs, and uncertainties in the aquatic acidification index. Quantified estimates of uncertainty vary according to the number of decision points ([Section IS.14.2.3](#)), including the method used and the input parameters under consideration; therefore, the analyses and discussion of

quantified uncertainty values will occur in the Risk and Exposure Assessment as scoped in the 2017 IRP ([U.S. EPA, 2017c](#)).

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## IS.14.1 Atmospheric Science

Estimating atmospheric deposition involves quantification of emissions, atmospheric concentrations, and deposition fluxes of the various species that make up atmospheric SO<sub>x</sub>, NO<sub>y</sub>, and NH<sub>x</sub>. This is accomplished with environmental measurements, model predictions, or hybrid approaches that combine measurements and modeling methods. There are a wide range of uncertainties across the environmental measurements and model parameters used to estimate atmospheric deposition fluxes. The largest uncertainties are those for dry deposition and ammonia emissions, whether measured or modeled. The smallest uncertainties are associated with ambient concentration measurements and continuously monitored stationary emissions like electric power plants.

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### IS.14.1.1 Emissions Uncertainty

Quantitative uncertainty estimates are not documented in the National Emissions Inventory (NEI), but uncertainties are often evaluated through separate efforts by comparing inventory predictions with measured long-term trends, statistical source apportionment methods, inverse chemical transport modeling, and comparison with satellite data ([Appendix 2.2.2](#)). SO<sub>2</sub> and NO<sub>x</sub> emission uncertainties for electricity-generating units, the major source of SO<sub>2</sub> and an important source of NO<sub>x</sub>, are in the 10–15% range because emissions are usually continuously monitored ([Appendix 2.2.3](#)). NO<sub>x</sub> emission uncertainties for mobile sources, the largest source of NO<sub>x</sub>, arise from differences in engine type, size, age, and maintenance, as well as fuel composition and emission control equipment. Overestimation of NO<sub>x</sub> emissions from mobile sources was proposed as an explanation for modeled NO<sub>x</sub> concentration bias in several studies. However, mixed results have been observed across several studies when modeled concentrations were compared with measurements. Estimates of NO<sub>x</sub> emissions uncertainties are in the 10–20% range for on-road gasoline and diesel vehicles, and up to 30% for off-road vehicles like ships, airplanes, and locomotives ([Appendix 2.2.3](#)). Spatial and temporal variability in soil NO<sub>x</sub> emissions can lead to uncertainty in emissions estimates. Soil emissions occur mainly during summer and across the U.S., but some areas, such as the central Corn Belt of the U.S., release more NO<sub>x</sub> emissions than others ([Appendix 2.2.3](#)).

In contrast, total NH<sub>3</sub> emissions uncertainties appear to be greater, underestimated by as much as a factor of two or more according to several recent studies ([Appendix 2.2.3](#)). The predominant sources, livestock operations and fertilizer application, exhibit large temporal and regional variability due to differences in climate conditions and farming practices. As a result, detailed models are required for estimating NH<sub>3</sub> emissions ([Appendix 2.2.2](#)), but data on local environmental conditions and farming practices necessary for good model performance are often not available. Large discrepancies between modeled and measured N concentrations and deposition rates have been attributed to uncertainties in NH<sub>3</sub> emissions ([Appendix 2.2.3](#)). Activity rates, including those for mobile source emissions, are also difficult to quantify, contributing to uncertainty in NH<sub>3</sub> emission estimates ([Appendix 2.2.3](#)).

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### IS.14.1.2 Atmospheric Measurement Uncertainty

Uncertainties in concentration and deposition measurements from network-based measurements are generally under 20%, and surface concentration uncertainties from satellite-based measurements typically somewhat higher. Concentration and deposition data are derived from several specialized national monitoring networks, including the national SO<sub>2</sub> monitoring network, the NCore network for multipollutant concentration monitoring including NO<sub>y</sub>, the Ammonia Monitoring Network, CASTNet for estimating dry deposition, and the National Trends Network for wet deposition ([Appendix 2.4.1](#)). Uncertainties are estimated from reports of precision in data quality reports where available, and otherwise from network data quality objectives.

For air concentration measurements used to estimate dry deposition, CASTNet measured precision was 2–5% for SO<sub>4</sub><sup>2-</sup>, 5–13% for NO<sub>3</sub><sup>-</sup>, and 2–6% for NH<sub>3</sub> in 2016 ([Appendix 2.4.5](#)). Additional uncertainty is associated with estimating dry deposition from NTN concentration data. Uncertainties of 30% for SO<sub>2</sub> and 40% for HNO<sub>3</sub> have been reported using a simple inferential approach ([Clarke et al., 1997](#)). However, single site determinations are of limited use because dry deposition fluxes are determined by several factors and can vary considerably over small spatial scales. In most recent efforts, dry and total deposition on a regional or national scale is usually modeled with CTMs ([Section IS.14.1.3](#)).

Precipitation concentration measurement precision and estimated wet deposition precision in the National Trends Network were less than 7% for SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> and less than 20% for NH<sub>3</sub>. PRISM (Parameter-elevation Regression on Independent Slopes Model) enhances spatial resolution using National Trends Network data to improve the creation of wet deposition maps ([Appendix 2.6](#)). Uncertainty for PRISM data sets has

been evaluated in the literature using cross validation and a 70% prediction interval for different data sets. NH<sub>3</sub> air concentration measurement methods used in AMoN were evaluated and found to have a precision of 10% ([Appendix 2.4.3](#)). Minimum performance specifications for SO<sub>2</sub> monitoring from the national SO<sub>2</sub> monitoring network include a precision of 2.0% ([Appendix 2.4.4](#)). Data quality objectives for NO<sub>y</sub> in the NCore network include a precision of 15% ([Appendix 2.4.2](#)). Uncertainty in satellite-based measurements depend on vertical profile, cloud fraction, cloud-top pressure, surface reflectivity, and extent of aerosol scattering. Estimates of 20% for NO<sub>2</sub> ([Appendix 2.4.2](#)) and 10–45% for SO<sub>2</sub> ([Appendix 2.4.4](#)) have been reported for cloud-free conditions.

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### IS.14.1.3 Atmospheric Modeling Uncertainty

The Community Multiscale Air Quality modeling system is probably the most widely used model in the U.S. for estimating atmospheric deposition. CMAQ accurately modeled total SO<sub>x</sub>, but partitioning resulted in overpredicting SO<sub>2</sub> and underpredicting SO<sub>4</sub><sup>2-</sup>. In a recent CMAQ evaluation, SO<sub>2</sub> concentrations were overestimated by 39 to 47%, and SO<sub>4</sub><sup>2-</sup> concentrations were underestimated by 9 to 17%, as annual averages over a range of 4 years compared to surface-based measurements. In addition, atmospheric NO<sub>3</sub><sup>-</sup> concentrations were overestimated by 22 to 26%, as annual averages over a range of 4 years compared to surface-based measurements ([Appendix 2.5.3](#)). Mixed results have been observed in several recent comparisons of CMAQ wet deposition estimates to network-based measurements, with average differences in modeled results and measurements ranging from ≤15 to 99% for NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and ≤15 to 60% for NH<sub>3</sub> ([Appendix 2.5.3](#)). Modeling methods for estimating dry and total deposition are still under development, and uncertainties have not been extensively evaluated or quantified. Recent sensitivity analysis results found less than 5% differences in total deposition estimates because of compensation of competing model processes, but extensive comparison of model results and measurements are not available ([Appendix 2.5.3](#)).

[Horn et al. \(2018\)](#) used deposition and forest inventory data (from 2000 to 2016) to assess the relationship between deposition and growth and survival of 71 tree species across the contiguous U.S. in a correlational analysis. Authors attempted to reduce uncertainty by accounting for other variables, either directly in their model or by quantifying and avoiding instances with high collinearity. The authors isolated the effects of N deposition from S deposition by adding S deposition explicitly into their models. Using variance inflation factors (VIFs), they also quantified the collinearity of N and S deposition against a suite of environmental variables that might have an effect. The analysis focused on the relationships of tree growth and survival to N and S deposition where the VIF was less

than or equal to 3. VIF values of 3–10 have been proposed as thresholds above which there is a potential for high collinearity ([Horn et al., 2018](#)). To what extent variables not included could have varied with deposition and had an effect, including ozone and drought, remained a key uncertainty.

[Clark et al. \(2018\)](#) analyzed exceedances of multiple types of CLs for the contiguous U.S. since 1800 and projecting out to 2025. The study authors discussed the uncertainty around CMAQ deposition estimates using CMAQ estimates starting in 1980. They noted that CMAQ may underestimate hot spots of deposition in space (e.g., concentrated deposition because of an orographic effect) or in time (e.g., from cloudbursts). CLs are an ecosystem response to deposition, and so any errors associated with deposition estimates would propagate through CLs. [Fenn et al. \(2010\)](#) found that CMAQ estimates and N in throughfall were similar under low throughfall conditions, but CMAQ underestimated N deposition when throughfall was high. [Clark et al. \(2018\)](#) noted that CMAQ is corrected using NADP data, but NADP sites do not provide complete spatial coverage. Remote sites are likely underrepresented.

In addition to measurable uncertainties associated with measurement precision or comparisons between models and measurements, there are also structural uncertainties due to incomplete understanding of the underlying science related to atmospheric deposition that are not possible to quantify. The main structural uncertainties associated with deposition estimates are canopy effects on NO<sub>x</sub> (including both bidirectional gas exchange and canopy reactions), bidirectional exchange of NH<sub>3</sub> with biota and soils, and processes determining transference ratios that relate average concentration to deposition ([Appendix 2.5](#)).

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## IS.14.2 Ecological Effects

Evaluation of ecological effects caused by acidification or eutrophication involves a suite of parameters and dose-response functions, both empirical and modeled. The quantitative uncertainty of empirically observed variables in ecology is determined by using statistics. A suite of mathematical statistical models is available to describe the variability among empirical observations and the strength of a cause and ecological effect relationship, the appropriate method to apply depends on the experimental design. Statistics for empirical data include calculation of probability, distributions, standard deviation, variance, *t*-tests, ANOVA, linear regression, spatial statistics, Bayesian analysis, and multivariate analysis, among others. In general, ecological endpoints determined by empirical studies to be affected by deposition were reported in the ISA if they were statistically significant; this means the magnitude of effect was larger than the estimated uncertainty.

Models of chemical and ecological processes, including biogeochemistry, provide representations of biological and geochemical interactions through mathematical expressions. The models used to characterize aquatic and terrestrial biogeochemistry response to N and S deposition can be complex, including many interacting variables. Model results are often compared to empirically collected data to confirm the model. Each of the input variables used in a biogeochemical model entails uncertainty. Model uncertainty is governed, in part, by how close the model predictions are to actual observations. Uncertainty in modeled results may arise from limitations in input data or from limitations in model assumptions. Statistical inference methodologies enable uncertainty analysis and determine the strength of the relation between a given uncertain input and the output (i.e., sensitivity analysis). For biogeochemistry models these methods include first-order sensitivity index, Monte Carlo technique, extended Fourier amplitude sensitivity test, Morris one-factor-at-a-time, and Bayesian analysis.

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#### **IS.14.2.1 Empirical Critical Loads**

Empirical N CLs for terrestrial and aquatic ecosystems reported in this ISA have been estimated using empirical data sets. The exact effects threshold may be determined using expert judgement. For example, if three levels of N addition are applied to a study site (10, 20, and 30 kg N/ha/yr) and an effect is noticed at 20 kg N/ha/yr, then the CL is estimated at <20 kg N/ha/yr. Another approach would be to fit a mathematical function to the observations, and a scientific judgement made to identify the level of deposition and/or N addition, or threshold, at which the ecological effect is considered to occur and which is likely to be biologically adverse.

There are some challenges associated with developing CLs that can result in uncertainty. First, because biological responses are often continuous, there can be a lack of an obvious cutoff between adverse and nonadverse effects. As a result, individual author groups have selected different response thresholds. For example, N CLs for lichens have been calculated for (1) deposition values associated with thallus N concentrations above the 97% distribution quantile observed for clean sites ([Fenn et al., 2008](#)), (2) community composition shifts from oligotroph to eutroph dominance ([Fenn et al., 2008](#)), (3) low probability of detecting regionally distributed sensitive species ([Root et al., 2015](#); [Geiser et al., 2010](#)), or (4) extirpation of oligotrophs ([Fenn et al., 2008](#)). Secondly, clean site data can be lacking in some ecoregions. For instance, few empirical data are available for sites in the eastern U.S. with deposition rates <4 kg N/ha/yr. This makes it difficult to quantify physiological or community compositional conditions that may have occurred in this region at deposition rates of 1–4 kg N/ha/yr.

The [Pardo et al. \(2011a\)](#) study provided a compilation of terrestrial and aquatic N CLs reported since the 2008 ISA. Uncertainty in the derivation of empirical CLs for N input as presented by [Pardo et al. \(2011a\)](#) arises in estimating the ambient (and perhaps historical) deposition loads and in estimating the biological effects caused by those deposition levels. According to [Pardo et al. \(2011a\)](#), sources of uncertainty in N deposition estimates for N CLs at the Ecoregion Level 1 scale include “(1) the difficulty of quantifying dry deposition of nitrogenous gases and particles to complex surfaces; (2) sparse data, particularly for arid, highly heterogeneous terrain (e.g., mountains); and (3) sites with high snowfall or high cloud water/fog deposition, where N deposition tends to be underestimated.” Examples of high uncertainty include high-elevation sites in the Rockies and Sierra Nevada mountains, due in part to highly uncertain estimates of dry deposition ([Appendix 2](#)). For sensitive receptors such as phytoplankton, shifts in high-altitude lakes, N deposition model bias may be close to, or exceed, predicted CL values ([Williams et al., 2017a](#)).

Physical, chemical, and ecological variability across lakes affect their response to N deposition and contribute to uncertainty of CL estimates ([Appendix 9.1.1.2](#)). A review by [Bowman et al. \(2014\)](#) noted that current N CLs for sensitive alpine systems may not be protective under future climate scenarios of warmer summer temperatures and a shorter duration of snow cover.

Between the publication of [Pardo et al. \(2011a\)](#) and the cutoff date for literature in this ISA (May 2017), some additional aquatic and terrestrial N CLs have been published ([Appendix 4](#); [Appendix 6.5](#)). [Simkin et al. \(2016\)](#) was not based on field addition or N gradient of deposition studies; instead, the methods were a spatial analysis of plant diversity using a large data set of over 15,000 forest, shrubland, and herbaceous sites across the U.S. Atmospheric N deposition varied nearly 20-fold across the site gradient. The study authors found that N deposition was negatively correlated with plant species richness at many locations, but positively correlated at others with most of the positive correlations in areas with low N deposition averaging 3 kg N ha/yr or less. [Simkin et al. \(2016\)](#) also estimated the uncertainty surrounding the mean CL estimates. For open canopy ecosystems, for example, they estimated a mean of 8.7 kg N ha/yr and provided 95% confidence intervals, which can be used as estimates of uncertainty, of 6.4 to 11.3 kg N ha/yr. For closed canopy systems, the mean of 13.4 kg N ha/yr was surrounded by a 95% confidence interval of 6.8 to 22.2 kg N ha/yr.

[Clark et al. \(2018\)](#) noted that many of the CLs used are empirically derived. Some of the uncertainties with these CLs are that they are often from one or two studies at a given location or area and extrapolated to a larger area, such as an entire Level 1 ecoregion. Thus, there is uncertainty about how representative these are for larger areas. As noted in

[Horn et al. \(2018\)](#), there also can be covariates unaccounted for that could affect estimates of CLs. CLs also do not generally account for historical effects that already might have affected the ecosystem. There are also uncertainties regarding process-based CLs, such as the terrestrial acidification CL. [Clark et al. \(2018\)](#) specifically pointed towards the existence of poor estimates of soil weathering despite the importance of soil weathering estimates for acidification CLs.

The majority of studies that evaluate terrestrial N CLs for N enrichment effects are based on observed response of a biological receptor to N deposition (or N addition as a proxy for deposition), without a known soil chemistry threshold that causes the biological effect. In contrast, CLs for acidification are typically based on the deposition amount that gives rise to a soil chemical indicator value which is known to cause an adverse biological effect. The link between soil chemical indicator and biological effect is based on empirical evidence ([Appendix 5](#)). The relationship between deposition and the biogeochemistry that causes effects on soil chemistry is typically modeled ([Appendix 4; Section IS.14.2](#)).

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## **IS.14.2.2 Modeled Critical Loads**

### **IS.14.2.2.1 Terrestrial and Aquatic Acidification: Biogeochemistry**

A variety of process models have been used to estimate past and future resource conditions under scenarios of acidification/recovery responses and critical and target loads, both aquatic and terrestrial. Models include simple approaches such as the simple mass-balance equation (SMBE), and dynamic models, such as PnET-BGC and ForSAFE, MAGIC, VSD, and VSD+ ([Appendix 4.5](#)). CLs for terrestrial and aquatic acidification are calculated by the model to determine the amount of deposition that alters soil or water chemistry to a threshold value known to have detrimental effects on a biological receptor.

Each of the several well-established models of terrestrial biogeochemistry used to evaluate soil acidification ([Appendix 4.5](#)) rely heavily on input or simulated values for base cation weathering (BCw) rate, one of the most influential yet difficult to estimate parameters in the calculation of critical acid loads of N and S deposition for protection against terrestrial acidification ([Appendix 4.5.1.1](#)). Obtaining accurate estimates of weathering rates is difficult because weathering is a process that occurs over very long periods of time, and the estimates on an ecosystem's ability to buffer acid deposition rely on accurate estimates of weathering. Various approaches can be used to estimate BCw, including the empirical soil clay approach, the PROFILE model [e.g., [Phelan et al. \(2014\)](#)], the F-factor approach ([U.S. EPA, 2009c](#)), and calibration of a dynamic model

such as MAGIC [e.g., [Povak et al. \(2014\)](#); [McDonnell et al. \(2014b\)](#)]. There are new studies on estimating BCw, including evaluation of uncertainty ([Whitfield et al., 2018](#); [Futter et al., 2012](#)). When applying PROFILE to upland forests in the U.S., [Whitfield et al. \(2018\)](#) found the greatest uncertainty in BCw estimate was due to the particle size class-based method used to estimate the total specific surface area on which weathering reactions can take place.

The uncertainty of forest soil CLs for acidification in U.S. calculated using simple mass-balance equations (SMBE) was investigated by [Li and McNulty \(2007\)](#). The results included a quantification of how 17 of the model's parameters contributed to the uncertainty and indicated that uncertainty in the CLs came primarily from components of base cation weathering and acid-neutralizing capacity, whereas the most critical parameters were BCw base rate, soil depth, and soil temperature. The study authors concluded that improvements in estimates of these factors are crucial to reducing uncertainty and successfully scaling up SMBE for national assessments (see [Appendix 4.6](#)).

Several dynamic models are commonly used to model terrestrial soil acidification ([Appendix 4.5](#)). [Tominaga et al. \(2009\)](#) conducted a Monte Carlo multiple-model evaluation of the dynamic models MAGIC, SAFE, and VSD and found that given the same deposition scenario, the three models (without calibration) simulate changes in soil and soil solution chemistry differently, but the basic patterns were similar. The study authors also found the greatest differences in model outputs were attributed to the cation exchange submodel. [Bonten et al. \(2015\)](#) compared how well the common types of dynamic models used to evaluate terrestrial soils (VSD, MAGIC, ForSAFE, and SMARTml) quantified several variables including soil S, soil pH, soil ANC, BC, base saturation, and Al ([Appendix 4.5.3](#)).

Uncertainty analysis of a dynamic model (VSD) used for CL based on soil chemistry chemical limits showed that the main drivers of uncertainty were largely dependent on the chemical criterion selected [[Appendix 5.5.3.3](#); [Reinds and de Vries \(2010\)](#)]. For example, base cation weathering, deposition, and the parameters describing the H-Al equilibrium in the soil solution were the main sources of uncertainty in the estimates of maximum CLs for S ( $Cl_{max}[S]$ ) based on the Al:Bc criterion of 1.0, and uncertainty in  $Cl_{max}(S)$  based on ANC was completely determined by base cation inputs. The denitrification fraction was the most important source of uncertainty for the maximum CLs of N ( $Cl_{max}[N]$ ). Calibration of VSD reduced the levels of uncertainty for all CLs and criteria.

[Fakhraei et al. \(2017b\)](#) reviewed sensitivity and uncertainty analysis techniques (e.g., first-order sensitivity index, Monte Carlo technique, extended Fourier amplitude

sensitivity test, Morris one-factor-at-a-time, and Bayesian analysis) in the context of a biogeochemistry model. The study authors applied these techniques to determine the uncertainty and sensitivity of the PnET-BGC model calculation of TMDLs of acidifying deposition that occur in high-elevation, acid-impaired streams in GSMNP ([Fakhraei et al., 2017a](#)). Sensitivity analyses showed that modeled estimates of maximum allowable acidifying deposition loads were most sensitive to uncertainty in model input parameters of air temperature, precipitation quantity, and rate of calcium weathering. Importantly, as more uncertainty was incorporated into model input parameters ( $\pm 5$  to  $\pm 10$  to  $\pm 20\%$  uncertainty), estimates of allowable deposition loads to protect aquatic ecosystem recovery decreased in magnitude ([Fakhraei et al., 2017a](#)).

#### **IS.14.2.2.2 Biogeochemistry and Plant Biodiversity Linked Modeling**

Plant biodiversity models, such as VEG and PROPS, have been coupled to dynamic biogeochemical models, such as ForSAFE and VSD+ ([Mcdonnell et al., 2018b](#); [Mcdonnell et al., 2018a](#); [Phelan et al., 2016](#)). ForSAFE-VEG is an older and more broadly applied model than VSD + PROPS. There are some key differences between VEG and PROPS. Plant species in the VEG component of ForSAFE-VEG are defined by mathematical equations based on expert opinion regarding such parameters as plant needs for moisture, sunlight, and N supply to represent unobservable fundamental niches. In the PROPS, statistical relationships based on empirical data are used to characterize plant species, which are more likely to approximate real-world niches influenced by competition among species. These model chains are subject to the same constraints and uncertainties as the biogeochemical models on their own, plus those of the plant response modules.

#### **IS.14.2.2.3 Aquatic Eutrophication Modeling**

Many of the models that estimate N loads to the coastal zone from land-based inputs (agricultural practices, sewage, atmospheric deposition, natural lands) and freshwater inflow have been compared, and there is a good deal of knowledge about their limitations and uncertainties ([McCrackin et al., 2013](#); [Alexander et al., 2008](#)). A National Research Council review determined that these models are hydrodynamically complex and tend to be site specific. Thus, they are difficult to apply broadly ([NRC, 2000](#)).

The SPARROW model application used only wet N deposition. A large amount of N from nonpoint source urban influences (most likely due primarily to the dry deposition of exhaust N gases) often approximately doubles the importance of N deposition as an N source to higher order river systems ([Howarth, 2008a, b](#)).

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### IS.14.2.3 Additional Key Considerations for Critical Loads

The choice of model for CL estimation, or for scenario projection, depends largely on the availability of time, data, and resources. Major decisions inherent in the modeling efforts include:

- Empirical observation or application of a model
- Steady-state or dynamic model
- Statistical or process-based model
- Protection against acidification or nutrient N enrichment
- Site-specific, regional, or national spatial scale
- Resources to be protected (i.e., stream, lake, soil, vegetation, aquatic biota)
- Chemical indicator(s) of adverse effects (e.g., water ANC, water  $\text{NO}_3^-$ , soil BS)
- Critical level(s) for selected indicator(s)
- Time frame of evaluation (i.e., ambient, 2050, long-term steady state)

Each of these decision points introduces additional uncertainties, data needs, and potential assessment errors. [U.S. EPA \(2008a\)](#) summarized CL research and monitoring needs identified by [U.S. EPA \(2006b\)](#) at the time of the previous (2009) U.S. EPA Risk and Exposure Assessment.

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### IS.14.3 Aquatic Acidification Index

Detailed analysis of uncertainty in the AAI equation can be found in Appendix F of the 2011 Policy Assessment for the Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur ([U.S. EPA, 2011a](#)). The AAI is made up of components including ecosystem effects; dose-response relationships; underlying ecosystem sensitivity to acid deposition, biogeochemical, atmospheric and deposition processes; and characterization of ecosystem services. Some degree of uncertainty exists in all of the components of the AAI. Overall, the 2011 Policy Assessment found, on balance, low uncertainty in the information and processes associated with linkages from ecological effects to atmospheric conditions through deposition and ecosystem modeling. However, it acknowledged the need to improve certainty of several components including nitrogen and sulfur deposition processes in CMAQ, natural emissions of  $\text{NO}_x$  from lightning processes, and improving the amount of samples of CL estimates at several ecoregions ([U.S. EPA, 2011a](#)).

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# APPENDIX 1    QUALITY ASSURANCE AND INTRODUCTION TO APPENDICES

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## 1.1    Quality Assurance Summary

The use of quality assurance (QA) and peer review helps ensure that the U.S. EPA conducts high-quality science assessments that can be used to help policymakers, industry, and the public make informed decisions. Quality assurance activities performed by the U.S. EPA ensure that environmental data are of sufficient quantity and quality to support the Agency's intended use. The ISA for Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter-Ecological Criteria is classified as a Highly Influential Scientific Assessment (HISA), which is defined by the Office of Management and Budget (OMB) as a scientific assessment that is novel, controversial, or precedent-setting, or has significant interagency interest (OMB, 2004). OMB requires a HISA to be peer reviewed before dissemination. To meet this requirement, the U.S. EPA engages the Clean Air Scientific Advisory Committee (CASAC) as an independent federal advisory committee to conduct peer reviews. Both peer-review comments provided by the CASAC panel and public comments submitted to the panel during its deliberations about the external review draft were considered in the development of this ISA.

Agency-wide, the U.S. EPA Quality System provides the framework for planning, implementing, documenting, and assessing work performed by the Agency, and for carrying out required quality assurance and quality control (QA/QC) activities. Additionally, the Quality System covers the implementation of the U.S. EPA Information Quality Guidelines (U.S. EPA, 2002). This ISA follows all Agency guidelines to ensure a high-quality document.

Within the U.S. EPA, Quality Assurance Project Plans (QAPPs) are developed to ensure that all Agency materials meet a high standard for quality. U.S. EPA has developed a Program-level QAPP (PQAPP) for the ISA Program to describe the technical approach and associated QA/QC procedures associated with the ISA Program (PQAPP ID# L-HEEAD-0030253-QP-1-0). All QA objectives and measurement criteria detailed in the PQAPP have been employed in developing this ISA. Quality assurance checks were conducted on numerical entries used in the appendices, and at a minimum, the numbers obtained from every tenth reference cited in the appendices were verified against the original source by an independent scientist for accuracy. Furthermore, publicly available databases (e.g., National Emissions Inventory, Air Quality System database) from which data was used in analyses were verified to have their own QA processes in place. U.S. EPA QA staff are responsible for the review and approval of all quality-related

documentation. Because this is a Highly Influential Scientific Assessment, U.S. EPA QA staff performed a Technical System Audit on the ISA in June 2018 and August 2019. These audits verified that the appropriate QA/QC procedures and reviews were adequately performed and documented.

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## 1.2 Introduction to the Appendices

The appendices and [Integrated Synthesis](#) serve different purposes in this ISA. The [Integrated Synthesis](#) is meant to summarize the key messages derived from assessment of the policy relevant science of NO<sub>y</sub>, SO<sub>x</sub>, and PM in this review of the secondary National Ambient Air Quality Standards. It provides a general introduction to the purpose, process, development, and organization of the ISA as well as highlights connections, concepts, and changes based on new evidence and causality. In addition, the [Integrated Synthesis](#) provides a discussion of uncertainty and a synthesis of information on the recovery of ecosystems from N and S deposition.

While the purpose of the [Integrated Synthesis](#) is to synthesize, integrate, and provide key messages, the purpose of the appendices is to provide a more detailed description of the state of science for specific topic areas. [Appendix 1](#) is an introduction to the purpose and organization of [Appendix 2–Appendix 16](#). [Appendix 2](#) characterizes the sources, atmospheric processes, and the trends in ambient concentrations and deposition of NO<sub>y</sub>, SO<sub>x</sub>, and PM. [Appendix 3](#) describes the direct effects of NO<sub>y</sub> and SO<sub>x</sub> gases on plants and lichens. [Appendix 4–Appendix 6](#) describe the effects of N and S deposition on biogeochemistry and the biological effects of acidification and N enrichment in terrestrial environments. [Appendix 7](#) describes the effects of N and S deposition on aquatic biogeochemistry. [Appendix 8–Appendix 10](#) characterize the biological effects of freshwater acidification, freshwater N enrichment, and N enrichment in estuaries and near-coastal systems. [Appendix 11](#) describes the effects of N deposition on wetlands, and [Appendix 12](#) characterizes the ecological effects of S as a nutrient. [Appendix 13](#) presents information on climate modification of ecosystem response to N and S, while [Appendix 14](#) discusses ecosystem services. [Appendix 15](#) is a review of the ecological effects of forms of PM, not related to N or S deposition. Finally, [Appendix 16](#) presents case studies for six locations in the U.S. (southern California, northeastern U.S., Rocky Mountain National Park, southeastern Appalachia, Tampa Bay, and the Adirondacks) where data are sufficient to well characterize the ecological effects of N and S deposition. These sites would therefore make good candidates to assess risk and exposure by exploring linkages across various effects and ecosystems-types in a specific location.

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## APPENDIX 2 SOURCE TO DEPOSITION

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### 2.1 Introduction

In this appendix, emphasis is placed on those species subject to atmospheric processes relevant for review of the air quality criteria and associated welfare-based secondary National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen, oxides of sulfur, and/or particulate matter (PM). As such, this appendix largely focuses on examining the fundamental and applied science of atmospheric processes relevant to assessing environmental exposures and effects associated with atmospheric deposition of nitrogen (N) and sulfur (S) species, including those present in PM.<sup>1</sup> Together this information serves as a prologue to the detailed descriptions of the evidence of ecological effects from oxidized and reduced N and oxidized S, including those present in PM, that follow in later appendices.

Recent advances in research on N and S emissions sources, atmospheric transformation and transport, measurement and modeling techniques, atmospheric loadings, and deposition processes relevant to this review of the NAAQS are evaluated in this appendix. N and S species of interest are generally classified into three groups: oxidized nitrogen, reduced nitrogen, and oxidized sulfur. While NO<sub>2</sub> and SO<sub>2</sub> are the most well known as air pollutants, research on the entire range of oxides of nitrogen and sulfur is considered for review of the air quality criteria. Reduced nitrogen is also discussed because it strongly influences the atmospheric deposition of NO<sub>Y</sub> and SO<sub>X</sub> as well as the chemistry of PM formation. Oxidized nitrogen, reduced nitrogen, and oxidized sulfur all have particulate forms (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>), which together account for a large fraction of PM mass ([U.S. EPA, 2019](#)), as well as gas-phase components that act as major precursors to PM. Thus, a consideration of the combined effects of oxides of nitrogen, oxides of sulfur, and PM requires an understanding of the atmospheric processes involving oxidized nitrogen, reduced nitrogen, and oxidized sulfur.

Oxidized nitrogen species considered here range from nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), collectively referred to as NO<sub>X</sub>, to higher order organic and inorganic oxidation products, collectively referred to as NO<sub>Z</sub> (e.g., pNO<sub>3</sub>, HNO<sub>3</sub>, HONO, PAN, other organic nitrates). NO<sub>Z</sub> is especially relevant when considering nutrient addition to ecosystems and the acidification of surface waters. NO<sub>X</sub> and NO<sub>Z</sub> together are referred to

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<sup>1</sup> Since ecological effects of PM are governed mainly by PM composition, the most relevant PM species (nitrate and sulfate) are also species that are derived from sulfur and nitrogen oxide precursors, and there is a high degree of overlap in the discussion of the impacts of NO<sub>Y</sub> and SO<sub>X</sub>, and the impacts of PM<sub>2.5</sub>. The PM ISA ([U.S. EPA, 2009a](#)) provides more extensive information about the atmospheric processes for total PM mass.

as  $\text{NO}_Y$  (i.e.,  $\text{NO}_X + \text{NO}_Z = \text{NO}_Y$ ). Nitrous oxide ( $\text{N}_2\text{O}$ ) is an oxide of nitrogen, but it is not included as a component of  $\text{NO}_Y$ .  $\text{N}_2\text{O}$  contributes to stratospheric ozone depletion and climate forcing [AR5; [IPCC \(2013\)](#)], but it contributes little to N deposition, and is not included in this appendix.

Reduced nitrogen species are  $\text{NH}_3$  and  $\text{NH}_4^+$  as well as reduced organic nitrogen compounds.  $\text{NH}_3$  and  $\text{NH}_4^+$  together are referred to as  $\text{NH}_X$  (i.e.,  $\text{NH}_3 + \text{NH}_4^+ = \text{NH}_X$ ). Reduced nitrogen contributes to acidification and N enrichment, and it also has a key role in neutralizing acidity in cloud, fog, and rainwater as well as aqueous aerosol particles formed from atmospheric oxidation of  $\text{SO}_2$  and  $\text{NO}_X$ . Additionally,  $\text{NH}_3$  is a precursor for atmospheric particulate matter, reacting with gas-phase nitric acid ( $\text{HNO}_3$ ) to form ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), a major component of N deposition in many areas of the U.S. For this assessment,  $\text{NO}_Y$  and  $\text{NH}_X$  are grouped together as total reactive nitrogen,  $\text{N}_r$  (i.e.,  $\text{NO}_Y + \text{NH}_X = \text{N}_r$ ).  $\text{N}_r$  does not include nitrous oxide and reduced organic nitrogen compounds. However, to the extent it is available, information on the sources, abundances, and fate of reduced organic nitrogen is included in the sections that follow.

Gaseous oxides of sulfur ( $\text{SO}_X$ ) is defined to include sulfur monoxide ( $\text{SO}$ ), sulfur dioxide ( $\text{SO}_2$ ), sulfur trioxide ( $\text{SO}_3$ ), and disulfur monoxide ( $\text{S}_2\text{O}$ ). Of these only  $\text{SO}_2$  is present in the lower troposphere at concentrations relevant for environmental considerations. However,  $\text{SO}_2$  interacts with particles and cloud drops and is oxidized to sulfate.  $\text{SO}_2$  and sulfate ( $\text{SO}_4^{2-}$ ) account for much of the acidification of surface water in the U.S. and together these make up total oxides of sulfur discussed in this appendix ( $\text{SO}_X$ ).

Particulate matter (PM) impacts discussed in this document are also mainly focused on N and S containing species, which together usually make up a large fraction of the fine PM mass in many areas of the U.S. and have better understood and potentially greater ecological impacts than other PM components. PM is usually classified into two size fractions which differ in their physical and chemical characteristics, atmospheric behavior, and health and environmental effects. These are  $\text{PM}_{2.5}$ , particles smaller than 2.5  $\mu\text{m}$  in diameter, and  $\text{PM}_{10-2.5}$ , particles with diameter between 2.5 and 10  $\mu\text{m}$ . Ecological impacts of PM depend largely on its composition ([U.S. EPA, 2009a, 2004](#)). Together  $\text{PM}_{2.5}$  and  $\text{PM}_{10-2.5}$  make up  $\text{PM}_{10}$ . PM contains numerous individual components representing a wide range of chemical and physical properties. However, in most areas of the U.S.  $\text{PM}_{2.5}$  mass is composed mainly of sulfate, nitrate, and organic materials. In contrast,  $\text{PM}_{10-2.5}$  is composed of crustal material similar in composition to soil in the area where the  $\text{PM}_{10-2.5}$  is found, as well as sea salt in coastal areas. There is little discussion of  $\text{PM}_{10-2.5}$  effects in this document because in most rural and remote areas  $\text{PM}_{10-2.5}$  is largely due to natural sources like soil and sea salt.

There are several other reasons for focusing on the sulfate and nitrate fraction of  $PM_{2.5}$  mass in this document in addition to the observation that they often account for most  $PM_{2.5}$  mass. Together they also usually account for an even greater fraction of  $PM_{2.5}$  in rural and remote areas that make up most of the U.S. land mass over which effects in this document are relevant. While organic matter can also account for a large fraction of  $PM_{2.5}$ , it is composed of a wide variety of individual compounds that cannot be identified at a molecular level, making it difficult to assess ecological impacts. Also, there is little information on organic PM impacts, except for individual compounds that make minor contributions to mass. As a result, the main contributors to  $PM_{2.5}$  mass for which ecological impacts can be readily assessed are limited to sulfate and nitrate, which are also components of total oxides of sulfur and oxides of nitrogen, respectively. Since ecological effects of PM are governed mainly by PM composition, the most relevant PM species (nitrate and sulfate) are also species that are derived from sulfur and nitrogen oxide precursors, and there is a high degree of overlap in the discussion of the impacts of  $NO_y$  and  $SO_x$ , and the impacts of  $PM_{2.5}$ .

In addition to nitrogen (N) and sulfur (S) and their transformation products, other PM components such as trace metals and organics are deposited to ecosystems and may subsequently impact biota. Evidence for effects of PM on ecological receptors include direct effects of airborne PM on radiative flux and both direct and indirect effects of deposited particles. Direct effects include alteration of leaf processes from deposition of PM (“dust”) to vegetative surfaces ([U.S. EPA, 2009a](#)). Indirect effects encompass physiological responses associated with uptake of PM components and alterations to ecosystem structure and function (see [Appendix 15](#)).

Much of the discussion in sections dealing with chemistry, measurement, and deposition (both wet and dry) focus on sulfuric acid ( $H_2SO_4$ ) and  $HNO_3$ , which have been long established as the major species contributing to acid rain. Other N and S species that either hydrolyze to form acids are also included, along with organic acids, to the extent that they contribute substantively to acidification of terrestrial (see [Appendix 5](#)) and aquatic environments (see [Appendix 8](#)) and/or N enrichment (see [Appendix 6](#), [Appendix 7](#), [Appendix 10](#), and [Appendix 11](#)).

Major sources of the precursors ( $NO_x$ ,  $SO_2$ ) to the formation of  $HNO_3$  and  $H_2SO_4$  include on- and off-highway vehicles and electricity-generating units (EGUs).  $SO_2$  is oxidized to  $H_2SO_4$  either in the gas phase or cloud water by several well-known mechanisms.  $NO_2$  is oxidized to  $HNO_3$ , which can either deposit as  $HNO_3$  or interact with  $NH_3$  to form particulate  $NH_4NO_3$ .  $NH_4NO_3$  can exhibit semivolatile behavior that can substantially alter the distance over which  $NH_3$  and  $HNO_3$  can travel. Reduced organic nitrogen species, which could have large agricultural sources, can constitute a substantial fraction

of N delivered to ecosystems by precipitation. In areas where the rainwater pH is greater than about 4.5, pH is not exclusively controlled by N and S species, as organic acids such as formic, acetic, and oxalic acids can be major contributors to the acidity of rainwater.

A wide variety of N containing compounds, consisting of oxidized and reduced organic and inorganic species contribute to wet and dry deposition. In general, deposition of reduced (organic + inorganic) N exceeds that of oxidized N across the contiguous U.S. (CONUS). Nationwide, deposition of N species occurs mainly by dry deposition of  $\text{HNO}_3$  and  $\text{NH}_3$ . The pattern is more complex for S in that for large areas, mainly in the central U.S., wet deposition tends to dominate over dry deposition. However, in some regions mostly in the west, dry deposition of mainly  $\text{SO}_2$  makes a greater contribution than wet deposition.

Precipitation chemistry has been monitored at a large number of sites across the U.S. for several decades as part of the National Atmospheric Deposition Program (NADP). Concentrations of inorganic gas and particulate phase N and S species have been monitored across the U.S. since 1990 by the Clean Air Status and Trends Network (CASTNET). These concentrations are used in atmospheric models to infer dry deposition (i.e., the transfer of gaseous and particulate pollutants from the atmosphere to the surface by impaction through turbulent motions and gravitational settling). Starting in 2007, monitoring of  $\text{NH}_3$  was initiated at a subset of CASTNET sites. Cloud deposition, which can account for the bulk of deposition at high elevations in mountainous areas, is monitored at two locations on a regular basis, but has been the subject of shorter term field studies in various locations in the U.S.

Although the pH of rainwater has increased noticeably across the U.S., coincident with notable decreases in the wet deposition of nitrate and sulfate since 1990, there are still widespread areas, mainly in the eastern U.S., affected by acid precipitation. Deposition of total nitrogen has not reflected the continuing decrease in  $\text{NO}_x$  emissions, largely because deposition of  $\text{NH}_3$  has increased. Large areas, at least one-third of the contiguous U.S. (CONUS), are estimated to receive at least 10 kg/ha/yr wet + dry deposition of reactive nitrogen species. This estimate is likely too low because reduced organic nitrogen species are not measured by the routine monitoring networks or considered in air quality models such as U.S. EPA's Community Multiscale Air Quality (CMAQ) modeling system.

Three of the four major contributors to inorganic N deposition are included in the definitions of either oxides of nitrogen or particulate matter:  $\text{HNO}_3$  is an oxide of nitrogen,  $\text{NH}_4^+$  is a PM component, particulate  $\text{NO}_3^-$  is both a PM component and an oxide of nitrogen. The fourth major contributor,  $\text{NH}_3$ , is neither an oxide of nitrogen nor a component of particulate matter. In a recent comparison, the contribution of  $\text{NH}_3$  to total inorganic N deposition ranged from 19% in locations in the Northwest U.S. to 63% in

locations in the Southwest U.S., and was generally higher in summer than in winter ([Li et al., 2016d](#)). In general, the majority of inorganic N deposition was accounted for by oxides of nitrogen and particulate matter in the Northwest, Northeast, Southeast, and Rocky Mountains, but the contribution of oxides of nitrogen and particulate matter was roughly equivalent to contributions from NH<sub>3</sub> in the Upper Midwest, Florida, and smaller in the Southwest ([Li et al., 2016d](#)). However, because NH<sub>3</sub> is a PM precursor, it can also be definitively stated that inorganic N deposition is entirely accounted for by oxides of nitrogen, PM components, and PM precursors.

Since the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria* [hereafter referred to as the 2008 ISA; [U.S. EPA \(2008a\)](#)], there have been a number of new developments. These apply to methods, such as data-model fusion to integrate information for deposition across the U.S.; the use of chemistry-transport models linking deposition to ambient air quality; the expansion of CASTNET monitoring to include NH<sub>3</sub> and NO<sub>y</sub> at selected sites and intercomparisons of monitoring methods with research grade instruments; and advances being made in satellite-based measurements in conjunction with chemistry-transport model simulations of tropospheric NO<sub>2</sub>, SO<sub>2</sub>, and NH<sub>3</sub> that will allow mapping of dry deposition over remote areas with spatial resolution of ~10 km × 10 km. These new developments are described in the following sections of this appendix. [Appendix 2.2](#) considers sources and emissions of N, S, and PM to the atmosphere. [Appendix 2.3](#) summarizes the atmospheric chemical transformations of N and S compounds and formation of PM that occur during transport from sources to deposition to the surface. [Appendix 2.4](#) describes measurement of relevant atmospheric species, including national monitoring networks and methods. [Appendix 2.5](#) discusses the use of chemical transport models to estimate deposition. [Appendix 2.6](#) shows the geographic distributions of atmospheric concentrations and deposition of N, S, and PM.

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## 2.2 Sources of Nitrogen and Sulfur Compounds and Particulate Matter to the Atmosphere

This section describes advances in our understanding of NO<sub>x</sub>, NH<sub>3</sub>, and SO<sub>2</sub> emissions. [Appendix 2.2.1](#) describes annual national emissions of each species based mainly on the 2014 National Emissions Inventory (NEI). [Appendix 2.2.2](#) describes methods of estimating emissions. Methods for major sources of SO<sub>2</sub> and NO<sub>x</sub> are reliable and have remained largely the same since the last review. The same is true to an extent for direct PM emissions. However, there have been fundamental changes in methods for estimating NH<sub>3</sub> emissions, and these are described in some detail. [Appendix 2.2.3](#) describes emission uncertainties, including recent comparisons between NEI data and alternative

methods of estimating emissions. Geographic distributions of emissions are presented in [Appendix 2.5](#), where they can be more directly compared with concentration and deposition data.

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## 2.2.1 National Emissions by Source

N and S containing compounds contributing to deposition can be either primary (i.e., directly emitted from sources) or secondary (i.e., produced from atmospheric reactions involving precursor species directly emitted from sources). Major primary species include NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub>, and reduced organic nitrogen (RON).

[Table 2-1](#) shows nationwide emissions of NO<sub>x</sub>, SO<sub>2</sub>, and NH<sub>3</sub> by source category compiled from the 2014 National Emissions Inventory (NEI) and other sources. Emissions estimates are not available for RON. For the most part, NO<sub>x</sub>, SO<sub>2</sub>, and NH<sub>3</sub> are each emitted by different sources. NO<sub>x</sub> emissions come from several important sources. Highway vehicles are the largest source category of NO<sub>x</sub> emissions nationwide, but off-highway vehicles, EGUs, other stationary fuel combustion, industrial processes, fires, and biogenic emissions from soil are all substantial contributors to total NO<sub>x</sub> emissions. Lightning is not included in the NEI, but it can also contribute substantially to total NO<sub>x</sub> emissions. Although lightning is shown as a relatively modest source of NO<sub>x</sub>, most production by lightning occurs during the summer and is the highest in the south-central and southwestern U.S. ([Zhang et al., 2012a](#)).

NH<sub>3</sub> originates mainly from agricultural sources, which account for ~80% of its emissions nationwide. Major sources are livestock waste, including confined animal feeding operations, and soils, after addition of N containing fertilizers. Fertilizer application occurs mainly during spring and summer. Emissions from livestock waste are roughly three times those from fertilizer application. In addition to NH<sub>3</sub>, reduced organic compounds such as urea and a wide range of proteins and other biological components are also emitted as the result of agricultural activity. [Xing et al. \(2013\)](#) observed that in contrast to SO<sub>2</sub>, NO<sub>x</sub>, and other pollutants, total national emissions of NH<sub>3</sub> increased from 1990 to 2010. The authors attributed this to agricultural emissions, including livestock, which they also identified as the dominant source of NH<sub>3</sub> emissions in the continental U.S. However, regionally the relative importance of agricultural and vehicle emissions is likely to be variable. The deposition of reduced nitrogen can be three times higher near roads ([Bettez et al., 2013](#)), and motor vehicles can be a substantial contributor to total NH<sub>3</sub> emissions in urban areas ([Baum et al., 2001](#)).

**Table 2-1 Emissions of NO<sub>x</sub> (nitric oxide + nitrogen dioxide), sulfur dioxide, and ammonia by source category for 2017 (Teragrams<sup>a</sup> N, S/yr).**

	NO <sub>x</sub>	SO <sub>2</sub>	NH <sub>3</sub>
Highway vehicles	1.0	0	0.1
Off-highway	0.7	0.1	<0.1
Utilities (fuel combustion)	0.3	0.6	<0.1
Other stationary (fuel combustion)	0.3	0.1	<0.1
Industrial and other processes	0.4	0.4	0.2
Livestock waste	0	0	1.9
Fertilizer application	0	0	0.7
Fires: wild, prescribed and agricultural	0.4	0.1	0.3
Biogenic	1.4	-- <sup>b</sup>	<0.1 <sup>c</sup>
<b>Total</b>	<b>3.3</b>	<b>1.2</b>	<b>3.2</b>

N = nitrogen; NH<sub>3</sub> = ammonia; NO<sub>x</sub> = the sum of nitric oxide and nitrogen dioxide; S = sulfur; SO<sub>2</sub> = sulfur dioxide; yr = year.

<sup>a</sup>1 Teragram = 1 × 10<sup>9</sup> kg.

<sup>b</sup>Not applicable.

<sup>c</sup>[Bouwman et al. \(1997\)](#).

Source: <https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data> update except as noted.

SO<sub>2</sub> emissions are dominated by stationary sources burning fossil fuels, particularly EGUs, which contribute about half of total nationwide SO<sub>2</sub> emissions. SO<sub>2</sub> emissions densities in most counties east of the Mississippi River are larger than in most counties in the West (see [Appendix 2.6.5](#)).

Emissions of NO<sub>x</sub> and SO<sub>2</sub> have decreased appreciably in recent years. National emissions of NO<sub>x</sub> have decreased by 61%, and national SO<sub>2</sub> emissions by 89% from 1990 to 2017 ([OAQPS-Emissions Inventory and Analysis Group, 2016](#)). Further details of declining emissions for these species can be found in the ISAs for health effects for NO<sub>x</sub> and SO<sub>2</sub> ([U.S. EPA, 2017d, 2016f](#)). In contrast, nationwide primary PM<sub>2.5</sub> and PM<sub>10</sub> emissions estimates have changed little between the 2002 NEI ([U.S. EPA, 2009a](#)) and the 2017 NEI ([U.S. EPA, 2020a](#)), with national PM<sub>2.5</sub> emissions estimates decreasing from 5.8 to 5.7 MMT, and PM<sub>10</sub> emissions estimates decreasing from 21.6 to 17.1 MMT. National annual NH<sub>3</sub> emissions have fluctuated as a result changes in both emissions and

methods of estimating emissions. However, no clear trend is evident in national NH<sub>3</sub> emissions, with estimates for 1990 and 2017 differing by less than 1%.

Not included in [Table 2-1](#) are primary emissions of PM<sub>2.5</sub> and PM<sub>10</sub>. Nationwide PM<sub>10</sub> emissions according to the 2014 NEI totaled 17.0 MMT. This is somewhat higher than the SO<sub>2</sub>, NO<sub>x</sub>, and NH<sub>3</sub> emissions in [Table 2-1](#), but 85% of these were from dust and fires, dominated by soil and organic matter. By comparison, total nationwide PM<sub>2.5</sub> primary emissions totaled 5.3 MMT based on the 2014 NEI. This is comparable to the totals for NO<sub>x</sub>, SO<sub>2</sub> in [Table 2-1](#) when it is considered that emissions in [Table 2-1](#) are given in terms of mass of N and S and does not include oxygen, while PM<sub>2.5</sub> emissions are based on total mass. However, primary PM<sub>2.5</sub> emissions are also dominated by dust (i.e., agricultural dust and road dust) and fires (i.e., wildfires, prescribed fires, and agricultural fires), which together account for two-thirds of total nationwide PM<sub>2.5</sub> primary emissions. PM<sub>2.5</sub> from these source categories are mainly crustal material (dust) and organic matter (fires).

As described in [Appendix 2.1](#), in rural and remote areas secondary PM<sub>2.5</sub> formed from NO<sub>x</sub> and SO<sub>2</sub> account for a greater fraction of PM<sub>2.5</sub> than primary PM<sub>2.5</sub>. The fraction of PM<sub>2.5</sub> accounted for by NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> formed from SO<sub>2</sub> and NO<sub>x</sub> in various U.S. locations is discussed in [Appendix 2.3](#). The NO<sub>x</sub>, SO<sub>2</sub>, and NH<sub>x</sub> emissions listed in [Table 2-1](#) cannot be used to quantitatively estimate the amount of secondary PM formed because the precursors are not completely converted to PM. However, they provide not only an estimate of emissions that lead to total NO<sub>y</sub> and SO<sub>x</sub>, but also provide an estimate of the emissions that can be used in conjunction with atmospheric models to estimate PM<sub>2.5</sub> concentrations (see [Appendix 2.5](#)). The emissions estimated in [Table 2-1](#) are ultimately responsible for a large fraction of PM<sub>2.5</sub> in many areas, and it is the fraction of PM mass (i.e., SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) for which ecosystem impacts are best understood.

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## 2.2.2 Methods of Estimating Emissions

The source categories used in [Table 2-1](#) represent groups of similar NEI source sectors. Highway Vehicles comprise all on-road vehicles, including light-duty as well as heavy-duty vehicles, both gasoline and diesel powered. Off-highway vehicles and engines include aircraft, commercial marine vessels, locomotives, and nonroad equipment. Utilities (Fuel Combustion), also identified as electric power-generating units (EGUs), are mostly coal burning, but some facilities burn natural gas and other fuels. Other Stationary (Fuel Combustion) includes commercial/institutional, industrial, and residential combustion of biomass, coal, natural gas, oil, and other fuels. Industrial and Other Processes include a variety of different industries, including chemical

manufacturing, cement manufacturing, and oil and gas production. The other processes included in this category include gasoline stations and terminals, commercial cooking, road and construction dust, solvent use, and waste disposal. Agriculture includes both fertilizer application and livestock waste emissions. Fires include wildfires, prescribed fires, and agricultural field burning. The biogenic category includes emissions from vegetation and soil. Both nitrifying and denitrifying organisms in the soil can produce NO<sub>x</sub>, mainly in the form of NO.

Emissions data for each source category listed in [Table 2-1](#) are from the 2014 National Emissions Inventory (NEI), Version 1. The NEI is a national compilation of criteria air pollutant and hazardous air pollutant emissions. The process of estimating emissions is explained for each source in a detailed technical support document for the inventory ([U.S. EPA, 2016b](#)). The NEI is maintained to support the NAAQS, and the Clean Air Act requires states to submit emissions to the U.S. EPA as part of their State Implementation Plans (SIPs). The Air Emissions Reporting Rule (AERR) requires agencies to report all sources of emissions, except fires and biogenic sources. Reporting of open fire sources, such as wildfires, is encouraged, but not required. Data in the NEI come from a variety of sources. The emission values are predominantly from state, local, and tribal agencies and are used wherever they are available, unless there are gaps or problems with submitted data. U.S. EPA quality assures and augments the data provided by states to assist with data completeness using separate augmentation procedures for each source as described in detail in a technical support document to fill in gaps for sources and/or pollutants that are often not reported by state, local, and tribal agencies. The intent is to create the most complete inventory for use in air quality modeling, national rule assessments, international reporting, and other reports. QA procedures and acceptance criteria are detailed in the NEI technical support document ([U.S. EPA, 2016b](#)).

For nonpoint sources, U.S. EPA provides tools that state, local, and tribal agency staff can use to generate emission estimates. For the 2014 NEI, the U.S. EPA developed emission estimates for many nonpoint sectors in collaboration with a consortium of inventory developers from various state agencies regional planning organizations called the Nonpoint Method Advisory (NOMAD) Committee. More detailed NOMAD subcommittees were established to collaborate on methods and emission factors for key nonpoint source categories/sectors, including oil and gas exploration and production, residential wood combustion, agricultural NH<sub>3</sub> sources (including fertilizer and livestock), and industrial and commercial/institutional fuel combustion, among other sources. The U.S. EPA also generates emission estimates as stand-alone data sets covering biogenics, agricultural livestock, fertilizer application, nonroad mobile sources, rail emissions, and commercial marine vessel ports and in-transit (underway) sources. U.S. EPA data sets for sources and pollutants are used only for sources not provided by

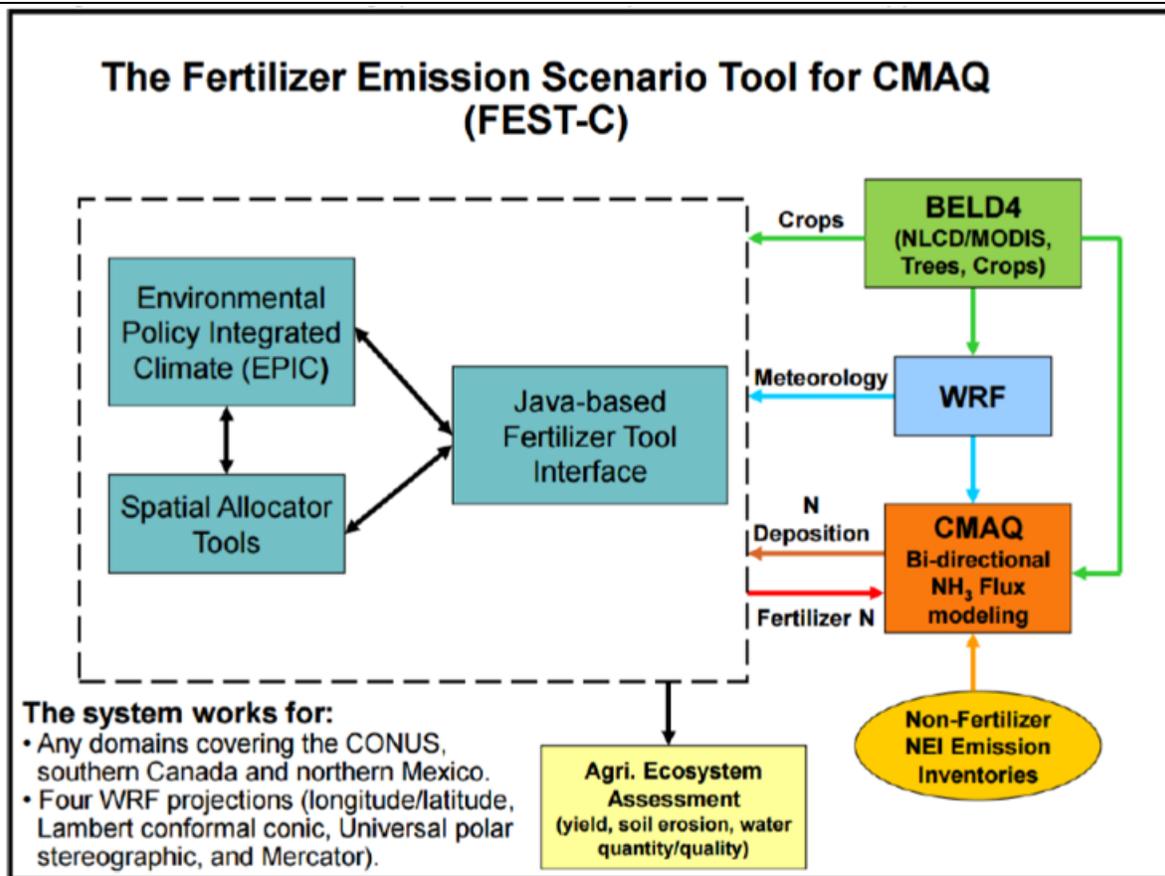
state, local, and tribal data. Tools and methods for estimating emissions from a given source, including EGUs, agricultural livestock, fertilizer application, mobile sources, agricultural and wildland fires (wildfires + prescribed fires), and wood combustion, were described in the 2014 NEI technical support document ([U.S. EPA, 2016b](#)).

The 2014 NEI technical support document provides considerable detail on emission factors and emission estimation methods by source used to generate the data in [Table 2-1 \(U.S. EPA, 2016b\)](#). Methods for estimating PM<sub>2.5</sub> and PM<sub>10</sub> emissions from dust and fire, the two largest national sources, are derived from experimental emission factors along with source specific information (e.g., crop type and tilling frequency for agricultural dust, vehicle weight and miles traveled for unpaved road dust) using source specific equations available in the NEI technical support document. These methods are largely well-established, although they have been updated to accommodate satellite data and emissions modeling improvements, particularly in the case of fire emissions.

Methods for estimating emissions from electric power-generating units and mobile sources, the largest sources of SO<sub>2</sub> and NO<sub>x</sub>, are also well established, and emissions from these sources are decreasing. In contrast, ammonia emissions in the U.S. are increasing ([Butler et al., 2016](#)), and significant uncertainties in the magnitude as well as spatial and temporal variability of NH<sub>3</sub> emissions estimates were reported in the 2008 ISA ([U.S. EPA, 2008a](#)). Two new methods for estimating ammonia emissions from fertilizer applications and livestock waste are highly relevant to understanding NH<sub>x</sub> sources and deposition are provided here as examples, but a similar level of detail is given in the NEI technical support document for other sources of NH<sub>3</sub>, SO<sub>2</sub>, and NO<sub>x</sub>, and a thorough reading of that document is necessary for a full description of emissions estimation methods used to construct [Table 2-1 \(U.S. EPA, 2016b\)](#).

Soil and fertilizer emissions are treated differently in the NEI for NH<sub>3</sub> and NO<sub>x</sub>. For NH<sub>3</sub>, fertilizer application is recognized as a major source for which emissions are specifically estimated, and emissions from fertilizer application are estimated only for NH<sub>3</sub>. The approach to calculating emissions from fertilizer application in the 2014 NEI is a completely new methodology to estimate ammonia (NH<sub>3</sub>) emissions from agricultural soils. The approach to estimate 2014 fertilizer emissions consists of these steps: (1) run the Fertilizer Emissions Scenario Tool for CMAQ FEST-C (v1.2; <https://www.cmascenter.org/fest-c/>) and the bidirectional version of CMAQ (v5.0.2; <https://www.cmascenter.org/>) to produce year 2011 nitrate (NO<sub>3</sub>), ammonium (NH<sub>4</sub><sup>+</sup>, including urea), and organic (manure) nitrogen (N) fertilizer usage estimates, and gaseous ammonia NH<sub>3</sub> emission estimates respectively; (2) calculate county-level emission factors for 2011 as the ratio of bidirectional CMAQ NH<sub>3</sub> fertilizer emissions to FEST-C total N fertilizer application; (3) run FEST-C to produce year 2014 NO<sub>3</sub>, NH<sub>4</sub><sup>+</sup> (including

Urea), and organic (manure) nitrogen fertilizer usage estimates; and (4) multiply county-level 2014 FEST-C total fertilizer estimates by the 2011 emission factors to estimate 2014 NH<sub>3</sub> emissions. FEST-C reads land use data from the Biogenic Emissions Land Use Dataset (BELD) Version 4, meteorological variables from the Weather Research and Forecasting (WRF v3.7.1) model (<https://www.mmm.ucar.edu/weather-research-and-forecasting-model>) and nitrogen deposition data from a previous or historical average CMAQ simulation. The Environmental Policy Integrated Climate (EPIC) modeling system (<http://epicapex.tamu.edu/>) provides information regarding fertilizer timing, composition, application method, and amount. [Figure 2-1](#) provides a comprehensive flowchart of the complete EPIC/FEST-C/WRF modeling system.

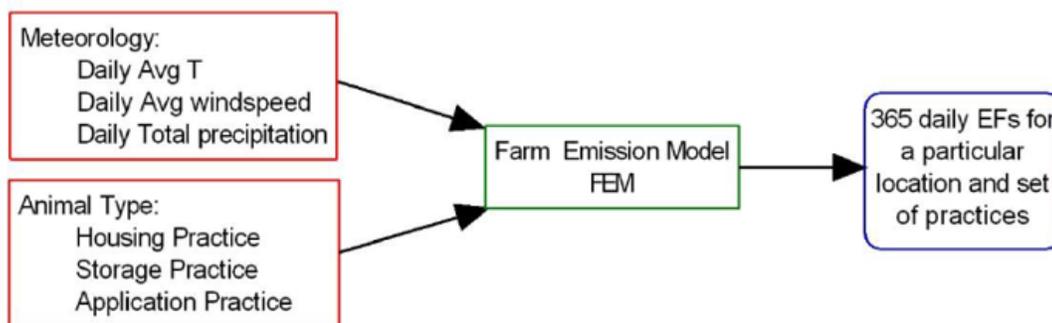


Source: [U.S. EPA \(2016b\)](#).

**Figure 2-1 Modeling system used to compute 2014 Fertilizer Application Emissions.**

Fertilizer application can also lead to NO<sub>x</sub> emissions, but it does not dominate soil emissions of NO. Biogenic emissions of NO are computed based on 2014 meteorology data from the Weather Research and Forecasting (WRF) model version 3.8 (WRF v3.8) and using the Biogenic Emission Inventory System, Version 3.61 (BEIS 3.61) model, based on land use and vegetation data ([U.S. EPA, 2016b](#)). The contribution of fertilizers to soil NO<sub>x</sub> emissions is not estimated in the NEI, but it has been estimated as 10% globally ([Hudman et al., 2012](#)). Biogenic emissions of NH<sub>3</sub> are not estimated in the NEI, but aside from fertilizer application it is a minor contributor, as shown in [Table 2-1](#). Further details on estimating biogenic NO<sub>x</sub> emissions are given in the NEI Technical Support Document ([U.S. EPA, 2016b](#)).

Livestock waste is another important source of ammonia in the U.S. In the 2014 NEI, the U.S. EPA has updated the methodology for ammonia emissions from the housing/grazing, storage and application of manure from beef cattle, dairy cattle, swine, broiler chicken, and layer chicken production. Cows, swine, and chickens account for 95% of national NH<sub>3</sub> emissions from livestock waste in 2014. The approach to estimate 2014 livestock NH<sub>3</sub> emissions from these animals consists of these general steps: (1) estimate 2014 county-level animal populations using 2012 and 2014 USDA agricultural census data; (2) use a model developed by Carnegie-Mellon University ([McQuilling and Adams, 2015](#); [Pinder et al., 2004a](#); [Pinder et al., 2004b](#)) to produce daily resolved, climate-level emission factors for a particular distribution of management practices for each county and animal type, as expressed as emissions/animal; and (3) multiply the county animal populations by the daily emission factor for each county and animal type to estimate emissions per day and sum daily emissions across the entire year for each county and SCC to produce annual emissions for use in the NEI. The model inputs and outputs are shown in [Figure 2-2](#).



Source: [U.S. EPA \(2016b\)](#).

**Figure 2-2 Process to produce specific location and practice specific daily emission factors for livestock waste.**

Similar details are given for estimating emissions for major sources of NO<sub>x</sub> and SO<sub>2</sub> in the NEI technical support document ([U.S. EPA, 2016b](#)), including EGUs, on-road mobile sources, marine vessels, locomotives, other nonroad sources, airports, rail yards, landfills, agricultural and wildland fires, wood combustion, other fuel residential and industrial fuel combustion, charcoal grilling, waste disposal, vegetation and soil, and other sources. Air emissions data from the 2014 Toxic Release Inventory (TRI) were also used in the 2014 NEI to supplement point source NH<sub>3</sub> emissions provided to the U.S. EPA by state, local, and tribal agencies. The TRI is a U.S. EPA database containing data on disposal or other releases including air emissions of over 650 toxic chemicals from approximately 21,000 facilities. Data are submitted annually by U.S. facilities that meet TRI reporting criteria.

### 2.2.3 Evaluation and Uncertainty

As described in the 2008 ISA ([U.S. EPA, 2008a](#)), emissions from different sources in the NEI are estimated with a wide range of methods that include direct measurements, indirect measurements, model predictions, and assumptions. Because there are unknown, incomplete, and variable emission rates, as well as unknown sources that are not represented, the NEI reflects an on-going process of updating increasing or declining emissions, improving estimation methods, and filling data gaps as measurements become available or understanding of emissions changes. Often, steps are taken to reduce errors in estimation as they are discovered, resulting in improved estimates as uncertainties are found. For example, the estimate of [Gilliland et al. \(2003\)](#) that annual NEI NH<sub>3</sub> was 37%

higher than estimates based on modeled  $\text{NH}_4^+$  deposition led to the development of lower emission factors for nondairy cows and swine ([U.S. EPA, 2008a](#)). Because of these unknowns and limitations, quantitative uncertainty estimates based on probability density functions or other statistical methods are not provided with NEI data. Instead, emission factors receive a rating based on the reliability of methods used for determining the emission factor. The rating is based on both the number of representative sources and the characteristics of the data used to determine the emission factor, but it does not imply statistical error bounds or confidence intervals for the emission factor ([U.S. EPA, 1996](#)).

As an alternative, uncertainties are often evaluated through separate efforts using a variety of techniques. These techniques include comparing inventory predictions with measured long-term trends, comparing emission estimates derived from principle component analysis or other statistical methods, comparing emissions estimated by inverse modeling of chemical transport models, and comparison with satellite data ([U.S. EPA, 2008a](#)). The distinction between the inventory compilations like the NEI and alternative satellite- and model-based methods of estimating emissions is generally described in terms of bottom-up and top-down estimates. The entries in emissions inventories are obtained using a bottom-up approach, in which entries are based on emissions factors, activity rates, and control device efficiency for various source types. This contrasts to a top-down approach in which measurements of pollutant concentrations from satellites, aircraft, or surface monitors are used to constrain a priori estimates of emissions using a chemistry-transport model (CTM).

Because of this variety of top-down approaches and the number of separate studies resulting in a wide range of estimated uncertainties, there is no single estimate of uncertainty that applies to either total emissions or emissions from individual sources in [Table 2-1](#). However, reports from numerous publications on emissions inventory evaluation have resulted in a wide range of uncertainty estimates for application to NEI data, and these were summarized in the 2008 ISA ([U.S. EPA, 2008a](#)). Across all sources, total  $\text{NO}_x$  emissions estimates from satellite data ranged from “highly consistent” with NEI estimates ([Martin et al., 2006](#)) to 68% higher than NEI estimates ([Jaegle et al., 2005](#)). Fewer estimates of individual source emissions were evaluated, with  $\text{NO}_x$  emissions both higher and lower than estimates using other methods.

Some recent work has shown summertime over-prediction of model  $\text{NO}_x$  estimates using recent U.S. EPA inventories (e.g., 2008 and 2011) when compared against monitored ambient concentrations ([Canty et al., 2015](#); [Anderson et al., 2014a](#)). [Appel et al. \(2017\)](#) found in their simulations that  $\text{NO}_x$  model over-estimates in summer were greatly diminished or reversed in other seasons. [Anderson et al. \(2014a\)](#) and [Travis et al. \(2016\)](#) concluded that emissions of  $\text{NO}_x$  from mobile sources are being overestimated and are

the source of this bias. Studies over Texas ([Souri et al., 2016](#); [Tang et al., 2015](#)) suggested a smaller or no bias in on road NO<sub>x</sub> emissions compared to [Anderson et al. \(2014a\)](#) and [Travis et al. \(2016\)](#), and suggested that both high and low biases in other NO<sub>x</sub> source categories (e.g., area sources, point sources, soil NO) impact model/measurement discrepancies. [Marr et al. \(2013\)](#) used near-road measurements to also conclude that mobile source NO<sub>x</sub> emissions in U.S. EPA's 2008 NEI agreed well with measurements (i.e., within 3%). The cause of discrepancies between measured and modeled concentrations are difficult to diagnose because the emission modeling process and associated photochemical modeling is complex. Researchers are continuing to investigate this question.

There can be higher uncertainties for specific sources. For example, about 60% of the total NO<sub>x</sub> emitted by soils nationwide is estimated to occur in the central Corn Belt of the U.S. Spatial and temporal variability in soil NO<sub>x</sub> emissions can lead to uncertainty in emissions estimates. Soil emissions occur mainly during summer and across the entire country, including areas where anthropogenic emissions are low. Emission rates depend primarily on fertilization amount, soil temperature, and moisture. Models of NO<sub>x</sub> emissions from soils [e.g., [Hudman et al. \(2012\)](#)] include these dependencies, but most measurements on which they are based are made at temperatures <30°C. However, in agricultural areas subjected to very high temperatures (>40°C) like the Imperial Valley, CA, emissions factors for NO following fertilizer application ranged from 1.8 to 6.6%, as compared to estimates of typically ~1 to 2% ([Oikawa et al., 2015](#)). [Oikawa et al. \(2015\)](#) also suggested that in many areas of the Southwest, the NEI overestimates anthropogenic emissions at the expense of soil emissions and that these soil emissions have a noticeable effect on ozone formation. [Travis et al. \(2016\)](#) estimated that combustion accounts for 68% of NO<sub>x</sub> emissions in the Southeast in summer, with the remainder from soils. These results indicate that soil emissions need to be better understood. Estimating emissions from highway vehicles can also be challenging because there is a wide variation in emissions between different vehicles.

Activity rates and uncertainties for NH<sub>3</sub> are difficult to quantify, and estimates have yet to be made for reduced organic nitrogen. NH<sub>3</sub> emission estimates are generally more uncertain than NO<sub>x</sub> and SO<sub>2</sub> emission estimates because of the variety of agricultural practices used, re-emission after deposition, and the dispersed nature of agricultural processes, as well as the complex influences of meteorology on processes controlling transformation and removal of nitrogen species on spatial and temporal emission patterns. As described in [Appendix 2.5.2](#), NO<sub>2</sub> and NH<sub>3</sub> can be both emitted from and deposited to soils, water, or vegetation depending on their atmospheric concentrations and characteristics of the underlying surface.

Mixed results were reported in evaluating the total NH<sub>3</sub> emissions estimates in the 2008 ISA ([U.S. EPA, 2008a](#)). However, as described above, there have been major changes in estimation methods for the most important ammonia sources since that report, and more recently [Paulot et al. \(2014\)](#) showed that a range of published bottom-up and top-down estimates of annual total U.S. ammonia emissions agreed within 10%. The NEI national estimate of 2.3 Tg NH<sub>3</sub> from [Table 2-1](#) was within 20% of the average across all estimates of  $2.8 \pm 0.2$  Tg NH<sub>3</sub> reported by [Paulot et al. \(2014\)](#). However, in the same comparison there was a divergence in the timing of the seasonal maximum, and agreement varied considerably temporally and spatially ([Paulot et al., 2014](#)).

Most SO<sub>2</sub> emissions originate from point sources having well-known locations and identifiable fuel streams. Uncertainties in annual emissions were estimated to range from 4 to 9% for SO<sub>2</sub> and slightly larger for NO<sub>x</sub> from the same point sources identified in the 1985 NAPAP inventories for the U.S. ([Placet et al., 1990](#)).

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## 2.3 Atmospheric Chemistry of Nitrogen and Sulfur Species and Particulate Matter (PM)

The atmospheric chemistry of N and S species relevant for the production of ecosystem nutrients and acidic species was extensively reviewed in the 2008 ISA ([U.S. EPA, 2008a](#)). The main findings from that review and key findings from more recent studies and reviews are included here. [Appendix 2.3.1](#) describes atmospheric NO<sub>x</sub> chemistry and the formation of HNO<sub>3</sub>. [Appendix 2.3.2](#) describes atmospheric sulfur oxide chemistry and the formation of H<sub>2</sub>SO<sub>4</sub>. [Appendix 2.3.3](#) reviews the role of ammonia as the most important atmospheric base for neutralizing atmospheric nitric and sulfuric acids and forming PM. The chemistry of all of these species largely controls the extent of acid deposition as well as the fraction of nitrogen in particulate matter, which in turn determines deposition rate and transport distance. The remaining sections review atmospheric organic sulfur and nitrogen compounds ([Appendix 2.3.4](#)), atmospheric organic acids ([Appendix 2.3.5](#)), and formation of PM<sub>2.5</sub> ([Appendix 2.3.6](#)).

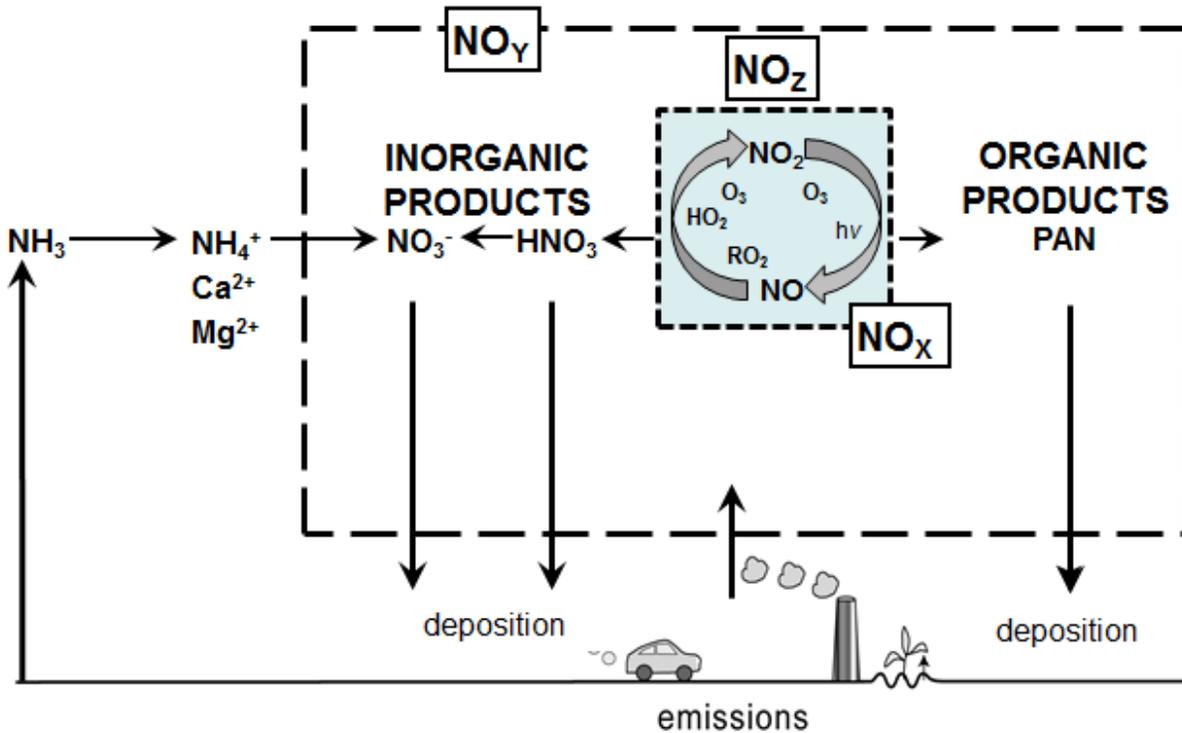
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### 2.3.1 Nitrogen Oxides

NO<sub>x</sub> (NO + NO<sub>2</sub>) is the precursor for oxidized nitrogen species that contribute to acidic deposition. More specific details on the chemistry and transformation of NO<sub>x</sub> can be found in the *2016 ISA for Oxides of Nitrogen—Health Criteria* ([U.S. EPA, 2016f](#)) and for SO<sub>x</sub> in the *2008 ISA for Sulfur Oxides* ([U.S. EPA, 2017d](#)). Hence, those topics are only briefly recounted here with special reference to the secondary NO<sub>x</sub> and SO<sub>x</sub>

NAAQS. Oxidized nitrogen species ( $\text{NO}_Y$ ) are introduced into the atmosphere as  $\text{NO}_X$ , mainly from fossil fuel combustion as described in [Appendix 2.2](#). [Figure 2-3](#) summarizes the atmospheric reactions of  $\text{NO}_X$ , showing rapid inter-conversion of  $\text{NO}$  and  $\text{NO}_2$  in sunlight, with slower formation of more oxidized organic and inorganic products ( $\text{NO}_Z$ ).

A large number of oxidized nitrogen species in the atmosphere are formed from the oxidation of  $\text{NO}$  and  $\text{NO}_2$  (shown in the inner box). These include nitrate radicals ( $\text{NO}_3$ ), nitrous acid ( $\text{HONO}$ ), nitric acid ( $\text{HNO}_3$ ), dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), nitryl chloride ( $\text{ClNO}_2$ ), peroxyntiric acid ( $\text{HNO}_4$ ), peroxyacetyl nitrate (PAN) and its homologues (PANs), other organic nitrates, such as isoprene- and monoterpene-derived nitrates, and particulate nitrate ( $\text{pNO}_3^-$ ). These species (and  $\text{NH}_3$ ) are characterized by large differences in their solubilities ([Table 2-2](#)), which determine their ability to be taken up by cloud droplets, airborne particles, and moist surfaces.



Ca<sup>2+</sup> = calcium ion; HNO<sub>3</sub> = nitric acid; HO<sub>2</sub> = hydroperoxy radicals; hv = energy of solar photon with frequency v;  
Mg<sup>2+</sup> = magnesium; NH<sub>3</sub> = ammonia; NH<sub>4</sub><sup>+</sup> = ammonium; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; NO<sub>3</sub><sup>-</sup> = nitrate ion; NO<sub>x</sub> = the sum of NO and NO<sub>2</sub>; NO<sub>z</sub> = oxidation products of NO<sub>x</sub>; NO<sub>y</sub> = NO<sub>x</sub> + NO<sub>z</sub>; O<sub>3</sub> = ozone; PAN = peroxyacetyl nitrate; RO<sub>2</sub> = organic peroxy radicals.

Note: The inner shaded box contains NO<sub>x</sub> (NO + NO<sub>2</sub>). The outer box contains other species (NO<sub>z</sub>) formed from reactions of NO<sub>x</sub>. All species shown in the outer and inner boxes are collectively referred to as NO<sub>y</sub> by the atmospheric sciences community.

Source: CPHEA.

**Figure 2-3 Schematic diagram showing pathways for reactive nitrogen species in ambient air.**

**Table 2-2 Henry's law coefficients for selected reactive nitrogen species at 25°C in water.**

Compound	Coefficient (mol/kg/bar)
HNO <sub>3</sub>	2.6 × 10 <sup>6</sup>
HONO	49
NO	0.0019
NO <sub>2</sub>	0.012
PAN	4.1
NH <sub>3</sub>	61

1 bar = 10<sup>5</sup> Pa; C = Celsius; HNO<sub>3</sub> = nitric acid; HONO = nitrous acid; NH<sub>3</sub> = ammonia; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; PAN = peroxyacetyl nitrate.

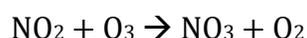
Source: adapted from [Sutton et al. \(2011\)](#).

Reactions producing more oxidized forms of nitrogen (NO<sub>z</sub>) involve mainly O<sub>3</sub>, OH, and organic radicals with NO and NO<sub>2</sub>. The reaction of NO<sub>2</sub> with OH leads directly to HNO<sub>3</sub>:

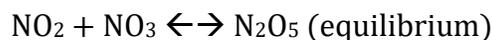


**Equation 2-1**

The reaction of NO<sub>2</sub> with O<sub>3</sub> produces nitrate radical (NO<sub>3</sub>), which reacts further to form dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), and ultimately also produces HNO<sub>3</sub>:



**Equation 2-2**



**Equation 2-3**



**Equation 2-4**

The relative importance of these two paths for producing HNO<sub>3</sub> is strongly location and seasonally dependent, with the first path dominating when OH radicals are abundant (during the day) and the second during the night and under cold conditions. [Warneck \(1999\)](#) estimated that most HNO<sub>3</sub> is formed in the sunlit portions of clouds by the reaction of NO<sub>2</sub> with OH, with much smaller amounts from the pathway involving N<sub>2</sub>O<sub>5</sub> hydrolysis. Because it is highly soluble, HNO<sub>3</sub> is taken up by particles or cloud droplets to form NO<sub>3</sub><sup>-</sup> and is also deposited onto moist surfaces, such as on vegetation. HNO<sub>3</sub> also

recycles back to NO<sub>2</sub> in the gas phase by photolysis and reaction with OH radicals, but on timescales longer than that for uptake by cloud droplets, particles, and the surface.

Whereas photolysis of HNO<sub>3</sub> is slow ( $\tau \sim 10^6$  s) in the gas phase, it can be two orders of magnitude faster on moist surfaces ([Ye et al., 2016](#)), releasing NO<sub>2</sub> and/or HONO back to the atmosphere.

NO<sub>2</sub> reacts with organic peroxy radicals to form organic nitrates such as peroxyacetyl nitrate (PAN) and its homologues as shown on the right side of [Figure 2-3](#); other RO<sub>2</sub>NO<sub>2</sub> compounds are much less stable than PANs. NO and NO<sub>3</sub> radicals also react with organic radicals produced by the oxidation of isoprene and monoterpenes to form a wide range of organic nitrates. Considering the troposphere as a whole, most of the mass of NO<sub>z</sub> shown in [Figure 2-3](#) is in the form of PAN and HNO<sub>3</sub>. However, organic nitrates such as isoprene- and monoterpene-derived nitrates increase in importance in the planetary boundary layer (PBL), and are likely to be dominant in vegetated areas ([Kim et al., 2015a](#); [Min et al., 2014](#)).

In forested areas, the initial step in the production of isoprene nitrates (INs) is most often the reaction of isoprene with OH radicals to produce isoprene peroxy radicals. These can react with HO<sub>2</sub> radicals, other RO<sub>2</sub> radicals, or isomerize to produce a variety of organic compounds. They can also react with NO to produce multifunctional organic nitrates. Lifetimes on the order of one to a few hours can be estimated for these first generation INs based on their reactions with OH radicals and O<sub>3</sub> ([Lockwood et al., 2010](#); [Paulot et al., 2009](#)). The reaction products can further react with NO (after internal rearrangement) to form secondary organic nitrates such as ethanal nitrate, methacrolein nitrate, propanone nitrate, and methyl vinyl ketone nitrate. The second-generation organic nitrates are more stable than the first-generation INs because they lack a double carbon (C = C) bond. Obviously, the relative importance of pathways forming nitrates or other products depends on the ambient concentrations of NO and other oxides of nitrogen for which many key experimental details are still lacking. During the SEAC<sup>4</sup>RS measurement campaign, which took place in the summer of 2013 in the southeastern U.S., [Travis et al. \(2016\)](#) found that these two pathways were of comparable importance.

In addition to oxidation initiated by OH radicals, isoprene is also oxidized by NO<sub>3</sub> radicals. [Rollins et al. \(2009\)](#) determined a yield of first-generation carbonyl nitrates of 70% based on experiments in large reaction chambers. These first-generation nitrates can further react with NO, leading to the production of second-generation organic (alkyl) nitrates. [Mao et al. \(2013\)](#) estimated that the global mean lifetime is ~5 days for these second-generation organic nitrates. [Mao et al. \(2013\)](#) also suggested that the export of INs and other organic nitrates followed by their decomposition is potentially a larger source of NO<sub>x</sub> to the boundary layer of the western North Atlantic Ocean than the export

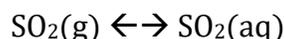
of PANs. Some INs are low enough in volatility that they can partition to the particle phase [e.g., [Rollins et al. \(2009\)](#)]. Once in the particle phase, the INs hydrolyze to form HNO<sub>3</sub> and an alcohol, with a rate constant that correlates strongly with the acidity of the particles ([Rindelaub et al., 2015](#); [Jacobs et al., 2014](#)).

In addition to considering the chemistry of isoprene-derived nitrates during SEAC<sup>4</sup>RS, [Fisher et al. \(2016\)](#) considered the formation of organic nitrates derived from the oxidation of monoterpenes with either one or two double bonds. Their modeling results suggest that isoprene- and monoterpene-derived nitrates account for 25 to 50% and ~10% of total organic nitrates and that production of isoprene- and monoterpene-derived nitrates account for ~20% of the net loss of NO<sub>x</sub> emitted in the Southeast during summer. [Fisher et al. \(2016\)](#) also noted that production of organic nitrates involving biogenic VOCs is the dominant NO<sub>x</sub> sink only in areas where elevated levels of biogenic VOCs coincide with low NO<sub>x</sub> levels (otherwise the major sink would be formation of HNO<sub>3</sub>). As a result, these processes will represent only a minor pathway for NO<sub>x</sub> loss. In any event, as with isoprene-derived nitrates, monoterpene-derived nitrates are also mainly taken up by particles with formation of HNO<sub>3</sub>. Uptake by particles was estimated by [Fisher et al. \(2016\)](#) to account for ~60% of the removal of gas-phase organic nitrates, with ~20% recycled back to NO<sub>x</sub> and another 15% deposited to the surface.

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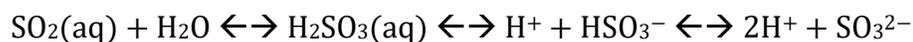
### 2.3.2 Sulfur Oxides

SO<sub>2</sub> is the only gas phase form of SO<sub>x</sub> (SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>) emitted in the tropospheric boundary layer at concentrations of concern for environmental exposures ([U.S. EPA, 2008c](#)). It reacts in both the gas phase and in aqueous solution in clouds and particles to form SO<sub>4</sub><sup>2-</sup>. As described in the 2008 ISA ([U.S. EPA, 2008a](#)), the steps involved in aqueous-phase oxidation of SO<sub>2</sub> begins with dissolution of SO<sub>2</sub> following [Jacobson \(2002\)](#):



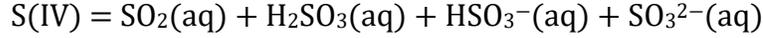
Equation 2-5

and is followed by formation and dissociation of H<sub>2</sub>SO<sub>3</sub>:



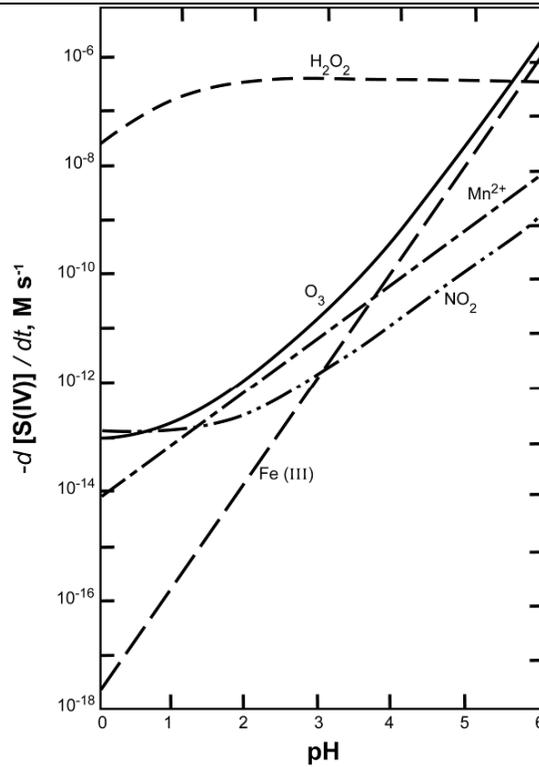
Equation 2-6

Dissolved SO<sub>2</sub> thus rapidly partitions into four forms with the same oxidation state, with their relative concentrations dependent on pH:



Equation 2-7

S(IV) is then oxidized to  $\text{SO}_4^{2-}$  in cloud water primarily by either  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , and  $\text{O}_2$  in the presence of dissolved Fe(III). Reaction with  $\text{H}_2\text{O}_2$  is most important at pH less than about 5.3, and reaction with either dissolved  $\text{O}_3$  or with  $\text{O}_2$  catalyzed by Fe(III) becomes most important at pH greater than about 5.3, as shown in [Figure 2-4 \(Seinfeld and Pandis, 1998\)](#).



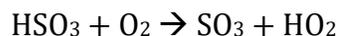
aq = aqueous; Fe(III) = iron (oxidation number III);  $\text{H}_2\text{O}_2$  = hydrogen peroxide; Mn(II) = manganese (oxidation number II);  $\text{NO}_2$  = nitrogen dioxide;  $\text{O}_3$  = ozone; S(IV) = sulfur (oxidation number IV);  $\text{SO}_2$  = sulfur dioxide.  
 Concentrations assumed are:  $[\text{SO}_2(\text{g})] = 5$  ppb;  $[\text{NO}_2(\text{g})] = 1$  ppb;  $[\text{H}_2\text{O}_2(\text{g})] = 1$  ppb;  $[\text{O}_3(\text{g})] = 50$  ppb;  $[\text{Fe(III)(aq)}] = 0.3$   $\mu\text{M}$ ;  $[\text{Mn(II)(aq)}] = 0.03$   $\mu\text{M}$ .  
 Source: [Seinfeld and Pandis \(1998\)](#).

**Figure 2-4** Rate of conversion of sulfur (IV) to sulfur (VI) by different oxidation paths as a function of pH.

The remaining  $\text{SO}_2$  is oxidized to  $\text{H}_2\text{SO}_4$  in the gas phase with a characteristic timescale of ~10 days [based on  $\text{OH} = 10^6/\text{cm}^3$  and rate coefficient =  $1.3 \times 10^{-12}/\text{cm}^3/\text{molec}/\text{s}$ ; [Sander et al. \(2011\)](#)] following a multistep process:



Equation 2-8



Equation 2-9

and/or by



Equation 2-10

where sCI is a stabilized Criegee intermediate ([Berndt et al., 2012](#); [Mauldin et al., 2012](#); [Welz et al., 2012](#)) and products refer to other organic radicals. Criegee radicals are produced by the reaction of alkenes with  $\text{O}_3$  during both night and day. The relative importance of the OH and sCI pathways depends in large measure on the local concentration of alkenes, in particular biogenic alkenes. [Welz et al. \(2012\)](#) also raised the possibility that Criegee radicals might be important for the oxidation of  $\text{NO}_2$  to form nitrate radicals.  $\text{SO}_3$  produced by either path further reacts to form gas-phase  $\text{H}_2\text{SO}_4$  via



Equation 2-11

Because  $\text{H}_2\text{SO}_4$  is extremely soluble, it is removed rapidly by transfer to the aqueous phase of particles and cloud droplets.

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### 2.3.3 Acid Neutralization by Ammonia

As the most common soluble base in the atmosphere,  $\text{NH}_3$  plays a key role in neutralizing the acidity in ambient particles and in cloud, fog, and rainwater resulting from dissolution of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , and the weak acidity due to organic acids. The atmospheric lifetime of  $\text{NH}_3$  with respect to oxidation by OH radicals is ~2 months [based on  $\text{OH} = 10^6 \text{ molec/cm}^3$  and rate coefficient =  $1.6 \times 10^{-13} \text{ /cm}^3 \text{ /molec/s}$ ; [Sander et al. \(2011\)](#)]. As a result, uptake by cloud droplets, particles, and the surface is favored over reaction with OH radicals. [Xu and Penner \(2012\)](#) estimated a globally averaged lifetime for  $\text{NH}_3$  of ~11 hours as a result of these processes, implying strong spatial and temporal variability of  $\text{NH}_3$  concentrations.

Sulfuric acid can be partly or totally neutralized by  $\text{NH}_3$ . [Seinfeld and Pandis \(1998\)](#) defined two regimes: (1) ammonia poor  $[\text{TA}] < 2 [\text{TS}]$  and (2) ammonia rich  $[\text{TA}] > 2 [\text{TS}]$ , where TA and TS refer to total ammonia, ammonium and sulfate concentrations in gas, aqueous, and solid forms. In the first regime, there is partial neutralization; sulfate is in the form of  $(\text{NH}_4)\text{HSO}_4$ , the vapor pressure of  $\text{NH}_3$  is very low, equilibrium favors

formation of ammonium sulfate over ammonium nitrate, any nitrate is driven to the gas phase, and ammonium nitrate levels are low (or even zero). In the second regime, sulfate is in the form of  $(\text{NH}_4)_2\text{SO}_4$ , and any  $\text{NH}_3$  left over could react with  $\text{HNO}_3$  to form  $\text{NH}_4\text{NO}_3$ . However, this conceptual model neglects interactions with organic compounds. Analysis of data by [Kim et al. \(2015a\)](#) from the SEAC<sup>4</sup>RS field study and the Chemical Speciation Network (CSN) during August–September of 2013 indicates that the extent of neutralization of sulfuric acid and acidic sulfate by ammonium was incomplete in the Southeast despite an excess of atmospheric  $\text{NH}_3$ . [Kim et al. \(2015a\)](#) suggested that uptake of  $\text{NH}_3$  is inhibited by organic compounds in particles. This suggestion is in accord with laboratory studies of [Liggio et al. \(2011\)](#) who found that organic compounds, especially terpenes and *n*-alkanes on particle surfaces are effective in inhibiting  $\text{NH}_3$  uptake by particles.

$\text{NH}_4\text{NO}_3$  is in thermodynamic equilibrium with gas-phase  $\text{NH}_3$  and  $\text{HNO}_3$ . The equilibrium constant is extremely sensitive to variations in relative humidity and temperature such that it varies over several orders of magnitude depending on atmospheric conditions, but in general, lower temperature and higher relative humidity (e.g., during winter) shifts the equilibrium towards condensed phase  $\text{NH}_4\text{NO}_3$ . The effects on phase partitioning are pronounced because of the large variation in the equilibrium constant,  $K$ , ( $\sim 10\text{--}10^3$  ppb<sup>2</sup>) between summer and winter conditions in many locations. Also, as noted by [Malm et al. \(2016\)](#),  $\text{NH}_4\text{NO}_3$  can volatilize and reform multiple times during transport away from sources of  $\text{NH}_3$  and  $\text{HNO}_3$ . Because the atmospheric lifetimes of  $\text{NH}_3$ ,  $\text{HNO}_3$ , and  $\text{NH}_4\text{NO}_3$  differ substantially from each other, local conditions of temperature and relative humidity, by implication, control how far these species can travel.

Although the above considerations apply to particles in general, it should be remembered that the mass of airborne particles is present in two distinct size fractions, each with its own characteristic composition [see [U.S. EPA \(2019\)](#)]. These differences determine the size fraction in which  $\text{pNO}_3^-$  will be found. Because  $\text{SO}_4^{2-}$  is found mainly in the fine particle mode these considerations tend to apply more to the atmospheric fine mode. Displacement of HCl (and other hydrohalic acids) from marine aerosol (found typically in the coarse mode) by gas-phase  $\text{HNO}_3$  has long been known to occur, resulting in particulate nitrate ( $\text{pNO}_3^-$ ) being associated with sodium in the coarse mode in many coastal areas. [Brimblecombe and Clegg \(1988\)](#) provided a detailed evaluation of the thermodynamic data and a discussion of this process. [Wolff \(1984\)](#) found that coarse-mode  $\text{pNO}_3^-$  is formed by adsorption of  $\text{HNO}_3$  on basic soil particles (i.e., those containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). These distinctions between the behavior of  $\text{pNO}_3^-$  in the fine and coarse modes are important as deposition rates for these two size modes can differ

appreciably and there can be large differences in the ratio of fine to coarse  $\text{pNO}_3^-$  as shown in [Appendix 2.5.2.1](#).

The composition of rainwater and of particles is strongly affected by pH. As described above, pH determines the distribution of S(IV) species in cloud water, rainwater and the aqueous phase of particles. This in turn impacts their oxidation processes ([Appendix 2.3.2](#)), the solubility of trace metals, and the partitioning of weak acids among other factors. As the most abundant base in the atmosphere,  $\text{NH}_3$  has a strong influence on pH of cloud water. However, the role of  $\text{NH}_3$  as a base is limited to atmospheric processes. Once deposited in soil, oxidation of  $\text{NH}_3$  and  $\text{NH}_4^+$  to  $\text{NO}_3^-$  (during nitrification) produces an amount of  $\text{H}^+$  equivalent to  $\text{HNO}_3$  deposition [[Scheffe et al. \(2014\)](#) and references therein].

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#### 2.3.4 Organic Nitrogen and Sulfur

In addition to deposition of  $\text{NO}_y$  and  $\text{NH}_x$ , the deposition of other nitrogen compounds, in particular dissolved organic nitrogen (DON) also occurs. Proteins, amino acids, urea, amines, and other DON compounds can contribute to acidification in soils and be an important source of nutrients to terrestrial and aquatic environments ([Jickells et al., 2013](#); [Cape et al., 2011](#); [Cornell, 2011b](#); [Sutton et al., 2011](#)). The content of organic nitrogen in particles and rainwater can be characterized in two ways. First, it can be calculated as the difference between total N as measured by total elemental analysis [e.g., [Bronk et al. \(2000\)](#)] minus  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . In the second way, the content of organic nitrogen in particles and rainwater can be characterized by measuring the concentrations of individual species. However, the number of species constituting DON at a particular location can be quite large. For example, [Altieri et al. \(2009a\)](#) detected several thousand organic N containing species in precipitation samples collected in New Jersey and found the overall composition was consistent with oligomerization of amino acids; in most compounds, N was in reduced form.

[Cornell \(2011a\)](#) estimated based on measurements reported in 58 published studies that organic N constitutes 35% of total N in rainwater in North America. [Jickells et al. \(2013\)](#) estimated based on data from a number of measurement sites ( $n = 115$  globally), that average DON in rainwater contributes ~25% of the flux of total nitrogen. They also reasoned that because it is correlated with total nitrogen in rainwater ( $R^2 = 0.57$ ), which has a large anthropogenic component, DON might also have a large anthropogenic component. Further description of DON measured at sites in the CONUS are deferred to [Appendix 2.6.2](#).

A large number of organosulfates (R-O-SO<sub>3</sub>H) have been detected in rainwater samples ([Altieri et al., 2009b](#)). However, their abundances could not be determined. [Tolocka and Turpin \(2012\)](#) estimated that organic sulfates could contribute up to 5 to 10% of organic mass on average to particle mass based on measurements taken at 12 sites across the U.S. [Liao et al. \(2015\)](#) found that organic sulfates accounted a few percent of particulate sulfate, mainly from the two most abundant forms, isoprene epoxydiol sulfate and glycolic acid sulfate. Organic sulfates such as these have high acid dissociation constants and are expected to act as singly charged species.

Phytoplankton emit copious amounts of dimethyl sulfide, which can be oxidized to sulfur dioxide and to methanesulfonic acid. The SO<sub>2</sub> that is formed can then be a source of H<sub>2</sub>SO<sub>4</sub> in coastal areas.

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### 2.3.5 Organic Acids

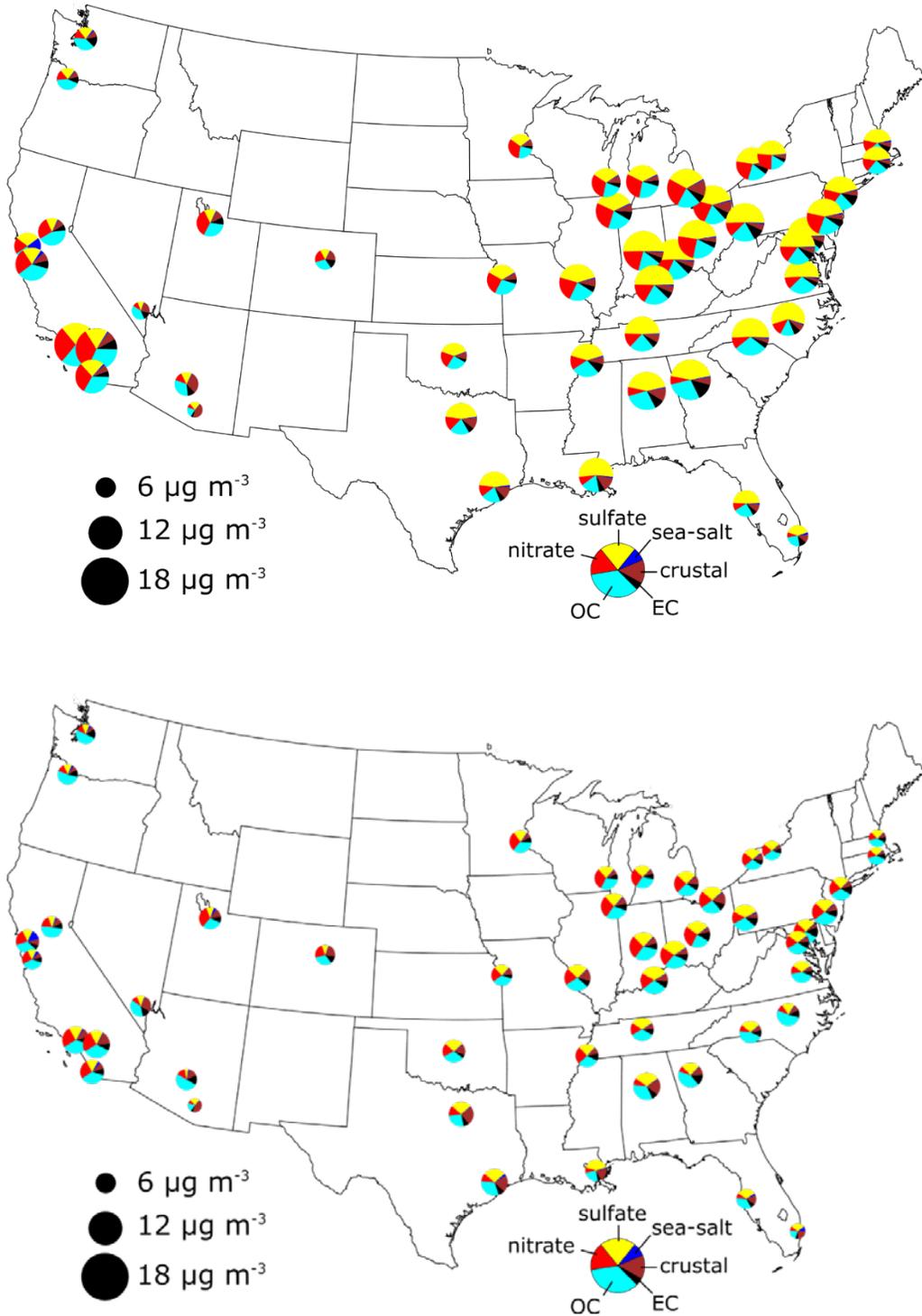
The effects of deposition of acidic sulfur and nitrogen should be considered in the context of a more complete description of the composition of rainwater, including organic acids. However, organic acids are not routinely measured by monitoring networks because they are unstable with respect to microbial degradation following collection. As a result, data for organic acids in rainwater are sparse. Formic and acetic acids are typically the most abundant organic acids found in rainwater in the U.S. ([Willey et al., 2011](#); [Avery et al., 2006](#); [Talbot et al., 1990](#)). They are largely secondary in origin (i.e., produced in the atmosphere by the photochemical oxidation of biogenic and anthropogenic hydrocarbons). [Paulot et al. \(2011\)](#) suggested that isoprene oxidation is the largest global source of formic and acetic acids. These acids are also produced by the oxidation of ethane and propylene emitted in automobile exhaust. Their abundances in rainwater and their effects on pH are not negligible. For example, [Willey et al. \(2011\)](#) found that formic acid (pK<sub>a</sub> = 3.75) and acetic acid (pK<sub>a</sub> = 4.76) were the major organic acids present and contributed ~22 and 5%, respectively, of free acidity (mean pH = 4.65) in rainwater samples collected at Wilmington, NC in 2008. In addition, other organic acids (e.g., oxalic acid, lactic acid) have been found to be present at much lower levels at this site ([Avery et al., 2006](#)). [Vet et al. \(2014\)](#) noted that organic acids should be monitored in areas where the concentration of H<sup>+</sup> is <5 µeq/L (or pH ≥ 5.3). As will be seen in [Appendix 2.6](#), this condition is met in areas like the Northwest where concentrations of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in rainwater are low. Even in areas where the effects of organic acid neutralization by NH<sub>4</sub><sup>+</sup> might be small, the vapor pressures of some organic acids (e.g., oxalic acid) would be reduced by orders of magnitude, resulting in increased uptake of the organic acid from the gas phase and growth of particles ([Ortiz-Montalvo et al., 2014](#); [Paciga et al., 2014](#)).

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## 2.3.6 Particulate Matter (PM)

The chemistry of  $\text{NO}_x$  and  $\text{SO}_2$  described in [Appendix 2.3.1](#) and [Appendix 2.3.2](#), and the neutralization reactions of  $\text{NH}_3$  described in [Appendix 2.3.3](#) are relevant not only to understanding the distribution of  $\text{NO}_y$  and  $\text{SO}_x$  species, but also in explaining a large fraction of  $\text{PM}_{2.5}$  in most of the U.S. [Figure 2-5](#) shows  $\text{PM}_{2.5}$  composition in numerous U.S. locations. In all locations  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  account for a substantial fraction, and in many cases the majority, of  $\text{PM}_{2.5}$ . In general,  $\text{SO}_4^{2-}$  accounts for an increasing fraction of  $\text{PM}_{2.5}$  moving east or south, and  $\text{NO}_3^-$  for a greater fraction moving west or north. [Figure 2-5](#) also shows that  $\text{PM}_{2.5}$  concentrations are lower and  $\text{SO}_4^{2-}$  accounts for a much greater fraction of  $\text{PM}_{2.5}$  mass in 2003–2005 than in 2013–2015. This reflects the steep decline in  $\text{SO}_2$  emissions over this period ([Appendix 2.2.1](#)) and demonstrates that it has greatly impacted  $\text{PM}_{2.5}$  composition and concentration in the U.S.

The decrease in  $\text{SO}_4^{2-}$  contribution is so large that in many locations where  $\text{SO}_4^{2-}$  was the greatest contributor to  $\text{PM}_{2.5}$  mass in 2003–2005, organic carbon was more abundant in 2013–2015. However, as described in [Appendix 2.1](#), organic matter does not contribute as much to acidification or nutrient enrichment as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  still account for the majority of  $\text{PM}_{2.5}$  mass in many locations. The remaining mass of  $\text{PM}_{2.5}$  is composed of elemental carbon, sea salt (mostly Na and Cl), and crustal material (Si and Al are most abundant elements). Monitoring methods and spatial and temporal trends for  $\text{PM}_{2.5}$  species are further developed in the 2019 PM ISA ([U.S. EPA, 2019](#)). There is much less information on  $\text{PM}_{10}$  or  $\text{PM}_{10-2.5}$  composition because of the lack of routine monitoring on the scale that has been implemented for  $\text{PM}_{2.5}$  species.



Source: U.S. EPA 2016 analysis of Air Quality System network data 2003–2005.

**Figure 2-5 Contributions of organic carbon (OC), elemental carbon (EC), sulfate, nitrate, sea salt, and crustal components to  $\text{PM}_{2.5}$  at selected sites (A) 2003–2005 (B) 2013–2015.**

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## 2.4 Concentration and Deposition Measurements

An extensive review of techniques for measuring  $\text{NO}_x$ ,  $\text{NO}_z$ ,  $\text{NO}_y$ ,  $\text{NH}_x$ , and  $\text{SO}_x$  appeared in the 2008 ISA ([U.S. EPA, 2008a](#)). Updates to techniques for measuring  $\text{NO}_x$ ,  $\text{NO}_y$ , and  $\text{SO}_x$  species can be found in the latest ISAs for Oxides of Nitrogen ([U.S. EPA, 2016f](#)), Sulfur Oxides ([U.S. EPA, 2017d](#)), and PM, including  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and  $\text{PM}_{10-2.5}$  ([U.S. EPA, 2019](#)) Health Criteria, to which the reader is referred for details. In the following sections, measurements of  $\text{NO}_x$ ,  $\text{SO}_2$ , and PM in national networks are only briefly discussed and the measurement of species most relevant to acid and nutrient deposition and measurement methods for wet and dry deposition are the main focus. [Appendix 2.4.1](#) explains the roles of various national and regional monitoring networks in place to support the NAAQS or to collect data used for estimating acid and nutrient deposition. [Appendix 2.4.2](#), [Appendix 2.4.3](#), and [Appendix 2.4.4](#) describe methods used to measure gas-phase oxides of nitrogen, reduced nitrogen, and sulfur oxides that are not based on filter collection. Each of these sections is divided into separate discussions of the methods used in monitoring networks, remote sensing methods, and recent advances in research methods and other methods that are effective for intensive field studies but impractical for routine monitoring. Satellite-based remote sensing methods are useful because network coverage is often sparse and satellite-based measurements are becoming a more widely used alternative to ground-based measurements. [Appendix 2.4.5](#) describes filter-based methods used in CASTNET and other networks for mainly particulate species, but also for some gases, including  $\text{HNO}_3$  and  $\text{SO}_2$ . [Appendix 2.4.6](#) describes wet and dry deposition measurement and recent advances.

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### 2.4.1 Monitoring Networks

Federal Reference Methods (FRMs) have been established and national monitoring networks put in place for  $\text{NO}_2$  as the indicator of oxides of nitrogen,  $\text{SO}_2$  as the indicator of sulfur oxides, and  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  as indicators for PM. These methods and networks are described in detail in recent ISAs for Oxides of Nitrogen ([U.S. EPA, 2016f](#)), Sulfur Oxides ([U.S. EPA, 2017d](#)), and Particulate Matter ([U.S. EPA, 2019](#)) Health Criteria. However, in general the large fractions of N and S deposition accounted for by species other than  $\text{NO}_2$  and  $\text{SO}_2$  make measurements of these indicator species alone inadequate for estimating deposition amounts of total oxides of nitrogen and total sulfur oxides. Similarly, it has long been established that wet deposition of S is usually dominated by  $\text{SO}_4^{2-}$  rather than  $\text{SO}_2$  ([Dana, 1980](#)). In this respect,  $\text{PM}_{2.5}$  monitoring is potentially useful because it efficiently collects the range of PM species involved in acidification and N deposition. However, variability of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  as a fraction of total  $\text{PM}_{2.5}$  presents a

challenge for relating  $PM_{2.5}$  mass to these effects. An additional challenge is the estimate of deposition from  $PM_{2.5}$  concentrations, because of the strong dependence of deposition flux on particle size (see [Appendix 2.5.2](#)) and general unavailability of size distribution measurements.

In principle, a multipurpose, multipollutant monitoring network could efficiently meet the needs of estimating N and S deposition and air monitoring for ecosystem protection, while at the same time addressing other national air monitoring priorities. Such a network could include measurements of other N and S species besides  $NO_2$  and  $SO_2$  as well as other species that are otherwise not routinely monitored to better understand a variety of air pollution processes. This is the overall concept behind the National Core Network (NCore), a newly developed multipollutant monitoring network, and measurements of  $NO_Y$  and  $NH_3$  were included as NCore monitoring in part because of their relevance to atmospheric deposition ([Scheffe et al., 2009](#)). NCore has been operating since January 1, 2011 and has 80 monitoring sites designed for measuring multiple pollutants ([Weinstock, 2012](#)). The network provides a core of sites that measure  $SO_2$ ,  $NO_2$ ,  $NO_Y$ , and PM components including ammonium, nitrate, and sulfate, but with sparser coverage than the FRM networks for  $SO_2$  or  $NO_2$ . Because  $NO_Y$  is measured rather than  $NO_X$ , and because of collocated  $SO_2$  and  $SO_4^{2-}$  measurements, ambient concentrations of both  $NO_Y$  and  $SO_X$  can be determined from NCore data, so that these data can be used to estimate total deposition of oxides of nitrogen and sulfur. However, because of the wide range of deposition velocities for different species,  $NO_Y$  measurements alone are not sufficient for estimating deposition and species concentrations are also necessary. A further disadvantage is that most NCore sites are located in urban areas.

Instead of using NCore or the national  $NO_2$ ,  $SO_2$ , and PM monitoring networks, national scale N and S deposition have relied on monitoring networks specifically designed for estimating deposition. [Table 2-3](#) lists monitoring networks that have been used for recent estimates of atmospheric N and S deposition for the NADP ([Schwede and Lear, 2014a](#)).

**Table 2-3 Summary of monitoring networks used by [Schwede and Lear \(2014a\)](#).**

Network	Chemical Species	Period of Record	Website
CASTNET	Concentration: HNO <sub>3</sub> , SO <sub>2</sub> , pSO <sub>4</sub> <sup>2-a</sup> , pNO <sub>3</sub> <sup>-a</sup> , pNH <sub>4</sub> <sup>+a</sup>	2000–2012	<a href="http://epa.gov/castnet/javaweb/index.html">http://epa.gov/castnet/javaweb/index.html</a>
AMoN	Concentration: NH <sub>3</sub>	2008–2012	<a href="http://nadp.slh.wisc.edu/amon/">http://nadp.slh.wisc.edu/amon/</a>
SEARCH	Concentration: HNO <sub>3</sub> , SO <sub>2</sub> , NH <sub>3</sub>	2005–2011	No longer in operation
NTN	Wet deposition: SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	2000–2012	<a href="http://nadp.slh.wisc.edu/ntn/">http://nadp.slh.wisc.edu/ntn/</a>

<sup>a</sup>pSO<sub>4</sub><sup>2-</sup> is particulate sulfate concentration, pNO<sub>3</sub><sup>-</sup> is particulate nitrate concentration, pNH<sub>4</sub><sup>+</sup> is particulate ammonium concentration.

Note: Summary of data from monitoring networks used in the methodology.

Source: [Schwede and Lear \(2014a\)](#).

Wet deposition is estimated as the product of pollutant concentration in precipitation and precipitation depth (e.g., in rain or snow). Concentration in precipitation is currently measured as a weekly average by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) across a national network of 250 sites using a standard precipitation collector described in the 2008 ISA ([U.S. EPA, 2008a](#)). The NADP precipitation network was initiated in 1978 to collect data on amounts, trends, and distributions of acids, nutrients, and cations in precipitation. It expanded to meet the needs of the National Acid Precipitation Assessment Program established in 1981 to understand causes and effects of acid precipitation. The NTN is the only network providing a long-term record of precipitation chemistry across the U.S. Sites are mainly located away from urban areas and pollution sources. An automated collector ensures that the sample is exposed only during precipitation (wet-only sampling). Species measured are free acidity (H<sup>+</sup> as pH), conductance, calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), chloride (Cl<sup>-</sup>), and ammonium (NH<sub>4</sub><sup>+</sup>). Relatively high confidence has been assigned to wet deposition estimates because of established capabilities for measuring relevant chemical components in precipitation samples ([U.S. EPA, 2011a](#)). The Atmospheric Integrated Research Monitoring Network (AIRMoN) started in 1992 and measures the same species as the NTN, but on a daily rather than weekly basis.

In contrast, direct measurements of dry deposition flux are rare and difficult, and dry deposition fluxes of gases and particles are estimated from concentration measurements by an inferential technique described in the 2008 ISA ([U.S. EPA, 2008a](#)). In the

inferential model approach, the deposition of a pollutant is accomplished by introducing a resistance component to account for the individual chemical and biological processes that control pollutant adsorption and capture at natural surfaces ([Hicks et al., 1987](#)).

Concentrations are measured in the Clean Air Status and Trends Network (CASTNET), which was established under the 1991 Clean Air Act Amendments to assess trends in acidic deposition. CASTNET is a long-term environmental monitoring network with 95 sites located throughout the U.S. and Canada, managed and operated by the U.S. EPA in cooperation with other federal, state, and local partners ([www.epa.gov/castnet](http://www.epa.gov/castnet)) including six Native American tribes. CASTNET is the only network in the U.S. that provides a consistent, long-term data record of acidic dry deposition fluxes. It complements the NTN, and nearly all CASTNET sites are collocated with or near an NTN site. Together, these two monitoring programs are designed to provide data necessary to estimate long-term temporal and spatial trends in total deposition (dry and wet) as well as ecosystem health. Species measured in CASTNET include: O<sub>3</sub>, SO<sub>2</sub>, HNO<sub>3</sub> in the gas phase and SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> in particles.

While CASTNET data are more useful for estimating dry deposition than data from FRM networks, monitors are generally sparse and deposition is only determined for discrete locations. Also, not all of the species that contribute to total sulfur and nitrogen deposition are measured in CASTNET ([Schwede et al., 2011](#)). Despite these disadvantages, CASTNET data still be very useful if used in combination with modeled data ([Schwede et al., 2011](#)). NH<sub>3</sub> is not measured in CASTNET, but the National Atmospheric Deposition Program (NADP) deployed a separate NH<sub>3</sub> monitoring network (AMoN) using Radiello<sup>®</sup> passive samplers starting in the fall of 2007 at 16 sites; currently there are more than 60 active AMoN sites, two-thirds of which are located at CASTNET sites.

A limitation of dry deposition derived from CASTNET and other dry deposition networks is that results cannot be spatially interpolated because of the complexity of the deposition field ([Schwede and Lear, 2014a](#); [Baumgardner et al., 2002](#)). Combined with the sparse coverage of the network, this complexity restricts the capability of routine monitoring networks to provide data on dry deposition. To some extent, this limitation can be addressed by considering data from other networks.

The remaining network in [Table 2-3](#) is the Southeastern Aerosol Research and Characterization network (SEARCH), which was a highly instrumented network of four urban and four rural stations in Alabama, Florida, Georgia, and Mississippi that was terminated in 2016 ([Hansen et al., 2003](#)). The four rural SEARCH sites have been used for dry deposition estimates. SEARCH began as a public-private collaboration in early 1998 and has continued operation with several objectives, including understanding

processes governing PM<sub>2.5</sub> and copollutants emissions, transport, and deposition in the southeastern U.S.

One additional network that has been identified as potentially suitable for use in future deposition estimates ([Schwede et al., 2011](#)) is the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The IMPROVE network consists of more than 100 monitoring sites in national parks and other remote locations and is primarily focused on visibility impairment, but has also provided a reliable, long-term record of particulate mass and species components. Several other monitoring networks are operated either by the U.S. EPA or jointly with other federal agencies; species measured and other details for networks making measurements relevant for deposition are shown in [Naess \(2016\)](#). Even if concentration data from other networks are combined with CASTNET data, large areas of the U.S. are still relatively far away from, or in a different environment than, the nearest monitor.

Another deficiency of both the NTN and CASTNET is that not all species that contribute to total sulfur and nitrogen deposition are measured. Reliable measurements of NO<sub>y</sub> and NO<sub>2</sub> concentrations, especially at the low concentrations observed in many areas far from sources, are crucial for evaluating the performance of three-dimensional, chemical transport models of oxidant and acid production in the atmosphere. To meet this need, NO<sub>y</sub> monitors have been installed at six sites in CASTNET as part of the NCore program. At most sites, however, NO<sub>2</sub> is not currently monitored in CASTNET. The same is true for HNO<sub>2</sub> and peroxyacyl nitrates, which can also contribute significantly to total gas-phase reactive nitrogen. These species can be important contributors to N deposition locally, especially near populated areas. Neither the NTN nor CASTNET monitor reduced organic nitrogen compounds, which can also contribute significantly to N deposition (see [Appendix 2.3.4](#)). The sparse geographic coverage and lack of measurements for key species in these networks along with the awareness of modeling uncertainties led to the initiation of the Total Deposition Science Committee [TDEP; [NADP \(2016\)](#)] to develop hybrid approaches to improve estimates of atmospheric deposition. The TDEP approach is described in [Appendix 2.6](#).

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## 2.4.2 NO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>y</sub>

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### 2.4.2.1 Network Monitoring

As described in [Appendix 2.4.1](#), a nationwide monitoring network is in place for routine monitoring of NO<sub>2</sub>, and NO<sub>y</sub> is measured in the nationwide NCore network. NO<sub>2</sub> is

routinely measured using the FRM chemiluminescence method based on the catalytic reduction of  $\text{NO}_2$  to NO, followed by reaction NO with  $\text{O}_3$ . However, the reduction of  $\text{NO}_2$  to NO on the  $\text{MoO}_x$  catalyst substrate also reduces other oxidized nitrogen compounds (i.e.,  $\text{NO}_z$  compounds shown in the outer box of [Figure 2-3](#)) to NO. This interference by  $\text{NO}_z$  compounds has long been recognized following [Winer et al. \(1974\)](#) who found NO was also produced by catalytic reduction of  $\text{HNO}_3$ , PAN, and organic nitrates using this method. As a result of their experiments, [Winer et al. \(1974\)](#) concluded that, “the  $\text{NO}_x$  mode of commercial chemiluminescent analyzers must be viewed to a good approximation as measuring *total* gas-phase ‘oxides of nitrogen,’ not simply the sum of NO and  $\text{NO}_2$ .” Numerous later studies, as noted in the ISA for Oxides of Nitrogen ([U.S. EPA, 2016f](#)), have confirmed this conclusion. Further details were also described in the 2008 ISA ([U.S. EPA, 2008a](#)).

Commercially available  $\text{NO}_x$  monitors have been converted to  $\text{NO}_y$  monitors by moving the molybdenum oxide catalyst substrate to interface directly with the sample inlet to improve the efficiency of reduction of  $\text{NO}_z$  compounds susceptible to loss on inlet surfaces.  $\text{NO}_x$  concentrations cannot be considered as a universal surrogate for  $\text{NO}_y$ . However, near sources of fresh combustion emissions, such as highways, most of the  $\text{NO}_y$  is present as  $\text{NO}_x$ . To the extent that all the major oxidized nitrogen species can be reduced quantitatively to NO, measurements of  $\text{NO}_y$  concentrations should be more reliable than those for  $\text{NO}_x$  concentrations, particularly at typical ambient levels of  $\text{NO}_2$ . Exceptions might apply in locations near  $\text{NO}_x$  sources, where  $\text{NO}_x$  measurements are likely to be less biased and confidence in measurement accuracy increases.

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#### **2.4.2.2 Remote Sensing**

Satellite-based methods have also been used to measure  $\text{NO}_2$ . Remote sensing by satellites is especially useful in areas where surface monitors are sparse. Retrieving  $\text{NO}_2$  column abundances from satellite data typically involves three steps: (1) determining the total  $\text{NO}_2$  integrated line-of-sight (slant) abundance by spectral fitting of measurements of backscattered solar radiation, (2) removing the stratospheric contribution by using data from remote regions where the tropospheric column abundance is small, and (3) applying an air mass factor to convert tropospheric slant columns into vertical columns. The retrieval uncertainty is largely determined by steps 1 and 2 over remote regions where there is little tropospheric  $\text{NO}_2$ , and by step 3, over regions of elevated tropospheric  $\text{NO}_2$  ([Boersma et al., 2004](#); [Martin et al., 2002](#)). Satellite retrievals are largely limited to cloud fractions <20%. A hybrid approach using data for  $\text{NO}_2$  tropospheric column abundances obtained by the Ozone Monitoring Instrument (OMI) on the Aura satellite coupled with results from the GEOS-Chem, global-scale, three-dimensional, chemistry-transport model

has been developed by [Lamsal et al. \(2008\)](#) with updates by [Lamsal et al. \(2010\)](#). In this approach, the surface mixing ratio divided by the column abundances calculated by the GEOS-Chem model are used as the scaling factors to derive surface mixing ratios from satellite-measured column abundances. This method provides estimates of surface NO<sub>2</sub> concentrations that are especially useful in data-sparse regions. The algorithm used to derive the tropospheric columns of NO<sub>2</sub> is given in [Bucsela et al. \(2013\)](#). Note that this algorithm was recently shown to produce NO<sub>2</sub> column abundances that are too high by ~20% ([Marchenko et al., 2015](#)). There have also been advances in satellite remote sensing of NH<sub>3</sub> with the implementation of Cross-Track Infrared Sounder Satellite measurements ([Kharol et al., 2018](#)).

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### 2.4.2.3 Research and Nonroutine Methods

Alternatively, multiple methods for observing components of NO<sub>y</sub> have been developed and evaluated in some detail. As a result of these methods, as applied in the field and the laboratory, knowledge of the chemistry of odd-N species has evolved rapidly. Recent evaluations of methods can be found in [Arnold et al. \(2007\)](#) for HNO<sub>3</sub>, [Wooldridge et al. \(2010\)](#) for speciated PANs, and [Pinto et al. \(2014\)](#) for HONO. However, it is worth reiterating that the direct measurements of NO are still the most reliable of all.

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## 2.4.3 Ammonia

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### 2.4.3.1 Network Monitoring

The recently implemented AMoN for monitoring ammonia was described in [Appendix 2.4.1](#). The passive sampling method relies on diffusion across a membrane onto an absorbing substrate, which for NH<sub>3</sub> is H<sub>3</sub>PO<sub>3</sub>. The sampling period in AMoN is 2 weeks. [Puchalski et al. \(2011\)](#) compared the results from three passive samplers with annular denuder systems (taken to be the reference method). The median relative percentage difference between the Radiello passive samplers and the denuder systems was -37% and the coefficient of variation among triplicate Radiello samplers was 10%. [Puchalski et al. \(2015\)](#) further compared 2-week samples collected at five sites over the course of a year by Radiello passive samplers with collocated annular denuder systems (ADS) with different configurations. The mean relative percentage difference between the ADS and AMoN samplers was -9% to be compared to a precision of 5% for both the ADS and AMoN samplers. Ammonia was also been measured as a part of the SEARCH

network (see [Appendix 2.4.1](#)) from 2004 to 2016 by 24-hour collection on citric acid denuders and laboratory analysis with U.S. EPA method 350.1, based on chemiluminescence from reaction with indophenol ([Edgerton et al., 2007](#)).

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### 2.4.3.2 Remote Sensing

In addition to these in situ techniques, remote sensing techniques have also been used to measure NH<sub>3</sub>. The Tropospheric Emission Spectrometer (TES) on the Aura satellite [[Shephard et al. \(2011\)](#), and references therein; [Beer et al. \(2008\)](#)] and the Infrared Atmospheric Sounding Interferometer (IASI) on the MetOp-A satellite ([Van Damme et al., 2014](#)) measured spectral features in the  $\nu_2$  vibrational band centered at around 950/cm (the so-called atmospheric window in the infrared). Operating specifications for TES (spectral resolution, 0.06/cm; footprint  $5.3 \times 8.3$  km<sup>2</sup>; 0.15–0.20 K noise) are generally better than for IASI (spectral resolution, 0.50/cm; footprint  $12 \times 12$  km<sup>2</sup>; 0.15–0.20 K noise). Although TES has higher spectral resolution, it has less dense spatial coverage. Unlike satellite detection of atmospheric molecules by backscattered solar radiation (e.g., NO<sub>2</sub> and SO<sub>2</sub>), NH<sub>3</sub> is detected in the thermal infrared spectral range, so data for both day and night can be obtained (satellite overpasses at the Equator at approximately 1:30 a.m. and 1:30 p.m. for TES and 9:30 a.m. and 9:30 p.m. for IASI). The sensitivity of the IR sounding technique for NH<sub>3</sub> increases with the thermal contrast between the surface and the temperature of the air in the lower troposphere, and thus the daytime crossing allows for increased detectability of NH<sub>3</sub> ([Clarisse et al., 2010](#)). NH<sub>3</sub> is confined largely to the planetary boundary layer (PBL), with much lower concentrations aloft in the free troposphere. TES retrievals are most sensitive to NH<sub>3</sub> at atmospheric pressures between 700 and 900 hPa. The TES level of detectability for NH<sub>3</sub> is given by a profile with a peak concentration of 1 ppbv, or equivalently a constant mixing ratio of 0.4 ppbv distributed over the pressure range of maximum sensitivity, provided there is substantial thermal contrast.

[Pinder et al. \(2011\)](#) found that TES retrievals of NH<sub>3</sub> in the PBL captured the spatial and seasonal variability of NH<sub>3</sub> over eastern North Carolina measured by surface observations. Similarly, [Sun et al. \(2015a\)](#) found that column abundances measured by TES over the San Joaquin Valley agreed with those measured by upward looking instruments at the surface to within 2% and to within 6% for aircraft measurements. TES columns were also shown to be reasonably well correlated ( $R^2 = 0.67$ ) with median NH<sub>3</sub> measured at the surface by quantum cascade laser, thereby demonstrating the ability of the satellite-based measurements to capture spatial variability in NH<sub>3</sub> between individual pixels.

[Alvarado et al. \(2011\)](#) derived emissions factors for NH<sub>3</sub> in biomass burning plumes over Canada using data from TES. Using data from IASI [R'Honi et al. \(2013\)](#) found total column abundances for NH<sub>3</sub> in the plumes of Russian wildfires during the summer of 2010 that were two orders of magnitude larger than background values.

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### 2.4.3.3 Research and Nonroutine Methods

Ambient instruments with much higher time resolution were compared by [Schwab et al. \(2007\)](#) and [von Bobruzki et al. \(2010\)](#). [Schwab et al. \(2007\)](#) conducted a laboratory-based intercomparison of ambient NH<sub>3</sub> instruments with seven instruments using six methods sampling from a common manifold, including tunable diode laser (TDLAS) absorption spectrometer, wet scrubbing long-path absorption photometer (LOPAP), wet effusive diffusion denuder (WEDD), ion mobility spectrometer (IMS), Nitrolux laser acousto-optical absorption analyzer, and a modified CL analyzer. [Schwab et al. \(2007\)](#) reported that all instruments agreed to within ~25% of the expected calibration value, with the exception of the CL analyzer which suffered from problems related to its MoO<sub>x</sub> conversion of NO<sub>z</sub> to NO.

[von Bobruzki et al. \(2010\)](#) conducted a field intercomparison of ambient NH<sub>3</sub> measurements with 11 instruments using 8 methods including 3 wet techniques (annular rotating batch denuders, 1 with offline analysis and 2 with online analysis [AMANDA, AiRRmonia]), 2 Quantum Cascade Laser Absorption Spectrometers (c-QCLAS, DUAL-QCLAS), 2 photo-acoustic spectrometers, a cavity ring down spectrometer, a chemical ionization mass spectrometer, an ion mobility spectrometer, and an open-path Fourier transform infrared spectrometer. This study was unique in that the surrounding field was fertilized with urea halfway through the campaign to increase average concentrations of NH<sub>3</sub> from 10 to 100 ppb. Overall,  $R^2$  was >0.84 with respect to the ensemble mean for all instruments over the entire range of concentrations (<120 ppb), with slopes ranging from 0.67 to 1.13. Higher variability was found at lower concentrations (<10 ppb) with  $R^2 > 0.52$  and slopes ranging from 0.42 to 1.15. Perhaps the most consistent agreement between two instruments was found for the c-QCLAS and AiRRmonia ( $R^2 = 0.91$ , slope = 0.86, intercept = 0.84 ppb for NH<sub>3</sub> <10 ppb; and  $R^2 = 0.91$ , slope = 0.83, intercept = 0.34 ppb over the entire range of NH<sub>3</sub> concentrations).

Nitrolux-100 denuders were used both in the intercomparison study of [von Bobruzki et al. \(2010\)](#) and in the one by [Puchalski et al. \(2011\)](#). Compared to the ensemble mean, the slope was 0.97, the intercept was 1.86 ppb, and  $R^2 = 0.98$  over the entire concentration range. As noted by [von Bobruzki et al. \(2010\)](#), comparisons of this sort only show relative performance of the instruments and not a functional relationship to a standard.

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## 2.4.4 Sulfur Dioxide

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### 2.4.4.1 Network Monitoring

In the nationwide monitoring network for SO<sub>2</sub>, SO<sub>2</sub> is routinely measured by pulsed UV fluorescence. This technique is a Federal Equivalence Method (FEM). The method's principles and potential interferences have been described in detail in the 2008 ISA ([U.S. EPA, 2008a](#)). However, measurements using this method are not as widely used as measurements from the CASTNET. In the CASTNET, SO<sub>2</sub> is collected by capturing it on filters and measured as sulfate following procedures described in [Appendix 2.4.5](#).

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### 2.4.4.2 Remote Sensing

In addition to the above in situ methods, satellite-based measurements have also been used to measure tropospheric SO<sub>2</sub> and to infer surface SO<sub>2</sub> concentrations with the aid of the GEOS-Chem chemistry-transport model ([Nowlan et al., 2014](#); [Lee et al., 2011](#)). Tropospheric column abundances of SO<sub>2</sub> are obtained by the Ozone Monitoring Instrument (OMI) on the Aura satellite or the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) on Envisat and are combined with results from the GEOS-Chem, global-scale, three-dimensional, chemistry-transport model to derive surface concentrations of SO<sub>2</sub> (as they are for NO<sub>2</sub>). [Lee et al. \(2011\)](#) associated annual mean surface mixing ratios of SO<sub>2</sub> derived from the hybrid satellite/model technique with ambient measurements of SO<sub>2</sub>, ( $R^2 = 0.66$  and  $0.74$ , slope =  $0.70$  and  $0.93$ ,  $n = 121$  and  $115$ , for OMI and SCIAMACHY, respectively).

The algorithms used to derive vertically integrated SO<sub>2</sub> abundances in the troposphere undergo continuing refinement. For example, [Theys et al. \(2015\)](#) applied an algorithm based on differential optical absorption spectroscopy ([Platt and Stutz, 2008](#)) combined with a radiative transfer model. [Li et al. \(2013\)](#) developed an algorithm based on principal components analysis, which has replaced the earlier standard algorithm developed by [Krotkov et al. \(2008\)](#). The methods applied by [Theys et al. \(2015\)](#) and [Li et al. \(2013\)](#) are designed to be operational for retrieving SO<sub>2</sub> in the PBL with an estimated detection limit of ~0.5 Dobson units (1 DU =  $2.69 \times 10^{16}$  molec/cm<sup>2</sup> corresponding to a concentration of ~3 ppb if SO<sub>2</sub> is well mixed in a 2-km-deep mixed layer), or about half that in the older standard method. [Table 2-4](#) summarizes sources of uncertainty for individual OMI measurements of NO<sub>2</sub> and SO<sub>2</sub>.

**Table 2-4 Sources of uncertainty for individual Ozone Monitoring Instrument measurements in the study of [Nowlan et al. \(2014\)](#).**

Source	NO <sub>2</sub>	SO <sub>2</sub>
OMI fitting error	~10 <sup>15</sup> molec/cm <sup>2</sup>	~10 <sup>16</sup> molec/cm <sup>2</sup>
Air mass factor	20%	15–45%
Stratospheric correction	2 × 10 <sup>14</sup> molec/cm <sup>2</sup>	N/A
SO <sub>2</sub> offset correction	N/A	2 × 10 <sup>14</sup> molec/cm <sup>2</sup>
Profile shape	30%	10%

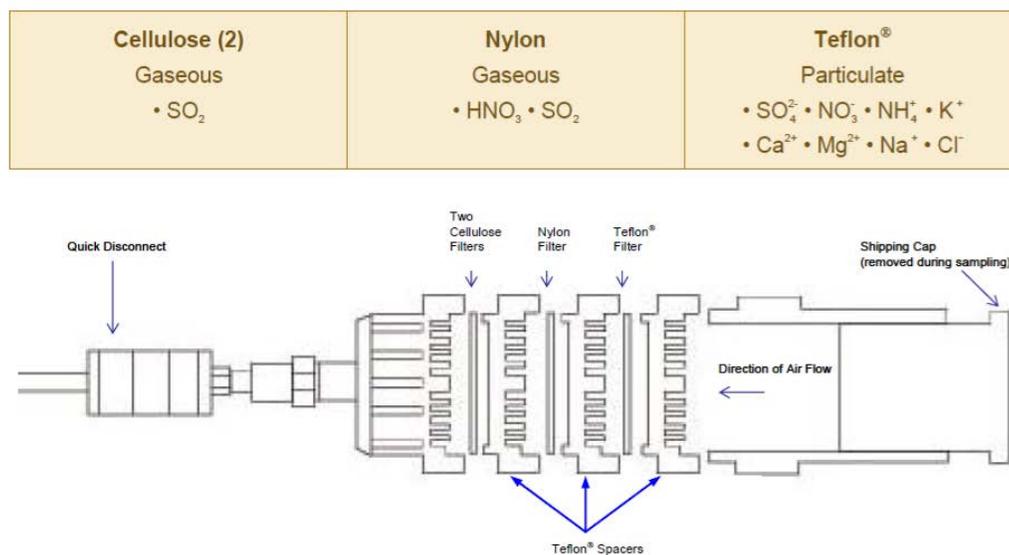
molec = molecules; N/A = not applicable; NO<sub>2</sub> = nitrogen dioxide; OMI = Ozone Monitoring Instrument; SO<sub>2</sub> = sulfur dioxide.  
Source: [Nowlan et al. \(2014\)](#).

The errors in the column measurements result mainly from uncertainties in the vertical profiles of NO<sub>2</sub> and SO<sub>2</sub>, cloud fraction, cloud pressure, surface reflectivity, and particles used in the calculation of air mass factor. A correction is required to account for NO<sub>2</sub> in the stratosphere (produced from N<sub>2</sub>O oxidation and cosmic ray interactions dissociating with N<sub>2</sub>). The SO<sub>2</sub> offset correction refers to a global background correction arising from issues in spectral fitting, such as spectral correlations with O<sub>3</sub> and stray light within the instrument.

#### 2.4.5 Filter-Based Concentration Measurements

As described in [Appendix 2.4.1](#), most measurements used for estimating deposition are from CASTNET, rather than from monitoring networks based on FRM and FEM methods. The CASTNET filter pack is shown in [Figure 2-6](#). Particulate matter is collected on the open-face Teflon filter, extracted in deionized water, and analyzed by ion chromatography (IC) for sulfate, nitrate, ammonium, and other species identified in [Figure 2-6](#). In the CASTNET filter pack, gases are collected downstream of the particulate species, with nitric acid collected on nylon filters and analyzed as NO<sub>3</sub><sup>-</sup> by ion chromatography, and SO<sub>2</sub> on carbonate impregnated cellulose filters and analyzed as SO<sub>4</sub><sup>2-</sup> by ion chromatography. Extensive intercomparisons of CASTNET methods with other measurement methods were described in the 2008 ISA ([U.S. EPA, 2008a](#)).

**Figure I-4 Three-Stage Filter Pack**



Ca<sup>2+</sup> = calcium ion; Cl<sup>-</sup> = chloride; HNO<sub>3</sub> = nitric acid; K<sup>+</sup> = potassium ion; Mg<sup>2+</sup> = magnesium ion; Na<sup>+</sup> = sodium ion; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>2</sub> = sulfur dioxide; SO<sub>4</sub><sup>2-</sup> = sulfate.

Air flows from right to left.

Source: [MACTEC \(2010\)](#).

**Figure 2-6 Clean Air Status and Trends Network filter pack.**

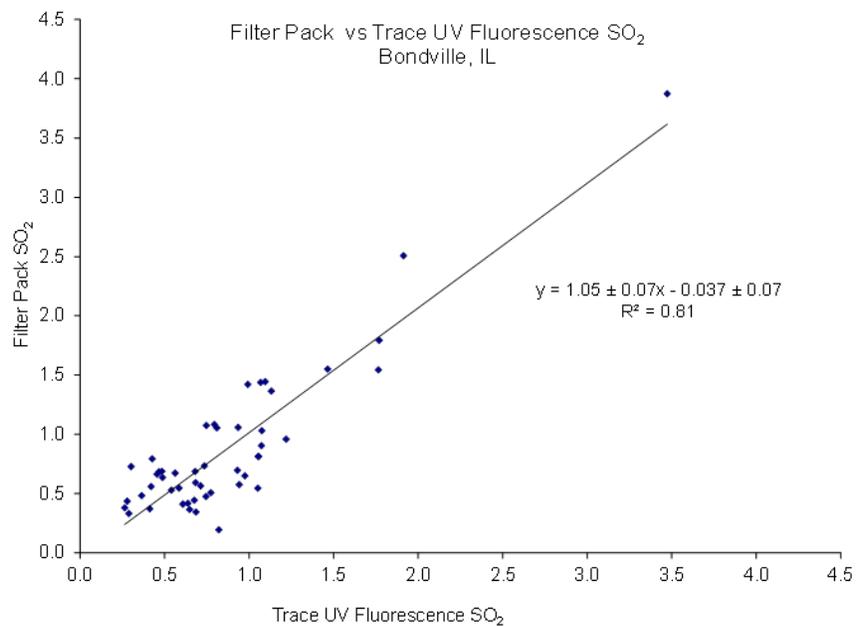
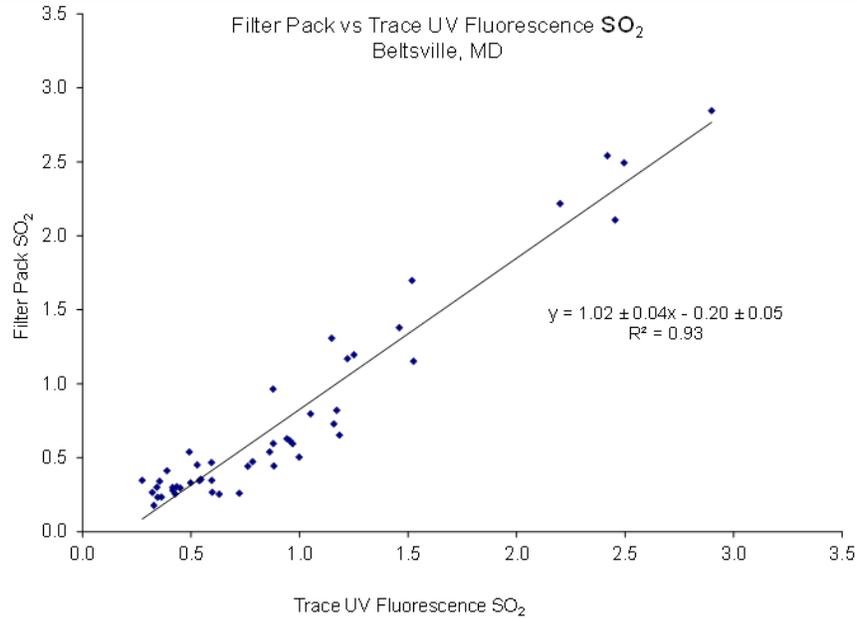
As can be seen in [Figure 2-6](#), SO<sub>2</sub> is measured by the CASTNET filter pack by IC analysis of extracts from the cellulose filters. Because the nylon filter adsorbs some of the SO<sub>2</sub> ([Sickles et al., 1999](#); [Sickles and Hodson, 1999](#)), SO<sub>4</sub><sup>2-</sup> is also measured on nylon and added to the SO<sub>2</sub> (expressed as SO<sub>4</sub><sup>2-</sup>) collected on the backup cellulose-fiber filters.

Uncertainties in CASTNET data are reported quarterly in a quality assurance report ([U.S. EPA, 2016c](#)). Precision is determined as the absolute value of quarterly or annually aggregated relative percentage difference for duplicate sample pairs collected with collocated samplers at two sites. Data quality objectives for ammonium, nitrate, and sulfate are within 20%, but reported precision for 2016 was well under this target, 2–5% for sulfate, 5–13% for nitrate, and 2–6% for ammonium, where the range reflects that there are two sites. Analytical accuracy was reported within 2% based on spiked calibration verification samples. Further detail on uncertainty and data quality can be found in ([U.S. EPA, 2016c](#)). Additional unknown uncertainty is associated with volatilization of NH<sub>4</sub><sup>+</sup> from collected PM. Substantial loss during sampling can occur because collected NH<sub>4</sub>NO<sub>3</sub> in PM is in a temperature dependent equilibrium with NH<sub>3</sub> and HNO<sub>3</sub> (see [Appendix 2.3.3](#)), leading to volatilization of both species after PM

collection. Loss of  $\text{NH}_4^+$  during sampling was thoroughly reviewed in the 2008 ISA ([U.S. EPA, 2008a](#)).

Results of an intercomparison of weekly average  $\text{SO}_2$  data (ppbv) collected by the CASTNET filter pack and trace level  $\text{SO}_2$  monitors during all of 2014 at Bondville, IL and Beltsville, MD are shown in [Figure 2-7 \(AMEC Environment & Infrastructure, 2015\)](#).

In addition to CASTNET,  $\text{pSO}_4^{2-}$ ,  $\text{pNO}_3^-$  are monitored in the Chemical Speciation Network (CSN), and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. Sampling and measurement methods for these networks were described in detail by [Solomon et al. \(2014\)](#). In the CSN network,  $\text{pNH}_4^+$  is also measured, but as for CASTNet, it may be subject to volatilization error (volatilization of  $\text{NO}_3^-$  is corrected).



SO<sub>2</sub> = sulfur dioxide; UV = ultraviolet.

Results for Beltsville, MD are shown in the upper panel and results for Bondville, IL are shown in the lower panel.

**Figure 2-7 Comparison between weekly average measurements of sulfur dioxide using the Clean Air Status and Trends Network filter pack and the trace ultraviolet pulsed fluorescence monitor in 2014.**

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## 2.4.6 Deposition Measurements

Wet deposition is estimated as the product of pollutant concentration in precipitation and precipitation depth (e.g., in rain or snow; see [Appendix 2.4.1](#)). Concentration in precipitation is currently measured by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) across a national network of sites using a standard precipitation collector described in the 2008 ISA ([U.S. EPA, 2008a](#)).

Relatively high confidence has been assigned to wet deposition estimates because of established capabilities for measuring relevant chemical components in precipitation samples ([U.S. EPA, 2011a](#)). Measurement precision determined as the average absolute percentage differences of replicate samples in the 2016 annual quality assurance report was 1% or less for sulfate, nitrate, and ammonium, and absolute percentage difference was no greater than 5% for sulfate and ammonium or 7% for nitrate for any single sample pair ([U.S. EPA, 2016c](#)). Bias determined from internal blind samples was 2% or less for sulfate and nitrate, and 6% or less for ammonium ([U.S. EPA, 2016c](#)).

In contrast, direct measurements of dry deposition flux are rare and difficult. Methods for estimating dry deposition from field measurements fall into two major categories: surface analysis methods, which include all types of estimates of contaminant accumulation on surfaces of interest, and atmospheric deposition rate methods, which use measurements of contaminant concentrations in the atmosphere and micrometeorological measurements of atmospheric turbulence ([U.S. EPA, 2008a](#)). Emphasis here is placed on the latter class of methods, which are more widely applicable because the accumulation methods are subject to limitations such as the site specificity of the measurements and the restriction to elements that are largely conserved within the vegetative system. Dry deposition estimates using atmospheric deposition rate methods are based on field measurements of a species or particle concentration gradient along with a measurement or estimate of its turbulent diffusivity under the field conditions of the measurement ([Myles et al., 2012](#); [Businger, 1986](#)). Examples include eddy covariance and aerodynamic gradient techniques ([U.S. EPA, 2008a](#)). In the eddy covariance method, flux is calculated from the covariance between fluctuations in wind velocity and concentration. Historically, empirical estimates of deposition for wind tunnel and field conditions often have not agreed well with theoretical predictions, probably because transport phenomena and turbulence structure near surfaces are not well characterized ([U.S. EPA, 2004](#)). However, improvement of dry deposition measurements is an active research area, both to reduce measurement uncertainties and to improve modeling capabilities by better understanding deposition processes and their parameterization in chemical transport models.

Progress in improving measurement capabilities has been triggered by the development of continuous air sampling measurement techniques with higher sensitivity and temporal

resolution, with the objective of improving costs and measurement quality using atmospheric deposition rate measurement methods. Concluding that the main reason for the shortage of dry deposition measurements is the expense and complexity of measurement methods, [Almand-Hunter et al. \(2015\)](#) tested a dynamic flux chamber using automated, inexpensive multispecies gas flux monitoring system for measurement of a variety of pollutants, including NO<sub>x</sub>, that would be needed to contend with the large spatial and temporal variability in air-surface exchange rates of reactive compounds. A dynamic chamber system was also developed to allow measurements of NO, NO<sub>2</sub>, and O<sub>3</sub> measurements so that compensation points and deposition velocities (see [Appendix 2.5.2](#)) could be estimated ([Breuninger et al., 2012](#)).

As part of a series of measurements to be tested at several CASTNET sites, [Rumsey and Walker \(2016\)](#) evaluated the ability of the MARGA 2S (Monitoring for AeRosols and GAses) system to simultaneously measure fluxes of NH<sub>3</sub>-HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> using the aerodynamic gradient method to allow for an assessment of the errors due to the instability of the particle phase, as well as SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, to allow for the investigation of ammonium sulfate neutralization and codeposition between SO<sub>2</sub> and NH<sub>3</sub>. Over a range of meteorological conditions, median flux uncertainty was found to range from ≈31% for NH<sub>3</sub> to ≈120% for NH<sub>4</sub><sup>+</sup>. The flux gradient technique was also applied to a forest clearing as an example of a complex ecosystem with the objectives of improving deposition rate accuracy and model parameterization for SO<sub>2</sub> ([Myles et al., 2012](#)). Deposition velocities fluctuated considerably with a mean of 1.00 ± 0.48 cm/s, and the large variation was not fully captured by estimates from widely used models ([Myles et al., 2012](#)). Uncertainties in canopy resistance, including stomatal and nonstomatal processes were identified as probable sources of uncertainty ([Myles et al., 2012](#)).

This approach has been successfully applied to measurements of a wide variety of species. However, it is less suitable for HNO<sub>3</sub> and NH<sub>3</sub> because they are subject to interactions with inlet surfaces of measuring devices. For example, in one study a correction factor of 1.62 was reported for inlet surface interactions ([Breuninger et al., 2012](#)). To address the problem of loss of HNO<sub>3</sub>, NH<sub>3</sub>, and other substances that interact with sampling inlet surfaces during measurement, [Roscioli et al. \(2016\)](#) developed a method to passivate inlet surfaces and thereby overcome this difficulty by allowing for more rapid response measurements. [Min et al. \(2014\)](#) determined the net flux of NO and NO<sub>2</sub> (at a frequency of 5 Hz) over a forest with estimated total systematic uncertainties of <8 and <6%, and random errors of <25 and <21%, respectively.

Measurement methods are well developed for ideal conditions of flat, homogeneous, and extensive landscapes and for chemical species for which accurate and rapid sensors are available ([U.S. EPA, 2008a](#)). However, the strong dependence of dry deposition on

surface characteristics, which are highly spatially variable, causes in situ measurements to be limited in applicability, especially in areas of high topographic relief [e.g., [Weathers et al. \(2006\)](#)]. The lifetime in the boundary layer (~1 km depth) for rapidly depositing species is ~1 day, implying that distances from source to deposition are relatively short and that the deposition flux depends strongly on the nature and strength of nearby sources. Deposition also shows strong temporal variability on timescales ranging from diurnal to seasonal, as do wind regimes affecting a particular site. In addition, cost and logistics make the eddy covariance and aerodynamic gradient techniques impractical for monitoring networks.

Instead, dry deposition fluxes of gases and particles are estimated in CASTNET and by chemistry-transport models, such as CMAQ, by an inferential technique described in the 2008 ISA ([U.S. EPA, 2008a](#)). In the inferential model approach, the deposition of a pollutant is estimated by introducing a resistance component to account for the individual chemical and biological processes that control pollutant adsorption and capture at natural surfaces ([Hicks et al., 1987](#)). Ambient pollutant concentrations of  $O_3$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $SO_2$ , and  $HNO_3$  are routinely collected at CASTNET dry deposition sites. Deposition velocities based on local meteorological measurements were calculated using the Multi-Layer Model (MLM) at U.S. EPA-sponsored CASTNET sites until 2010, when meteorological measurements were discontinued at all but five U.S. EPA CASTNET sites. Dry deposition fluxes are still reported at sites with discontinued meteorological measurements using historical data. A disadvantage to this approach is that relevant atmospheric species are not routinely measured. For example,  $NO_2$  and peroxyacetyl nitrate, which together consistently contribute 15 to 25% of estimated oxidized nitrogen dry deposition, are not measured at CASTNET sites. Even for those species that are routinely measured, network spatial coverage is sparse ([U.S. EPA, 2011a](#)).

Satellite-based measurements offer a potential means of greater coverage, but only a limited number of deposition related applications have been described. [Nowlan et al. \(2014\)](#) combined satellite data with modeled  $NO_2$  and  $SO_2$  surfaces and vertically integrated concentrations and deposition velocities to estimate deposition fluxes.  $SO_2$  dry deposition fluxes compared well with surface network-based deposition fluxes. Uncertainties in depositional flux estimates in this approach result from the combined uncertainties in the satellite-derived surface concentrations and model-derived deposition velocities and were estimated to be ~30% on average for both  $NO_2$  and  $SO_2$  over land. In the absence of routine measurements, dry deposition is often modeled with CMAQ or other modeling tools using relevant emissions, meteorological, and land use data, rather than estimated from measured concentration measurements ([U.S. EPA, 2011a](#)).

Modeling dry deposition is particularly challenging over varying terrain and under extremely stable conditions such as those occurring at night. Under optimal conditions over a relatively small area where dry deposition measurements have been made, uncertainties on the order of  $\pm 30\%$  have been reported and larger uncertainties are likely when the surface features in the built environment are not well known or when the surface comprises a patchwork of different surface types, as is common in the eastern U.S. ([U.S. EPA, 2008a](#)). For this reason, dry deposition is routinely estimated from concentration measurements, usually from CASTNET data ([Appendix 2.4.5](#)) using a hybrid approach based on both measured and modeled data ([Appendix 2.6](#)).

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## 2.5 Modeling Chemistry, Transport, and Deposition

In this section, advances in modeling transport and deposition of species relevant to acid and nutrient deposition are discussed, along with research progress on understanding underlying transport and deposition processes. The use of chemical transport models (CTMs) to model deposition was discussed extensively in the 2008 ISA ([U.S. EPA, 2008a](#)). Relevant new research and improvements in CTM modeling in general are described in [Appendix 2.5.1](#). [Appendix 2.5.2](#) discusses environmental processes relevant to understanding and modeling acid and nutrient deposition. [Appendix 2.5.2.1](#) begins with an overview of fundamental processes of atmospheric deposition of gases and particles, along with deposition velocities for some key gas-phase species. It also contains discussions of research advances in three key processes that serve as major structural uncertainties (lack of knowledge of the underlying science) in modeling deposition: NO<sub>x</sub> canopy processes, which involve both bidirectional gas exchange and NO<sub>x</sub> chemistry ([Appendix 2.5.2.2](#)); bidirectional exchange of ammonia ([Appendix 2.5.2.3](#)); and transference ratios relating average ambient concentration to deposition flux ([Appendix 2.5.2.4](#)). [Appendix 2.5.3](#) discusses model evaluation and uncertainty, including comparisons between CTM and network-based wet deposition results.

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### 2.5.1 Advances in Chemistry-Transport Model (CTM) Modeling

To understand the lifetime and fate of the varied forms of atmospheric sulfur and nitrogen from emission to deposition, it is necessary to account for both atmospheric transport and chemical transformations. CTMs simulate the relevant atmospheric transport processes (e.g., horizontal and vertical advection and diffusion), as well as chemistry, aerosol physics, deposition, and cloud processes. The 2008 ISA ([U.S. EPA, 2008a](#)) provided a detailed description of the CTM models and their application to estimating deposition. Continental-scale CTMs include CMAQ ([Appel et al., 2017](#)) and CAMx ([Koo et al.,](#)

2015), while GEOS-Chem (Zhang et al., 2012a) is an example of a global-scale model. Most major regional-scale, air-related modeling efforts at U.S. EPA use the Community Multiscale Air Quality (CMAQ) modeling system (Byun and Schere, 2006; Byun and Ching, 1999). Recent updates to CTM model design, and in particular to CMAQ, are described here.

A number of complex atmospheric processes influence pollutant behavior between emission and deposition and must be taken into account to achieve good model performance. A variety of mechanisms operating over a wide range of spatial and temporal scales transport heat, water, and pollutants horizontally and vertically through the atmosphere. These mechanisms range from local-scale circulations (e.g., urban heat islands) to hemispheric-scale transport by the jet stream. Long-range transport of pollutants in the lower free troposphere associated with large-scale synoptic systems is possible because flows are largely uncoupled from surface friction. Flows in the upper planetary boundary layer (PBL), especially during the day, might not be as effective for transporting pollutants over long distances because air can be mixed down to the surface by turbulence. If these pollutants react with surface material or are taken up by vegetation, they can be removed within a relatively short distance from their sources.

In addition to wind velocity, the distance scale for transport of a pollutant that is relatively stable in the troposphere with respect to gas-phase reactions (i.e., chemical lifetime > a few days) depends strongly on the pollutant's interactions with solid and liquid surfaces and subsequent chemical transformations. Because NO and NO<sub>2</sub> are only slightly soluble, they can be transported over longer distances in the gas phase than can more soluble species like HNO<sub>3</sub> (and its anhydride, N<sub>2</sub>O<sub>5</sub>) and NH<sub>3</sub> that are depleted by deposition to moist surfaces or taken up more readily on aqueous surfaces of particles or on cloud drops. For example, measurements of the ratio of NH<sub>3</sub> to CH<sub>4</sub> in the San Joaquin Valley indicate substantial loss of NH<sub>3</sub> to the surface within a few km of sources of these gases (Miller et al., 2015), consistent with an NH<sub>3</sub> lifetime of minutes to a few hours in this environment. On the other hand, a combination of models, remote sensing, and in situ measurements over the eastern U.S. indicate an atmospheric lifetime for SO<sub>2</sub> of 19 ± 7 hours in summer increasing to 58 ± 20 hours in winter (Lee et al., 2011), which indicates the potential for much longer-range transport of SO<sub>2</sub>.

Numerous advances in atmospheric science have been codified in CTMs, including gas-phase oxidant chemistry relevant for the formation of aerosol precursors and dry deposition by gravitational settling (Nolte et al., 2015), improved representation of meteorological processes in CTMs and interactions with aerosols (Tuccella et al., 2015), and improved algorithms for understanding the influence of weather on emissions of ammonia from agricultural lands (Flechar et al., 2013). Over the U.S. and Europe,

substantial reductions in sulfur dioxide and nitrogen oxides have created an opportunity to compare the model results with the trends in ambient observations ([Banzhaf et al., 2015](#); [Xing et al., 2015](#); [Civerolo et al., 2010](#)). Studies have shown that CMAQ is skilled at capturing the seasonal and long-term changes in sulfate PM<sub>2.5</sub> and nitrate PM<sub>2.5</sub> as well as total PM<sub>2.5</sub> mass; however, the model performs less well for seasonal variability in nitrate PM<sub>2.5</sub>, owing to uncertainties in ammonia emission trends ([Banzhaf et al., 2015](#); [Xing et al., 2015](#)).

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## 2.5.2 Modeling Deposition

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### 2.5.2.1 Wet and Dry Deposition of Gases and Particles

Considerable advances in both our understanding of atmospheric deposition and modeling approaches to characterize it have taken place recently. Deposition is a complicated process influenced by numerous atmospheric and deposition surface properties, as well as chemical reactions and other processes that take place within canopies of vegetation.

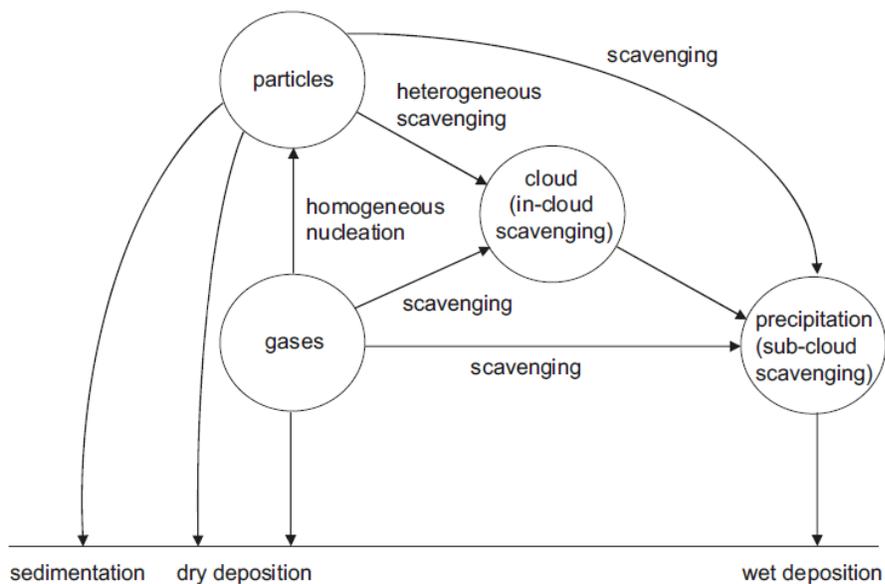
In [Figure 2-8](#), [Möller \(2014\)](#) illustrated the pathways that transfer gaseous and particulate pollutants from the atmosphere to the surface by deposition. Wet deposition occurs when particulate and gaseous species are removed by cloud drops or by falling precipitation (washout). Dry deposition occurs when they are removed without precipitation by processes like turbulence and gravitational settling. In mountainous areas, a third important type of deposition occurs, referred to as occult deposition ([Dollard et al., 1983](#)), which is not shown in [Figure 2-8](#), and results from the impaction of droplets in fogs or clouds on vegetation. Wet deposition is determined as the simple product of concentration in precipitation and precipitation rate. Receptor (i.e., vegetation) surface properties have little effect on wet deposition. Dry deposition is more difficult to determine. It can be described as a flux  $F_d$ , the mass of pollutant deposited per unit area of the Earth's surfaces where it deposits, or a deposition velocity that relates the dry deposition flux  $F_d$  to a pollutant's ambient concentration:

$$F_d = v_d C$$

Equation 2-12

where  $C$  is the pollutant's concentration in mass in per unit volume, and  $v_d$  is the deposition velocity, which relates a pollutant's deposition flux to its ambient concentration.

Dry deposition of gases depends on leaf area, surface resistance to gas uptake, interactions with biota through both stomatal and plant surface pathways, and atmospheric reactivity, which can vary among depositing gases. Measurements of average dry deposition velocities for gases over land surfaces are shown in [Table 2-5](#), and an indication of the seasonal variability of deposition velocities over different land surface types can be seen in [Table 2-6](#), which shows the variability in  $v_d$  for  $\text{SO}_2$ . Deposition velocities of other species are also expected to be spatially and temporally variable.



Source: [Möller \(2014\)](#).

**Figure 2-8** Schematic diagram showing mechanisms for transferring pollutants from the atmosphere to the surface.

**Table 2-5 Average dry deposition velocities (cm/s) for several gases over land surfaces.**

Substance	SO <sub>2</sub>	NO	NO <sub>2</sub>	HNO <sub>3</sub>	O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	CO	NH <sub>3</sub>
$v_d$	0.8	<0.02	0.02	3	0.6	2	<0.02	1

CO = carbon monoxide; H<sub>2</sub>O<sub>2</sub> = hydrogen peroxide; HNO<sub>3</sub> = nitric acid; NH<sub>3</sub> = ammonia; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; O<sub>3</sub> = ozone; s = second; SO<sub>2</sub> = sulfur dioxide;  $v_d$  = deposition velocities.

Source: [Möller \(2014\)](#).

**Table 2-6 Deposition velocity (cm/s) for sulfur dioxide averaged over different land use types for summer and winter.**

	Farmland		Grassland		Dec. Forest		Con. Forest		Urban		Water	
	Su	Wi	Su	Wi	Su	Wi	Su	Wi	Su	Wi	Su	Wi
Wet	1.0	1.0	1.0	1.0	3.0	1.5	2.0	2.0	1.0	1.0	0.5	0.5
Dry	0.7	0.5	0.6	0.4	1.5	0.5	0.7	0.5	0.1	0.1	0.5	0.5
Snow	--	0.	--	0.1	--	0.2	--	0.2	--	0.1	--	0.1

Con. = coniferous; Dec. = deciduous; Su = summer; Wi = winter.

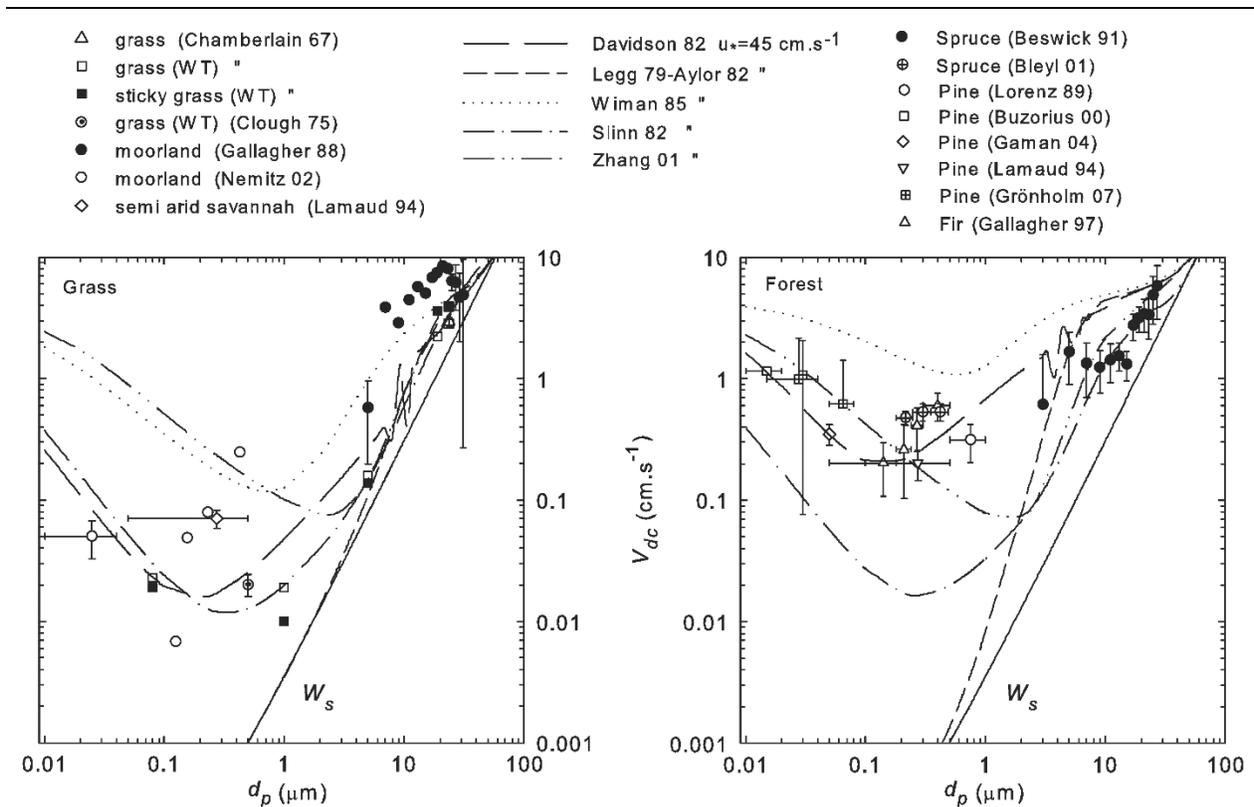
Source: [Möller \(2014\)](#).

A wide range of deposition velocities is observed among different atmospheric gas-phase species. HNO<sub>3</sub> is an example of gas with straightforward deposition behavior. It sticks easily to vegetative surfaces, i.e., there is a negligible surface resistance to HNO<sub>3</sub> uptake by vegetation, and its deposition rates are independent of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the leaf cuticle as well as leaf surfaces. The HNO<sub>3</sub>  $v_d$  typically exceeds 1 cm/s and exhibits a diel pattern controlled by turbulence characteristics of midday maxima and lower values at night in the more stable boundary layer ([U.S. EPA, 2008a, 2004](#)). In contrast, NO<sub>2</sub> interaction with vegetation is more complicated. The uptake rate by foliage is related to stomatal conductance and is more variable. It may also be associated with concentrations of reactive species such as ascorbate in the plant tissue that react with NO<sub>2</sub>. At very low NO<sub>2</sub> concentrations, emission from foliage is observed. Internal NO<sub>2</sub> appears to derive from plant N metabolism, and there is evidence for a compensation point, typically near

~1 ppb, at which uptake and emission rates are equal and net flux is zero ([U.S. EPA, 2008a](#)).

Dry deposition of PM is influenced by a number of variables, including particle diameter, atmospheric stability, deposition surface roughness, and the shape, stickiness, roughness, and cross-sectional area of leaves. Greater roughness and leaf shape complexity increase deposition. The diversity of particle sizes, atmospheric conditions, and surface characteristics makes it difficult to estimate dry deposition ([U.S. EPA, 2008a, 2004](#)). The appreciable effects of particle size, local micrometeorological conditions and surface characteristics on deposition velocity can be seen in [Figure 2-9](#). The key to measurements of  $v_d$  over surfaces covered by low vegetation is given in the left column and over forest in the right column. These measurements are compared to six model formulations which are shown as lines in the center column.

For particles  $>10 \mu\text{m}$ ,  $v_d$  varies between 0.5 and 1.1 cm/s, and a minimum particle  $v_d$  of 0.03 cm/s exists for particles in the size range 0.1 to 1.0  $\mu\text{m}$ , while deposition of particles from the atmosphere to a forest canopy has been estimated as 2 to 16 times greater than deposition in adjacent open terrain like grasslands or other low vegetation ([U.S. EPA, 2004](#)).



$d_p$  = aerodynamic diameter of particle;  $v_{dc}$  = deposition velocity;  $W_s$  = Stokes settling velocity.

Notes: [Chamberlain \(1967\)](#); [Clough \(1975\)](#); [Gallagher et al. \(1988\)](#); [Nemitz et al. \(2002\)](#); [Lamaud et al. \(1994b\)](#); [Davidson et al. \(1982\)](#); [Legg and Powell \(1979\)](#); [Aylor \(1982\)](#); [Wiman and Ågren \(1985\)](#); [Zhang et al. \(2001\)](#); [Beswick et al. \(1991\)](#); [Lorenz and Murphy \(1989\)](#); [Buzorius et al. \(1998\)](#); [Gaman et al. \(2004\)](#); [Lamaud et al. \(1994a\)](#); [Grönholm et al. \(2007\)](#); [Gallagher et al. \(1997\)](#).

Closed symbols correspond to wet or sticky surfaces or liquid particles; open symbols to dry surfaces or solid particles.

Source: [Petroff et al. \(2008\)](#).

**Figure 2-9 Modeled and measured deposition velocities over grass (left figure) and coniferous forest canopies (right figure) for particles of density  $1 \text{ gm/cm}^3$  depositing under similar friction velocity ( $u^*$ ) ( $35 < u^* < 56 \text{ cm/s}$ ).**

### 2.5.2.2 NO<sub>x</sub> Canopy Processes

There are a number of ways that landscape characteristics influence the deposition process ([U.S. EPA, 2008a, 2004](#)). In terrain containing extensive vegetative canopies, any material deposited via precipitation to the upper stratum of foliage is likely to be intercepted by several foliar surfaces before reaching the soil. Deposition velocity ( $v_d$ ) is usually greater for a forest than for a nonforested area and greater for a field than for a water surface. The upwind leading edges of forests, hedgerows, and individual plants are

primary sites of coarse particle deposition, and upper canopy foliage tends to receive maximum exposure to coarse and fine particles, but foliage within the canopy tends to receive primarily fine particles ([U.S. EPA, 2008a, 2004](#)). Several  $N_r$  species are deposited to vegetation, among them  $HNO_3$ ,  $NO_2$ , PAN (and other  $RONO_2$ ), and  $NH_3$ .

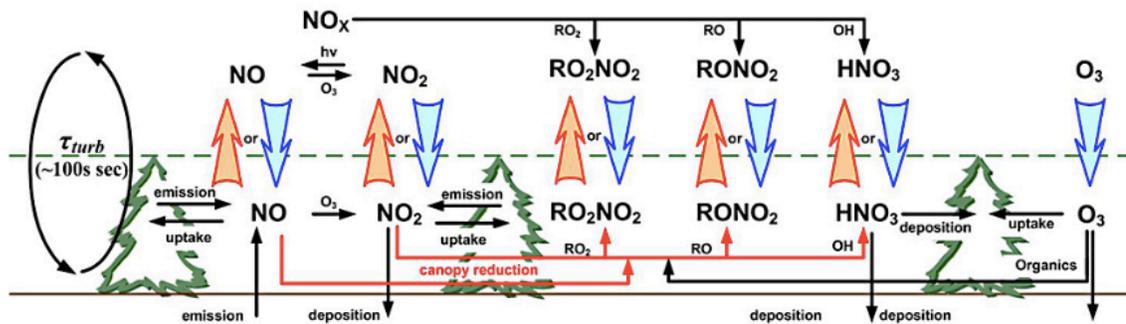
Wet, dry, and occult deposition all contribute N and S species to the forest canopy in varying proportions. Deposited species can react on surfaces within the canopy, be taken up by vegetation through stomata, be resuspended during stormy weather, or simply pass through the canopy to the forest floor. Surface characteristics can influence foliar uptake, chemical transformation, and resuspension. Landscape characteristics can affect wet deposition via orographic effects and by the closer aerodynamic coupling to the atmosphere of tall forest canopies as compared to the shorter shrub and herbaceous canopies. The rainwater that passes directly through a canopy or is initially intercepted by aboveground vegetative surfaces and subsequently drips from the canopy is measured as throughfall. The fraction of the precipitation that drains from outlying leaves and branches and is channeled to the stem of plants is classified as stemflow. Throughfall and stemflow inputs constitute the majority of incident precipitation in forests and can account for 70 to 90% of incoming precipitation in most cases, with the remainder lost to interception within the canopy ([Levia and Frost, 2003](#)). Compared to wet deposition measurements in the open, the magnitude of deposition from throughfall and stemflow can either be smaller (e.g., from evaporation from canopy surfaces) or larger (e.g., from resuspension of previously deposited material). The type of vegetation is important for characterizing throughfall. For example, [Templer et al. \(2015a\)](#) found that the cycling of N, particularly the rate of throughfall for  $NH_4^+$ , is significantly different in conifer compared to deciduous forest sites. Rainfall introduces new wet deposition and also redistributes previously dry-deposited particles throughout the canopy. Intense rainfall may contribute substantial total particulate inputs to the soil, but it also removes bioavailable or injurious pollutants from foliar surfaces, while low-intensity events may enhance foliar uptake through the hydrating of some previously dry-deposited particles ([U.S. EPA, 2004](#)).

Chemistry within the canopy can also be important. Very fast measurements of  $NO_2$  flux are confounded by the rapid interconversion of NO and  $NO_2$  with  $O_3$ , and the biosphere also interacts with  $NO_x$  through hydrocarbon emissions and their subsequent reactions to form multifunctional  $RONO_2$ , including isoprene nitrates, which can account for a substantial fraction of total N deposition.  $NO_2$  emissions also show UV dependence, and both photo-induced and dark production of  $HNO_2$  from  $NO_2$  have been observed on leaf surfaces, especially wet surfaces, although there is no consensus concerning chemical mechanisms ([U.S. EPA, 2008a](#)). It was recently reported that  $NO_2$  deposition velocities would have been overestimated by up to 80% if  $NO_2$  photolysis had not been considered

([Breuninger et al., 2012](#)). Both biotic interactions and reaction chemistry further complicate our understanding of N deposition and our ability to estimate deposition velocity.

Some species, most prominently  $\text{HNO}_3$ , can be characterized by unidirectional exchange, whereas bidirectional exchange is more appropriate for most other species. Bidirectional exchange is often described in terms of a compensation point, defined as the ambient concentration above which a net uptake of the trace gas occurs and below which the trace gas is released ([Ganzeveld et al., 2002](#)). A two-pathway process description can be used to describe bidirectional exchange in a forest canopy [e.g., [Fowler et al. \(2009\)](#); [Loubet et al. \(2001\)](#)]: (1) a stomatal pathway, which is bidirectional and modeled using a stomatal compensation point and (2) a plant surface pathway, which denotes exchange with water or waxes on the plant surface.

Understanding the exchange of reactive nitrogen species in the forest canopy has always been challenging. One of the most comprehensive studies focusing on this question has been the Biosphere Effects on AeRosols and Photochemistry Experiment (BEARPEX) conducted in 2009 ([Min et al., 2014](#)) that examined fluxes and transformations of  $\text{NO}_x$  within a forest canopy on the western slope of the Sierra Madre Range in 2009. The study's results, shown schematically in [Figure 2-10](#), indicate the existence of active chemical interactions within the forest canopy in which  $\text{NO}$  emitted from soil or transported from elsewhere is oxidized to  $\text{NO}_2$  and then to peroxy and alkyl nitrates and  $\text{HNO}_3$ . These pathways represent alternative mechanisms to plant uptake that have the net effect of reducing the soil  $\text{NO}$  that escapes the forest canopy as  $\text{NO}_x$  is converted to peroxy nitrates and alkyl nitrates that can be transported to the atmosphere above the canopy on very short time scales ( $\sim 100$ s of seconds). The fraction of  $\text{NO}$  emitted by soil that can be lost to the atmosphere above the canopy depends on the relative time scales for transport through the canopy versus chemical transformation and foliar uptake. Likewise,  $\text{NO}$  or  $\text{NO}_2$  transported from elsewhere can also be oxidized to organic nitrates within the canopy. The organic nitrates formed can either be taken up within the canopy or transported upward through the forest canopy to act as reservoirs of  $\text{NO}_x$  that can reform downwind.



HNO<sub>3</sub> = nitric acid; hv = solar photon; OH = hydroxyl radical; NO = nitric oxide; NO<sub>2</sub> = nitrogen dioxide; NO<sub>x</sub> = sum of NO and NO<sub>2</sub>; O<sub>3</sub> = ozone; RO = alkoxy radicals; RO<sub>2</sub> = organic peroxy radicals; RONO<sub>2</sub> = alkyl nitrates; RO<sub>2</sub>NO<sub>2</sub> = peroxy nitrates.

Bold arrows in blue (downward) and red (upward) represent the direction of the flux of each species across the canopy surface. Red thin arrows within canopy indicate the nitrogen oxides removal processes within the canopy in addition to plant uptake.

Source: [Min et al. \(2014\)](#).

**Figure 2-10 Schematic of the interactions involved in the exchange of nitrogen oxides between the atmosphere and the forest canopy as identified by [Min et al. \(2014\)](#).**

The organic nitrates consist in large measure of isoprene- and monoterpene-derived nitrates. [Nguyen et al. \(2015\)](#) measured fluxes of organic nitrates on a tall tower in the Talladega National Forest (AL) in June 2013 as part of the Southern Oxidant and Aerosol Study (SOAS). They found that fluxes of organic nitrogen formed by reactions of nitrogen oxides (NO, NO<sub>2</sub>, NO<sub>3</sub>) with isoprene and monoterpene oxidation products constituted ~15% of the flux of oxidized N to the forest canopy, with most of the rest from HNO<sub>3</sub>.

### 2.5.2.3 Bidirectional Exchange of NH<sub>3</sub>

NH<sub>3</sub> can also be both emitted and deposited from plants and soils in a bidirectional exchange. [Farquhar et al. \(1980\)](#) observed the existence of a compensation point for ammonia due to gas exchange through the stomata of leaves. NH<sub>3</sub> in the stomata results from dissociation equilibria of NH<sub>4</sub><sup>+</sup> produced physiologically in the leaves, followed by equilibrium partitioning into air in the stomata ([Sutton et al., 1998](#)). Further research indicated that NH<sub>3</sub> deposition rates to leaf surfaces were often faster than stomatal uptake ([Sutton et al., 1993](#)) and that NH<sub>3</sub> can both react to form particulate NH<sub>4</sub><sup>+</sup> and evaporate from deposited PM within the canopy ([Nemitz et al., 2004](#); [Brost et al., 1988](#)). Moisture and plant type are strong influences, because deposition is more efficient on wet surfaces ([Sutton et al., 1995](#)), evaporation occurs under drying conditions ([Fowler et al., 2009](#)),

and plant emissions are controlled by the physiological importance of  $\text{NH}_4^+$  in intercellular fluids of plants ([Sutton et al., 1998](#)). Copollutants also play a role because  $\text{NH}_3$  deposition is enhanced by the presence of atmospheric acids like  $\text{SO}_2$  ([Sutton et al., 1995](#); [McLeod et al., 1990](#)).

The complex pattern of  $\text{NH}_3$  sources and sinks with strong horizontal gradients of  $\text{NH}_3$  concentration ([Fowler et al., 2009](#)) presents problems for simple bidirectional exchange models ([Sutton et al., 1998](#)). These problems have been addressed through the concept of a canopy compensation point to include exchange with leaf surfaces ([Flechard et al., 1999](#); [Sutton et al., 1998](#)), as well as decomposing leaf litter and soil surfaces ([Nemitz, 2000](#)) in addition to stomatal exchange to describe bidirectional exchange ([Burkhardt et al., 2008](#); [Sutton et al., 1998](#)). Emission flux is particularly high from recently fertilized soils ([Fowler et al., 2009](#); [Sutton et al., 1998](#)) and after leaf-cutting events ([Nemitz et al., 2009](#)).

According to the 2008 ISA ([U.S. EPA, 2008a](#)), large areas of the U.S. are very near the  $\text{NH}_3$  compensation point for most of the year, resulting in a highly dynamic air-surface flux, which is prone to shifts in magnitude and direction. Bidirectional  $\text{NH}_3$  fluxes with some periods of deposition and some periods of emission are typical for fertilized and grazed agricultural ecosystems, while forests and other unfertilized ecosystems are usually sinks for  $\text{NH}_3$  ([Fowler et al., 2009](#)). Smaller emissions can also occur in semi natural ecosystems ([Fowler et al., 2009](#)).

Recently, regional scale modeling studies began to include canopy compensation points and parameterize bidirectional exchange ([Kruit et al., 2012](#); [Dennis et al., 2010](#); [Kruit et al., 2010](#)), and a bidirectional exchange model for  $\text{NH}_3$  based on observations from North Carolina field sites ([Walker et al., 2013](#)) was developed for the CMAQ modeling system and an agroecosystem model was included in CMAQ Version 5.0 to estimate  $\text{NH}_3$  emissions, transport, and deposition from agricultural practices ([Bash et al., 2013](#)). Including bidirectional exchange in deposition modeling substantially improves agreement between modeling results and ambient observations. A large bias of  $-19\%$  has been observed in annual wet deposition of  $\text{NH}_4^+$  when modeling results were compared with ambient measurements without bidirectional exchange included in the model ([Appel et al., 2011](#)).  $\text{NH}_4^+$  was underestimated throughout the year, but the largest underestimations were for winter and spring in the Eastern U.S. ([Appel et al., 2011](#)). The  $\text{NH}_4^+$  wet deposition bias was reduced by a factor 3, from  $-19$  to  $-6\%$ , by including bidirectional exchange in CMAQ ([Appel et al., 2011](#)).

Poor temporal and spatial representation of  $\text{NH}_3$  emissions in areas with fertilizer application was also identified as a source of bias ([Appel et al., 2011](#)). When CMAQ was coupled with the U.S. Department of Agriculture's (USDA) Environmental Policy

Integrated Climate (EPIC) agroecosystem model to improve characterization of fertilizer emissions in annual simulations, NH<sub>3</sub> dry deposition decreased by 45%, total NH<sub>x</sub> deposition decreased by 15%, and total N deposition decreased by 5% compared to modeling without bidirectional exchange ([Bash et al., 2013](#)). In sensitivity tests of key parameters in dry deposition modeling, the largest uncertainty was observed for the change of unidirectional to bidirectional flux, but uncertainties of 5% or less in total nitrogen deposition were reported ([Dennis et al., 2013](#)). Although this is a small difference nationwide, changes can locally be up to 50%, and only 66% of the 12 × 12 grid cells modeled showed changes of less than 10% ([Dennis et al., 2013](#)).

Recent modeling studies have also improved insight into local areas and conditions under which bidirectional flux most strongly affects deposition estimates. For example, accounting for bidirectional flux resulted in a 17% increase in NH<sub>3</sub> emissions from agricultural operations ([Massad et al., 2010](#)) compared with a 5% increase in domain-wide NH<sub>3</sub> emissions ([Dennis et al., 2013](#)). Increases in NH<sub>3</sub> emissions from including bidirectional flux in semi natural ecosystems mostly occurred in areas of the western U.S. with low emissions, where emissions were not included in existing inventories. Seminal ecosystems in the eastern U.S. isolated from agricultural emissions exhibited changes of less than 1%. Seasonal differences were also observed, with greater NH<sub>3</sub> emissions observed in summer and winter, but emissions up to 45% lower in fall and in spring when bidirectional exchange was included ([Bash et al., 2013](#)).

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#### 2.5.2.4 Transference Ratios

Ratios of modeled or measured concentrations of SO<sub>x</sub> and NO<sub>y</sub> to their deposition, or transference ratios (TR<sub>SO<sub>x</sub></sub>, TR<sub>NO<sub>y</sub></sub>) were proposed by [Scheffe et al. \(2011\)](#) as a means to link ambient air quality to deposition, and can be extended to NH<sub>x</sub>. Transference ratios for NO<sub>y</sub>, SO<sub>x</sub>, and NH<sub>x</sub> are given by:

- $TR_{NO_y} = (\text{annual wet} + \text{dry deposition of } NO_y) / \text{annual average ambient concentration of } NO_y$
- $TR_{SO_x} = (\text{annual wet} + \text{dry deposition of } SO_x) / \text{annual average ambient concentration of } SO_x$
- $TR_{NH_x} = (\text{annual wet} + \text{dry deposition of } NH_x) / \text{annual average ambient concentration of } NH_x$

These ratios are expressed in units of distance/time (as a velocity). In the 2011 Policy Analysis for the NO<sub>x</sub>/SO<sub>x</sub> NAAQS review ([U.S. EPA, 2011a](#)), the transference ratios were multiplied by measured ambient concentrations of NO<sub>y</sub> and SO<sub>x</sub> to estimate a flux.

The transference ratio is an aggregate of multiple forms of nitrogen or sulfur. For example, the transference ratio for  $\text{NO}_Y$  includes  $\text{NO}_2$  and  $\text{HNO}_3$ , which have very different deposition rates, chemical reaction rates, and atmospheric lifetimes. Close to emission sources where fresh  $\text{NO}_X$  emissions have had little time to react, the ratio of  $\text{HNO}_3$  to  $\text{NO}_2$  is smaller than farther from emission sources. Accordingly, there is considerable spatial and temporal variability ([Sickles et al., 2013](#)) in transference ratios, in part governed by the relative abundance of compounds with short and relatively longer atmospheric lifetimes.

In practice, a regional modeling approach using a modeling system such as CMAQ or CAMx is used in the calculation of transference ratios by simulating the relevant transport processes discussed in [Appendix 2.5.1](#). [Sickles and Shadwick \(2013\)](#) estimated that  $\text{TR}_{\text{SO}_X}$  and  $\text{TR}_{\text{NO}_Y}$  could be given to within 25–35% of observed values using observations of atmospheric concentration and deposition at some monitoring sites in the eastern U.S. The study noted that accounting for year-to-year variability in precipitation could lower the uncertainty. The transport processes described in [Appendix 2.5.1](#) imply that wet deposition should not necessarily be well correlated with surface concentrations due to differences in the direction or spatial extent of transport in the boundary layer compared to cloud levels. Dry deposition fluxes are more directly related to surface concentrations. In a follow-on study, [Sickles et al. \(2013\)](#) calculated transference ratios using measurements from CASTNET and NADP monitoring networks with CMAQ model results and found the relative difference ranged from –37 to 64%. The authors caution that this range should not be considered a definitive assessment of uncertainty because relative differences do not reflect the extent to which the monitor is representative of the grid-cell average modeled by CMAQ.

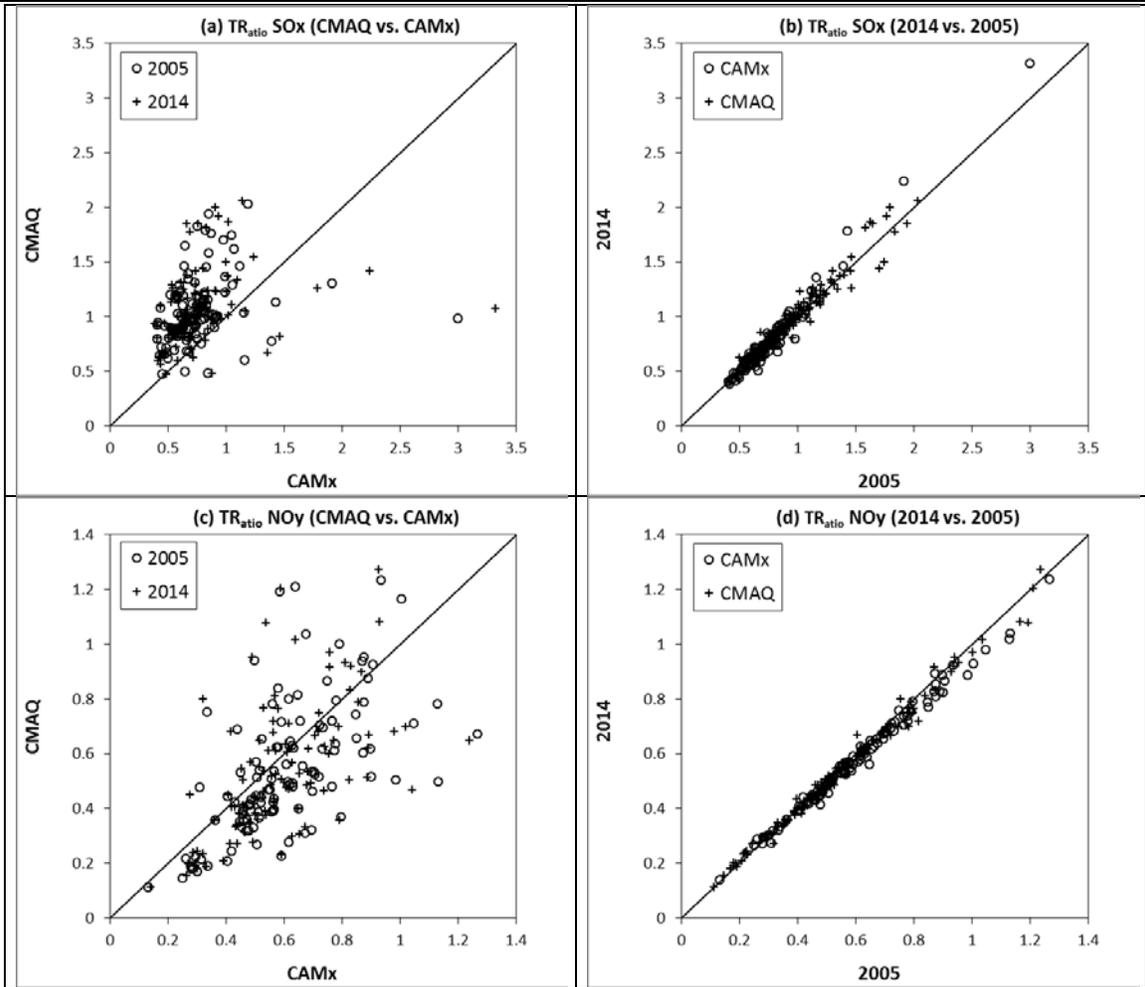
[Koo et al. \(2012\)](#) and [Koo et al. \(2015\)](#) raised the issue of model dependence on the calculation of depositing species and transference ratios. [Koo et al. \(2012\)](#) compared model results for concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$ , and  $\text{NO}_3^-$  and corresponding dry deposition fluxes from CMAQ and CAMx to those measured at CASTNET sites. They also compared model results for wet deposition to NADP/NTN measurements. On an annualized basis, mean normalized errors (MNEs) in gas-phase concentrations ranged from ~25 to ~100%. MNEs in dry deposition were much larger and ranged from ~50 to >300% and MNE in wet deposition ranged from ~40 to ~100% with no clear preference for one model over another. MNE for  $\text{NH}_4^+$  in dry and wet deposition ranged from ~35 to 70%. [Koo et al. \(2012\)](#) also found evidence for spatial variability in  $\text{TR}_{\text{SO}_X}$  and  $\text{TR}_{\text{NO}_Y}$  across the U.S. and within selected ecosystems (roughly a few hundred km across).

[Koo et al. \(2015\)](#) compared simulations of transference ratios computed using CMAQ and CAMx for two model years, 2005 and 2014, (see [Figure 2-11](#)) and found that  $\text{TR}_{\text{SO}_X}$

was much higher in CMAQ than in CAMx; however, differences were much smaller for  $TR_{NO_Y}$ .  $R^2$  values for  $TR_{NO_Y}$  between the two models was 0.37 for 2005 and 0.33 for 2014. For  $TR_{SO_X}$ ,  $R^2$  was 0.073 for 2005 and 0.072 for 2014. Note that each point shown in [Figure 2-11](#) represents the average over  $365 \times 24$  model entries and are dissimilar to measurement artifacts. The outlying point (in the lower right) is from the Weminuche Wilderness IMPROVE site (WEMI) in the Rockies and likely is the result of the difficulty mesoscale models have in simulating precipitation and flow patterns in areas of high relief and indicates further work is needed in this regard. Note that the disagreement in  $TR_{SO_X}$  by CMAQ is mostly due to an error in CMAQ emissions of  $SO_2$  that has since been corrected. There is no consistent geographic pattern of agreement or disagreement between the two simulations.

A more complete understanding of the causes of differences between model simulations requires understanding the differences in how major chemical and physical processes have been parameterized, thus underscoring the importance of accurately representing emissions, transport, chemistry, and deposition. Both models used different modules to represent these processes. In addition, these results might imply that the metrics used need further scrutiny. Note again that the results shown in [Koo et al. \(2012\)](#) and [Koo et al. \(2015\)](#) were obtained using older versions of CMAQ and CAMx and that CTMs are continually undergoing improvement. In this regard, detailed comparisons with observations and intercomparisons between the most current versions of these models might help explain these findings.

[Koo et al. \(2015\)](#) also found very small differences between simulations for model years 2005 and 2014 from either CMAQ or CAMx for both  $NO_Y$  and  $SO_X$ , indicating the ratios are relatively invariant at least over an annual time scale. This result is not surprising, because with the long averaging time, concentrations and deposition rates can better track emissions changes.



CAMx = Comprehensive Air Quality Model with Extensions; CMAQ = Community Multiscale Air Quality;  $\text{NO}_y$  = oxides of nitrogen;  $\text{SO}_x$  = sulfur oxides;  $\text{TR}_{\text{ratio}}$  = transference ratio.

Source: Adapted from [Koo et al. \(2015\)](#).

**Figure 2-11 Scatterplots showing transference ratios for oxidized nitrogen and sulfur oxides comparing the Community Multiscale Air Quality model to the Comprehensive Air Quality Model with Extensions in (a) and (c) and comparing 2005 to 2014 in (b) and (d).**

To summarize, recent studies have found that using transference ratios for estimating the deposition flux from atmospheric measurements has lower uncertainty when applied at an annual timescale. The transference ratio can vary spatially, and an estimate of uncertainty and variability depends on the spatial scale of interest. Finally, previous studies have highlighted some of the uncertainties when using models to calculate the transference

ratio, but a comprehensive assessment of uncertainty is not available. When the transference ratio is calculated using observations of atmospheric concentrations from monitoring networks, the deposition flux for oxidized sulfur and oxidized nitrogen can be estimated to within 25 to 35%.

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### 2.5.3 Model Evaluation and Uncertainty

CMAQ model estimates were recently compared to monitoring network observations and results were reported as normalized mean bias statistics ([U.S. EPA, 2011a](#), [2009c](#)). Total nitrate concentrations were overestimated by CMAQ, with predictions averaged over each of 4 years ranging from 22 to 26% higher than observed concentrations ([U.S. EPA, 2011a](#)). Model performance was described as good for total SO<sub>x</sub>, but the ability to partition SO<sub>x</sub> into sulfate and SO<sub>2</sub> was identified as an area that needed improvement ([U.S. EPA, 2011a](#)). SO<sub>2</sub> concentrations were overestimated, with CMAQ predictions ranging from 39 to 47% higher than observed concentrations. Sulfate concentrations were underestimated, with CMAQ predictions ranging from 9 to 17% lower than observed concentrations ([U.S. EPA, 2011a](#)). A disadvantage of this type of comparison is that modeled concentrations are outputted for a 12 × 12 km grid, while measured concentrations are from a single point within that grid.

Wet deposition estimates from CTMs were extensively evaluated using wet deposition data collected over the U.S. as part of the National Atmospheric Deposition Program's National Trends Network. [Simon et al. \(2012\)](#) summarized model evaluation studies published before 2010, and [Table 2-7](#) summarizes the studies since 2010.

While measurements comparing model outputs to observations provide one perspective on the uncertainty in the fate and transport of atmospheric N and S, another approach to quantifying uncertainty is to estimate the sensitivity of the model results with respect to the uncertain range of parameters relevant to deposition calculations. A study by [Dennis et al. \(2013\)](#) examined a range of uncertainties relevant to dry deposition using the CMAQ model. This study found little change (<5%) in total deposition, despite changes in dry deposition parameters because competing processes in the model tended to rebalance and compensate. Changes in a single grid cell were as large as 20%.

There are also structural uncertainties that are difficult to assess in applying CTM models to estimate deposition. The main structural uncertainties are associated with canopy effects of NO<sub>x</sub>, bidirectional exchange of NH<sub>3</sub>, and transference ratios that relate average concentration to deposition. These factors are discussed in [Appendix 2.5.2](#).

**Table 2-7 Reported comparisons of chemical transport models and observations of nitrogen and sulfur wet deposition**

Reference	Bias/Error	Model	Metric
<a href="#">Appel et al. (2011)</a>	7.9% normalized mean bias	CMAQ	Annual, wet deposition, sulfate, continental U.S.
<a href="#">Appel et al. (2011)</a>	-12.8% normalized mean bias	CMAQ	Annual, wet deposition, ammonium, continental U.S.
<a href="#">Appel et al. (2011)</a>	-12.8% normalized mean bias	CMAQ	Annual, wet deposition, ammonium, continental U.S.
<a href="#">Appel et al. (2011)</a>	-15% normalized mean bias	CMAQ	Annual, wet deposition, nitrate, continental U.S.
<a href="#">Appel et al. (2011)</a>	0.5 kg/ha median bias	CMAQ	Annual, wet deposition, nitrate, continental U.S.
<a href="#">Zhang et al. (2012a)</a>	6.5% mean normalized bias	GEOS-Chem	Annual, wet deposition, sulfate, continental U.S.
<a href="#">Zhang et al. (2012a)</a>	10% mean normalized bias	GEOS-Chem	Annual, wet deposition, nitrate, continental U.S.
<a href="#">Zhang et al. (2012a)</a>	7.4% mean normalized bias	GEOS-Chem	Annual, wet deposition, ammonium, continental U.S.
<a href="#">Koo et al. (2012)</a>	45 to 99% normalized mean error	CMAQ	Annual, wet deposition, sulfate, continental U.S.
<a href="#">Koo et al. (2012)</a>	38 to 99% normalized mean error	CMAQ	Annual, wet deposition, nitrate, continental U.S.
<a href="#">Koo et al. (2012)</a>	45 to 66% normalized mean error	CMAQ	Annual, wet deposition, ammonium, continental U.S.
<a href="#">Williams et al. (2017a)</a>	0.34 kg ha <sup>-1</sup> mean error	CMAQ	Annual, wet deposition, inorganic nitrogen, Pacific Northwest

## 2.6 Geographic Distribution of Concentration and Deposition

Maps of national distributions of emissions, atmospheric concentrations, and deposition fluxes of relevant species are presented in this section. The first two sections are limited to deposition maps and are intended to provide a broad overview of the extent and recent trends for acid deposition ([Appendix 2.6.1](#)) and total nitrogen deposition, including relative contributions of reduced and oxidized nitrogen ([Appendix 2.6.2](#)). The subsequent three sections contain data on geographic distributions of emissions, ambient

concentrations and deposition of oxidized nitrogen ([Appendix 2.6.3](#)), reduced nitrogen ([Appendix 2.6.4](#)), and sulfur oxides ([Appendix 2.6.5](#)), including key species in each of these classes.

Emission maps in [Appendix 2.6.3](#), [Appendix 2.6.4](#), and [Appendix 2.6.5](#) are from U.S. EPA's National Emissions Inventory described in [Appendix 2.2](#). Ambient concentration maps in these sections are from a variety of sources, depending on the availability of data. Deposition maps in [Appendix 2.6.1](#), [Appendix 2.6.2](#), [Appendix 2.6.3](#), [Appendix 2.6.4](#), and [Appendix 2.6.5](#) are based on the approach of [Schwede and Lear \(2014a\)](#) which combines measured and modeled values to produce spatially aggregated maps of wet, dry, and total (wet plus dry) deposition of nitrogen and sulfur species across the U.S. Wet deposition is based on concentrations measured in rainwater collected at NADP/NTN monitoring sites combined with precipitation estimates interpolated by PRISM (Parameter-elevation Regression Slopes Model) using inverse distance weighting (IDW). In their approach to dry deposition, [Schwede and Lear \(2014a\)](#) measured values of species concentrations in air at monitoring site locations and used bias-corrected modeling results from CMAQ (currently at 12-km horizontal resolution) to fill in gaps between sites and provide composition and deposition information for species not measured (PANs, NO<sub>2</sub>, and HONO) in the routine monitoring networks. Distributions of species that undergo dry deposition are derived mainly by fusion of data from the Clean Air Status and Trends Network (CASTNET), the National Atmospheric Deposition Program (NADP), Ammonia Monitoring Network (AMoN), and the Southeastern Aerosol Research and Characterization (SEARCH) network. Parameterizations in CMAQ are used to calculate deposition velocities for gases and particles ([Pleim and Ran, 2011](#)). Note that CMAQ includes bidirectional exchange for NH<sub>3</sub> ([Bash et al., 2012](#)), but not for other species such as NO<sub>2</sub>. Dry deposition fluxes are then combined with wet fluxes to estimate total deposition. Details on interpolation, special treatment for particulate species calculations, and procedures to correct for bias are described in detail by [Schwede and Lear \(2014a\)](#).

Efforts have also been made to achieve greater consistency by relying more heavily on WRF/CMAQ simulations for estimating wet deposition. Effects of biases in CMAQ wet deposition are corrected by adjusting the modeled wet deposition by the ratio of observed precipitation interpolated by PRISM to WRF precipitation. In this approach, it is assumed that the ratio of observed to modeled precipitation is well correlated with the ratio of observed to modeled wet deposition, but not (necessarily) that wet deposition scales linearly with precipitation ([Appel et al., 2011](#)). Likewise, estimates of dry deposition could be obtained using CMAQ evaluated by comparison with monitoring results.

This approach resulted from efforts to improve estimates of atmospheric deposition by advancing the science of measuring and modeling atmospheric wet, dry, and total deposition of atmospheric species. Recognizing that the thin geographic coverage and the lack of species measurements described in [Appendix 2.4.6](#) are not ideal for estimating dry deposition on a national scale, the NADP established the Total Deposition Science Committee (TDEP) with this mission in 2011, with an initial goal of providing estimates of total S and N deposition across the U.S. for use in estimating critical loads and other assessments, where loading results in the acidification and eutrophication of ecosystems ([NADP, 2016](#)). Following this hybrid approach to mapping total deposition that combines measured and modeled values, measured values are given more weight at the monitoring locations, and modeled data are used to fill in spatial gaps and provide information on chemical species that are not measured by routine monitoring networks. This effort provides continuous spatial and temporal coverage of total deposition estimates in the U.S., something previously unavailable ([NADP, 2016](#)).

Limitations to the TDEP approach are: (1) interpolation leads to a minimization of extreme values and a lower than actual variability, (2) data are limited to sites that meet network completion criteria, (3) discontinuities in trends can occur for intermittent monitoring data, (4) characterization of wet and dry organic nitrogen components is uncertain and likely incomplete, (5) deposition in urban areas is not well represented because the monitoring sites used are primarily in rural areas, and (6) occult deposition is not well understood and might not be characterized accurately. An additional potential drawback is that a mass balance is not maintained, although the mass balance error was small in a similar effort combining measured wet deposition and bias corrected modeled deposition ([Schwede and Lear, 2014a](#)).

Differences in wet deposition of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  and N + S expressed as  $\text{H}^+$  equivalents between the two, 3-year periods 1989–1991 and 2012–2014 across the U.S. are shown in [Figure 2-13](#), [Figure 2-27](#), [Figure 2-34](#), and [Figure 2-43](#). These figures are based on data obtained by the NADP/NTN. The maps were constructed by summing gridded values and then taking the difference between the two, 3-year averages using data from the NADP website. These maps are meant to provide a general indication of large-scale features in the patterns and long-term changes in deposition, with potential for error from extensive interpolation between monitoring sites, which are often distant from each other. The TDEP values shown on the maps are derived from NADP/NTN wet deposition measurements at 4-km resolution coupled with CMAQ results for dry deposition at 12 km. [Weathers et al. \(2006\)](#) found evidence for substantial spatial variability in deposition with altitude, generally at smaller scales than used for TDEP. In particular, they found evidence for factors of 4–6 variability in N and S deposition throughout Acadia National Park (121 km<sup>2</sup>) and Great Smoky Mountains National Park

(2,074 km<sup>2</sup>); deposition rates averaged over the two parks were ~70% higher than inferred using only in situ point measurements. As might be expected, deposition increased with elevation because of the increased importance of cloud deposition and dry deposition (due to higher winds and hence increased turbulence). As noted by the NADP, uncertainty within maps of wet deposition varies geographically and has not been quantified.

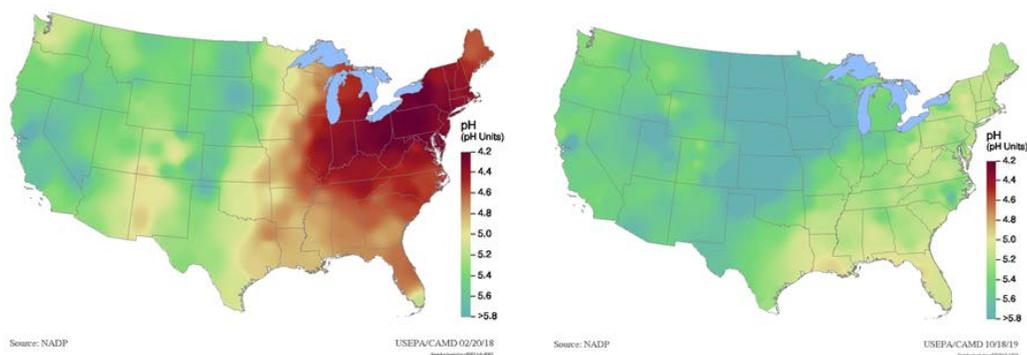
[Appendix 2.6.6](#) and [Appendix 2.6.7](#) summarize concentration and deposition data from other approaches. [Appendix 2.6.6](#) describes distributions of dry deposition of NO<sub>2</sub> and SO<sub>2</sub> from satellite-based measurements of tropospheric vertical column abundance and model input derived by [Nowlan et al. \(2014\)](#). [Appendix 2.6.7](#) describes recent estimates of background concentrations, deposition fluxes, and sources and methods used to obtain them.

Additional maps on the portion of the NADP website dedicated to the Total Deposition (TDEP) program (<http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>) are shown in [Appendix 2.7](#). They present a comprehensive overview of changes in various parameters related to deposition from 2000–2018. Each map shows two 3-year periods, 2000–2002 and 2016–2018. Although uncertainty has not been fully characterized using the TDEP approach, they are instructive because they give an indication of how various estimates carried out with the same approach have changed over the past decade.

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## 2.6.1 pH and H<sup>+</sup> Equivalents

Long-term trends in rainwater pH over the CONUS between the two periods 1989 to 1991 and 2016 to 2018 are shown in [Figure 2-12](#). Substantial improvement in the quality of rainwater in terms of pH has occurred from the earlier to the later period. [Figure 2-12](#) is a remarkable demonstration of the effectiveness of the Clean Air Act Amendments, showing that the steep reductions of NO<sub>x</sub> and SO<sub>2</sub> emissions described in [Appendix 2.2](#) coincide with a sharp decline in pH.



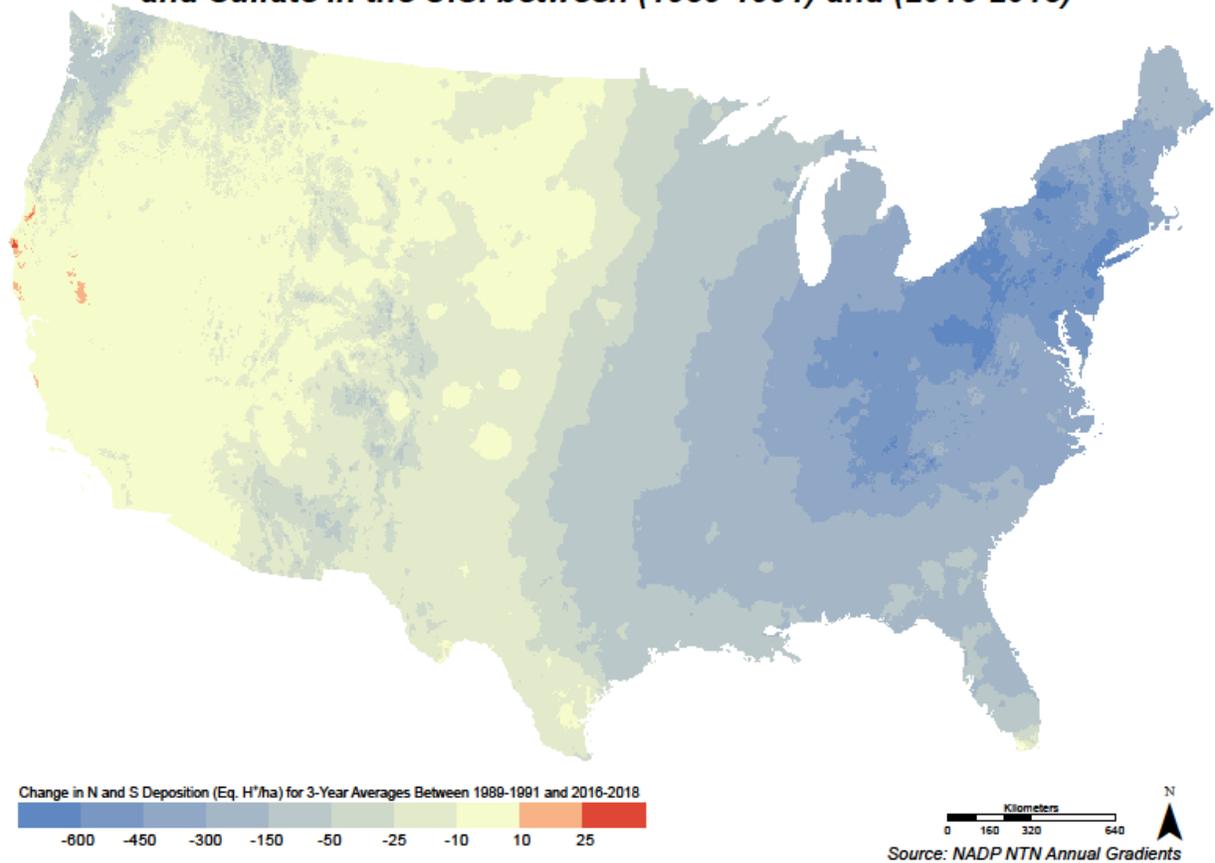
Source: NADP/U.S. EPA/CAMD. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-12 (Left) pH of rainwater, 1989–1991; (Right) pH of rainwater, 2016–2018.**

However, there are areas, especially in the eastern U.S. near the upper Ohio River Valley, where the pH of rainwater is still much lower than the reference pH of  $\sim 5.65$  (for equilibrium with  $\text{CO}_2$ ) that has often been used as a benchmark when characterizing the excess acidity of rainwater. (Note that the reference  $\text{CO}_2$  concentration used to determine this value is 316 ppm, atmospheric  $\text{CO}_2$  concentrations are now over 400 ppm, resulting in a lowering of pH by  $\sim 0.05$  units.) As noted by [Galloway et al. \(1976\)](#), the major contributors to free acidity in rainwater for  $\text{pH} < 5.6$  are the strong mineral acids  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . However, weak acids (e.g., organic acids) can contribute substantively to free acidity at pH levels seen throughout much of the U.S. (see [Appendix 2.3.5](#)). For example, concentrations of formic acid and acetic acid ( $\text{pK}_a = 3.75, 4.76$ ) measured in rainwater at  $\text{pH} \sim 5$  by [Avery et al. \(2006\)](#) are on the order of  $10 \mu\text{M}$ , which is comparable to concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  measured in rainwater. Additionally, in areas like the Northwest where the pH of stream water can be around or even larger than 5.6, acidification of streams by  $\text{CO}_2$  might also need to be considered ([Ou et al., 2015](#)).

The change in acid loading ( $\text{H}^+$  equivalents) due to wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$  ions in precipitation expressed as  $\text{H}^+$  equivalents between the two, 3-year periods 1989–1991 and 2016–2018 across the U.S. based on data obtained by the NADP/NTN is shown in [Figure 2-13](#). Substantial decreases in acid loading are seen in the eastern U.S., with most of the central and western U.S. showing smaller negative changes or essentially no change.

**Change in Nitrogen and Sulfur Wet Deposition from Nitrate, Ammonium, and Sulfate in the U.S. between (1989-1991) and (2016-2018)**



eq = H<sup>+</sup> equivalent; H<sup>+</sup> = hydrogen ion.

Source: CPHEA analysis of CASTNET/CMAQ/NTN/AMON/SEARCH data.

**Figure 2-13** Difference in wet deposition of nitrate, ammonium, and sulfate expressed as hydrogen ion equivalents (eq/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018.

This map was constructed by summing gridded values and then taking the difference between the two, 3-year averages using data from the NADP website. Although instructive, these results should be viewed with some caution, as errors are incurred because development of a map spanning the CONUS requires extensive interpolation between monitoring sites, which are often distant from each other. As noted by the NADP, uncertainty within maps of wet deposition varies geographically and has not been quantified. Therefore, these maps are meant to provide a general indication of large-scale features in the patterns and long-term changes in deposition.

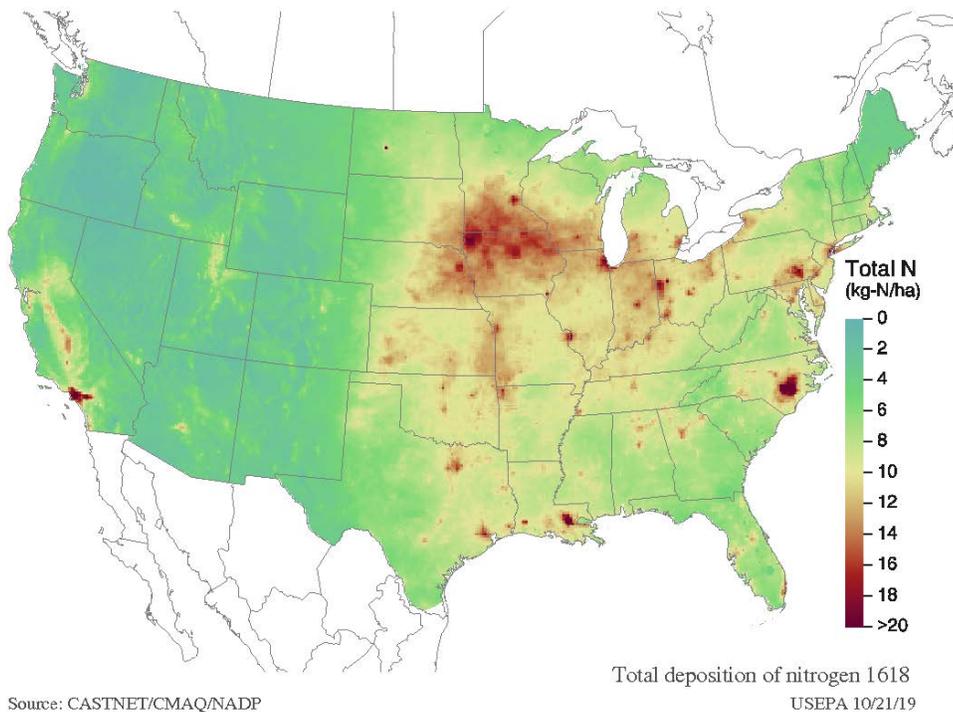
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## 2.6.2 Total Nitrogen

[Figure 2-14](#) shows total deposition of N averaged over 2016–2018. This is determined from the sum of dry and wet deposition for all  $\text{NO}_Y$  and  $\text{NH}_X$  species considered by CMAQ. Fluxes are based on the method developed by [Schwede and Lear \(2014a\)](#) as outlined above and are given in terms of kg N/ha/yr.

As can be seen from [Figure 2-14](#), the highest deposition of nitrogen occurs in a broad swath across the Midwest, and in more localized patches across the U.S. Total N deposition can be put in context by comparing the deposition amounts in [Figure 2-14](#) to estimates of critical load, which is the N deposition amount below which no significant harmful effects on sensitive elements of the environment occur. These are typically below 10 kg N/ha/yr and can be as low as 2–3 kg N/ha/yr in both eastern and western locations ([Lee et al., 2016](#); [Ellis et al., 2013](#)), amounts which are firmly below the estimated deposition amounts in [Figure 2-14](#) over wide areas of the U.S. [Ellis et al. \(2013\)](#) observed that critical loads were exceeded in 24 of 45 parks, and [Lee et al. \(2016\)](#) observed that critical loads were exceeded at more locations in the western U.S., but by larger amounts in the eastern U.S.

Inspection of [Figure 2-15a](#) and [Figure 2-15b](#) shows that many of these areas are dominated either by deposition of  $\text{NH}_X$  emitted mainly by agriculture (e.g., California's Central Valley, Upper Midwest), or  $\text{NO}_Y$  resulting from oxidation of nitrogen oxides emitted mainly by combustion sources (e.g., the Northeast, Southwest). As might be expected when considering all forms of  $\text{NO}_Y$ , total deposition tends to be much higher near urban and suburban areas. Note also that deposition of  $\text{N}_r$ , based on the hybrid measurements/modeling approach, is dominated by reduced forms across the CONUS as a whole. This is consistent with Cross-Track Infrared Sounder Satellite measurements ([Appendix 2.4.2.2](#)) combined with dry deposition modeling to show that  $\text{NH}_3$  deposition fluxes were greater than  $\text{NO}_Y$  in most regions of North America ([Kharol et al., 2018](#)). [Figure 2-16](#) illustrates how this has changed over time by comparing trends in oxidized and reduced nitrogen deposition and changes in contributions of major species and type of deposition from 2000–2017 ([NADP, 2019](#)).



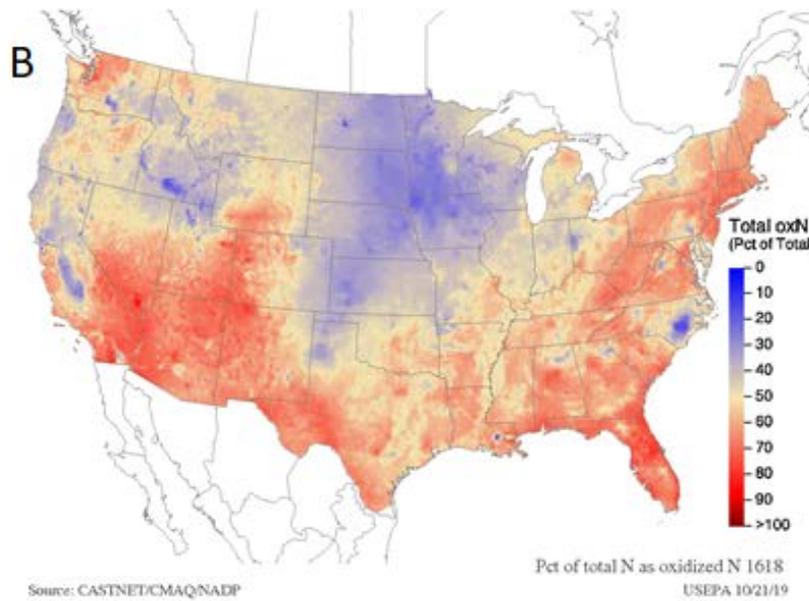
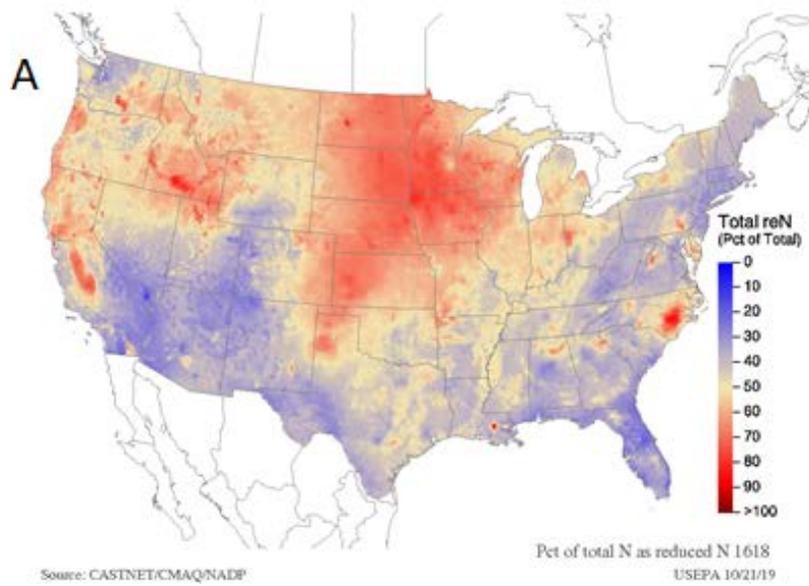
N = nitrogen; Nr = reactive nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-14 Total (wet + dry) deposition of nitrogen (kg N/ha/yr) over the contiguous U.S. 2016–2018.**

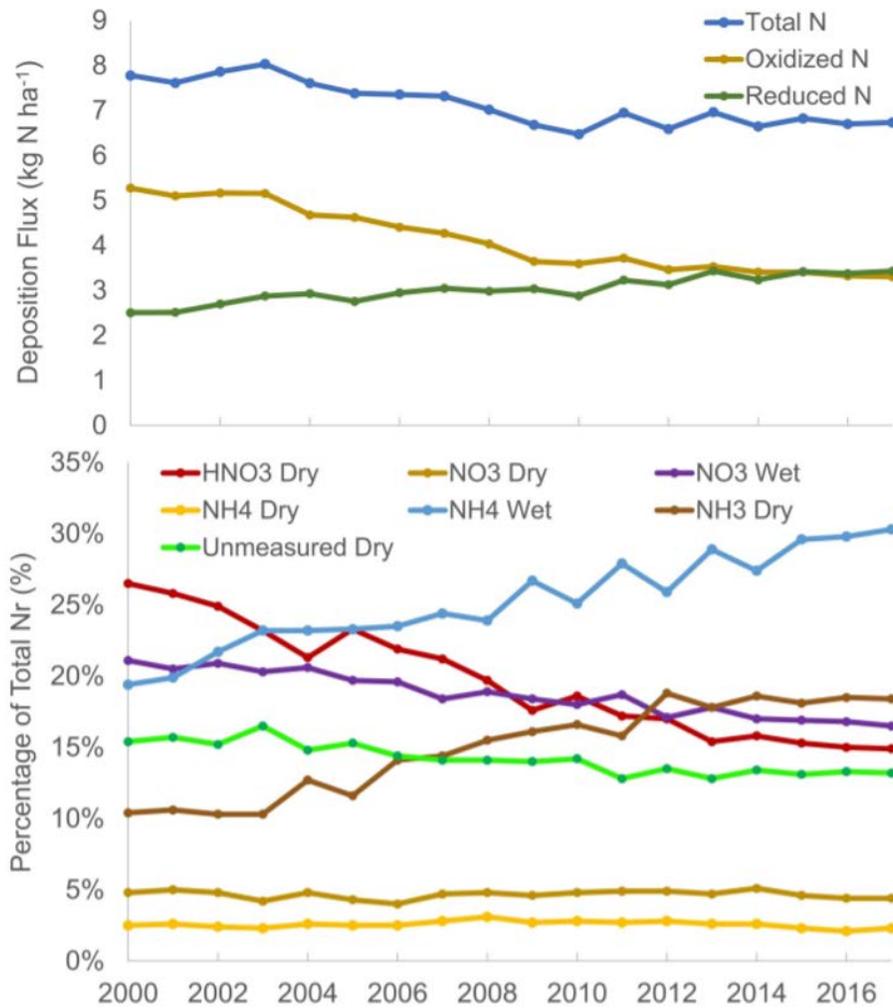
Dry deposition of gas-phase N (as  $\text{HNO}_3$  and  $\text{NH}_3$ ) exceeds dry deposition of particulate forms ( $\text{pNO}_3^-$ ,  $\text{NH}_4^+$ ) over most of the CONUS according to the hybrid method. Overall, deposition of N is mainly as reduced forms, with a maximum over the north-central U.S. The Central Valley of California, northern Utah, and eastern North Carolina are among other areas of high deposition of reduced N. In general, dry deposition of N, in either oxidized or reduced form, exceeds wet deposition across the CONUS. However, as discussed in earlier sections, uncertainties for dry deposition are likely much larger than for wet deposition.

Also as mentioned earlier, several species potentially important for deposition are not measured in CASTNET. [Figure 2-17](#) shows dry deposition for oxidized nitrogen species (e.g., PAN, other organic nitrates, HONO) calculated by CMAQ.



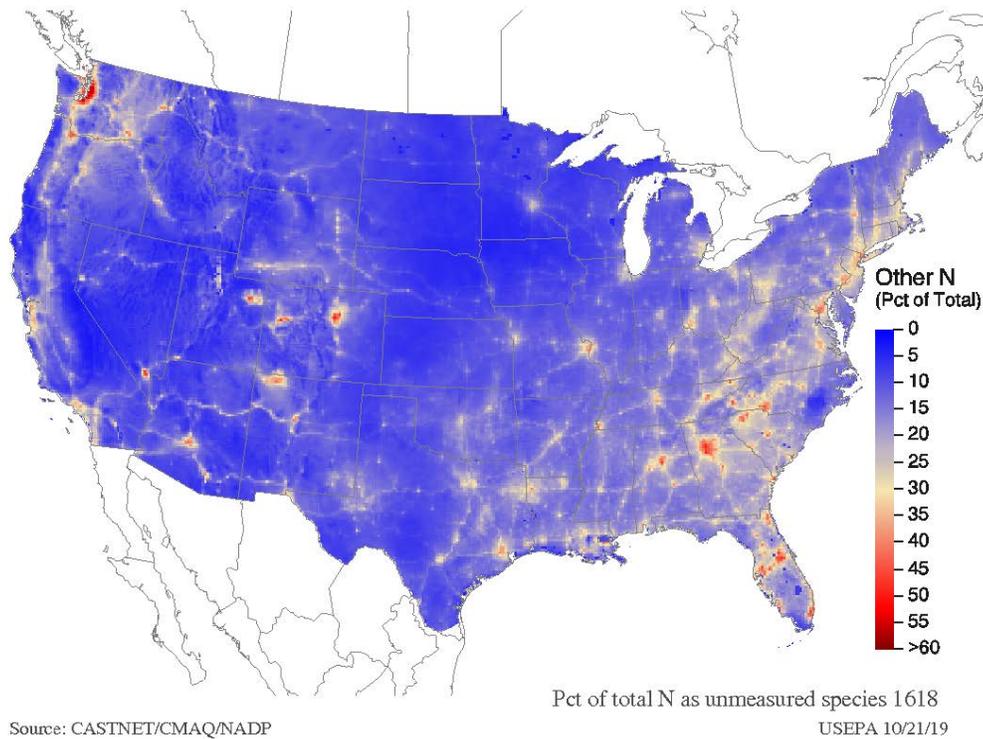
Note: We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-15 (A) Percentage of total nitrogen deposition as reduced inorganic nitrogen over the contiguous U.S. 2016–2018. (B) Percentage of total nitrogen deposition as oxidized nitrogen over the contiguous U.S. 2016–2018.**



Source: (NADP, 2019).

**Figure 2-16 Trends in U.S. total deposition flux of total nitrogen, oxidized nitrogen, reduced nitrogen, and major nitrogen species 2000–2017.**



N = nitrogen.

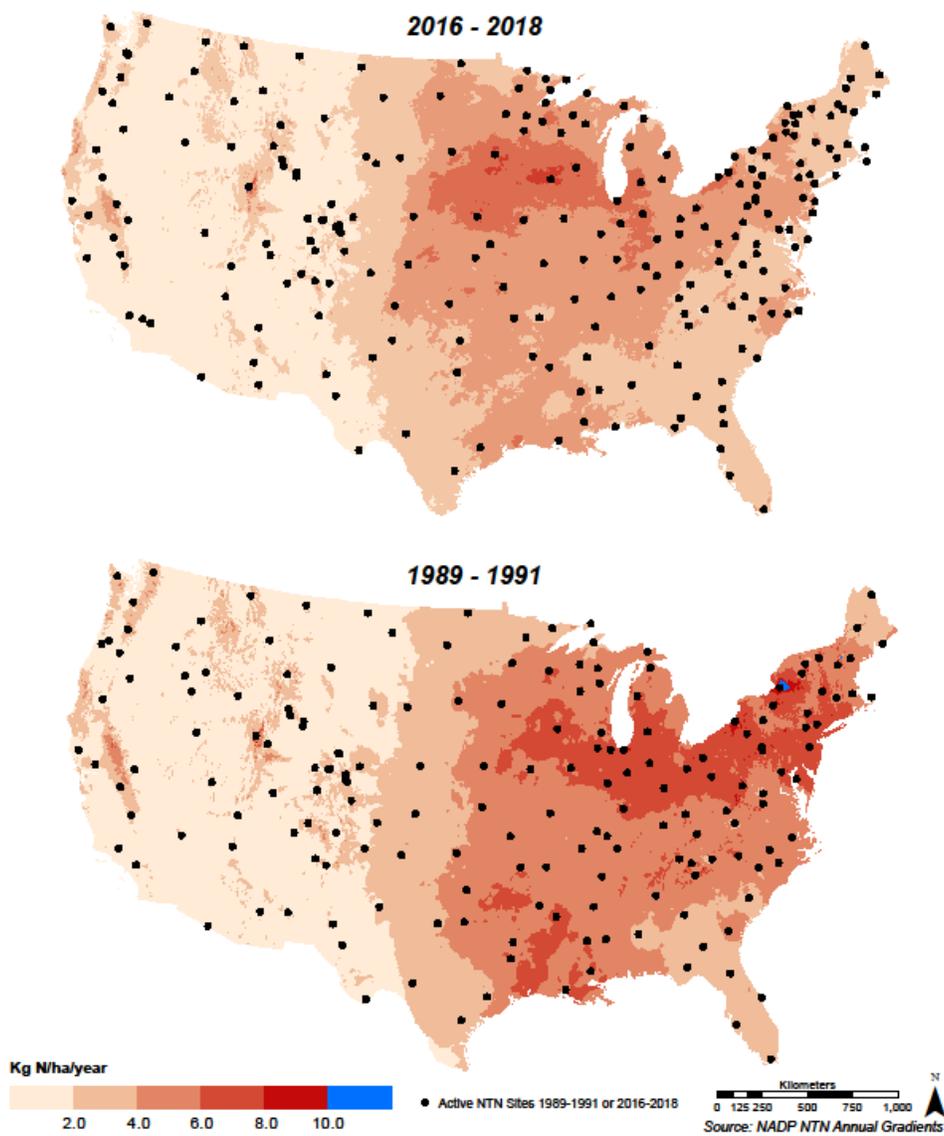
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-17 Three-year average percentage of total nitrogen deposition by species (i.e., those species that are not measured in the networks) simulated by the Community Multiscale Air Quality modeling system for 2016–2018.**

As seen in [Figure 2-17](#), deposition of these species can contribute substantially to N deposition, especially near strong sources, in particular large urban areas. [Turnipseed et al. \(2006\)](#) also indicated that not accounting for these species can result in significant underestimates of N deposition.

[Figure 2-18](#) illustrates the long-term trend in total wet deposition of N ( $\text{NH}_4^+ + \text{NO}_3^-$ ) by showing maps for two 3-year periods (2016–2018 and 1989–1991) binned in increments of 2 kg N/ha/yr for comparison to critical loads estimates. Although it is apparent that N wet deposition has decreased overall across the U.S., there are areas showing increases. Also shown are NTN sites active during either period.

**Sum  $\text{NO}_3^-$  and  $\text{NH}_4^+$  Wet Deposition by 3-Year Averages**



N = nitrogen;  $\text{NH}_4^+$  = ammonium;  $\text{NO}_3^-$  = nitrate; NTN = National Trends Network.  
Source: CPHEA analysis of CASTNET/CMAQ/NTN/AMON/SEARCH data.

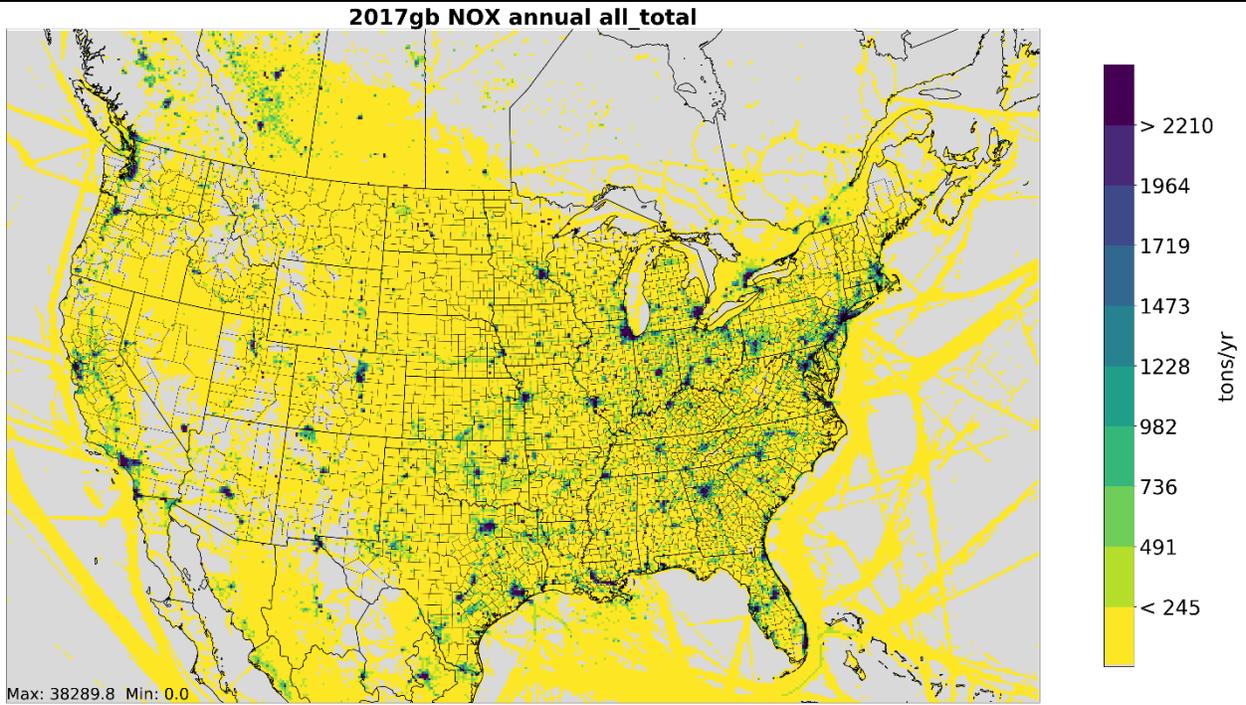
**Figure 2-18** Wet deposition of ammonium + nitrate (kg N/ha/yr) over the contiguous U.S. in two, 3-year periods, 2016 to 2018 and 1989 to 1991. Also shown are active National Trends Network sites in either period.

Studies at individual sites (e.g., on the coast of North Carolina) have shown that about 30% of wet deposition of N consisted of organic N, 20–30% of which was then available to primary producers on timescales of hours to days ([Peierls and Paerl, 1997](#)). In addition, [Benedict et al. \(2013\)](#) found that wet deposition of organic nitrogen contributed 18% of total quantified reactive nitrogen deposition and 25% of wet nitrogen deposition at Rocky Mountain National Park between November 2008 and November 2009. Trends in total (wet + dry) deposition of total ( $\text{NO}_Y + \text{NH}_X$ ) nitrogen between 2000 and 2018 are described with maps in [Appendix 2.7](#).

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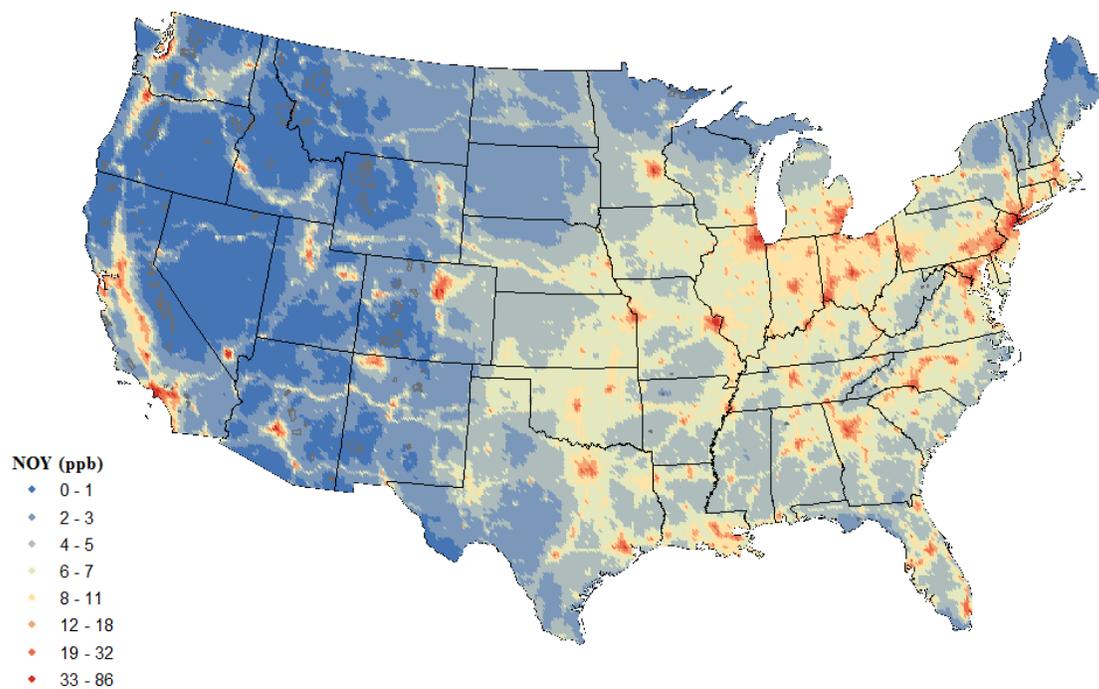
### 2.6.3 Oxidized Nitrogen

The geographic distribution of annual U.S.  $\text{NO}_X$  emissions for 2017 is shown in [Figure 2-19](#). Areas of higher emissions are apparent in urban areas and along the major travel routes between them, especially in the eastern U.S. and states along the west coast. The distribution of ambient  $\text{NO}_Y$  concentrations is shown in [Figure 2-20](#). However, because  $\text{NO}_Y$  is only measured at a small number of sites, this map is based solely on CMAQ model output. Although these model results for  $\text{NO}_Y$  are not as up to date as the network concentration measurement results or the modeled deposition of  $\text{NO}_Y$  component species that follow in this section, the same basic patterns observed for emissions also apply to ambient concentrations, with higher concentrations in the eastern U.S. than in the western U.S., as well as along the west coast, in urban areas and along major travel routes. The distribution of  $\text{NO}_2$  (shown in [Figure 2-21](#)) is derived from satellite data (OMI) and output from the GEOS-Chem model using the method outlined in [Appendix 2.6.3](#). Distributions of  $\text{HNO}_3$ ,  $\text{pNO}_3^-$ ,  $\text{pNH}_4^+$ ,  $\text{SO}_2$ , and  $\text{pSO}_4^{2-}$  are based on data from the CASTNET. Note, however, that because of artifacts relating to measurement of  $\text{HNO}_3$  and  $\text{pNO}_3^-$  ([Appendix 2.4.5](#)), the measurement of total nitrate ( $\text{TN} = \text{HNO}_3 + \text{pNO}_3^-$ ) is judged to be more reliable than measurements of its components.



Source: OAQPS analysis of [U.S. EPA \(2020a\)](#) data.

**Figure 2-19** Geographic distribution of annual U.S. NO<sub>x</sub> emissions in 2017.

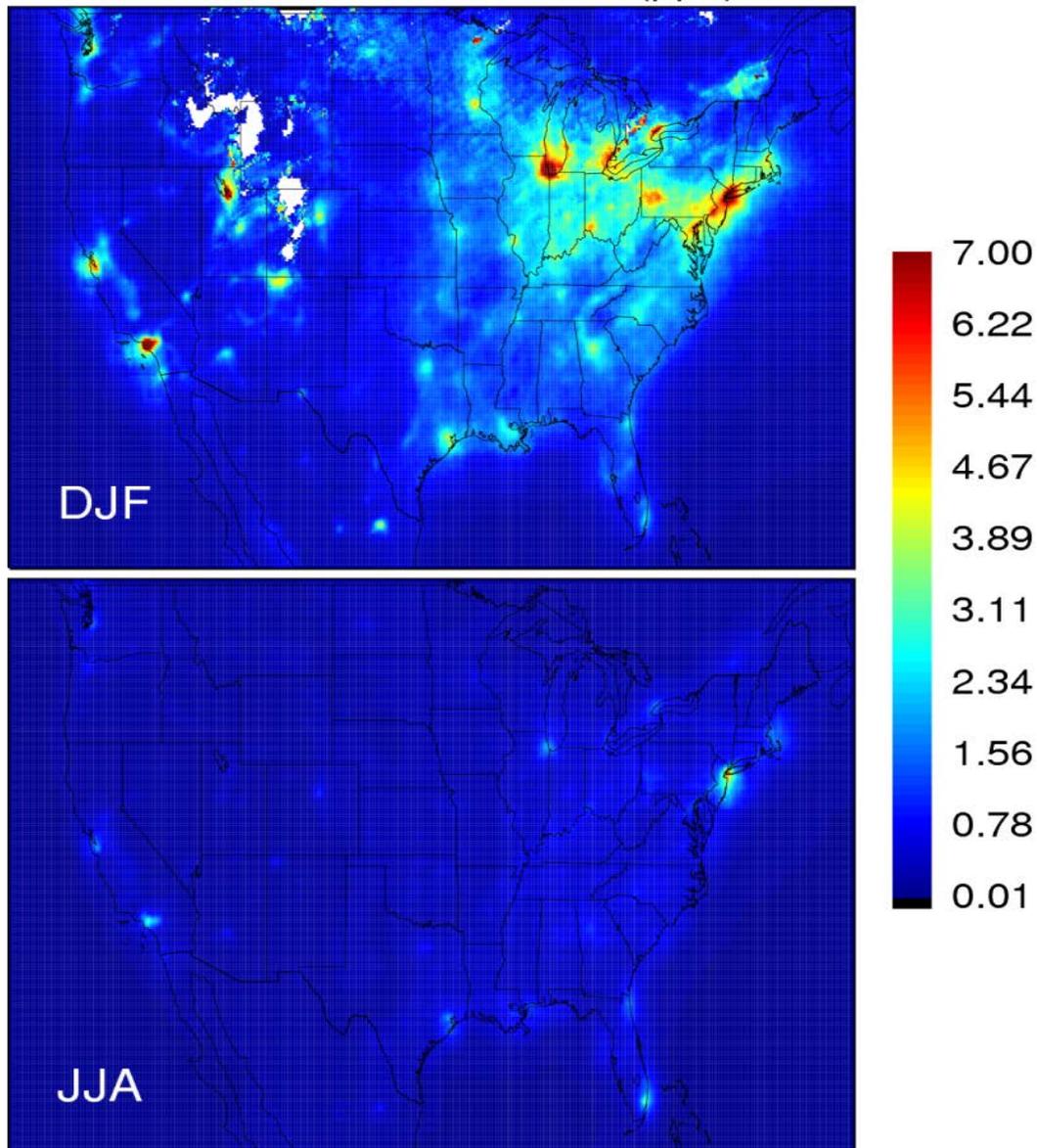


NO<sub>y</sub> = oxidized nitrogen species.

Source: U.S. EPA/OAQPS.

**Figure 2-20**      **Distribution of annual average total oxidized nitrogen species concentrations for 2011 simulated by Community Multiscale Air Quality modeling system.**

## OMI-derived surface NO<sub>2</sub> (ppb)



DJF = December, January, February; JJA = June, July, August; NO<sub>2</sub> = nitrogen dioxide; OMI = Ozone Monitoring Instrument.

Note: Images shown were constructed by Dr. Lok Lamsal of Universities Space Research Association from data obtained by the OMI on the Aura satellite (<http://aura.gsfc.nasa.gov/scinst/omi.html>) using the algorithm described in [Bucseles et al. \(2013\)](#). Output from the GEOS-Chem, global-scale, three-dimensional, chemistry-transport model to derive surface concentration fields from the satellite data as described in [Lamsal et al. \(2008\)](#) and [Lamsal et al. \(2010\)](#).

Top panel (winter: December, January, February). Lower panel (summer: June, July, August).

**Figure 2-21** Seasonal average surface nitrogen dioxide mixing ratios in parts per billion for winter (upper panel) and summer (lower panel) derived by the Ozone Monitoring Instrument/GEOS-Chem model for 2009–2011. The Ozone Monitoring Instrument has an overpass at approximately 1:30 p.m. local standard time.

As seen in the figure, the highest values are found in and around urban areas. In general, much broader areas of high concentrations ( $>5$  ppb) are found in the eastern U.S., with many areas in the western U.S. subjected to concentrations  $<1$  ppb, which implies that concentrations of components that might pose a hazard are also lower than 1 ppb because  $\text{NO}_Y$  refers to the sum of oxidized N species.

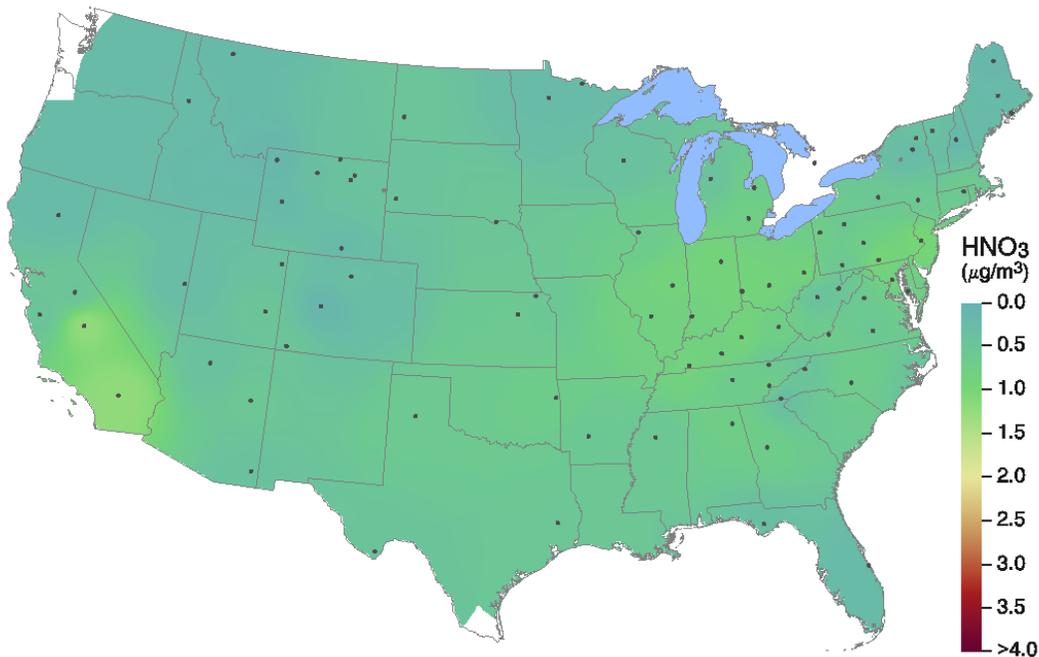
[Figure 2-21](#) through [Figure 2-23](#) describe geographic concentration patterns for  $\text{NO}_Y$ ,  $\text{HNO}_3$ , and  $\text{pNO}_3^-$ . [Figure 2-21](#) shows seasonal average  $\text{NO}_2$  concentrations derived using the hybrid (OMI-satellite/GEOS-Chem-model) approach described in [Appendix 2.4.2.2](#). Large variability in  $\text{NO}_2$  concentrations is apparent in [Figure 2-21](#). As expected, the highest  $\text{NO}_2$  concentrations are seen in large urban regions, such as in the Northeast Corridor, and lowest values are found in sparsely populated regions located mainly in the West. Minimum hourly values can be less than  $\sim 10$  ppt, leading to a large range between maximum and minimum concentrations. Although overall patterns of spatial variability are consistent with the current understanding of the behavior of  $\text{NO}_2$ , there are limitations in the satellite retrievals (see [Appendix 2.4.2.2](#)). Surface  $\text{NO}_2$  concentrations tend to be higher in January than in July, largely reflecting lower planetary boundary layer heights in winter. Such seasonal variability is also evident on a local scale, as measured by surface monitors. For example, in Atlanta, GA,  $\text{NO}_X$  measurements also exhibited higher concentrations in winter and lower concentrations in summer, when  $\text{NO}_X$  is more rapidly removed by photochemical reactions. For example, see [U.S. EPA \(2008b\)](#). 98th percentile  $\text{NO}_2$  concentrations from the national  $\text{NO}_2$  monitoring network, which has monitors mainly in urban areas, decreased by 53% from 1990 to 2017.

[Figure 2-22](#) shows ambient concentrations of  $\text{HNO}_3$ . Elevated concentrations of  $\text{HNO}_3$  are notable in southern California, the Midwest, the south-central U.S., and the Mid-Atlantic states. Conversion of  $\text{NO}_2$  to  $\text{HNO}_3$  takes place over a timescale of 1 to several hours, during which time appreciable transport can occur.

[Figure 2-23](#) shows 3-year average concentrations of particulate nitrate ( $\text{pNO}_3^-$ ) across the CONUS. Average  $\text{pNO}_3^-$  concentrations were highest in the Upper Midwest with a notable maximum at the junction of Iowa, Wisconsin, Missouri, and Illinois. The high values in the Upper Midwest are expected to be found during winter for reasons noted in [Appendix 2.3.3](#). Elevated levels were also observed in central California in the San Joaquin Valley, central Pennsylvania, central Florida, and through much of the Midwest. Based on IMPROVE and CSN monitoring network data, ammonium nitrate concentrations are highest in California and the Midwest ([Hand et al., 2012c](#)).

[Figure 2-24](#) shows decreasing trends in particulate  $\text{NO}_3^-$  based on CASTNET monitoring data for 34 eastern U.S. and 16 western U.S. monitoring sites, showing on average a 51% decrease in the eastern U.S. and a 37% decrease in the western U.S. from 1989 to 2017

(U.S. EPA, 2017b). It is worth noting that at several monitoring sites in the IMPROVE network in the central and northern Great Plains,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are increasing at a rate of over 5% per year (Hand et al., 2012a). Hand et al. (2012a) suggested that this increase might be related to oil and gas exploration and production in the region, transport from oil and gas fields in Alberta, and also to expansion of EGUs to meet the demands of population growth.



Source: CASTNET

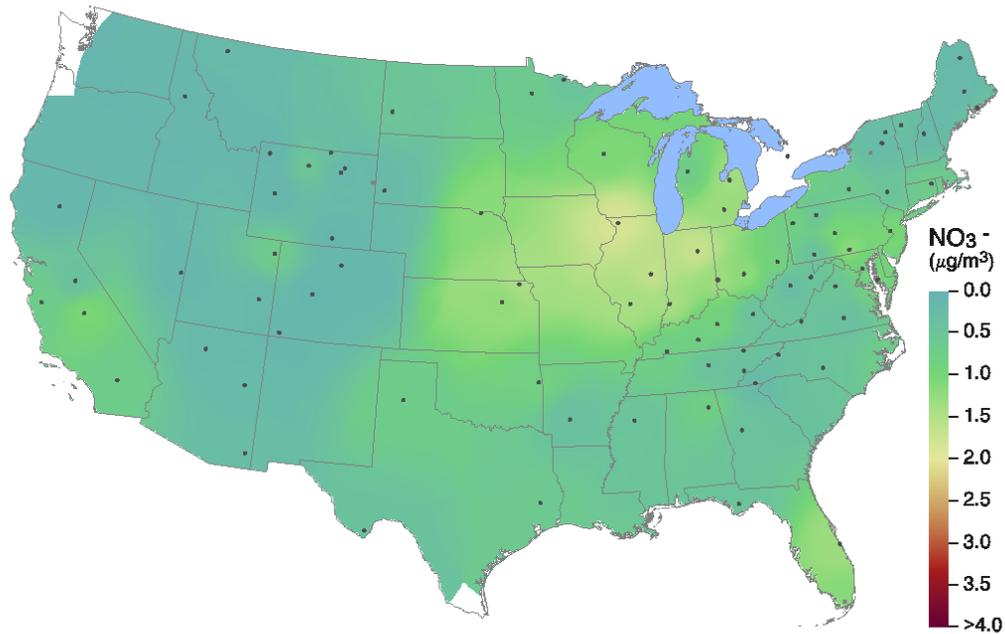
USEPA/CAMD 09/10/19  
file:///c:/castnet/png/1618/0/noc3\_--1618

$\text{HNO}_3$  = nitric acid.

Concentrations of nitric acid ( $\mu\text{g}/\text{m}^3$ ) can be converted to mixing ratios (parts per billion) to rough approximation at normal temperature and pressure by multiplying by 0.38.

Source: CASTNET/U.S. EPA-CAMD.

**Figure 2-22 Three-year average (2016–2018) surface concentrations of nitric acid based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots).**



Source: CASTNET

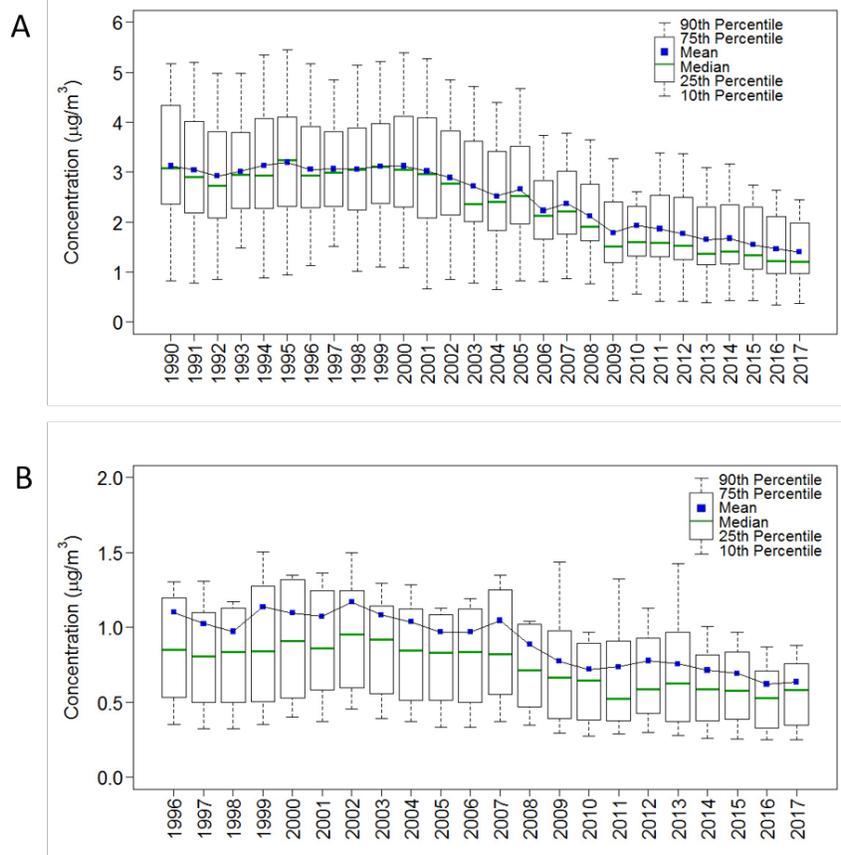
USEPA/CAMD 09/10/19

file:///c:/castnet/png/1618/no3\_c-1618

$\text{NO}_3^-$  = nitrate.

Source: CASTNET/U.S. EPA-CAMD.

**Figure 2-23 Three-year average (2016–2018) surface concentrations of particulate nitrate based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots).**

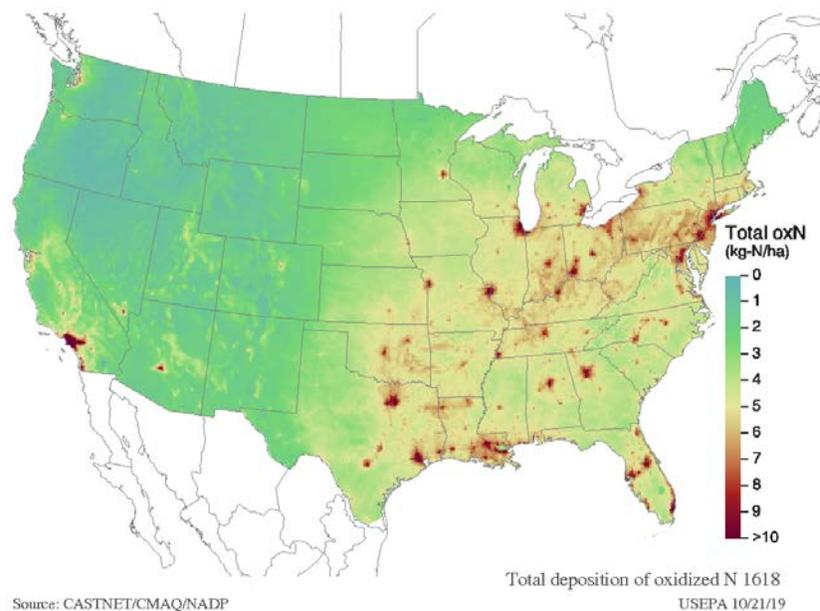


Source: (U.S. EPA, 2017b).

**Figure 2-24 Trends in particulate nitrate concentration 1990–2017: (A) average eastern U.S. concentration based on 34 sites; (B) average western concentration based on 16 sites.**

Figure 2-25 shows the depositional flux of  $\text{NO}_Y$  over the CONUS for 2016–2018. In constructing Figure 2-25 and maps that include  $\text{pNO}_3^-$  deposition estimates, the assumption was made that 80% of  $\text{pNO}_3^-$  is in the fine mode and 20% is in the coarse mode. Note also, the monitors in CASTNET do not use size-selected inlets. As shown in Figure 2-9 (Appendix 2.5.2.1), the deposition velocity of particles increases dramatically with particle size due to gravitational settling, resulting in higher deposition rates than calculated if  $\text{pNO}_3^-$  were found mainly in the fine mode. However, there is displacement of  $\text{HNO}_3$  by acid S species in fine particles as occurs in the eastern U.S. due to much higher emissions of  $\text{SO}_2$  than in the western U.S. [e.g., Wolff (1984); especially in coastal areas where displacement of  $\text{Cl}^-$  in marine aerosol occurs]. Under these circumstances higher levels of  $\text{pNO}_3^-$  would be found in coarse mode particles (see Appendix 2.3.3). In

a field study in Tampa Bay, FL, , measured and modeled (using CMAQ) concentrations of  $\text{HNO}_3$  and  $\text{pNO}_3^-$  in  $\text{PM}_{10-2.5}$  were much higher than  $\text{pNO}_3^-$  in  $\text{PM}_{2.5}$ . [Wolff \(1984\)](#) found that most  $\text{pNO}_3^-$  (as  $\text{NH}_4\text{NO}_3$ ) is found in the fine mode in Denver but in the coarse mode (associated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in measurements made in Detroit and rural South Dakota, Louisiana, and Virginia. [Blanchard et al. \(2013\)](#) found a range of 32 to 63% for the fraction of  $\text{pNO}_3^-$  in  $\text{PM}_{10-2.5}$  versus  $\text{PM}_{2.5}$  particles in the Southeast. [Lee et al. \(2008\)](#) found that most  $\text{pNO}_3^-$  was in the coarse mode at Grand Canyon and Great Smoky Mountains, corroborating earlier findings at Yosemite and Big Bend national parks. They also found that both coarse and fine mode  $\text{pNO}_3^-$  were important at Brigantine National Wildlife Refuge, NJ and San Geronio Wilderness Area, CA. [Lefer and Talbot \(2001\)](#) also found that  $\text{NO}_3^-$  sampled at Harvard Forest, MA between March and October was mainly found in the coarse mode with a mass median diameter of  $4.8 \pm 1.5 \mu\text{m}$ . These results indicate considerable regional variability in the ratio of  $\text{pNO}_3^-$  in the fine and coarse modes and consequently additional uncertainty in estimates of  $\text{pNO}_3^-$  deposition.



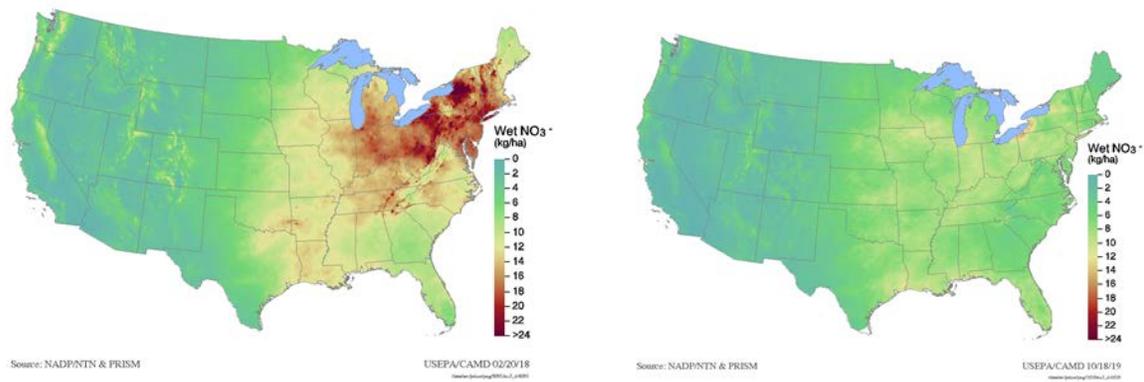
oxN = oxidized nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-25 Total oxidized nitrogen deposition over the contiguous U.S. 2016–2018.**

[Figure 2-26](#) and [Figure 2-27](#) show decreases in wet deposition of  $\text{NO}_3^-$  at most locations in the U.S. These decreases are associated with  $\text{NO}_x$  emissions control measures since the passage of the 1990 Clean Air Act amendments. However, some areas, located mainly in the West show increases. As noted earlier, [Hand et al. \(2012a\)](#) suggested that this increase might be related to oil and gas exploration and production in the region, transport from oil and gas fields in Alberta, and also to expansion of motor vehicles and EGUs to meet the demands of population growth. The large area with the strongest increases in the north-central U.S. corresponds to oil and gas operations in the Bakken Shale region. Trends in total (wet + dry) deposition of oxidized nitrogen between 2000 and 2013 are described with maps in [Appendix 2.7](#).

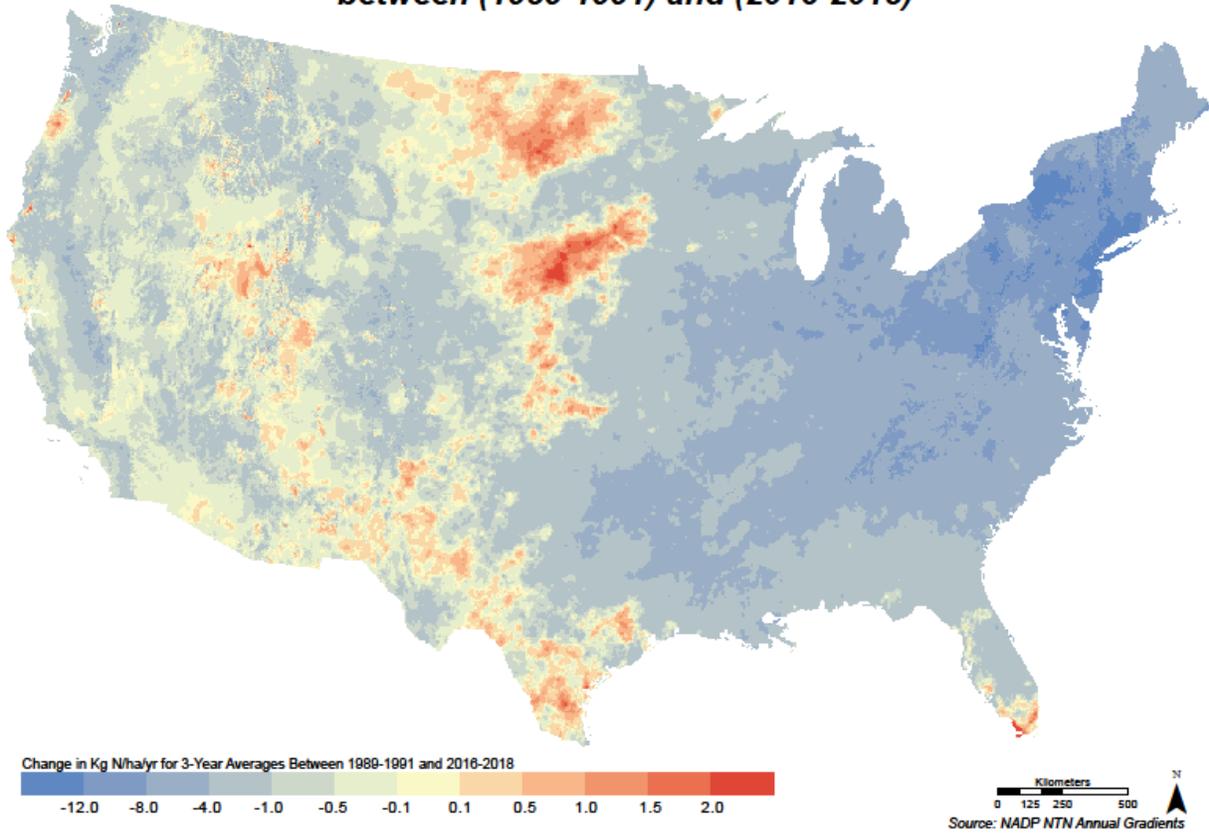
Overall, total U.S. oxidized nitrogen deposition has decreased since 2000, reflecting the substantial decline in nitrogen oxides emissions, as indicated in [Figure 2-28 \(NADP, 2019\)](#).



Source: NADP/U.S. EPA/CAMD.

**Figure 2-26** (Left) nitrate wet deposition, 1989–1991; (Right) nitrate wet deposition, 2016–2018.

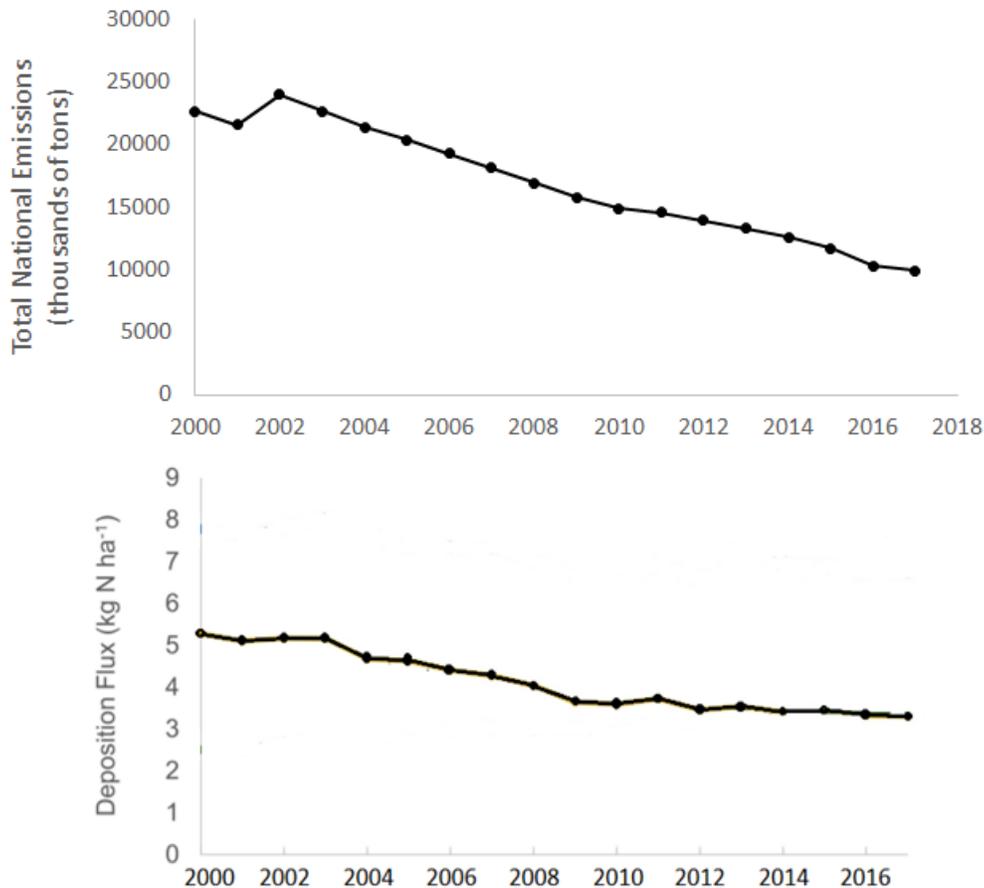
**Change in  $\text{NO}_3^-$  Wet Deposition in the U.S.  
between (1989-1991) and (2016-2018)**



N = nitrogen;  $\text{NO}_3^-$  = nitrate.

Source: CPHEA analysis of CASTNET/CMAQ/NTN/AMON/SEARCH data.

**Figure 2-27** Difference in wet deposition of nitrate (kg N/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. The range of positive values is smaller than that for negative values.



Source: (A) [U.S. EPA \(2020a\)](#), (B) [NADP \(2019\)](#).

**Figure 2-28 Trends in oxidized nitrogen emissions and deposition 2000–2017: (A) total national emissions; (B) national average total deposition flux.**

## 2.6.4 Reduced Nitrogen

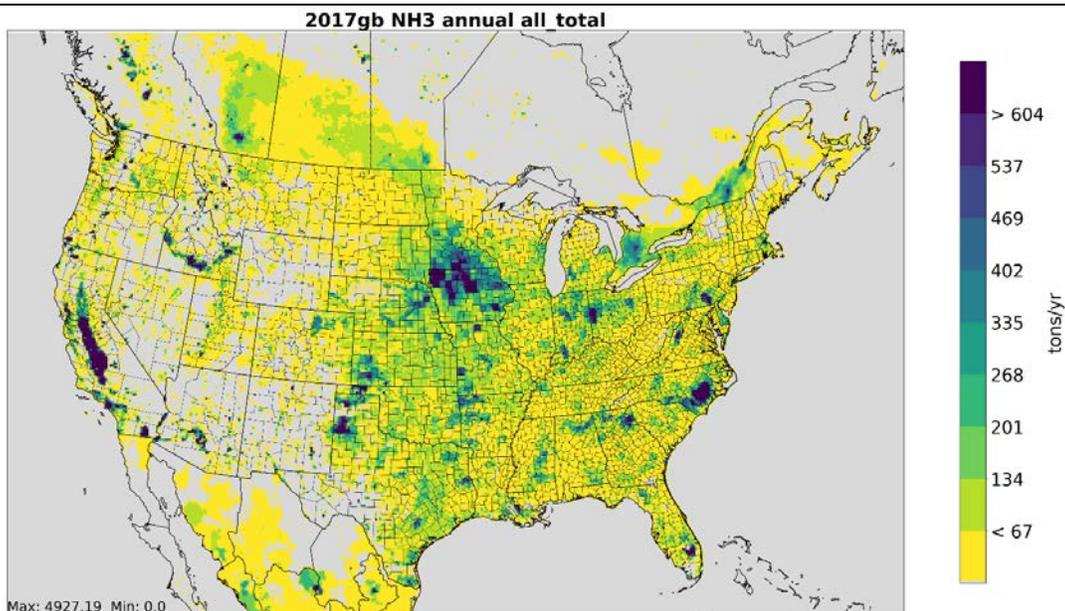
[Figure 2-29](#) shows the geographic distribution of annual total  $\text{NH}_3$  emissions. The observed pattern is somewhat different than for  $\text{NO}_x$  emissions ([Appendix 2.6.3](#)), reflecting the widely distributed and rural nature of  $\text{NH}_3$  emissions, compared to  $\text{NO}_x$  emissions, which are largely urban or from large point sources. Widespread areas of high emissions are in the Midwest, California, and several other hot spots.

[Figure 2-30](#) and [Figure 2-31](#) show maps for the concentrations of the reduced inorganic nitrogen species,  $\text{NH}_3$  and  $\text{pNH}_4^+$ . The distribution of  $\text{NH}_3$  was obtained from the Ammonia Monitoring Network (AMoN). The highest concentrations of  $\text{NH}_3$  were

measured in Salt Lake City, UT at  $16.9 \mu\text{g}/\text{m}^3$ . All other annual average concentrations for 2017 were lower than  $5 \mu\text{g}/\text{m}^3$  except eastern North Carolina. The Salt Lake City site is located near feed lots, perhaps explaining in large part why levels were much higher there than at other sites. In general, areas with the highest  $\text{NH}_3$  concentrations in [Figure 2-30](#) correspond well with areas of the highest  $\text{NH}_3$  emissions, as shown in [Figure 2-29](#). Note that confidence in the magnitude and inter-monitor precision of  $\text{NH}_3$  measurements has increased since the 2008 ISA ([U.S. EPA, 2008a](#)), also see [Appendix 2.4.3.1](#). However, sparseness of the monitoring network still presents uncertainty in describing the nationwide distribution of  $\text{NH}_3$  concentrations. National  $\text{NH}_3$  monitoring is too recent for evaluating long-term concentration trends. In the Southeastern U.S., SEARCH network observations indicated slight upward trends in ammonia concentrations from 2004–2012, but the trend was statistically significant at only monitoring site ([Saylor et al., 2015](#)).

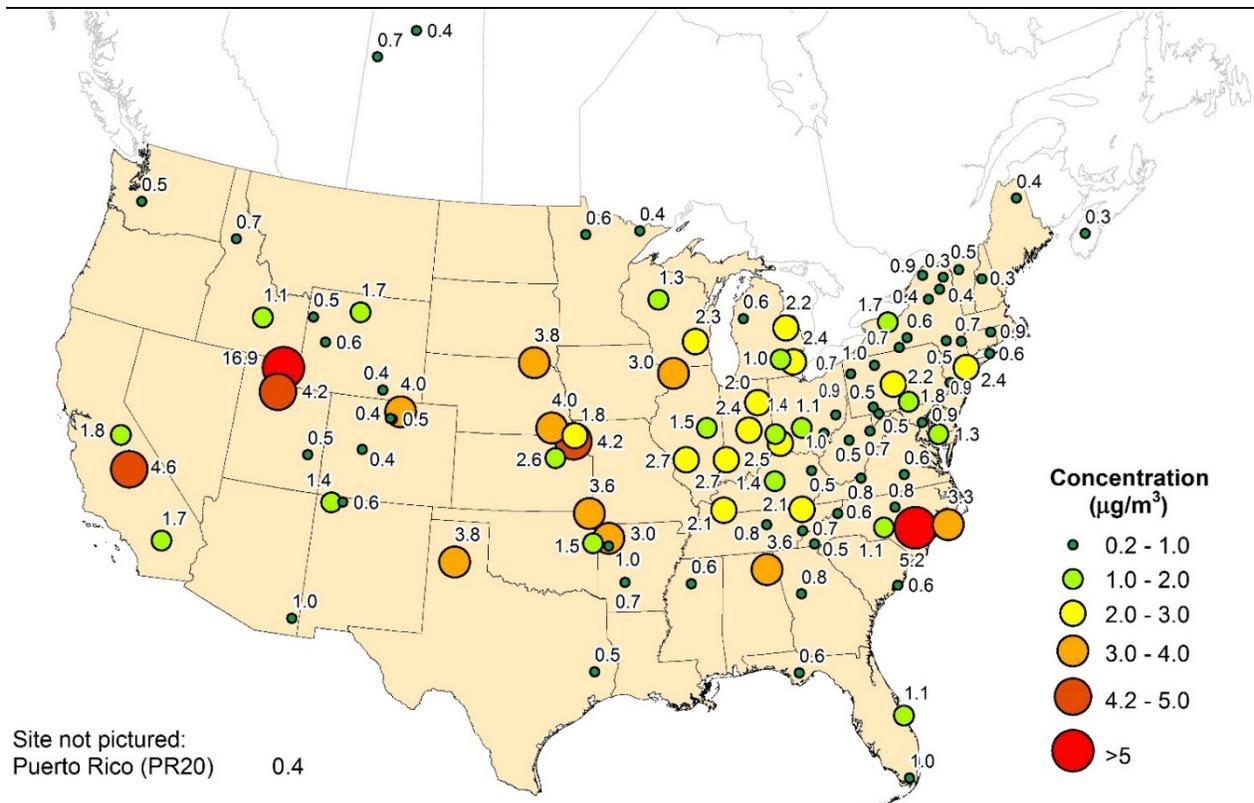
Particulate  $\text{NH}_4^+$  concentrations were obtained from CASTNET and were highest in Illinois-Indiana-western Ohio, along with high values in central Pennsylvania and central California. These locations correspond generally to the highest concentrations of  $\text{pNO}_3^-$  and moderate-to-high concentration locations for  $\text{NH}_3$ .

[Figure 2-32](#) shows the depositional flux of  $\text{NH}_x$  over the CONUS 2016–2018.



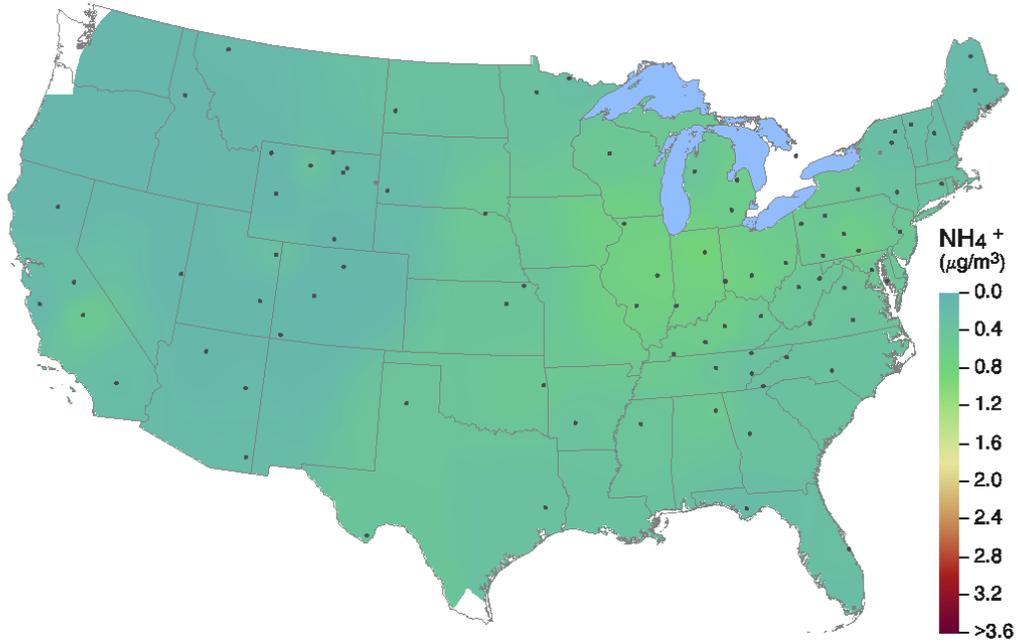
Source: OAQPS analysis of [U.S. EPA \(2020a\)](#) data.

**Figure 2-29 Geographic distribution of annual U.S. ammonia ( $\text{NH}_3$ ) emissions in 2017.**



AMoN = Ambient Ammonia Monitoring Network;  $\text{NH}_3$  = ammonia.  
Source: ([U.S. EPA, 2017b](#)).

**Figure 2-30** Average (2017) surface concentration of ammonia obtained by the Ambient Ammonia Monitoring Network at select Clean Air Status and Trends Network sites. Concentrations of ammonia ( $\mu\text{g}/\text{m}^3$ ) can be converted to mixing ratios (parts per billion) to rough approximation at normal temperature and pressure by multiplying by 1.4.



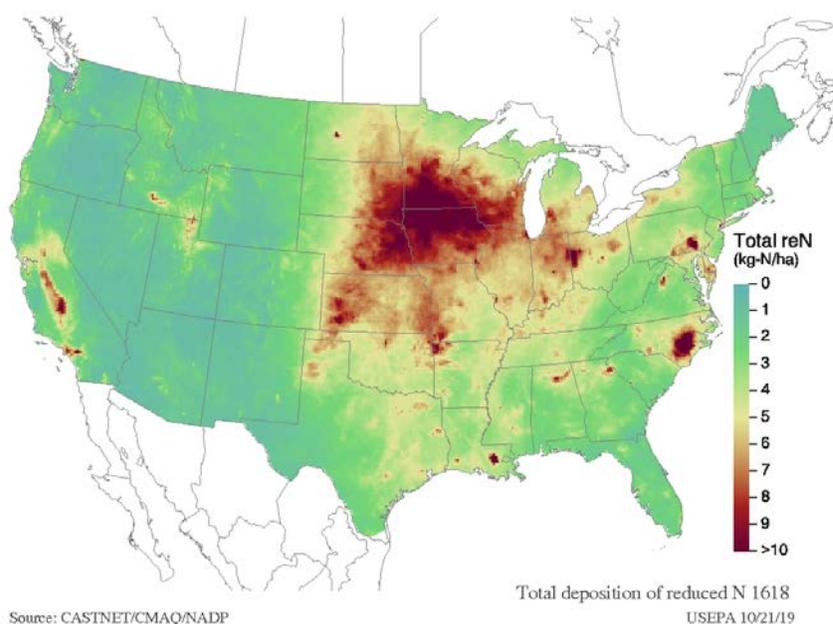
Source: CASTNET

USEPA/CAMD 09/10/19  
[https://www.epa.gov/castnet/pmg/1618/nh4\\_m\\_1618](https://www.epa.gov/castnet/pmg/1618/nh4_m_1618)

$\text{NH}_4^+$  = ammonium.

Source: CASTNET/U.S. EPA-CAMD.

**Figure 2-31** Three-year average (2016–2018) surface concentrations of particulate ammonium ( $\mu\text{g}/\text{m}^3$ ) based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots).



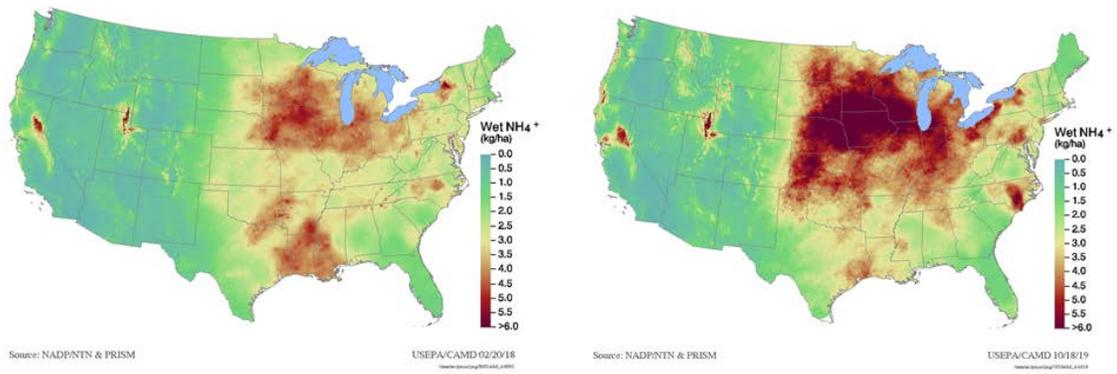
reN = reduced nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-32 Total reduced inorganic nitrogen deposition over the contiguous U.S. 2016–2018.**

[Figure 2-33](#) and [Figure 2-34](#) shows large increases in wet deposition of  $\text{NH}_4^+$  throughout the north-central U.S. with hot spots along the eastern Great Lakes, eastern Pennsylvania and North Carolina, the Texas gulf coast, and parts of Utah and California. The situation is more nuanced than shown in that some sites show small increases and others small decreases. In general, large-scale increases in wet deposition of  $\text{NH}_4^+$ , rather than decreases, are seen across the U.S. in agreement with the analysis of [Li et al. \(2016d\)](#). Trends in total (wet + dry) deposition of reduced nitrogen between 2000 and 2013 are described with maps in [Appendix 2.7](#).

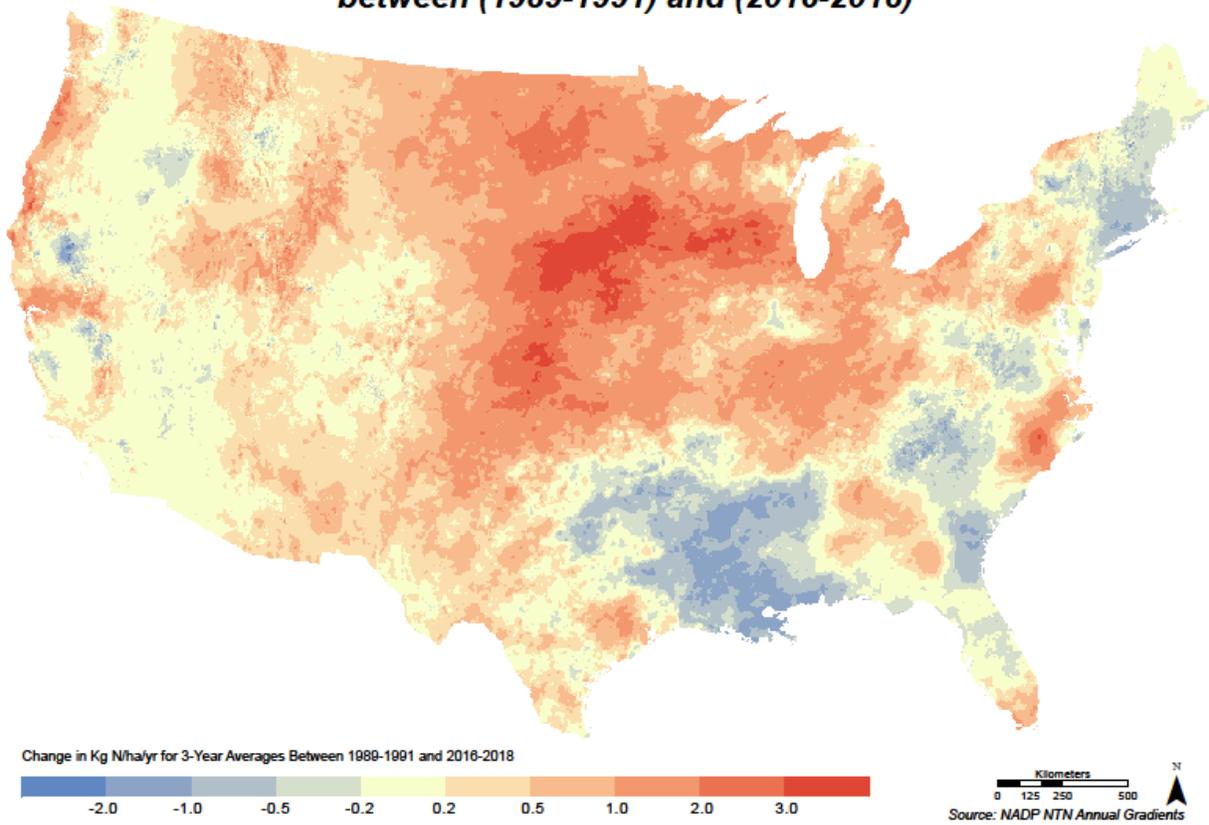
Overall, total U.S. reduced nitrogen deposition has slightly increased since 2000, even though annual national  $\text{NH}_3$  emissions data have fluctuated with no obvious trend during this period. However, during the last few years both national  $\text{NH}_3$  emissions and total reduced nitrogen deposition estimates have increased, as indicated in [Figure 2-35 \(NADP, 2019\)](#).



Source: NADP/U.S. EPA/CAMD.

**Figure 2-33** (Left) ammonium wet deposition, 1989–1991; (Right) ammonium wet deposition, 2016–2018.

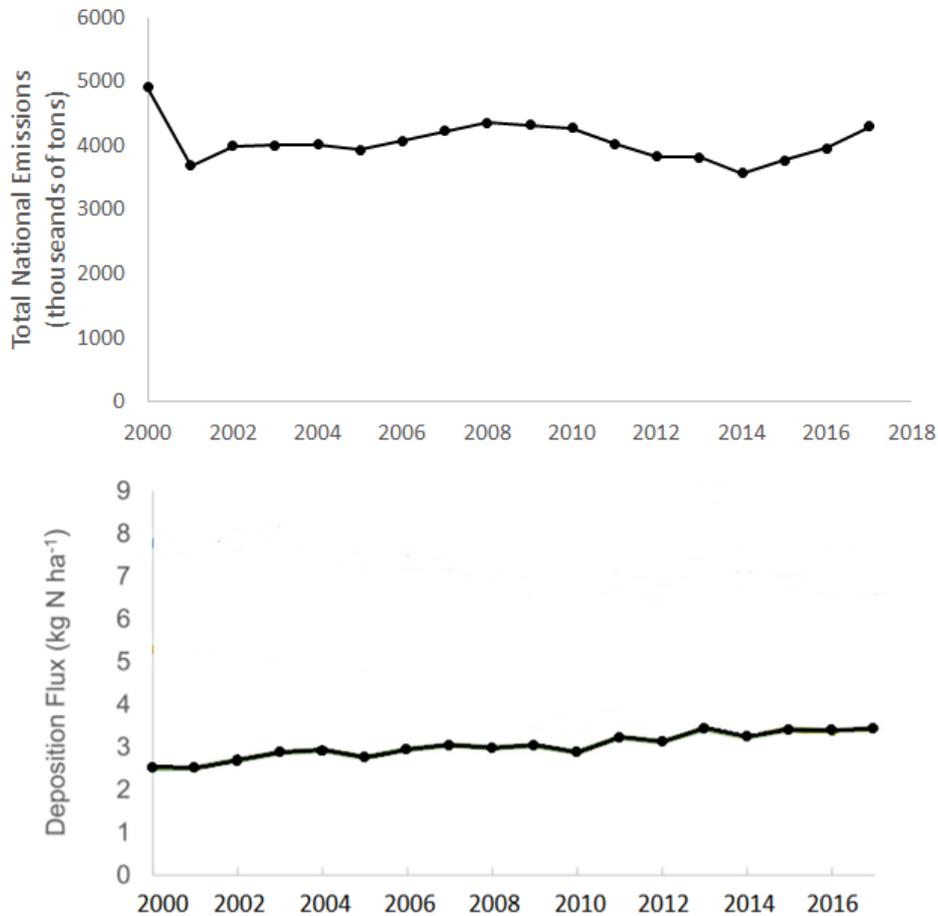
**Change in  $\text{NH}_4^+$  Wet Deposition in the U.S.  
between (1989-1991) and (2016-2018)**



N = nitrogen;  $\text{NH}_4^+$  = ammonium.

Source: CPHEA analysis of CASTNET/CMAQ/NTN/AMON/SEARCH data

**Figure 2-34** Difference in wet deposition of ammonium (kg N/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018.

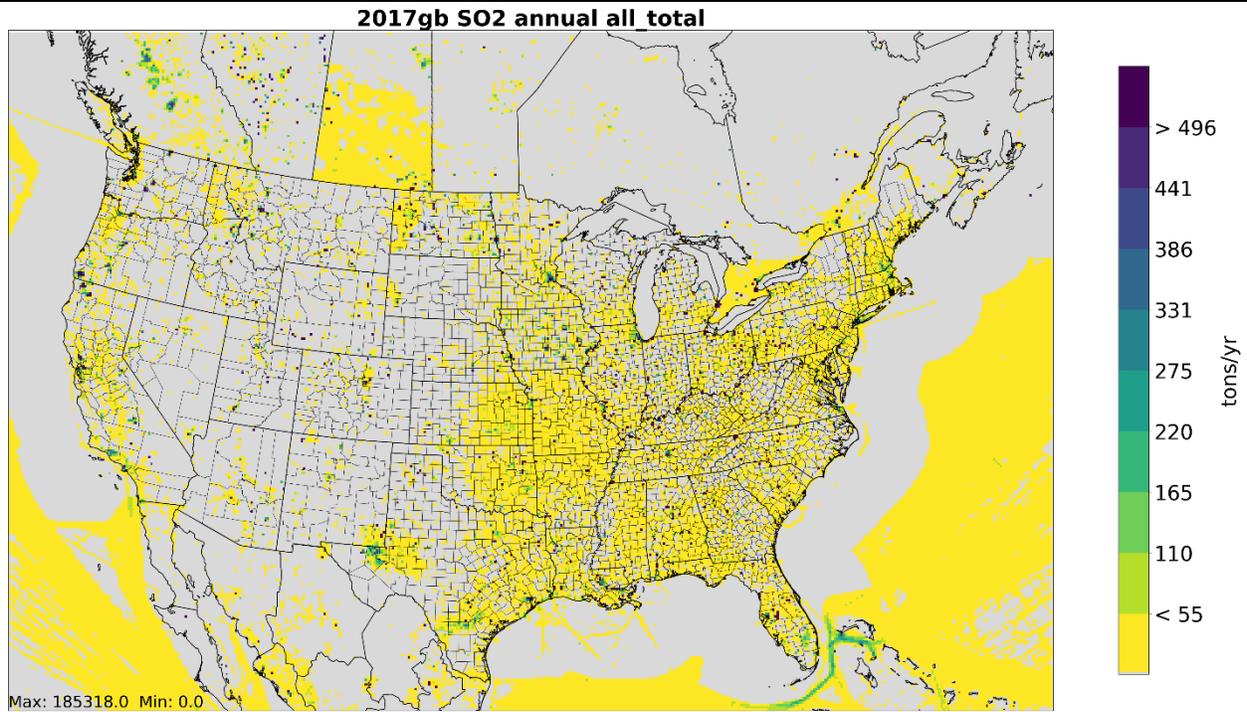


Source: (A) [U.S. EPA \(2020a\)](#), (B) [NADP \(2019\)](#).

**Figure 2-35 Trends in reduced nitrogen emissions and deposition 2000–2017: (A) total national NH<sub>3</sub> emissions; (B) national average reduced nitrogen deposition flux.**

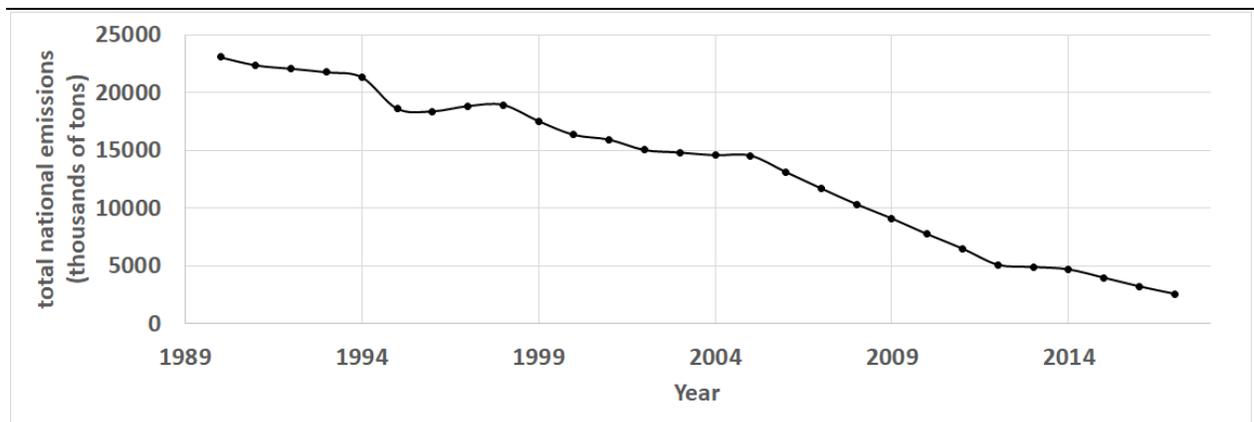
## 2.6.5 Sulfur Oxides

[Figure 2-36](#) shows the west-to-east increasing gradient in SO<sub>2</sub> emissions, with greater emissions in most areas east of the Mississippi than in the West. Widespread areas of high emissions are in the Northeast and Mississippi Valley. [Figure 2-37](#) shows that sulfur dioxide emissions have declined by 89% from 1990 to 2017 and continue to decline steeply ([U.S. EPA, 2020a](#)).



Source: OAQPS analysis of [U.S. EPA \(2020a\)](#).

**Figure 2-36** Geographic distribution of annual U.S. sulfur dioxide (SO<sub>2</sub>) emissions by county from the 2017 National Emissions Inventory.



Source: [\(U.S. EPA, 2020a\)](#).

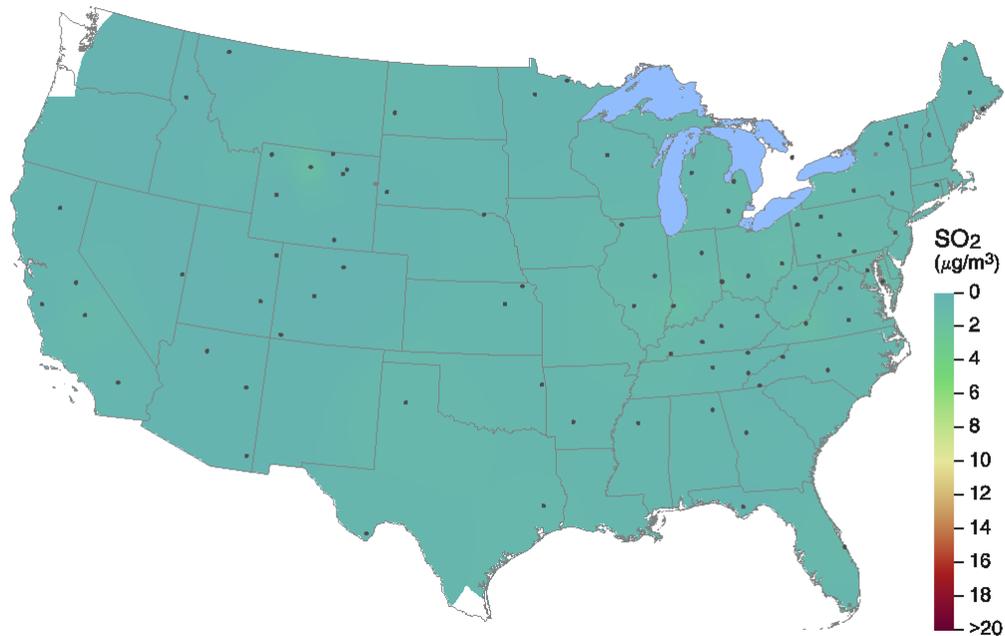
**Figure 2-37** Trends in total national sulfur dioxide emissions.

[Figure 2-38](#) and [Figure 2-39](#) show the distribution of atmospheric concentrations of gas-phase SO<sub>2</sub> and particulate phase SO<sub>4</sub><sup>2-</sup>. Concentrations have decreased substantially over the last decade throughout the eastern U.S. Comparison between the national SO<sub>2</sub> distributions ([Figure 2-38](#)) for 2016–2018 and the ones for 1989–1991 and 2003–2005 presented in the 2008 ISA ([U.S. EPA, 2008a](#)) demonstrated continual decreases in SO<sub>2</sub> concentrations across the nation.

Both concentrations and seasonal variability of sulfate are substantially higher in the eastern U.S. than in the West ([Hand et al., 2012c](#)). The higher concentrations in the eastern U.S. are consistent with greater emissions indicated in [Figure 2-36](#). Based on air pollution monitoring network data (IMPROVE and CSN), sulfate concentrations on a national scale are steadily decreasing across the U.S. Between 1992 and 2010, annual mean sulfate concentrations at rural sites decreased fairly consistently at a rate of –2.7% per year. This decline has become even steeper more recently, with annual mean concentrations decreasing by an average of –4.6% per year from 2002 to 2010. The decrease appears to be due to decreasing SO<sub>2</sub> emissions from power plants ([Hand et al., 2012b](#)). While the nationwide trend is for a reduction in sulfate concentrations, there are seasonal and regional increasing trends, specifically in the central and northern Great Plains in winter, and in the western U.S. in spring ([Hand et al., 2012a](#)). Both sulfate and nitrate are increasing at a rate of over 5% per year at several monitoring sites in the central and northern Great Plains ([Hand et al., 2012c](#)).

[Figure 2-40](#) shows trends based on CASTNET data for SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations for 34 eastern and 16 western U.S. monitoring sites. An average SO<sub>2</sub> concentration decline of 89% was observed in the eastern U.S. and a 45% decrease was observed on average for the western U.S. from 1989–2017. For the same monitoring sites, SO<sub>4</sub><sup>2-</sup> concentrations decreased by 75% in the eastern U.S. and 35% in the western U.S. on average ([U.S. EPA, 2017b](#)).

[Figure 2-41](#) shows wet plus dry deposition of SO<sub>x</sub> (SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>) over the CONUS. Greater deposition occurs over the Ohio River Valley (southeastern Ohio, West Virginia, and western Pennsylvania), Gulf coast (Texas and Louisiana), and Northern Great Plains (North Dakota), than in other areas of the U.S. [Figure 2-42](#) shows a good deal of spatial variability in the percentage of dry deposition across the CONUS. In the Mid-Atlantic states, dry deposition of SO<sub>2</sub> is dominant and dry deposition of pSO<sub>4</sub><sup>2-</sup> is very minor component of dry deposition of SO<sub>x</sub>. Wet deposition dominates in the Pacific Northwest, northern New England and in general in the central U.S. Note that deposition of organic sulfur species (e.g., methane sulfonic acid) or SO<sub>2</sub> and/or SO<sub>4</sub><sup>2-</sup> produced by the oxidation of organic S species is not included.



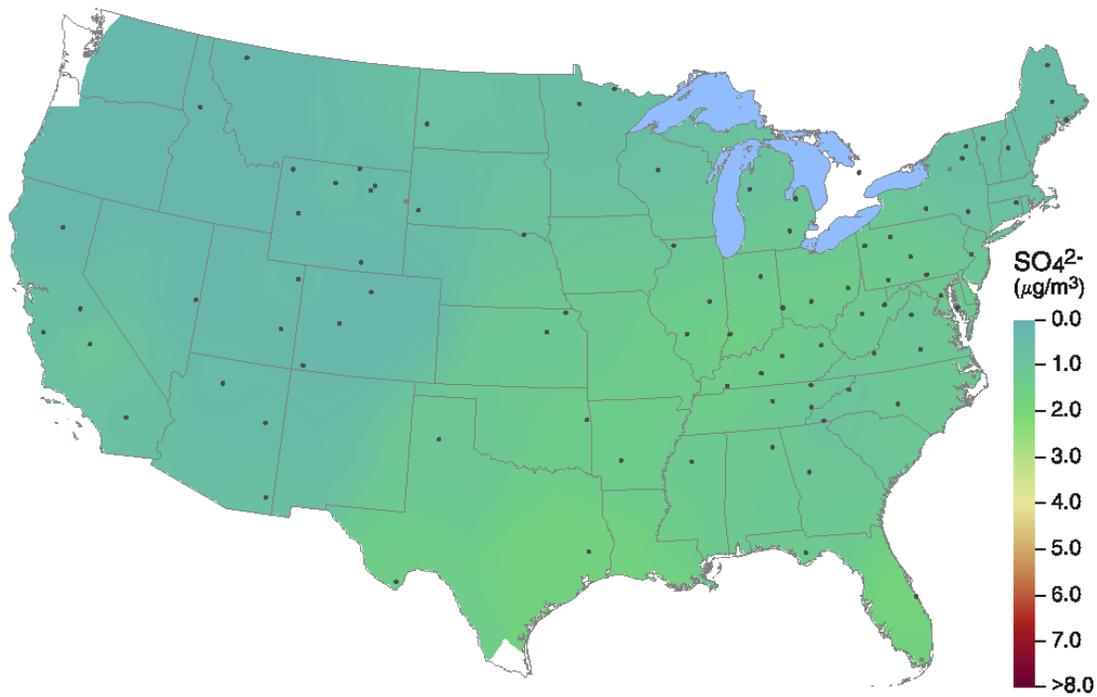
Source: CASTNET

USEPA/CAMD 09/10/19  
/data/arc/castnet/pm10/so2\_1618/so2\_1618

SO<sub>2</sub> =sulfur dioxide.

Source: CASTNET/U.S. EPA-CAMD.

**Figure 2-38** Three-year average (2016–2018) surface concentrations of sulfur dioxide obtained by fusion of monitoring data obtained at Clean Air Status and Trends Network sites (black dots) and Community Multiscale Air Quality model system results. Concentrations ( $\mu\text{g}/\text{m}^3$ ) can be converted to mixing ratios (parts per billion) at normal temperature and pressure) to rough approximation by multiplying by 0.37.



Source: CASTNET

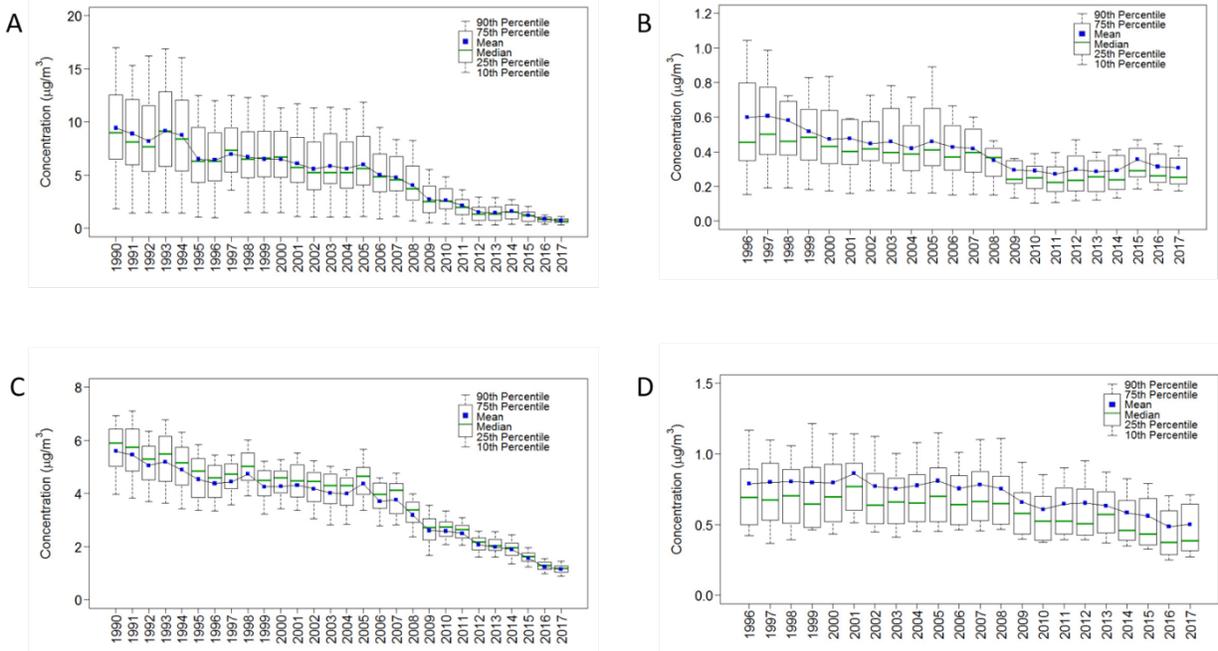
USEPA/CAMD 09/10/19

/data/arc/castnet/png/1618/so4\_c-1618

SO<sub>4</sub><sup>2-</sup> = sulfate.

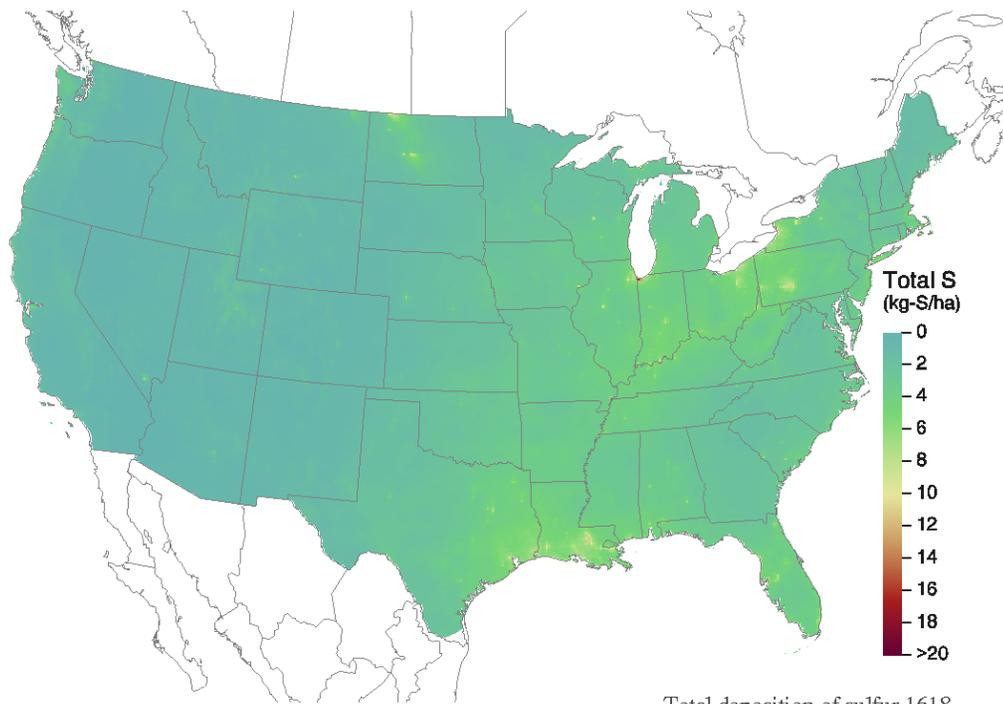
Source: CASTNET/U.S. EPA-CAMD.

**Figure 2-39** Three-year average (2016–2018) surface concentrations of particulate sulfate based on monitoring data obtained at Clean Air Status and Trends Network sites (black dots).



Source: ([U.S. EPA, 2017b](#)).

**Figure 2-40 Trends in oxides of sulfur oxides concentrations 1990–2017:**  
**(A) average eastern U.S. SO<sub>2</sub> concentration based on 34 sites;**  
**(B) average western U.S. SO<sub>2</sub> concentration based on 16 sites;**  
**(C) average eastern U.S. sulfate concentration based on 34 sites;**  
**(D) average western U.S. sulfate concentration based on 16 sites.**



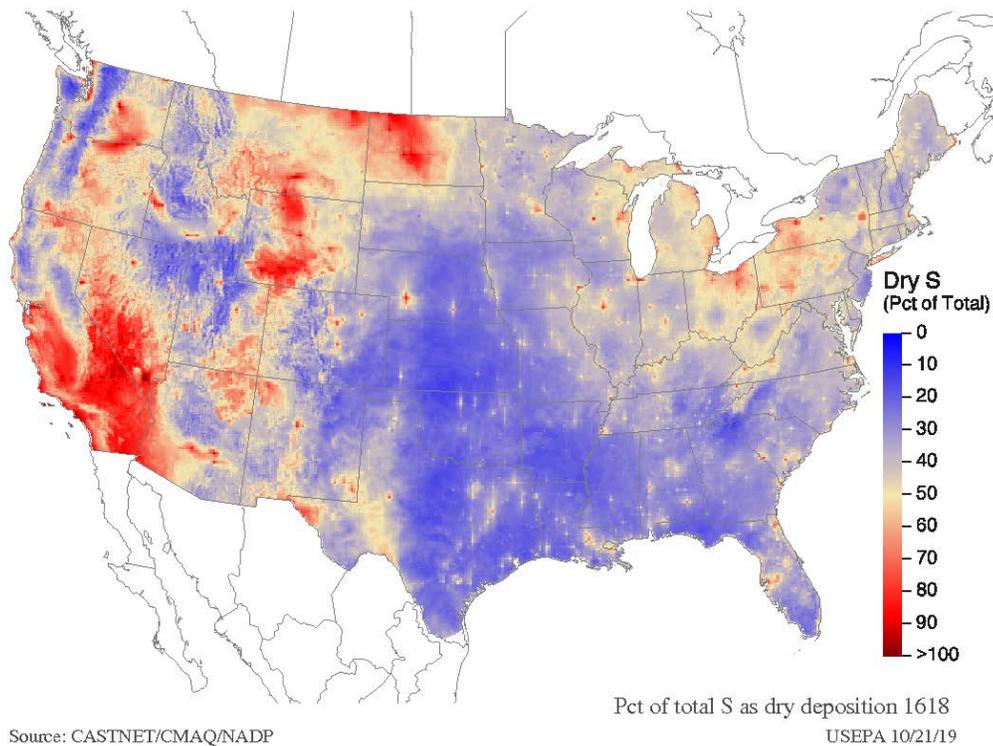
Source: CASTNET/CMAQ/NADP

Total deposition of sulfur 1618  
USEPA 10/21/19

S = sulfur.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-41 Total deposition of sulfur (kg S/ha/yr) over the contiguous U.S. 2016–2018.**

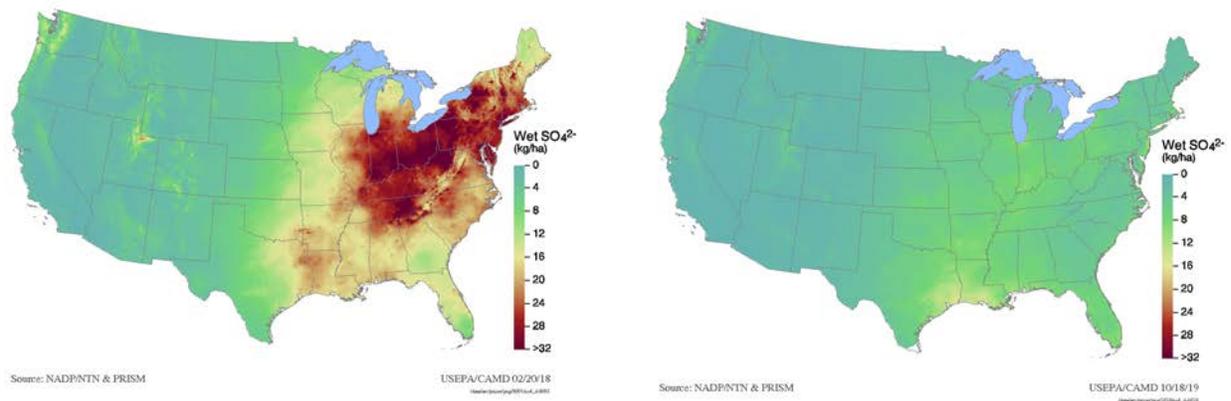


S = sulfur.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

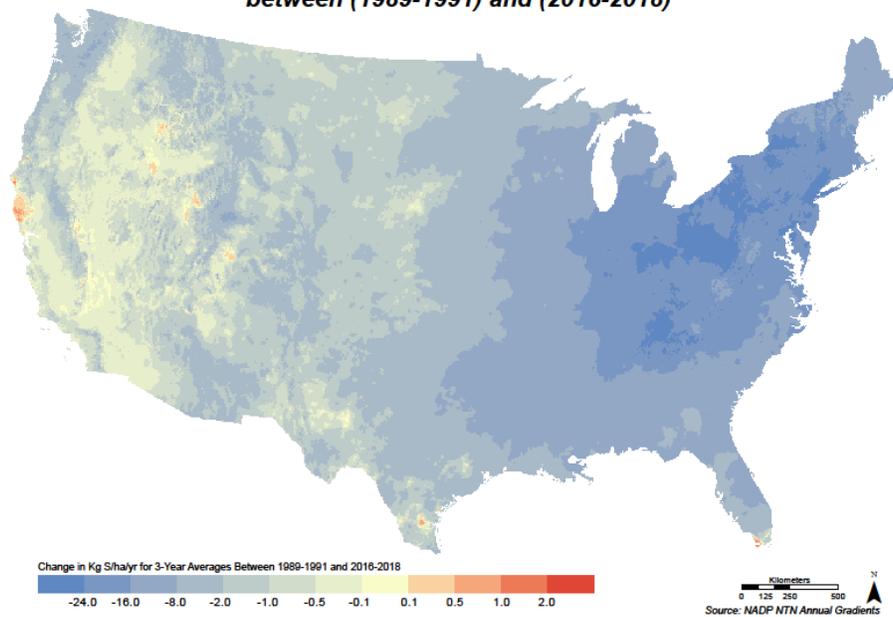
**Figure 2-42 Percentage of deposition of total sulfur as dry deposition over the contiguous U.S. 2016–2018.**

[Figure 2-43](#) and [Figure 2-44](#) show that the pattern for changes in wet deposition of  $\text{SO}_4^{2-}$  is similar to that for  $\text{NO}_3^-$  with strongest decreases in the East, but with many areas in the western U.S. showing some increase. Reasons for this increase are similar to those for  $\text{NO}_3^-$  as noted by [Hand et al. \(2012a\)](#).



**Figure 2-43** (Left) sulfate wet deposition, 1989–1991; (Right) sulfate wet deposition, 2016–2018.

**Change in  $SO_4^{2-}$  Wet Deposition in the U.S. between (1989-1991) and (2016-2018)**



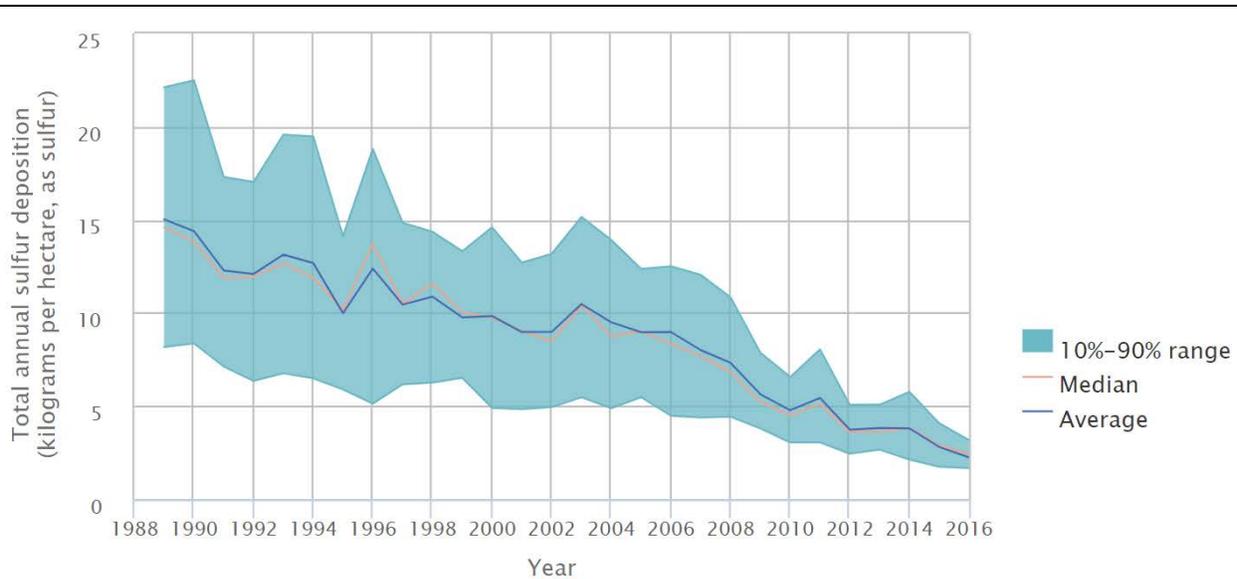
S = sulfur;  $SO_4^{2-}$  = sulfate.

Source: CPHEA analysis of CASTNET/CMAQ/NTN/AMON/SEARCH data.

**Figure 2-44** Difference in wet deposition of sulfate (kg S/ha/yr) over the contiguous U.S. between 1989 to 1991 and 2016 to 2018. The range of positive values is much smaller than for negative values.

The increases in wet deposition of  $\text{SO}_4^{2-}$  in the north-central U.S. correspond to those for  $\text{NO}_3^-$  and are in the immediate vicinity of the Bakken Shale. There is a high degree of interannual variability in deposition in some areas, especially those showing increases (e.g., Logan, UT/Idaho), making source attribution difficult. Trends in total (wet + dry) deposition of sulfur between 2000 and 2018 are described with maps in [Appendix 2.7](#).

Overall, U.S. sulfur deposition has decreased since 2000, reflecting the steep decline in  $\text{SO}_2$  emissions. This is especially evident in the eastern U.S., where  $\text{SO}_2$  emissions are higher (see [Figure 2-36](#)) and concentrations have decreased more rapidly than in the western U.S. (see [Figure 2-40](#)). [Figure 2-45](#) shows the decreasing trend of sulfur deposition for 34 CASTNET monitoring sites in the western U.S.



Coverage: 34 monitoring sites in the eastern U.S.

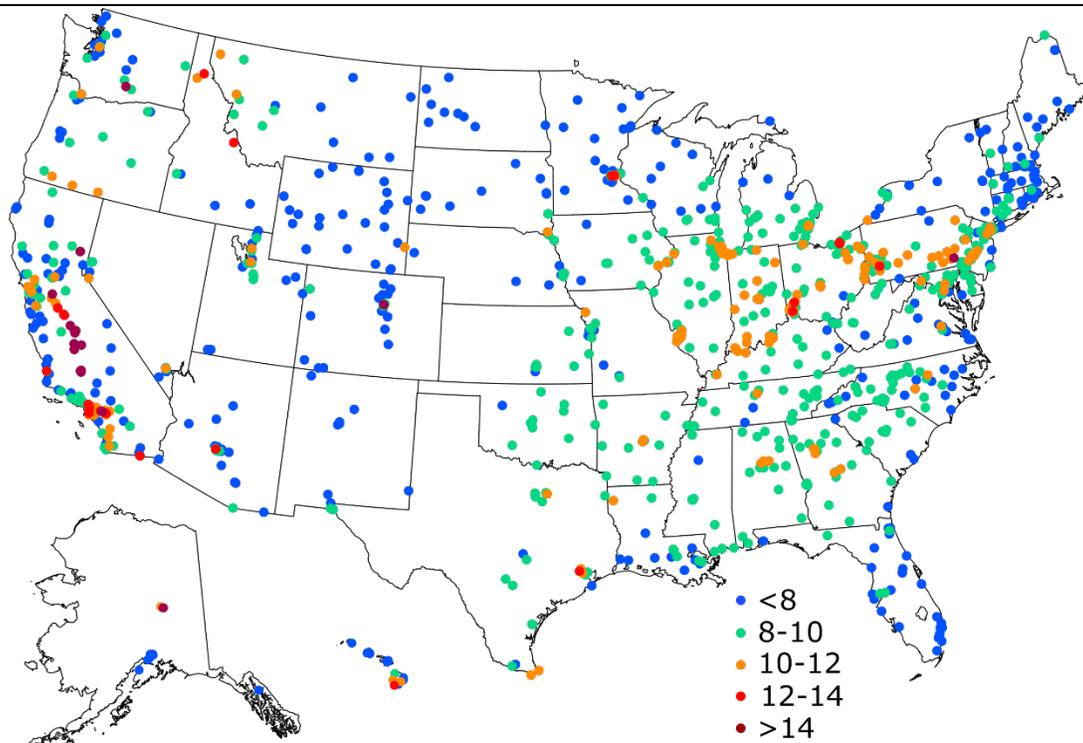
Source: [\(U.S. EPA, 2020b\)](#).

**Figure 2-45 Trends in average sulfur deposition flux for 34 monitoring sites in the eastern U.S. 1989–2017.**

## 2.6.6 Particulate Matter (PM)

[Figure 2-46](#) shows the 3-year mean of the 24-hour  $\text{PM}_{2.5}$  concentrations for  $\text{PM}_{2.5}$  network monitoring sites across the U.S. from 2013–2015. Emissions are not shown

because the majority of  $PM_{2.5}$  mass is often produced by atmospheric reactions (see [Appendix 2.3](#)). Some of the highest  $PM_{2.5}$  concentrations are in the San Joaquin Valley and the Los Angeles-South Coast Air Basin of California. However, in general 3-year average 24-hour  $PM_{2.5}$  concentrations are higher in the Eastern U.S. than in the western U.S. An area of the highest concentrations in the Eastern U.S. can be seen in the Ohio Valley. From [Appendix 2.3.6](#) is the same area where  $SO_4^{2-}$  and  $NO_3^-$  account for the greatest fraction of  $PM_{2.5}$ , indicating that at least in the eastern U.S., the highest  $PM_{2.5}$  concentrations also correspond to PM with greatest the fraction of mass accounted for by  $SO_4^{2-}$  and  $NO_3^-$ .

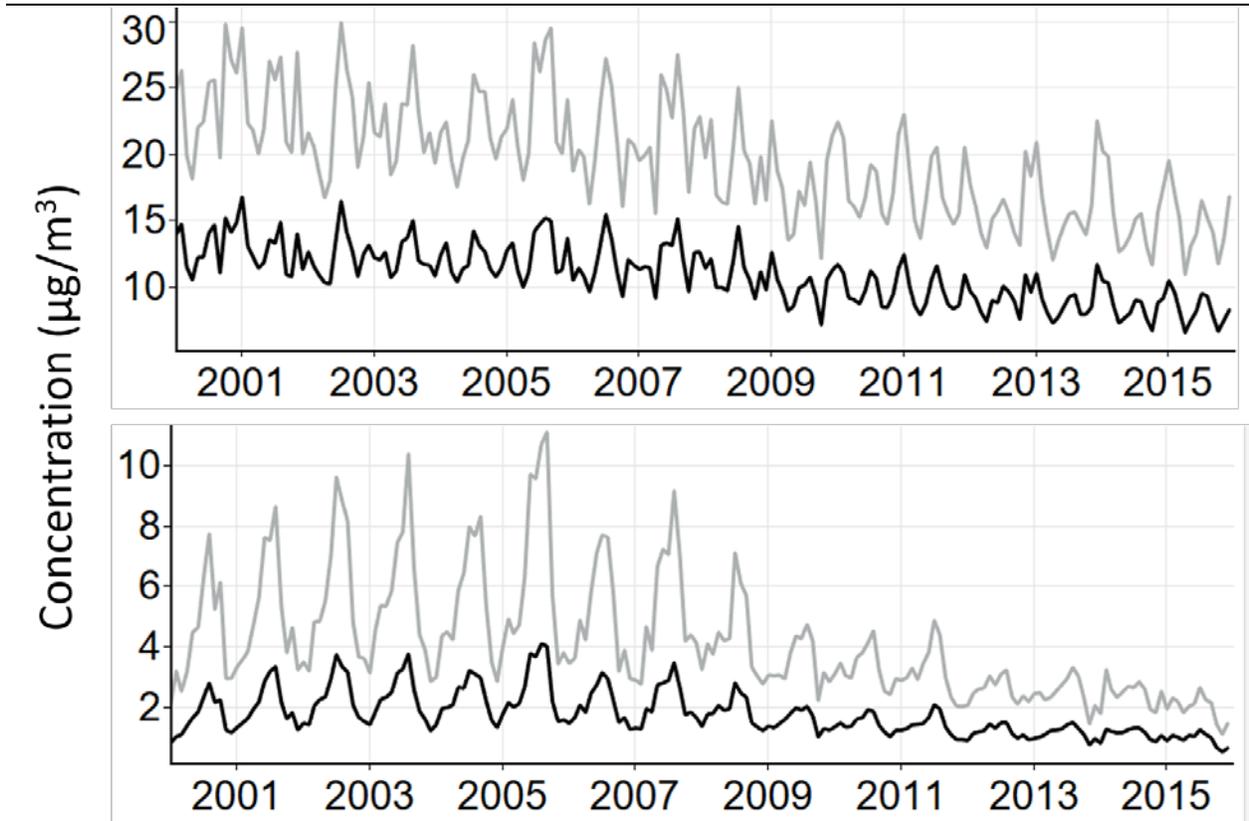


Source: ([U.S. EPA, 2019](#)).

**Figure 2-46** Three-year average concentrations of particulate matter smaller than 2.5 μm diameter ( $PM_{2.5}$ ) 2013–2015.

A further indication that the fraction of mass contributed by  $SO_4^{2-}$  and  $NO_3^-$  may increase with increasing  $PM_{2.5}$  concentration is demonstrated by [Figure 2-47](#). [Figure 2-47](#) shows that a decrease in national average  $PM_{2.5}$  between 2000 and 2016 is paralleled by a similar decrease in  $SO_4^{2-}$ . Since  $SO_4^{2-}$  has been the most abundant component of  $PM_{2.5}$ , the steep decline in  $SO_2$  emissions ([Appendix 2.2](#)) has led to a sharper decrease in  $SO_4^{2-}$

concentrations than in concentrations of other  $PM_{2.5}$  components. As indicated by [Figure 2-46](#), in those areas where  $SO_4^{2-}$  concentrations remain high, the  $SO_4^{2-}$  fraction of  $PM_{2.5}$  mass is also still high in the eastern U.S.

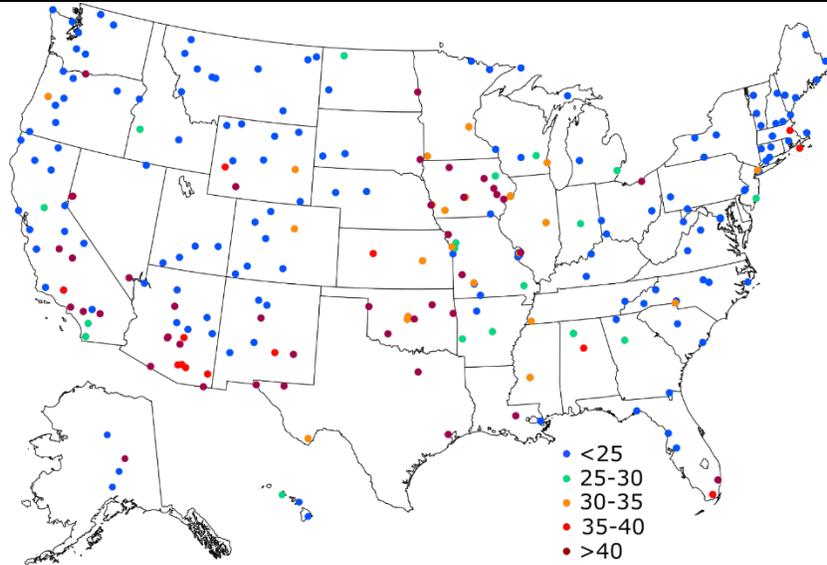


Notes: Black = mean, gray = 90th percentile.

Source: [Chan et al. \(2018\)](#).

**Figure 2-47 National monthly average concentrations of particulate matter smaller than 2.5 µm diameter ( $PM_{2.5}$ ; top) and sulfate in  $PM_{2.5}$  (bottom) from 2000–2016 (concentrations in  $\mu\text{g}/\text{m}^3$ ).**

For completeness, [Figure 2-48](#) shows  $PM_{10-2.5}$  concentrations. The highest concentrations are observed in Southwest and Great Plains. These are the same areas where crustal material accounts for the greatest fraction of  $PM_{2.5}$  as described in [Appendix 2.3.6](#), and  $PM_{10-2.5}$  is also largely composed of crustal material, which has little impact on acid or nutrient deposition.



Source: ([U.S. EPA, 2019](#)).

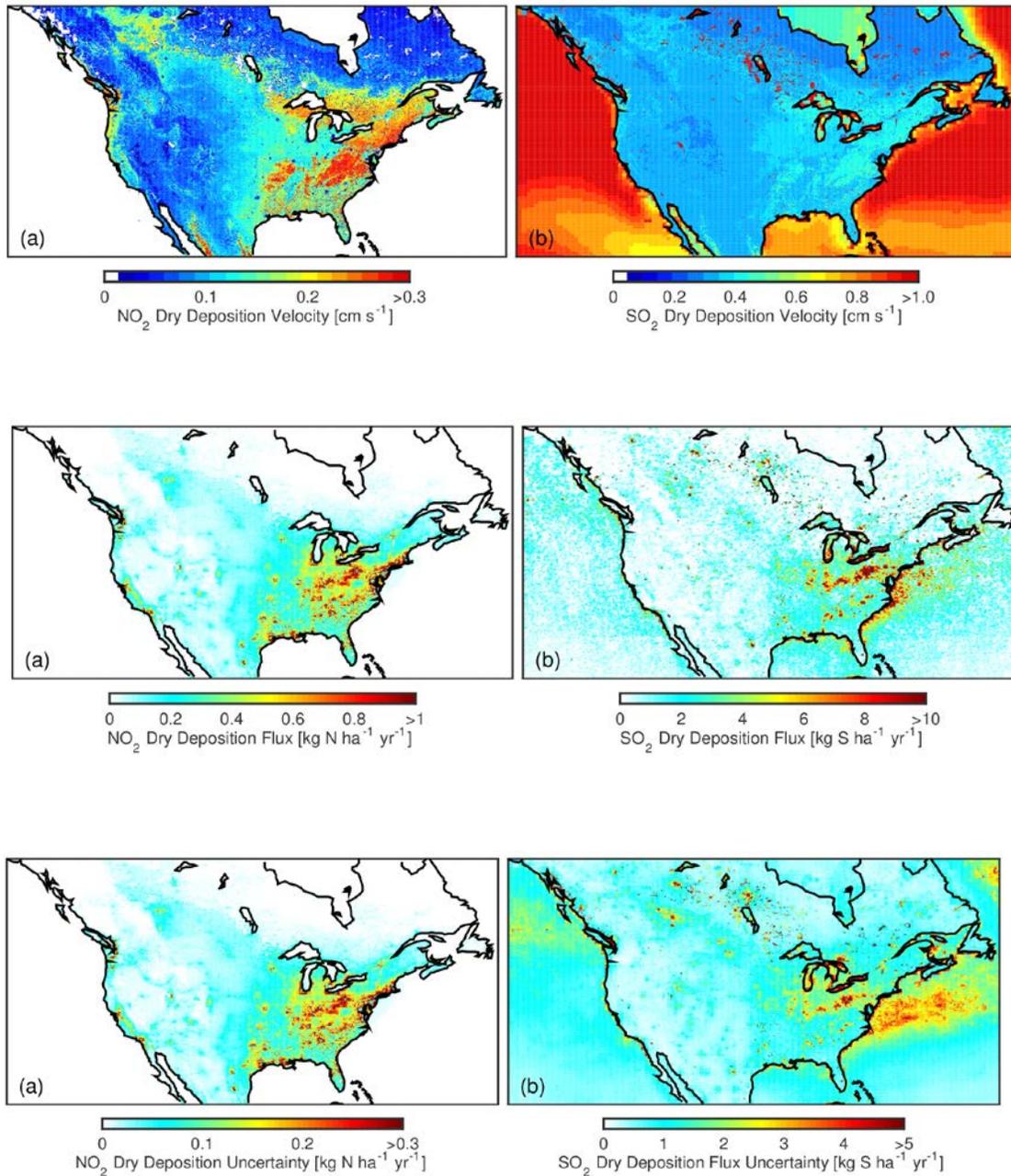
**Figure 2-48 98th percentile concentrations for PM<sub>10-2.5</sub> between 2013–2015.**

### 2.6.7 Distributions of Dry Deposition of Nitrogen Dioxide and Sulfur Dioxide Derived Using Satellite-Based Measurements and Chemistry Transport Models

[Figure 2-49](#) shows the annual average dry deposition velocities and fluxes of NO<sub>2</sub> and SO<sub>2</sub> for 2005 to 2007 and their estimated uncertainties derived by [Nowlan et al. \(2014\)](#) using data derived from the Ozone Monitoring Instrument (OMI) on board the Aura satellite and model parameters from the GEOS-Chem three-dimensional, chemistry-transport model.

As shown in [Figure 2-49](#), higher fluxes for both NO<sub>2</sub> and SO<sub>2</sub> occur in the East than in the West. In particular, there is a band of high dry deposition for NO<sub>2</sub> and SO<sub>2</sub> along the Ohio River. High depositional fluxes for NO<sub>2</sub> are also seen along the Northeast Corridor and in scattered locations throughout the East. In addition, there is a noticeable plume of SO<sub>2</sub> over the western Atlantic Ocean. Average, relative uncertainty in the flux estimates for both NO<sub>2</sub> and SO<sub>2</sub> are ~30% over land and are not much higher over the Atlantic Ocean south of Massachusetts and Nova Scotia. Increased SO<sub>2</sub> deposition, especially near shore, is expected based on the likelihood of off-shore transport of SO<sub>2</sub> and NO<sub>2</sub> along with other pollutants by synoptic weather systems. Note that bidirectional exchange for NO<sub>2</sub> (and a number of other gases) has not been implemented yet in GEOS-Chem or

in CMAQ. Note also that in this study, the algorithms used to derive NO<sub>2</sub> and SO<sub>2</sub> columns are older than more recent ones with lower detection limits. These results, however, do illustrate the potential of the hybrid, satellite/model approach for mapping deposition at the continental scale.



N = nitrogen;  $\text{NO}_2$  = nitrogen dioxide; S = sulfur;  $\text{SO}_2$  = sulfur dioxide.

Source: [Nowlan et al. \(2014\)](#).

**Figure 2-49** Top panel: modeled deposition velocities for nitrogen dioxide and sulfur dioxide for 2005 to 2007; middle panel satellite-model estimates of annual mean dry deposition fluxes of nitrogen dioxide and sulfur dioxide; bottom panel: uncertainties in estimates.

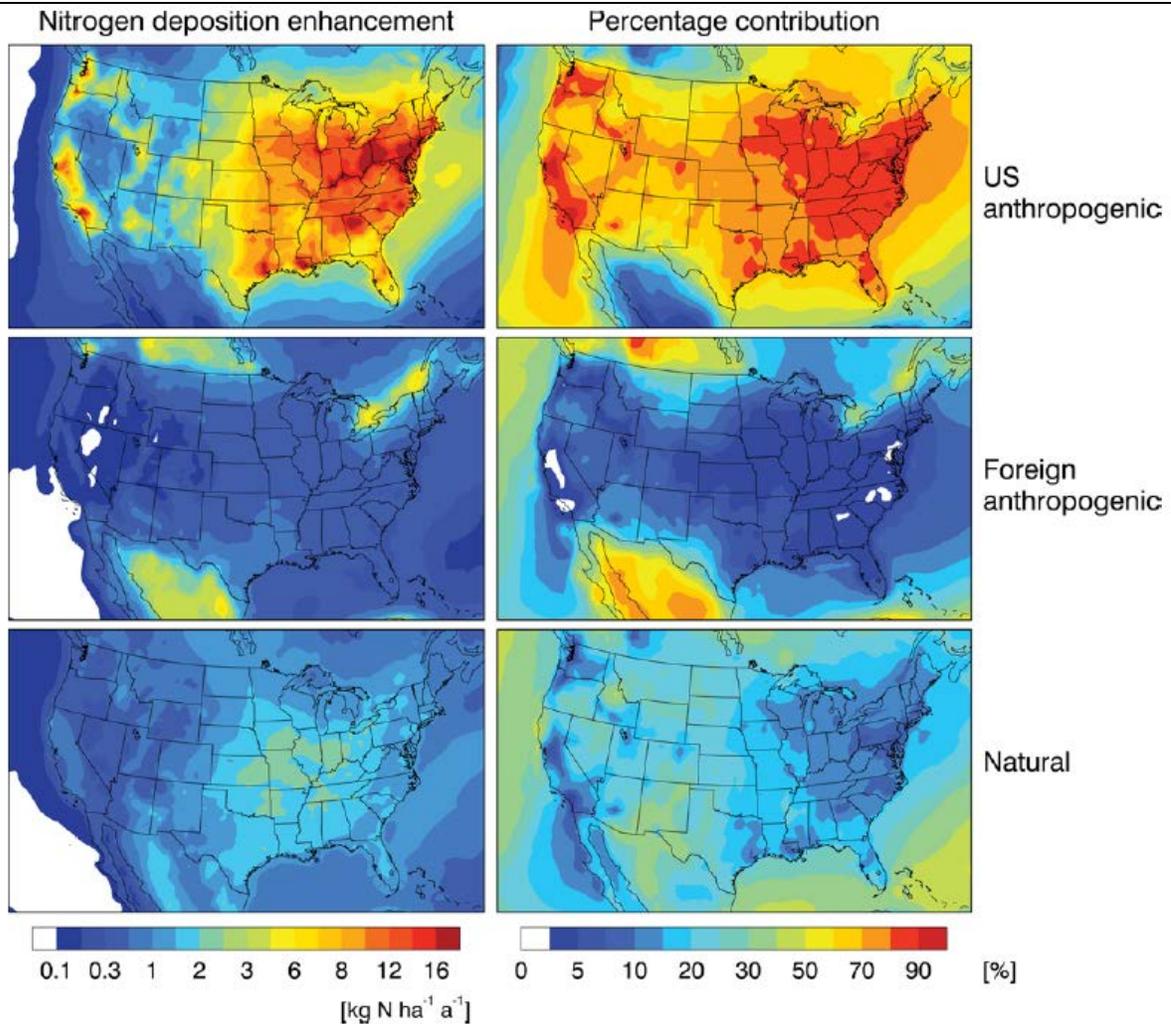
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## 2.6.8 Background Concentrations and Deposition

Background refers here to those concentrations or fluxes that do not result from U.S. anthropogenic emissions. Background sources of N include natural sources like lightning, wildfires, and emission from soils. Background sources of SO<sub>x</sub> include natural sources, such as volcanos or oxidation of reduced sulfur species (H<sub>2</sub>S, [CH<sub>3</sub>]<sub>2</sub>S) emitted in anaerobic environments, and anthropogenic sources from outside the U.S. Background levels so defined facilitate separation of pollution levels that can be controlled by U.S. regulations (or through international agreements with neighboring countries) from levels that are generally uncontrollable by the U.S.

[Kim et al. \(2014a\)](#) found increases in nitrate concentrations in the mixed layer of the North Pacific Ocean, extending to near-shore areas off the west coast of the U.S., with attendant changes in the status of N limitation. Because NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are so highly soluble, they are likely to be removed in rain during ascent before trans-Pacific transport. Because SO<sub>2</sub> is much less soluble than NH<sub>3</sub>, it can be transported to the free troposphere by the warm conveyor belt system before it is oxidized to SO<sub>4</sub><sup>2-</sup> in cloud droplets or on the surfaces of mineral dust particles. The survivability of nitrate is intermediate, depending on the form the nitrate takes.

[Zhang et al. \(2012a\)](#) computed N deposition rates from background sources and from domestic anthropogenic sources using GEOS-Chem. According to their estimates, most of the eastern U.S. and parts of states along the Pacific Coast received >10 kg/ha/yr N deposition. The version of GEOS-Chem used (8.2.3) is the same as described in [Zhang et al. \(2011a\)](#) and used in the 2013 ISA for Ozone and Other Photochemical Oxidants ([U.S. EPA, 2013c](#)). [Figure 2-50](#) shows contributions from domestic anthropogenic, foreign anthropogenic, and natural emissions to total (wet + dry) annual nitrogen deposition over the CONUS for 2006 calculated by [Zhang et al. \(2012a\)](#) using the GEOS-Chem global scale CTM with a horizontal resolution of 1/2° by 2/3°.



Source: [Zhang et al. \(2012a\)](#).

**Figure 2-50** Contributions to oxidized and reduced nitrogen deposition from U.S.: anthropogenic (top), foreign anthropogenic (middle), and natural sources (bottom).

The upper panel of [Figure 2-50](#) shows that the highest values from U.S. anthropogenic sources are found in the eastern U.S., in and downwind of the Ohio River Valley, and in and around urban areas. The middle panel of [Figure 2-50](#) shows the highest contributions from foreign anthropogenic sources in regions of the CONUS bordering Canada and Mexico. Note the band of the highest contributions in upper New York State as a result of emissions in southern Canada. There is also some indication in the Pacific Northwest of smaller contributions due to transport from Eurasia. The pattern of N deposition in the simulation for natural sources in [Figure 2-50](#) (bottom panel), however, shows maximum

deposition throughout the central U.S., with the highest values over the Midwest, reflecting a combination of  $\text{NO}_y$  emissions from lightning in the south-central U.S., from biomass burning throughout the Southeast, and from soils, mainly in the Midwest. The background contribution to N deposition is typically <30% over the eastern U.S. and typically 30 to 50% in the western U.S. where N deposition is already lower. Overall, according to these simulations, U.S. anthropogenic emissions account for 78% of  $\text{N}_r$  deposition over the CONUS. Foreign anthropogenic emissions and natural emissions account for 6 and 16% respectively of total N deposition in this model simulation.

Background concentrations of  $\text{SO}_2$  were calculated using the MOZART-2 global model of tropospheric chemistry (Horowitz et al., 2003) and were presented in the 2008 ISA for Sulfur Oxides (U.S. EPA, 2008c). Background  $\text{SO}_2$  concentrations are estimated to be below 10 parts per trillion (ppt) over much of the U.S. Maximum background concentrations of  $\text{SO}_2$  of ~30 ppt are found in the western U.S. In the Northwest, where there are large geothermal sources of  $\text{SO}_2$ , the contribution of background sources to total  $\text{SO}_2$  is 70 to 80%; however, absolute  $\text{SO}_2$  concentrations are still on the order of ~2 ppb or less. With the exception of the West Coast, where volcanic  $\text{SO}_2$  emissions cause high background concentrations, background sources contribute <1% to present-day  $\text{SO}_2$  concentrations in surface air in the CONUS. Over the eastern U.S., the predicted background contribution to  $\text{SO}_x$  deposition was <10% and even smaller (<1%) where present-day  $\text{SO}_x$  deposition is the highest. The predicted contribution of background sources to S deposition was the highest in the western U.S. at >20% because of the geothermal sources of  $\text{SO}_2$  and oxidation of DMS in surface water of the eastern Pacific. In comparison, values observed at several relatively remote sites cited in the 2008 ISA for Sulfur Oxides (U.S. EPA, 2008c) ranged from 20 to 40 ppt.

As noted earlier, volcanic sources of  $\text{SO}_2$  in the U.S. are found in the Pacific Northwest, Alaska, and Hawaii. The greatest potential domestic effects from volcanic  $\text{SO}_2$  occur on the island of Hawaii. Nearly continuous venting of  $\text{SO}_2$  from Mauna Loa and Kilauea produces  $\text{SO}_2$  in high concentrations of ~5 ppm lasting for periods of up to 1 hour [see Figure 2-34 and Figure 2-35 in the 2008 ISA for Sulfur Oxides; U.S. EPA (2008c)] at two national park sites near the Kilauea caldera and the nearby east rift zone. The latter emits several times as much  $\text{SO}_2$  as the Kilauea caldera. The two measurement sites within the national park are <3 km from the summit emission source and ~10 km from the east rift source and are affected by the two sources during southerly and easterly winds. A number of communities and population centers are within the same distance from the east rift gas source that affects these two monitoring sites. When the normal trade wind flows are disrupted, emissions from the sources can be brought directly to these various communities. Because these communities are located at a similar distance from the large east rift emission source as the national park monitoring stations, it is

probable that these communities are subjected to SO<sub>2</sub> concentrations as high as those measured within Hawaii Volcanoes National Park.

When considering emission sources further afield, intercontinental transport of O<sub>3</sub> and PM has been the focus of efforts by the Task Force on Hemispheric Transport of Air Pollution (HTAP). To the extent that N and S species are transported along with O<sub>3</sub> and PM, they also contribute to deposition following subsidence to the surface. Modeling studies estimate that only a small fraction of nitrogen and sulfur emissions are transported to and deposited within a continent different than the source of the emissions ([Stock et al., 2013](#); [Roy et al., 2012](#); [Sanderson et al., 2008](#)). Global-scale modeling results reported in the 2008 ISA ([U.S. EPA, 2008a](#)) and in the latest ISAs for Oxides of Nitrogen Health Criteria ([U.S. EPA, 2016f](#)) and Sulfur Oxides Health Criteria ([U.S. EPA, 2017d](#)) also indicate that intercontinental transport of oxidized and reduced nitrogen, SO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup> are likely minor background sources of these species. Of greater importance are localized emissions from natural sources. These include emissions of NO from soils and lightning and emissions of SO<sub>2</sub> from geothermal and biogenic sources.

Background PM that would occur in the U.S. in the absence of anthropogenic emissions originates from natural and international sources. Natural sources include windblown dust, wildfires, and sea salt. International contributions include intercontinental transport of dust, wildfire smoke, and pollution as well as transboundary transport of these contributors from Canada and Mexico. Background PM includes both primary and secondary natural and anthropogenic contributions and usually makes a relatively small contribution to urban annual average PM<sub>2.5</sub> concentrations. However, it is an important contributor to PM<sub>2.5</sub> concentrations in the southwestern U.S. and affects PM<sub>2.5</sub> concentrations elsewhere on an episodic basis. Background contributions to PM<sub>10-2.5</sub> can be substantial, as it is generally dominated by dust and sea salt ([U.S. EPA, 2019](#)).

Estimated PM<sub>2.5</sub> background concentrations were estimated to be less than 1 µg/m<sup>3</sup> on an annual basis, with maximum daily average values in a range from 3 to 20 µg/m<sup>3</sup> and a peak of 63 µg/m<sup>3</sup> at the nine national park sites across the U.S. ([U.S. EPA, 2009a](#)).

According to the 2019 PM ISA ([U.S. EPA, 2019](#)), there has not been a similar national-scale effort to update background PM<sub>2.5</sub> concentration estimates since the 2009 PM ISA, but there has been considerable research focused on better understanding the sources and processes that influence background contribution to PM<sub>2.5</sub> in the U.S. Background PM can be viewed as a combination of two conceptually separate components: 1) a baseline component characterized by reasonably consistent distribution of daily values each year, with some variability by region and season, and 2) an episodic component consisting of infrequent contributions from high-concentration events, including volcanic eruptions, wildland fires, and dust storms. On average, natural sources

including soil dust and sea salt have been estimated to account for approximately 10% of U.S. urban PM<sub>2.5</sub> ([U.S. EPA, 2019](#)). However, PM concentrations of several hundred µg/m<sup>3</sup> in areas impacted by wildland fires and >5,000 µg/m<sup>3</sup> during intense dust storms were reported in the 2019 PM ISA, and longer fire seasons resulting from invasive species, historical fire management practices, more frequent droughts, and extreme heat have led to more large fires ([U.S. EPA, 2019](#)). Intercontinental transport contributes 0.05 to 0.15 µg/m<sup>3</sup> to annual average PM<sub>2.5</sub> concentrations in the U.S. Although concentrations are typically less than 1 µg/m<sup>3</sup> at U.S. sites, episodic contributions as high as 20 µg/m<sup>3</sup> have been estimated ([U.S. EPA, 2019](#)).

Just as pollutants can be transported into the U.S., they can also be transported outward. For example, wet deposition of pollutants emitted in eastern North America occurs over the North Atlantic Ocean. Deposition of N species is an important source of nutrients to the western North Atlantic ([Zamora et al., 2011](#)). [Dennis et al. \(2013\)](#), based on CMAQ modeling results, estimated that ~1/3 of oxidized N emissions and slightly less than 1/3 of NH<sub>3</sub> emissions in the U.S. are transported out over the North Atlantic Ocean. Although the average pH of rainwater at Bermuda is ~5, reflecting deposition of acidic species emitted in North America, this additional source of acidity is at most only ~2% of that due to anthropogenic CO<sub>2</sub> ([Bates and Peters, 2007](#)).

With well-validated models, it is possible to compare the relative role of different emission and removal processes. Adjoint models ([Henze et al., 2009](#)) are particularly useful for understanding the relative contribution of emission sources to dry and wet deposition of different nitrogen and sulfur containing compounds. For example, [Lee et al. \(2016\)](#) found that half of nitrogen deposition at Federal Class I areas, such as national parks, can be attributed to emission sources within 500 km and 90% of nitrogen deposition is due to emission sources within 1,500 km. [Malm et al. \(2013\)](#) simulated conservative tracer transport from ammonia source regions with the GEOS-Chem model to estimate that roughly equal amounts of ammonia deposition in Rocky Mountain National Park (RMNP), CO was from within or outside Colorado, with most of the transport into Colorado coming from the West. [Thompson et al. \(2015\)](#) reported that 40% reduced nitrogen deposition in RNMP was from outside Colorado.

Background rainwater pH and background deposition in remote areas worldwide has considerably lower H<sup>+</sup> and N deposition levels than in more populated areas, as described in [Appendix 2.6](#). [Galloway et al. \(1982\)](#) measured the pH of rainwater at five remote sites worldwide and measured pH values ranging from 4.8 to 5.0. At some sites, acidity was attributed to long-range transport of acid sulfate, while at others a mixture of strong and weak acids attributed to both anthropogenic and natural sources was observed. They concluded that a pH of 5 was a good lower limit estimate for natural contributions. [Curtis](#)

[et al. \(2018\)](#) estimated nitrogen and sulfur deposition in remote inland areas of Greenland and reported 0.13 to 0.19 kg N/ha/yr for total nitrogen, 0.8 to 0.11 kg N/ha/yr for  $\text{NO}_3^-$ , 0.05 to 0.09 kg N/ha/yr for  $\text{NH}_4^+$ , and 0.08 to 0.13 kg S/ha yr for  $\text{SO}_4^{2-}$ .

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## 2.7 Supplemental Material on Changes in Deposition since 2000

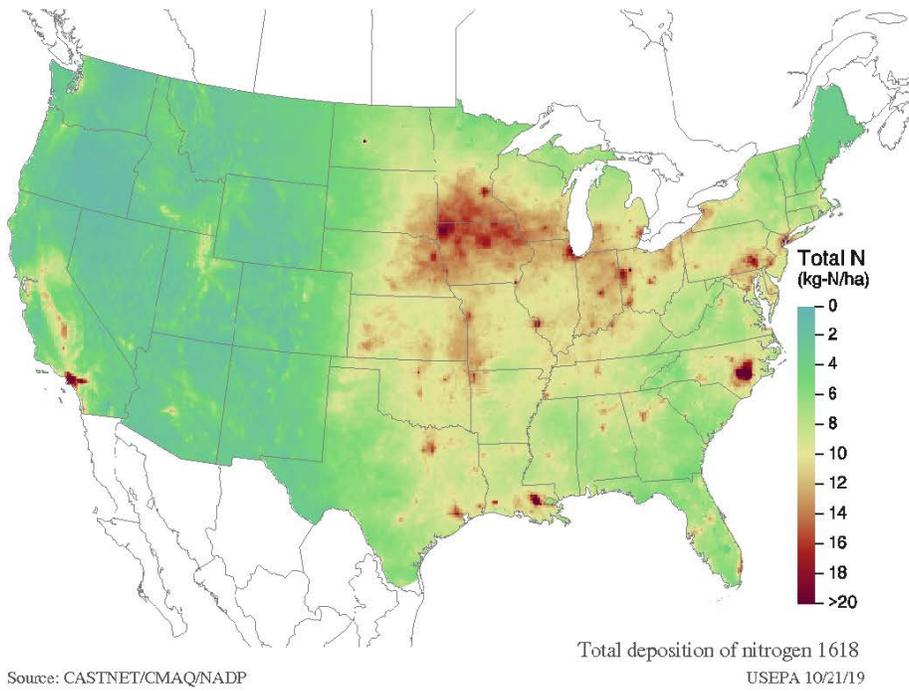
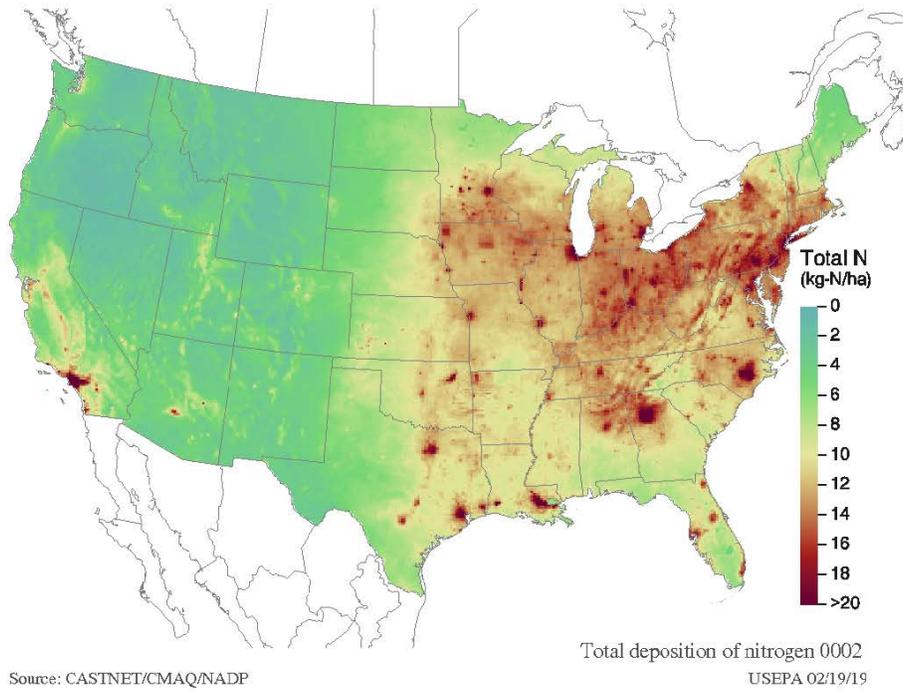
Maps on the portion of the NADP website dedicated to the Total Deposition (TDEP) program (<http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>) and shown in this section present a comprehensive overview of changes in various parameters related to deposition over 2000–2018. Changes between two, 3-year periods, 2000 through 2002 and 2016 through 2018 are summarized in this section. The most notable changes in the geographical distribution of total (wet + dry) deposition of  $\text{NO}_Y + \text{NH}_X$  between these two time periods are the large increase in total deposition of N in the upper Midwest centered in Iowa and Minnesota, with an accompanying decrease in a large area further east, extending from Illinois and Indiana to Pennsylvania and further south (see [Figure 2-51](#)). There are also shifts in the distribution of wet and dry deposition in these areas (see [Figure 2-52](#), [Figure 2-53](#), and [Figure 2-54](#)). Deposition of oxidized nitrogen has declined markedly throughout the eastern U.S. and southern California between the periods 2000–2002 and 2016–2018 (see [Figure 2-55](#), [Figure 2-56](#), [Figure 2-57](#), and [Figure 2-58](#)) due mainly to large decreases in dry deposition of total nitrate ( $\text{TNO}_3 = \text{HNO}_3 + \text{pNO}_3^-$ ; see [Figure 2-59](#)). The decreases in total nitrate deposition across the CONUS are generally due to decreases in  $\text{HNO}_3$  deposition (see [Figure 2-60](#)). Decreases in dry deposition of  $\text{pNO}_3^-$  have generally been smaller, reflecting the smaller contribution of  $\text{pNO}_3^-$  to  $\text{TNO}_3$ . Exceptions include areas such as Florida, Texas, and southern California where dry deposition of  $\text{pNO}_3^-$  has been much greater than  $\text{HNO}_3$  in the earlier period and has decreased substantially (see [Figure 2-61](#)). Other N species, mainly  $\text{NO}_2$  also show large decreases (see [Figure 2-62](#) and [Figure 2-63](#)), especially near urban source areas. Using OMI data, [Krotkov et al. \(2016\)](#) found decreases in column (vertically integrated) abundances of  $\text{NO}_2$  of ~40% from 2005 to 2014 over the U.S.

In contrast to deposition of oxidized N, deposition of reduced inorganic N has seen large increases (see [Figure 2-64](#) and [Figure 2-65](#)). Several areas, including the upper Midwest and San Joaquin Valley, have increased markedly in size or intensity (see [Figure 2-64](#)) between the two periods. Dry deposition of  $\text{NH}_3$  has been the major contributor to the increase (see [Figure 2-66](#)), and although dry deposition of  $\text{pNH}_4^+$  has largely decreased between the two periods (see [Figure 2-67](#)), the greater contribution of  $\text{NH}_3$  has resulted in an overall increase of total reduced nitrogen deposition in affected areas. Between the two periods, emissions of  $\text{NO}_X$  have decreased resulting in lower formation rates of  $\text{HNO}_3$  that could react with  $\text{NH}_3$  to form  $\text{pNH}_4\text{NO}_3$ .

Deposition of oxidized and reduced N have undergone geographic shifts with corresponding shifts in the contributions of each to total N deposition on regional and smaller scales (compare [Figure 2-55](#) and [Figure 2-56](#) to [Figure 2-64](#) and [Figure 2-65](#)). For example, deposition of oxidized N in the Northeast has decreased substantially, but deposition of reduced N has increased in the central U.S. Sizable shifts are also seen in the fractional contributions of total N deposition as dry deposition of both oxidized and reduced forms (compare [Figure 2-58](#) and [Figure 2-69](#)).

Declines in the deposition of S since 2000 have also occurred, particularly in the Ohio River Valley (see [Figure 2-70](#)), with generally much smaller declines in wet deposition (see [Figure 2-71](#)) than for dry deposition (see [Figure 2-72](#)). The proportion of S dry deposited has also decreased, especially in the Ohio Valley and the rest of the eastern U.S. (see [Figure 2-73](#)). Dry deposition of both SO<sub>2</sub> and pSO<sub>4</sub><sup>2-</sup> have both decreased in areas with the greatest deposition ([Figure 2-74](#) and [Figure 2-75](#)). These decreases are consistent with those derived by [Krotkov et al. \(2016\)](#) who detected decreases in the column (vertically integrated) abundance of SO<sub>2</sub> of ~75 % for the period 2005 to 2014 over the Ohio River Valley and southwestern Pennsylvania. These decreases reflect reductions in emissions mandated by the Clean Air Act Amendments and other regulatory requirements.

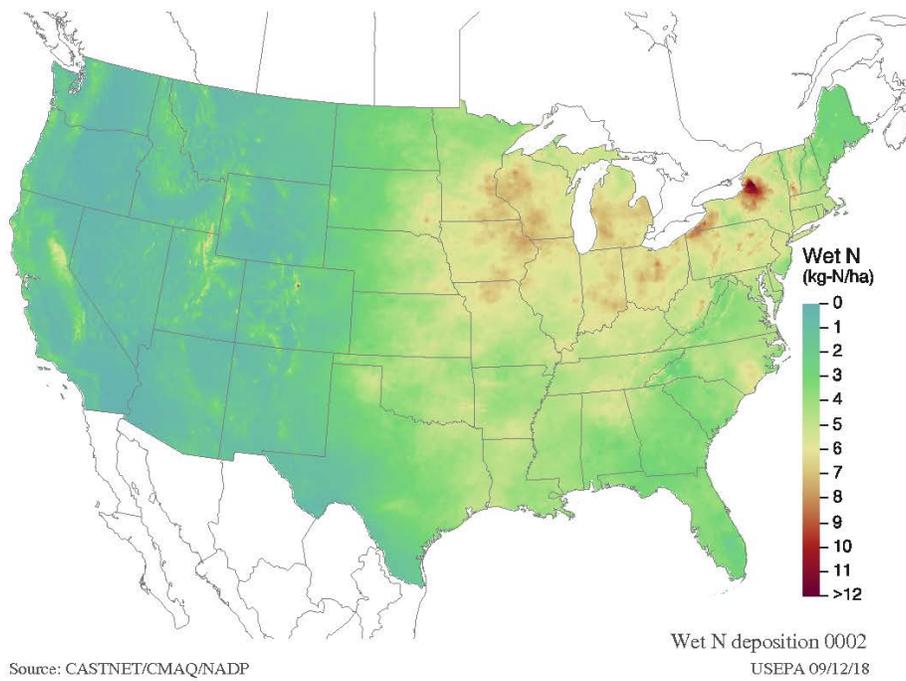
As noted earlier, these estimates of change in deposition were derived from CMAQ output and data from measurement networks. Each of these components has its own set of uncertainties, and the estimates of deposition and the changes over time should be viewed in this light.



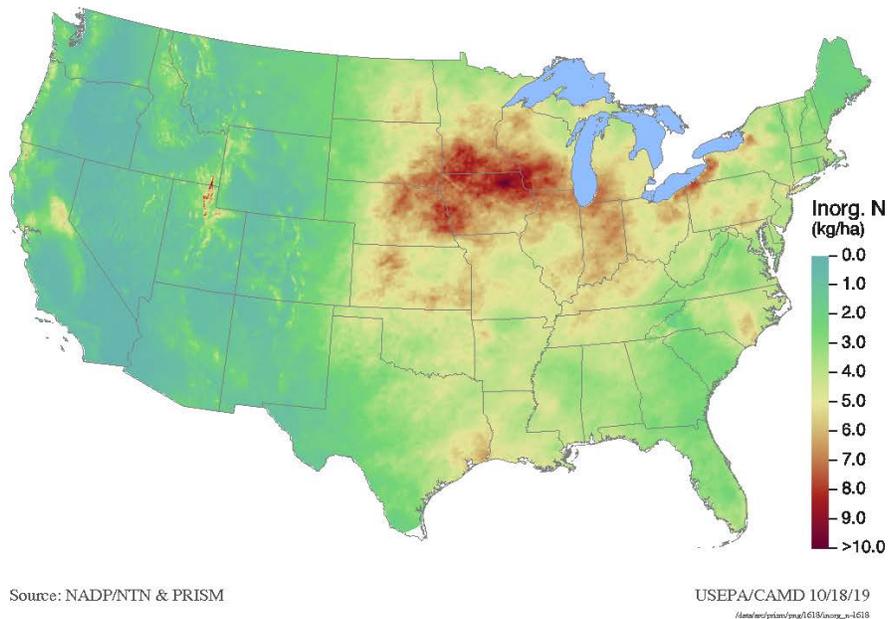
N = nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-51 Wet plus dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



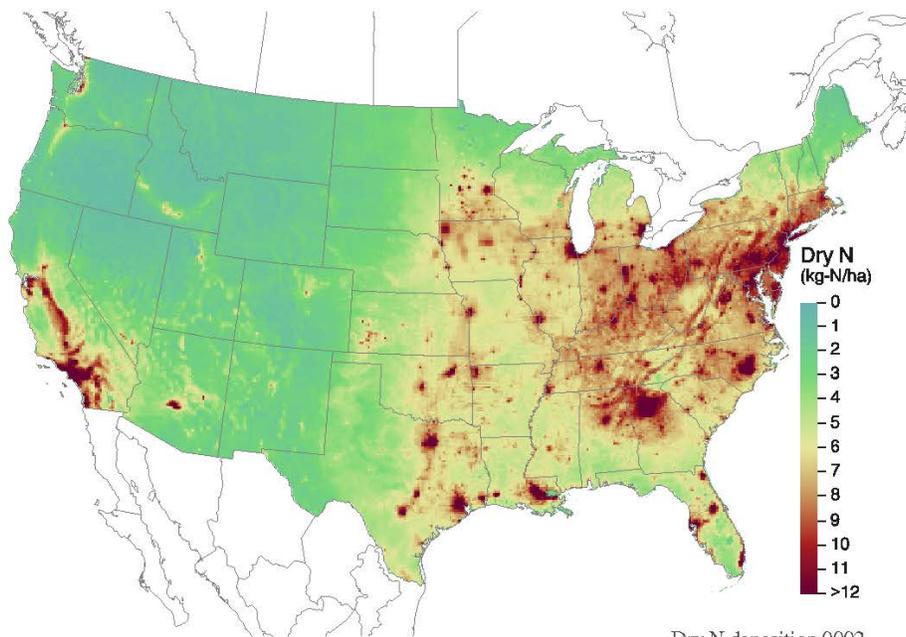
Source: CASTNET/CMAQ/NADP



Source: NADP/NTN & PRISM

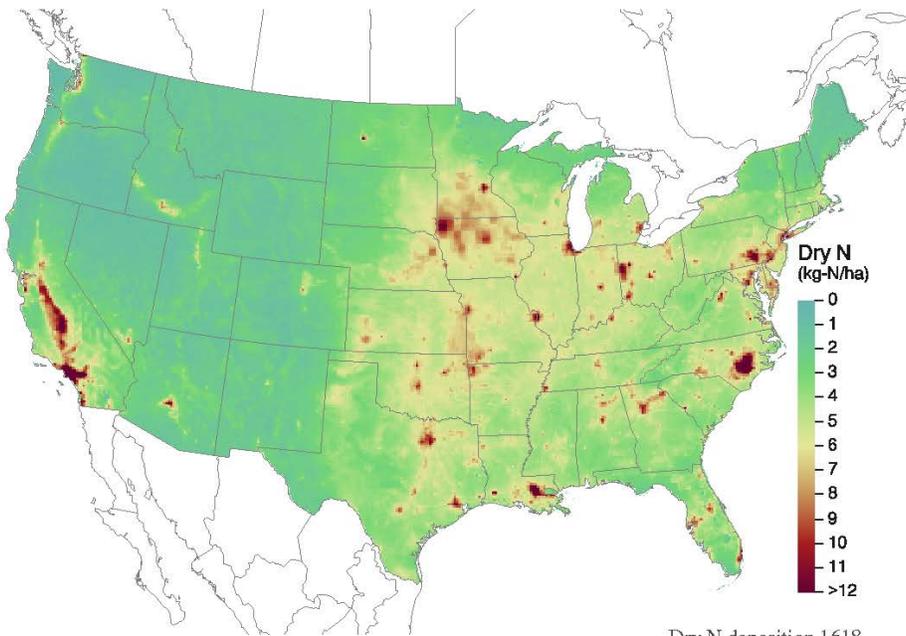
N = nitrogen.  
Source: CASTNET/CMAQ/NTN/AMON/SEARCH.

**Figure 2-52 Wet deposition of total nitrogen over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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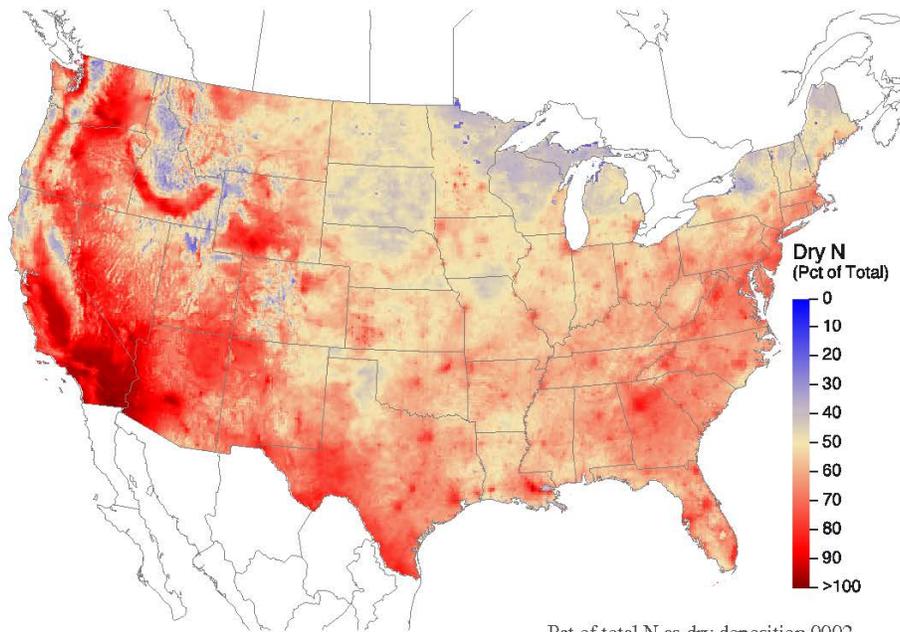
Source: CASTNET/CMAQ/NADP

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N = nitrogen.

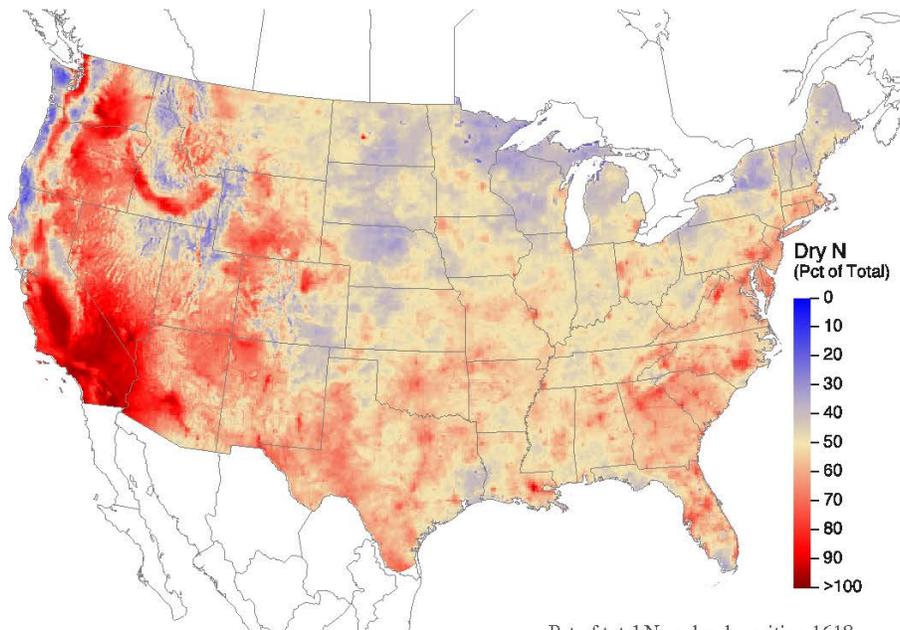
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-53 Dry deposition of total nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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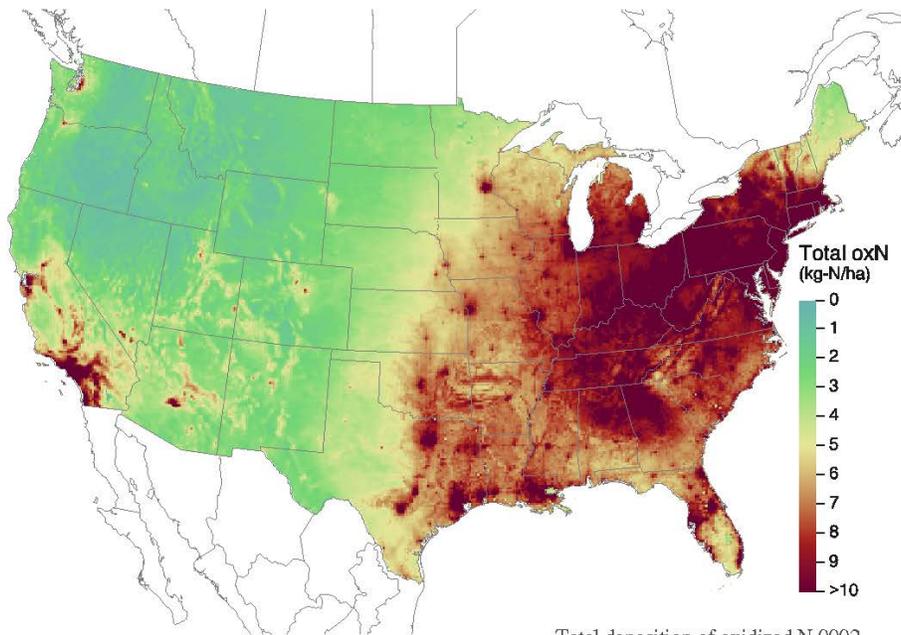
Source: CASTNET/CMAQ/NADP

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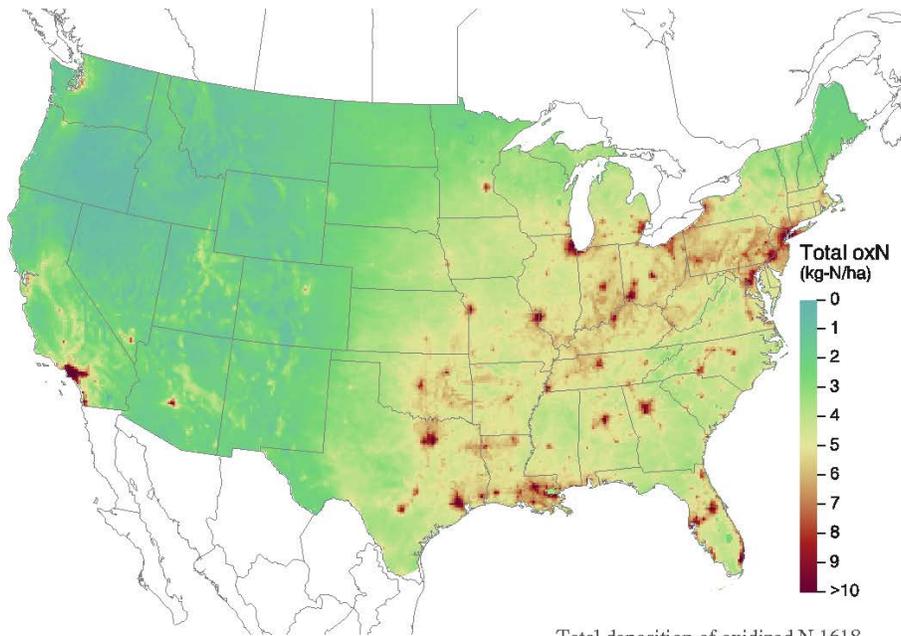
N = nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-54 Percent of total nitrogen as dry deposition over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

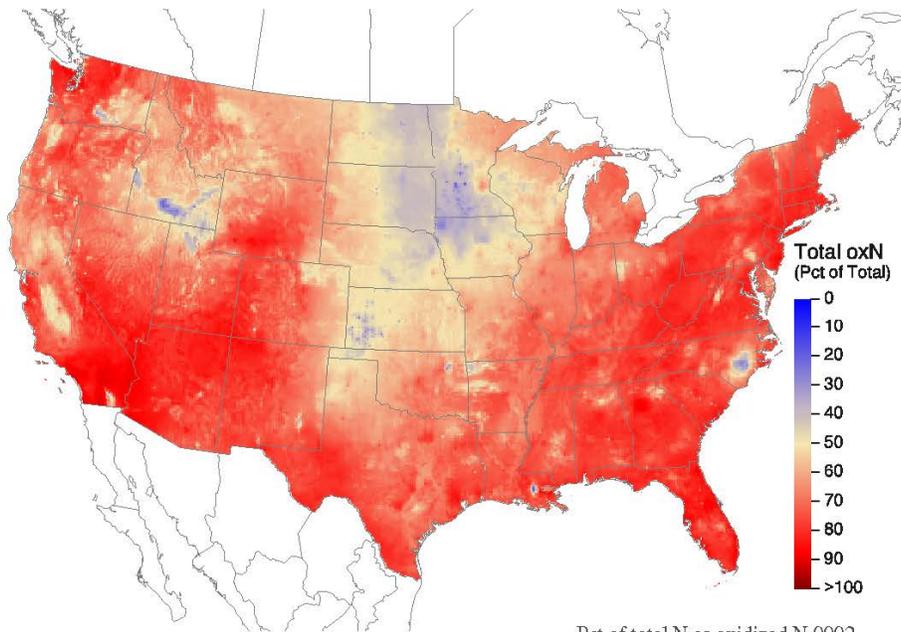


Source: CASTNET/CMAQ/NADP

oxN = oxidized nitrogen.

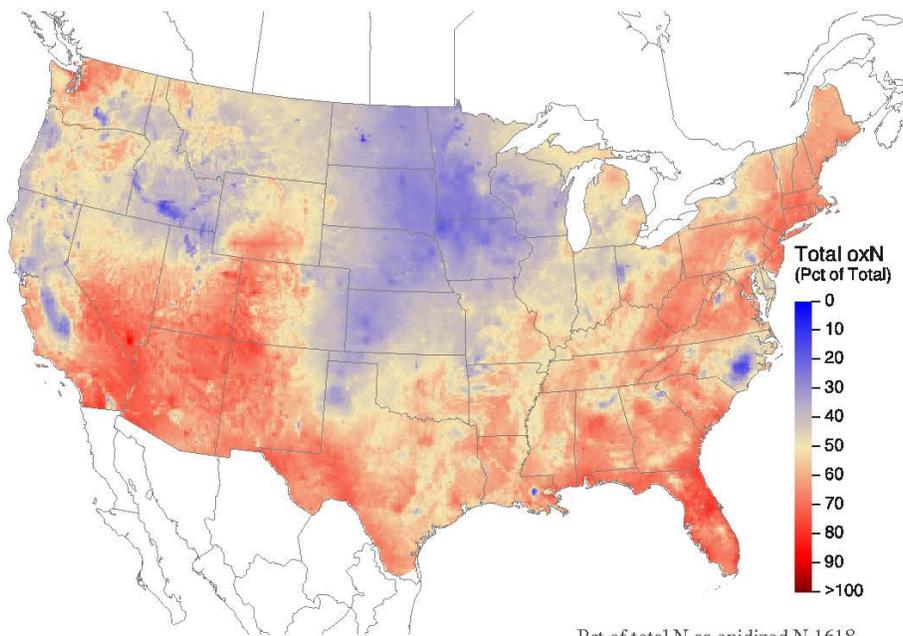
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-55 Wet plus dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Pct of total N as oxidized N 0002  
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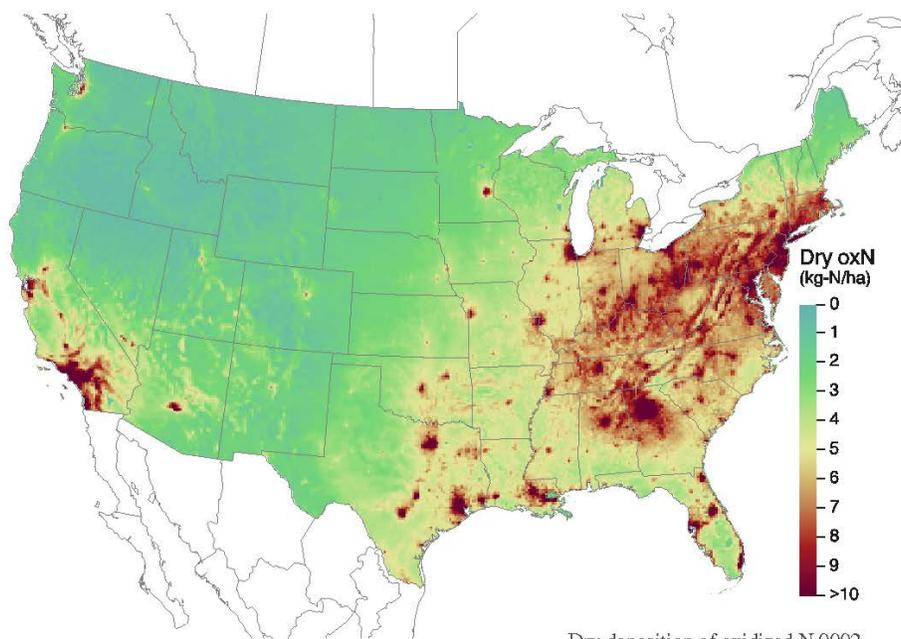
Source: CASTNET/CMAQ/NADP

Pct of total N as oxidized N 1618  
USEPA 10/21/19

oxN = oxidized nitrogen.

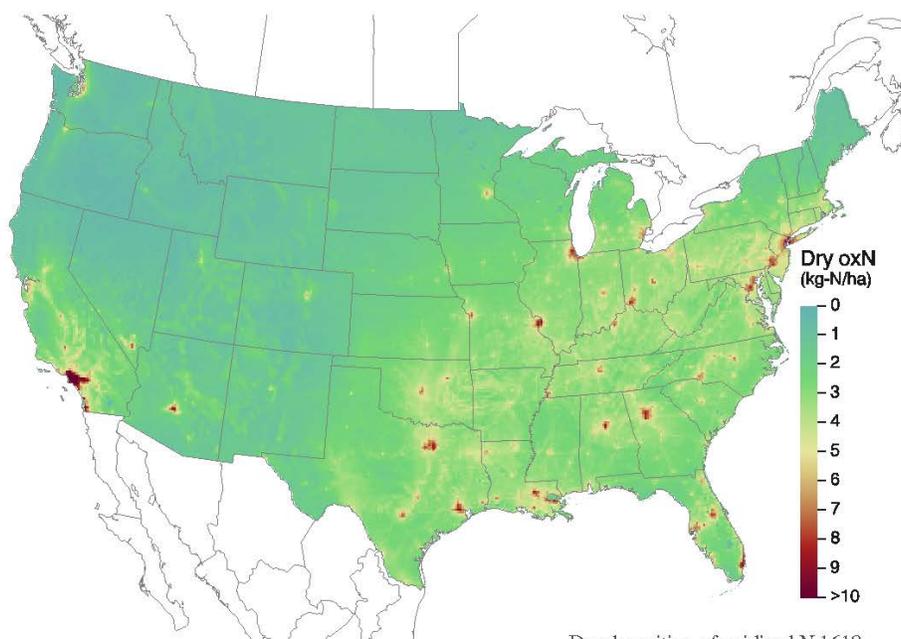
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-56 Percent of total nitrogen as oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry deposition of oxidized N 0002  
USEPA 09/12/18



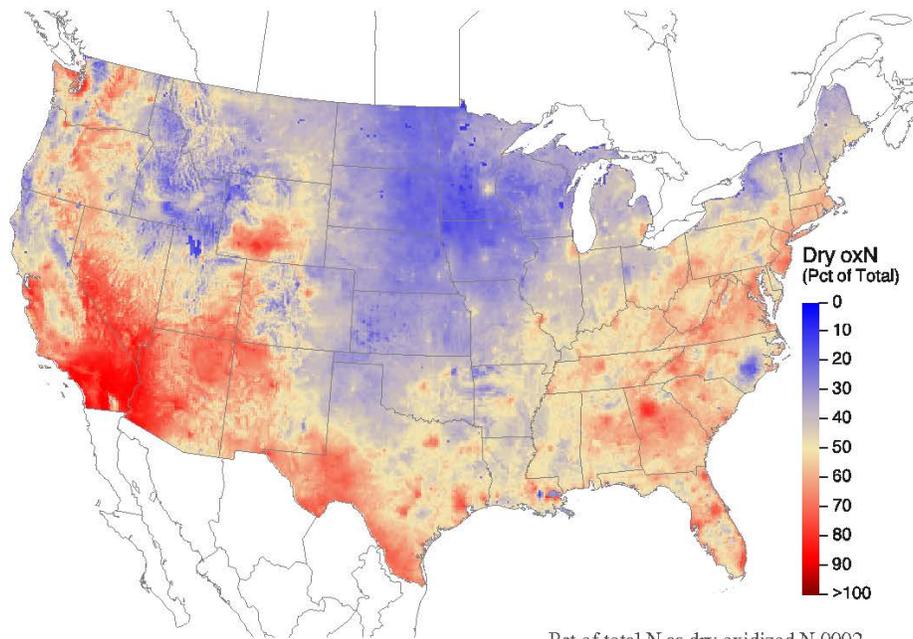
Source: CASTNET/CMAQ/NADP

Dry deposition of oxidized N 1618  
USEPA 10/21/19

oxN = oxidized nitrogen.

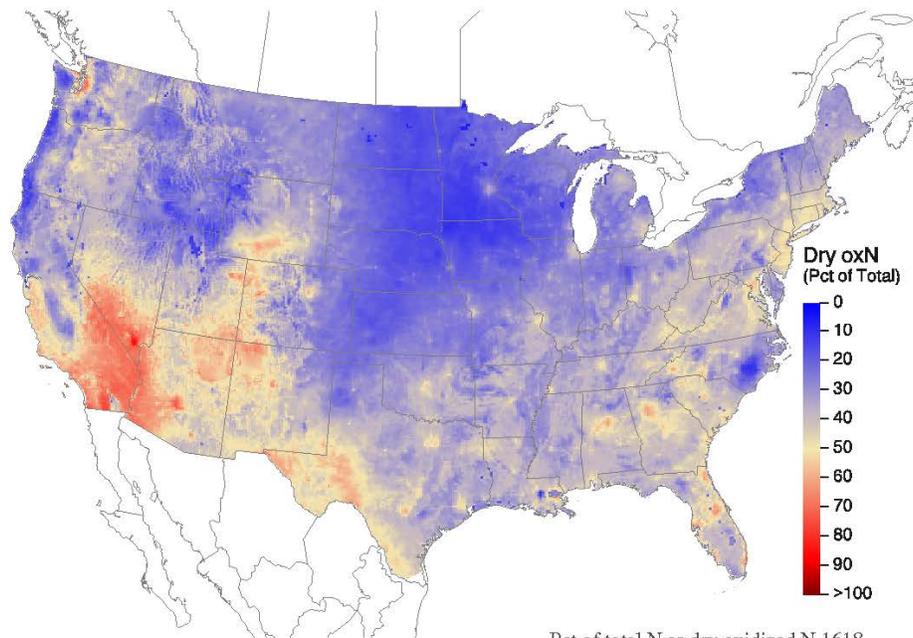
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-57 Dry deposition of oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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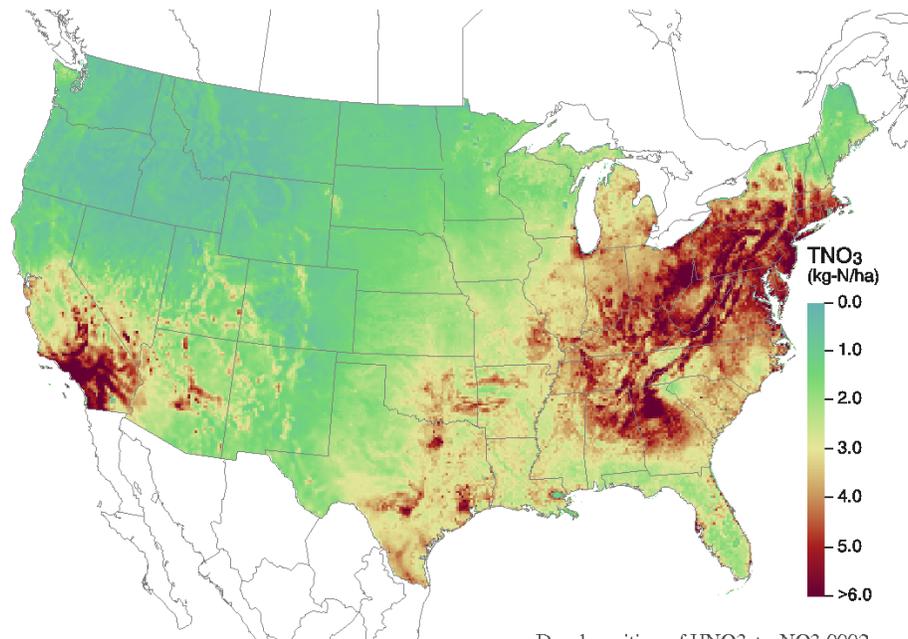
Source: CASTNET/CMAQ/NADP

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oxN = oxidized nitrogen.

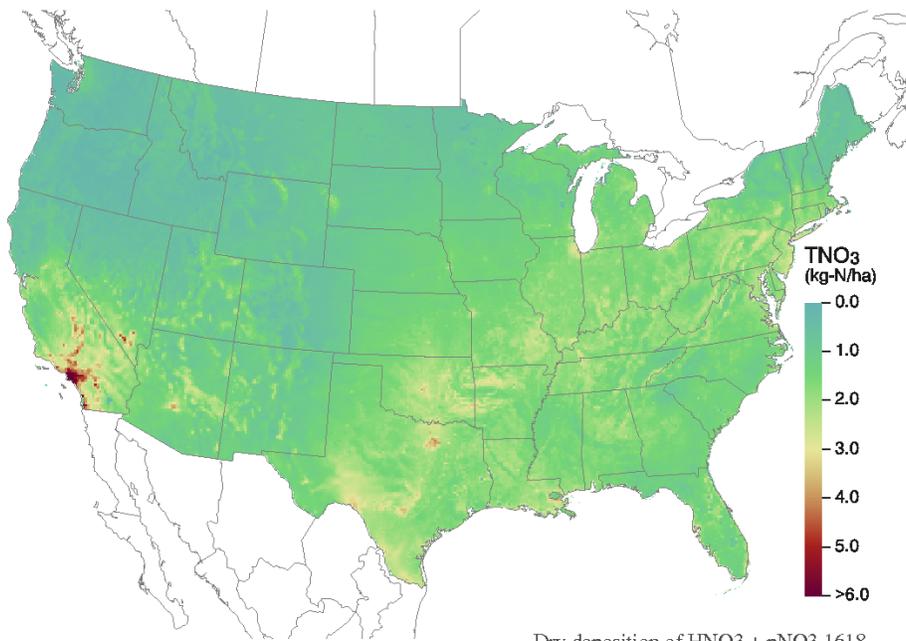
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-58 Percent of total nitrogen dry deposited as oxidized nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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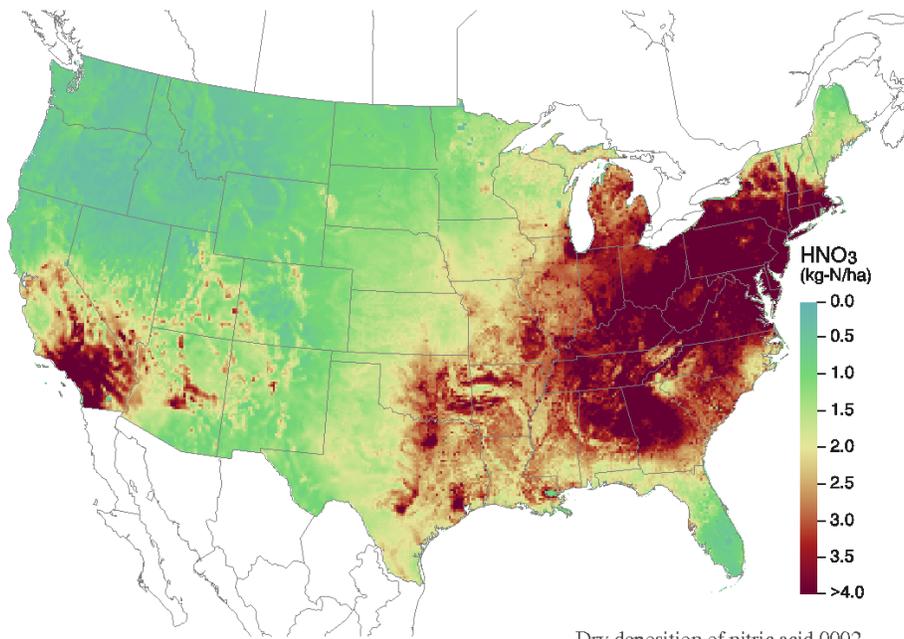
Source: CASTNET/CMAQ/NADP

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TNO<sub>3</sub> = nitric acid and particulate nitrate.

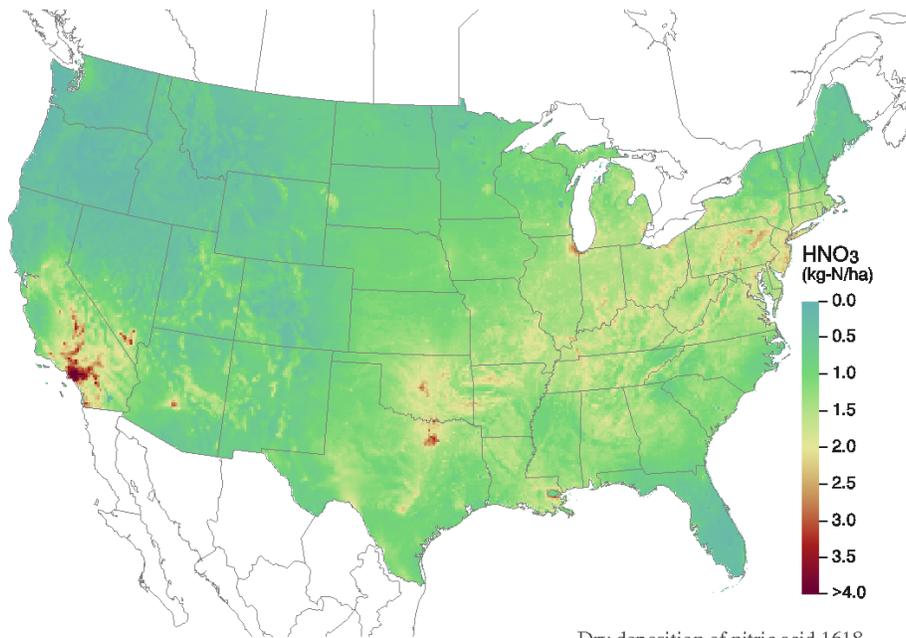
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-59 Combined dry deposition of nitric acid and particulate nitrate over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry deposition of nitric acid 0002  
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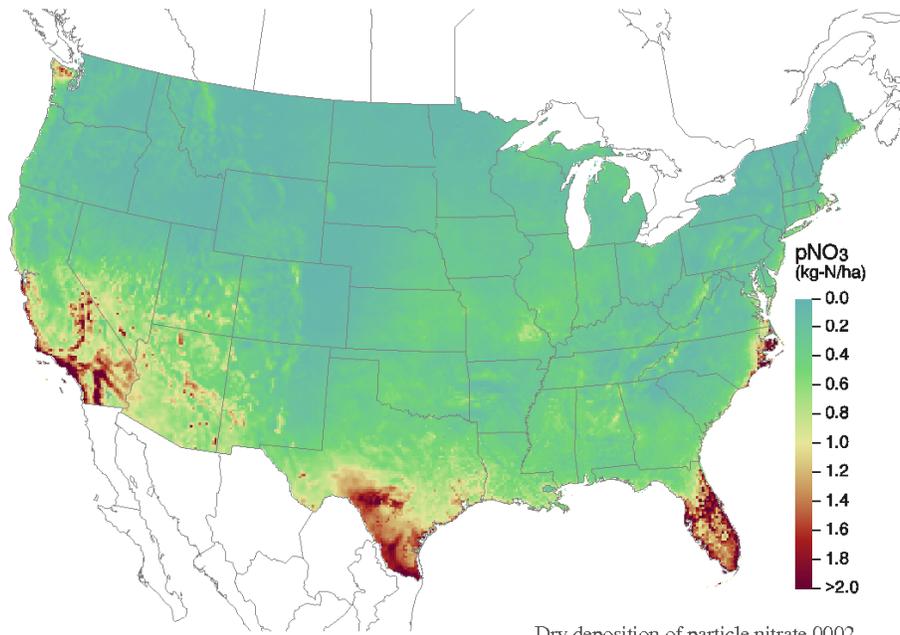
Source: CASTNET/CMAQ/NADP

Dry deposition of nitric acid 1618  
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HNO<sub>3</sub> = nitric acid.

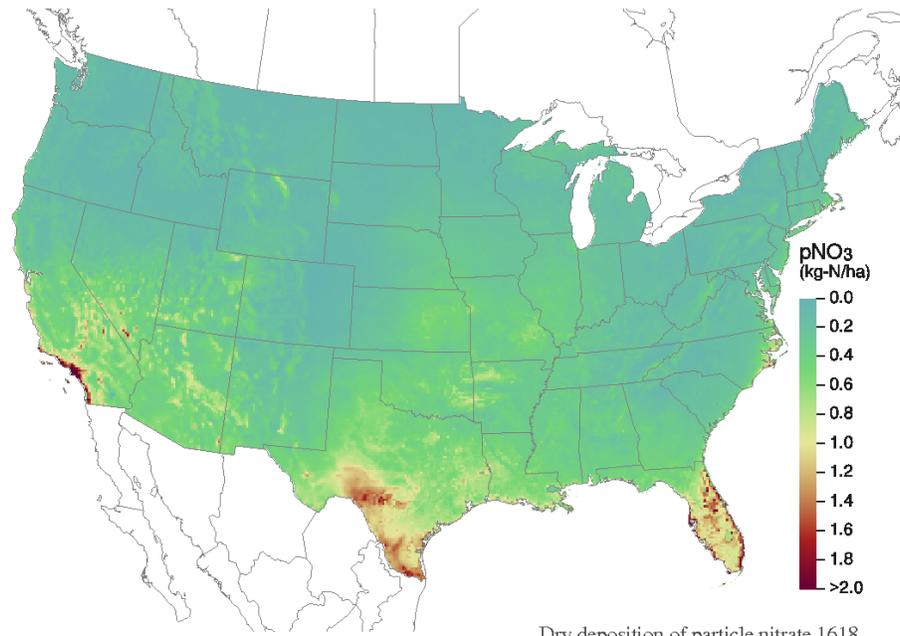
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-60 Dry deposition of nitric acid over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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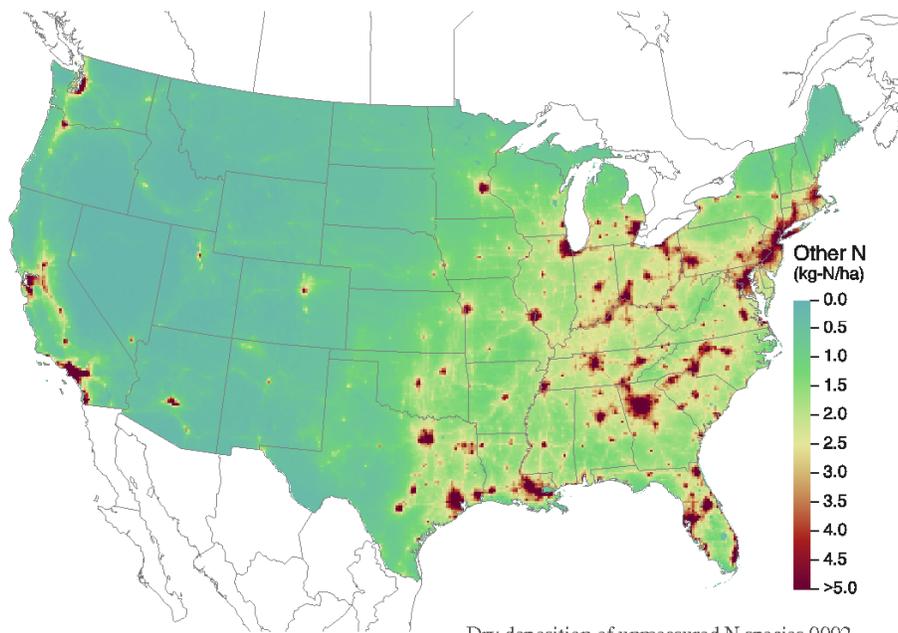
Source: CASTNET/CMAQ/NADP

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pNO<sub>3</sub> = particulate nitrate.

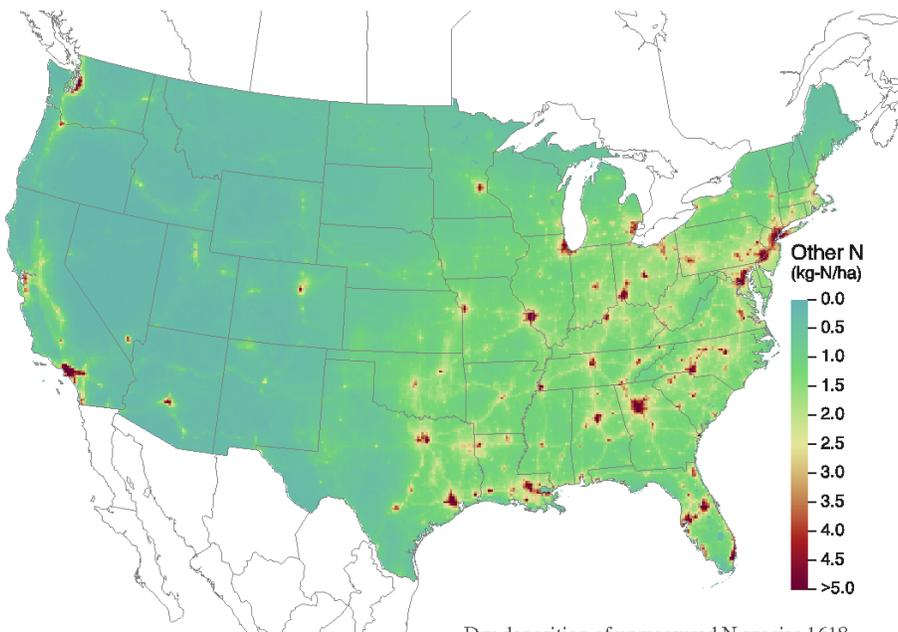
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-61 Dry deposition of particulate nitrate over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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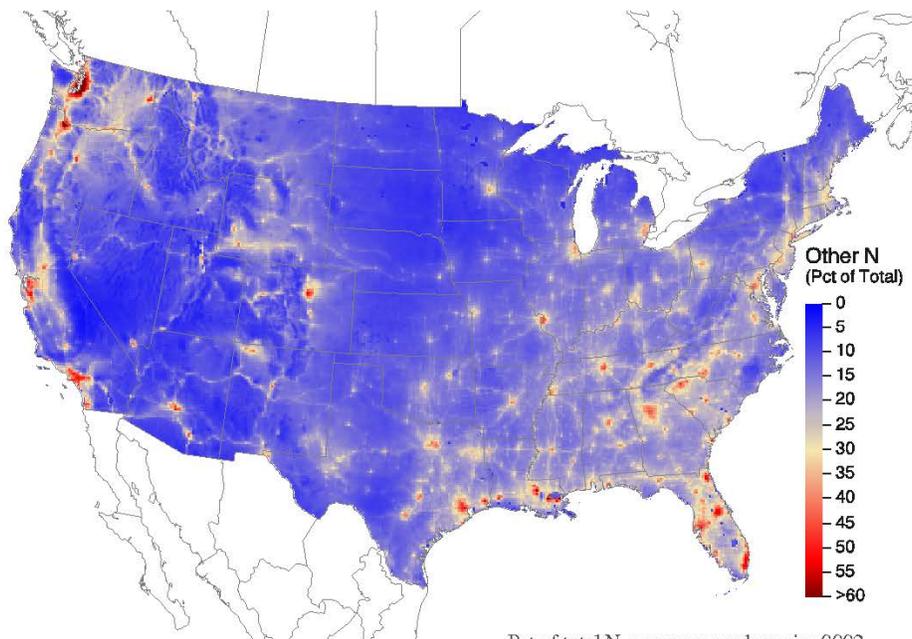
Source: CASTNET/CMAQ/NADP

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N = nitrogen.

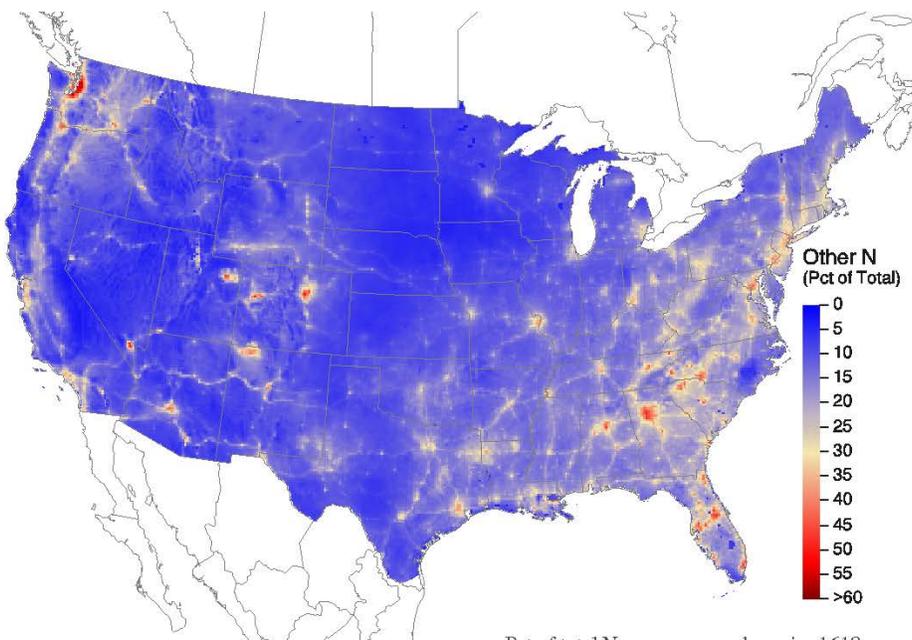
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-62 Dry deposition of modeled (unmeasured) nitrogen species over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Pct of total N as unmeasured species 0002  
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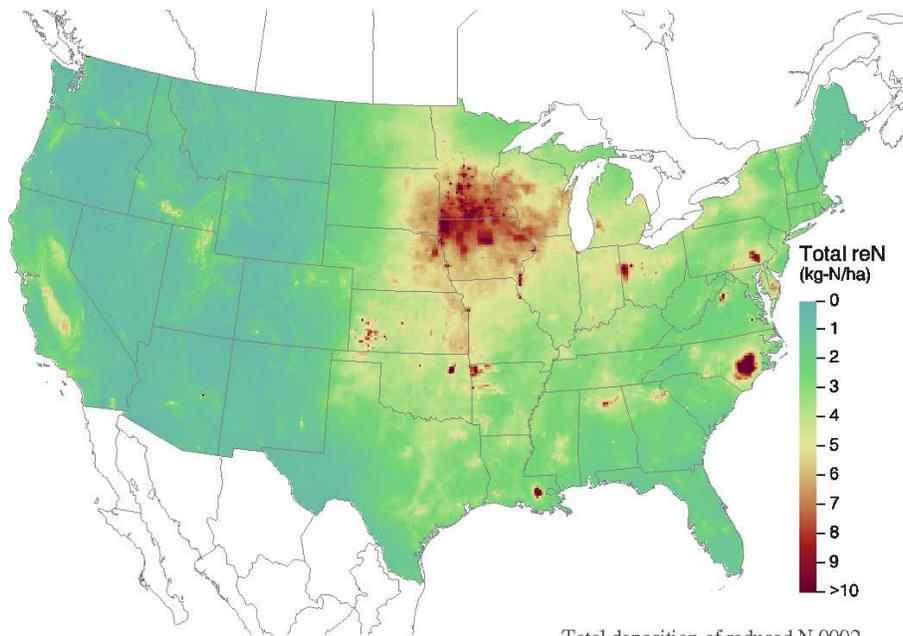
Source: CASTNET/CMAQ/NADP

Pct of total N as unmeasured species 1618  
USEPA 10/21/19

N = nitrogen.

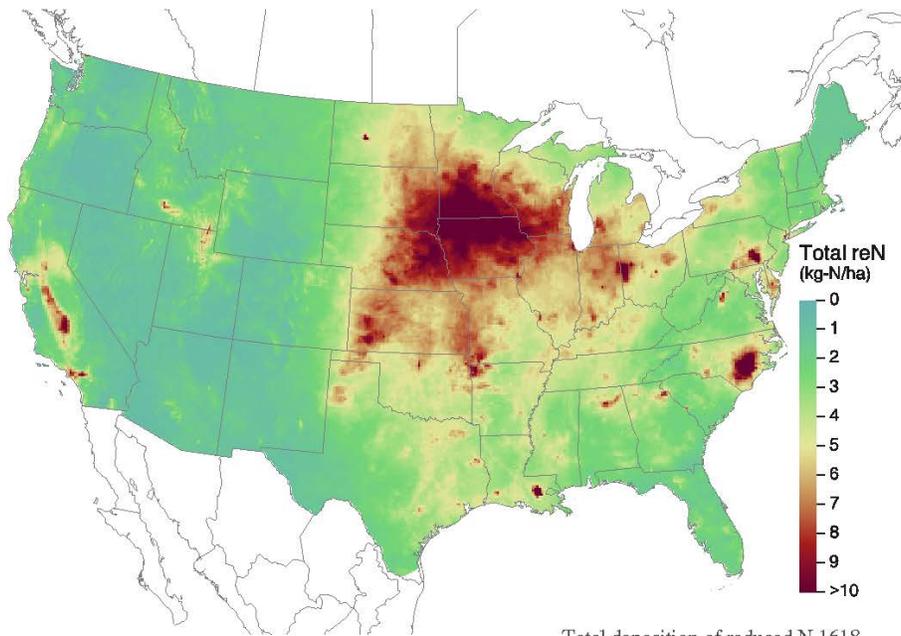
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-63 Percent of total nitrogen as modeled (unmeasured) species over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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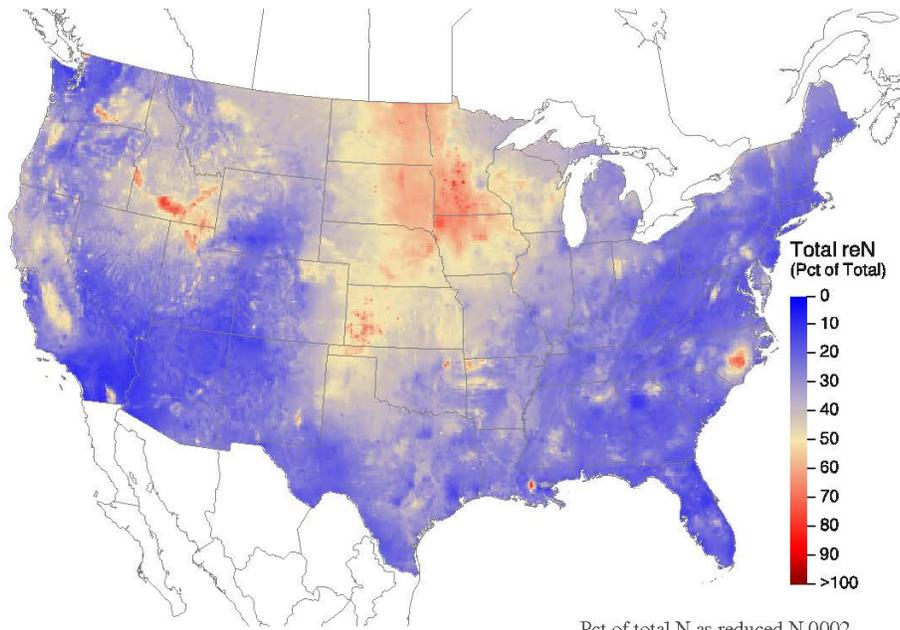
Source: CASTNET/CMAQ/NADP

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reN = reduced nitrogen.

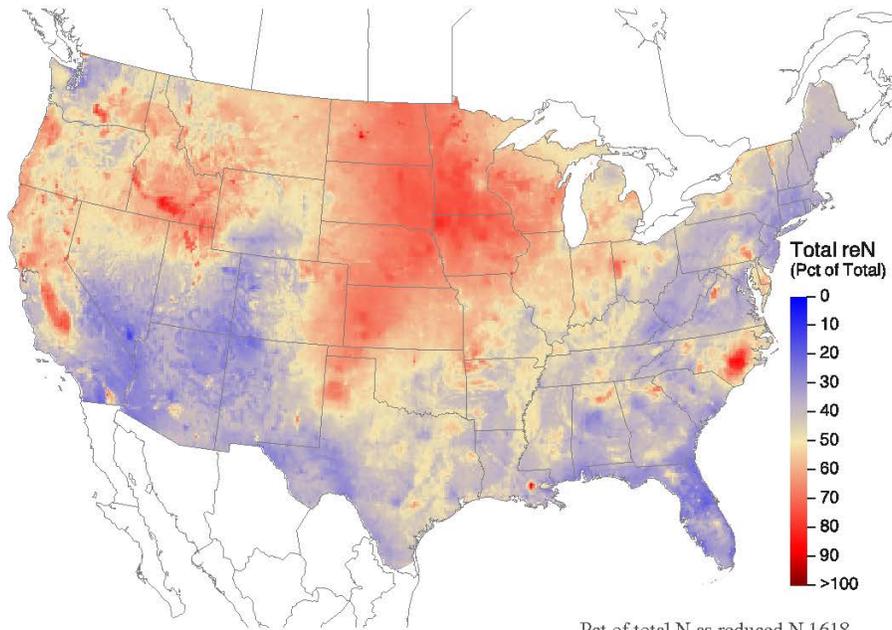
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-64 Wet plus dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Pct of total N as reduced N 0002  
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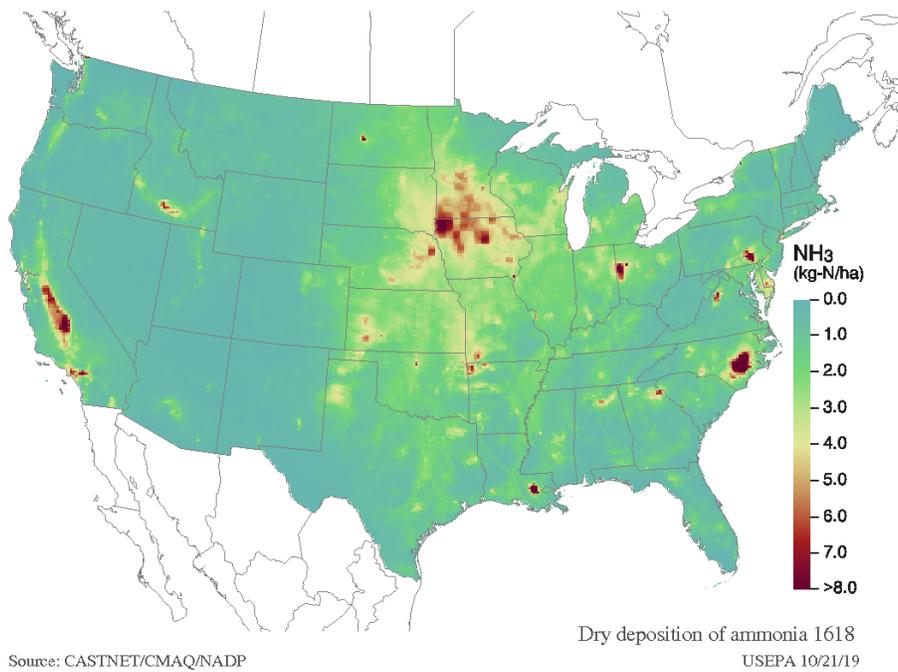
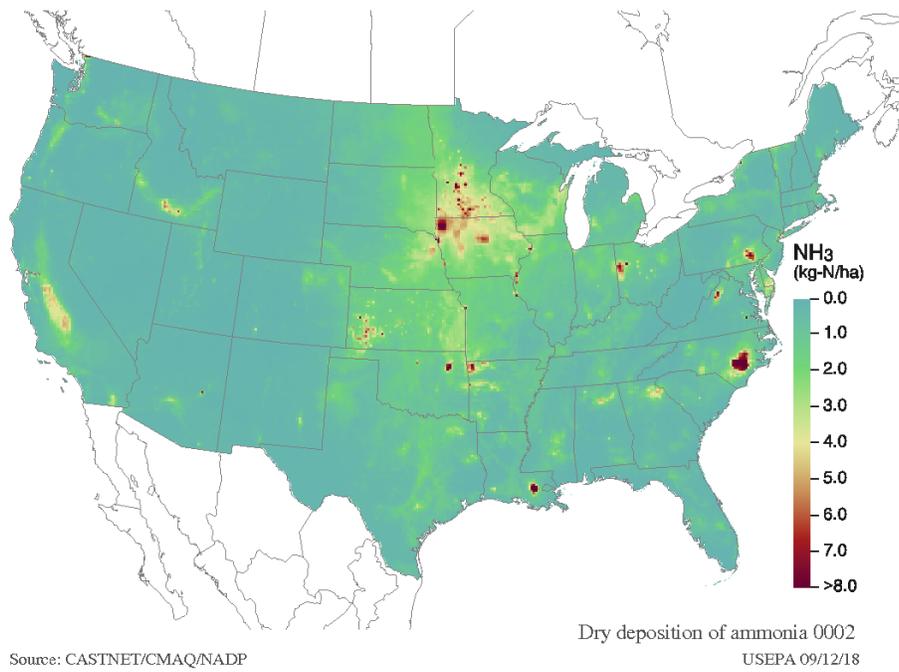
Source: CASTNET/CMAQ/NADP

Pct of total N as reduced N 1618  
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reN = reduced nitrogen.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

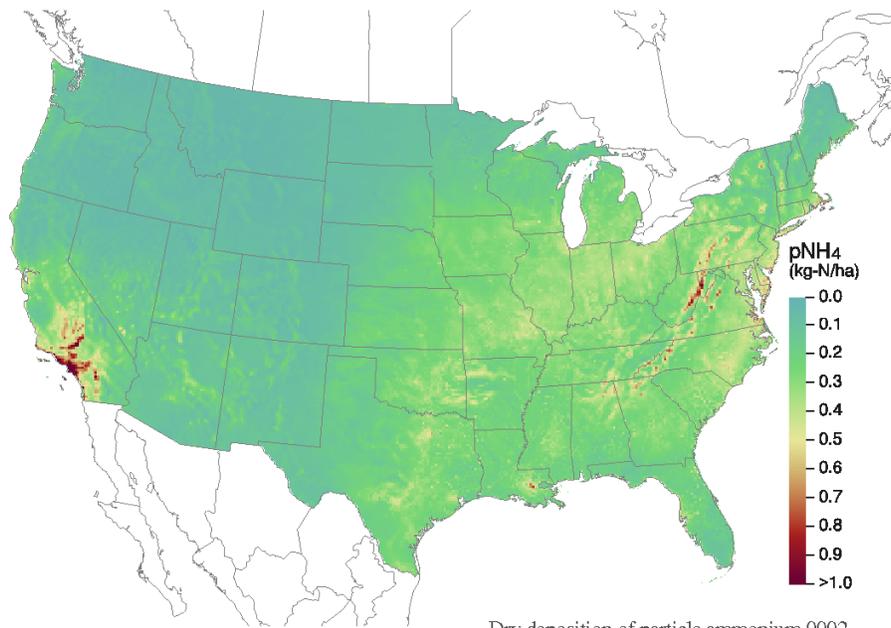
**Figure 2-65 Percent of total nitrogen deposition by reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



NH<sub>3</sub> = ammonia.

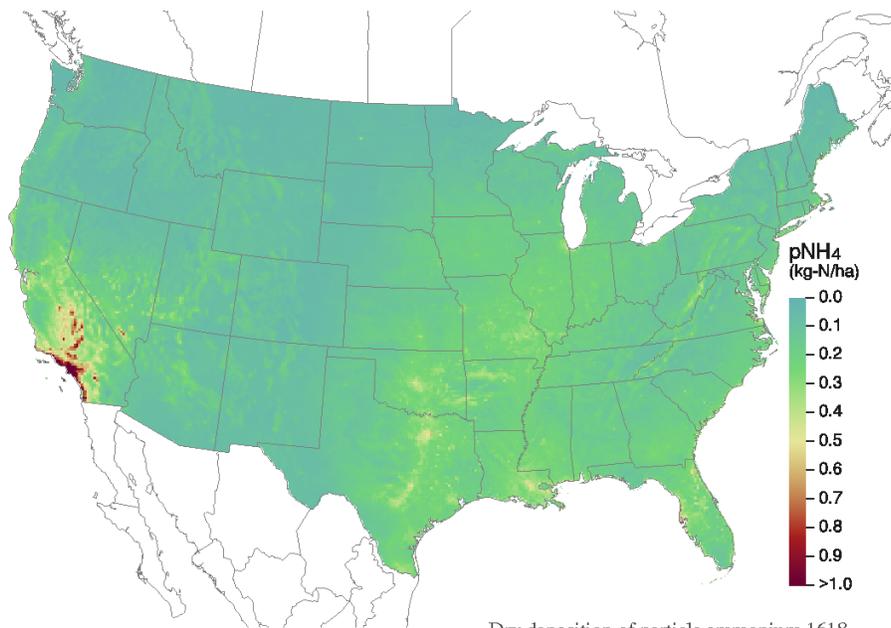
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-66 Dry deposition of ammonia over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry deposition of particle ammonium 0002  
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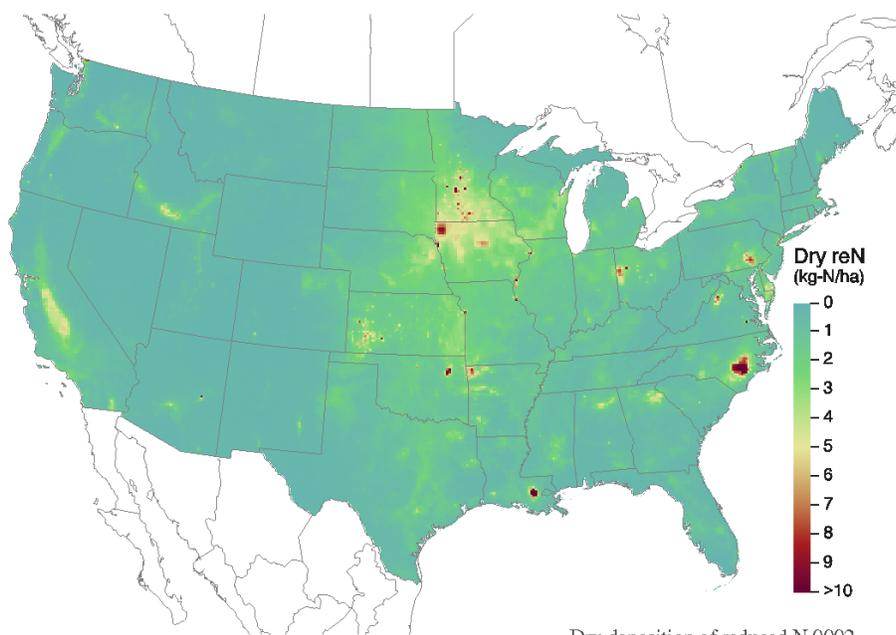
Source: CASTNET/CMAQ/NADP

Dry deposition of particle ammonium 1618  
USEPA 10/21/19

pNH<sub>4</sub> = particulate ammonium.

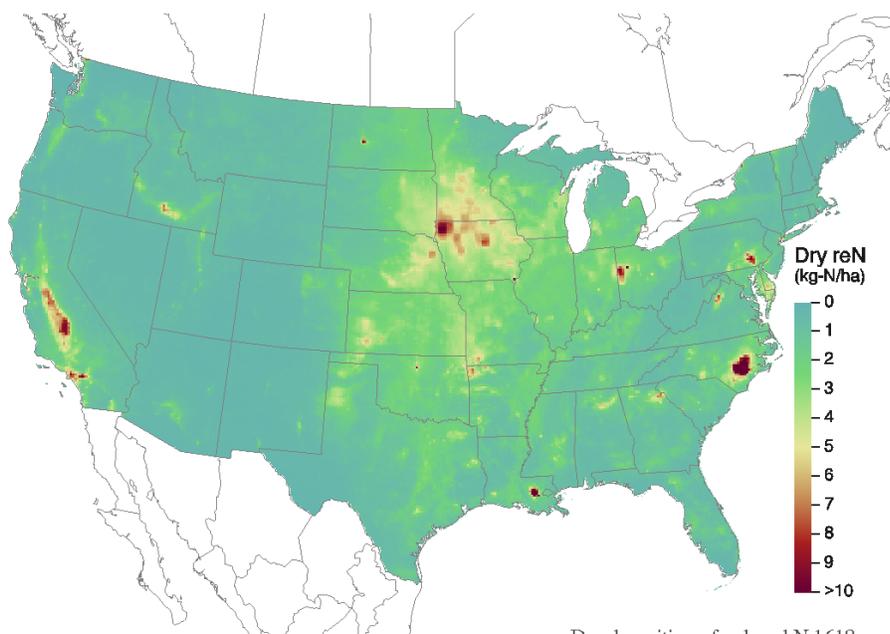
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-67 Dry deposition of particulate ammonium over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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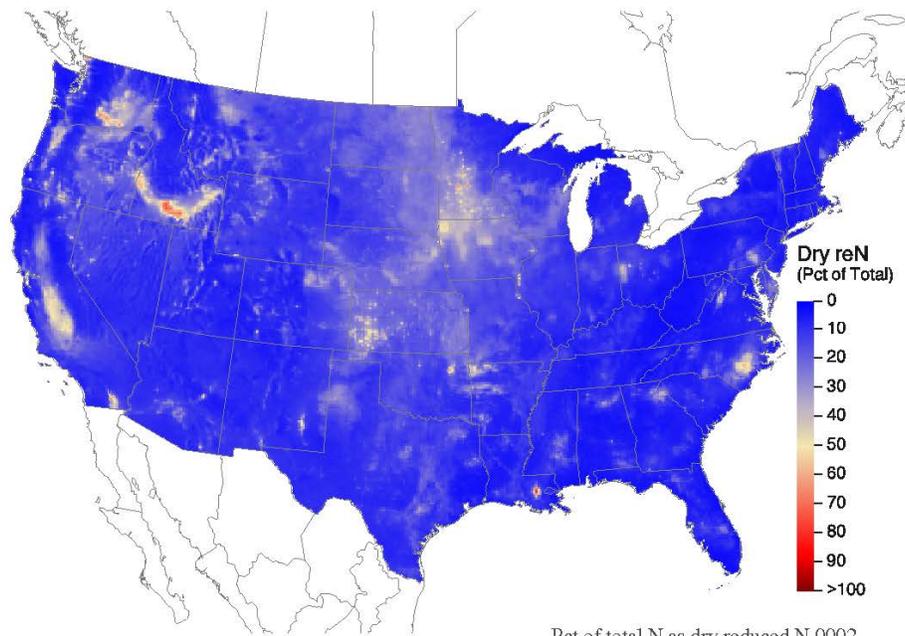
Source: CASTNET/CMAQ/NADP

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reN = reduced nitrogen.

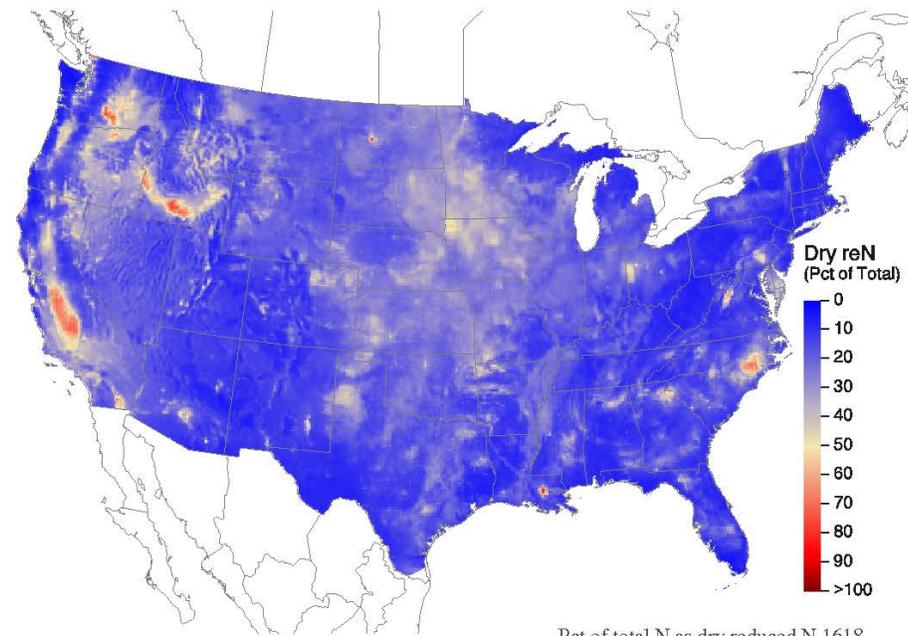
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-68 Dry deposition of reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

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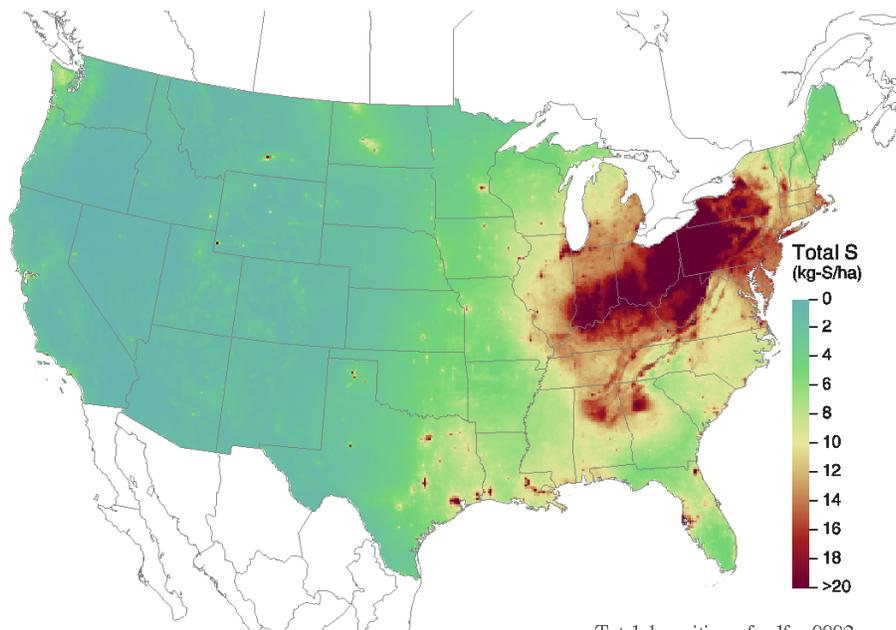
Source: CASTNET/CMAQ/NADP

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reN = reduced nitrogen.

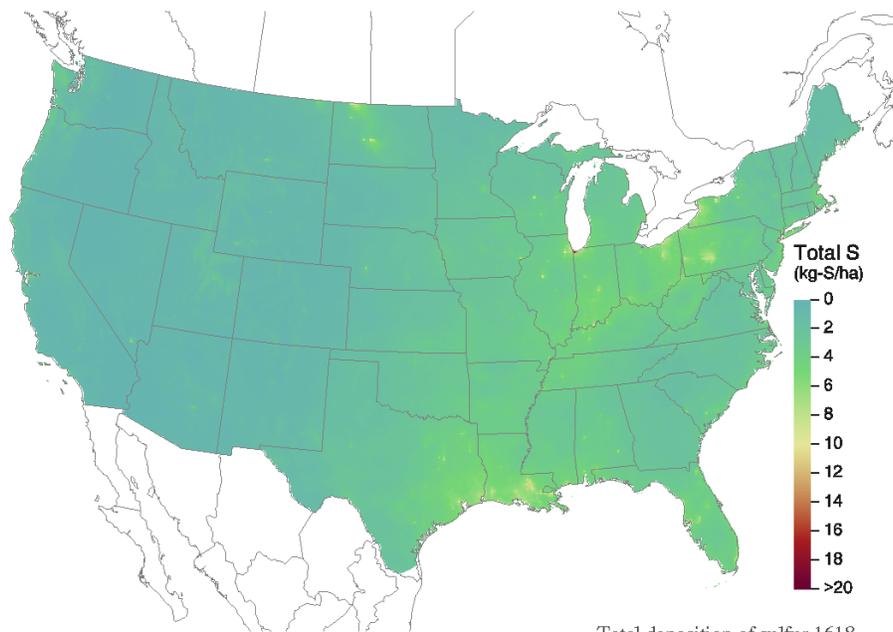
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-69 Percent of total nitrogen deposition by dry reduced (inorganic) nitrogen over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Total deposition of sulfur 0002  
USEPA 09/12/18



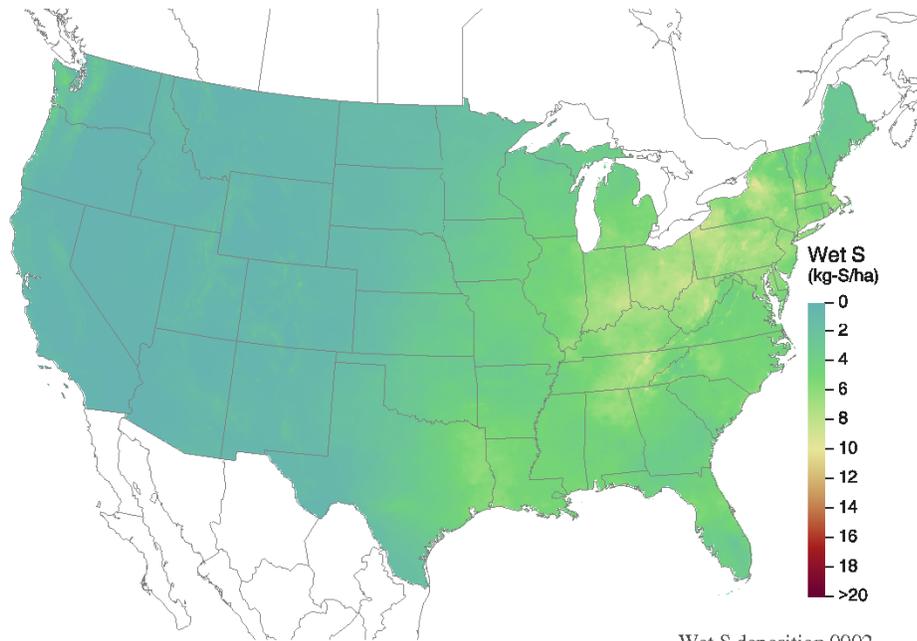
Source: CASTNET/CMAQ/NADP

Total deposition of sulfur 1618  
USEPA 10/21/19

S = sulfur.

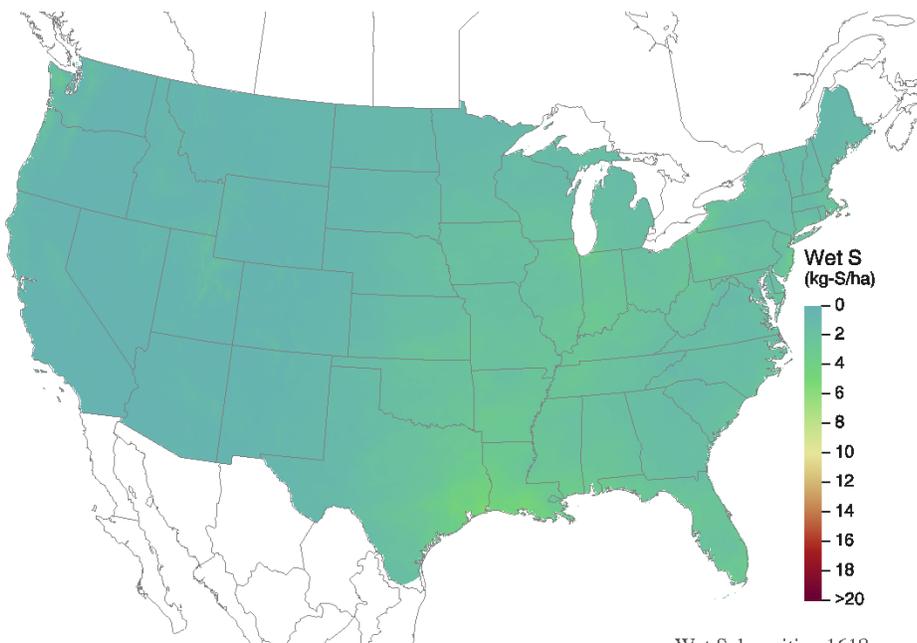
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-70 Wet plus dry deposition of total sulfur over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Wet S deposition 0002  
USEPA 09/12/18



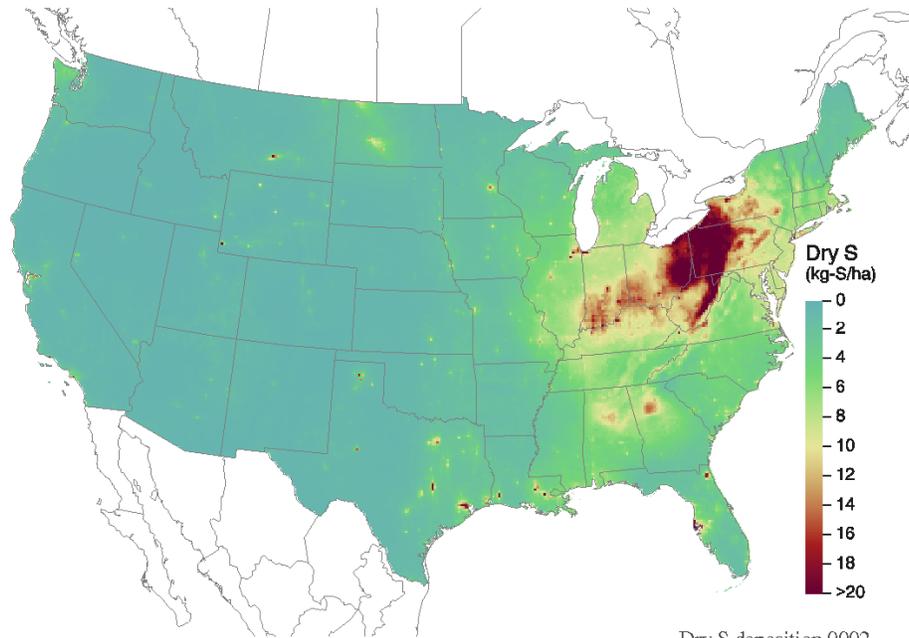
Source: CASTNET/CMAQ/NADP

Wet S deposition 1618  
USEPA 10/21/19

S = sulfur.

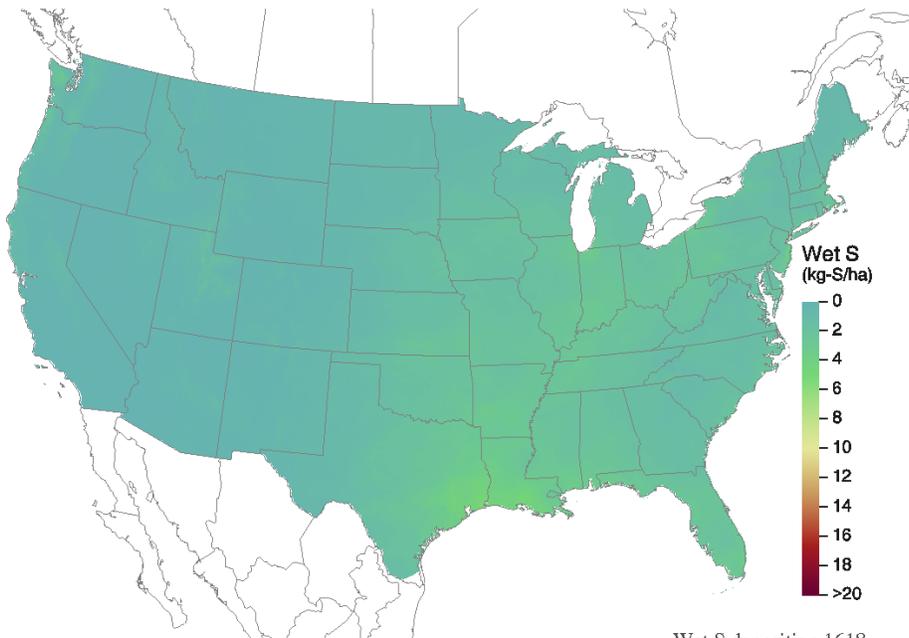
Source: CASTNET/CMAQ/NTN/AMON/SEARCH.

**Figure 2-71 Wet deposition of total sulfur over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry S deposition 0002  
USEPA 09/12/18



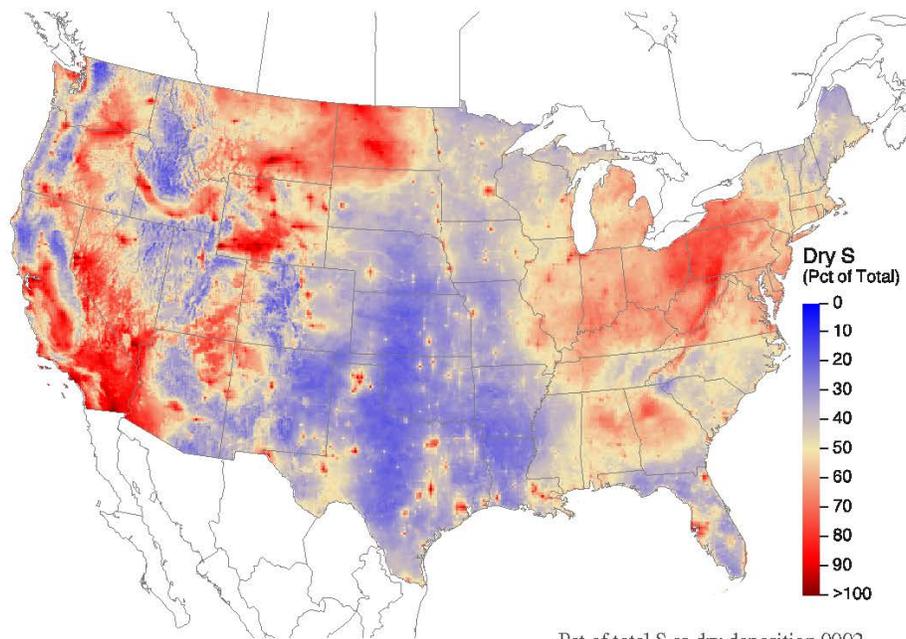
Source: CASTNET/CMAQ/NADP

Wet S deposition 1618  
USEPA 10/21/19

S = sulfur.

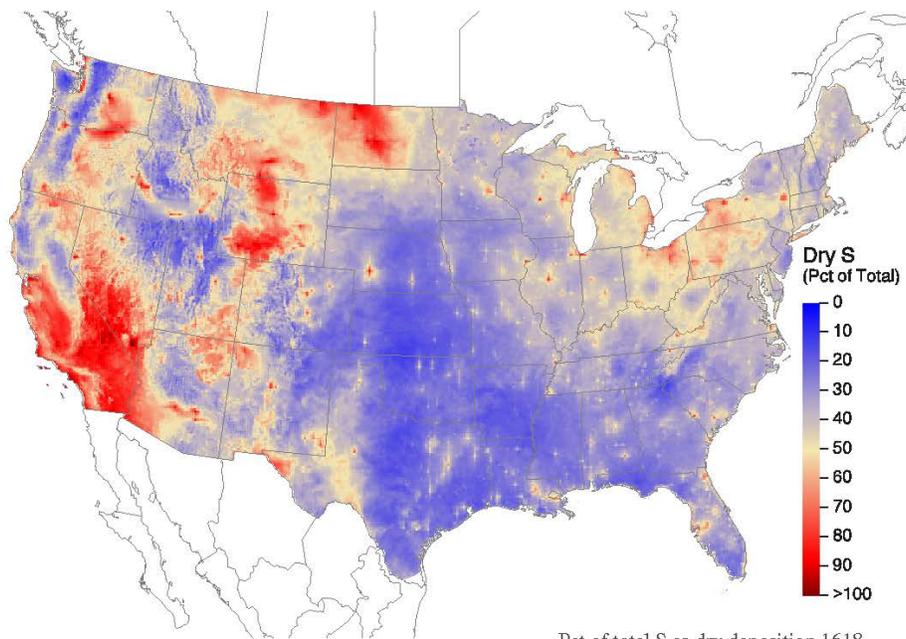
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-72 Dry deposition of total sulfur over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

USEPA 09/12/18



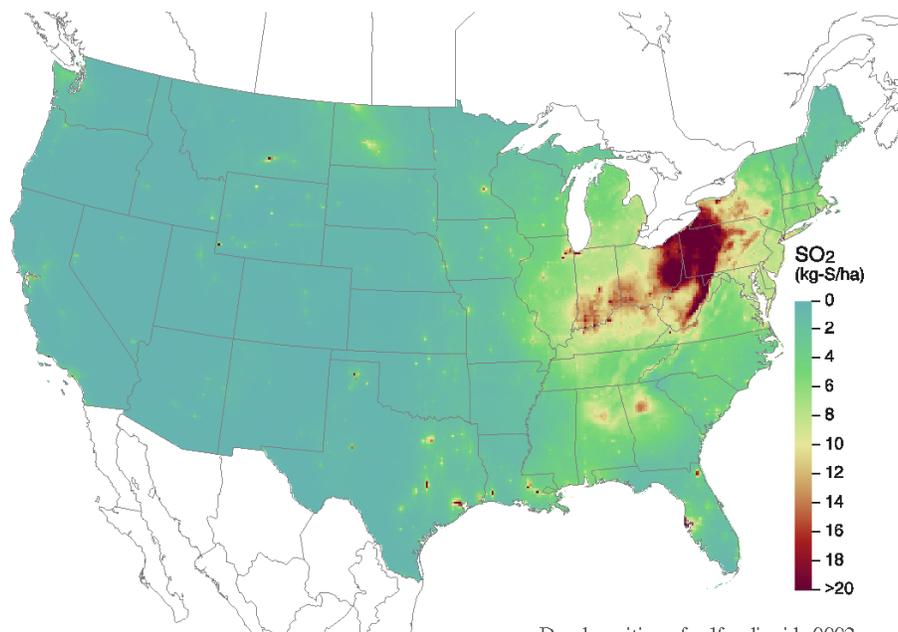
Source: CASTNET/CMAQ/NADP

USEPA 10/21/19

S = sulfur.

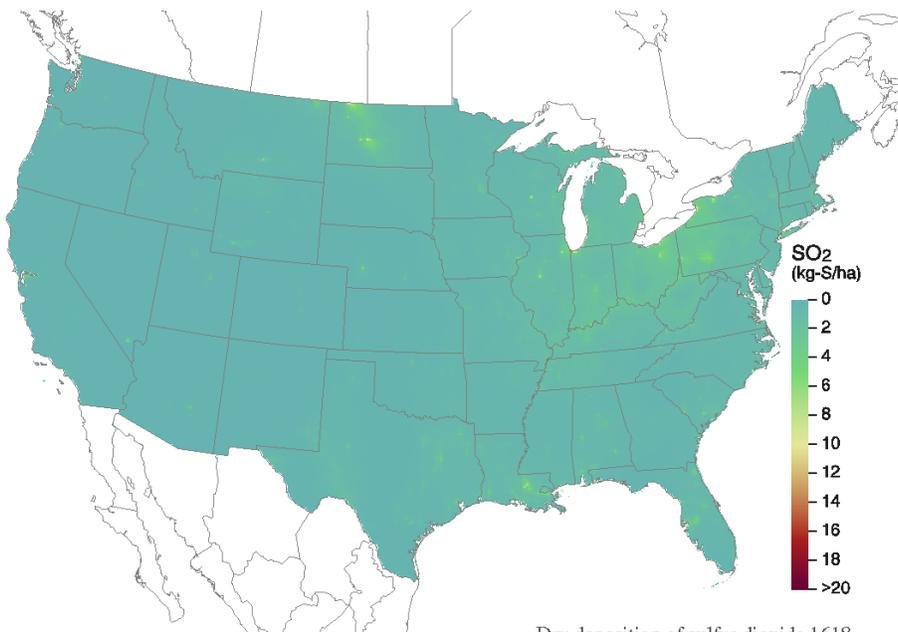
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-73 Percent of total sulfur deposition by dry deposition over 3-year periods. Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry deposition of sulfur dioxide 0002  
USEPA 09/12/18



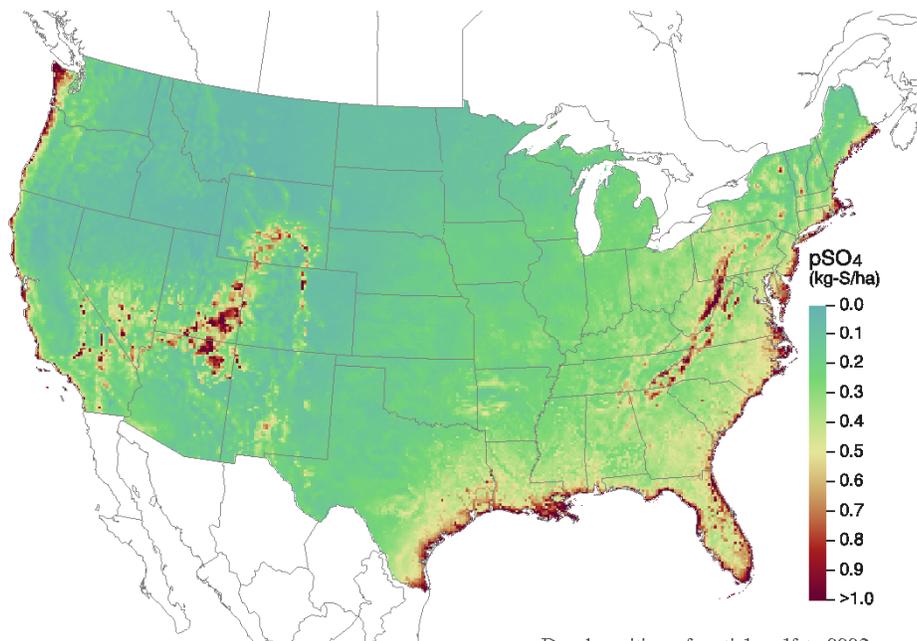
Source: CASTNET/CMAQ/NADP

Dry deposition of sulfur dioxide 1618  
USEPA 10/21/19

SO<sub>2</sub> = sulfur dioxide.

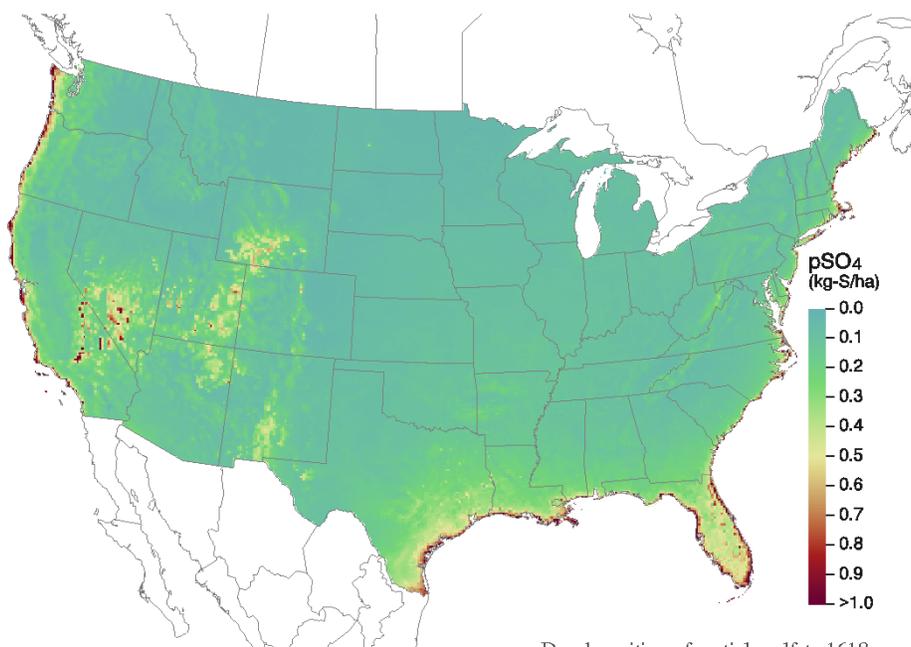
Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-74 Dry deposition of sulfur dioxide over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**



Source: CASTNET/CMAQ/NADP

Dry deposition of particle sulfate 0002  
USEPA 09/12/18



Source: CASTNET/CMAQ/NADP

Dry deposition of particle sulfate 1618  
USEPA 10/21/19

pSO<sub>4</sub> = particulate sulfate.

Source: CASTNET/CMAQ/NTN/AMON/SEARCH. We acknowledge the Total Deposition (TDep) Science Committee of the National Atmospheric Deposition Program (NADP) for their role in making the TDep data and maps available.

**Figure 2-75 Dry deposition of particulate sulfate over 3-year periods.  
Top: 2000–2002; Bottom: 2016–2018.**

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## APPENDIX 3 DIRECT PHYTOTOXIC EFFECTS OF GASEOUS OXIDIZED NITROGEN AND SULFUR ON VEGETATION

This appendix provides a brief overview of the exposure and phytotoxic effects of gaseous forms of oxidized nitrogen (N) and sulfur (S) compounds on vegetation. The main focus of this ISA is understanding the ecological impact of oxidized N and S and that the major effects of these compounds on ecosystems are through acidifying deposition and N enrichment deposition. However, direct effects of gaseous oxidized N and S could augment the effects of deposition on vegetation, and direct effects of gaseous N and S may be apparent in some areas. The effect of sulfur dioxide (SO<sub>2</sub>) gas on vegetation is discussed in [Appendix 3.2](#). [Appendix 3.3](#) discusses the effects of nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and peroxyacetyl nitrate (PAN) on vegetation. [Appendix 3.4](#) presents information on the direct effects of nitric acid (HNO<sub>3</sub>) vapor on vegetation, including lichens. A summary section with causal determinations based on a synthesis of the body of information on the biological effects of exposure to these gases is presented in [Appendix 3.5](#).

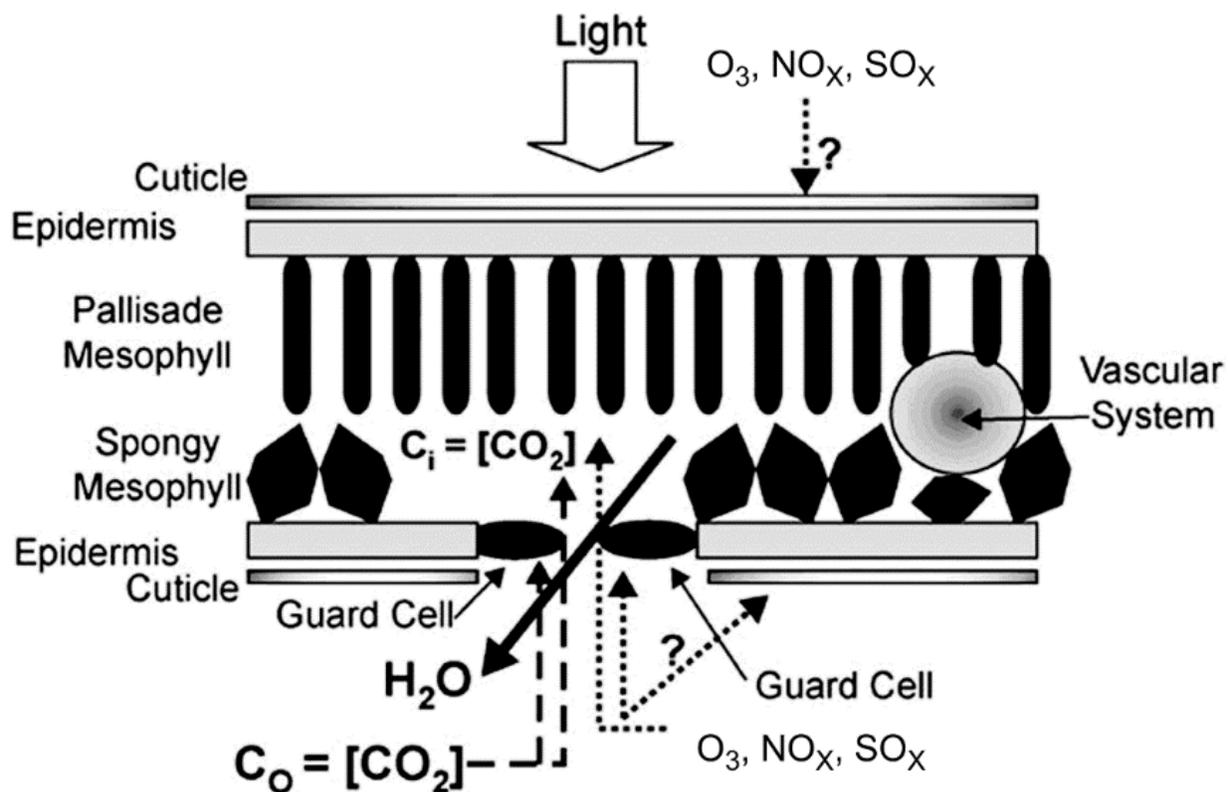
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### 3.1 Introduction

The effects of gaseous pollutants such as SO<sub>2</sub>, NO<sub>2</sub>, NO, HNO<sub>3</sub>, and ozone (O<sub>3</sub>) on vegetation have been studied since at least the early 19th century ([Holmes et al., 1915](#); [Haywood, 1905](#)). Methodologies have been developed to study the effects of gaseous exposures to these pollutants in the laboratory, greenhouse, and in the field. The methodologies to study the effects of gaseous pollutants on vegetation have been recently reviewed in the 2013 Ozone ISA and 2006 Ozone AQCD [Air Quality Criteria Document; [U.S. EPA \(2013c\)](#); [U.S. EPA \(2006a\)](#)]. A thorough description of the methodologies used to expose vegetation to gaseous pollutants can be found in Section 9.2 of the 2013 Ozone ISA ([U.S. EPA, 2013c](#)), AX9.1 of the 2006 Ozone AQCD ([U.S. EPA, 2006a](#)), and Section 9.2 in the 1993 Oxides of Nitrogen AQCD ([U.S. EPA, 1993](#)).

Uptake of gaseous pollutants in a vascular plant canopy is a complex process involving adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants penetrate into leaves primarily in gaseous forms through the stomata. The surface cuticle provides a protective barrier to gaseous pollutant exposure, although there is evidence for limited uptake across the cuticle ([Zhang et al., 2003](#); [Kerstiens et al., 1992](#)). Pollutants must be transported from the bulk air to the leaf boundary layer to reach

the stomata. The transport of pollutants through a boundary layer into the stomatal region is by diffusion. Studies of transport through the boundary layer are based on aerodynamic concepts and usually relate to smooth surfaces that are not typical of leaf-surface morphology ([Gates, 1968](#)). Once through the boundary layer, the gas enters the leaf through the stomata. The entry of gases into a leaf is dependent upon gas-phase chemical processes and physical characteristics of surfaces, including stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as humidity, temperature, light intensity, and water availability. When the stomata are closed, as occurs under dark or drought conditions, resistance to gas uptake is very high and the plant has a very low degree of susceptibility to injury ([Figure 3-1](#)). The stomatal control of uptake of gaseous pollutants is described in more detail in AX9.2 of the 2006 Ozone AQCD ([U.S. EPA, 2006a](#)) and Section 9.3.1.5 of the 1993 Oxides of Nitrogen AQCD ([U.S. EPA, 1993](#)). Note that unlike vascular plants, mosses and lichens do not have a protective cuticle barrier to gaseous pollutants, which is a major reason for their sensitivity to gaseous S and N.



C<sub>i</sub> = internal CO<sub>2</sub> in leaf; C<sub>o</sub> = CO<sub>2</sub> of the atmospheric air; CO<sub>2</sub> = carbon dioxide; H<sub>2</sub>O = water; SO<sub>x</sub> = sulfur oxides; NO<sub>x</sub> = oxides of nitrogen; O<sub>3</sub> = ozone.

Source: U.S. Environmental Protection Agency ([U.S. EPA, 2008a](https://www.epa.gov/2008a)).

**Figure 3-1** The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial) leaf surface. Carbon dioxide, oxides of sulfur, oxides of nitrogen, and ozone gases generally enter by diffusion through the guard cells (or stomata) on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).

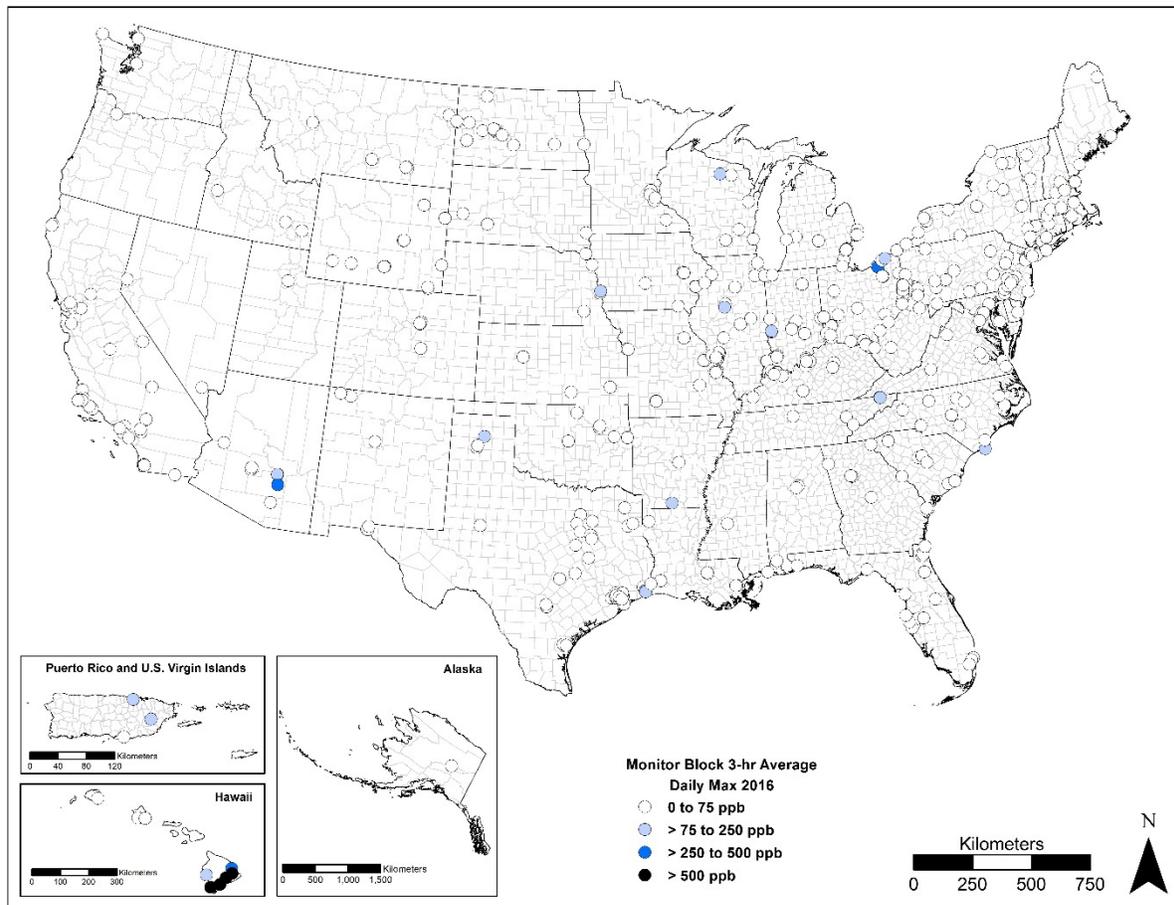
### 3.2 Direct Phytotoxic Effects of Sulfur Dioxide on Vegetation

It has been known since the early 1900s that exposure to SO<sub>2</sub> can cause plant damage and death ([Wislicenus, 1914](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1363144/)). The large sources of historic SO<sub>2</sub> emissions were ore smelters. Sulfides in the ore were oxidized during smelting and resulted in large releases of SO<sub>2</sub>. Emissions from large ore smelters in the U.S. and Canada resulted in large areas denuded of vegetation surrounding these facilities ([Thomas, 1951](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1363144/); [Swain, 1949](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1363144/)). Much of the

damage to the vegetation was due to acute effects of high concentrations of SO<sub>2</sub>. However, as early as 1923, researchers recognized that SO<sub>2</sub> might decrease plant growth without producing acute symptoms of foliar injury ([Stoklasa, 1923](#)). In the 1950s through the early 1980s, there was much research on the effects of SO<sub>2</sub> on vegetation, as well as the interaction with pollutants such as O<sub>3</sub> and NO<sub>2</sub>. Since then, there has been much less research on the effects of SO<sub>2</sub> on vegetation, especially in the U.S., due to the decreasing ambient concentrations of SO<sub>2</sub> [[U.S. EPA \(2012a\)](#); see [Figure 3-2](#) for max 3-hour SO<sub>2</sub> concentrations for 2016]. The effects of SO<sub>2</sub> on vegetation are summarized below.

Currently, SO<sub>2</sub> is the only criteria pollutant with a secondary NAAQS distinct from the primary standard. Other criteria air pollutants produce adverse welfare effects, but the secondary and primary NAAQS have been set to be identical. The SO<sub>2</sub> NAAQS is to protect acute foliar injury resulting from SO<sub>2</sub> exposure. The standard is a 3-hour average of 0.50 ppm and was promulgated in 1971 to protect against the adverse effects of acute foliar injury in vegetation. The 1982 AQCD for Particulate Matter and Sulfur Oxides concluded that controlled experiments and field observations of vegetation supported retaining this secondary standard ([U.S. EPA, 1982b, d, 1971](#)).

Acute foliar injury usually occurs within hours of exposure, involves a rapid absorption of a toxic dose, and involves a collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and is usually a result of variable SO<sub>2</sub> exposures over the growing season. After entering the leaf, SO<sub>2</sub> is converted to sulfite (SO<sub>3</sub><sup>2-</sup>) and bisulfite (HSO<sub>3</sub><sup>-</sup>) ions, which may be oxidized to sulfate (SO<sub>4</sub><sup>2-</sup>). Sulfate is about 30 times less toxic than sulfite and bisulfite. The conversion of sulfite and bisulfite to sulfate results in net H<sup>+</sup> production in the cells. [Kropff \(1991\)](#) proposed that the appearance of SO<sub>2</sub>-induced leaf injury was likely due to a disturbance of intracellular pH regulation. [Kropff \(1991\)](#) listed several studies in which the pH of homogenates of leaf cells only shifted towards greater acidity when plants were lethally damaged from long-term SO<sub>2</sub> exposures ([Jäger and Klein, 1977](#); [Grill, 1971](#); [Thomas et al., 1944](#)). The appearance of foliar injury can vary significantly among species and growth conditions (which affect stomatal conductance). Currently, there is no regular monitoring for SO<sub>2</sub> foliar injury effects in the U.S.



Source: U.S. Environmental Protection Agency 2016 analysis of data from state and local air monitoring stations.

**Figure 3-2** Map of maximum 3-hour daily max average sulfur dioxide concentration reported at Air Quality System monitoring sites for 2016.

Besides foliar injury, long-term lower SO<sub>2</sub> concentrations can result in decreased photosynthesis, growth, and yield of plants. These effects are cumulative over the growing season and are often not associated with visible foliar injury. As with foliar injury, the effects of these injuries vary among species and growing environment. The 1982 Particulate Matter and Oxides of Sulfur (PM-SO<sub>x</sub>) AQCD summarized the concentration-response information available at the time ([U.S. EPA, 1982b](#)). Effects on growth and yield of vegetation were associated with increased SO<sub>2</sub> exposure concentration and time of exposure. However, that document concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Because ambient SO<sub>2</sub> concentrations declined and focus on O<sub>3</sub> vegetation effects research increased, relatively few studies have emerged to better

inform a metric and levels of concern for effects of SO<sub>2</sub> on growth and productivity of vegetation.

SO<sub>2</sub> is considered to be the primary factor causing the death of lichens in many urban and industrial areas, with fruticose lichens being more susceptible to SO<sub>2</sub> than many foliose and crustose species ([Hutchinson et al., 1996](#)). Damage to lichens in response to SO<sub>2</sub> exposure includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K<sup>+</sup> absorption, and structural changes ([Hutchinson et al., 1996](#); [Belnap et al., 1993](#); [Farmer et al., 1992](#)). Significant reductions in lichen photosynthesis have been measured at concentrations as low as 91 ppb over 2–4 hours ([Sanz et al., 1992](#); [Huebert et al., 1985](#)). Damage to the algal component of the thallus is evidenced by its discoloration. The entire thallus dies soon after algal cells are damaged ([Hutchinson et al., 1996](#)). At higher concentrations, SO<sub>2</sub> deactivates enzymes by chemical modification, leading to reduced metabolic activity and loss of membrane integrity ([Nieboer et al., 1976](#); [Ziegler, 1973](#)). In addition, SO<sub>2</sub> binds to the central metal atoms of enzymes, adversely affecting membrane function and cell osmolality. SO<sub>2</sub> also competitively inhibits bicarbonate (HCO<sub>3</sub><sup>-</sup>) and dihydrogen phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) interactions with enzymes ([Hutchinson et al., 1996](#)). Low pH increases the toxicity of SO<sub>2</sub> action ([Farmer et al., 1992](#)). The toxic effects of atmospheric deposition of SO<sub>2</sub> are lessened when lichens are attached to a substrate, typically bark or rock, that has high pH or superior buffering capacity ([Richardson and Cameron, 2004](#)). [van Herk \(2001\)](#) evaluated relationships between bark pH and air pollution levels as two significant variables affecting epiphytic lichen composition and concluded that bark pH was the primary factor regulating the distribution of acidophilic species in the Netherlands. In studies of unpolluted areas, differences in bark chemistry also affect the presence and distribution of epiphytes ([Farmer et al., 1992](#)). Indirect changes to bark pH, caused by acidification and high SO<sub>2</sub> concentrations, also affect lichen distribution ([Farmer et al., 1992](#)). More recently, [Geiser and Neitlich \(2007\)](#) reported that direct SO<sub>2</sub> damage to lichens in the Pacific Northwest may have been confined to major urban areas such as Seattle, Portland, and Bellingham. However, lichen monitoring plots were not colocated with SO<sub>2</sub> monitors and the authors were not able to quantify SO<sub>2</sub> exposure. More information on the N effects reported in this study is found in [Appendix 6.3.7](#) and [Appendix 6.5.2](#).

More recent research has been performed in areas of Europe where ambient SO<sub>2</sub> concentrations are generally higher than in the U.S. Since the 2008 ISA, several studies in Germany and some eastern European countries have indicated that direct effects of SO<sub>2</sub> caused growth reductions in trees during the last century ([Cavlovic et al., 2015](#); [Hauck et al., 2012](#); [Rydval and Wilson, 2012](#); [Elling et al., 2009](#)). [Elling et al. \(2009\)](#) evaluated a large database providing long-term growth records of 1,010 silver firs (*Abies*

*alba*), long-term climate records, and long-term air pollution data from 51 sites in southern Germany. In this analysis, silver fir growth was influenced by SO<sub>2</sub> pollution more than any other factor in the second half of the last century. The study authors also reported an almost immediate increase in growth in response to falling SO<sub>2</sub> emissions in the 1980s. This rapid response indicates a direct effect of gaseous SO<sub>2</sub> rather than an indirect effect of soil acidification, which would have a longer response time. Annual average concentrations above 10 µg SO<sub>2</sub>/m<sup>3</sup> (approximately 4 ppb) appeared to reduce growth of silver fir. (See [Figure 2-15](#) for recent concentrations in the continental U.S.). In a later publication, [Bošela et al. \(2014\)](#) argued a combination of SO<sub>2</sub> and NO<sub>x</sub> gas emissions has historically reduced growth in silver fir in the western Carpathian Mountains of the Czech Republic.

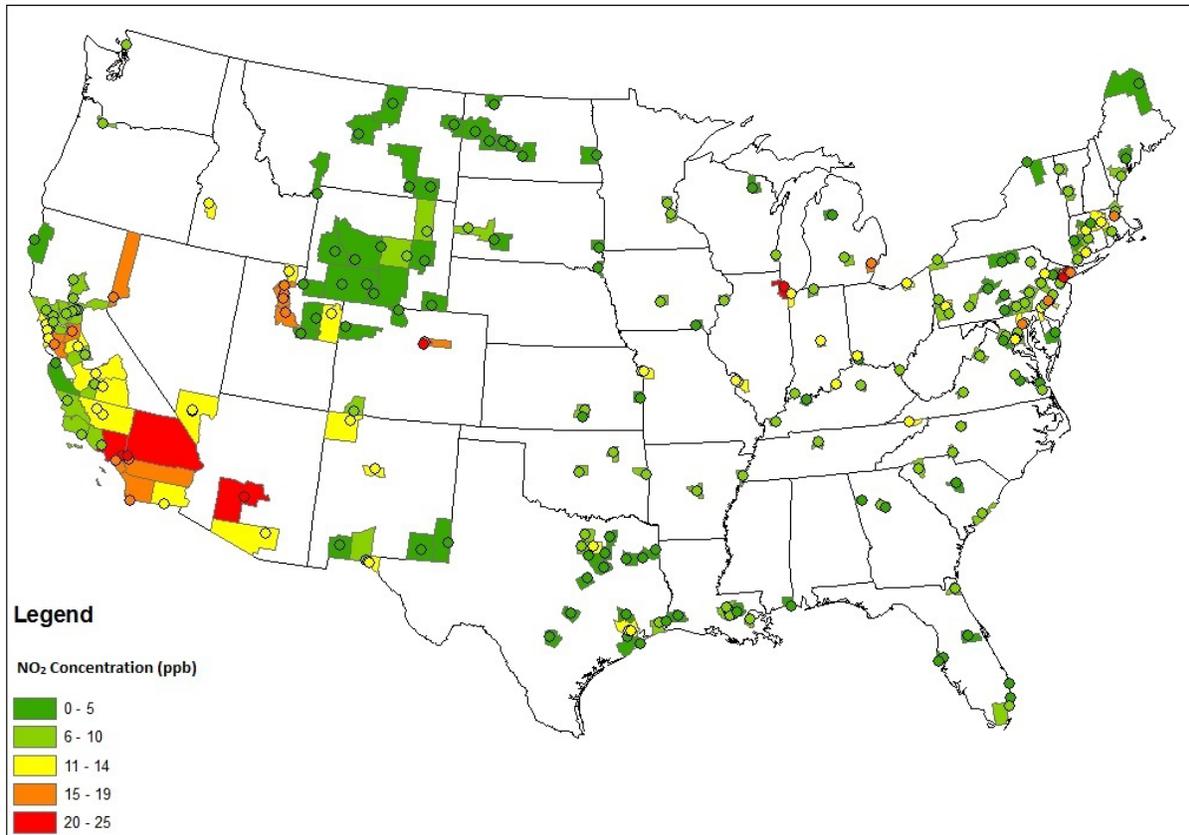
A similar gaseous SO<sub>2</sub> effect on tree growth may have been occurring in the eastern U.S. Using tree ring analysis, [Thomas et al. \(2013\)](#) reported significant growth increases in old-growth eastern red cedar (*Juniperus virginiana*) in West Virginia following decreases in SO<sub>2</sub> emissions since 1980. Growth continued to increase as SO<sub>2</sub> emissions further declined in the 1990s and 2000s. [Thomas et al. \(2013\)](#) also found evidence of physiological changes in response to SO<sub>2</sub> emissions. The authors attributed the growth response to an indirect effect of decreasing acidifying deposition, and thus, recovery from soil acidification. However, a historical record of acidifying deposition was not available. As in Europe, the trees studied in West Virginia also had a relatively rapid recovery in response to declining SO<sub>2</sub> emissions that could indicate the effects were from direct exposure to gases in the atmosphere rather than soil acidification. Further, a response to this study from other researchers suggested that the eastern red cedars in the West Virginia study were found on a limestone outcrop that could be well buffered from soil acidification ([Schaberg et al., 2014](#)). This study may indicate that gaseous SO<sub>2</sub> alone or in combination with other gases may have inhibited red cedar growth. See [Appendix 5.2.1.3](#) for further discussion of this study.

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### **3.3 Direct Phytotoxic Effects of Nitric Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate**

In sufficient concentrations, nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) can have phytotoxic effects on plants by decreasing photosynthesis and inducing visible foliar injury ([U.S. EPA, 1993](#)). The current secondary (welfare) and primary (human health) standard for oxides of nitrogen is a NO<sub>2</sub> annual mean of 0.053 ppm. See [Figure 3-3](#) for recent concentrations of NO<sub>2</sub>. The 1993 Oxides of Nitrogen AQCD concluded that concentrations of NO<sub>2</sub> or NO in the atmosphere are rarely high enough to have phytotoxic effects on vegetation ([U.S. EPA, 1993](#)). Since the 1993 Oxides of Nitrogen

AQCD, very little new research has been done on these phytotoxic effects to alter this conclusion ([Bender and Weigel, 2011](#)). However, it is known that these gases alter the N cycle in some ecosystems, especially in the western U.S., and contribute to N saturation ([Sparks, 2009](#); [Fenn et al., 2003a](#); [Bytnerowicz and Fenn, 1996](#)). See [Appendix 6.1](#) for a discussion of the nutrient effects of N.



NO<sub>2</sub> = nitrogen dioxide.

Note: Concentrations indicated are the highest concentration in the county and do not represent countywide concentrations.

Source: U.S. Environmental Protection Agency 2014 analysis of data from state and local air monitoring stations ([U.S. EPA, 2016f](#)).

**Figure 3-3**      **Map of U.S. annual average nitrogen dioxide concentrations for 2013.**

In general, NO and NO<sub>2</sub> enters leaves through the stomata ([Saxe, 1986](#)). However, the leaf cuticle could be an important receptor for NO<sub>2</sub>, and there is evidence of transport of NO and NO<sub>2</sub> across isolated cuticles ([Lendzian and Kerstiens, 1988](#)). Several studies

have demonstrated that plant canopies can directly assimilate N in the form of  $\text{NO}_2$ , but canopy uptake of  $\text{NO}_2$  is generally small relative to total plant uptake ([Vallano and Sparks, 2008](#); [Ammann et al., 1995](#); [Nussbaum et al., 1993](#); [Segschneider et al., 1993](#); [von Ballmoos et al., 1993](#); [Hanson et al., 1989](#)). After entering the leaves,  $\text{NO}_2$  dissolves in the extracellular water of the substomatal cavity to form  $\text{HNO}_2$  and  $\text{HNO}_3$ , which then dissociate to form  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  ([Bytnerowicz et al., 1998](#)). Both cell and tonoplast membranes contain ATP-dependent  $\text{H}^+$  pumps, and the tonoplast pumps are strongly inhibited by  $\text{NO}_3^-$  ([Bytnerowicz et al., 1998](#)). If extra protons are deposited in vacuoles of the plant cells during normal cellular regulation, then additional acidity will occur in combination with additional  $\text{NO}_3^-$ . This combination can cause disruptions in cellular control ([Taylor and MacLean, 1970](#)).  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) are metabolized to amino acids and proteins through a series of enzymatic reactions mainly involving  $\text{NO}_3^-$  and nitrite reductases ([Amundson and MacLean, 1982](#)). The ability of plants to reduce  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to amino acids and proteins determines the potential of the plant to detoxify NO and  $\text{NO}_2$  ([Wellburn, 1990](#)). Reduction of  $\text{NO}_3^-$  takes place outside of the chloroplast while the reduction of  $\text{NO}_2^-$  is coupled with the light reactions of photosynthesis. Therefore, when leaves are exposed to NO and  $\text{NO}_2$  in the dark, highly phytotoxic levels of  $\text{NO}_2^-$  accumulate and may lead to greater toxicity to NO and  $\text{NO}_2$  at night ([Amundson and MacLean, 1982](#)). Exposure to NO produces both  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in the leaves, but the rate of  $\text{NO}_3^-$  accumulation is much slower than  $\text{NO}_2^-$ . Thus, plants exposed to high NO could be at risk to elevated concentrations of  $\text{NO}_2^-$  ([Wellburn, 1990](#)). More detailed information on the cellular effects of NO and  $\text{NO}_2$  can be found in the 1993 Oxides of Nitrogen AQCD.

The functional relationship between ambient concentrations of NO or  $\text{NO}_2$  and a specific plant response, such as foliar injury or growth, is complex. Factors such as inherent rates of stomatal conductance and detoxification mechanisms and external factors, including plant water status, light, temperature, humidity, and the particular pollutant exposure regime, all affect the amount of a pollutant needed to cause symptoms of foliar injury. Plant age and growing conditions and experimental exposure techniques also vary widely among studies quantifying the response of plants to  $\text{NO}_2$ . An analysis conducted in the 1993 Oxides of Nitrogen AQCD of over 50 peer-reviewed reports on the effects of  $\text{NO}_2$  on foliar injury indicated that plants are relatively resistant to  $\text{NO}_2$ , especially compared to foliar injury caused by exposure to  $\text{O}_3$  ([U.S. EPA, 1993](#)). With few exceptions, visible injury has not been reported at concentrations below 0.20 ppm, and these exceptions occurred when the cumulative duration of exposures extended to 100 hours or longer. At 0.25 ppm, increased leaf abscission was reported on navel orange trees (*Citrus sinensis*), but only after exposures in excess of 1,000 hours ([Thompson et al., 1970](#)). Green bean (*Phaseolus vulgaris*) plants used as bioindicators of  $\text{NO}_2$  injury in Israel developed foliar injury symptoms when ambient concentrations exceeded 0.5 ppm ([Donagi and Goren,](#)

[1979](#)). In most plants, injury occurred in less than 1 day only when concentrations exceeded 1 ppm ([U.S. EPA, 1993](#)). In recent years (2011–2013), ambient hourly NO<sub>2</sub> concentrations in the U.S. have been well below the exposures in the above studies with maximum highest 1-hour daily concentrations less than 0.075 ppm [see Section 2.5.2 of [U.S. EPA \(2016f\)](#)].

Decreased rates of photosynthesis have been recorded in experimental exposures of plants to both NO and NO<sub>2</sub>, but usually at concentrations significantly higher than would normally be encountered in ambient air. For example, [Sabaratnam et al. \(1988\)](#) reported that soybeans (*Glycine max*) exposed 7 hours/day for 5 days showed an increase in photosynthesis at a concentration of 0.2 ppm but a decrease in net photosynthesis at a concentration of 0.5 ppm. Short-term exposures of soybean to 0.6 ppm NO<sub>2</sub> for 2 to 3 hours also had no effect on net photosynthesis ([Carlson, 1983](#)). Most plants appear to be more susceptible to NO than to NO<sub>2</sub>, as shown by [Saxe \(1986\)](#), who exposed a variety of horticultural plants raised in greenhouses (species of *Hedera*, *Ficus*, *Hibiscus*, *Nephrolepis*, and *Dieffenbachia*) to both NO and NO<sub>2</sub>. [Saxe \(1986\)](#) reported that decreases in net photosynthesis occurred at doses of NO that were 22 times less than that for NO<sub>2</sub>. However, these decreases in net photosynthesis required concentrations as high as 1 ppm NO for 12 hours to elicit a response in these plants.

In the 1970s and 1980s, hundreds of studies were conducted on the effects of NO<sub>2</sub> on growth and yield of plants. These studies varied widely in plant species, growing conditions, exposure equipment, concentrations, durations, exposure regimes, and environmental conditions during exposures. No clear dose-response relationships for exposure to NO<sub>2</sub> and reductions in growth and/or yield of plants emerged from these experiments. Readers are referred to the analysis of over 100 studies conducted in the 1993 Oxides of Nitrogen AQCD. A few key studies are highlighted in this section. The growth of several plant species appears to be susceptible to concentrations of NO<sub>2</sub> less than 0.2 ppm, particularly when exposure occurs during low light conditions. For example, nearly continuous exposure to 0.1 ppm NO<sub>2</sub> for 8 weeks significantly reduced growth of Kentucky blue grass [*Poa pratensis*; [Ashenden \(1979\)](#); [Whitmore and Mansfield \(1983\)](#)]. Eight species of tree seedlings were exposed to 0.1 ppm NO<sub>2</sub> for 6 hours/day for 28 days, resulting in reduced shoot or root growth in two species, white ash (*Fraxinus americana*) and sweetgum (*Liquidambar styraciflua*), reduced height growth in two clones of loblolly pine (*Pinus taeda*), and no effects on the other species ([Kress and Skelly, 1982](#)). No effects of NO<sub>2</sub> at 0.1 ppm or lower were observed on numerous other species, including potato (*Solanum tuberosum*), black poplar (*Populus nigra*), radish (*Raphanus sativus*), soybean, or peas [*Pisum sativum*; [U.S. EPA \(1993\)](#)]. No effects of NO<sub>2</sub> were observed on soybeans grown in field plots subjected to a series of 10 episodic exposures averaging 0.4 ppm for 2.5 or 3 hours ([Irving et al., 1982](#)).

Numerous studies have reported negative effects on growth of a variety of plants exposed to 0.5 ppm NO<sub>2</sub> and above ([U.S. EPA, 1993](#)), but these concentrations are very high relative to current ambient levels of NO<sub>2</sub> (see [Appendix 2.6.1](#)).

The 1993 Oxides of Nitrogen AQCD reviewed the extensive literature on the effects of NO<sub>2</sub> in combination with other gaseous air pollutants, particularly SO<sub>2</sub> and O<sub>3</sub>, and concluded that combinations of pollutants can cause foliar injury or decreases in photosynthesis at concentrations lower than those associated with NO<sub>2</sub> acting alone. However, the plant responses occur at concentrations much higher than typically found in ambient air in the U.S. ([U.S. EPA, 1993](#)). In addition, the presence of NO<sub>2</sub> in studies combining other gases did not produce symptoms different from those caused by the dominant pollutant, either SO<sub>2</sub> or O<sub>3</sub>, such that a plant response produced by combinations of NO<sub>2</sub> with other air pollutants in the field would be difficult, if not impossible, to distinguish from those of the other single pollutants ([U.S. EPA, 1993](#)).

Since the 1993 Oxides of Nitrogen AQCD was completed, most new research on NO<sub>2</sub> exposure to vegetation has taken place in Europe and other areas outside the U.S. For example, foliar NO<sub>3</sub> reductase activity was increased in Norway spruce (*Picea abies*) growing near a highway in Switzerland with average exposures of about 0.027 ppm compared to trees growing 1,300 m away from the highway with NO<sub>2</sub> exposures less than 0.005 ppm ([Ammann et al., 1995](#)). This result was consistent with other studies on Norway spruce in the field and laboratory ([von Ballmoos et al., 1993](#); [Thoene et al., 1991](#)). [Muller et al. \(1996\)](#) found that the uptake rate of NO<sub>3</sub><sup>-</sup> by roots of Norway spruce seedlings was decreased by exposure to 0.1 ppm of NO<sub>2</sub> for 48 hours. Similarly, soybean plants grown in Australia had decreased NO<sub>3</sub> uptake by roots and reduced growth of plants exposed to 1.1 ppm of NO<sub>2</sub> for 7 days ([Qiao and Murray, 1998](#)). In a Swiss study, poplar (*Populus × euramericana*) cuttings exposed to 0.1 ppm of NO<sub>2</sub> for approximately 12 weeks resulted in decreased stomatal density and increased specific leaf weight, but did not result in other effects such as leaf injury or a change in growth ([Günthardtgoerg et al., 1996](#)). However, NO<sub>2</sub> enhanced negative effects of ozone on poplars, including leaf injury, when the pollutants were applied in combination ([Günthardtgoerg et al., 1996](#)).

Since the 2008 ISA for Oxides of Nitrogen and Oxides of Sulfur-Ecological Criteria [hereafter referred to as the 2008 ISA ([U.S. EPA, 2008a](#))], very few studies have been published on the direct effects of NO and NO<sub>2</sub> on vegetation. [Hu et al. \(2015b\)](#) exposed clonal hybrid poplar (*Populus alba × Populus berolinensis*) saplings to 4 ppm of NO<sub>2</sub>. The authors reported significant declines in photosynthesis and dark respiration with exposures of 48 hours. They also reported stomatal dysfunction at this level of exposure resulting in partial stomatal closure and a decline in stomatal conductance. However, 4 ppm of NO<sub>2</sub> is very high relative to current ambient levels of NO<sub>2</sub> in the U.S. (see

[Appendix 2.6.1](#)). These results are consistent with past studies of plants with relatively high NO<sub>2</sub> exposure.

As part of a broad study of N deposition of a native serpentine grassland in California, [Vallano et al. \(2012\)](#) exposed five native grasses and forbs (*Plantago erecta*, *Layia gaillardoides*, *Lasthenia californica*, *Vulpia microstachys*, and *Cryptantha flaccida*) and the most common invasive grass *Lolium multiflorum* to NO<sub>2</sub> and soil N addition. The plants were exposed in a growth chamber to very low levels of NO<sub>2</sub> (0.03 ppm) to simulate recent ambient air concentrations for this ecosystem. At this relatively low NO<sub>2</sub> exposure, no significant effects were found on shoot biomass, root biomass, photosynthesis, or stomatal conductance. The authors reported that despite not finding species responses to NO<sub>2</sub> exposure, the additive effects of NO<sub>2</sub> combined with soil N on plant performance indicate that uptake of NO<sub>2</sub> may play a role in species responses to increasing N deposition. The authors found that the combined NO<sub>2</sub> and N addition resulted in a strong positive growth and competitive response in the invasive *Lolium*. This result is consistent with previous findings that low levels of NO<sub>2</sub> that are not phytotoxic to plants can add to the N load to an ecosystem from uptake through leaves ([Sparks, 2009](#)).

In a study in the Grand Canyon National Park, AZ, [Kenkel et al. \(2016\)](#) found that NO<sub>x</sub> concentrations measured by Ogawa passive samplers were about 52% higher along roadsides than 30 m away from the road. The pattern of the amount of <sup>15</sup>N in pinyon pine (*Pinus edulis*) mirrored the concentration gradient of NO<sub>x</sub> concentrations from the road, indicating that the vegetation is taking up N from the vehicle traffic in the park. The authors reported that sustained chronic N deposition on this arid environment could result in deleterious effects for these ecosystems.

Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant that often co-occurs with O<sub>3</sub> during high photochemical episodes and that has been shown to cause injury to vegetation [see reviews by [Cape \(2003\)](#), [Kleindienst \(1994\)](#), and [Temple and Taylor \(1983\)](#)]. Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species include spinach, Swiss chard, lettuces, and tomatoes ([Temple and Taylor, 1983](#)). Petunias (*Petunia hybrida*) have also been characterized as sensitive to PAN exposures and have been used as bioindicators in areas of Japan ([Nouchi et al., 1984](#)). Controlled experiments have also shown significant negative effects on the net photosynthesis and growth of petunias and kidney beans (*Phaseolus vulgaris*) after exposure of 30 ppb of PAN for 4 hours on each of 3 alternate days ([Cape, 2003](#); [Izuta et al., 1993](#)). As mentioned previously, it is known that oxides of N, including PAN, could be altering the N cycle in some ecosystems, especially in the western U.S.,

and contributing to N saturation ([Fenn et al., 2003a](#); [Bytnerowicz and Fenn, 1996](#)). Although PAN continues to persist as an important component of photochemical pollutant episodes, there is little evidence in recent years to suggest that PAN poses a significant risk to vegetation in the U.S.

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### 3.4 Direct Phytotoxic Effects of Nitric Acid

Relatively little is known about the direct effects of HNO<sub>3</sub> vapor on vegetation. Recent information on HNO<sub>3</sub> concentrations are given in [Appendix 2.6.3](#). The deposition velocity of HNO<sub>3</sub> is very high compared to other pollutants (see [Table 2-2](#)) and HNO<sub>3</sub> may be an important source of N for plants ([Hanson and Garten, 1992](#); [Hanson and Lindberg, 1991](#); [Vose and Swank, 1990](#)). This deposition could contribute to N saturation of some ecosystems close to sources of photochemical smog ([Fenn et al., 1998](#)). For example, in mixed conifer forests of the Los Angeles basin mountain ranges, HNO<sub>3</sub> has been estimated to provide 60% of all dry deposited N ([Bytnerowicz et al., 1998](#)). Since the 2008 ISA, a controlled exposure study ([Padgett et al., 2009a](#)) reported that 10 to 60% of the HNO<sub>3</sub> retained by foliage was incorporated into the biologically active N pool. The remainder of the HNO<sub>3</sub> was bound to foliar surfaces. This new study provides further evidence for HNO<sub>3</sub> as a contributor of biologically available N to southern California forests.

[Norby et al. \(1989\)](#) reported that exposure of 75 ppb of HNO<sub>3</sub> for 1 day increased nitrate reductase activity in red spruce (*Picea rubens*) foliage. In another study, foliar nitrate reductase activity was also increased in California black oak (*Quercus kelloggii*), canyon live oak (*Quercus chrysolepis*), and ponderosa pine (*Pinus ponderosa*) seedlings with exposure to 65 to 80 ppb of HNO<sub>3</sub> for 24 hours ([Krywult and Bytnerowicz, 1997](#)). Because the induction of nitrate reductase activity is a step in a process leading to the formation of organic N compounds (amino acids), the nitrate from HNO<sub>3</sub> could function as an alternative source of N for vegetation ([Calanni et al., 1999](#)). However, in plants under stress, the reduction of nitrate to amino acids consumes energy needed for other metabolic processes.

At high ambient concentrations, HNO<sub>3</sub> can cause vegetation damage. Seedlings of ponderosa pine and California black oak subjected to short-term exposures from 50–250 ppb of HNO<sub>3</sub> vapor for 12 hours showed deterioration of pine needle cuticle at 50 ppb in light ([Bytnerowicz et al., 1998](#)). Oak leaves, however, appeared to be more resistant to HNO<sub>3</sub> vapor, with 12-hour exposures in the dark at 200 ppb producing damage to the epicuticular wax structure ([Bytnerowicz et al., 1998](#)). The observed changes in wax chemistry caused by HNO<sub>3</sub> and accompanying injury to the leaf cuticle

([Bytnerowicz et al., 1998](#)) may predispose plants to various environmental stresses such as drought, pathogens, and other air pollutants. Because elevated concentrations of HNO<sub>3</sub> and ozone co-occur in photochemical smog ([Solomon et al., 1988](#)), synergistic interactions between the two pollutants are possible ([Bytnerowicz et al., 1998](#)). Note, however, that the experiments described above were observed at relatively short-term exposures at above ambient concentrations of HNO<sub>3</sub>. Studies of long-term effects of lower air concentrations that more closely approximate ambient HNO<sub>3</sub> are needed.

Since the 2008 ISA, [Padgett et al. \(2009b\)](#) investigated dry deposition of HNO<sub>3</sub> on the foliage of ponderosa pine, white fir (*Abies concolor*), California black oak, and canyon live oak in southern California. Using a chamber system within a greenhouse, leaves and needles were exposed to control (0 µg/m<sup>3</sup> HNO<sub>3</sub>), moderate (30 to 60 µg/m<sup>3</sup> peak HNO<sub>3</sub>), and high (95 to 160 µg/m<sup>3</sup> peak HNO<sub>3</sub>) concentrations. The high concentrations represented a high ambient concentration that occurs periodically in California. The experimental exposures resulted in a suite of damage symptoms that intensified with increasing exposure. The exposures caused substantial perturbations to the epicuticular surfaces of foliage of all four tree species studied. The damage caused by dry deposition may leave foliage more vulnerable to other copollutants such as ozone.

It has been suspected that HNO<sub>3</sub> may have caused a dramatic decline in lichen species in the Los Angeles basin ([Nash and Sigal, 1999](#)). The suggestion was strengthened by transplant of *Ramalina* lichen species from clean air habitats (Mount Palomar and San Nicolas Island) to analogous polluted habitats in the Los Angeles basin and observing death of the lichens over a few weeks in the summer ([Boonpragob and Nash, 1991](#)). Associated with this death was a massive accumulation of H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the lichen thalli ([Boonpragob et al., 1989](#)). [Riddell et al. \(2008\)](#) exposed healthy *R. menziesii* thalli to moderate (8–10 ppb) and high (10–14 ppb) HNO<sub>3</sub> in month-long fumigations and reported a significant decline in chlorophyll content and carbon exchange capacity compared to thalli in control chambers. Thalli treated with HNO<sub>3</sub> showed visual signs of bleaching and by Day 28 were clearly damaged and dead. The damage may have occurred through several mechanisms, including acidification of pigments and cell membrane damage ([Riddell et al., 2008](#)). The authors concluded that *R. menziesii* has an unequivocally negative response to HNO<sub>3</sub> concentrations common to ambient summer conditions in the Los Angeles air basin. They believed it was very likely that HNO<sub>3</sub> contributed to the disappearance of this sensitive lichen species from the Los Angeles air basin, as well as other locations with arid conditions with high HNO<sub>3</sub> deposition loads ([Riddell et al., 2008](#)).

Since the 2008 ISA, there have been more studies published on HNO<sub>3</sub> effects on lichen in the Los Angeles basin. [Riddell et al. \(2012\)](#) studied six lichen species with differing

morphology and physiology that were collected near the Los Angeles basin. All were found to be sensitive to HNO<sub>3</sub> exposures (daily peak levels near 50 ppb) in controlled chambers. Measurements of effects included decreased chlorophyll content and chlorophyll fluorescence, decreased photosynthesis and respiration, and increased electrolyte leakage. The species showed differential sensitivity to the HNO<sub>3</sub> exposures ([Riddell et al., 2012](#)). In the same study, lichens were not reported to be sensitive to ozone exposure. This study adds to evidence that the main agent of decline of lichen in the Los Angeles basin is HNO<sub>3</sub> exposure.

In another study, [Riddell et al. \(2011\)](#) resampled 18 plots from a 1976–1977 study in the Los Angeles basin. The 1976–1977 study ([Sigal and Nash, 1983](#)) had documented an air pollution-related 50% decline of lichens described and collected in the same region in the early 1900s ([Hasse, 1913](#)). In the 2008 resampling, [Riddell et al. \(2011\)](#) found community shifts, declines in the most pollutant-sensitive lichen species, and increases in abundance of nitrogen-tolerant lichen species compared to 1976–1977. The authors also reported that these lichen communities have not recovered from the damaged state of the late 1970s, and the 2008 survey data suggest that lichen communities are further degrading. This recent observational field study further supports the evidence air pollutants such as HNO<sub>3</sub> may be causing declines in lichens in the Los Angeles basin.

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### 3.5 Direct Phytotoxic Effects of Reduced Nitrogen Gases

Ammonia gas (NH<sub>3</sub>) can have direct phytotoxic effects. [Section 2.6.4](#) discusses recent concentrations of NH<sub>3</sub> in the U.S. The literature on effects of NH<sub>3</sub> exposure to vegetation is limited in the U.S., where fumigation studies using NH<sub>3</sub> are particularly lacking. Reduced N gases such as ammonia are not criteria air pollutants or oxides of N and therefore are not the focus of this review of the gas-phase effects. However, there are similar phytotoxic effects to oxides of N, and NH<sub>3</sub> can be a source of N nutrient effects. This section briefly covers these ammonia effects.

As with other gases, NH<sub>3</sub> is taken up through the leaf stomata in higher plants. The uptake increases as ambient air concentrations rise. In higher plants, NH<sub>3</sub> dissolves into the mesophyll and becomes toxic if the rate of uptake exceeds the ability of a plant to detoxify and assimilate NH<sub>3</sub>. This can depend on the N content of the plant, species of plant, and age of leaf ([Krupa, 2003](#)). Direct visible damage to foliage has been reported at relatively high concentrations of NH<sub>3</sub> [annual averages of about 110 ppb; 77 µg/m<sup>3</sup>; [Bytnerowicz et al. \(1998\)](#); [Van der Eerden \(1982\)](#)]. Historically, field studies on phytotoxic effects of NH<sub>3</sub> have generally been performed in Europe in close proximity to livestock farms and manure storage facilities ([Van der Eerden, 1982](#)). Because of the

rapid deposition and transformation of NH<sub>3</sub>, effects have been generally found close to sources.

Ammonia exposure can also directly affect bryophytes and lichens. These nonstomatal plants have acidic surfaces that facilitate the deposition of NH<sub>3</sub>. Several European studies have reported effects on lichen and bryophytes and have found them to be more sensitive to NH<sub>3</sub> than higher plants ([Cape et al., 2009](#)). Often less tolerant lichens disappear and are replaced by more tolerant species.

In a recent study, [Sheppard et al. \(2011\)](#) reported the effects of ammonia on vegetation in a Whim peat bog in Scotland that included stomatal and nonstomatal plants. A free air release system created a gradient of ammonia from 70 kg NH<sub>3</sub>/ha/yr down to 3–4 kg NH<sub>3</sub>/ha/yr. Three years exposure to 20–56 kg NH<sub>3</sub>/ha/yr led to large declines in species cover of *Calluna vulgaris* (a flowering shrub), *Sphagnum capillifolium* (a bryophyte), and *Cladonia portentosa* (a lichen). The authors reported that the effects were due to direct uptake by the foliage and interactions with other stresses. Whim peat bogs do not occur in the U.S. (see [Appendix 11](#) for more discussion of peat bogs), but this study may provide information about potential effects of NH<sub>3</sub> in other areas relevant to U.S. ecosystems. Studies at this site ([Sheppard et al., 2009](#); [Sheppard et al., 2008](#)) and other European studies ([Wolseley et al., 2006](#)) have been referenced as evidence for changing the European critical level to protect bryophytes, lichens, and herbaceous plants ([Cape et al., 2009](#)).

Besides being potentially phytotoxic to vegetation, NH<sub>3</sub> exposure can lead to more N inputs into plants and ecosystems through foliage uptake. In general, N content of leaves increases with NH<sub>3</sub> exposure ([Krupa, 2003](#)). Ammonia deposition that leads to N enrichment is an important consideration when evaluating total N deposition. These N nutrient effects to vegetation are discussed in [Appendix 6](#).

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## 3.6 Summary

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### 3.6.1 Sulfur Dioxide

The current secondary standard for SO<sub>2</sub> is a 3-hour average of 0.50 ppm, which is designed to protect against acute foliar injury in vegetation. There has been limited research on acute foliar injury since the 1982 PM-SO<sub>x</sub> AQCD, and there is no clear evidence of acute foliar injury below the level of the current standard. The limited

research since 2008 adds more evidence on acute effects of SO<sub>2</sub> on vegetation but does not change conclusions from the 2008 ISA on the levels producing the effects.

Effects on growth and yield of vegetation are associated with increased SO<sub>2</sub> exposure concentration and time of exposure. The 1982 PM-SO<sub>x</sub> AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Very few studies have been reported on the effects of SO<sub>2</sub> on growth of U.S. vegetation since the 1982 PM-SO<sub>x</sub> AQCD. Recent studies from eastern Europe indicate recovery of tree growth correlated to falling SO<sub>2</sub> concentrations since the 1980s. [Elling et al. \(2009\)](#) reported that annual SO<sub>2</sub> concentrations of 4 ppb appeared to reduce silver fir (*Abies alba*) growth. There may be similar effects of SO<sub>2</sub> emissions on trees in West Virginia ([Thomas et al., 2013](#)), but more research is needed to further investigate the mechanisms of the apparent recovery of tree growth to link this phenomenon with declines in ambient SO<sub>2</sub> that have occurred since the 1980s.

Limited new evidence from 2008 to the present continue to support the causal findings of the 2008 ISA. As a whole, **the body of evidence is sufficient to infer a causal relationship between gas-phase SO<sub>2</sub> and injury to vegetation.**

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### 3.6.2 Nitrogen Oxide, Nitrogen Dioxide, and Peroxyacetyl Nitrate

It is well known that in sufficient concentrations, NO, NO<sub>2</sub>, and PAN can have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury ([U.S. EPA, 1993](#)). However, the 1993 Oxides of Nitrogen AQCD concluded that concentrations of NO, NO<sub>2</sub>, and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation ([U.S. EPA, 1993](#)). Since the 1993 Oxides of Nitrogen AQCD, very little new research has been performed on these phytotoxic effects at concentrations currently observed in the U.S.

Since the 2008 ISA ([U.S. EPA, 2008a](#)), very few studies have been published on the direct effects of NO, NO<sub>2</sub>, and PAN on vegetation; thus, **the body of evidence is sufficient to infer a causal relationship between gas-phase NO, NO<sub>2</sub>, and PAN and injury to vegetation.**

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### 3.6.3 Nitric Acid

The 2008 ISA reported experimental exposure of HNO<sub>3</sub> resulted in damage to the leaf cuticle of pine and oak seedlings, which could predispose those plants to other stressors such as drought, pathogens, and other air pollutants ([U.S. EPA, 2008a](#)). Since the 2008

ISA, [Padgett et al. \(2009b\)](#) investigated dry deposition of HNO<sub>3</sub> on the foliage, with findings that supported the earlier research. The 2008 ISA also reported several lines of evidence in lichen studies, including transplant and controlled exposure studies, indicating that past and current HNO<sub>3</sub> concentrations contributed to the decline in lichen species in the Los Angeles basin ([U.S. EPA, 2008a](#)). Since the 2008 ISA, there have been more exposure and field survey studies published on the effects of HNO<sub>3</sub> on lichen in the Los Angeles basin ([Riddell et al., 2012](#); [Riddell et al., 2011](#)). These new studies continue to support the causal findings of the 2008 ISA. As a whole, **the body of evidence is sufficient to infer a causal relationship between gas-phase HNO<sub>3</sub> and changes to vegetation.**

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## APPENDIX 4 SOIL BIOGEOCHEMISTRY

This appendix characterizes how nitrogen (N) and sulfur (S) deposition contribute to total loading of N and S in the soils of nonagricultural terrestrial ecosystems ([Appendix 4.2](#)) and how this loading causes soil acidification and eutrophication by altering soil chemical pools and processes ([Appendix 4.3](#)). Additional topics are discussed, including soil monitoring and databases ([Appendix 4.4](#)), soil biogeochemistry models ([Appendix 4.5](#)), national-scale soil sensitivity to N and S deposition ([Appendix 4.6](#)), climate modification of soil response to N ([Appendix 4.7](#)), and a summary ([Appendix 4.8](#)). The effects of altered soil biogeochemistry on terrestrial biota due to soil acidification and eutrophication are discussed in [Appendix 5](#) and [Appendix 6](#), respectively. Soil biogeochemistry that has been altered by N may also be linked to aquatic biogeochemistry, which is discussed in [Appendix 7](#).

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### 4.1 Introduction

The *2008 ISA for Oxides of Nitrogen and Oxides of Sulfur—Ecological Criteria* (hereafter referred to as the 2008 ISA) documented that the main effects of N and S deposition on terrestrial soils were N enrichment and acidification. Since the 2008 ISA, there is new evidence on how deposition contributes to total N and S loading in terrestrial ecosystems, as well as the effects of deposition on soil chemical pools and processes. This evidence is from addition, gradient, and time-series studies. Many of the new studies focus on the effects of N deposition, with relatively little work focusing on S deposition. There are improved models to evaluate ecosystem responses to deposition, most of which are applicable at watershed scales. Some may be applied regionally. Soil N enrichment and soil acidification occur in sensitive ecosystems across the U.S. at recent levels of deposition. Decreasing emissions of S have led to early signs of recovery from soil acidification in some northeastern watersheds; however, areas in the Southeast do not show any appreciable recovery of soils. There are no signs of recovery of N enrichment effects in soils. Critical load (CL) determinations for soils have been made at the ecoregion scale for  $\text{NO}_3^-$  leaching and some soil acidification indicators. **The body of evidence is sufficient to infer a causal relationship between N and S deposition and alteration of soil biogeochemistry in terrestrial ecosystems**, which is consistent with the conclusions of the 2008 ISA.

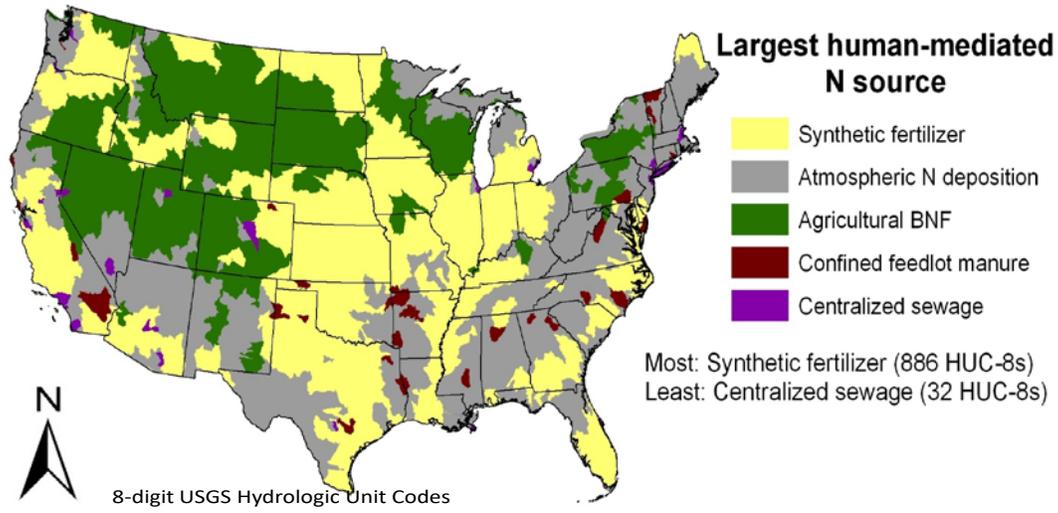
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## 4.2 Nitrogen and Sulfur Sources to Soil

The 2008 ISA documented that atmospheric deposition is the main source of anthropogenic N to nonagricultural and nonurban terrestrial ecosystems and headwater streams. In 2008 it was well known that the global pool of reactive N ( $N_r$ ) had increased over the previous century, largely due to three main causes: (1) widespread cultivation of legumes, rice, and other crops that support bacteria capable of converting diatomic nitrogen gas ( $N_2$ ) to organic N through biological N fixation; (2) fossil fuel combustion converting atmospheric  $N_2$  and fossil N to total oxidized N ( $NO_Y$ ); and (3) the Haber-Bosch process, which converts nonreactive  $N_2$  to  $N_r$  for N fertilizer production and some industrial activities ([Galloway et al., 2003](#); [Galloway and Cowling, 2002](#)). Food production was known to account for much of the conversion of  $N_2$  to  $N_r$ . N was shown to be geographically redistributed through food shipment to meet human needs and often returned to the environment via wastewater.  $N_r$  was known to accumulate in the environment on local, regional, and global scales ([Galloway et al., 2003](#); [Galloway and Cowling, 2002](#); [Galloway, 1998](#)) in the atmosphere, soil, and water ([Galloway and Cowling, 2002](#)), with a multitude of effects on humans and ecosystems ([Townsend et al., 2003](#); [Rabalais, 2002](#); [van Egmond et al., 2002](#); [Galloway, 1998](#)). The term the “N cascade” was coined to refer to the sequence of transfers, transformations, and environmental effects ([Galloway et al., 2003](#); [Galloway and Cowling, 2002](#)).

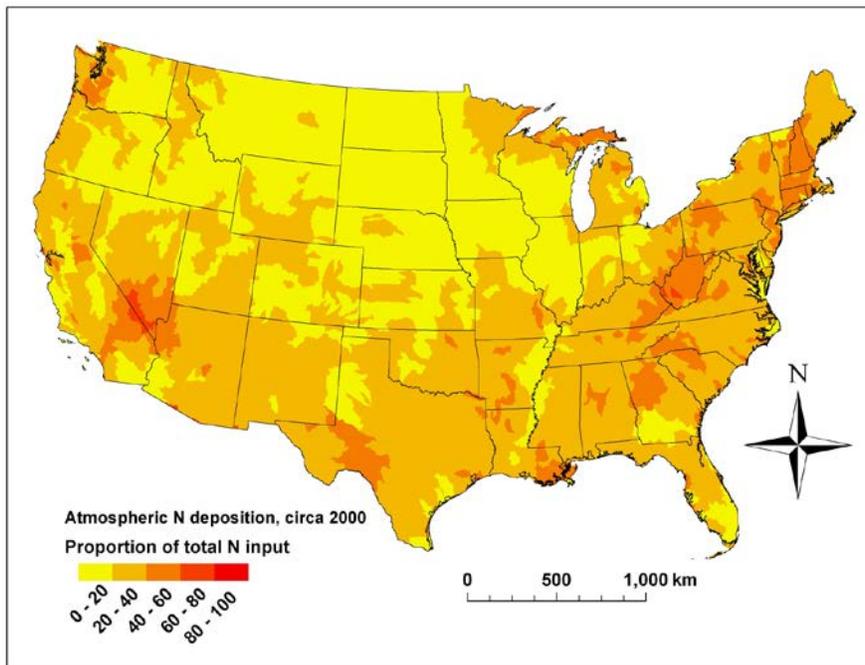
Since 2008, a number of estimates have been made of the relative contribution of sulfate, oxidized N, and reduced N from atmospheric deposition. The most recent estimates are summarized in [Appendix 2](#). Maps showing the geographic distribution of deposition are presented for total acidifying (N + S) deposition ([Figure 2-12](#)), total N deposition ([Figure 2-13](#)), and total S deposition ([Figure 2-31](#)). Maps depicting how the relative contribution of oxidized and reduced N species varies across the U.S. are presented in [Figure 2-14](#).

Several new studies have been published since the 2008 ISA on the source of N inputs to ecosystems; however, no new studies on S sources to ecosystems have been identified. [Sobota et al. \(2013\)](#) quantified sources and fluxes of reactive N inputs to U.S. lands and waterways and found human-mediated N inputs are spatially heterogeneous across the country, ranging up to 34.6-fold the background N input across all of the 8-digit hydrologic unit codes (HUC-8s). Across the contiguous U.S. (CONUS), synthetic N fertilizer and atmospheric N deposition are the largest and second-largest overall human-mediated N inputs to ecosystems, and the single largest sources in 41 and 33% of HUC-8s, respectively ([Figure 4-1](#) and [Figure 4-2](#)).



BNF = biological nitrogen fixation; HUC-8 = 8-digit hydrologic unit code; N = nitrogen; USGS = U.S. Geological Survey.  
Source: Map presented in [Sobota et al. \(2013\)](#).

**Figure 4-1** Dominant sources of nitrogen across the U.S. at 8-digit hydrologic unit codes.



N = nitrogen.  
Source: Modified from data presented in [Sobota et al. \(2013\)](#).

**Figure 4-2** Percentage of nitrogen input from nitrogen deposition at 8-digit hydrologic unit codes.

At the global scale, [Fowler et al. \(2013\)](#) estimated the relative contributions of five sources of N that contribute to emissions and deposition, all of which are predicted to change through the end of this century. Two new studies, both in the western U.S., have confirmed that N from the weathering of sedimentary and metasedimentary rock can be a source of N to some ecosystems ([Montross et al., 2013](#); [Morford et al., 2011](#)), although [Sobota et al. \(2013\)](#) suggested that anthropogenic sources of N are more significant at the landscape scale.

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### 4.3 Soil Pools and Processes

Eutrophication and acidification are two biogeochemical processes that can occur in response to the inputs of N and S deposition. These processes can alter the biogeochemistry in terrestrial ecosystems, and they may occur either in sequence or simultaneously in a given geographic area. N driven eutrophication is typically indicated by N accumulation (e.g., increased soil N concentrations or decreased C:N ratios). These indicators of N accumulation are directly linked to biological effects in the soil, including changes in microbial-mediated decomposition and nitrification. N added to terrestrial ecosystems can also be lost through leaching from the soil, typically as nitrate ( $\text{NO}_3^-$ ), or through emissions to the atmosphere, primarily via denitrification ([Galloway et al., 2003](#); [Galloway and Cowling, 2002](#)). Denitrification is a microbial process that reduces  $\text{NO}_3^-$  to either unreactive  $\text{N}_2$  gas, nitrogen oxide (NO), or the potent greenhouse gas nitrous oxide ( $\text{N}_2\text{O}$ ). S addition to an ecosystem typically causes S accumulation and variable amounts of leaching from the soil, which in turn leads to acidification because demand for S as a nutrient is low compared to human-caused soil stores of organic and inorganic S.

Soil acidification results from the accumulation of hydrogen ions ( $\text{H}^+$ ). This occurs naturally through the production of carbonic acid and organic acids, as well as through plant cation uptake ([Charles and Christie, 1991](#); [Turner et al., 1991](#)). The rate of soil acidification can increase as a result of soil acidification caused by the deposition of the inorganic acids  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . In addition,  $\text{NH}_x$  deposition contributes to soil acidification by stimulating nitrifying bacteria that derive energy by oxidizing the  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . A byproduct of nitrification is the production of a  $\text{H}^+$  ion, but whether there is a net effect on soil acidity depends upon the fate of the  $\text{NO}_3^-$ . If the  $\text{NO}_3^-$  is leached with a base cation, then the  $\text{H}^+$  is left behind and the soil become more acidic. If, however, the  $\text{NO}_3^-$  is denitrified, then the  $\text{H}^+$  from nitrification is neutralized by  $\text{OH}^-$  generated by denitrification. Likewise, if  $\text{NO}_3^-$  is taken up by a plant root, the root will exude an  $\text{OH}^-$  in exchange.

Decreases in soil pH attributable to acid deposition have been documented throughout the U.S. ([Sullivan et al., 2006b](#); [Bailey et al., 2005](#); [Johnson et al., 1994b](#); [Johnson et al., 1994a](#)). Inorganic and organic acids can be neutralized by soil weathering or base cation exchange, in addition to denitrification. However, because soils vary in their capacity to neutralize incoming acidity, the effects of acidification have been heterogeneous across the U.S. In addition, pollutant loadings vary across the U.S. The primary chemical effects of acidification in soils that have biological effects include the loss of important base cation nutrients such as Ca and Mg, as well as the mobilization of aluminum (Al) cations of varied speciation, several of which are toxic to many organisms. The quantities of precipitation and runoff are important determinants of base cation leaching and acidification ([Van Breemen et al., 1984](#)). The accelerated loss of base cations through leaching, decrease in base saturation, and decreased in soil solution Ca:Al ratio all serve as indicators of soil acidification.

Studies published since the 2008 ISA augment our knowledge of previously identified effects of N addition on soils. The following sections document the empirical evidence of N effects on multiple pools, processes, and indicators associated with the general effects of N enrichment and eutrophication ([Table 4-1](#)). These sections summarize the empirical effects of N and S addition on soil biogeochemistry, often based on results from addition or gradient studies. The publications summarized here present information on multiple processes and indicators; therefore, individual papers are often discussed in more than one section.

**Table 4-1 Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N-Driven Nutrient Enrichment	Acidification	Appendix of ISA that Discusses Each Endpoint
<b>PROCESS</b>			
N saturation	X	X	<a href="#">4.3.2</a>
Soil N accumulation	X	X	<a href="#">4.3.2</a>
NO <sub>3</sub> <sup>-</sup> leaching	X	X	<a href="#">4.3.2</a>
S accumulation and adsorption		X	<a href="#">4.3.3</a>
SO <sub>4</sub> <sup>2-</sup> leaching		X	<a href="#">4.3.3</a>
Base cation release/depletion		X	<a href="#">4.3.4</a>
Al mobilization		X	<a href="#">4.3.5</a>
Nitrification	X	X	<a href="#">4.3.6</a>
Denitrification	X		<a href="#">4.3.6</a>
Decomposition/mineralization	X	X	<a href="#">4.3.7</a> and <a href="#">4.3.8</a>
DOC leaching	X	X	<a href="#">4.3.9</a>
<b>INDICATOR</b>			
Soil [N]	X	X	<a href="#">4.3.2</a>
Soil C:N ratio	X	X	<a href="#">4.3.6</a> and <a href="#">4.3.7</a>
Soil base saturation		X	<a href="#">4.3.4</a>
Soil Bc:Al ratio		X	<a href="#">4.3.5</a>
Fungi:bacteria ratio	X		<a href="#">4.3.11</a>

Al = aluminum; Bc = base cation; C = carbon; DOC = dissolved organic carbon; ISA = Integrated Science Assessment; N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate.

### 4.3.1 Nitrogen Pathways and Pools

The 2008 ISA documented that N is stored primarily in the soil in forest ecosystems, and soil N often exceeds 85% of the total ecosystem N ([Cole and Rapp, 1981](#); [Bormann et al.,](#)

1977). Experimental  $^{15}\text{N}$  addition studies showed that trees typically take up only a small fraction of added  $^{15}\text{N}$ ; most is retained in the soil N pool (Providoli et al., 2005; Templer et al., 2005; Nadelhoffer et al., 1999a; Tietema et al., 1998). However, these experiments were criticized for applying  $^{15}\text{N}$  directly to the soil surface, thereby precluding direct canopy uptake of N from wet or dry deposition and limiting inference for N deposition effects (Sievering et al., 2000; Sievering, 1999). Forest canopies take up an average of 16% of total atmospheric N input (Lovett, 1992), but this uptake could be considerably higher (up to 90%) in some N limited forests with large epiphyte loads (Klopatek et al., 2006). It is unclear how much of the N from deposition retained by vegetation was used in photosynthetic enzymes and would thus contribute to increased productivity (Bauer et al., 2004).

Most soil N is contained in organic matter, typically bound in organo-mineral complexes or large-molecular-weight organic compounds (Schmidt et al., 2011; Schimel and Bennett, 2004). These pools of N are not directly available for uptake by plants or microbes, and the relative immobility of these compounds means they contribute little to the leaching loss of N into ground or surface waters. To enter the actively cycling portion of the ecosystem N pool, recalcitrant organic N must be converted into inorganic forms (e.g.,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) or small-molecular-weight organic compounds (e.g., amino acids, amino sugars), typically through the activity of extracellular enzymes produced by soil microorganisms. The size of this N pool often controls net primary productivity (NPP; see Appendix 6), but plants compete with microorganisms for available N.

Since 2008 there is new research using  $^{15}\text{N}$  to trace pathways and pools in ecosystems (Table 4-2), including a new paper confirming the previous conclusion that ecosystem N is primarily stored in forest mineral soil (Perakis et al., 2011). There is also new evidence that litter is the largest sink for added N in grasslands, shrublands, and wetlands (Templer et al., 2012).

New studies have also been conducted tracing pathways of N in ecosystems through time. In Swiss grasslands, N addition increased ecosystem N storage in plant biomass, both in living plant biomass as well as litter, but did not affect soil N (Bassin et al., 2015). In a temperate forest ecosystem in Switzerland, application of  $^{15}\text{N}$  tracer in a solution to simulate wet deposition showed increased dissolved organic N and enrichment of soil microbes and plant roots within the first day. When plots were resampled a year later, litter and soil pools, particularly soil organic matter, were enriched with the N tracer (Morier et al., 2008). These results confirm that deposited N is incorporated rapidly into ecosystem pools and is stored primarily in litter and recalcitrant organic matter in the soil.

**Table 4-2 Pathways and pools.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
Mineralization	Semiarid	Southern California	Up to 35–45 for N	Two applications per yr of 30 kg N	N fertilizer additions resulted in faster gross N cycling rates. Greater net release or greater net immobilization of N was observed at different sampling times and likely related to seasonality of C availability.	<a href="#">Sirulnik et al. (2007b)</a>
N pools	Temperate hardwood forest	Swiss Prealps	16		The litter layer retained approximately 19–28% of the <sup>15</sup> N tracer after 1 day. The authors concluded that the processes relevant for the fate of atmospherically deposited N take place rapidly and that N recycling within the microbe-plant-soil organic matter system prevents further losses in the long term.	<a href="#">Morier et al. (2008)</a>
N turnover times	Semiarid grassland	Not specified	Not specified	5 as NH <sub>4</sub> NO <sub>3</sub>	Model for N cycling was developed using observations of <sup>15</sup> N. The temporal dynamics of <sup>15</sup> N fractions (labeled-N fractions) in plant and microbial biomass are closely tied to the turnover time of these N pools	<a href="#">Dijkstra (2009)</a>
N pathway		Höglwald, Bavaria, Germany	45		After two to three decades of high loads of N deposition, a new equilibrium was reached, characterized by substantial losses of N to the groundwater (approximately 20 kg NO <sub>3</sub> <sup>-</sup> ) and to the atmosphere (16 kg N in form of N <sub>2</sub> O, NO, and N <sub>2</sub> ). Ecosystem N retention is dominated by microbial immobilization, which was about a factor of three higher than plant N uptake.	<a href="#">Kreutzer et al. (2009)</a>
N pathway	Simulated northern hardwood forest	Michigan, Great Lakes region	7 to 12	30	Tracing <sup>15</sup> NO <sub>3</sub> <sup>-</sup> revealed that N accumulated in soil organic matter by first flowing through soil microorganisms and plants, and that the shedding of <sup>15</sup> N-labeled leaf litter enriched soil organic matter.	<a href="#">Zak et al. (2008)</a>

**Table 4-2 (Continued): Pathways and pools.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
N pools	Temperate forest	Oregon coast range	2.0	None	Mineral soil accounted for 96–98% of total ecosystem N. Soil water $^{15}\text{NO}_3^-$ patterns suggested a shift in relative N losses from denitrification to $\text{NO}_3^-$ leaching as N accumulated, and simulations identified $\text{NO}_3^-$ leaching as the primary N loss pathway that constrains maximum N accumulation.	<a href="#">Perakis et al. (2011)</a>
N pools	Soil $^{15}\text{N}$	Global	Varied across 48 studies	Varied across 48 studies	A meta-analysis of studies at 48 sites across four continents shows the largest sinks for $^{15}\text{N}$ tracers among ecosystem types were organic soil in forests (35.5%, n = 31) and foliage in tundra (12.1%, n = 3). Litter was the largest sink in grasslands (25.5%, n = 9), shrublands (33.8%, n = 6), and wetlands (34.1%, n = 2).	<a href="#">Templer et al. (2012)</a>
N pools	Common garden experiment, five broadleaved tree species	Denmark	13 to 19 for broadleaf forest 18 to 26 for Norway Spruce		Tree species influenced N cycling and $^{15}\text{N}$ patterns through multiple species-specific traits. The type of mycorrhiza association, light regime, and ground vegetation differed between ash and sycamore and beech, lime, oak, and Norway spruce.	<a href="#">Callesen et al. (2013)</a>
Pools and pathway N uptake	Subalpine (seminatural) pasture	Alp Flix, a high plateau near Sur, Grosons, Switzerland	4	0, 5, 10, 25, and 50 as $\text{NH}_4\text{NO}_3$	Plant N pools increased by 30–40% after N addition, while soil pools remained unaffected.	<a href="#">Bassin et al. (2015)</a>
N cycling	All	Global	Not specified	None	Synthesis of recent literature that did not include new quantitative analysis.	<a href="#">Niu et al. (2016)</a>

**Table 4-2 (Continued): Pathways and pools.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
Throughfall NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , and SO <sub>4</sub> <sup>2-</sup> Base cations Dry N deposition	<i>Quercus ilex</i> forests ranging from Mediterranean climate to a drier, more seasonal climate		Not specified	None	Rainfall and net NH <sub>4</sub> <sup>+</sup> throughfall were negatively correlated at all sites. Rainfall and net NO <sub>3</sub> <sup>-</sup> -N throughfall correlation varied between negative and positive. Rainfall and net SO <sub>4</sub> <sup>2-</sup> throughfall were positively correlated at wet sites and negatively correlated at the drier site.	<a href="#">Aguillaume et al. (2017)</a>
Canopy throughfall	Holm oak forests ( <i>Quercus ilex</i> L.) in the north, center, and north-east of the Iberian Peninsula	Europe-Iberian Peninsula	Wet deposition ranged between 1.2 to 5.8, and dry deposition ranged from 1.5 to 14		Canopies retained ranged between 0.5 and 12 ka/ha/yr. Both NH <sub>4</sub> <sup>+</sup> and NO <sub>3</sub> <sup>-</sup> showed higher retention at the agricultural and rural sites (50–60%) than at sites located close to big cities (20–35%).	<a href="#">Avila et al. (2017)</a>

<sup>15</sup>N = Nitrogen-15; N = nitrogen; NO = nitric oxide; N<sub>2</sub>O = nitrous oxide; NO<sub>2</sub> = nitrogen dioxide; NO<sub>3</sub><sup>-</sup> = nitrate; <sup>15</sup>NO<sub>3</sub><sup>-</sup> = Nitrogen-15-labeled nitrate; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; yr = year.

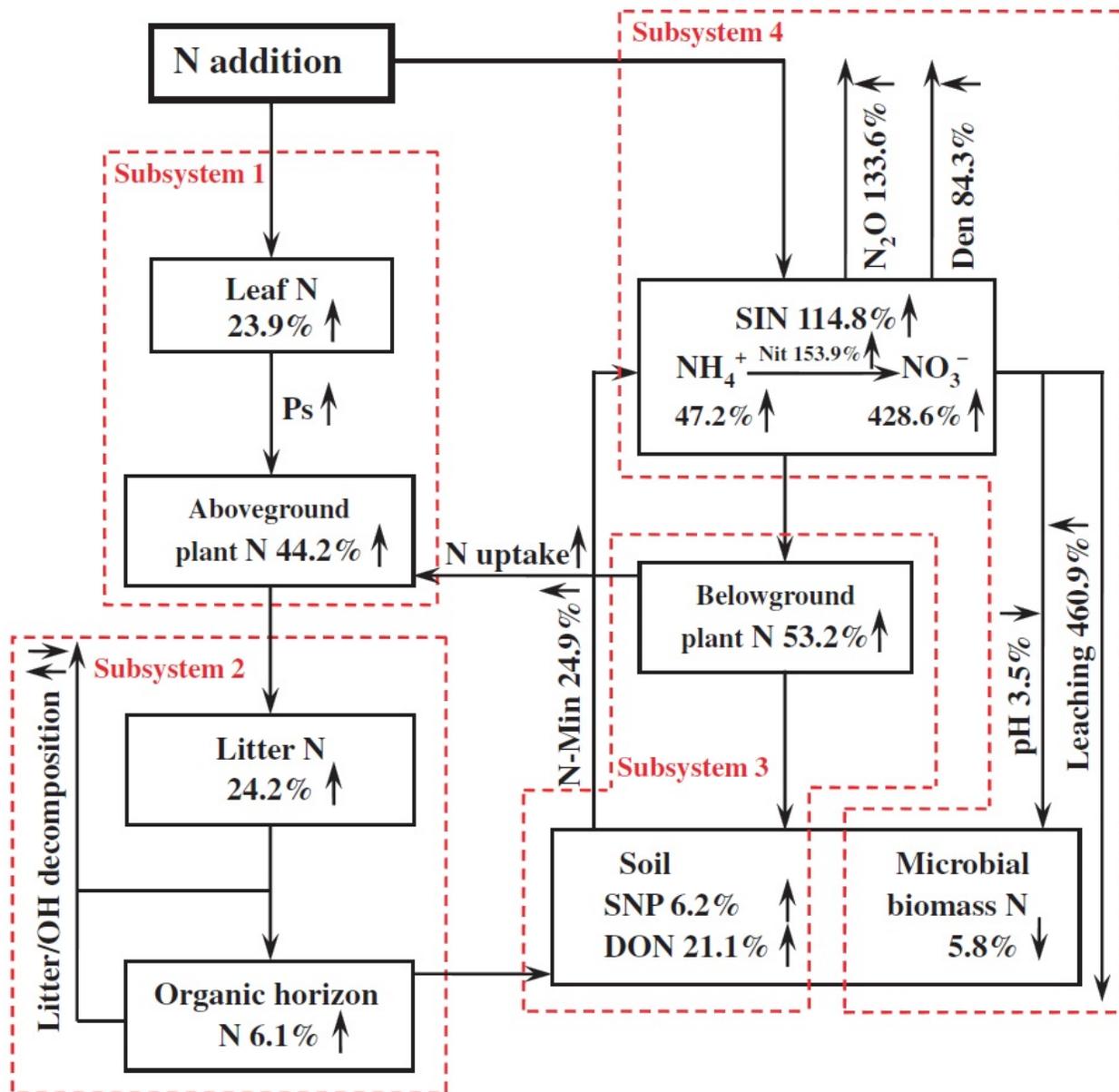
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### 4.3.2 Nitrogen Accumulation, Saturation, and Leaching

In the 2008 ISA, a documented indicator of terrestrial N driven eutrophication was the accumulation of N in soil. Atmospherically deposited N can accumulate in soil as inorganic N or by incorporating N into organic matter. The ability of atmospheric N pollution to cause an accumulation of N in soil is indicated by a positive correlation between the atmospheric deposition rate and total N concentration in the Oa horizon observed at sites in New York, Vermont, New Hampshire, and Maine ([Driscoll et al., 2001b](#)). Accumulation of soil N as a result of N deposition has been either documented or suggested to occur across large areas of the U.S. ([Aber et al., 2003](#)) including semiarid ecosystems ([Padgett et al., 1999](#)). There is also evidence for soil N accumulation from mass-balance studies of experimental N additions ([Campbell et al., 2004b](#)). Further evidence that atmospheric deposition increased the availability of N in soil is provided by the strong negative correlation between atmospheric N deposition and the C:N ratio of the Oa soil horizon across the northeastern U.S. ([Aber et al., 2003](#)). Soil N accumulation is linked to increased N leaching.

New studies ([Table 4-3](#)) confirm that, across terrestrial ecosystem types, N addition increases soil N concentrations. In semiarid shrublands in southern California, [Vourlitis and Fernandez \(2012\)](#) observed that N additions increased soil N. [Lu et al. \(2011a\)](#) conducted a meta-analysis of N cycle responses to N additions using data from 206 peer-reviewed studies. They observed mean increases in N leaching, soil inorganic N, soil total N pool, as well as increases in the litter N, organic horizon N, and mineral soil N; the only pool that decreased was microbial N ([Figure 4-3](#)).

Thresholds of N deposition associated with the onset of elevated  $\text{NO}_3^-$  leaching have been previously identified. Atmospheric deposition of 8 to 10 kg N/ha/yr resulted in the onset of  $\text{NO}_3^-$  leaching to surface waters throughout the eastern U.S. Slightly lower N deposition levels (5–10 kg N/ha/yr) led to  $\text{NO}_3^-$  leaching in the Rocky Mountains, and this was attributable to colder temperatures, shorter growing season, slow soil development, extensive exposed bedrock, and rapid melting of large snowpacks ([Williams and Tonnessen, 2000](#); [Williams et al., 1996c](#); [Baron et al., 1994](#)). Lastly, deposition loads of 17 kg N/ha/yr led to the onset of  $\text{NO}_3^-$  leaching in the Sierra Nevada and San Bernardino mountains ([Fenn et al., 2008](#)).



Den = denitrification; DON = dissolved organic N; N = nitrogen; N-min = net N mineralization; Nit = nitrification; Ps = photosynthesis; SIN = soil inorganic N; SNP = soil N pool.

Source: [Lu et al. \(2011a\)](#).

**Figure 4-3** A conceptual framework for the responses of the ecosystem nitrogen (N) cycle to nitrogen (N) addition.

The 2008 ISA documented that N saturation occurred when the input of N to the terrestrial ecosystem chronically exceeded the uptake capacity of the soils and biota, causing a large fraction of the incoming N to leach from soils to surface waters ([Stoddard, 1994](#); [Aber et al., 1989](#)). N saturation had been observed or suggested to occur across large areas of the U.S. ([Adams et al., 2000](#); [Aber et al., 1998](#); [Adams et al., 1997](#); [Peterjohn et al., 1996](#); [Cook et al., 1994](#); [Edwards and Helvey, 1991](#); [Aber et al., 1989](#)).

New evidence ([Table 4-3](#)) from an N tracer study confirms that N retention varies across ecosystem types and is highest in shrublands (89.5%) and wetlands (84.8%), followed by forests (74.9%), and grasslands [51.8%; [Templer et al. \(2012\)](#)]. Other significant factors affecting long-term  $^{15}\text{N}$  recovery (a proxy for N retention in N tracer studies) were mycorrhizal association (ericoid > ecto > arbuscular), plant growth form, and site history (less retention on former agricultural sites). The influence of biotic processes on N retention is evident at smaller scales. Among nine forested sites along an urban-to-rural landscape gradient in the Boston, MA area, throughfall inorganic N deposition increased with proximity to the urban core, with inorganic N deposition rates positively correlated with rates of soil inorganic N leaching across the sites ([Rao et al., 2014](#)). Measurements of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  in soil  $\text{NO}_3^-$  leachate indicated no clear relationship between microbial nitrification and proximity to the urban core—evidence that factors other than N availability influenced N processing. Overall, it is clear from recent research that N retention is strongly influenced by biotic factors (e.g., mycorrhizae, plant growth form) and environmental conditions (e.g., precipitation).

Leaching of N tends to increase with increasing N addition. Where  $^{15}\text{N}$  tracer studies were conducted as part of N addition experiments, the N additions decreased  $^{15}\text{N}$  retention. In  $^{15}\text{N}$  studies with multiple N addition treatments, a negative correlation between retention and the rate of N additions was observed ([Templer et al., 2012](#)). In Europe, [Dise et al. \(2009\)](#) documented approximately 95% of forests receiving less than 8 kg N/ha/yr still had leaching, typically less than 1 kg N/ha/yr. Additional work on monitoring data in Sweden by [Khalili et al. \(2010\)](#) showed a clear sudden increase in  $\text{NO}_3^-$  leaching in regions where N deposition exceeded 7.5 kg/ha/yr ([Appendix 4.4](#)). In the U.S. there are new studies modeling N leaching in eastern U.S. forests [[Phelan et al. \(2016\)](#); [Fakhraei et al. \(2016\)](#); [Table 4-3](#)].

N leaching is an indicator of ecosystem N saturation. New studies ([Table 4-3](#)) suggest the N saturation concept ([Aber et al., 1998](#)) may need revision in response to observations of N cycling in temperate forests ([Lovett and Goodale, 2011](#)) and chaparral ([Homyak et al., 2014](#)). [Lovett and Goodale \(2011\)](#) proposed a new model of N saturation that distinguished capacity N saturation, in which the vegetation and soil sinks for N have been filled, from kinetic N saturation, in which the plant and soil sinks are accumulating

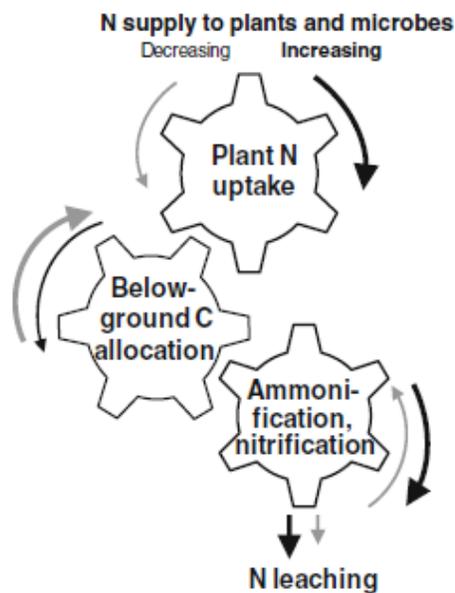
N, but the rate of N accumulation is slower than the N input rate. One implication of this new model is that  $\text{NO}_3^-$  leaching can occur even if the ecosystem N retention capacity has not yet been saturated, as is observed at many sites [e.g., [Lovett and Goodale \(2011\)](#); [Talhelm et al. \(2012\)](#); [Homyak et al., 2014](#)]. New information confirms the applicability of the capacity N saturation concept in northwest forests ([Perakis and Sinkhorn, 2011](#)), although the new idea of kinetic N saturation is particularly useful in describing N cycling processes in California chaparral ([Homyak et al., 2014](#)). At chaparral sites, N added during the dry season is lost from the ecosystem, while N added during the growing season is retained in plant biomass ([Vourlitis and Pasquini, 2009](#); [Grulke et al., 2005](#)). In these systems, water scarcity limits plant productivity, microbial C availability, and denitrification, all of which cause  $\text{NO}_3^-$  to be flushed from surface soils during large precipitation events ([Menon et al., 2010](#)). Large leaching losses of N in arid ecosystems are evidence for kinetic saturation.

New research highlights the importance of deposition of N from mobile sources along roadsides ([Fenn et al., 2018](#); [Bettez et al., 2013](#)). The higher deposition along roadsides in Cape Cod, MA was associated with a two- to fourfold greater rate of nitrate leaching from the soils. Approximately 15% less N from deposition was retained 10 m from the road than sites more distant removed from the road. N deposition contribution to N in the watershed may be underestimated by 13–25% when roadside deposition and the associated leaching are not included. In a U.S. nationwide evaluation of on road emissions of ammonia, [Fenn et al. \(2018\)](#) found  $\text{NH}_4^+:\text{NO}_3^-$  ratios in urban deposition reflected elevated  $\text{NH}_3$  from emissions, and that on-road  $\text{NH}_3$  emissions exceeded agricultural emissions in locations where 40% of the population resides.

New research highlights the role of the microbial community in N saturation. [Kopáček et al. \(2013\)](#) developed a conceptual model in which N saturation is associated with shifts in the microbial community, namely a decrease in the fungi-to-bacteria ratio, and a transition from N to C limitation. In N enriched systems, three mechanisms could lead to lower amounts of bioavailable dissolved organic C (DOC) for the microbial community and to C limitation: (1) lower plant allocation of nutrients to roots in response to increased nutrient availability, leading to a decrease in plant exudates; (2) chemical suppression of DOC solubility by soil acidification; and (3) enhanced bacterial mineralization of DOC due to increased abundance of electron acceptors in the form of  $\text{NO}_3^-$  in anoxic soil. In support of this model, recent studies indicate that N retention in semiarid shrublands is driven more by spatial and temporal variations in labile C availability than exceedance of N storage capacity ([Vourlitis and Fernandez, 2015](#)). Furthermore, [Högberg et al. \(2013\)](#) found that forest soils with low concentrations of  $\text{NO}_3^-$  and Al had a higher fungi:bacteria ratio compared with stands having higher concentrations of  $\text{NO}_3^-$  and Al (negative correlation,  $r = -0.857$ ). Fungi:bacteria ratio,

and a second indicator, stem growth, explained 70% of the variation in N and Al leaching (see broader discussion of N effects on microbial community composition in [Appendix 6](#)).

[Högberg et al. \(2013\)](#) proposed a hypothetical model to account for the effects of N supply on plant N uptake and belowground C allocation, microbial production of inorganic N, and N leaching ([Figure 4-4](#)). Shifts in N mineralization, nitrification, and leaching from forests might occur in response to N loading as a result of decreasing tree allocation of C to belowground roots, and ultimately, to ectomycorrhizal fungi and other C limited soil microbes. When N supply increases, ectomycorrhizal fungi and other rhizosphere microbes become progressively more C limited, and their abundance and activity decline. Microbial assimilation of N diminishes, and N mineralization increases, whereas the fungi:bacteria ratio decreases. Increasing  $\text{NH}_4^+$  levels and decreasing organic C supply stimulate leaching, and denitrification. Increasing N loading can alter plant C allocation, causing shifts in microbial activity and community composition that in turn increase  $\text{NO}_3^-$  leaching from the ecosystem ([Figure 4-4](#)).



C = carbon; N = nitrogen.

Thick arrows indicate an increasing rate whereas thin arrows mean decreasing rate. Nitrogen supply increases are indicated by black arrows.

Source: [Högberg et al. \(2013\)](#).

**Figure 4-4** A hypothetical model to account for the effects of nitrogen supply on plant nitrogen uptake and belowground carbon allocation, microbial production of inorganic nitrogen, and nitrogen leaching.

**Table 4-3 Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
N leaching	Forest	248 sites (plot and catchment scale) from 15 countries in Europe	Varied	Not reported	<b>Gradient:</b> The most consistent indicators of N leaching were throughfall N deposition, organic horizon C:N ratio, and mean annual temperature. Sites receiving low levels of N deposition (8 kg N/ha/yr) showed very low output fluxes of N. In general, the models successfully predicted N leaching (mean of $\pm 5$ kg N/ha/yr between observed and predicted) from forests at early to intermediate stages of N saturation but not from N saturated sites.	<a href="#">Dise et al. (2009)</a>
N accumulation N leaching	Mesic desert	Spanish Spring Valley, NV	Not specified	None	<b>Field experiment:</b> Concluded that vadose soil resources (water and organic C) are rare. Unused $\text{NO}_3^-$ from low biological demand is transported and accumulated in the deeper vadose zone with occasional deep leaching events.	<a href="#">Menon et al. (2010)</a>
N saturation	Oak forest	Southeastern New York State	9	100 $\text{NH}_4\text{NO}_3$ (1996–1999) 50 $\text{NH}_4\text{NO}_3$ (2000–2006)	<b>Conceptual model:</b> New N saturation model based on an N addition study of an oak forest in southeastern New York State.	<a href="#">Lovett and Goodale (2011)</a>
N accumulation	Meta-analysis		Varied	Varied	<b>Meta-analysis:</b> N cycle responses to N additions using data from 206 peer-reviewed studies and observed a mean increase in N soil pools except microbial biomass N ( <a href="#">Figure 4-12</a> ).	<a href="#">Lu et al. (2011a)</a>

**Table 4-3 (Continued): Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
N saturation N accumulation N mineralization nitrification	Douglas fir forest	Oregon coast range	2.0	None	<b>Gradient:</b> This is a test of the N saturation theory along a natural N gradient. Higher N content of surface (0–10 cm) soil was linearly related to higher net N mineralization. Lower pH was related to lower nitrification. The ratio of net to gross N mineralization to higher nitrification increased along the gradient, indicating progressive saturation of microbial N demand.	<a href="#">Perakis and Sinkhorn (2011)</a>
N leaching	Douglas fir forest	Oregon coast range	2.0	None	<b>Gradient:</b> Hydrologic N losses were dominated by dissolved organic N at low N sites, with increased nitrate loss causing a shift to dominance by nitrate at high N sites, particularly where net nitrification exceeded plant N demands.	<a href="#">Perakis and Sinkhorn (2011)</a>
N leaching	48 sites across four continents  Grassland, forest, wetland, shrubland	Global	Varied across 48 studies	Varied across 48 studies	<b>Meta-analysis:</b> The greatest recoveries of ecosystem <sup>15</sup> N tracer occurred in shrublands (mean, 89.5%) and wetlands (84.8%) followed by forests (74.9%) and grasslands (51.8%).	<a href="#">Templer et al. (2012)</a>
Soil N, C:N	Chaparral and coastal sage scrub (CSS)	Southern California	6–8.1	56 to 58	<b>Addition:</b> In this 6-yr field experiment, chaparral and CSS vegetation communities were found to have the capacity to immobilize 6.2 and 11.9 g N/m <sup>2</sup> /yr, respectively. Soil extractable N increased significantly after 7–10 g/m <sup>2</sup> of cumulative N exposure, resulting in a simultaneous increase in the N concentration and a decline in the C:N ratio of shrub tissue. Similar results were observed for the surface litter pool and litter production but at a higher cumulative N exposure.	<a href="#">Vourlitis and Fernandez (2012)</a>

**Table 4-3 (Continued): Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
NO <sub>3</sub> <sup>-</sup> leaching	Forest	Cape Cod, MA	Annual throughfall deposition was 8.7 (±0.4) and 6.8 (±0.5) TDN at sites 10 and 150 m away from the road	None	<b>Roadside gradient:</b> 25 to 30% higher N deposition to forests 10 m away from roads on Cape Cod, compared to hundreds of meters away from the road; the higher deposition was associated with a two to four-fold greater rate of nitrate leaching from the soils. 73% of the deposition was retained in the forest away from roads, compared to 58% retention at 10 from the road. Results scaled to the entire watershed indicate an underestimate of the amount of N deposition to the watershed by 13–25% by not including roadside deposition and leaching.	<a href="#">Bettez et al. (2013)</a>
Soil [NO <sub>3</sub> <sup>-</sup> ] Soil [Al] Fungi:bacteria ratio	19 <i>Picea abies</i> (L.) Karst. Stands	South Sweden	Throughfall N includes wet and dry inputs and ranged from 2.7 to 19	Ammonium NO <sub>3</sub> <sup>-</sup> at 20	<b>Addition:</b> Microbial community composition in the organic horizon and soil solution chemistry below the rooting zone were highly correlated. Stands with low concentrations of NO <sub>3</sub> <sup>-</sup> and Al had higher fungi:bacteria ratio compared with stands with higher concentrations of NO <sub>3</sub> <sup>-</sup> and Al. Microbial community composition in the soil was more closely related to the soil solution than to the soil chemistry. The study found a significant negative correlation between the fungi:bacteria ratio in the soil and NO <sub>3</sub> <sup>-</sup> and Al in soil solution ( $r = -0.533$ and $-0.857$ , respectively).	<a href="#">Högberg et al. (2013)</a>
N saturation	None (theoretical)	None (theoretical)	Not specified	None	<b>Conceptual model:</b> N addition alleviates N limitation, and together with SO <sub>4</sub> <sup>2-</sup> deposition, causes soil acidification and increases availability of electron acceptors for soil microbial processes. Increasing N and SO <sub>4</sub> <sup>2-</sup> decreases fungal biomass, increases bacterial DOC mineralization, and decreases DOC leaching.	<a href="#">Kopáček et al. (2013)</a>

**Table 4-3 (Continued): Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
Decomposition	Deciduous forests	Catskills Mountains of southeastern New York	9.0	50 (NH <sub>4</sub> NO <sub>3</sub> )	<b>Addition:</b> NO <sub>3</sub> <sup>-</sup> leaching increased markedly in response to the N addition in all species, indicating that the addition rate of N exceeded the N retention capacity of vegetation and soils in these plots.	<a href="#">Lovett et al. (2013)</a>
NO <sub>3</sub> <sup>-</sup> leaching	Alpine	Rocky Mountain National Park (Niwot Ridge)	Not specified	Variable	<b>Review:</b> Nitrate leaching increases above 10 kg N/ha/yr deposition.	<a href="#">Bowman et al. (2014)</a>
Rate of soil N cycling	Alpine	Rocky Mountain National Park (Niwot Ridge)	Not specified	Variable	<b>Review:</b> The rate of soil N cycling increases above 15 kg/ha/yr deposition.	<a href="#">Bowman et al. (2014)</a>
Soil acidification and soluble Al	Alpine	Rocky Mountain National Park (Niwot Ridge)	Not specified	Variable	<b>Review:</b> Soil acidification and soluble aluminum increases above 25 kg/ha/yr deposition.	<a href="#">Bowman et al. (2014)</a>
N export	Forest	Ontario, Canada	Not reported	Not applicable	<b>Isotope:</b> Rain on snow, as it passes through the ecosystem, has a higher concentration of NO <sub>3</sub> <sup>-</sup> (throughfall/snowmelt average = 498 µg/L) compared with baseflow (average = 7.3 µg/L; average = 41 µg/L) and as a result, throughfall and snowmelt contribute the majority of NO <sub>3</sub> <sup>-</sup> export (average = 62%) during rain on snow events.	<a href="#">Casson et al. (2014b)</a>
NO <sub>3</sub> <sup>-</sup> leaching	Urban gradient		Urban sites 12.3 and nonurban 5.7		<b>Gradient:</b> The source of N leaching from five of nine sites was almost entirely from nitrification, indicating that the NO <sub>3</sub> <sup>-</sup> in leachate came from biological processes rather than directly passing through the soil. A significant proportion (17–100%) of NO <sub>3</sub> <sup>-</sup> leached from the other four sites came directly from the atmosphere.	<a href="#">Rao et al. (2014)</a>

**Table 4-3 (Continued): Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
N saturation/NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , total inorganic N, and SO <sub>4</sub> <sup>2-</sup> -S	Forest	White Mountains National Forest, Crawford Notch, NH; Lye Brook, VT in southern Green Mountain National Forest	6.6 to 6.7 N 8.1 to 8.5 SO <sub>4</sub> <sup>2-</sup>	Not applicable	<b>Isotope:</b> There was no significant biological production of NO <sub>3</sub> <sup>-</sup> via nitrification in the canopy. NO <sub>3</sub> <sup>-</sup> concentrations in streams were low and had natural <sup>18</sup> O abundances consistent with microbial production, demonstrating that atmospheric N is being biologically transformed while moving through these watersheds and that these forested watersheds are unlikely to be N saturated.	<a href="#">Templer et al. (2015b)</a>
N accumulation	Semiarid chaparral and CSS	Santa Margarita Ecological Reserve and the Sky Oaks Field Station	6 to 8	50	<b>Addition:</b> N enrichment significantly increased N accumulation but not microbial respiration.	<a href="#">Vourlitis and Fernandez (2015)</a>
N retention	Beech and Norway spruce forests	Solling, Germany	Direct total deposition not specified	None	<b>Field Time Series:</b> Two study plots observed that N retention decreased from 40 to 0–20 kg/ha/yr (from 1970s to current), indicating increasing N saturation.	<a href="#">Meesenburg et al. (2016)</a>
NO <sub>3</sub> <sup>-</sup> leaching and N availability	Eastern U.S. forests	Hubbard Brook Experimental Forest, NH, and Bear Brook Watershed, ME	Four modeling scenarios ranging from 7.4 to 103.9 keq/ha N and 7.8 to 149.1 keq/ha S from 1850–2100 with 0–95% decrease from 2010 to 2100	28.8 kg/hr/yr S and 25.2 kg/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	<b>Model:</b> Modeled scenarios at Hubbard Brook, NH received twice the N and S at Bear Brook, ME and resulted in the largest changes in soil base saturation, ANC, NO <sub>3</sub> <sup>-</sup> leaching, and N availability. Modeled recovery of soil chemistry and understory plant communities at both forests only occurred when N and S deposition were modeled at preindustrial levels.	<a href="#">Phelan et al. (2016)</a>
NO <sub>3</sub> <sup>-</sup> leaching	Mixed beech-pine forest	Neuglobsow Integrated Monitoring (IM) site, Germany	Total N wet deposition: 13.26 ± 2.01 kg N/ha/yr (1998–2013)	None	<b>Field observation:</b> Seepage water (120 cm) is estimated to contain at 2.38 kg N/ha/yr (96% as NO <sub>3</sub> <sup>-</sup> ).	<a href="#">Schulte-Bisping and Beese (2016)</a>

**Table 4-3 (Continued): Nitrogen accumulation, saturation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effect of Deposition	Reference
N immobilization	Restored tallgrass prairie	Prairie invasion and Climate Experiment (PRICLE) Loveland, CO	~1/3 of N added	5 g N/m <sup>2</sup> /yr urea. “Seasonal maximum 5-day cumulative rainfall” increased by 33% (2012) and 9% (2013)	<b>N Addition:</b> Nitrogen addition during plant growth accelerated subsequent mass loss of <i>Schizachyrium scoparium</i> litter and litter produced with N addition had a 65% greater N loss than ambient N litter in <i>Solidago canadensis</i> plots, indicating N addition accelerates N cycling.	<a href="#">Schuster (2016)</a>
N soil retention	Forest	Great Smoky Mountains National Park	5.1 kg N/ha/yr (36.5 mmolc /m <sup>2</sup> /yr), respectively.	None	<b>Model:</b> PnET-BGC was used to model 30 stream watersheds characterized by decreased SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition during 1981–2014 (81 and 53%) and predict stream recovery. Spruce-fir forests at higher elevations have limited N retention and exhibit N saturation due to elevated N deposition.	<a href="#">Fakhraei et al. (2016)</a>

Al = aluminum; C = carbon; cm = centimeter; CSS = coastal sage scrub; DOC = dissolved organic carbon; g = gram; ha = hectare; kg = kilogram; L = liter; m = meter; N = nitrogen; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; P = phosphorus; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; *r* = correlation coefficient; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

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### 4.3.3 Sulfate Accumulation, Adsorption, and Leaching

The 2008 ISA showed that  $\text{SO}_x$  deposition may be assimilated by vegetation or microbes, accumulate in the soil, or act as a mobile ion and leach out of the soil to aquatic ecosystems. Plant demand for S is typically low, particularly in comparison to the large pools of S stored in the soil in recalcitrant organic compounds; consequently, almost all S deposited in terrestrial ecosystems enters soil rather than plant pools. At many locations in the U.S. that receive high levels of S deposition, notably the glaciated Northeast and upper Midwest, much of the deposited S leaches through soils into streams and lakes. The physical process of charge balance pairs sulfate ( $\text{SO}_4^{2-}$ ) leaching with leaching of countercharged cations from the soil matrix, and this process contributes to acidification of soil, soil water, and surface water. As the base cations become depleted in the soil matrix, charge balance in the soil is maintained by an increase in acidic cations ( $\text{H}^+$  and inorganic Al), sometimes resulting in toxic conditions for plant roots and aquatic organisms ([Charles and Christie, 1991](#); [Turner et al., 1991](#)).

In the 2008 ISA, regional trends of  $\text{SO}_4^{2-}$  soil accumulation and leaching were identified in the U.S. In the Southeast, accumulation of atmospherically deposited S in soil resulted from  $\text{SO}_4^{2-}$  adsorption to soil particles as well as incorporation of S into soil organic matter through biological assimilation. Accumulated S can be slowly released from soil pools into drainage water, and this process can temporarily delay ecosystem recovery in response to decreases in S deposition ([Sullivan et al., 2004](#); [Elwood et al., 1991](#); [Turner et al., 1991](#)). In the Northeast, there was a demonstrated accumulation of S in soil ([Driscoll et al., 2001a](#)). Two new studies on  $\text{SO}_4^{2-}$  accumulation, leaching, and adsorption are described below ([Table 4-4](#)).

The net loss of S from soils is occurring in a number of northeastern watersheds in response to decreased levels of atmospheric S deposition. In a new study evaluating watersheds in the Northeast, [Mitchell and Likens \(2011\)](#) calculated that annual discrepancies in the watershed S budgets ( $\text{SO}_4^{2-}$  flux in drainage waters minus total atmospheric S deposition) have become more negative, indicating the increasing importance of the release of S from internal ecosystem sources. The release of S from forest soils is controlled (57%) by water flux and soil moisture ([Mitchell and Likens, 2011](#)).

In the southeastern U.S., [Rice et al. \(2014\)](#) calculated  $\text{SO}_4^{2-}$  mass balances for 27 forested, unglaciated watersheds from Pennsylvania to Georgia by using total atmospheric deposition (wet plus dry) as input. Unlike their counterparts in the northeastern U.S. and southern Canada, many of these watersheds still retain  $\text{SO}_4^{2-}$ . [Rice](#)

[et al. \(2014\)](#) predicted that many of the watersheds in the study will begin releasing  $\text{SO}_4^{2-}$  over the next two decades. The specific years when the watersheds cross over from retaining to releasing  $\text{SO}_4^{2-}$  correspond to a general geographical pattern from north to south of later net watershed release. For instance, the three watersheds in West Virginia have crossover years that ranged from 2006 to 2011, and crossover years for five of the watersheds in Virginia range from 2012 to 2021. The runoff ratio, computed as the ratio of annual mean discharge to annual mean precipitation, was the single best watershed-scale predictor of the crossover year ( $r^2 = 0.72$ ). Watersheds with higher runoff ratios tend to convert sooner from net retention to net release of  $\text{SO}_4^{2-}$  ([Rice et al., 2014](#)). More recently, [Fakhraei et al. \(2016\)](#) used PnET-BGC to model 30 stream watersheds during 1981–2014 in the Great Smoky Mountains National Park. Hindcast modeling (beginning ca. 1850) to 2014 showed that the soil  $\text{SO}_4^{2-}$  pools increased from 20.2 g/m<sup>2</sup> (preindustrial) to 145.6 g/m<sup>2</sup> (ambient median). Soils with high  $\text{SO}_4^{2-}$  adsorption capacity also had a faster rate of base cation depletion. In general, soils with high  $\text{SO}_4^{2-}$  adsorption capacity will have more  $\text{SO}_4^{2-}$  release for longer periods of time during the recovery period from acidification, thereby having a faster rate of base cation depletion compared to soils with low  $\text{SO}_4^{2-}$  adsorption capacity during the recovery period.

**Table 4-4 Sulfate adsorption, accumulation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Sulfate adsorption and cation leaching	Upland forests, low-lying areas and wetlands	Athabasca oil sands region (AOSR) in Alberta, Canada	Not specified	None	<b>Field comparison:</b> SO <sub>4</sub> <sup>2-</sup> adsorption capacity was relatively low (50 to 500 mg SO <sub>4</sub> <sup>2-</sup> /kg) in both watersheds as compared to other acid-sensitive soils in eastern North America.	<a href="#">Jung et al. (2011)</a>
S budget	Varied	15 sites southeastern Canada and northeastern U.S.	~0.1 to 14		<b>Long-term deposition:</b> The net annual fluxes of SO <sub>4</sub> <sup>2-</sup> showed a strong relationship with hydrology; the sensitivity of S budgets is likely greatest in watersheds with the greatest wetland area, which are particularly sensitive to drying and wetting cycles.	<a href="#">Mitchell et al. (2011)</a>
Sulfate accumulation and leaching	Forest	HBEF in the White Mountains of New Hampshire	~7 to 20	None	<b>Long-term deposition:</b> S released from internal sources is increasing over time. Watershed wetness, as a function of log <sub>10</sub> annual water flux explained 57% (n = 157) of the annual variation for four watersheds. The biogeochemical control of annual SO <sub>4</sub> <sup>2-</sup> export in stream water draining from forested watersheds has shifted from control by atmospheric S deposition to soil moisture driven by climate.	<a href="#">Mitchell and Likens (2011)</a>

**Table 4-4 (Continued): Sulfate adsorption, accumulation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
SO <sub>4</sub> <sup>2-</sup> leaching	Watersheds ranging from Pennsylvania to Georgia	27 forested, unglaciated watersheds	Not specified	None	<b>Long-term deposition:</b> Calculated SO <sub>4</sub> <sup>2-</sup> mass balances for 27 watersheds showed that over the next two decades, many of the study's watersheds will begin releasing SO <sub>4</sub> <sup>2-</sup> . The single most important variable that explained the crossover year was the runoff ratio, defined as the ratio of annual mean stream discharge to precipitation.	<a href="#">Rice et al. (2014)</a>
Soil SO <sub>4</sub> <sup>2-</sup>	Forest	Great Smoky Mountains National Park	3.1 kg S/ha/yr (19.3 mmolc/m <sup>2</sup> /yr)	None	<b>Model:</b> PnET-BGC used to model 30 stream watersheds during 1981–2014 when SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition decreased (81 and 53%, resp.). Hindcast modeling (beginning ca. 1850) increased soil pools of SO <sub>4</sub> <sup>2-</sup> from 20.2 g/m <sup>2</sup> (preindustrial) to 145.6 g/m <sup>2</sup> (current median).	<a href="#">Fakhraei et al. (2016)</a>
Base saturation	Forest	Great Smoky Mountains National Park, U.S.	5.1 kg N/ha/yr (36.5 mmolc/m <sup>2</sup> /yr)	None	<b>Model:</b> PnET-BGC used to model 30 stream watersheds during 1981–2014 when SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition decreased (81 and 53%, resp.). High capacity SO <sub>4</sub> <sup>2-</sup> adsorbing soils depleted base saturation faster.	<a href="#">Fakhraei et al. (2016)</a>
Soil SO <sub>4</sub> <sup>2-</sup>	Boreal forest	Sweden	Not specified	None	<b>Time series:</b> In an analysis of 10 yr of data, riparian zone soil SO <sub>4</sub> <sup>2-</sup> was observed to decrease from 2003–2012.	<a href="#">Ledezma et al. (2016)</a>

**Table 4-4 (Continued): Sulfate adsorption, accumulation, and leaching.**

Process/Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Soil SO <sub>4</sub> <sup>2-</sup>	Maritime pine forest plantation	Northwest Spain	Not specified	None	<b>Field experiment:</b> The soil parent material (slate, biotitic schist, mica schist, and granite) did not significantly affect soil solution SO <sub>4</sub> <sup>2-</sup> ( <i>p</i> = 0.39).	<a href="#">Eimil-Fraga et al. (2016)</a>

AOSR = Athabasca oil sands region; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

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#### 4.3.4 Base Cation Leaching and Exchange

In the 2008 ISA, it was known that acidifying deposition changes concentrations of exchangeable base cations in soil by accelerating natural rates of base cation leaching until stores become depleted ([Lawrence et al., 1999](#); [Cronan et al., 1978](#)). Base cations include the essential plant nutrients (e.g., Ca, Mg, and K), and the loss of exchangeable base cations from the soil may have adverse effects on flora. When  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  leaching occur in equal magnitude to base cation leaching, the drainage water is not acidified. However, in the process of neutralizing the acidity of drainage water, base cation release from soil eventually can cause decrease of the base saturation of the soil. Soil base saturation expresses the concentration of exchangeable bases (Ca, Mg, potassium [K], sodium [Na]) as a percentage of the total cation exchange capacity (which includes exchangeable  $\text{H}^+$  and inorganic Al).

Under conditions of low soil base saturation (approximately <20%) and elevated concentrations of strong acid anions, Al is mobilized from soil to drainage water ([Cronan and Schofield, 1990](#); [Reuss, 1983](#)), with potentially harmful consequences for sensitive terrestrial plants and aquatic organisms ([Appendix 7](#)) throughout the food web ([Appendix 4.3.6](#)).

Leaching of base cations by acidifying deposition has been documented in sensitive regions in the U.S., including the Adirondack Mountains, New England, the Catskill Mountains, and northwestern Pennsylvania ([U.S. EPA, 2008a](#)). Base cation loss increases the sensitivity of the watershed to further acidifying deposition. Watersheds that were capable of fully neutralizing a particular level of acidifying deposition in the past may no longer be capable of fully neutralizing that level today or in the future due to the cumulative effect of acidifying deposition on soil base saturation.

Base saturation values less than 10% predominate in the soil B-horizon in the areas in the U.S. where soil and surface water acidification from acidifying deposition have been most pronounced, including conifer and hardwood forests in the Adirondack Mountains ([Sullivan et al., 2006b](#)), red spruce forests throughout the Northeast ([David and Lawrence, 1996](#)), hardwood forests in the Allegheny Plateau ([Bailey et al., 2004](#)), and conifer and hardwood forests in the southern Appalachian Mountains ([Sullivan et al., 2003](#)). In a study of sugar maple decline throughout the Northeast, [Bailey et al. \(2004\)](#) found threshold relationships between base cation availability in the upper B soil horizon and sugar maple mortality at Ca saturation less than 2%, and Mg saturation less than 0.5% ([Bailey et al., 2004](#)). The authors concluded that base saturation varied as a function of topography, geologic parent material, and acidifying deposition.

New publications further support findings from the 2008 ISA that N and S deposition cause base cation depletion from soils ([Table 4-5](#)). In the Rocky Mountains, [Lieb et al. \(2011\)](#) observed that soil acid buffering capacity decreased as N inputs increased (40% decrease at highest N input). An acidification threshold was calculated for significant loss of soil acid buffering capacity of around 28 kg N/ha/yr. In another U.S. study, long-term trends in base cation depletion at Bear Brook Watershed, ME, showed N and S addition over a 17-year time period (while ambient S deposition was simultaneously decreasing) resulted in little evidence of continued soil exchangeable base cation depletion or recovery [expected because of decreasing S deposition; [SanClements et al. \(2010\)](#)]. A study of the forest understory herb community in West Virginia found that N addition lowered plant-available Ca and, to a lesser degree, Mg, but not K, illustrating how biogeochemical cycling of forest ecosystems is altered ([Gilliam et al., 2016a](#)).

A meta-analysis of 107 studies found N addition alters the availability of base cations in terrestrial and aquatic ecosystems ([Lucas et al., 2011](#)): although short-term N and S deposition cause base cation depletion, long-term trends across all studies are unclear and may be affected by confounding disturbances. Evaluating the strength of these results is difficult because they are based on averages from various biome types and there are few long-term studies.

Field studies in forests in Europe confirm that N deposition and N addition lower soil pH and decrease base cations ([Chen et al., 2015](#); [Ferretti et al., 2014](#)). As acidifying deposition decreased, base cation concentration in the soil increased ([Berger et al., 2016](#)). Two studies from grasslands in Asia report mixed results, with N addition causing base cation levels to decrease in one study ([Chen et al., 2015](#)) and increase in another ([Tian et al., 2016b](#)). A study of European grasslands found that base cation depletion increased with N addition over a 10-year period, leading to a loss of 23 to 35% of total available bases ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) from the soil and acidifying it by 0.2 to 0.4 pH units ([Horswill et al., 2008](#)).

Base cation weathering rates are uncertain, but substantial advancements have been made in this field since the 2008 ISA ([Appendix 4.5.1.1](#)). New model estimates have been published for two forested areas in Canada ([Williston et al., 2016](#); [Watmough et al., 2014](#)).

Major sources of base cations to ecosystems are either from atmospheric deposition or weathering from soils. Two additional studies from Spain considered the sources of base cations in ecosystems from deposition ([Aguillaume et al., 2017](#)) or as compared with sources from different types of soil parent material ([Eimil-Fraga et al., 2016](#)).

Additional literature that evaluates how base cation depletion from acidification may recover in response to the addition of base cations to the soil is also noted here; however, this literature does not describe the effects of N and S deposition, but rather a method for recovering ecosystems to a more natural state. This literature includes several publications from a 15-year Ca addition study at Hubbard Brook Experimental Forest (HBEF), NH ([Shao et al., 2016](#); [Johnson et al., 2014](#); [Green et al., 2013](#); [Nezat et al., 2010](#)).

**Table 4-5 Base cation leaching and exchange.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Base cation depletion Soil pH Soil [Al], [Fe], [Mg]	Grasslands	Peak District National Park, England	Not specified	Plots treated for 8 to 10 yr with 0, 35, or 140 N as NH <sub>4</sub> NO <sub>3</sub>	<b>Addition:</b> Treatments caused grassland soils to lose 23 to 35% of their total available bases (Ca <sup>2+</sup> , Mg <sup>2+</sup> , K <sup>+</sup> , and Na <sup>+</sup> ), and they became acidified by 0.2 to 0.4 pH units. Al, Fe, and Mn were mobilized and taken up by limestone grassland forbs and were translocated down the acid grassland soil. Mineral N availability increased in both grasslands and many species showed foliar N enrichment. N deposition depletes base cations from grassland soils.	<a href="#">Horswill et al. (2008)</a>
Base cation depletion	Hardwood forest	Eastern U.S., Bear Book watershed, ME		28.8 S and 25.2 N as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	<b>Addition:</b> Compared treated and untreated watersheds after N and S manipulation over a 17-yr time period. Found little evidence of continued soil exchangeable base cation concentration depletion or recovery, possibly because a 1998 ice storm increased litterfall and accelerated mineralization, obscuring temporal trends in soil chemistry.	<a href="#">SanClements et al. (2010)</a>
Base cation depletion Critical load	Forest stands with mature white ash	Niwot Ridge in southern Rocky Mountains	8	20, 40, 60 N	<b>Addition:</b> Soil acid buffering capacity decreased with increasing N inputs (40% decrease at highest input), and was associated with a decrease in pH, loss of extractable Mg <sup>2+</sup> and increases in Mn and Al <sup>3+</sup> . The threshold at which acidification occurred was around 28 kg N/ha/yr.	<a href="#">Lieb et al. (2011)</a>
Base cation depletion	Boreal forest, temperate forest, tropical forest, and grassland	107 sites globally	Not specified	Median N addition across the studies was 38, and 71% of the studies added 70 or less	<b>Meta-analysis:</b> Evaluation of 107 independent studies to determine whether N fertilization alters the availability of base cations (Bc) in terrestrial and stream ecosystems. Results suggest N fertilization may accelerate Bc loss from terrestrial ecosystems over time periods less than 5 yr.	<a href="#">Lucas et al. (2011)</a>

**Table 4-5 (Continued): Base cation leaching and exchange.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Base cation leaching	Jack pine ( <i>Pinus banksiana</i> ) and aspen ( <i>Populus tremuloides</i> ) in upland forests and black spruce ( <i>Picea mariana</i> ) in low-lying areas and wetlands.	Athabasca oil sands region (AOSR), Alberta, Canada	Not specified for AOSR	30 N, 30 S (2006 through 2009)	<b>Addition:</b> No evidence of N saturation in the studied forest ecosystem after 4 yr of N and S additions. No long-term increase of inorganic N concentrations in the soil; leaching of N beyond the main rooting zone in the soil profile was minimal, and tree growth was increased by N addition, all indications of N limitation in the studied forest stand. However, exchangeable Ca <sup>2+</sup> and Mg <sup>2+</sup> concentrations in the surface mineral soil layer were reduced by N and S additions because of increased cation leaching associated with increased SO <sub>4</sub> <sup>2-</sup> leaching caused by S addition and increased nutrient uptake associated with increased tree growth resulting from N addition.	<a href="#">Jung and Chang (2012)</a>
Hydrologic flowpath	Forest	HBEF, NH	Not specified	41 metric tons of the mineral wollastonite (CaSiO <sub>3</sub> ) was applied to an 11.8-hectare watershed	<b>Addition:</b> The flow path of the added Ca was followed through time. The deepest flowpaths to the streams were penetrated by 3–9 yr after application. It was estimated that only ~360 kg out of 19 metric tons of Ca applied as wollastonite had been exported from the watershed in stream flow 9 yr after its application and it would take 1,000 yr for all of the added Ca to be transported from the watershed.	<a href="#">(Nezat et al. (2010)</a>
Evapotranspiration	Forest	HBEF, NH	Not specified	1,028 kg Ca/ha (as wollastonite) in 1999	<b>Field observation:</b> 25, 18, and 19%, evapotranspiration, increased in years 1–3 after addition and then returned to pretreatment levels. Watershed soil retained Ca from the wollastonite, indicating a watershed-scale fertilization effect on transpiration. That response is unique in being a measured manipulation of watershed runoff attributable to fertilization.	<a href="#">Green et al. (2013)</a>

**Table 4-5 (Continued): Base cation leaching and exchange.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Total Ca, exchangeable Ca, cation exchange capacity, base saturation	Forest	Hubbard Brook Experimental Forest, NH	Not specified	1,028 kg Ca/ha (as wollastonite) in 1999	<b>Field observation:</b> Compared to conditions before the 1999 Ca addition, total Ca increased 596% in the Oie-horizon in 2000, 81% in the Oa-horizon in 2002, and 146% in the 0–10 cm mineral soil in 2006.  Oie-horizon exchangeable Ca tripled in 2000 and remained significantly higher through 2010. Significant increases occurred in 2002 in Oa; modest increases measured in upper mineral soil in 2006 and 2010. Total Ca pool in O-horizon and mineral soils was 250 kg/ha greater than pretreatment. In total, 92.4% of Ca added was estimated to dissolve and enter the ecosystem as labile Ca. Cation exchange capacity CEC increased by 106% in the Oie-horizon in 2010 but decreased 52 and 32% in the Oa and mineral soil. Oie, Oa, and mineral soil base saturation rose 69, 84, and 58%, resp. by 2010.	<a href="#">Johnson et al. (2014)</a>
pH Base cations	Forest soils	Italy	4.5 to 28.8 throughfall N (NO <sub>3</sub> <sup>-</sup> + NH <sub>4</sub> <sup>+</sup> )	Not applicable	<b>Gradient:</b> Exchangeable base cations and pH decreased with increasing N deposition, and foliar nutrient N ratios (especially N:P and N:K) increased. Comparison between bulk open-field and throughfall data suggested possible canopy uptake of N, levelling out for bulk deposition >4–6 kg/ha/yr.	<a href="#">Ferretti et al. (2014)</a>
Bc weathering rate	Boreal plains	NE Alberta, Canada	S = 118, NH <sub>4</sub> <sup>+</sup> = 93, NO <sub>3</sub> <sup>-</sup> = 49 in units of mmolc m <sup>2</sup> /yr	Not applicable	<b>Modeling:</b> base cation weathering rate estimated for 63 sites using PROFILE was 17 mmolc m <sup>2</sup> /yr, however acidification was not expected because base cations from fugitive dust sources were a comparatively high 250 mmolc m <sup>2</sup> /yr, offsetting much of the acidifying input of N and S deposition.	<a href="#">Watmough et al. (2014)</a>
pH Soil N Base cations Fungi:bacteria ratio Belowground biomass Microbial community Structure	Semiarid grassland	Mongolia	Not specified	0, 17.5, 52.5, 105.0, 175, and 280 NH <sub>4</sub> NO <sub>3</sub> fertilizer	<b>Addition:</b> Soil pH decreased across the N addition gradient by 0.3–1.8 units in 2010 and by 0.1–1.7 units in 2011. Decreased concentrations of mineral cations Ca <sup>2+</sup> , Mg <sup>2+</sup> , and Na <sup>+</sup> were observed. The observed increases in above- and belowground biomass and changes in plant community structure were mainly (57–69%) attributed to the increase in soil N availability and changes in soil base cations. N addition increased the fungi:bacteria ratio by 5–18% in 2010 and by 2–10% in 2011.	<a href="#">Chen et al. (2015)</a>

**Table 4-5 (Continued): Base cation leaching and exchange.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Base saturation		Adirondack Mtns. region, NY	SO <sub>4</sub> <sup>2-</sup> = 290.3–365.7 eq/ha/yr; NO <sub>3</sub> <sup>-</sup> = 172. 5–233.5 eq/ha/yr	None	<b>Model:</b> PnET-BGC was used to evaluate biophysical factors that affect CLs of acidity. Model simulations included a range of future scenarios of decreases in atmospheric nitrate, ammonium, and sulfate deposition from the present to 2,200; historical forest harvesting; supply of naturally occurring organic acids; and variations in lake hydraulic residence time.  Assuming the current soil base saturation of 6.4%, a decrease in SO <sub>4</sub> <sup>2-</sup> deposition from 0 to 100% resulted in a soil percentage BS range of 6.2 to 15.3%, respectively, after 200 yr. (Preindustrial soil percentage BS ~22%).	<a href="#">Zhou et al. (2015c)</a>
Bc	Predominantly beech	Vienna Woods, Austria	Not specified locally	None	<b>Time Series:</b> In 1984 and 2012, soil samples were taken from 20 cm downhill and 3 m away from the base of a beech tree stem. Exchangeable Ca <sup>2+</sup> , Mg <sup>2+</sup> , and pH increased in 0–5 cm soil from 1984 to 2012. Recovery appeared delayed in deeper soils. Foliar base cations Ca, Mg, and K decreased. (Foliar K declined the most at 48%).	<a href="#">Berger et al. (2016)</a>
Bc	Maritime pine forest	Northwest Spain	Not specified	None	<b>Field observation:</b> The soil parent material (slate, biotitic schist, mica schist, and granite) significantly affected base cation concentrations.	<a href="#">Eimil-Fraga et al. (2016)</a>
Foliar base cation	Eastern U.S. temperate, hardwood forest herbaceous layer ( <i>Viola rotundifolia</i> , <i>Rubus allegheniensis</i> )	Fernow Experimental Forest, WV	~10 kg N/ha/yr (wet)	35 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	<b>N Addition:</b> Foliar measurements were used as a proxy for soil micronutrient availability under N addition. Excess N lowered plant-available Ca and, to a lesser degree, Mg, but not K. N addition significantly affected Ca:Al ratios in <i>Viola</i> sp. and <i>Rubus</i> sp.	<a href="#">Gilliam et al. (2016a)</a>

**Table 4-5 (Continued): Base cation leaching and exchange.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Soil solution Bc	Forest	Hubbard Brook Experimental Forest, NH	Not specified	1,028 kg Ca/ha (as wollastonite) in 1999	<b>Field observation:</b> Significant increase in soil Ca concentrations. Increases in pH and ANC and decreases in inorganic Al in the Oa, Bh, and Bs soil horizons. Ca:Al ratios ranging from 1 to 5.3 in the Oa-, Bh-, and Bs-horizons before treatment increased significantly after Ca addition, with the greatest increase occurring in the Oa-horizon. Average 2000–2011 Ca fluxes in soil solution across the study area’s three subwatersheds ranged from 26.4 + 3.2 mmol/m <sup>2</sup> /yr to 29.9 + 4.2 mmol/m <sup>2</sup> /yr. The weighted average percentage increase in Ca fluxes for the three subwatersheds from 1999–2011 were 139, 91, and 97% for Oa-, Bh-, and Bs-horizons, respectively.	<a href="#">Shao et al. (2016)</a>
Soil Bc	Temperate grassland	Mongolia, China	1.6 mg N/m <sup>2</sup> /yr (not specified if wet or total)	1, 2, 4, 8, 16, 32, 64 g N/m <sup>2</sup> /yr (urea)	<b>N Addition:</b> Soil exchangeable Mn <sup>2+</sup> , Fe <sup>3+</sup> , and Al <sup>3+</sup> concentrations increased linearly with N addition.	<a href="#">Tian et al. (2016b)</a>
Bc weathering	Forest	NW British Columbia, CAN (Kitmat and Prince Rupert)	0–80 meq SO <sub>4</sub> <sup>2-</sup> /m <sup>2</sup> /yr and 0–30 meq N/m <sup>2</sup> /yr	None	<b>Model:</b> Weathering rates were modeled by PROFILE and A2M solver using empirical soil data to parameterize the models. Rates ranged between 19 and 393 meq/m <sup>2</sup> /yr (average: 76) in the top 50 cm of soil in Prince Rupert and between 24 and 118 meq/m <sup>2</sup> /yr (average: 57 meq/m <sup>2</sup> /yr) in Kitimat.	<a href="#">Williston et al. (2016)</a>
Bc deposition	Mediterranean holm-oak ( <i>Quercus ilex</i> ) forests ranging from the typical Mediterranean climate to a drier, more seasonal climate	Spain	Not specified	None	<b>Field observation:</b> In wetter forest sites, 55–65% of total base cation deposition was wet deposition. Rainfall and net throughfall were positively correlated for leaching for K <sup>+</sup> and uptake for NH <sub>4</sub> <sup>+</sup> at all sites. Variable response between sites was found for Na <sup>+</sup> , Ca <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> and Cl <sup>-</sup> . The authors suggest that the interplay of dry deposition, leaching, and uptake at the canopy was different depending on site climate and air quality characteristics.	<a href="#">Aguillaume et al. (2017)</a>

Al = aluminum; AOSR = Athabasca oil sands region; Bc = base cations; BCE = exchangeable base cations; Ca<sup>2+</sup> = calcium ion; Fe = iron; g = gram; ha = hectare; K<sup>+</sup> = potassium ion; kg = kilogram; m = meter; Mg<sup>2+</sup> = magnesium ion; N = nitrogen; Na<sup>+</sup> = sodium ion; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

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#### 4.3.5 Aluminum Mobilization

The 2008 ISA documented that when soil base saturation is 15 to 20% or lower, acidifying deposition can mobilize inorganic Al, which can lead to its leaching into soil solution and into surface waters ([Cronan and Schofield, 1990](#); [Reuss and Johnson, 1985](#); [Reuss, 1983](#)). Leaching of inorganic Al is an extremely important effect of acidifying deposition because some forms of inorganic monomeric Al, including  $\text{Al}^{3+}$  and various hydroxide species, are toxic to tree roots, fish, algae, and aquatic invertebrates ([Appendix 5](#) and [Appendix 8](#)). Increased concentrations of exchangeable inorganic Al in the soil have been identified through repeated sampling in the U.S. and Europe over periods ranging from 17 to 41 years in studies by [Billett et al. \(1990\)](#), [Falkengren-Grerup and Eriksson \(1990\)](#), [Bailey et al. \(2005\)](#), and [Lawrence et al. \(1995\)](#).

The negative biological effects of Al mobilization are discussed in [Appendix 5](#); in general, Al disrupts Ca uptake by tree roots ([Shortle and Smith, 1988](#)). Substantial evidence of this relationship has been provided through field studies ([Kobe et al., 2002](#); [Minocha et al., 1997](#); [Shortle et al., 1997](#); [McLaughlin and Tjoelker, 1992](#); [Schlegel et al., 1992](#)) and laboratory studies ([Cronan and Grigal, 1995](#); [Sverdrup and Warfvinge, 1993](#)). These studies make clear that high inorganic Al concentration in soil water can be toxic to plant roots. The toxic response is often related to the concentration of inorganic Al relative to the concentration of Ca, expressed as the molar ratio of Ca to inorganic Al in soil solution. From an exhaustive literature review, [Cronan and Grigal \(1995\)](#) estimated a 50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. They estimated a 100% risk for adverse effects on growth at a molar ratio value Ca:Al <0.2 in soil solution and minimal to no risk is thought to occur at Ca:Al >10.

New studies on Al in soils are summarized in [Table 4-6](#) and include an investigation of long-term soil solution chemistry trends in Hubbard Brook Experimental Forest ([Fuss et al., 2015](#)), an investigation of the influence of increasing dissolved organic matter (DOM) on toxic inorganic Al ( $\text{Al}_i$ ) concentration in 52 Adirondack and Hubbard Brook watersheds ([Fakhraei and Driscoll, 2015](#)), an investigation of the effects of soil parent material on Al ([Eimil-Fraga et al., 2016](#)), a model comparison of three models' predictions of soil solution Al concentrations in three monitored Swiss and German forests ([Bonten et al., 2015](#)), and a study showing that N addition increased Al mobilization on grasslands in England ([Horswill et al., 2008](#)).

[Fakhraei and Driscoll \(2015\)](#) evaluated the influence of increasing DOM on  $\text{Al}_i$  concentration in the Adirondacks and Hubbard Brook. The authors linked a PnET-BGC

model chemical equilibrium subroutine with an optimization algorithm. They determined that accounting for the increasing concentration of DOM (as acid deposition decreases and ANC increases) and its binding capacity for  $Al_i$  is necessary in the model to avoid substantial overestimation of available toxic  $Al_i$  in waters. In an empirical study, [Fuss et al. \(2015\)](#) found that  $Al_i$  in soil solution in the mineral horizon decreased over the period of 1984–2011 (also discussed in the recovery [Appendix 4.6.1](#)).

**Table 4-6 Aluminum mobilization.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Base cation depletion Soil pH Soil [Al], [Fe], [Mg]	Grasslands	Peak District National Park, England,	Not specified	Plots treated for 8 to 10 yr with 0, 35, or 140 N as NH <sub>4</sub> NO <sub>3</sub>	<b>Addition:</b> Treatments caused the grassland soils to lose 23 to 35% of their total available bases and acidify by 0.2 to 0.4 pH units. Al, Fe, and Mn were mobilized and taken up by limestone grassland forbs and were translocated down the acid grassland soil.	<a href="#">Horswill et al. (2008)</a>
Al <sub>i</sub> , DOM, DOC	Lakes	Adirondack Long-Term Monitoring (ATLM) Program lakes	Variable	None	<b>Model:</b> A PnET-BGC chemical equilibrium subroutine was linked with an optimization algorithm. Accounting for the increasing concentration of dissolved organic matter (DOM) as acid deposition decreases and ANC increases, DOM's binding capacity for Al is necessary to avoid substantial overestimation of toxic Al <sub>i</sub> in waters.	<a href="#">Fakhraei and Driscoll (2015)</a>
Al <sub>i</sub>	Forest and streams	Hubbard Brook Experimental Forest, NH	Variable	None	<b>Field observation/elevation gradient:</b> Al <sub>i</sub> in soil solution in the mineral horizon decreased over the period of 1984–2011.	<a href="#">Fuss et al. (2015)</a>
Al	Forest	Three Swiss forest monitoring sites	Not specified	None	<b>Model:</b> VSD modeled soil solution Al concentrations are substantially smaller than measured ones. However, VSD only calculates free Al <sup>3+</sup> , whereas measurements also include other Al species as Al hydroxides, Al fluorides, and Al complexed by DOM.	<a href="#">Bonten et al. (2015)</a>
Al	Spruce forest	Bechtel, Switzerland	Not specified	None	<b>Model:</b> ForSAFE-modeled Al <sup>3+</sup> was in the range of the measured soil solution values at 20 cm depth (1990–2005)	<a href="#">Bonten et al. (2015)</a>

**Table 4-6 (Continued): Aluminum mobilization.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Al, Ca and protons	Norway spruce forest	Long-term monitoring site in Germany	Not specified	None	<b>Model:</b> SMARTml results showed that modeled Al <sup>3+</sup> , Ca <sup>2+</sup> , and H <sup>+</sup> agree with measured values in soil solution (1990–2005).	<a href="#">Bonten et al. (2015)</a>
Total Al, reactive Al	Maritime pine forest	Northwest Spain	Not specified	None	<b>Field Observation:</b> The soil parent material (slate, biotitic schist, mica schist, and granite) significantly affected total and reactive Al in soil solution. Total Al ranged from 17.2 to 64.2 µmol/L ( $p = 0.0006$ ). The concentration was significantly higher for soil developed from mica schist developed soil than granite and biotitic schist.	<a href="#">Eimil-Fraga et al. (2016)</a>

Al = aluminum; Al<sub>i</sub> = toxic inorganic Al; AOSR = Athabasca oil sands region; Bc = base cations; BCE = exchangeable base cations; Ca<sup>2+</sup> = calcium ion; Fe = iron; g = gram; H<sup>+</sup> = hydrogen ion; ha = hectare; K<sup>+</sup> = potassium ion; kg = kilogram; m = meter; Mg<sup>2+</sup> = magnesium; N = nitrogen; Na<sup>+</sup> = sodium ion; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

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### 4.3.6 Nitrification and Denitrification

Nitrification is the microbial oxidation of ammonia or ammonium to form nitrite followed by the oxidation of the nitrite to form  $\text{NO}_3^-$ . The 2008 ISA documented that oxidation of ammonia into nitrite is performed by two groups of organisms, ammonia-oxidizing bacteria and ammonia-oxidizing archaea. The rate of nitrification is controlled by numerous factors, including substrate availability (presence of  $\text{NH}_4^+$ ), aeration (availability of  $\text{O}_2$ , often as well-drained soils with <60% soil moisture), and acidity (pH). N addition may increase nitrification, which is often stimulated in soils with a C:N ratio below about 20 to 25 (Ross et al., 2004; Aber et al., 2003). The microbial process of autotrophic nitrification is an acidifying process, releasing 2 moles of hydrogen ion ( $\text{H}^+$ ) per mole of  $\text{NH}_4^+$  converted to  $\text{NO}_3^-$  (Reuss and Johnson, 1986). As the N cycle becomes enriched through cumulative N addition, N becomes more abundant, competition among organisms for N decreases, net nitrification rates often increase, and  $\text{NO}_3^-$  can leach from the soil (Aber et al., 2003; Aber et al., 1989).

Soils with a C:N ratio below about 20 to 25 are associated with stimulated mineralization, nitrification, and cation leaching (Ross et al., 2004; Aber et al., 2003). This observation makes the C:N ratio an especially useful field measurement that provides a relative index rather than a quantitative rate of N leaching (Ross et al., 2004). C:N ratios in the forest floor are generally inversely related to acidifying deposition levels, although the relationship is stronger for hardwood stands than conifer stands (Aber et al., 2003). The C:N ratio is a reliable and relatively straightforward measure for identifying forest ecosystems that may be experiencing soil acidification and base leaching as a result of N input and increased nitrification.

Denitrification is the microbial process that transforms  $\text{NO}_3^-$  by anaerobically reducing it to nitrite ( $\text{NO}_2^-$ ), nitric oxide (NO), the greenhouse gas nitrous oxide ( $\text{N}_2\text{O}$ ) and  $\text{N}_2$ . The 2008 ISA documented that in terrestrial ecosystems, denitrification mainly occurs in oxygen-depleted soils (e.g., during periods of water saturation), groundwater, and riparian zones. Soil pH has a marked effect on denitrification, with lower rates in acidic as compared with alkaline conditions (Yamulki et al., 1997). Soil denitrification and  $\text{N}_2\text{O}$  production and consumption are extremely variable in time and space (McClain et al., 2003).

New information published since 2008 is summarized in Table 4-7. New empirical work along an N deposition gradient in Oregon found that nitrification increased with increasing N deposition (Perakis and Sinkhorn, 2011); likewise, denitrification increased with N deposition in northeastern forests (Morse et al., 2015a). In a deposition exclusion

study in Europe, after two decades of deposition exclusion, net nitrification and  $\text{NO}_3^-$  concentration in soils were not detectable, and in fact, the soil switched from a net source of  $\text{NO}_y$  to a net sink ([Eickenscheidt and Brumme, 2012](#)).

A growing body of information indicates that increased N deposition also alters the soil microbial community ([Freedman et al., 2013](#)). Discussion of this is provided in [Appendix 6](#). [Marusenko et al. \(2013\)](#) explored the role of fungi in  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  production in soils from regions across the southwestern U.S. and found that fungi are significant sources of  $\text{N}_2\text{O}$  production in soils in semiarid grasslands and deserts. [Russow et al. \(2008\)](#) found that soils with high soil organic matter adsorbed added  $\text{NH}_4^+$ , making it difficult to determine microbial activity.

Several new syntheses evaluated N addition effects on denitrification and nitrification in terrestrial ecosystems ([Yang et al., 2017](#); [Bouwman et al., 2013](#); [Lu et al., 2011a](#); [Liu and Greaver, 2009](#)). Globally, the amount of N removed from ecosystems by denitrification may be higher in terrestrial ecosystems than from groundwater or riparian zones ([Bouwman et al., 2013](#)); however, other older estimates have indicated more denitrification may occur in riparian wetlands and in first-order streams than in terrestrial ecosystems ([Van Breemen et al., 2002](#)), although the authors acknowledged this estimate likely underestimated terrestrial N. [Liu and Greaver \(2009\)](#) showed that N addition significantly increased denitrification from all ecosystems tested (coniferous forest, deciduous forest, tropical forest, wetland, grassland) except heathland. Among the five chemical forms of N fertilizer added to ecosystems in studies,  $\text{NO}_3^-$  showed the strongest stimulation of  $\text{N}_2\text{O}$  emission ([Figure 4-5](#)). [Lu et al. \(2011a\)](#) further confirmed that N addition stimulates nitrification and denitrification ([Figure 4-6](#)). Using data extracted from 206 peer-reviewed papers, the meta-analysis showed that the largest changes caused by N addition in the ecosystem N cycle were increased nitrification (154%), nitrous oxide emission (134%), and denitrification (84%). In addition, [Yang et al. \(2017\)](#) evaluated N cycling in five biomes in California and found a strong ( $r^2 = 0.34$ ) significant linear correlation between  $\text{NO}_3^-$  and nitrification rates. They also found a strong negative relationship between gross nitrification and soil C:N in forests that had soil C:N ratios greater than 20. However, the authors noted that not all forests have such high soil C:N ratios as those in their study that were dominated by coniferous trees. Coniferous forests generally have higher litter C:N ratios than deciduous forests, and deciduous forests with lower C:N ratios may also have negative relationship with C:N and nitrification.

**Table 4-7 Nitrification and denitrification.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Nitrification and denitrification	Agricultural black earth soils (haplic chernozem); two sites: high and normal SOM	Central Germany	Not specified	81.3 (KNO <sub>3</sub> , Ca[NO <sub>3</sub> ] <sub>2</sub> ); 80 kg (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	<b>Isotopic tracer:</b> Addition of <sup>15</sup> N revealed denitrification of NO <sub>3</sub> <sup>-</sup> represents the main pathway of soil N <sub>2</sub> O release. On average, 76 and 54% of N <sub>2</sub> O was emitted during denitrification from soils with high and normal SOM content, respectively. Denitrification contributed, on average, only 17 and 12% of released NO from soil with high and normal SOM content, respectively.	<a href="#">Russow et al. (2008)</a>
Nitrification	Spruce plantation	Höglwald, Bavaria, Germany	30 (two decades)	None	<b>Time series:</b> Dynamic internal N cycle within the soil, driven by growth and death of the microbial biomass, which turns over approximately seven-fold each year.	<a href="#">Kreutzer et al. (2009)</a>
Denitrification	Agricultural crop, forest, grassland, wetland, tundra, heathland, and desert	Global	Not specified	10 to 562	<b>Meta-analysis:</b> Analysis of 313 observations across all ecosystems show N addition increased N <sub>2</sub> O emission by 216%.	<a href="#">Liu and Greaver (2009)</a>
Nitrification Denitrification	Agriculture and nonagriculture	Not specified	Mean = 105 Tg N/yr	0 to >100	<b>Meta-analysis:</b> included 206 papers on responses of ecosystem N cycle in response to N addition. Increases in nitrification (154%), N <sub>2</sub> O emission (134%), and denitrification (84%) were found. Increased N <sub>2</sub> O emissions and N leaching under N addition tended to export the N out of the systems rather than benefit plant uptake over the long term, suggesting a leaky terrestrial N system.	<a href="#">Lu et al. (2011a)</a>

**Table 4–7 (Continued): Nitrification and denitrification.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Nitrification and denitrification Microbial N demand	Temperate hardwood and conifer forests (unfertilized)	Nine sites in the north-central Oregon coast range, U.S.	Not specified	None	<b>Soil and foliar N gradient:</b> As future reductions in N deposition to polluted sites occurs, symptoms of N saturation are most likely to persist where soil N content remains elevated. Temperate and hardwood forests of the north-central Oregon coast range showed the ratio of net to gross N mineralization and nitrification increased along the gradient, indicating progressive saturation of microbial N demands at high soil N.	<a href="#">Perakis and Sinkhorn (2011)</a>
Nitrification	Common garden experiment, five broadleaved tree species	Denmark	13 to 19 for broadleaf forest; 18 to 26 for Norway spruce		<b>Isotopic tracer:</b> Litter $\delta^{15}\text{N}$ was positively correlated with N status based on nitrification, as well as other factors. A linear relationship was found between fungal mycelia production and net nitrification rate in lab incubations of soils collected in the field.	<a href="#">(Callesen et al., 2013)</a>
Denitrification	Forested watershed	Pond Branch in Maryland, U.S.	$10 \pm 4$	None	<b>Isotopic tracer:</b> Spatial and temporal extrapolations of measured rates suggest that a minimum of 16–27% of atmospheric N deposition is lost to denitrification.	<a href="#">Duncan et al. (2013)</a>
Fungal nitrification and denitrification	Semiarid grasslands	Arizona and New Mexico	Not specified	10 g soil to a 100 mL solution of 50 mmol/L $(\text{NH}_4)_2\text{SO}_4$ , 0.2 mol/L $\text{K}_2\text{HPO}_4$ , and 0.2 mol/L $\text{KH}_2\text{PO}_4$ , with a pH of 7.2.	<b>Moisture X biocide:</b> Fungi are significant sources of $\text{N}_2\text{O}$ production in soils from semiarid grasslands and deserts, expanding evidence that fungi play a vital role in the N cycle of arid lands.	<a href="#">Marusenko et al. (2013)</a>

**Table 4–7 (Continued): Nitrification and denitrification.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Denitrification	Agricultural land and natural ecosystems	Global	24 to 46 Tg N/yr from 1900–2050	Not applicable	<b>Model:</b> N <sub>2</sub> production from denitrification increased from 52 to 96 Tg/yr between 1900 and 2000, and N <sub>2</sub> O emissions increased from 10 to 12 Tg N/yr. The scenarios suggest a further increase to 142 Tg N <sub>2</sub> and 16 Tg N <sub>2</sub> O–N/yr by 2050. Riparian buffer zones are an important source of N <sub>2</sub> O, contributing an estimated 0.9 Tg N <sub>2</sub> O–N/yr in 2000.	<a href="#">Bouwman et al. (2013)</a>
Nitrification and denitrification Microbial community	Sugar maple dominated northern hardwood forest	Upper Michigan	15 to 20	30 kg N in the form of NaNO <sub>3</sub> pellets delivered to the forest floor over the growing season	<b>Addition:</b> NO <sub>3</sub> <sup>-</sup> addition to forest stands across a 500-km climatic gradient decreased the abundance and richness of key protein-coding genes in archaea and bacteria responsible for N fixation, ammonification, denitrification, and assimilatory NO <sub>3</sub> <sup>-</sup> reduction; the same was true for bacterial genes mediating nitrification and dissimilatory NO <sub>3</sub> <sup>-</sup> reduction.	<a href="#">Freedman et al. (2013)</a>
Denitrification	Northern hardwood forest	HBEF, White Mountain National Forest, NH	6 to 8	None	<b>Method comparison:</b> Both the isotopic tracer and gas-flow soil core method indicate that denitrification is higher and N <sub>2</sub> O:N <sub>2</sub> ratios are lower (<0.02) than previously thought in the northern hardwood forest and that short-term abiotic and biotic transformations of atmospheric N deposition to gas are significant in this ecosystem.	<a href="#">Kulkarni et al. (2014)</a>

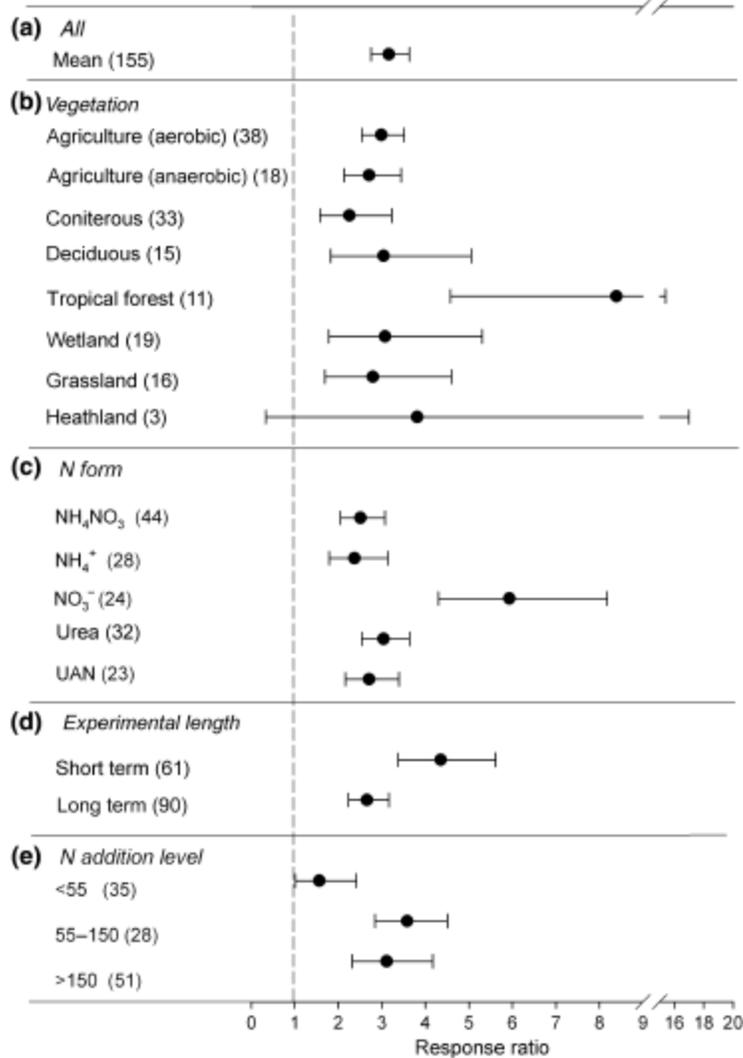
**Table 4–7 (Continued): Nitrification and denitrification.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Nitrification	Mixed hardwood forested headwater catchments	South-central Ontario, Canada	Average NO <sub>3</sub> <sup>-</sup> N deposition 2.78 ± 1.22; average NH <sub>4</sub> <sup>+</sup> N deposition 3.90 ± 1.39	Not applicable	<p><b>Time series:</b> Seasonal differences in nitrification were largely driven by temperature, soil moisture, and inorganic N concentration in soil.</p> <p>Annual nitrification fluxes were almost two orders of magnitude greater than N deposition or NO<sub>3</sub><sup>-</sup> leaching. Nitrification rates scaled up to annual catchment-scale production of NO<sub>3</sub><sup>-</sup>; the resulting fluxes are 64.9 ± 8.7 and 59.7 ± 3.1 kg N/ha/yr, which greatly exceed seasonal inputs in deposition.</p> <p>Rates of nitrification and mineralization were similar, indicating that almost all mineralized N is converted to NO<sub>3</sub><sup>-</sup> (ranging from 71 to 99%).</p>	<a href="#">Casson et al. (2014a)</a>
Nitrification denitrification	Deciduous and coniferous forests	Ontario, Canada; New Hampshire; and Maine	Three sites along a gradient: 4.5, 7, and 11	Not applicable	<p><b>Gradient:</b> N gas flux increased systematically with natural N enrichment from soils with high nitrification rates.</p> <p>N gas fluxes were linked to patterns of N availability in forests; results do not suggest that these fluxes respond to increases in atmospheric N deposition at the study sites.</p>	<a href="#">Morse et al. (2015a)</a>

**Table 4–7 (Continued): Nitrification and denitrification.**

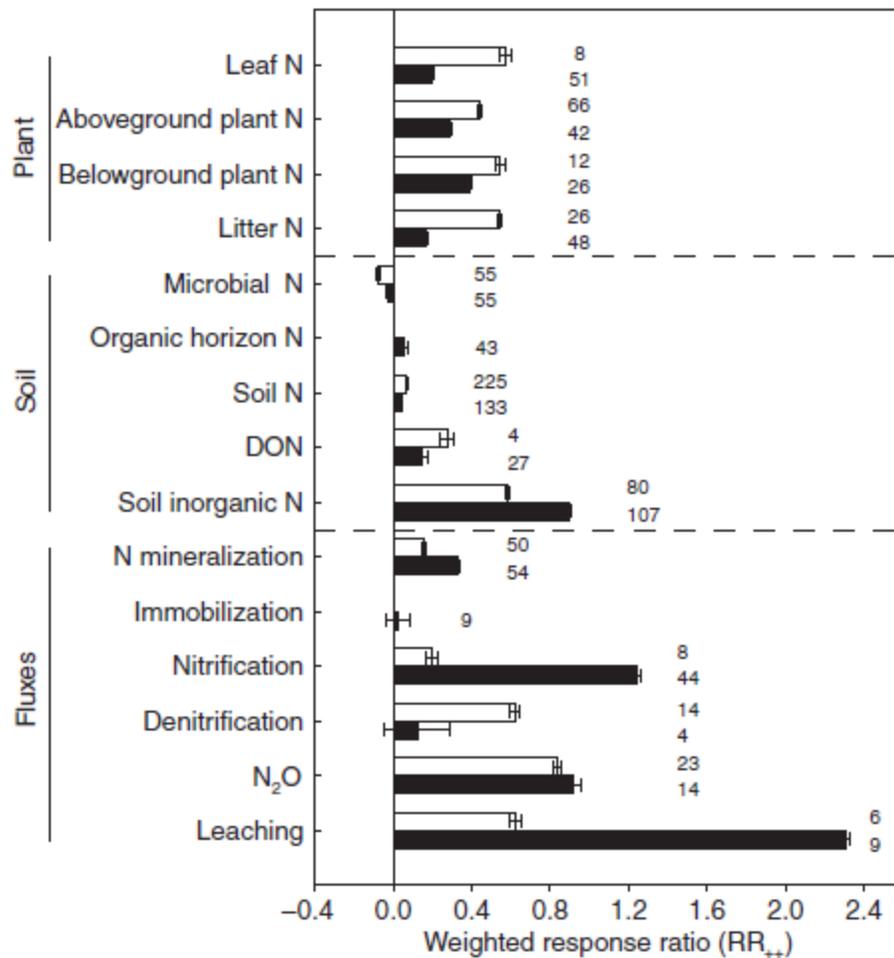
Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Nitrification C:N	Five biome classes in California: desert, grassland, shrubland, forest, wetland	California	0.6–18.4 kg N/ha/yr	Grassland soil: 76.4 kg N/ha/yr as NPK (29:3:4); desert soil: 60 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> ; shrubland soil: 60 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub>	<b>N Addition:</b> Across biomes, a positive correlation of gross nitrification to soil NO <sub>3</sub> <sup>-</sup> ( $r^2 = 0.34$ ) and a negative correlation to soil C:N ( $r^2 = 0.31$ ) was observed.  No correlation was found between gross N mineralization and nitrification. Deserts had the lowest gross N mineralization rates and exhibited similar nitrification rates to the shrublands and grasslands. Only 15% of NH <sub>4</sub> <sup>+</sup> produced was nitrified in the forests compared to 47 to 86% in the other biomes. This suggests that NH <sub>4</sub> <sup>+</sup> production rates did not limit nitrifiers in the forests, but rather, that another factor limited nitrifier activity.	<a href="#">Yang et al. (2017)</a>

Ca(NO<sub>3</sub>)<sub>2</sub> = calcium nitrate; g = gram; HBEF = Hubbard Brook Experimental Forest; K<sub>2</sub>HPO<sub>4</sub> = dipotassium phosphate; KH<sub>2</sub>PO<sub>4</sub> = monopotassium phosphate; KNO<sub>3</sub> = potassium nitrate; L = liter; mL = milliliter; mmol = millimole; mol = mole; N = nitrogen; N<sub>2</sub> = molecular nitrogen; N<sub>2</sub>O = nitrous oxide; N<sub>2</sub>O-N = nitrogen from nitrous oxide; NaNO<sub>3</sub> = sodium nitrate; NH<sub>4</sub><sup>+</sup> = ammonium; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO = nitric oxide; NO<sub>3</sub><sup>-</sup> = nitrate; SOM = soil organic matter; Tg = teragram yr = year.



N = nitrogen; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; UAN = urea and ammonium nitrate fertilizer. The data are expressed as the mean response ratio with 95% confident intervals. The numbers of studies included are indicated in parentheses.  
 Source: [Liu and Greaver \(2009\)](#).

**Figure 4-5 Effects of nitrogen addition on biogenic nitrous oxide emission.**



N = nitrogen; N<sub>2</sub>O = nitrous oxide; RR = response ratio.

Bars represent RR<sub>++</sub> ± SE. The vertical line is drawn at log<sub>e</sub>RR = 0. The sample size for each variable is shown next to the bar.

Source: [Lu et al. \(2011a\)](#).

**Figure 4-6** The weighted response ratio for the responses to nitrogen addition for fluxes and pools related to the ecosystem nitrogen cycle in agricultural (open bars) and nonagricultural (closed bars) ecosystems.

### 4.3.7 Decomposition

Decomposition is a general term that refers to the breakdown of organic matter ([Schlesinger, 1997](#)). Decomposition is an important part of N and C cycling that can be altered by N deposition. Decomposition rates correlate with ratios of C:N, lignin:N, and

lignin:cellulose in litter, all of which may be altered by N deposition. The addition of N can stimulate the decomposition of labile compounds that degrade during the initial stages of decomposition, but added N can suppress the decomposition of more recalcitrant material. Evidence for this is widespread in forests but has not yet been well documented in grasslands and other ecosystems. Since 2008, there are new addition studies and meta-analyses to better understand the mechanisms and response trends.

The 2008 ISA documented that the soil microbial community (bacteria and fungi) are the main decomposers of organic matter. Both the microbial community composition and microbial enzyme activity can dynamically respond to shifts in inorganic nutrient and substrate availability ([Compton et al., 2004](#); [Carreiro et al., 2000](#)); the shift reflects the nutrient and energy limitation of the microbial community. Litter decay rates are also well established to correlate with ratios of C:N, lignin:N, or lignin:cellulose in litter ([Hobbie, 2008](#); [Aerts, 1997](#); [Melillo et al., 1982](#)). These chemical traits are strong predictors of litter decay, accounting for over 73% of the variation in litter decomposition rates worldwide ([Zhang et al., 2008](#)).

Traditionally, carbon dioxide (CO<sub>2</sub>) is measured as an indication of soil respiration and a proxy for decomposition. Since the 2008 ISA, analysis of microbial enzymes and genes in the soil have been used to identify microbial activity and determine how it relates to decomposition. Numerous studies have been published since 2008 describing how N addition affects the decomposition of organic C and N ([Table 4-8](#)).

**Table 4-8 Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Decomposition	Sugar maple hardwood forest	Bear Brook Watershed in eastern Maine		1,800 eq/ha/yr of (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	<b>N + S Addition:</b> Caused increased N concentration in leaves and faster short-term decomposition.	<a href="#">Hunt et al. (2008)</a>
Enzyme activity Decomposition	Eight annual herb species	Controlled ecosystem (litter bags placed in annual herb-based microcosm ecosystems)	2.0 and 44.0		<b>Growth chamber:</b> N deposition increased soil enzyme activity known to breakdown cellulose (cellobiosidase, β-glucosidase and β-xylosidase).	<a href="#">Manning et al. (2008)</a>
Enzyme activity Decomposition	Northern hardwood forest	Michigan	6.8 to 11.8	30 NO <sub>3</sub> <sup>-</sup>	<b>N Addition:</b> N addition altered rates of organic matter decomposition by suppressing the soil enzymes responsible for litter degradation when litter has a higher N concentration. This causes an increase in surface soil C storage.	<a href="#">Pregitzer et al. (2008)</a>
Enzyme activity Decomposition	Forests grasslands	Central Minnesota	Not specified	100 (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> Generally stimulated activities of cellulose degrading enzymes in litter and soil, but had no effect on lignin degrading enzyme activity. N addition had a negative or neutral effect on litter and SOM decomposition in the same sites, with no correspondence between effects of N on enzyme activity and decomposition across sites.	<a href="#">Keeler et al. (2009)</a>
Enzyme activity	Northern hardwood forest	Catskill Mountains of New York, U.S.		50 (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> Identified that patterns in microbial community structure and function were more strongly influenced by tree species than by fertilization.	<a href="#">Weand et al. (2010)</a>
Soil respiration Decomposition	Forest	Global		Varied	<b>Meta-analysis:</b> N additions decreased root respiration, heterotrophic respiration, and soil CO <sub>2</sub> but had no effect on litter decomposition.	<a href="#">Janssens et al. (2010)</a>

**Table 4–8 (Continued): Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Soil respiration	Temperate broadleaf and mixed forest, temperate conifer forest, boreal forest, tropical forest, grassland, wetland, tundra, desert, and arctic	Global		Varied	<b>Meta-analysis:</b> N additions decreased heterotrophic respiration but had no effect on total soil respiration.	<a href="#">Liu and Greaver (2010)</a>
Enzyme activity Decomposition	Forest and grasslands	U.S.	None	None	<b>Synthesis:</b> Data from 28 ecosystems show resources to produce the enzymes phenol oxidase and $\beta$ -1,4-glucosidase are uncoupled. This indicates that the increasing recalcitrance of organic matter decreases C and nutrient availability and slows microbial growth.	<a href="#">Sinsabaugh and Shah (2011)</a>
Enzyme activity Decomposition	Mature black spruce forest in upland boreal ecosystem	Central Alaska	Not specified	Years 2009 = 200 (NH <sub>4</sub> NO <sub>3</sub> ) Years 2010 = 100 (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> N fertilization may alter decomposer community structure by favoring a shift toward cellulose- and mineral-N users. Cellulose degrading microbes (decomposers) were competitively dominant under N fertilization.	<a href="#">Talbot and Treseder (2012)</a>
Enzyme activity Decomposition	Sugar maple forests	Michigan	Not specified	30	<b>Meta-analysis:</b> N addition increased cellulose decomposition by 9% and decreases lignin decomposition rates by 30%. Overall, N increases the amount of litter mass entering the humus pool and leads to increases in soil C storage under experimental N deposition.	<a href="#">Whittinghill et al. (2012)</a>
Enzyme activity Decomposition	Northern hardwood forest	Minnesota			<b>N Addition:</b> Accelerated the initial decomposition rate. Faster initial decomposition rates corresponded to higher activity of polysaccharide-degrading enzymes and greater relative abundances of Gram-negative and Gram-positive bacteria. Later in decomposition, externally supplied N slowed decomposition, increasing the fraction of slowly decomposing litter, reducing lignin-degrading enzyme activity, and relative abundances of Gram-negative and Gram-positive bacteria.	<a href="#">Hobbie et al. (2012)</a>

**Table 4–8 (Continued): Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Decomposition	Deciduous forests	Catskill Mountains of southeastern New York, U.S.	9.0	50 mg N/ha/yr N (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> N addition caused decrease in mineralization and nitrification and an increase in forest floor C pools and C:N, indicating that N addition increased C sequestration in the organic horizons of the soil, most significantly in hemlock plots.	<a href="#">Lovett et al. (2013)</a>
Enzymes Decomposition	Northern hardwood forest	Upper Michigan	15 to 20	30	<b>N Addition:</b> Caused slower organic matter decay and altered microbial community composition and function. Observed a decrease in the abundance and richness of key protein-coding genes in archaea and bacteria responsible for N fixation, ammonification, denitrification, and assimilatory NO <sub>3</sub> <sup>-</sup> reduction; the same was true for bacterial genes mediating nitrification and dissimilatory NO <sub>3</sub> <sup>-</sup> reduction.	<a href="#">Freedman et al. (2013)</a>
Enzymes Decomposition	Sugar maple forests	Michigan	5.8 to 7.3	30	<b>N Addition:</b> (1) significantly altered the composition of actinobacterial and fungal genes mediating plant and fungal cell wall depolymerization; (2) significantly decreased the richness and diversity of genes involved in the depolymerization of starch (~12%), hemicellulose (~16%), cellulose (~16%), chitin (~15%), and lignin (~16%); and (3) resulted in small changes in community composition (25% difference in fungi; 18% in actinobacteria).	<a href="#">Eisenlord et al. (2013)</a>
Enzymes Decomposition	Northern hardwood forest	Upper Michigan	15 to 20	30 as six equal applications of NaNO <sub>3</sub> pellets delivered to the forest floor over the growing season	<b>N Addition:</b> Observed that atmospheric N deposition increases saprotrophic bacterial laccase-like multicopper oxidases (LMCOs). These results suggest a plausible mechanism by which anthropogenic N deposition has reduced decomposition, increased soil C storage, and accelerated phenolic DOC production.	<a href="#">Freedman and Zak (2014)</a>
Decomposition fungal residue	Forest	Switzerland	Not specified	7 (NH <sub>4</sub> NO <sub>3</sub> ) 70 (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> Promoted the production of new fungal residues but slowed the decomposition of old residues in forest soil fractions. Preservation of old microbial residues could be due to decreased N limitation of microorganisms and therefore a reduced dependence on organic N sources.	<a href="#">Griepentrog et al. (2014)</a>

**Table 4–8 (Continued): Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Enzyme activity	Northern hardwood and softwood forest	Bear Brook Watershed (BBWM), ME, U.S.		25.5	<b>N Addition:</b> After 22 yr of N addition, N enrichment had little effect on microbial enzyme activity in terrestrial compartments, even across varying degrees of organic matter recalcitrance.	<a href="#">Mineau et al. (2014)</a>
Soil respiration	Multiple biomes	Global		Varied	<b>Meta-analysis:</b> N addition significantly increased soil respiration by 2.0% across all biomes but decreased respiration by 1.44% in forests and increased it by 7.84 and 12.4% in grasslands and croplands, respectively ( $p < 0.05$ ).  The response ratios of soil respiration to N addition were positively correlated with mean annual temperature (MAT), most significant when MAT was less than 15°C. N addition largely altered root and microbial biomass and soil C content, which are likely the mechanisms behind the altered soil respiration.	<a href="#">Zhou et al. (2014a)</a>
Decomposition	Grassland	Minnesota, Nebraska, Iowa, Kansas; Colorado	3.1 to 18	100	<b>N Addition:</b> Decreased microbial respiration of OM by as much as 29% relative to control plots, and consequently, decreased C loss from this pool.	<a href="#">Riggs et al. (2015)</a>
Decomposition	Forest	Great Lakes region	6.8 to 11.8	30 as NaNO <sub>3</sub>	<b>N Addition:</b> Fine root biochemistry was less responsive than leaf litter to long-term simulated N deposition. Fine roots were the dominant source of difficult-to-decompose plant C fractions entering the soil.  When combined with litter production, simulated N deposition increased N flux through leaf litter by an average of 29% but did not affect fine root N flux.	<a href="#">Xia et al. (2015)</a>
Enzyme activity	Subalpine forest	Loch Vale watershed (LVWS) is in Rocky Mountain National Park (RMNP) on the eastern edge of the Colorado Front Range.	3–4 kg N/ha/yr (wet)	25 kg NH <sub>4</sub> NO <sub>3</sub> /ha/yr (1996–present)	<b>N Addition:</b> There were no changes in the C degrading enzyme activity in response to fertilization, while the N degrading enzyme activity was enhanced with elevated activity of leucine aminopeptidase (LAP) and marginally significant increase in N-acetyl-β-glucosaminidase (NAG) with N fertilization.	<a href="#">Boot et al. (2016)</a>

**Table 4–8 (Continued): Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Enzyme activity	Northern hardwood forest	Michigan	5.9–7.4 kg N/ha/yr (not specified if wet, dry, or total)	30 kg NaNO <sub>3</sub> /ha/yr (beginning in 1994)	<b>N Addition:</b> This long-term experiment found N deposition decreased the activity reduced the activity of extracellular enzymes mediating plant cell wall decay.	<a href="#">Freedman et al. (2016)</a>
Soil respiration	Northern hardwood forest	White Mountain National Forest, NH; Bartlett, Hubbard Brook, and Jeffers Brook Forests	8 kg N/ha/yr (wet + dry) (20th century average at HBEF)	30 kg N/ ha/yr (NH <sub>4</sub> NO <sub>3</sub> ), 10 kg P/ha/yr (NaH <sub>2</sub> PO <sub>4</sub> ), or N + P (treatments in year 2011)	<b>N Addition:</b> The greatest reduction in soil respiration on N and N + P fertilized plots occurred on the sites with lowest pretreatment soil N mineralization and litterfall N flux. Nutrient additions did not significantly affect either fine root turnover (minirhizotrons) or microbial respiration (laboratory incubations).	<a href="#">Kang et al. (2016)</a>
Decomposition	Restored tallgrass prairie	Prairie Invasion and Climate Experiment (PRICLE) Loveland, CO	~1/3 of N added	5 g N/m <sup>2</sup> /yr urea. “Seasonal maximum 5-day cumulative rainfall” increased by 33 (2012) and 9% (2013)	<b>N Addition:</b> Increasing rainfall variability and N addition can stimulate litter decomposition in tall grass prairie.	<a href="#">Schuster (2016)</a>
Decomposition	All ecosystems	Global	Not specified	Not specified	<b>Meta-analysis:</b> 198 peer-reviewed journal articles found N addition did not significantly alter litter decomposition, soil respiration (except for wetlands, +28.26%), and microbial respiration (except for forests, +9.08).	<a href="#">Yue et al. (2016)</a>

**Table 4–8 (Continued): Decomposition.**

Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Addition kg/ha/yr	Effect of Deposition	Reference
Decomposition	Mixed hardwood forest dominated by black and red oak ( <i>Quercus velutina</i> and <i>Q. rubra</i> )	Chronic Nitrogen Amendment Study (CNAS) located at the Harvard Forest Long-Term 57 Ecological Research (LTER) site in Petersham, MA, USA		50–150	Changes in litter decay by was generally lower in the N treatment microbes compared to control microbes for the same species, a response not readily reversed when N microbial isolates were grown in low N environments. Changes in fungal behaviors accompany and perhaps drive previously observed N induced shifts in fungal diversity, community composition, and litter decay dynamics.	<a href="#">van Diepen et al. (2017)</a>
Decomposition	Forest	Scotland	14–16 kg N/ha/yr	1.18 g <sup>15</sup> N in 4m plot	Litter decomposition is a larger source of N for trees than simulated N deposition.	<a href="#">Nair et al. (2017)</a>

BBWM = Bear Brook Watershed; C = carbon; DOC = dissolved organic carbon; ha = hectare; kg = kilograms; LMCO = Laccase-like multicopper oxidase; mg = milligrams; N = nitrogen; <sup>15</sup>N = nitrogen-15; NaNO<sub>3</sub> = sodium nitrate; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; <sup>15</sup>NO<sub>3</sub><sup>-</sup> = nitrogen-15-labeled nitrate; OM = organic matter; S = sulfur; SOM = soil organic matter; yr = year.

The body of knowledge published since the 2008 ISA indicates the effects of N on decomposition rates are inconsistent among studies. New field work supported the concept that N deposition suppresses decomposition ([Riggs et al., 2015](#); [Zak et al., 2008](#)). Likewise, [Kang et al. \(2016\)](#), in a large-scale N addition study of 13 northern hardwood forests in the U.S., supported the findings that N addition decreases forest respiration and further identified the greatest reduction in soil respiration on N fertilized plots occurred on the sites with lowest pretreatment soil N mineralization and litterfall N flux ([Kang et al., 2016](#)). In contrast, meta-analysis that evaluated the central tendencies of N addition on total soil respiration in forest biomes reported inconsistent results, including an increase ([Yue et al., 2016](#)), decrease ([Zhou et al., 2014a](#)), and no effect ([Liu and Greaver, 2010](#)). Meta-analyses that looked for the central tendencies of terrestrial soil respiration to N addition also have inconsistent results; two meta-analyses found that N did not alter total soil respiration in terrestrial soils ([Yue et al., 2016](#); [Liu and Greaver, 2010](#)), another identified an increase ([Zhou et al., 2014a](#)), and only one identified a decrease ([Janssens et al., 2010](#)). The different results in the meta-analyses reflect slightly different selection criteria the authors used to determine which studies to include in the analyses. Among biomes, differences in soil respiration may result largely from stimulation of autotrophic respiration by N addition to croplands and grasslands compared with no significant change for forests, and a simultaneous decline in heterotrophic/microbial respiration in most biomes [[Liu and Greaver \(2010\)](#); [Zhou et al. \(2014a\)](#), with the exception of croplands, tropical forests, and boreal forests].

One proposed mechanism for reduced microbial decay under increased N deposition is a shift in the species composition of the microbial community with the consequence of decreased lignin decomposition. Lignin is an organic polymer, particularly important in cell wall formation of vascular plants. Under N addition, the microbial community would shift from basidiomycete fungal activity, some of which oxidize lignin in plant detritus and polyphenols in SOM to CO<sub>2</sub>, to more metabolism by bacteria and ascomycete fungi (cellulose degraders), which only partially oxidize these organic substrates ([Freedman and Zak, 2014](#); [Zak et al., 2011](#)). There is new evidence to support this theory in northeastern hardwood forests in the U.S. where N enrichment increases the species richness and diversity of ascomycetes generally [cellulose degraders; [Morrison et al. \(2016\)](#)], with evidence that observed changes in decay abilities were not readily reversed when N isolates were grown in control environments, indicating that the fungal community may not recover quickly following the cessation of N enrichment [[van Diepen et al. \(2017\)](#); see [Appendix 6](#)].

There is new evidence to support that lignolytic enzyme activity decreases under N addition ([Freedman et al., 2016](#); [Keeler et al., 2009](#); [Manning et al., 2008](#)). This trend is also supported by a meta-analysis by [Whittinghill et al. \(2012\)](#), who found that N

addition decreased lignin decomposition rates by 30% and increased cellulose decomposition by 9%. Fine roots are likely the dominant source of difficult-to-decompose plant carbon fractions entering the soil, and this pattern appears to be widespread in boreal and temperate forests ([Xia et al., 2015](#)).

There are cases in which N addition causes no change in enzyme activity of microbes; for example, the hardwood and softwood forests growing in the Bear Brook Watershed in Maine ([Mineau et al., 2014](#)) and C degrading enzymes in a subalpine forest ([Boot et al., 2016](#)). Another study in the Catskill Mountains of New York State found that patterns in microbial community structure and function (detected by enzyme activity) were more strongly influenced by the tree species present than by fertilization ([Weand et al., 2010](#)).

Microbial decomposition response to N addition may also change through time. The 2008 ISA documented an N addition study lasting longer than 2 years that indicated that a shift can occur from stimulation to depression of decomposition over time ([Knorr et al., 2005](#)). In a study looking at changes through time of the organic layer, [Hobbie et al. \(2012\)](#) suggested N deposition in forest ecosystems may decrease mean residence times of active fractions in fresh litter, while increasing those of more slowly decomposing fractions, including more processed litter. In boreal forests, [Talbot and Treseder \(2012\)](#) found a transition over time from competition among decomposers to high cellulase activity and suppressed lignin loss under N fertilization. The trend suggests that, in N limited systems, N fertilization may alter decomposer community structure by favoring a shift toward cellulose- and mineral-N users.

There is also new evidence that experimental N deposition significantly decreased the richness and diversity of microbial genes involved in the depolymerization of starch (12%), hemicellulose (16%), cellulose (16%), chitin (15%), and lignin (16%) ([Eisenlord et al., 2013](#)).

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#### 4.3.8 Nitrogen Mineralization

Mineralization refers to processes that release carbon as CO<sub>2</sub> and nutrients in inorganic form. Nitrogen mineralization is the process by which organic N is converted to plant-available inorganic forms. The 2008 ISA documented that the rate of mineralization may be influenced by numerous factors including C:N of soil organic matter, soil pH, and the microbial community. N mineralization has been shown to increase with increasing N addition ([Aber et al., 1998](#)), often up to 1.6 times the control ([Gundersen et al., 1998](#)).

New publications ([Table 4-9](#)) support that soil N mineralization increases with N addition across terrestrial ecosystems ([Lu et al., 2011a](#)), specifically in temperate forests ([Nave et](#)

[al., 2009a](#)), likely due to increases in dissolved organic nitrogen (DON), the size of the N pool in the soil, and decreases in C:N ratios. The forest floor responds differently than the deeper mineral soil layer [[Figure 4-7](#); [Nave et al. \(2009a\)](#); [Lovett et al. \(2013\)](#)].

In two forested headwater catchments in Ontario, [Casson et al. \(2014a\)](#) found that N mineralization and nitrification rates were similar, indicating that almost all mineralized N was converted to  $\text{NO}_3^-$  (ranging from 71 to 99%) in catchments they studied. While [Bade et al. \(2015\)](#) found in old-growth spruce forests, lower N mineralization occurred in the more open patches than the closed ones. Possible reasons were reduced litter supply and lower canopy N interception in gaps in this forest under exposure to high N deposition. Further studies in other old-growth forests are needed to better understand the mechanisms causing long-term change in N cycling with forest development.

In desert shrublands, [Rao et al. \(2009\)](#) found that N deposition may increase production and/or alter litter C:N ratios that increase soil C. There was an inverse relationship between the C:N ratio and total N mineralized, yet a positive relationship between organic C and total N with mineralization. These results indicate that microbial activity in low productivity arid land soils is primarily limited by C and secondarily limited by N.

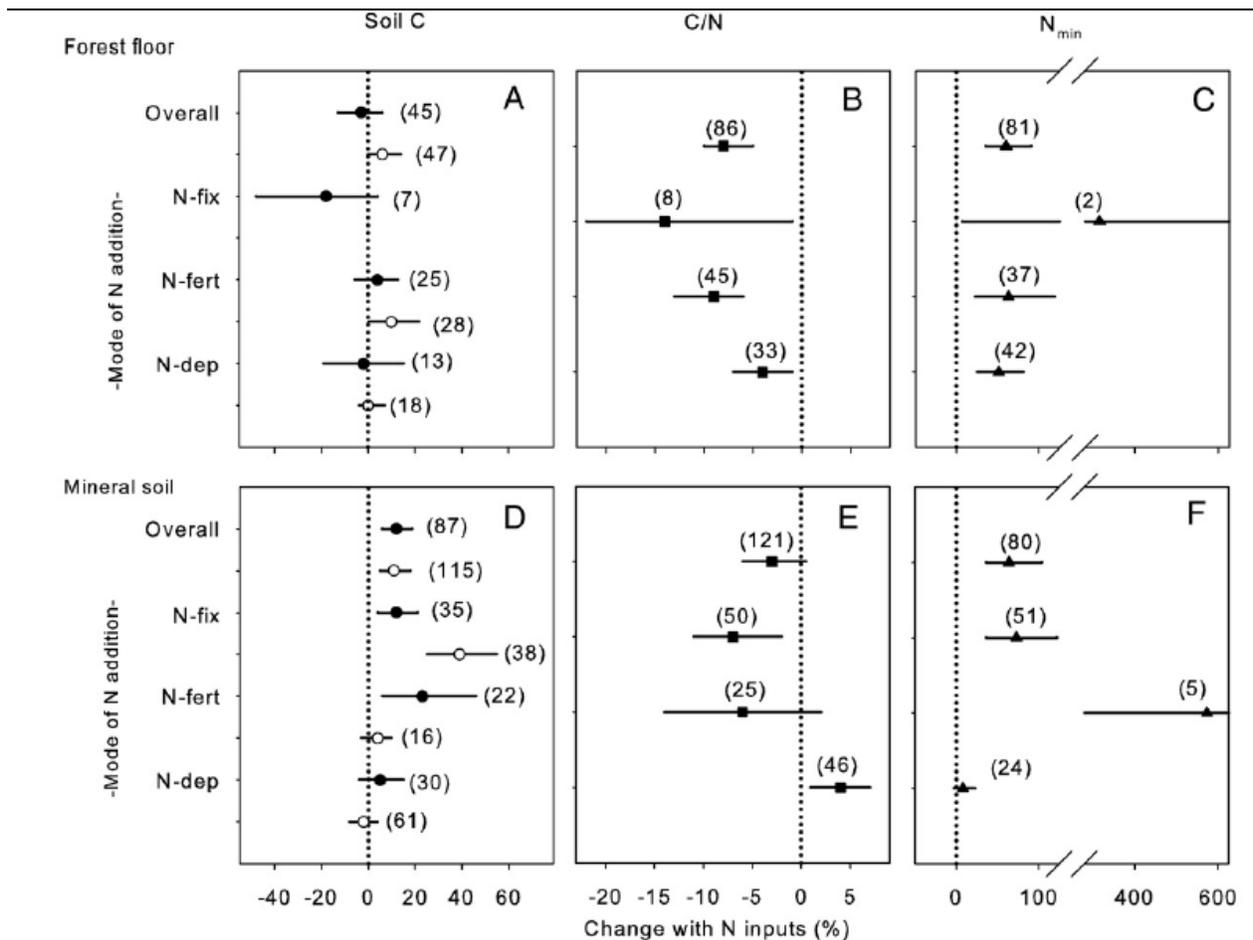
**Table 4-9 Nitrogen mineralization.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Mineralization	Semiarid	Southern California, U.S.	Up to 35–45 for N	Two applications per year of 30 kg N	N is mineralized at a faster rate from grass litter enriched in N as a result of N deposition.	<a href="#">Sirulnik et al. (2007a)</a>
Mineralization	Semiarid	Southern California, U.S.	Up to 35–45 for N	Two applications per year of 30 kg N	When significantly lower microbial N was reported in fertilized plots it corresponded to faster net N mineralization. When higher microbial N was observed in fertilized plots it corresponded to net immobilization (though not significantly faster), thus corroborating evidence that the microbial community was taking up more N in fertilized plots. These rates may have corresponded to C availability, which was not measured.	<a href="#">Sirulnik et al. (2007b)</a>
Mineralization soil [N] soil [Ca]	Mixed hardwood stands	Adirondack Mountains, NY, U.S.	Not specified	None	<b>Ca Gradient:</b> The exchangeable Ca coupled with soil moisture, soil organic matter, and ambient temperature accounted for 61% of the variability in extractable inorganic N across 11 sites. The influence of Ca on soil inorganic N may be through interactions between soil Ca concentrations and species composition, which in turn affect the quality of litter available for N mineralization.	<a href="#">Page and Mitchell (2008)</a>
Decomposition Enzyme activities	Spruce forest	Germany	8.5		<b>N Exclusion:</b> Some N cycling enzymes increased activities, whereas others decreased under reduced N treatment.	<a href="#">Enowashu et al. (2009)</a>
N mineralization	Desert	Joshua Tree National Park	2.7 to 14.4		Calculated soil N from deposition was directly correlated with measured soil C and N and decreasing C:N ratios.	<a href="#">Rao et al. (2009)</a>

**Table 4–9 (Continued): Nitrogen mineralization.**

Process Endpoint	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
N mineralization	Temperate forests.	Northeastern U.S.	Varies	Varies	<b>Meta-analysis:</b> Overall, N inputs increased soil C (+7.7%) and N mineralization (+62%), while decreasing C:N (-4.9%).	<a href="#">Nave et al. (2009a)</a>
N mineralization	Forest			50 (6 yr of N addition)	<b>N Addition:</b> There was a significant decline in potential N mineralization and nitrification rates in the mineral horizon but not in the forest floor.	<a href="#">Lovett et al. (2013)</a>
N mineralization	Terrestrial ecosystems		Varies	Varies	<b>Meta-analysis:</b> included 206 papers on responses of ecosystem N cycle caused by N addition. N addition increased mineralization rates.	<a href="#">Lu et al. (2011a)</a>
N mineralization	Douglas fir forest	Oregon coast range	2.0	None	Aboveground N uptake by plants increased with net N mineralization, peaking at 35 kg N/ha/yr.	<a href="#">Perakis and Sinkhorn (2011)</a>
Net N mineralization and nitrification rates/NH <sub>4</sub> <sup>+</sup> N, soil NO <sub>3</sub> <sup>-</sup> , stream NO <sub>3</sub> <sup>-</sup>	Mixed hardwood forested headwater catchments	Muskoka-Haliburton district of south-central Ontario, Canada	NO <sub>3</sub> <sup>-</sup> deposition 2.78 ± 1.22; NH <sub>4</sub> <sup>+</sup> deposition 3.90 ± 1.39	Not applicable	In all seasons, rates of nitrification were similar to rates of total mineralization, indicating that almost all mineralized N is converted to NO <sub>3</sub> <sup>-</sup> in both soil types (ranging from 71 to 99%).	<a href="#">Casson et al. (2014a)</a>
N mineralization, ammonification, nitrification/NO <sub>3</sub> <sup>-</sup>	Natural (unmanaged) old-growth Norway spruce forest	Harz National Park in central Germany	27 (open areas) 47 (closed forest)	Not applicable	Net N mineralization (and ammonification) rates were higher in the closed stands of the optimum and overmature stages than in the more open decay and regeneration stages. Only a small proportion of NH <sub>4</sub> <sup>+</sup> was oxidized to NO <sub>3</sub> <sup>-</sup> in the acidic soils.	<a href="#">Bade et al. (2015)</a>
Net litter mineralization	Forest	Scotland	14–16 kg N/ha/yr	1.18 g <sup>15</sup> N per 4m plot	Three times as much <sup>15</sup> N was retained in the O and A soil layers when N was derived from litter decomposition than from mineral N additions.	<a href="#">Nair et al. (2017)</a>

C = carbon; Ca = calcium; ha = hectare; kg = kilogram; N = nitrogen; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; yr = year.



C = carbon; C/N = carbon-to-nitrogen ratio; N = nitrogen; N-dep = nitrogen deposition; N-fert = nitrogen-fertilization; N-fix = nitrogen-fixing vegetation; N<sub>min</sub> = nitrogen mineralization.

Points are means ± bootstrapped 95% confidence intervals, with number of studies in parentheses. Groups with confidence intervals overlapping the dotted reference line (0% change) show no significant effects of N addition. Soil carbon responses to nitrogen inputs are shown separately for pool sizes (filled symbols) and concentrations (open symbols). For each response parameter, the effects of nitrogen inputs are shown overall, and for individual modes of nitrogen addition, including the establishment of nitrogen-fixing vegetation, large-dose nitrogen-fertilization, and simulated chronic nitrogen deposition. Note that points plotted in panels C and F have 95% confidence intervals with upper-bounds beyond the x-axis maximum.

Source: [Nave et al. \(2009a\)](#).

**Figure 4-7** Effects of nitrogen inputs on soil carbon, carbon:nitrogen ratio, and minimum nitrogen in forest floors (panels A–C) and mineral soils (panels D–F).

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### 4.3.9 Dissolved Organic Carbon Leaching

The acid-base characteristics of dissolved organic matter (DOM) are an important part of understanding the recovery potential for soils, lakes, and streams impaired by acid deposition. The composition of DOM includes fulvic and humic acids, carboxylic acids, and amino acids; dissolved organic carbon (DOC) includes these organic acids. Here we focus on the DOC component of DOM. The many carboxylic groups of DOC make it chemically interact like a weak acid; therefore, DOC content may affect pH levels. In addition, [Fakhraei and Driscoll \(2015\)](#) emphasized the importance of predicting accurately the acid-base properties of recovering surface waters because, for example, the acidic components of DOC act as hosts for binding trace metals like toxic  $Al_i$  (for additional discussion on  $Al_i$  and DOM see [Appendix 4.3.5](#)).

In recent years, the DOC of many lakes and streams has risen, with the likely source being the soils in the adjacent terrestrial watershed. However, the mechanism causing the observed increase is unclear. The increase may be due to a combination of soil recovery from acidification, changes in climate (e.g., temperature and precipitation), and N deposition, among other mechanisms [for reviews see [Kalbitz et al. \(2000\)](#); [Evans et al. \(2005\)](#)]. New studies in the literature have investigated soil DOC response to acidification (N + S deposition) and/or looked at the effects of N addition; these studies will be the focus of the following discussion ([Table 4-10](#)). For a discussion of DOC in surface water see [Appendix 7](#).

**Table 4-10 Terrestrial dissolved organic carbon (DOC) leaching.**

Process	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
DOC	Bog, heathland, grassland, broadleaf and coniferous forest	Synthesis of 17 addition experiments in the northeastern U.S. and northern Europe	Ranged from 5–16 N dep	Ranged from 10 to 150 N (chemical forms for N varied)	<b>Synthesis:</b> N had inconsistent effect on DOC; however, the form of N applied indicates nonacidifying forms of N tend to increase DOC concentrations.	<a href="#">Evans et al. (2008)</a>
DOC	Temperate mixed and conifer forests, boreal forests, grasslands, tropical forests, arctic, wetlands, desert, and tundra	410 observations globally	Not specified	10 to 650	<b>Meta-analysis:</b> N addition increases short-term belowground C storage by increasing C content of the organic layer. N addition; increased DOC concentration (+18%); and increased C content of the organic soil layer (+17%) but not the mineral soil layer.	<a href="#">Liu and Greaver (2010)</a>
DOC	Norway spruce ( <i>Picea abies</i> ) forests	Southern Sweden	Not specified	Not specified	<b>Model:</b> The Stockholm Humic Model was used to model DOC solubility in soil water and predicted that DOC trends could vary between positive and negative depending on changes in pH, ionic strength, and soil Al pools.	<a href="#">Lofgren et al. (2010)</a>

**Table 4-10 (Continued): Terrestrial dissolved organic carbon (DOC) leaching.**

Process	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
DOC	Beech forest stands on calcareous soils	Swiss Jura mountain range	Not specified	5.5 (NH <sub>4</sub> NO <sub>3</sub> )	<b>N Addition:</b> Leaching of DOC from the litter layer was not affected by N additions, but DOC fluxes from the mineral soils at 5- and 10-cm depth were significantly reduced by 17%. <sup>13</sup> C indicated that litter-derived C contributed less than 15% of the DOC flux from the mineral soil, with N additions not affecting this fraction. Hence, the suppressed DOC fluxes from the mineral soil at higher N inputs can be attributed to reduced mobilization of nonlitter derived “older” DOC.	<a href="#">Hagedorn et al. (2012)</a>
DOC	None— theoretical	None— theoretical	Not specified	Not specified	<b>N Addition:</b> Increases mineralization causing the pool of bioavailable DOC to decrease. Consequently, relatively less bioavailable DOC remains for NH <sub>4</sub> <sup>+</sup> assimilation and immobilization in microbial biomass, leaving more NH <sub>4</sub> <sup>+</sup> for nitrifiers. As a result, internal NO <sub>3</sub> <sup>-</sup> production increased. The higher bacterial demand for DOC under elevated availability of N and electron acceptors comes into conflict with increasing chemical suppression of DOC solubility and bioavailability in the progressively acidifying soils and finally results in the C limitation of microbial metabolism.	<a href="#">Kopáček et al. (2013)</a>
DOC	Northern hardwood forest	Upper Michigan	15 to 20 kg N/ha/yr	30 (as six equal applications of NaNO <sub>3</sub> pellets delivered to the forest floor over the growing season)	<b>N Addition:</b> N addition accelerated phenolic DOC production.	<a href="#">Freedman and Zak (2014)</a>

**Table 4-10 (Continued): Terrestrial dissolved organic carbon (DOC) leaching.**

Process	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
DOC	Forest and streams	Hubbard Brook Experimental Forest, NH	Variable	None	<b>Field observation:</b> Concentrations of DOC showed statistically significant declines in the Oa soil solutions of all three elevation zones, and a subset of the Bs soil solutions over the period of 1984–2011.	<a href="#">Fuss et al. (2015)</a>
DCO	Lakes	Adirondack Long-Term Monitoring (ATLM) Program lakes at Huntington Forest and Whiteface Mountain, Adirondack Mountains, NY	Variable	None	<b>Field observation:</b> increasing DOC in 29 of 48 lakes as lake pH increased.	<a href="#">Driscoll et al. (2016)</a>
DOC	Forest and grassland	U.K.	Mean 1993 to 2010 gradients of deposition: S: 44 to 86 meq/m <sup>2</sup> /yr; N: 40 to 90 meq/m <sup>2</sup> /yr; Cl: 94 to 306 meq/m <sup>2</sup> /yr	None	<b>Modeling:</b> Using the MADOC model, the acidifying effect of S deposition was the predominant control on the observed soil water DOC trends. The relative importance of S and N loading depended on soil sensitivity to acidification, and on N limitation.	<a href="#">Sawicka et al. (2017)</a>

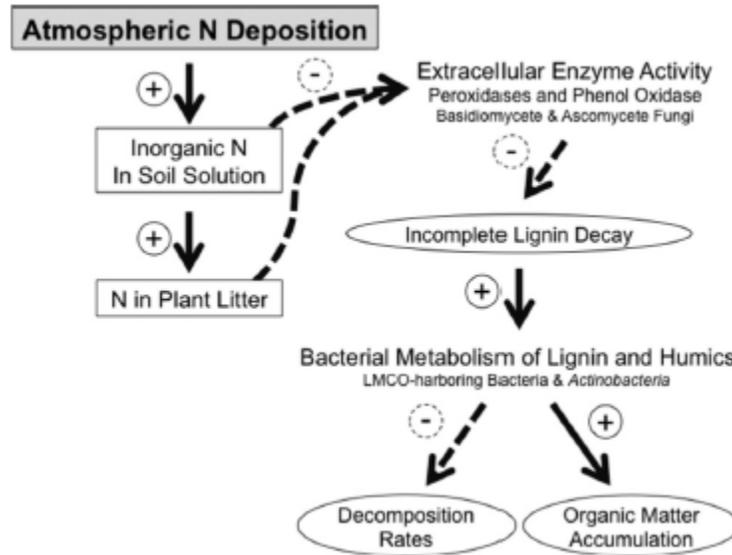
<sup>13</sup>C = carbon-13; C = carbon; DOC = dissolved organic carbon; ha = hectare; kg = kilogram; N = nitrogen; NaNO<sub>3</sub> = sodium nitrate; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; yr = year.

A number of studies suggest that recovery from acidification is driving the elevated levels of DOC. An inverse relationship between mineral and organic acid export to surface waters from soils was first proposed in the 1980s ([Krug and Frink, 1983](#)). Support for this theory is found in a range of laboratory experiments in which increases in both acidity and ionic strength (associated with a high  $\text{SO}_4^{2-}$  loading) have been shown to reduce soil solution DOC ([Kalbitz et al., 2000](#)). [Evans et al. \(2008\)](#) addressed whether elevated N deposition or recovery from acidification associated with decreasing S cause increased DOC loss from upland soil. Their analysis of a large experimental data set including 12 sites in the U.S. and northern Europe showed that although the response to N addition is inconsistent, DOC concentrations responded predictably to the chemical form of N added. DOC concentrations increased with  $\text{NaNO}_3$  additions or gaseous  $\text{NH}_3$  exposure and decreased with most  $\text{NH}_4^+$  salt additions. The authors cite the effect of the chemical form of N on acidity as a plausible mechanism and further conclude that their evaluation does not provide clear support for the role of N deposition as the sole driver of rising DOC, but is consistent with an acidity-change mechanism. [Evans et al. \(2008\)](#) also stated their finding is consistent with findings based on long-term monitoring data, that DOC increases in northern European and North American surface waters are substantially attributable to regional decreases in acidifying, primarily S, deposition ([Monteith et al., 2007](#); [Evans et al., 2005](#)). New studies also report that N addition has caused inconsistent changes to DOC, with N addition causing both increases ([Driscoll et al., 2016](#); [Liu and Greaver, 2010](#)) and decreases ([Fuss et al., 2015](#); [Hagedorn et al., 2012](#)).

In the Adirondack Long-term Monitoring Program, [Driscoll et al. \(2016\)](#) measured increasing DOC in 29 of 48 monitored lakes as lake ANC and pH increased. In contrast, decreases in DOC concentrations were observed in the soil solution from the Oa soil horizon at all sites, the Bs soil horizon soil solution of one site, and the stream water measured at the base of the watershed. These observations were attributed to recovery from acidification in the HBEF, NH ([Fuss et al., 2015](#)). [Fuss et al. \(2015\)](#) considered these results surprising and therefore reviewed European and U.S. research literature, found studies with similar observed trends, and identified a number of potential factors leading to this difference. While surface water DOC generally emanates from soil water DOC (with the possible exception of snowmelt), soil ionic strength and soil Al pools, as well as soil depth, may also influence DOC in soil solution ([Lofgren et al., 2010](#)). Decreasing ionic strength can decrease DOC; higher levels of organic aluminum complexes in soil can increase DOC solubility; and DOC in forest floor soil water may decrease at a faster rate than in mineral soil water. The authors did note that HBEF's rate of decreasing DOC concentrations appeared to be diminishing in the later 15 years of reporting.

Although most studies are on forests, [Sawicka et al. \(2017\)](#) used the MADOC model for three forested and three grassland and heath sites and observed that the acidifying effect of S deposition was the predominant control on the observed soil water DOC trends ([Sawicka et al., 2017](#)). The relative importance of S and N loading depended on soil sensitivity to acidification and on N limitation. In all N limited soils investigated, the modeled DOC increases over the monitoring period were dominated by the effects of recovery from acidification (higher DOC solubility), but the effects of N enrichment driving higher DOC production may have been important in the longer term. In contrast, reductions in nonmarine chloride deposition and the effects of long-term warming appeared to have been relatively unimportant.

Other work has further explored the mechanisms for how N addition (including nutrient as well as acidification effects) affects DOC ([Freedman and Zak, 2014](#); [Kopáček et al., 2013](#)). [Freedman and Zak \(2014\)](#) reported that atmospheric N deposition led to less microbial biodiversity and favored bacterial species in the forest floor that lead to reduced decomposition, increased soil C storage, and accelerated phenolic DOC production ([Figure 4-8](#)). [Kopáček et al. \(2013\)](#) observed that N addition, together with  $\text{SO}_4^{2-}$  deposition, increases the availability of electron acceptors for soil microbial processes. The chemical and microbial responses include an increase in bacterial mineralization creating DOC, increased N mineralization where N availability increases (with an increase in bacterial uptake of DOC), chemical suppression of DOC solubility and bioavailability in the progressively acidifying soils, and finally, the C limitation of microbial metabolism. Bacterial assimilation of  $\text{NO}_3^-$ , which depends on the stoichiometric  $\text{NO}_3^-$  to DOC ratio in the substrate, may initially increase with increasing  $\text{NO}_3^-$  concentrations, but then decrease due to a lower pool of bioavailable DOC.



N = nitrogen; LMCO = Laccase-like multicopper oxidase.

Source: [Freedman and Zak \(2014\)](#).

**Figure 4-8** Conceptual diagram of positive (solid arrows) and negative (dashed arrows) fluxes in nitrogen pools (squares) and carbon pools (ovals) and the biological processes (no border) that are affected by experimental nitrogen deposition.

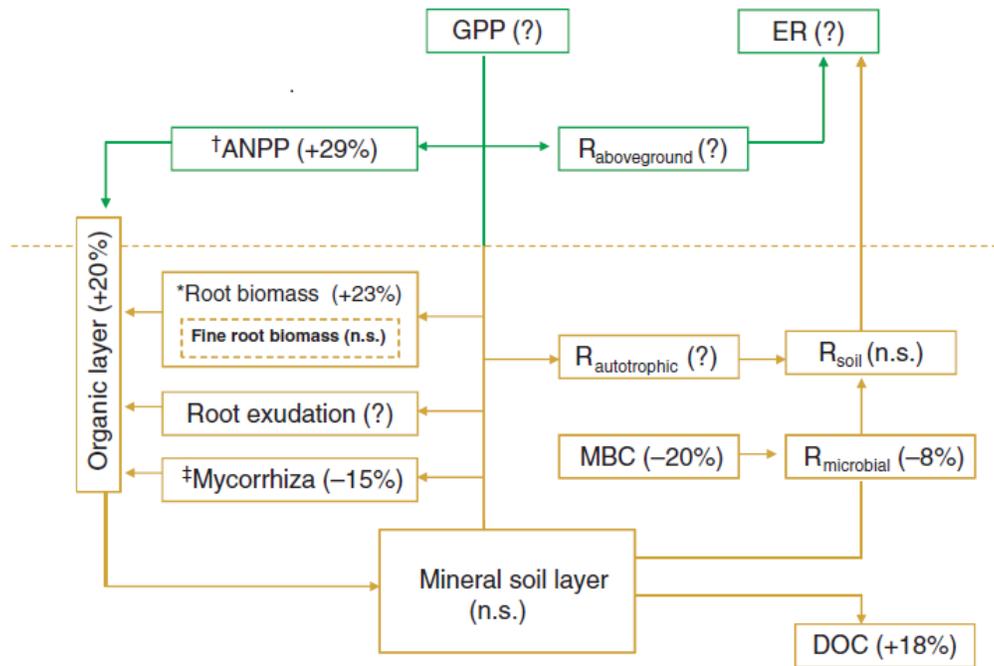
#### 4.3.10 Belowground Carbon Pools

In general, N enrichment influences C flux, C partitioning, and the amount of C sequestered by ecosystems. A number of studies have suggested that C sequestration increases with increasing N supply based on the changes in aboveground net primary production [ANPP; [LeBauer and Treseder \(2008\)](#); [Xia and Wan \(2008\)](#)]. However, about half of the C fixed annually by terrestrial vegetation is allocated to belowground pools. Many studies have shown that the belowground C cycle does not always mirror the aboveground cycle. For example, elevated CO<sub>2</sub> and N both have been shown to increase aboveground biomass production ([LeBauer and Treseder, 2008](#)). However, increases in aboveground plant production and greater aboveground litter inputs do not necessarily increase mineral soil C storage ([Talhelm et al., 2009](#); [Gielen et al., 2005](#); [Lichter et al., 2005](#)), and increases in soil C do not necessarily result from greater aboveground litter inputs ([Pregitzer et al., 2008](#)). This disparity indicates that it is inappropriate to extrapolate from aboveground responses to belowground processes. Aboveground plant biomass, once dropped from the canopy, is one of the major contributors to soil organic

matter accumulation ([Sullivan et al., 2007a](#)). ANPP generally increases with increasing N supply ([LeBauer and Treseder, 2008](#); [Xia and Wan, 2008](#)). However, this increase in C input may not cause an increase in belowground ecosystem C storage. This is because the output of C from the soil may be stimulated by N induced alteration of plant tissue chemistry or the ratio of root:shoot, each of which will change the rate of decomposition (see [Appendix 4.3.7](#)). Since the 2008 ISA was published there have been several new meta-analyses on the effects of N addition on belowground carbon pools ([Janssens et al., 2010](#); [Liu and Greaver, 2010](#)), each integrating information from numerous pools to improve the understanding of how N addition alters the carbon cycle belowground. Additional studies are summarized in [Table 4-11](#).

[Liu and Greaver \(2010\)](#) synthesized data from multiple terrestrial ecosystems to quantify the response of belowground C cycling under N addition ([Figure 4-9](#)). N addition increased aboveground litter inputs (+20%), but fine root litter inputs were unchanged. N addition inhibited microbial activity, as indicated by a reduction in microbial respiration (−8%) and microbial biomass carbon (−20%). Although soil respiration was not altered by N addition, dissolved organic carbon concentration increased (+18%), suggesting C leaching loss may increase. N addition increased the C content of the soil organic horizon (+17%) but not the mineral soil. The increase in organic horizon C was attributed to both increased litter input and decreased decomposition [inferred from the lower microbial respiration rates ([Liu and Greaver, 2010](#))].

Field studies provide additional support for the finding that soil carbon responds differently to N addition depending on the organic (vs. mineral) content of the soil, with organic content tending to decrease with increasing soil depth. In four northern hardwood forests spread across Michigan that received experimental N deposition (additional 30 kg N/ha/yr) for 10 years, [Pregitzer et al. \(2008\)](#) and [Zak et al. \(2008\)](#) reported significant increases in soil C, particularly within the soil organic horizon. These increases occurred despite no increase in aboveground litter production or root turnover. A  $^{15}\text{NO}_3^-$ -labeling experiment revealed that N accumulated in SOM by first flowing through soil microorganisms to plants, which then shed the leaves back to the detrital layer. In a meta-analysis including data from 72 north temperate forests, [Nave et al. \(2009a\)](#) found N addition increased soil C (+7.7%). The forest floor responded differently than the deeper mineral soil layer (5- to 100-cm depth) as increased soil C storage occurred only in the mineral soil (+12.2%), in contrast to the findings of [Liu and Greaver \(2010\)](#) and [Pregitzer et al. \(2008\)](#).



ANPP = aboveground net primary production; DOC = dissolved organic carbon; ER = ecosystem respiration; GPP = gross primary productivity; MBC = microbial biomass carbon; n.s. = nonsignificant;  $R_{\text{aboveground}}$  = aboveground respiration;  $R_{\text{autotrophic}}$  = soil autotrophic respiration;  $R_{\text{microbial}}$  = microbial respiration;  $R_{\text{soil}}$  = total soil respiration.

† data from [LeBauer and Treseder \(2008\)](#); \* data from [Xia and Wan \(2008\)](#); ‡ data from [Treseder \(2004\)](#).

Source: [Liu and Greaver \(2010\)](#).

**Figure 4-9 Estimation of the changes in carbon budget of terrestrial ecosystem under nitrogen addition.**

A new study has evaluated the consistency of N cycling in different ecosystems by synthesizing data across five biomes in California. The results indicated that, across biomes, N concentration in soil has a strong positive correlation to SOC ([Yang et al., 2017](#)). There are also new studies indicating N deposition increases SOM accumulation without altering the biochemical composition ([Zak et al., 2017](#)). New studies on how the response of belowground soil C to N is modified by temperature and precipitation has been published since the 2008 ISA ([Ni et al., 2017](#); [Greaver et al., 2016](#)) and is summarized in [Appendix 4.7](#).

**Table 4-11 Belowground carbon pools.**

Process	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
SOC	Soil	Great Britain	0–2 g N/m <sup>2</sup> /yr	None	<b>Model:</b> Using model N <sup>14</sup> CP for data from ~2,000 N limited field sites, it was predicted that, N deposition increased NPP between the years 1750 and 2010, increasing via detritus SOC by 1.2 kg C/m <sup>2</sup> (~10%). (The authors assumed ~30% error of estimated values.)	<a href="#">Tipping et al. (2017)</a>
SOC	Five biome classes in California: desert, grassland, shrubland, forest, wetland	California	0.6–18.4 kg N/ha/yr	Grassland soil: 76.4 kg N/ha/yr as NPK (29:3:4); desert soil: 60 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> ; shrubland soil: 60 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub>	<b>Synthesis:</b> Across biomes, total N concentration was strongly correlated to SOC ( $R^2 = 0.88$ ; $\log(y) = [0.81 \times \log(x)] - 1.10$ ).	<a href="#">Yang et al. (2017)</a>
SOC	Hardwood forest birch ( <i>Betula platyphylla</i> ) and aspen ( <i>Populus davidiana</i> )	Jilin province, China	23 kg N/ha/yr	0 kg N/ha/yr, 25 kg N/ha/yr, and 50 kg N/ha/yr	<b>N Addition:</b> This was a 6-yr fertilization study. The authors observed that fertilization decreased the fraction of macroaggregates (2–8 mm) and increased the fraction of 0.053–2 mm aggregates. ( $P = 0.01$ ). They concluded that N deposition (as simulated with fertilization) can increase formation of micro- and macroaggregates within macroaggregate soil and thus stabilize C.	<a href="#">Chen et al. (2017)</a>

**Table 4-11 (Continued): Belowground carbon pools.**

Process	Type of Ecosystem	Region	Ambient N/S Deposition kg/ha/yr	N/S Addition kg/ha/yr	Effect of Deposition	Reference
Soil organic matter	Sugar maple ( <i>Acer saccharum</i> )-dominated northern hardwood forests	North-south geographic range of sugar maple-dominated upper Great Lakes and eastern North America	6.8–11.8 kg N/ha/yr (wet + dry) across sites	30 kg NO <sub>3</sub> <sup>-</sup> -N/ha/yr (NaNO <sub>3</sub> )	<b>N Addition:</b> SOM accumulated as soil particulate organic matter occlusion at N addition sites.	<a href="#">Zak et al. (2017)</a>
Abundance of carboxyl, aryl, O/N-alkyl, and alkyl C in mineral soil (biochemical composition of forest floor [Oe/Oi-horizon ~4 cm] and organic matter)	Sugar maple ( <i>Acer saccharum</i> )-dominated northern hardwood forests	North-south geographic range of sugar maple-dominated upper Great Lakes and eastern North America	6.8–11.8 kg N/ha/yr (wet + dry) across sites	30 kg NO <sub>3</sub> <sup>-</sup> -N/ha/yr (NaNO <sub>3</sub> )	<b>N Addition:</b> Abundance of carboxyl and aryl C in forest floor differed across sites but the abundance of O/N-alkyl and alkyl C did not ( <i>P</i> = 0.10–0.80). No difference was observed in the proportion of aryl, O/N-alkyl, or alkyl C in mineral soil between ambient deposition and N addition sites. (Particulate organic matter's increased occlusion of organics may shift fungal and bacterial activity toward partial oxidation of organics without changing biochemistry of organic matter.)	<a href="#">Zak et al. (2017)</a>

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#### 4.3.11 New Biogeochemical Indicators

In this section, we report on new biogeochemical indicators reported in the literature since the 2008 ISA. Recent literature offering potential new indicators of biogeochemical change due to N and/or S deposition included fungal-to-bacterial ratio ([Högberg et al., 2013](#)) and syntaxonomic associations [[Wamelink et al. \(2011\)](#); [Table 4-12](#)].

[Högberg et al. \(2013\)](#) proposed soil microbial community indices as predictors of soil solution chemistry and N leaching in *Picea abies* spruce forests in southern Sweden. Stands with low concentrations of  $\text{NO}_3^-$  and  $\text{Al}^{3+}$  had higher fungi:bacteria ratios compared with stands with higher concentrations of  $\text{NO}_3^-$  and Al. They identified three promising microbial community indices as indicators of N leaching from forests; the soil fungi:bacteria ratio was the most important.

In a study in the Netherlands, [Wamelink et al. \(2011\)](#) examined whether the abiotic ranges of syntaxonomic units (associations) in terms of pH and  $\text{NO}_3^-$  concentration can be estimated and then, in principle, used to estimate critical loads for acid and N deposition. They used splines to estimate abiotic ranges of syntaxonomic units based on measured soil pH and  $\text{NO}_3^-$  concentration and vegetation relevés. They acknowledge it is not yet possible to directly estimate ranges for syntaxa for pH and  $\text{NO}_3^-$  on a large scale using this approach; however, indirectly estimated soil pH and  $\text{NO}_3^-$  concentrations are sufficiently available to derive ranges for many associations.

**Table 4-12 New biogeochemistry indicators.**

Endpoint	Nutrient Enrichment Indicator	Acidification Indicator	Deposition kg/ha/yr	Addition kg/ha/yr	Description/Direct Effect of Soil/Water Endpoint on Biological Effect	Reference
N leaching		X	Throughfall N includes wet and dry inputs and ranged from 2.7 to 19	20 (NH <sub>4</sub> NO <sub>3</sub> )	Microbial community composition in the organic layer of spruce forests and soil solution chemistry below the rooting zone was highly correlated. Stands with low concentrations of NO <sub>3</sub> <sup>-</sup> and Al were fungi dominated and had a higher fungi:bacteria ratio compared with stands with high concentrations of these leachates. Leaching stands had higher abundance of Gram-positive bacteria.	<a href="#">Högberg et al. (2013)</a>
Vegetation health	X	X	Not specified	None	Acknowledge the approach is not yet possible to directly estimate ranges for syntaxa for pH and NO <sub>3</sub> <sup>-</sup> on a large scale; however, indirectly estimated soil pH and NO <sub>3</sub> <sup>-</sup> concentrations are sufficiently available to derive ranges for many associations.	<a href="#">Wamelink et al. (2011)</a>

Al = aluminum; ha = hectare; kg = kilogram; N = nitrogen; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NO<sub>3</sub><sup>-</sup> = nitrate; yr = year.

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#### 4.3.12 Differential Effects of Reduced and Oxidized Nitrogen

Some biogeochemical process responses to N deposition have the potential to vary depending on whether the dominant form of deposited N was oxidized or reduced. We have focused on presenting meta-analyses as they synthesize the central tendencies of many studies. In some cases, the results for a given endpoint are not consistent among meta-analyses. [Table 4-13](#) summarizes the studies that look at the most common forms of N.

Additional studies include the observation by [Evans et al. \(2008\)](#) that DOC concentrations responded predictably to the chemical form of N used for manipulation, increasing with NaNO<sub>3</sub> additions or gaseous NH<sub>3</sub><sup>+</sup> exposure, and decreasing with most NH<sub>4</sub><sup>+</sup> salt additions ([Appendix 4.3.9](#)). The authors cite the effect of the chemical form of N on acidity as a plausible mechanism. [Ramirez et al. \(2010a\)](#) investigated whether soil microbes in three distinct soils (from aspen, pine, and grassland ecosystems) respond differently to six different reduced and oxidized N species, including NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>2</sub>)<sub>2</sub>CO (urea), KNO<sub>3</sub>, NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> (also discussed in [Appendix 6](#)). The authors found that all inorganic forms of N fertilizer significantly decreased microbial CO<sub>2</sub> production but that organic N (urea) decreased the respiration rate in forest soil only by 27% (aspen) and 11% (pine) and increased the grassland microbial respiration rate by 20%. They added that the soil pH change resulting from N addition did not appear to influence the observed decrease in the soils' microbial respiration rate.

[Jovan et al. \(2012\)](#) monitored tree trunk pH during their research on eutrophic lichen abundance in the Los Angeles air basin, oxidized forms of N (particularly HNO<sub>3</sub>) dominate dry deposition. They noted that NH<sub>3</sub> deposition would normally raise bark pH but in the arid, hot Mediterranean climate of the study area, high trunk pH dust raises bark pH.

**Table 4-13 The effects of different forms of inorganic nitrogen on biogeochemical processes and indicators according to meta-analyses. See [Table 6-1](#) for the effects of different forms of inorganic nitrogen on biological endpoints.**

Process/Indicator	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> NO <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>	Urea	UAN	Reference
Total soil C	NS	NS	NS	NS	NS	<a href="#">Liu and Greaver (2010)</a>
Total soil C	NS	↑	NS	NS	-	<a href="#">Yue et al. (2016)</a>
Soil DOC	↑	↑	NS	NS	-	<a href="#">Yue et al. (2016)</a>
Soil DOC	↑	NS	NS	↑	-	<a href="#">Liu and Greaver (2010)</a>
Organic layer C	NS	↑	-	↑	-	<a href="#">Liu and Greaver (2010)</a>
Soil respiration	NS	NS	NS	NS	NS	<a href="#">Yue et al. (2016)</a>
Soil respiration <sup>a</sup>	NS	NS	↑	NS	-	<a href="#">Liu and Greaver (2010)</a>
CH <sub>4</sub> emission	NS	NS	NS	NS	NS	<a href="#">Liu and Greaver (2009)</a>
CH <sub>4</sub> uptake	↓	↓	↓	↓	NS	<a href="#">Liu and Greaver (2009)</a>
N <sub>2</sub> O	↑	↑	↑	↑	↑	<a href="#">Liu and Greaver (2009)</a>
N Recovery	80%	85%	53%	-	-	<a href="#">Templer et al. (2012)</a>

<sup>a</sup>Not significant effect of the N mean for this endpoint; however, there was a significant difference among N forms.

↑ indicates significant increase.

↓ indicates significant decrease.

- indicates not reported.

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## 4.4 Soil Monitoring and Databases

There are several new studies using long-term monitoring data sets in the U.S. and Europe ([Table 4-14](#)). New studies in the U.S. include an analysis of 45 years of biogeochemical monitoring data ([Yanai et al., 2013](#)) and sulfur accumulation ([Mitchell and Likens, 2011](#)) at the HBEF, NH. At the Niwot Ridge LTER site, CO ([Lieb et al., 2011](#)), identify the effects of a decade of simulated N deposition in the southern Rocky Mountains.

[Yanai et al. \(2013\)](#) evaluated 45 years of biogeochemical monitoring data at the HBEF, NH. Since 1992, the ecosystem shifted to a net N sink ~8 kg N/ha/yr. There are several possible explanations: (1) gaseous N fluxes from the ecosystem in response to denitrification, (2) a budget discrepancy in the net error of the other measured and estimated stocks and fluxes, and/or (3) N accumulation in an unidentified ecosystem compartment.

As discussed in [Appendix 4.3.3](#), [Mitchell and Likens \(2011\)](#) examined the sulfur accumulation observed in over four decades of continuous long-term records for four watersheds in HBEF, NH and found that as S deposition declined, soil moisture became a more powerful control on S release from soils than did deposition.

At the southern Rocky Mountains Niwot Ridge LTER site, CO, [Lieb et al. \(2011\)](#) found a decade of simulated N deposition to alpine ecosystems caused ongoing changes in diversity and soil biogeochemistry, including lower soil acid buffering capacity, decreased concentrations of exchangeable  $Mg^{2+}$ , and increased concentrations of the potentially toxic cations  $Mn^{2+}$  and  $Al^{3+}$ . Their results suggested an N deposition threshold for the onset of acidification at this site of 28 kg N/ha/yr.

**Table 4-14 Biogeochemistry monitoring and databases.**

Process/ Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effects	Reference
Base cation (Bc) release soil [Al] soil [Mn] soil pH	Alpine soils	Niwot Ridge in the southern Rocky Mountains, CO, U.S.	6 to 8 (10 yr)	8, 28, 48, and 68 (NH <sub>4</sub> NO <sub>3</sub> )	<b>Addition:</b> Changes in diversity, lower soil acid buffering capacity, decreased concentrations of Mg <sup>2+</sup> , and increased concentrations of the potentially toxic cations Mn <sup>2+</sup> and Al <sup>3+</sup> . Results suggested an N deposition threshold of 28 kg N/ha/yr.	<a href="#">Lieb et al. (2011)</a>
Sulfate leaching [SO <sub>4</sub> <sup>2-</sup> ]	Northeastern forest	HBEF, NH, U.S.	Not specified	None	<b>Monitoring:</b> Over four decades of data were used to evaluate S budgets. Current declining inputs of atmospheric S and the higher outputs of SO <sub>4</sub> <sup>2-</sup> in drainage waters relative to precipitation inputs are driven by the S stored in the soil. Climatic change will potentially increase SO <sub>4</sub> <sup>2-</sup> mobilization and hence could slow the resultant recovery from acidification.	<a href="#">Mitchell and Likens (2011)</a>
N accumulation C:N soil [N]	Northern hardwood forest	HBEF, NH, U.S.	~7 (since 1992)	None	<b>Monitoring:</b> Since 1992, the ecosystem shifted to a net N sink, either storing or denitrifying ~8 kg N/ha/yr.	<a href="#">Yanai et al. (2013)</a>

**Table 4-14 (Continued): Biogeochemistry monitoring and databases.**

Process/ Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effects	Reference
NO <sub>3</sub> <sup>-</sup> leaching C:N (lake) C:N (mineral soil layer) TOC:TN	Boreal soils and lakes	Sweden	<3 to 17	None	<b>Gradient:</b> Significant relation found between C:N ratios of the organic soil layer and the ones of lake waters. Evidence found of N deposition having depressed the C:N ratios of lake waters more than the ones of organic soil layers. Clear sudden increase seen in NO <sub>3</sub> <sup>-</sup> leaching in regions where N deposition exceeded 7.5 kg/ha/yr.	<a href="#">Khalili et al. (2010)</a>
Oxidation of organic S in humic soils due to S dep Ratio of reduced to oxidized organic S	Grassland	Rothamsted Park Grass Experiment, Hertfordshire, England	Not specified	None	<b>Monitoring:</b> Analysis of the effects of atmospheric SO <sub>2</sub> emissions since the late 1800s found acidification led to a depletion of exchangeable Ca and Mg and an 8× increase in exchangeable Al.	<a href="#">Lehmann et al. (2008)</a>
Bc, N, and SO <sub>4</sub> <sup>2-</sup> flux soil solution [Al] soil solution Bc soil solution [Inorganic N] soil solution [SO <sub>4</sub> <sup>2-</sup> ] molar Bc:Al in soil solution	Forest, including beech and Norway spruce	Switzerland, Jura Mountains in southern Alps. The forests were not managed during the whole observation period	Between 2000 and 2007, mean (-0.02 to 1.99 kmol/ha/yr)	None	<b>Monitoring:</b> A decade (1995–2007) of monitoring data indicates acidifying deposition significantly decreased at three out of the nine study sites due to a decrease in total N deposition. In the soil solution, no trend in concentrations and fluxes of Bc, SO <sub>4</sub> <sup>2-</sup> , and inorganic N were found at most soil depths at five out of the seven sites, suggesting that the soil solution reacted very little to the changes in atmospheric deposition.	<a href="#">Pannatier et al. (2011)</a>

**Table 4-14 (Continued): Biogeochemistry monitoring and databases.**

Process/ Indicator	Type of Ecosystem	Region	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Effects	Reference
pH, ANC, base cations, Al <sub>i</sub> , Al <sub>o</sub>	Forest and streams	HBEF, NH	Variable	None	<b>Field observation:</b> Soil solution monitoring 1984–2011 at HBEF showed that: pH and ANC did not change significantly in the Oa-horizon but ANC increased in Bs-horizon. Total base cations decreased in Bs-horizon. Al <sub>o</sub> decreased and. Al <sub>i</sub> decreased in the 2 high-elevation subwatersheds.	<a href="#">Fuss et al. (2015)</a>

Al = aluminum; Al<sub>i</sub> = inorganic aluminum; Al<sub>o</sub> = organic aluminum; Bc = base cation; C = carbon; Ca = calcium; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; kmol = kilomole; Mg = magnesium; Mn = manganese; N = nitrogen; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>2</sub> = sulfur dioxide; SO<sub>4</sub><sup>2-</sup> = sulfate; TN = total nitrogen; TOC = total organic carbon; yr = year.

There are new studies evaluating long-term monitoring in Europe, including those looking at S dynamics in England ([Lehmann et al., 2008](#)) and N and S dynamics in Switzerland ([Pannatier et al., 2011](#)). In Sweden, [Khalili et al. \(2010\)](#) examined N and C interactions between boreal soils and lakes. [Lehmann et al. \(2008\)](#) found that soil acidification from the input of oxidized organic S proceeded much more rapidly than did recovery after reductions of atmospheric emissions and deposition. [Pannatier et al. \(2011\)](#) examined monitoring data at Swiss Long-Term Forest Ecosystem Research sites. The results suggested that the fluxes of  $\text{Bc}$ ,  $\text{SO}_4^{2-}$ , and inorganic N in soil solution reacted very little to the changes in atmospheric deposition. A stronger reduction in base cations compared to  $\text{Al}^{3+}$  was detected at two sites, possibly indicating that acidification of the soil solution was proceeding faster at these sites than the other sites. In Sweden, [Khalili et al. \(2010\)](#) examined samples collected in selected years between 1993 and 2005. Although they found a significant relation between C:N ratios of the organic soil layer and lake waters, the large-scale variations in soil C content were not directly linked to C concentrations in lake waters. Soil N seems to have leached in small amounts from the soils directly into the lakes in the form of  $\text{NO}_3^-$ .  $\text{NO}_3^-$  leaching showed a clear and sudden increase in regions where N deposition exceeded 7.5 kg/ha/yr.

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## 4.5 Models

The 2008 ISA described the most commonly applied soil biogeochemistry models in the U.S. used to track N and/or S deposition (Section A.3 of the 2008 ISA). The focus of [Appendix 4.5](#) is to update available information on several key models currently being used in the U.S. to assess the effects of S and N deposition on terrestrial ecosystem soil biogeochemistry. Steady-state models include steady-state simple mass-balance (SMB). Dynamic models include the Very Simple Dynamic (VSD) soil acidification model, MAGIC, PnET/BGC, and DayCent-Chem. One important input to these models is estimating base cation weathering (BCw), and there are new updates on two methods to estimate this parameter: Soil Texture Approximations (STA) and PROFILE.

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## 4.5.1 Updates to Key Previously Identified Models

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### 4.5.1.1 Soil Texture Approximation (STA) and PROFILE: Estimating Base Cation Weathering

Base cation weathering (BCw) rate is one of the most influential yet difficult to estimate parameters in the calculation of critical acid loads of N and S deposition for terrestrial systems. As discussed in [Appendix 4.3](#), acidifying deposition causes base cation leaching from soil. The supply of base cations is largely replenished by base cation weathering of minerals from rock within the ecosystems. Obtaining accurate estimates of weathering rates is difficult because weathering is a process that occurs over very long periods of time. There are some new studies on estimating BCw, including a study on the clay correlation-substrate method and PROFILE ([Koseva et al., 2010](#)), a new application of PROFILE in the U.S. ([Phelan et al., 2014](#)), and an evaluation of uncertainty in estimating BCw ([Futter et al., 2012](#)).

The clay correlation-substrate method, also called clay-based Soil Texture Approximation (STA), is an empirical steady-state model that has been used to estimate BCw rates for forest ecosystems in the U.S. because it is simple and has low data requirements. The STA method has an empirical function that was first developed for European soils and later adapted to soils in Canada and the U.S. The method estimates total base cation weathering rates (BCw, sum of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ), based on the relationship between established weathering classes and clay content of soils for different acidity classes—acidic, intermediate, and basic. An alternate steady-state model, PROFILE ([Sverdrup and Warfvinge, 1993](#)), may offer an improved method to estimate BCw rates. It is a transferable, process-based model that simulates the weathering rates of groups of minerals. PROFILE was developed in Sweden and is a mechanistic, steady-state kinetics model that calculates the weathering of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  in each horizon within a soil profile based on mineral specific chemical dissolution rates and site and soil conditions. Because PROFILE is a steady-state model, weathering rates calculated by PROFILE can be used with the SMB critical acid load model. One of the main limitations that has discouraged the wider adoption of PROFILE for BCw rate determinations in the U.S. is the large data requirements of the model ([Koseva et al., 2010](#)).

[Koseva et al. \(2010\)](#) reported on their evaluation and revision of the STA model for use in Canadian forests. The authors compared the performance of the STA model to PROFILE weathering estimates for soils at 75 sites in Canada. The relative ability of the STA and PROFILE models to provide reasonable weathering rates was evaluated using

base cation mass balances at a subset of sites in Ontario ( $n = 19$ ). Mineral weathering rates calculated with the STA method at 75 sites in Canada (6–367 eq/ha/yr) were up to 38 times lower (7 times on average) than rates estimated with PROFILE (143–2,119 eq/ha/yr,  $p < 0.0001$ ). Despite deviations from the 1:1 line, weathering estimates obtained using the STA method were significantly correlated using PROFILE weathering estimates ( $p < 0.05$ ). The authors concluded that the “revised” STA model they used may be more widely applicable in Canada, but not necessarily suited to all regions in the U.S. The uncertainty of the model is largely unknown, and the three equations of the clay correlation-substrate method require recalibration or revision when transferred to new locations. In addition, the STA equations were derived for young soils that developed following the Late Wisconsin glaciation ([Koseva et al., 2010](#)); the clay correlation-substrate model, which is based on clay content and parent material acidity, may not be suitable for older, more weathered soils that were not affected by the most recent glaciation and which cover the majority of the U.S. ([U.S. EPA, 2009c](#)).

PROFILE requires over 26 time series or site parameters as model inputs. The U.S. Geological Survey (USGS) recently completed a soil geochemical and mineralogical survey of the U.S. as part of the North American Soil Geochemical Landscapes Project. This project, hereafter referred to as the USGS Landscapes Project, included mineralogy analyses conducted on soil samples collected from 4,871 evenly spaced sites across the U.S. ([Smith et al., 2013](#)). These new data allow the PROFILE model to be applied at a larger scale. [Phelan et al. \(2014\)](#) evaluated PROFILE using national data sets as a method to estimate BCw rates for forests in the U.S., focusing on Pennsylvania as the first test state. The model was successfully applied at 51 forested sites across Pennsylvania. Weathering rates ranged from 11.9 to 924.5 meq/m<sup>2</sup>/yr and were consistent with soil properties and regional geology. The authors suggest that the method be applied to other locations to further evaluate the performance of the model.

A data set of published BCw rates was evaluated by [Futter et al. \(2012\)](#). The data set included 394 individual silicate mineral weathering rate estimates from 82 poorly buffered, silicate-mineral-dominated locations across the world where at least 3 published estimates of BCw were available. The researchers found uncertainty for the input data high relative to the estimated contribution of model parameter uncertainty of BCw weathering rate (meq/m<sup>2</sup>/yr) to overall variability related to PROFILE and MAGIC, ranging from 1.7 to 2.1 for the two models, respectively. The two models have been most widely used to make assessments of weathering rates for environmental decision making, and each represents the landscape differently. PROFILE provides estimates for shallow one-dimensional soil, whereas MAGIC integrates weathering processes for the whole catchment, including deep soil weathering. Therefore, lower weathering rate estimates are shown from PROFILE in comparison to MAGIC, which considers deep soil

weathering to constitute a potentially important source of Bc in catchment weathering ([Futter et al., 2012](#)).

[Whitfield et al. \(2018\)](#) evaluated major sources of uncertainty associated with using PROFILE for upland forests in the continental U.S. Mineral stoichiometry was not an important influence on BCw estimates (uncertainty < 1%). Characterizing B-horizon mineralogy by averaging A- and C-horizons was found to be a minor (< 5%) contributor to uncertainty in some areas, but where mineralogy is known to vary with depth the uncertainty can be large. Estimating mineral-specific surface areas had a strong influence on estimated BCw, however the greatest uncertainty in BCw estimates, was due to the particle size class-based method used to estimate the total specific surface area upon which weathering reactions can take place.

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#### 4.5.1.2 Steady-State Mass Balance

The 2008 ISA documented a model to assess CLs for acidification in forest soils based on simple mass-balance equations [SMBE; [McNulty et al. \(2007\)](#)]. This study estimated critical acid load and exceedance in soils at a 1-km<sup>2</sup> spatial resolution across the U.S. A second publication discussed the uncertainties associated with this model and national-scale assessment ([Li and McNulty, 2007](#)). The authors quantified uncertainty under natural variability in 17 model parameters and determined the relative contributions of each in predicting critical loads. The results indicated that uncertainty in the CLs came primarily from components of base cation weathering (BCw; 49%) and acid neutralizing capacity (46%), whereas the most critical parameters were BCw base rate (62%), soil depth (20%), and soil temperature (11%). The authors concluded that improvements in estimates of these factors are crucial to reducing uncertainty and successfully scaling up SMBE for national assessments. This work remains the best national-scale estimate of terrestrial soil acidification in the U.S. (see [Appendix 4.6](#)). A new study by [Posch et al. \(2011\)](#) is a regional application of SMB models, while several other studies using SMB have been published to determine acidification critical loads based on critical limits of Bc:Al and ANC ([Phelan et al., 2014](#); [Duarte et al., 2013](#); [Jung et al., 2013](#); [Whitfield and Watmough, 2012](#); [Forsius et al., 2010](#); [McNulty and Boggs, 2010](#); [Nasr et al., 2010](#)). The biological implications of these critical loads are discussed in [Appendix 5](#) and a summary of SMB CLs in the U.S. is presented in [Appendix 4.6](#).

[Posch et al. \(2011\)](#) published an article outlining SMB models for use in N deposition on ecosystem biodiversity. This approach has the well-established benefit of easy regional applicability, while incorporating specified critical chemical criteria to protect specified receptors. Rather than indicating an upper limit for deposition (i.e., critical load), linked

nutrient nitrogen and acidity chemical criteria for plant occurrence produce an “optimal” nitrogen and sulfur deposition envelope. This method is similar to the methods developed in the 2012 Policy Assessment for the Review of the secondary NAAQS for Oxides of N and S.

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#### **4.5.1.3 ForSAFE and ForSAFE-VEG**

The ForSAFE model ([Wallman et al., 2005](#)) is the biogeochemical simulator platform that simulates the cycles of carbon, nitrogen, base cations (Bc), and water in a forest ecosystem, including simulation of soil chemistry, tree growth, and soil organic matter accumulation or depletion. ForSAFE requires site-specific inputs of the physical properties of the soil (including mineralogy, hydrological parameters, density, depth, and stratification), tree type, and time series of atmospheric deposition and climatic data (temperature, light, and precipitation). The model gives monthly estimates of weathering rates, soil moisture, soil solution concentrations, uptake fluxes of N and Bc, litterfall, decomposition and mineralization, as well as photosynthesis and growth rates. ForSAFE-VEG is a composite model, in which the VEG module ([Sverdrup et al., 2007](#)) reads a set of five drivers (soil solution pH, Bc concentration, N concentration, ground level light, soil moisture) from ForSAFE, including air temperature, and uses them to estimate the relative abundance of a set of indicator plants at the site. The result is a model chain that can link changes in atmospheric deposition, climatic conditions, and land use to responses in the biogeochemistry and plant community composition at the site level, both historically and in the future. A new study by [Belyazid et al. \(2011a\)](#) revealed limitations in the model simulation of N concentrations in soil solution. The authors concluded that the biogeochemical model platform must be improved to simulate N processes more accurately before it is used to calculate CL for N deposition. The model overestimated the actual N concentrations in the soil solution. Several new applications of ForSAFE-VEG have been published ([Sverdrup et al., 2012](#); [Belyazid et al., 2011a](#)), and the results are discussed in [Appendix 5](#) and [Appendix 6](#).

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#### **4.5.1.4 Model of Acidification of Groundwater in Catchment (MAGIC)**

The Model of Acidification of Groundwater in Catchment [MAGIC; [Cosby et al. \(1985a\)](#); [Cosby et al. \(1985b\)](#); [Cosby et al. \(1985c\)](#)] is one of the most well-known dynamic models of aquatic and terrestrial acidification. It is a lumped-parameter model of soil and surface water acidification in response to atmospheric deposition based on process-level information about acidification. “Lumped-parameter” refers to the extent

that spatially distributed physical and chemical processes in the catchment are averaged or lumped together without affecting the model's reproduction of catchment response. Process-level information refers to how the model characterizes acidification into (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving  $\text{SO}_4^{2-}$  adsorption, cation exchange, dissolution-precipitation-speciation of aluminum, and dissolution-speciation of inorganic carbon and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. One strength of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time due to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils. The data requirements to run dynamic models like MAGIC are considerable. The equations that characterize the chemical composition of soil water in MAGIC contain 33 variables and 21 parameters. Data required to conduct dynamic modeling are not as available in as many places as the data required to conduct steady-state modeling.

[Oulehle et al. \(2012\)](#) presented a new formulation of the acidification model MAGIC that uses decomposer dynamics to link N cycling to C turnover in soils. In comparisons with earlier versions, the new formulation more accurately simulates observed short-term changes in  $\text{NO}_3^-$  leaching, as well as long-term retention of N in soils. The authors state that the new formulation gives a more realistic simulation of observed changes in N leaching. The new formulation also provides a reasonable simulation of the long-term changes in C and N pools (and C:N ratio) with SOM.

MAGIC has recently been used to calibrate BCw at 140 locations throughout the southern Appalachian Mountains, where input data were sufficient for running the dynamic model ([Povak et al., 2014](#)). Results were then extrapolated to the region. [McDonnell et al. \(2014b\)](#) used these calibrated regionalized BCw values as inputs for regional steady-state CL modeling.

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#### **4.5.1.5 Photosynthesis and Evapotranspiration—Biogeochemical (PnET-BGC)**

The Photosynthesis and Evapotranspiration—Biogeochemical (PnET-BGC) model is an integrated forest-soil-water model that has been used to assess the effects of air pollution and land disturbances on forest and aquatic ecosystems ([Gbondo-Tugbawa et al., 2001](#)). The model was developed by linking two submodels: PnET-carbon and nitrogen

[PnET-CN; [Aber et al. \(1997\)](#)] and BGC ([Gbondo-Tugbawa et al., 2001](#)). The main processes in the model include tree photosynthesis, growth and productivity, litter production and decay, mineralization of organic matter, immobilization of nitrogen, nitrification ([Aber et al., 1997](#)), vegetation and organic matter interactions of major elements, abiotic soil processes, solution speciation, and surface water processes ([Gbondo-Tugbawa et al., 2001](#)). The hydrologic algorithms used in PnET-BGC are summarized by [Aber and Federer \(1992\)](#) and [Chen and Driscoll \(2005\)](#). PnET-BGC has the capability of using multiple soil layers ([Chen and Driscoll, 2005](#)) to model seasonal variations in soil parameters and chemistry. Applications and conceptual advancements to the model published since 2008 are summarized in [Table 4-15](#).

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#### **4.5.1.6 DayCent-Chem**

DayCent-Chem links two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent ([Parton et al., 1998](#)), and the other of soil and water geochemical equilibrium, PHREEQC ([Parkhurst and Appelo, 1999](#)). The linked DayCent/PHREEQC model was created to capture the biogeochemical responses to atmospheric deposition and to explicitly consider those biogeochemical influences on soil and surface water chemistry. The linked model expands on DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions of many other chemical species in surface water.

**Table 4-15 Photosynthesis and Evapotranspiration—Biogeochemical (PnET-BGC) and DayCent.**

Region	Deposition	Model (Dynamic or Steady State)	Approach/Observation	Reference
HBEF, NH	526 eq S/ha/yr; 327 eq NO <sub>3</sub> <sup>-</sup> /ha/yr; ~522 eq NO <sub>3</sub> <sup>-</sup> + NH <sub>3</sub> /ha/yr	PnET-BGC	<b>Application:</b> Combination of multiple deposition scenarios of S, NO <sub>3</sub> <sup>-</sup> , and base cation deposition (0 to 100% decrease in 20% increments after 2008), as well as current climate and climate change scenarios to year 2100.	<a href="#">Wu and Driscoll (2010)</a>
HBEF, NH	Not specified	PnET-BGC	<b>Conceptual advancement:</b> PnET-BGC modified to include CO <sub>2</sub> .	<a href="#">Pourmokhtarian et al. (2012)</a>
San Bernadino Mtns., CA	Two sites: (1) 8.8 kg N/ha/yr; (2) 70 kg N/ha/yr	DayCent	<b>Conceptual advancement:</b> DayCent modified to include O <sub>3</sub> effects.	<a href="#">Bytnerowicz et al. (2013)</a>
Adirondack Long-term Monitoring Program (ALTM; 128 lakes)	Mean wet + dry dep. 2009–2011: S = 20–34 meq/m <sup>2</sup> /yr; N = 24–33 meq/m <sup>2</sup> /yr	PnET-BGC	<b>Application:</b> Controlling S deposition is more effective in promoting acidic lake recovery than controlling S + N deposition.  Reducing S dep. 60% beyond 2011 level is predicted to restore 28% of impaired lakes to ANC 20 µeq/L ≥ by 2050 and 60% of lakes by 2200. An ANC of 11 µeq/L can be achieved to 53% of lakes by 2050.	<a href="#">Fakhraei et al. (2014)</a>
Adirondack Mtns. Region, NY	SO <sub>4</sub> <sup>2-</sup> = 290.3–365.7 eq/ha/yr; NO <sub>3</sub> <sup>-</sup> = 172.5–233.5 eq/ha/yr		<b>Application:</b> PnET-BGC was used to evaluate biophysical factors that affect CLs and TLs of acidity for the Constable Pond watershed, as an example of a chronically acidic drainage lake in the Adirondack region of New York, U.S. These factors included a range of future scenarios of decreases in atmospheric nitrate, ammonium and sulfate deposition from present to 2200.	<a href="#">Zhou et al. (2015c)</a>
Great Smoky Mtns. National Park	6.8–27.8 kg S/ha/yr 6.1–16.6 kg N/ha/yr (2004–2008)	PnET-BGC	<b>Application:</b> Simultaneous reduction in SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition is more effective at increasing stream ANC than SO <sub>4</sub> <sup>2-</sup> alone. NO <sub>3</sub> <sup>-</sup> leaching continues as N deposition decreases. Stream recovery is delayed as NO <sub>3</sub> <sup>-</sup> facilitates desorption of legacy SO <sub>4</sub> <sup>2-</sup> that is adsorbed to acid soils.	<a href="#">Zhou et al. (2015b)</a>

**Table 4-15 (Continued): Photosynthesis and Evapotranspiration—Biogeochemical (PnET-BGC) and DayCent.**

Region	Deposition	Model (Dynamic or Steady State)	Approach/Observation	Reference
Great Smoky Mtns. National Park	3.1 kg S/ha/yr 5.1 kg N/ha/yr	PnET-BGC	<b>Application:</b> Due to soil SO <sub>4</sub> <sup>2-</sup> adsorption capacity, reducing NH <sub>4</sub> <sup>+</sup> deposition would be more effective in stream recovery than reducing NO <sub>x</sub> and SO <sub>2</sub> .	<a href="#">Fakhraei et al. (2016)</a>

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## 4.5.2 New Models (Published since 2008)

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### 4.5.2.1 SMARTml

SMARTml is an assemblage of surface complexation models (SCMs), which are used in predicting dynamics in soil chemistry without any site-specific calibration. In the first published application of SMARTml to a spruce forest site in Germany, model results matched observations well overall ([Bonten et al., 2011](#)). Simulations deviated from observations only for soil layers or parameters for which insufficient information was available. These positive results demonstrate the potential to further apply SCMs in dynamic modeling. Current results only refer to a single site, and the testing of SCMs for more cases with differences in soil types, depositions, and environmental conditions are needed to better understand the strengths of this model.

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### 4.5.2.2 Very Simple Dynamic (VSD) and VSD<sup>+</sup>

The Very Simple Dynamic (VSD) soil acidification model is the simplest extension of the steady-state SMB model into a dynamic model. It does this by including cation exchange and time-dependent N immobilization (accumulation). The VSD model is designed for sites with little available data and for applications on a large regional or continental scale. The model has a short execution time that allows rapid scenario analyses and the calculation of target loads (i.e., deposition targets), which result in a desired chemical condition in the soil (solution) in a specified year. [Posch and Reinds \(2009\)](#) developed a version of the VSD for steady-state critical load applications at the regional scale. Although simpler than other widely used dynamic models (such as MAGIC and SAFE), VSD contains the basic physical and chemical relationships common to all these models. However, the model's simplicity also means that some processes have either been left out altogether (e.g.,  $\text{SO}_4^{2-}$  sorption) and others strongly simplified (e.g., N cycling processes). As a consequence, VSD is not best suited for sites where  $\text{SO}_4^{2-}$  adsorption is important. Furthermore, the simple description of N processes does not allow simulating decreasing soil N pools (and increasing C:N ratios) under reduced N inputs.

[Bonten et al. \(2015\)](#) describe an extension of the VSD model, called VSD<sup>+</sup>, which includes an explicit description of C and N turnover. The VSD<sup>+</sup> model includes an explicit description of organic C and N turnover, whereas in the VSD model, N

immobilization depends on the N availability and C sequestration mostly depends on the N immobilization rate, which is controlled by user-prescribed C:N ratios. The VSD<sup>+</sup> model also includes S adsorption on soils. The authors apply VSD<sup>+</sup> to three forest stands, which differ in N deposition and soil C:N ratios. Results suggest that at some locations VSD<sup>+</sup> can accurately predict trends and absolute values of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations in soil and stream waters, soil C:N ratios and pH.

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#### 4.5.2.3 Soil Organic Matter

The Soil Organic Matter (SOM) model was developed as an alternative to the decomposition module of the PnET model for application in northeastern forests. It relies on empirical representations of litter decomposition and soil C turnover rates, and explicitly represents multiple soil horizons. [Tonitto et al. \(2014\)](#) examined the effect of N addition on SOM dynamics. Their model simulations suggested that ambient atmospheric N deposition at the forest has led to an increase in cumulative O-, A-, and B-horizons C stocks of 211 g C/m<sup>2</sup> (3.9 kg C/kg N) and 114 g C/m<sup>2</sup> (2.1 kg C/kg N) for hardwood and pine standards, respectively. They concluded that the model proved largely able to simulate soil C and N dynamics at their study site under control conditions and that field observations, mechanistic experiments, and model simulations suggest that the addition of N to forest ecosystems could have a substantial effect on forest soil C accumulation via suppression of organic matter decomposition.

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#### 4.5.2.4 ORCHIDEE—Carbon-Nitrogen

ORCHIDEE—Carbon-Nitrogen (O-CN) is a terrestrial biosphere model which has been developed from the land surface model ORCHIDEE and describes the N and C fluxes and stocks of vegetation and SOM for 10 natural plant functional types, as well as C<sub>3</sub> and C<sub>4</sub> croplands at a half-hourly timescale. [Zaehle \(2013\)](#) determined that the estimate C sequestration from the process-based O-CN model is lower than was found in earlier studies based on simple biogeochemical models and upscaling of field-based measurement, which have estimated C sequestration based on N deposition estimates as 0.4–0.7 Pg C/yr in 1990. The O-CN results were within the range of previous model simulations with the current generation of C-N cycle models (0.2–0.6 Tg N/yr). The authors believe the study provides an advance over previous assessments because it relies on a “process-based ecosystem model that integrates the key C-N cycle interactions and their coupling to biogeophysical processes, while considering the impacts of atmospheric (climate, CO<sub>2</sub>) and land cover changes.” Key uncertainties in the modeling include (1) the response of canopy-level photosynthesis to N additions, (2) changes in the allocation

patterns (root:shoot ratio), and (3) the competition of plants and soil microbes for the added (or reduced) amount of N.

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#### 4.5.2.5 Dynamic Model N<sup>14</sup>C

Dynamic model N<sup>14</sup>C is a plant-soil N and C cycling model that simulates terrestrial ecosystem responses to atmospheric N deposition ([Tipping et al., 2012](#)). The model includes four plant functional types: broadleaved and coniferous trees, herbs, and dwarf shrubs. It simulates net primary production (NPP); C and N pools; leaching of DOC, DON, and inorganic N; denitrification; and the radiocarbon contents of organic matter on an annual time step. The model simulates annual plant growth and turnover and soil C and N cycling and is reasonably successful at reproducing average results. However, for individual sites, there are no significant correlations for C pools or C:N ratios and only weak relationships for N pools and inorganic N leaching. Inorganic leaching has traditionally been considered one of the main indicators of N saturation (however, see new studies in [Appendix 4.3.2](#)) and therefore an important goal of N<sup>14</sup>C is to simulate its response to N enrichment.

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#### 4.5.2.6 Dynamic Simulation Model of Ecosystem Nitrogen

[Perakis and Sinkhorn \(2011\)](#) reported  $\delta^{15}\text{N}$  constraints on long-term N balances in temperate forests using a dynamic simulation model of ecosystem N and  $\delta^{15}\text{N}$ . Their model evaluated which combination of N input and loss pathways could produce a range of high ecosystem N contents characteristic of forests in the Oregon Coast Range, U.S. Ecosystem  $\delta^{15}\text{N}$  displayed a curvilinear relationship with ecosystem N content and largely reflected mineral soil, which accounted for 96–98% of total ecosystem N. Model simulations of ecosystem N balances parameterized with field rates of N leaching required long-term average N inputs that exceed atmospheric deposition and asymbiotic and epiphytic N<sub>2</sub>-fixation, and that were consistent with cycles of post-fire N<sub>2</sub>-fixation by early successional red alder. Soil water  $\delta^{15}\text{NO}_3^-$  patterns suggested a shift in relative N losses from denitrification to  $\text{NO}_3^-$  leaching as N accumulated, and simulations identified  $\text{NO}_3^-$  leaching as the primary N loss pathway that constrains maximum N accumulation.

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### 4.5.3 Comparative Analyses

[Tominaga et al. \(2009\)](#) used HBEF located in NH, as the setting to evaluate the performance of three uncalibrated process-oriented models. They performed a Monte

Carlo multiple-model evaluation framework of the dynamic models MAGIC, SAFE, and VSD. The greatest differences in model outputs were attributed to the cation exchange submodel, with Gapon exchange-based models retaining more base cations on the exchange complex and releasing less into solution, resulting in lower soil solution ANC values. Given the same deposition scenario, the three models (without calibration) simulate changes in soil and soil solution chemistry differently, but the basic patterns were similar.

[Bonten et al. \(2015\)](#) compared common dynamic models used to evaluate soils ([Table 4-16](#)). Comparisons are summarized in [Table 4-17](#).

**Table 4-16 Overview of properties of four dynamic soil chemistry models as characterized in [Bonten et al. \(2015\)](#).**

Features	VSD	MAGIC	ForSAFE	SMARTml
Number of soil layers	1	1–3	1–20	1–15 soil horizons
Temporal resolution	Annual	Annual/monthly	Monthly	Variable (day–yr)
Bc weathering	External input	Calibrated, or external-input	Submodel	External input
Forest nutrient uptake	External input	External input	Submodel	Submodel
Runoff-to-precipitation ratio	External input	External input	Fixed ratio	External input
Sulfate adsorption	Not included	Langmuir isotherm	Yes	At Fe/Al hydroxides using a 2pK-DDL model
N immobilization	Fractional, fixed, or external input	Fractional, fixed, or external input	Submodel	Submodel
Nitrification	100%	Fractional	Submodel	Submodel
Denitrification	Fractional, fixed	Fractional	None or submodel	Submodel
Soil N build-up controlled by C:N ratio	Yes	Yes	No	Submodel
CO <sub>2</sub> degassing in surface water	Yes	Yes	Yes	No surface water
Al(OH) <sub>3</sub> precipitation in stream	Yes	Yes	Yes	No surface water
Lumped base cations (Ca <sup>2+</sup> , Mg <sup>2+</sup> , and K <sup>+</sup> )	Yes	No	Yes	No
DOC dissociation model	Oliver or simple monoprotic	Triprotic	Oliver	NICA-Donnan

**Table 4-16 (Continued): Overview of properties of four dynamic soil chemistry models as characterized in Bonten et al. (2015).**

Features	VSD	MAGIC	ForSAFE	SMARTml
Cation exchange	Gaines-Thomas or Gapon	Gaines-Thomas	Gapon	OM: NICA-Donnan clay: Donnan gel hydroxides: 2pk DDL
Number of cation exchange equations	2	4	1	Not relevant
Ions in soil solution charge balance	12	28	16	Full speciation of ions in the soil solution
First appearance in the literature	2009	1985	1993	2011

**Table 4-17 Model comparison.**

Soil Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Modeled Observation	Reference
Soil S	Forest	Three Swiss forest monitoring sites	Not specified	In a comparison of four models VSD, MAGIC, ForSAFE, and SMARTml, ForSAFE-modeled S concentrations tended to be underestimated by the model.	<a href="#">Bonten et al. (2015)</a>
Soil pH	Forest	Three Swiss forest monitoring sites	Not specified	In a comparison of four models VSD, MAGIC, ForSAFE, and SMARTml, ForSAFE results indicated upper soil layers can have higher modeled pH than observed.	<a href="#">Bonten et al. (2015)</a>
Soil ANC and pH	Scots pine plantation	Long-term forest monitoring site in U.K. (Peak District of northern England)	Not specified	In a comparison of four models VSD, MAGIC, ForSAFE, and SMARTml, MAGIC successfully reproduced the trend in acidity (ANC and pH) in soil solution over the majority of the (ca. 1990s) monitoring period.	<a href="#">Bonten et al. (2015)</a>
Soil SO <sub>4</sub> <sup>2-</sup>	Spruce forest	Gårdsjön, Sweden	Not specified	In a comparison of four models VSD, MAGIC, ForSAFE, and SMARTml, ForSAFE modeling results showed SO <sub>4</sub> <sup>2-</sup> was slightly underestimated compared to measured SO <sub>4</sub> <sup>2-</sup> concentrations in soil solutions at 5-, 10-, and 20-cm depth (1990–2000).	<a href="#">Bonten et al. (2015)</a>
Soil SO <sub>4</sub> <sup>2-</sup>	Spruce forest	Bechtel, Switzerland	Not specified	In a comparison of four models VSD, MAGIC, ForSAFE, and SMARTml, ForSAFE-modeled soil SO <sub>4</sub> <sup>2-</sup> was reasonably well modeled at 20-cm depth but clearly below measured values at 100-cm depth (1990–2005).	<a href="#">Bonten et al. (2015)</a>

**Table 4-17 (Continued): Model comparison.**

Soil Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Modeled Observation	Reference
Ion concentrations, Al	Forest	Three Swiss forest monitoring sites	Not specified	Comparison of four models VSD, MAGIC, ForSAFE, and SMARTml. VSD reproduced the ion concentrations similar to measured values, however the modeled Al concentrations were substantially lower than measured ones. VSD only calculates free Al <sup>3+</sup> , whereas measurements also include other Al-species as Al-hydroxides and Al complexed by dissolved organic matter and fluoride.	<a href="#">Bonten et al. (2015)</a>
Base cations (nutrients Ca + Mg + K; Na; and Ca)	Spruce forest	Gårdsjön, Sweden; Bechtel, Switzerland; and long-term monitoring site in Germany	Not specified	ForSAFE results compared to observations. In Sweden, nutrient base cations were slightly underestimated compared to measured values in soil solution at 5-, 10-, and 20-cm depth (1990–2000), while Na <sup>+</sup> in soil solution was relatively well modeled at 5-, 10-, and 20-cm depth but less well in deeper soil. In Switzerland, base cations modeling results were “within the range of the measured values with a slight underestimation at 20-cm depth” (1990–2005). In Germany, Ca <sup>2+</sup> agreed with measured values in soil solution (1990–2005).	<a href="#">Bonten et al. (2015)</a>
Al	Spruce forest	Bechtel, Switzerland	Not specified	ForSAFE-modeled Al <sup>3+</sup> was “in the range of the measured soil solution values at 20-cm depth” (1990–2005).	<a href="#">Bonten et al. (2015)</a>
Al, Ca, and protons	Norway spruce forest	Long-term monitoring site in Germany	Not specified	SMARTml results showed that modeled Al <sup>3+</sup> , Ca <sup>2+</sup> , and protons agree with measured values observations in soil solution (1990–2005).	<a href="#">Bonten et al. (2015)</a>

**Table 4-17 (Continued): Model comparison.**

Soil Process/ Indicator	Type of Ecosystem	Region	Deposition kg/ha/yr	Modeled Observation	Reference
Base saturation	Forest	Great Smoky Mountains National Park	5.1 kg N/ha/yr (36.5 mmolc/m <sup>2</sup> /yr)	PnET-BGC used to model 30 stream watersheds during 1981–2014 when SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition decreased (81 and 53%, resp.). Hindcast modeling (beginning ca. 1850) showed decreased soil base saturation from 17.8% (preindustrial median) to 12.6% (current median).	<a href="#">Fakhraei et al. (2016)</a>

SO<sub>4</sub><sup>2-</sup> = sulfate; kg = kilogram; HBEF = Hubbard Brook Experimental Forest; S = sulfur; yr = year.

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## 4.6 National-Scale Sensitivity

The 2008 ISA documented that by the end of the 1980s, after nearly a decade of intensive research performed under the original National Acid Precipitation Assessment Program (NAPAP) research program, the regions of the U.S. with acid-sensitive waters and ecosystems were well recognized. These acid-sensitive ecosystems are generally located in upland mountainous terrain in the eastern U.S. and are underlain by weathering-resistant bedrock, such as granite or quartzite sandstone. The 2008 ISA documented maps of the U.S. that showed areas sensitive to acidification. However, similar maps for areas sensitive to the eutrophication effects of nitrogen were not available. Strong evidence was documented demonstrating that biogeochemical sensitivity to deposition-driven eutrophication and acidification is the result of historical loading, geologic/soil conditions (e.g., mineral weathering and S adsorption), and nonanthropogenic sources of N and S loading to the system. The 2008 ISA documented that there was no single deposition level applicable to all ecosystems in the U.S. that will describe the onset of eutrophication or acidification. Since the 2008 ISA, there are new publications commenting on recovery of terrestrial ecosystems at either the national scale ([NAPAP, 2011](#)) or in specific regions ([Lawrence et al., 2015a](#); [McDonnell et al., 2013](#); [Elliott et al., 2008](#)). One new paper evaluates national-scale terrestrial critical loads for nitrate leaching ([Pardo et al., 2011b](#)), but work on national-scale soil acidification published in 2007 remains the most recent national assessment of this effect ([McNulty et al., 2007](#)).

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### 4.6.1 Acidification Recovery

It is important to note that different chemical pools within the soil may recover from declining N and S atmospheric deposition at different rates. For example, soil solution Ca:Al ratio or  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  concentration are faster responding indicators than total N. Indicators that are linked to slow pools (such as soil percentage base saturations or soil C-to-N ratios) will have slow response times with regard to changes in atmospheric deposition. An indicator such as ANC which is influenced by both fast (solution) and slow (soil) pools has an intermediate response time. In addition to how indicators convey rates of recovery in different biogeochemical pools, recovery can be documented by empirical evidence and projected by models of recovery trajectories.

The most recent national-scale assessment of recovery from acidifying deposition was the National Acid Precipitation Assessment Program (NAPAP) report to Congress ([NAPAP, 2011](#)). NAPAP is a cooperative federal program first authorized in 1980 to coordinate acid rain research and report the findings to Congress. The NAPAP member agencies are

the U.S. EPA, the U.S. Department of Energy, the U.S. Department of Agriculture, the U.S. Department of Interior, the National Aeronautics and Space Administration, and the National Oceanic and Atmospheric Administration. The report concluded that few studies have evaluated terrestrial ecosystem health relative to acidification effects over time, and soils in the most acid-sensitive regions for which there is more data continue to acidify.

New evidence since the publication of the [NAPAP \(2011\)](#) is summarized in [Table 4-18](#). A new study supports the beginning of recovery from soil acidification in the northeastern U.S. ([Fuss et al., 2015](#); [Lawrence et al., 2015a](#)). [Fuss et al. \(2015\)](#) studied HBEF in NH and found indicators of recovery of acidification in soil solution measurements taken from 1984–2011. At the same site, [Phelan et al. \(2016\)](#) conducted a modeling study that showed current reductions in deposition generally halted further damage to soils and plants and resulted in no or only partial recovery.

In the southern Appalachian Mountains, modeling studies suggest current stress and recovery likely to take decades even under scenarios of large reductions in S deposition ([McDonnell et al., 2013](#); [Elliott et al., 2008](#)). [Rice et al. \(2014\)](#) calculated for many forested, unglaciated watersheds from Pennsylvania to Georgia will begin releasing  $\text{SO}_4^{2-}$  over the next two decades ([Appendix 4.3.3](#)). Unglaciated soils, like those that occur in the southeastern U.S., accumulate S that is slowly released from soil pools into drainage water, a process that temporarily delays ecosystem recovery in response to decreases in S deposition ([Appendix 4.3.3](#)).

The acid-base characteristics of DOC are an important part of understanding the recovery potential for soils, lakes, and streams impaired by acid deposition; these effects are discussed in [Appendix 4.3.9](#).

**Table 4-18 Recovery.**

Region	Type of Ecosystem	Empirical or Model	Approach/Observation	Reference
Southern Appalachian Mountains, NC	Forest soil	NuCM	<b>Model:</b> Modeled three S deposition simulations: current, 50% decrease, and 100% increase, at Joyce Kilmer (JK), Shining Rock (SR), and Linville Gorge (LG) wilderness areas. Low Ca:Al ratios results suggest that forests at SR and LG are significantly stressed under current conditions. The soil SO <sub>4</sub> <sup>2-</sup> retention is low, perhaps contributing to the high degree of acidification. The soils are very acidic and low in weatherable minerals. Even with large reductions in SO <sub>4</sub> <sup>2-</sup> and associated acid deposition, it may take decades before these systems recover from depletion of exchangeable Ca, Mg, and K.	<a href="#">Elliott et al. (2008)</a>
Southern Appalachian Mountains, U.S.	65 streams and their watersheds	MAGIC model	<b>Model:</b> A study used the MAGIC model to evaluate soil Bc status. Future S deposition reduction scenarios (6, 58, 65, and 78% reduction), and various changes in timber harvest, temperature, and precipitation were modeled. Each of the scenario projections indicated that median year 2100 soil exchangeable Ca will be at least 20% lower than preindustrial values. The simulations suggested that substantial mass loss of soil Bc has already occurred since preindustrial times. Soil Bc pools in the study region are expected to remain significantly below preindustrial conditions for more than 100 yr, regardless of changes in climate, S deposition, or timber harvest.	<a href="#">McDonnell et al. (2013)</a>
Great Smoky Mountains National Park, U.S.	Forest soils and streams	PnET-BGC	<b>Application:</b> Simultaneous reduction in SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition is more effective at increasing stream ANC than SO <sub>4</sub> <sup>2-</sup> alone. NO <sub>3</sub> <sup>-</sup> leaching continues as N deposition decreases (this is due to unmanaged forests). Stream recovery is delayed as NO <sub>3</sub> <sup>-</sup> facilitates desorption of legacy SO <sub>4</sub> <sup>2-</sup> that is adsorbed to acid soils.	<a href="#">Zhou et al. (2015b)</a>
Great Smoky Mountains National Park, U.S.	Forest soils and streams	PnET-BGC	<b>Model:</b> Modeling of 30 stream watersheds characterized by decreased SO <sub>4</sub> <sup>2-</sup> and NO <sub>3</sub> <sup>-</sup> deposition during 1981–2014 (81 and 53%) showed that stream recovery has been limited and delayed due to the high sulfate adsorption capacity of soils in the park resulting in a long lag time for recovery of soil chemistry.	<a href="#">Fakhraei et al. (2016)</a>

**Table 4-18 (Continued): Recovery.**

Region	Type of Ecosystem	Empirical or Model	Approach/Observation	Reference
Eastern Canada and the northeastern U.S.	Forest and streams	Recovery	<b>Field observation:</b> 27 sites exposed to reductions in wet $\text{SO}_4^{2-}$ deposition of 5.7–76%, over intervals of 8–24 yr. Results are decreased exchangeable Al in the O-horizon and increases in pH in the O and B-horizons at most sites. Among all sites, reductions in $\text{SO}_4^{2-}$ deposition were positively correlated with ratios of base saturation and negatively correlated with exchangeable Al ratios in the O-horizon. However, base saturation in the B-horizon decreased at one-third of the sites, with no increases.	<a href="#">Lawrence et al. (2015a)</a>
HBEF, NH	Forest and streams	Al <sub>i</sub> Recovery	<b>Field observation:</b> Slowed losses of base cations from soil and decreased mobilization of dissolved inorganic aluminum were observed. Stream water pH at the watershed outlet increased at a rate of 0.01 units/yr and the acid neutralizing capacity (ANC) gained 0.88 $\mu\text{eq/L/yr}$ . Dissolved organic carbon generally decreased in stream water and soil solutions. Both baseline and chronic acidification (measured during snowmelt) are recovering at this site.	<a href="#">Fuss et al. (2015)</a>
HBEF, NH, and Bear Brook Watershed, ME	Forests soils and plants	Model ForSAFE-VEG	<b>Model:</b> Only when future deposition to 2100 was returned to preindustrial levels was recovery of soil and plant community to 1900 conditions projected. Policy-based reductions in deposition generally halted further damage to soils and plants and resulted in no or only partial recovery.	<a href="#">Phelan et al. (2016)</a>
Adirondack Long-term Monitoring Program (ALTM; 128 lakes)	Forests soils and lakes	PnET-BGC	<b>Model:</b> Controlling S deposition is more effective at acidic lake recovery than controlling S + N deposition. Reducing N deposition is less effective because the resulting increase in soil pH leads to soil desorption of $\text{SO}_4^{2-}$ and other anions.  Reducing S dep. 60% beyond 2011 level is predicted to restore 28% of impaired lakes to $\text{ANC } 20 \mu\text{eq/L} \geq$ by 2050 and 60% of lakes by 2200. An ANC of 1 $\mu\text{eq/L}$ can be achieved to 53% of lakes by 2050.	<a href="#">Fakhraei et al. (2014)</a>

**Table 4-18 (Continued): Recovery.**

Region	Type of Ecosystem	Empirical or Model	Approach/Observation	Reference
Adirondack Mtns. Region, NY	Forests soils and lakes	PnET-BGC	<p><b>Model:</b> Decreasing <math>\text{SO}_4^{2-}</math> deposition is 4.6x more effective than <math>\text{NO}_3^-</math> decrease for years 2040–2050.</p> <p>Decreases in <math>\text{NO}_3^-</math> deposition is more effective at increasing lake ANC than an equal decrease in <math>\text{NH}_4^+</math> deposition.</p> <p>Due to the higher mass transfer coefficient for in-lake retention of <math>\text{NO}_3^-</math>, decreasing <math>\text{NO}_3^-</math> deposition decreases <math>\text{NO}_3^-</math> leaching but lowers ANC production.</p> <p>As <math>\text{SO}_4^{2-}</math> and <math>\text{NO}_3^-</math> deposition decrease, a significant lake DOC concentration increase has been observed. However, PnET-BGC does not consider the decrease in soil organic matter partitioning as acid deposition decreases and soil pH increases.</p>	<a href="#">Zhou et al. (2015c)</a>

MAGIC = Model for Acidification of Groundwater in Catchments; NuCM = Nutrient Cycling Model;  $\text{SO}_4^{2-}$  = sulfate; Ca = calcium; Mg = magnesium; K = Potassium; S = sulfur; Bc = base cation.

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## 4.6.2 Critical Loads

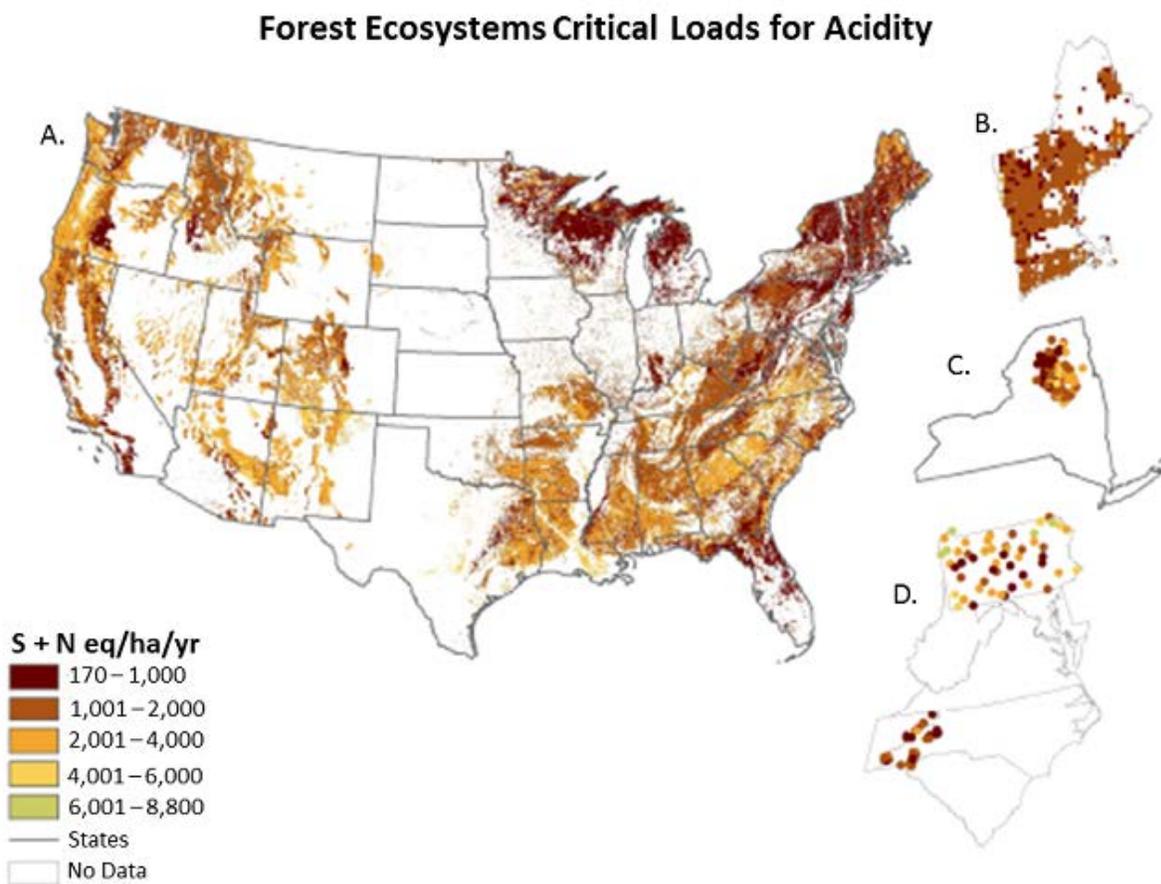
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### 4.6.2.1 Soil Acidification

The 2008 ISA included [McNulty et al. \(2007\)](#) a national assessment of soil critical loads for acidification calculated by a SMBE technique (see Section 4.5.1.8 of the 2008 ISA). The uncertainty associated with the SMBE technique was discussed in a second publication ([Li and McNulty, 2007](#)). In general, the SMBE predicted that 26% of U.S. forest soils have critical loads less than 1,000 eq/ha/yr. Low critical loads outside of New England, New York, and the Appalachian Mountain region are not necessarily problematic to forest health because acid deposition is much lower across most of the U.S. compared to these areas. Unfortunately, mountainous terrain comprises much of the area with very low forest soil critical loads. Mountain forests receive some of the highest local rates of acidic deposition.

No new publications are identified in this review on the subject of national-scale sensitivity; however, there are new reports on regional sensitivity. [Figure 4-10](#) is a map of soil CLs presented by [McNulty et al. \(2007\)](#) and updated with newer SMB modeling, where available ([McDonnell et al., 2014b](#); [Phelan et al., 2014](#); [Duarte et al., 2013](#); [Sullivan et al., 2011b](#); [Sullivan et al., 2011a](#)). [Duarte et al. \(2013\)](#) is a new evaluation of critical loads for terrestrial acidification in New England, U.S. The steady-state mass balance method is applied at over 4,000 plots. The acceptable ANC leaching rate was calculated based on the critical chemical criteria of no change in base saturation. Over 80% of the critical loads were between 850 and 2,015 eq/ha/yr. [Phelan et al. \(2014\)](#) evaluated PROFILE using national data sets as a method to estimate BCw rates for forests in the U.S., focusing on Pennsylvania as the first test state. The model paired with national data sets was successfully applied at 51 forested sites across Pennsylvania. The soil critical loads were evaluated using a Bc:Al value of 10.0. The CL values ranged from 4 to 10,503 eq/ha/yr. [Sullivan et al. \(2011a\)](#) used the dynamic model MAGIC to model terrestrial soil acidification in the Adirondacks, NY. Simulations were based on one driver of acidic deposition (S) and included evaluation of CLs for soil solution molar Bc:Al and Ca:Al ratio, two critical threshold levels (1 and 10), and two endpoint years of model simulation (2050 and 2100). Statistically selected lakes (n = 44) were modeled to represent a population of 1,320 sites. Nearly all (>93%) had a very low TL (<25 eq/ha/yr for the year 2100) when the protection threshold was set to BC:Al = 10, and the majority (>60%) had a high TL of (>100 eq/ha/yr for the year 2100) to achieve Bc:AL = 1. [Sullivan et al. \(2011b\)](#) calculated surface water CLs for 66 sites in the Blue Ridge

mountains (North Carolina, Tennessee, and South Carolina). CL were reported for surface waters; however, the MAGIC model was parameterized for all 66 sites including terrestrial geochemistry. [McDonnell et al. \(2014b\)](#) studied acidification in the southern Appalachians from northern Georgia to southern Pennsylvania and from eastern Kentucky and Tennessee to central Virginia and western North Carolina. Although soil critical loads were not reported in the publication, soil solution data are reported in [Figure 4-10](#).



eq = equivalent; ha = hectare; yr = year.

(A.) [McNulty et al. \(2007\)](#) critical loads are mapped at 1-km<sup>2</sup> grids (center map). For uncertainty, see [Li and McNulty \(2007\)](#).

(B.) [Duarte et al. \(2013\)](#) critical loads are mapped at 4-km<sup>2</sup> grids; (C. and D.) [Phelan et al. \(2014\)](#) critical loads are mapped for each sampling site (Pennsylvania). [McDonnell et al. \(2014b\)](#); [Sullivan et al. \(2011b\)](#); [Sullivan et al. \(2011a\)](#) critical loads are mapped as a single point at the center point of the watershed (New York and North Carolina).

Source: <http://nadp.slh.wisc.edu/committees/clad>.

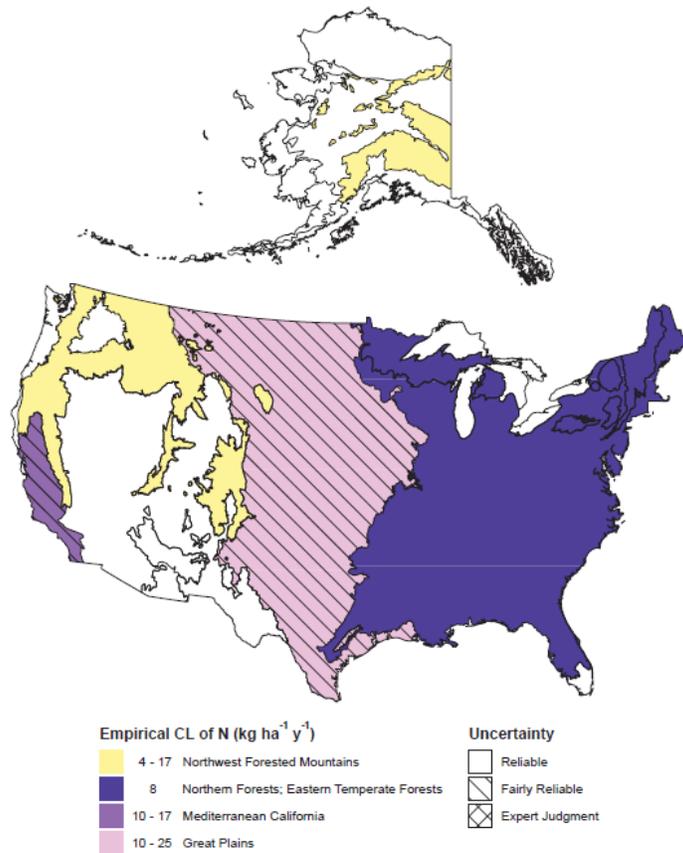
**Figure 4-10 Forest ecosystem critical loads for soil acidity related to base cation soil indicators.**

In the case of semiarid ecosystems of southern California, which are not highly sensitive to acidification, soils in high N deposition areas of chaparral and forested areas in the Los Angeles basin have acidified significantly ([Pardo et al., 2011b](#)).

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#### 4.6.2.2 Nitrate Leaching

[Pardo et al. \(2011b\)](#) documented the threshold N deposition value which caused increased  $\text{NO}_3^-$  leaching from forest ecosystems into surface water was 8 to 25 kg N/ha/yr. This information is summarized by ecoregion (Omernick Level 1) in [Figure 4-11](#). At 4 kg N/ha/yr, increasing  $\text{NO}_3^-$  was reported in the organic horizon in the Colorado Front Range, which suggests incipient N saturation. In the northeastern U.S., N budgets from 83 forested watersheds show that N retention averages 76% of incoming atmospheric-N deposition and decreases from 90% retention for sites receiving 7 kg N/ha/yr to 60% retention for sites receiving 11 kg N/ha/yr ([Aber et al., 2003](#)). The highest critical loads were reported for Mediterranean California mixed-conifer forests. Since the publication of [Pardo et al. \(2011b\)](#), new studies have been published on nitrate leaching in the U.S. (see [Appendix 4.3.2](#)); one critical load is from [Bowman et al. \(2014\)](#), who identify 10 kg N/ha/yr as the deposition level associated with nitrate leaching in RMNP. New evidence from Europe by [Dise et al. \(2009\)](#) shows approximately 95% of forests receiving less than 8 kg N/ha/yr have leaching of less than 1 kg N/ha/yr. In Sweden, [Khalili et al. \(2010\)](#) showed a clear sudden increase in  $\text{NO}_3^-$  leaching in regions where N deposition exceeded 7.5 kg/ha/yr.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

The range of critical loads based on increased nitrate leaching for each ecoregion. The hatch marks indicate increasing levels of uncertainty: no hatch marks for the most certain “reliable” category and single hatching for the “fairly reliable” category. White areas lack data for critical loads determination for nitrate leaching.

Source: [Pardo et al. \(2011b\)](#).

**Figure 4-11 Map of critical loads for nitrate leaching by ecoregion in the U.S.**

## 4.7 Modification of Terrestrial Soil Response to Nitrogen (N)

Biogeochemical responses to N deposition can be modified by many environmental factors including phosphorus, disturbance, stand age and climatic shifts in temperature and precipitation. Here we provide a very brief overview of these topics. [Appendix 13](#) provides an overview of modification of ecosystem response to N driven by climate, whereas this section describes a brief summary of how climate modifies terrestrial soil response to N.

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#### 4.7.1 Disturbance and Stand Age Effects on Nitrogen Retention

The 2008 ISA reported that varying degrees of N assimilation, leaching, and microbial transformation often reflect differences in N status among treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more ([Goodale and Aber, 2001](#)). Sites that have undergone disturbances that cause loss of soil N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and experimental inputs of N. Fire causes substantial N losses from ecosystems. Timber harvest contributes to nutrient removal from the ecosystem via biomass export and acceleration of leaching losses ([Mann et al., 1988](#); [Bormann et al., 1968](#)). In particular, logging contributes to loss of N and Ca<sup>2+</sup> from the soil ([Latty et al., 2004](#); [Tritton et al., 1987](#)). Fire has been shown to alter N retention by its effects on vegetation, leading to less interception of deposition, and soil characteristics; the effects on these processes may be seen for decades after fire occurs ([Kahl et al., 2007](#)). N retention capability often decreases with stand age, suggesting that older forests are more susceptible than younger forests to becoming N saturated ([Hedin et al., 1995](#)).

One new study has been published since 2008 on how disturbance affects N retention ([Vourlitis and Pasquini, 2008](#)). Fire did little to alter patterns of soil N enrichment from atmospheric N deposition; however, periodic fires have important implications for the structure and function of chaparral shrublands and their propensity to become N saturated under current and future N deposition and fire regimes.

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#### 4.7.2 Nitrogen and Phosphorus Interactions

Mechanisms driving terrestrial N versus P (phosphorus) limitations differ greatly since their sources and biogeochemical dynamics differ; therefore, there is variability across ecosystems ([Vitousek et al., 2010](#)). Organic N can be decomposed by a variety of enzymes to mineralize N from substrate; however, organic P relies on phosphatase enzymes to mineralize it, an enzymatic process that is independent of C respiration and N mineralization ([Marklein et al., 2016](#)).

Literature on N deposition's effect on N and P dynamics focuses on N and P cycling and the influence of N on phosphatase enzyme activity. Phosphatase is an enzyme released into the soil by organisms. It cleaves or hydrolyzes phosphorous (phosphoric acid) from substrate (soil, roots) to yield available phosphate for uptake ([Marklein et al., 2016](#)). The chemical structure of phosphatase includes N, therefore [Vitousek et al. \(2010\)](#) explained that N fertilization increases P cycling because it enables organisms to increase their extracellular phosphatase and, in turn, release more phosphate from soil organic matter.

There are some conflicting ideas of how N addition effects P in soils. N addition can acidify soil, therefore phosphatase activity may be suppressed by this mechanism, decreasing P release to soil ([Wang et al., 2016b](#)). In contrast, N addition can decrease the adsorption capacity of soil for P ions, thus increasing P availability and uptake by plants for productivity. It is also well known that N addition can increase litter decomposition, which may also increase P release/cycling rates. An increased supply of P can delay the onset of P limitation. It is important though to acknowledge that the type of N applied, application rate, and ecosystem type may influence the phosphatase activity ([Song et al., 2017](#)).

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### 4.7.3 Climate Modification of Acidification Effects on Soil

For soil acidification, potential future changes in the quantity and temporal distribution of precipitation and temperature (and their interactions) is expected to alter the wet-dry cycles that govern the timing and amount of acidic inputs in precipitation, microbial transformation in the soil, and the flush of acid anions from soils to surface waters.

There are two recent papers on the relationship between precipitation and sulfur in U.S. watersheds. [Rice et al. \(2014\)](#) indicated that hydrology, and specifically runoff, is an important controller of sulfate recovery in watersheds because drainage flushes the accumulated sulfur from the soil. As precipitation and runoff patterns change with a changing climate, this important process will be affected. Changing hydrology in the Northeast is well documented and underway, not just a future effect. Similarly, [Mitchell et al. \(2011\)](#) observed that following decades of changes in stream sulfate concentrations and fluxes that have been driven by atmospheric deposition, variation in stream sulfate is now being controlled by variations in precipitation inputs. Increased variation in precipitation will increase wetting and drying cycles that promote mineralization of sulfate from soil and subsequent methylation.

In general, if acid anions build up in soil during periods of drought, the eventual flushing likely causes a more potent acidification event ([Mosley, 2015](#); [Whitehead et al., 2009](#)). If the acidification event occurs during a time when sensitive biota or lifestages of biota are present, acidification may cause more adversity to these populations ([Kowalik et al., 2007](#)). Increases in storm frequency associated with global climate change ([Collins et al., 2013](#)) could increase the frequency and severity of acidification driven by high levels of sea salt deposition in coastal regions ([Wright and Schindler, 1995](#)). Although the mechanisms of interaction are unclear, increases in DOC concentrations in aquatic ecosystems across Europe and the U.S. have been linked to acidification, N cycling, and

climate change, with important implications for water quality and ecosystem function [[Evans et al. \(2008\)](#); see [Appendix 4.3.9](#)].

Warmer temperatures increase decomposition and nitrification. Nitrification will also increase with increased N supply caused by increased weathering or decomposition ([Booth et al., 2005](#)). The process of nitrification generates protons that increase the rate of nitrate and base cation leaching to drainage waters ([Murdoch et al., 1998](#)). The combined increase of  $\text{NO}_3^-$  leaching and loss of base cations has the potential to magnify acidification in forest soils ([Fernandez et al., 2003](#)). Soil weathering is typically the key buffer to acidic deposition ([Li and McNulty, 2007](#)), and while weathering is increased by both soil temperature and soil moisture ([Gwiazda and Broecker, 1994](#)), it is unclear whether any future change in the magnitude of temperature and precipitation will be enough to alter base cation supply or influence the acid-base balance of sensitive ecosystems. Furthermore, it is unclear whether increased supply of N in soils from either deposition, increased decomposition, or increased nitrogen fixation will negate the ameliorative effect of enhanced weathering. Some studies show that climate change will mitigate acidification through increased weathering ([Kopáček et al., 2017](#); [Belyazid et al., 2011a](#)), while others show that climate change will aggravate acidification although increased nitrification outpacing enhanced weathering ([Wu and Driscoll, 2010](#)). In general, increased temperature and precipitation will likely enhance inputs of buffering agents from weathering and deposition, but also increase inputs of acidifying agents from deposition and enhanced N cycling. The relative sensitivity of these opposing processes to a given change in climate remains unresolved.

Ecological effects of atmospheric nitrogen (N) and sulfur (S) deposition on two hardwood forest sites in the eastern United States were simulated in the context of a changing climate using the dynamic coupled biogeochemical/ecological model chain ForSAFE-VEG. The main driver of ecological effects was soil solution N concentration ([Mcdonnell et al., 2018a](#)).

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#### **4.7.4 Climate Modification of Nitrogen-Driven Eutrophication in Soil**

The following is a brief summary of how temperature, snow, and precipitation affect soil response to N. In addition, information is summarized on N effects on the flux of three GHGs ( $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ ) from terrestrial ecosystems.

Snow interacts with soil biogeochemistry in a number of ways, mostly by temperature shifts associated with snowpack and soil moisture flux during snowmelt. The highest flow and lowest ANC periods of the year tend to coincide with times of high snowmelt. This is when acidification is likely to occur. Snowpack insulates soils from frigid winter

air temperatures. With a warming climate, soils are expected to become colder and experience more winter soil freeze-thaw cycles as snow cover continues to decline.

A number of experiments have evaluated snow effects on soil N; these include studies on the timing, frequency, and severity (snow depth). [Contosta et al. \(2017\)](#) found evidence that in winters with more snow, a large pulse of  $\text{NO}_3^-$  may move from soils to streams when temperatures are too low/flows too high to allow for biological uptake. [Groffman et al. \(2001\)](#) conducted a snow manipulation experiment at HBEF and found mild late-season freezing increases soil  $\text{NO}_3^-$  levels by physical disruption (increased fine root mortality) causing reduced plant N uptake and reduced competition for inorganic N, allowing soil  $\text{NO}_3^-$  levels to increase even with no increase in net mineralization or nitrification. Later studies at the same site have shown that soil N mineralization rates were more strongly related to soil volumetric water content than to root biomass, snow or soil frost, or winter soil temperature ([Sorensen et al., 2016](#)), and the more freeze/thaw cycles anticipated with climate warming supported lower rates of N mineralization at HBEF ([Duran et al., 2016](#)). The effects of snow depth on soil N have been synthesized in a meta-analysis by [Li et al. \(2016c\)](#), who evaluated the central tendencies from 41 publications on 12 variables related to soil N. Results are that snow addition (increasing depth) significantly increased foliar N (+4.5%) and microbial N (MBN, +35.9%); however, snow removal did not significantly change under snow removal manipulation. Snow removal manipulation significantly decreased soil  $\text{N}_2\text{O}$  efflux (-34.1%) and nitrification (-24.8%). However, altered snow depth did not significantly affect soil dissolved organic N (DON), total inorganic N, nitrate, and N leaching. Because increasing snowpack depth promoted MBN, the unchanged, net N mineralization and soil ammonium content were probably due to limitation of the soil N availability and other soil abiotic factors rather than soil microbes.

[Greaver et al. \(2016\)](#) created a synthesis of meta-analyses to study the individual effects of either N, temperature, or precipitation on different pools and processes related to ecosystem C pools and fluxes ([Figure 13-2](#)). Nineteen different pools and processes were included in this analysis.

Initial findings are consistent with the biokinetic effects of warming; long-term data and meta-analyses show that soil respiration, including decomposition and microbial respiration, is stimulated by increasing temperature ([Lu et al., 2013](#); [Bond-Lamberty and Thomson, 2010](#); [Rustad et al., 2001](#)). Most empirical studies show rising temperature stimulates N release by mineralization ([Churkina et al., 2010](#)), which may be driven more by temperature effects on moisture ([Emmett et al., 2004](#)). In some dynamic land models, the additional N from mineralization will stimulate C uptake by plants even more than current N deposition ([Burd et al., 2016](#)). At the same time, increased N from

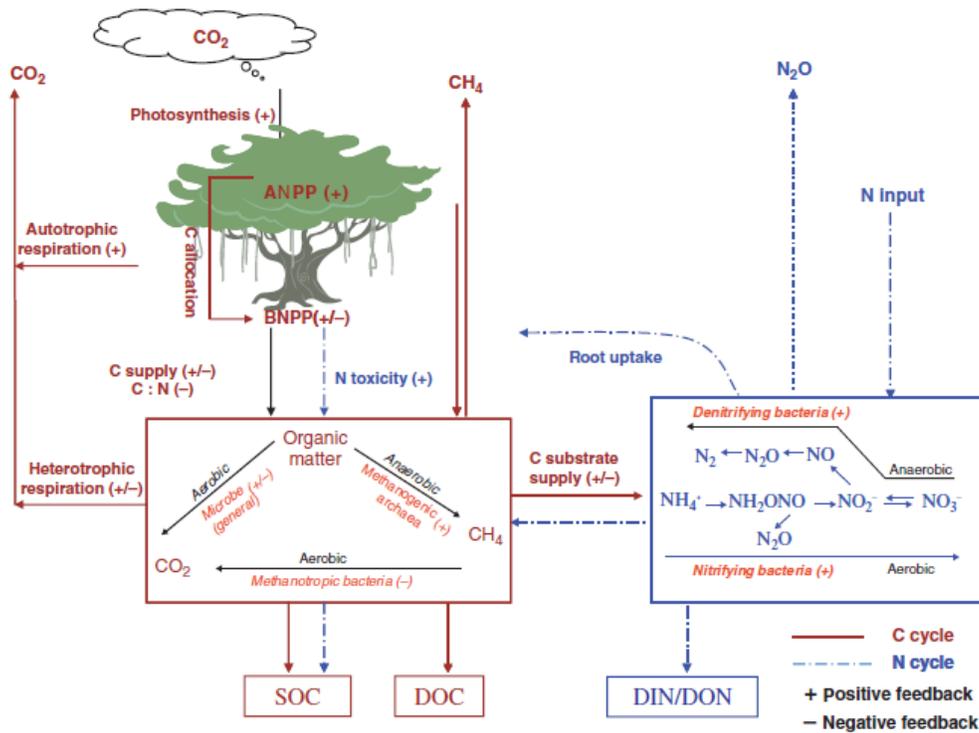
mineralization may cause N induced inhibition of decomposition, a feedback mechanism that might decrease the amount of N released and which is currently considered by a few models ([Gerber et al., 2010](#)). The mechanisms causing N driven reduction in decomposition are not well understood but are thought to result from changes in microbial community composition and the production of decomposition enzymes, as well as possible changes in the character and degradability of soil organic matter ([Conant et al., 2011](#); [Janssens et al., 2010](#)). Climate change could also affect decomposition rates by altering both available soil moisture and microscale connectivity among microorganisms, water, and nutrients within the soil matrix, which, in turn, may alter microbial processes ([Xiang et al., 2008](#)). Although there is no consensus about how dissolved organic carbon (DOC) in surface water is regulated overall, increasing N and temperature increase DOC concentrations ([Laudon et al., 2012](#)). While few meta-analyses have examined precipitation effects on the soil C cycle, precipitation tends to increase the root C pool ([Figure 13-2](#)).

[Ni et al. \(2017\)](#) created a meta-analysis to evaluate the interactions between warming and N deposition and found the interaction greatly increased the soil C input (+49%) compared with the single factor of either warming (+5%) or N deposition (+20%). Soil C loss was not significantly affected by the interaction of N and warming likely because increases in decomposition due to warming are offset by the decreases by N addition.

N addition alters fluxes of GHGs by regulating plant and microbial activities that are directly associated with GHG production and consumption processes ([Figure 4-12](#)). It is important to consider net ecosystem flux because consumption may be offset by production. For example, N addition stimulates plant growth in most ecosystems ([LeBauer and Treseder, 2008](#)), and may in turn increase C sequestration in plant biomass. On the other hand, maintenance respiration is positively correlated with tissue N content ([Reich et al., 2008](#)), and litter with higher N content also decomposes faster. Therefore, increased leaf N content under elevated N may result in higher C loss by increasing both autotrophic and heterotrophic respiration. Like CO<sub>2</sub>, ecosystems may consume and produce CH<sub>4</sub> and N<sub>2</sub>O, and the balance determines their net release.

[Liu and Greaver \(2009\)](#) conducted a meta-analysis of 313 observations across 109 studies to evaluate the effect of N addition on the flux of three GHGs: CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. The results indicated that N addition increased ecosystem carbon content of forests by 6%, marginally increased soil organic carbon of agricultural systems by 2% but had no significant effect on net ecosystem CO<sub>2</sub> exchange for nonforest natural ecosystems. Across all ecosystems, N addition increased CH<sub>4</sub> emission by 97%, reduced CH<sub>4</sub> uptake by 38%, and increased N<sub>2</sub>O emission by 216%. Most often, N addition is considered to increase forest C sequestration without consideration of N stimulation of GHG

production in other ecosystems. However, this study indicated that although N addition increased the global terrestrial C sink, the GHG benefits of an atmospheric CO<sub>2</sub> reduction could be largely offset (53–76%) by N stimulation of global CH<sub>4</sub> and N<sub>2</sub>O emission from multiple ecosystems.



ANPP = aboveground net primary productivity; BNPP = belowground net primary productivity; SOC = soil organic carbon; DOC = dissolved organic carbon; DIN = dissolved inorganic nitrogen; DON = dissolved organic nitrogen.  
Source: [Liu and Greaver \(2009\)](#).

**Figure 4-12** The potential mechanisms that regulate the responses of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) production and consumption to elevated nitrogen (N).

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## 4.8 Summary

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### 4.8.1 Sources

The effects of N and S deposition on soil biogeochemistry cause cascading effects on biological species. The biological effects are discussed in [Appendix 5](#) and [Appendix 6](#).

Since 2008, there have been a number of estimates of sulfate, oxidized nitrogen, and reduced nitrogen from atmospheric deposition. The most recent estimates are summarized in [Appendix 2](#), and maps showing the geographic distribution of deposition are presented for total acidifying deposition ([Figure 2-12](#)), total N deposition ([Figure 2-13](#)), and total S deposition ([Figure 2-31](#)). Maps depicting how the relative contribution of oxidized and reduced N species varies across the U.S. are presented in [Figure 2-14](#).

In the 2008 ISA, atmospheric deposition was identified as the main source of anthropogenic N, relative to other N sources, to nonmanaged terrestrial ecosystems. This has been confirmed by new studies on N sources to U.S. lands and waterways, which find human-mediated N inputs are spatially heterogeneous across the country, ranging from <1.0 to 34.6-fold the rate of background N input across the conterminous U.S. Synthetic N fertilizer and atmospheric N deposition are the largest and second-largest overall human-mediated N sources (the single largest sources in 41 and 33% of HUC-8s, respectively). There is no new information published on nondeposition sources of S in terrestrial ecosystems. S inputs from emissions to the atmosphere are discussed in [Appendix 2](#).

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### 4.8.2 Soil Processes and Indicators

Soil N enrichment and soil acidification are occurring in sensitive ecosystems across the U.S. at recent levels of deposition. Soil acidification is a natural process that can be accelerated by N and/or S deposition. A number of soil geochemical processes are associated with acidification ([Appendix 4.3](#) and [Table 4-19](#)). Base cations counterbalance acid anions. Base cations are added to a watershed by weathering and atmospheric deposition and are removed by leaching and (perhaps temporarily) by uptake into growing vegetation. Acidifying deposition can deplete exchangeable base cation pools in soils where acid deposition is high relative to base cation input. The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid)

controls the rate of base cation leaching from soil where rates of atmospheric deposition of S and N are low. In addition to increasing ion concentration in soil, inputs of S and N in acidifying deposition provide anions that are highly mobile, further accelerating the rates of base cation leaching. In addition, the deposition of reduced forms of N (e.g.,  $\text{NH}_x$ ) can stimulate nitrification, which is the microbial oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . This oxidation process acidifies soils because 2 moles of hydrogen ion ( $\text{H}^+$ ) are released per mole of  $\text{NH}_4^+$  converted to  $\text{NO}_3^-$ . Therefore, both chemically reduced and oxidized forms of N and S deposition contribute to terrestrial acidification. Several useful indicators of soil acidification ([Table 4-19](#)) include indicator thresholds related to biological responses, the biological basis of which are discussed in [Appendix 5](#).

It is clear from [Table 4-19](#) that some of the same processes and indicators associated with acidification are also associated with N enrichment. The N enrichment of terrestrial soils occurs in response to the input of exogenous N. The new studies on N deposition contribution to total N loading in terrestrial U.S. ecosystems are discussed in [Appendix 4.2](#).

The 2008 ISA documented that most N, often more than 85% of the total ecosystem N, is stored in the soil in temperate forest ecosystems. There is new evidence that soil litter is the largest N pool in grasslands, shrublands, and wetlands ([Appendix 4.3.1](#)). The ability of atmospheric deposition to increase soil N is indicated by a positive correlation between atmospheric deposition levels and total N concentration in the organic and mineral soil horizon. Soil N accumulation is linked to increased N leaching and decreased N retention ([Appendix 4.3.2](#)). Thresholds of N deposition that are associated with the onset of elevated  $\text{NO}_3^-$  leaching are discussed in [Appendix 4.6.2.2](#).

Recent work suggests that N leaching from soil can precede the complete saturation of the biotic and abiotic processes that retain N ([Appendix 4.3.2](#)). [Lovett and Goodale \(2011\)](#) proposed a model of N saturation in which  $\text{NO}_3^-$  leaching can occur even if the ecosystem N retention capacity has not yet been saturated, as is observed at many sites and supported by several new studies. Although N leaching may occur prior to saturation, N budgets from 83 forested watersheds in the northeastern U.S. show that N retention averages 76% of incoming N deposition. Nitrogen retention decreases from 90% retention for sites receiving 7 kg N/ha/yr to 60% retention for sites receiving 11 kg N/ha/yr, suggesting a range of response in which leaching is exacerbated in this region ([Aber et al., 2003](#)).

The 2008 ISA documented that N enrichment alters rates of microbial transformation of chemicals in the soil, such as increased rates of nitrification and denitrification, and altered rates of decomposition. The addition of N to terrestrial ecosystems can increase nitrification, an important process for soil acidification and the production of  $\text{NO}_3^-$ .

Nitrification is often stimulated in soils with a C:N ratio below approximately 20 to 25, and N deposition often causes the ratio to fall below this threshold. The  $\text{NO}_3^-$  created by nitrification may be leached or denitrified. In terrestrial ecosystems, denitrification of  $\text{NO}_3^-$  mainly occurs in saturated zones. Several syntheses have been published since 2008 evaluating N addition effects on denitrification and nitrification in terrestrial ecosystems ([Appendix 4.3.6](#)). A new meta-analysis shows N addition significantly increases denitrification from many types of ecosystems (coniferous forest, deciduous forest, tropical forest, wetland, grassland), except heathlands.

**Table 4-19 Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N-Driven Nutrient Enrichment	Acidification	The Effect of Deposition
<b>PROCESS</b>			
N saturation	X	X	New empirical evidence suggests revising the N saturation concept, because observed NO <sub>3</sub> <sup>-</sup> leaching can occur even if the ecosystem N retention capacity has not yet been saturated.
Soil N accumulation	X	X	New meta-analysis across ecosystem types confirms inorganic soil NO <sub>3</sub> <sup>-</sup> concentration increases with N addition. New gradient study confirms that N concentration increases with N deposition. New addition study confirms increased soil accumulation.
NO <sub>3</sub> <sup>-</sup> leaching	X	X	New meta-analysis confirms leaching increases with N addition. New regional-scale gradient analyses: <8 kg N/ha/yr onset of leaching <1 kg N/ha/yr in European forests. Second study suggests <7.5 kg N/ha/yr increases leaching in Swedish forests. New addition study: 9 to 14 kg N/ha/yr increase in inorganic N concentrations. New USFS critical loads for the onset of leaching: 8 to 10 kg N/ha/yr in eastern and western U.S., 17 kg N/ha/yr in the Sierra Nevada and San Bernardino Mountains.
S accumulation and adsorption		X	Some soils (notably in many watersheds in the SE U.S.) have the capacity to adsorb substantial quantities of S, with essentially no acidification of drainage water. Nevertheless, S adsorption capacity is finite and under continual high S deposition loading, the adsorptive capacity of soil will eventually be depleted. New studies of 27 watersheds in the SE indicates most will begin releasing SO <sub>4</sub> <sup>2-</sup> in the next two decades, and northeastern watersheds show a net loss of S from soils now in response to decreased levels of atmospheric S deposition.
SO <sub>4</sub> <sup>2-</sup> leaching		X	Atmospheric S deposition generally increases leaching of SO <sub>4</sub> <sup>2-</sup> to surface waters. The amount of deposition that causes the onset of leaching varies across the landscape.

**Table 4-19 (Continued): Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N-Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Base cation release/depletion		X	<p>Base cation (Ca, Mg, K, Na) release occurs in response to the input of acid anions (<math>\text{SO}_4^{2-}</math> and <math>\text{NO}_3^-</math>) from deposition. This proportional change in base cations relative to acid anions from N and S deposition is called the F-factor.</p> <p>New studies confirm base cation depletion continues to occur in the Rocky Mountains (threshold 28 kg N/ha/yr) and in U.K. grasslands, while in a northeastern forest, 17 yr of N addition did not cause further depletion. A meta-analysis indicates cation depletion occurs early after increased deposition of acid anions, which tapers off with time.</p>
Al mobilization		X	<p>&lt;15 to 20% soil base saturation is the threshold for inorganic Al mobilization from soil. This is an extremely important effect of acidifying deposition because inorganic monomeric Al, including <math>\text{Al}^{3+}</math> and various hydroxide species, is toxic to biota (<a href="#">Appendix 5</a>). Inorganic Al is minimally soluble at pH about 6.0, but solubility increases steeply at pH values below about 5.5.</p> <p>There have been no new studies on Al mobilization.</p>
Nitrification	X	X	<p>Nitrification releases 2 mol hydrogen ion (<math>\text{H}^+</math>) per mol <math>\text{NH}_4^+</math> converted to <math>\text{NO}_3^-</math>, acidifying soils. As soil inorganic N accumulates, net nitrification rates often increase, and <math>\text{NO}_3^-</math> can leach from the ecosystem.</p> <p>New N gradient and meta-analysis studies confirm N addition increases nitrification.</p>
Denitrification	X		<p>Denitrification is the microbial reduction of <math>\text{NO}_3^-</math> to nitrite (<math>\text{NO}_2^-</math>), nitric oxide (NO), the greenhouse gas nitrous oxide (<math>\text{N}_2\text{O}</math>), and <math>\text{N}_2</math>. It occurs under anaerobic conditions. In Europe, soil switched from a source to a sink after two decades of N deposition exclusion.</p> <p>New meta-analysis confirms N addition increases denitrification rates.</p>
DOC leaching	X	X	<p>Acidity of some surface waters is partly regulated by DOC concentrations. Soil acidification can suppress the natural production of DOC. In recent years, the DOC concentration of some lakes and streams has risen, with adjacent terrestrial ecosystems as the DOC source. However, the mechanism for this increase is unclear. It may be due to soil recovery from acidification or N deposition effects on decomposition.</p> <p>New studies include a meta-analysis and field addition studies.</p>

**Table 4-19 (Continued): Summary of key soil geochemical processes and indicators associated with eutrophication and acidification.**

Endpoint	N-Driven Nutrient Enrichment	Acidification	The Effect of Deposition
Decomposition/mineralization	X	X	Decomposition rates correlate with ratios of C:N, lignin:N, or lignin:cellulose in litter. The addition of N can stimulate the decomposition of labile compounds that degrade during the initial stages of decomposition, but added N can suppress the decomposition of more recalcitrant material. Evidence for this is widespread in forests but has not yet been well documented in grasslands and other ecosystems.  There are new addition studies and meta-analysis to better understand the mechanisms and response trends.
<b>INDICATOR</b>			
Soil [N]	X	X	Increasing N deposition increases concentration of N in soil and reflects soil N accumulation that may be assimilated by organisms or mobilized via leaching.
Soil C:N ratio	X	X	Increasing N deposition decreases the C:N in plant tissue, causing cascading effects during decomposition on microbial transformation, especially nitrification, leading to increased NO <sub>3</sub> <sup>-</sup> leaching.  THRESHOLD: <20 to 25 associated with elevated rates of nitrification and elevated risk of nitrate leaching in the U.S. and <25 to 30 for increased NO <sub>3</sub> <sup>-</sup> leaching in Europe.
Soil base saturation		X	Increasing N + S deposition decreases the soil pool of exchangeable base cations.  THRESHOLD: <15 to 20% is the value at which exchange ion chemistry is dominated by inorganic Al and may cause injury to vegetation (see <a href="#">Appendix 5</a> ).
Soil Bc:Al ratio		X	Increasing N + S deposition decreases the soil pool of exchangeable base cations, often decreasing the Ca:Al ratio.  THRESHOLD: Ca:Al <1.0 to 10 causes physiological stress and decreased growth and survival of sensitive plant species (see <a href="#">Appendix 5</a> ).
Fungi:bacteria ratio	X		New indicator since 2008 ISA: Increasing N deposition decreases the fungi-to-bacteria ratio and causes a transition from N to C limitation among soil food webs.

Al = aluminum; Bc = base cation; C = carbon; Ca = calcium; DOC = dissolved organic carbon; H<sup>+</sup> = hydrogen ion; ha = hectare; K = potassium; kg = kilogram; Mg = magnesium; N = nitrogen; N<sub>2</sub> = molecular nitrogen; N<sub>2</sub>O = nitrous oxide; NE = northeast; NH<sub>4</sub><sup>+</sup> = ammonium; NO = nitric oxide; NO<sub>2</sub><sup>-</sup> = nitrite; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SE = southeast; yr = year.

The effects of N on decomposition, which is the breakdown of organic matter, is an active area of research ([Appendix 4.3.7](#)). Within the soil microbial community, bacteria and fungi are the primary decomposers of organic matter. Both microbial community composition (see [Appendix 6](#)) and microbial enzyme activity can respond dynamically to shifts in inorganic nutrient and substrate availability, reflecting the nutrient and energy limitation of the microbial community. Litter decay rates are also well established to correlate with ratios of C:N, lignin:N, or lignin:cellulose in litter. These chemical traits have been shown to account for over 73% of the variation in litter decomposition rates worldwide. Based on these observations, it could be assumed that added N would stimulate decomposition and the loss of C from soil pools. There is now widespread evidence, however, that the stimulatory effects of N on decomposition are limited to the early stages of mass loss, when more labile compounds are degraded. During the later stages of decomposition when the rates of mass loss are slow and controlled by the degradation of recalcitrant compounds, the addition of N slows decomposition. This slowing of decomposition appears to be a consequence of decreases in the production of some extracellular enzymes by fungi. It is clear that N additions generally decrease respiration from soil heterotrophs, but this may not decrease total soil respiration because heterotrophic respiration accounts for only a portion of soil CO<sub>2</sub> efflux.

Several new meta-analyses have been published since 2008 on N addition effects on belowground carbon cycling ([Appendix 4.3.10](#)). About half of C fixed annually by terrestrial vegetation is allocated to belowground C pools; therefore, it is important to understand how N affects belowground C to better understand changes in plant physiology, plant growth, and ecosystem C cycling ([Appendix 6](#)). Many studies have shown that changes in the belowground C cycle do not always match the aboveground C cycle. Therefore, it is inappropriate to extrapolate from aboveground responses to belowground processes.

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### 4.8.3 Monitoring

Several new studies use long-term monitoring data sets. [Yanai et al. \(2013\)](#) evaluated 45 years of biogeochemical monitoring data at the HBEF, NH. From 1966 to 1977, more N was accumulating in living biomass than was input by atmospheric deposition; the missing N source was attributed to N fixation. Since 1992, biomass accumulation has been negligible, and the ecosystem shifted to a net missing N sink of ~8 kg N/ha/yr, which the authors hypothesized may not be the result of N retention, but may be due to gaseous N fluxes in response to N deposition or uncertainty the amount of N in the mineral soil. [Mitchell and Likens \(2011\)](#) examined sulfur accumulation observed in over four decades of continuous long-term record for four watersheds, showing that the

biogeochemical control of annual  $\text{SO}_4^{2-}$  export in stream water draining from forested watersheds has shifted from control by atmospheric S deposition to soil moisture driven by climate (reported in [Appendix 4.3.3](#)). At the Niwot Ridge LTER, CO, [Lieb et al. \(2011\)](#) found that a decade of simulated N deposition to alpine ecosystems caused ongoing changes in diversity and soil biogeochemistry, including lower soil acid buffering capacity, decreased concentrations of  $\text{Mg}^{2+}$ , and increased concentrations of the potentially toxic cations  $\text{Mn}^{2+}$  and  $\text{Al}^{3+}$ . Their results suggested an N deposition threshold of 28 kg N/ha/yr.

There are new studies on long-term monitoring in Europe, including investigations of S dynamics in England ([Lehmann et al., 2008](#)), N and S dynamics in Switzerland ([Pannatier et al., 2011](#)), and N and C interactions between boreal soils and lakes in Sweden ([Khalili et al., 2010](#)). Notably, [Khalili et al. \(2010\)](#) found a significant relationship between C:N ratios of the organic soil layer and C in lake waters, and a clear sudden increase in  $\text{NO}_3^-$  leaching in regions where N deposition exceeded 7.5 kg N/ha/yr.

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#### 4.8.4 Models

The most commonly used ecosystem models in the U.S. were described in the 2008 ISA. Here we focus on the several primary models that are currently being used in the U.S. to assess the effects of S and N deposition on terrestrial ecosystems. One important input to these models are estimates of base cation weathering (BCw). There are new updates on two methods to estimate this parameter: Soil Texture Approximations (STA) and PROFILE. Steady-state models include steady-state mass balance equations (SMBE), while dynamic models include the VSD and  $\text{VSD}^+$ , MAGIC, NuCM, PnET/BGC, and DayCent-Chem.

Base cation weathering rate is one of the most influential yet difficult to estimate parameters in the calculation of critical acid loads of nitrogen (N) and sulfur (S) deposition for terrestrial systems. Commonly used models include STA, a simple empirical steady-state model with low data requirements, and PROFILE, a mechanistic, steady-state kinetics model that requires 26 input parameters. There is a new study on estimating BCw. [Koseva et al. \(2010\)](#) confirmed that the STA equations were derived for young soils that developed following the Late Wisconsin glaciation and may not be suitable for older, more weathered soils that were not affected by the most recent glaciation and which cover the majority of the U.S. ([U.S. EPA, 2009c](#)). The larger data set required to run PROFILE prohibits applying the model to many parts of the U.S. However, a recent soil geochemical data set compiled by the USGS has made it possible to apply PROFILE in the U.S. The initial application in 51 forested sites across

Pennsylvania indicates this technique may be appropriate for applications nationwide ([Phelan et al., 2014](#)). The uncertainty associated with the calculation of BCw has recently been evaluated by [Futter et al. \(2012\)](#), who estimated that the contribution of model parameter uncertainty to overall variability related to PROFILE and MAGIC (a dynamic model that typically uses PROFILE for initial estimates of BCw) was relatively small.

Estimates of BCw are input parameters in soil acidification models. The simplest acidification models are the steady-state mass balance models. The 2008 ISA documented a model based on simple mass-balance equations (SMBE) to assess critical loads for acidification in U.S. forest soils ([McNulty et al., 2007](#)). A second publication discussed the uncertainties associated with this model and national-scale assessment ([Li and McNulty, 2007](#)). The results indicated that uncertainty in the critical load came primarily from components of BCw (49%) and acid neutralizing capacity (46%), whereas the most critical parameters were BCw base rate (62%), soil depth (20%), and soil temperature (11%). The authors concluded that improvements in estimates of these factors are crucial to reducing uncertainty and successfully scaling up SMBE for national assessments. [Posch et al. \(2011\)](#) discussed a regional application of SMB models.

Dynamic models are typically applied to much smaller spatial areas than steady-state models because they require more data and parameterization. The VSD model is the simplest extension of the steady-state SMB model into a dynamic model that is designed for sites with few data available and applications on a large regional or continental scale. [Posch and Reinds \(2009\)](#) developed a version of the VSD for steady-state critical load applications at the regional scale. The ForSAFE model [Wallman et al. \(2005\)](#) simulates the cycles of carbon, nitrogen, base cations (Bc), and water in a forest ecosystem, while simultaneously simulating soil chemistry, tree growth, and soil organic matter accumulation or depletion. ForSAFE-VEG ([Sverdrup et al., 2007](#)) is a composite model that can link changes in atmospheric deposition, climatic conditions, and land use to responses in the biogeochemistry and plant community composition at the site level, both historically and into the future. [Belyazid et al. \(2011a\)](#) stated that the biogeochemical model platform must be improved to simulate N processes more accurately before being applied to calculate critical loads. The model overestimated the actual N concentrations in the soil solution. Several new applications of ForSAFE-VEG were published [[Belyazid et al. \(2011a\)](#); [Sverdrup et al. \(2012\)](#); [McDonnell et al. \(2013\)](#)], and the results are discussed in [Appendix 5](#) and [Appendix 6](#)].

MAGIC ([Cosby et al., 1985a](#); [Cosby et al., 1985c](#); [Cosby et al., 1985b](#)) is one of the most well-known dynamic models of aquatic acidification. An update to MAGIC by [Oulehle et al. \(2012\)](#) gives a more realistic simulation of observed changes in N leaching. The new formulation also provides a reasonable simulation of the long-term changes in C and N

pools (and C:N ratio) with SOM. PnET-BGC is an integrated forest-soil-water model that has been used to assess the effects of air pollution and land disturbances on forest and aquatic ecosystems; it uses a new conceptual advancement that incorporates CO<sub>2</sub> dynamics into the model. DayCent-Chem links two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent ([Parton et al., 1998](#)), and the other of soil and water geochemical equilibrium, PHREEQC ([Parkhurst and Appelo, 1999](#)). There is a new conceptual advancement for DayCent which now includes O<sub>3</sub> ([Bytnerowicz et al., 2013](#)). The Nutrient Cycling Model (NuCM) was developed to synthesize current understanding of nutrient cycling in forests and to predict how forests respond to changing S and N atmospheric deposition rates. No revisions to these models have been identified.

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#### 4.8.5 National-Scale Sensitivity

The 2008 ISA documented that by the end of the 1980s, after nearly a decade of intensive research performed under the original NAPAP, the regions of the U.S. with many acid-sensitive waters and ecosystems were well recognized. These acid-sensitive ecosystems are generally located in upland mountainous terrain in the eastern U.S. and are underlain by weathering-resistant bedrock like granite or quartzite sandstone. However, similar work characterizing areas sensitive to the eutrophication effects of nitrogen is not available. Typically, all terrestrial ecosystems are sensitive to N deposition.

There is strong evidence to show that biogeochemical sensitivity to N-driven eutrophication and acidification from atmospheric deposition is the result of historical loading, geologic/soil conditions (e.g., mineral weathering and S adsorption), and nonanthropogenic sources of N and S loading to the system. No single deposition level is applicable to all ecosystems in the U.S. that will describe the onset of eutrophication or acidification. Ecosystem sensitivity is heterogeneous.

New publications have commented on recovery of terrestrial ecosystems from acidification at the national scale ([NAPAP, 2011](#)), specifically in the Northeast ([Phelan et al., 2016](#); [Fuss et al., 2015](#); [Lawrence et al., 2015a](#)), and the lack of recovery in the southern Appalachian Mountains ([Fakhraei et al., 2016](#); [Zhou et al., 2015b](#); [McDonnell et al., 2013](#); [Elliott et al., 2008](#)). Work on national-scale soil acidification published in 2007 remains the most recent national assessment of this effect ([McNulty et al., 2007](#)); however, [Figure 4-10](#) is a map of soil CLs that updates ([McNulty et al., 2007](#)) with newly available modeling ([McDonnell et al., 2014b](#); [Phelan et al., 2014](#); [Duarte et al., 2013](#); [Sullivan et al., 2011b](#); [Sullivan et al., 2011a](#)).

New critical loads for nitrate leaching in forest ecosystems reported by [Pardo et al. \(2011b\)](#) ranges from 8 to 25 kg N/ha/yr across ecoregions (Omernick Level 1) in the U.S. ([Figure 4-11](#)). At 4 kg N/ha/yr, increasing  $\text{NO}_3^-$  was reported in the organic horizon in the Colorado Front Range, which suggests incipient N saturation. In the northeastern U.S., N budgets from 83 forested watersheds show that N retention averages 76% of incoming atmospheric-N deposition and decreases from 90% retention for sites receiving 7 kg N/ha/yr to 60% retention for sites receiving 11 kg N/ha/yr ([Aber et al., 2003](#)). The highest critical loads were reported for Mediterranean California mixed-conifer forests. Since the publication of [Pardo et al. \(2011b\)](#), new studies have been published on nitrate leaching (see [Appendix 4.3.2](#)). Evidence from Europe by [Dise et al. \(2009\)](#) showed approximately 95% of forests receiving less than 8 kg N/ha/yr have leaching of less than 1 kg N/ha/yr. In Sweden, [Khalili et al. \(2010\)](#) showed a clear sudden increase in  $\text{NO}_3^-$  leaching in regions where N deposition exceeded 7.5 kg/ha/yr.

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#### 4.8.6 Climate Modification of Soil Response to Nitrogen Addition

Soil biogeochemistry response to N deposition can be modified by climatic shifts in temperature and precipitation. For soil acidification, potential future changes in the quantity and temporal distribution of precipitation and temperature (and their interactions) is expected to alter the wet-dry cycles that govern the timing and amount of acidic inputs in precipitation, microbial transformation in the soil, and the flush of acid anions from soils to surface waters. In general, increased temperature and precipitation will likely enhance inputs of buffering agents from weathering and deposition, but also increase inputs of acidifying agents from deposition and enhanced N cycling. The relative sensitivity of these opposing processes to a given change in climate remains unresolved.

Snow interacts with soil biogeochemistry in a number of ways, mostly by temperature shifts associated with snowpack and soil moisture flux during snowmelt ([Duran et al., 2016](#); [Sorensen et al., 2016](#); [Groffman et al., 2001](#)). The highest flow and lowest ANC periods of the year tend to coincide with times of high snowmelt. This is when acidification is likely to occur. Snowpack insulates soils from frigid winter air temperatures. With a warming climate, soils are expected to become colder and experience more winter soil freeze-thaw cycles as snow cover continues to decline. There have been a number of experiments evaluating how snow effects soil N; these include studies on the timing, frequency, and severity [snow depth; [Li et al. \(2016c\)](#)].

[Greaver et al. \(2016\)](#) created a synthesis of meta-analyses to study the effects of either N, temperature, or precipitation on different pools and processes related to ecosystem C responses to these variables and to gain some insight as to the direction and magnitude of

the change observed ([Figure 13-2](#)). Nineteen different pools and processes were included in this analysis. [Liu and Greaver \(2009\)](#) conducted a meta-analysis of 313 observations across 109 studies of terrestrial and wetland ecosystems to evaluate the effect of N addition on the flux of three GHGs (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O). This study indicated that although N addition increased the global terrestrial C sink, the GHG benefits of an atmospheric CO<sub>2</sub> reduction could be largely offset (53–76%) by N stimulation of global CH<sub>4</sub> and N<sub>2</sub>O emission from multiple ecosystems. The authors noted that N addition alters fluxes of GHGs by regulating plant and microbial activities that are directly associated with GHG production and consumption processes. It is therefore extremely important to consider total ecosystem flux of GHGs because consumption may be offset by production, even within the same ecosystem

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## APPENDIX 5 BIOLOGICAL EFFECTS OF TERRESTRIAL ACIDIFICATION

This appendix characterizes the biological effects of acidifying deposition of nitrogen (N) and sulfur (S) to terrestrial ecosystems. [Appendix 5.2](#) discusses effects on trees and forests ([Appendix 5.2.1](#)), understory plants and grasslands ([Appendix 5.2.2](#)), lichens ([Appendix 5.2.3](#)), soil biota ([Appendix 5.2.4](#)), and fauna ([Appendix 5.2.5](#)). The characteristics, distribution and extent of sensitive ecosystems is presented in [Appendix 5.3](#). Next, [Appendix 5.4](#) presents the application of terrestrial acidification models. Finally, levels of deposition at which effects are manifested is discussed in [Appendix 5.5](#), including a discussion of critical loads ([Appendix 5.5.3](#)). Climate modification of acidifying deposition effects is discussed in [Appendix 5.6](#). A summary section with causal determinations based on a synthesis of new information and previous evidence of biological effects of terrestrial acidification is presented in [Appendix 5.7](#).

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### 5.1 Introduction

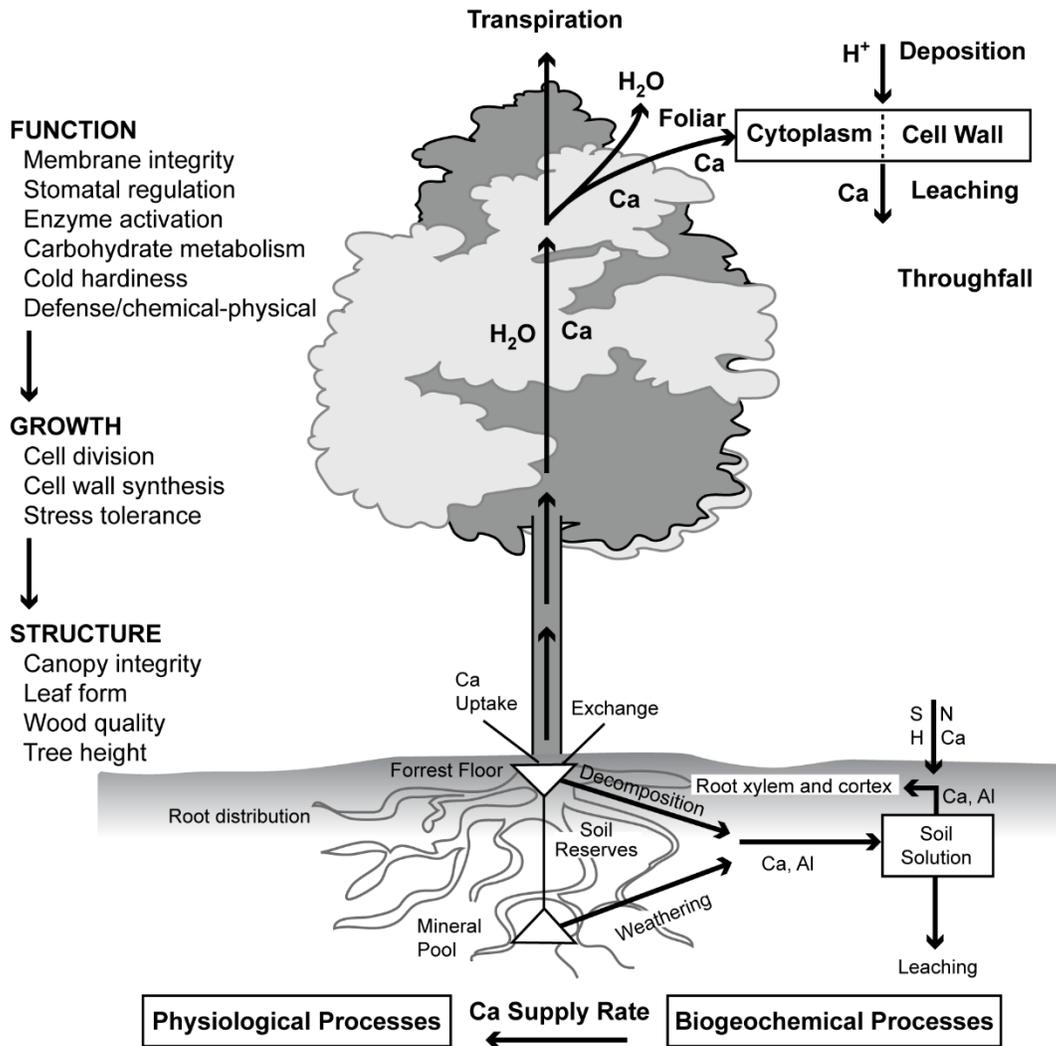
Changes in biogeochemical processes caused by acidifying deposition of N and S to terrestrial systems ([Appendix 4](#)) are linked to changes in terrestrial biota and have significant ramifications for biological functioning of these ecosystems. In the *2008 ISA for Oxides of Nitrogen and Oxides of Sulfur—Ecological Criteria* (hereafter referred to as the 2008 ISA), the evidence was sufficient to infer a causal relationship between acidifying N and S deposition and changes in terrestrial biota. The strongest evidence for a causal relationship comes from studies of terrestrial systems exposed to elevated levels of acidifying deposition that show decreased plant health, reduced plant vigor, and/or loss of terrestrial biodiversity. In multiple studies, consistent and coherent evidence has shown that acidifying deposition can affect terrestrial ecosystems by causing direct effects on plant foliage and indirect effects associated with changes in soil chemistry (Section 3.2.2.3 of 2008 ISA). Biological indicators with reported responses to acidifying deposition and conditions created by acidifying deposition include forest trees, shrubs, lichens, grasslands, and Arctic and alpine tundra.

Acidifying deposition can affect terrestrial ecosystems via direct effects on plant foliage and indirect effects associated with changes in soil chemistry ([Figure 5-1](#)). Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum (Al) toxicity and decreased ability of plant roots to take up base cations (especially calcium [Ca]) and water from the soil ([Cronan and Grigal, 1995](#)). Acidifying deposition to acid-sensitive soils can cause soil acidification, increased mobilization of Al from soil

to drainage water, and depletion of the pool of exchangeable base cations in the soil (see [Appendix 4.3.4](#) and [Appendix 4.3.5](#) for descriptions of these processes). Effects on the soil and direct effects of acidifying deposition on foliage can influence the response of plants to climatic stresses such as drought and cold temperature. The effects of acidifying deposition can also influence the sensitivity of plants to other stresses, including insect pests and disease ([Joslin et al., 1992](#)).

Since publication of the 2008 ISA, the overarching understanding of terrestrial acidification has not appreciably changed. More recent research has confirmed and strengthened this understanding and provided more quantitative information, especially across the regional landscape. This appendix highlights findings from the literature after the completion of the 2008 ISA. A number of studies have evaluated the relationships between soil chemistry indicators of acidification and ecosystem biological endpoints ([Table 5-6](#)). Much of the new literature reviewed in [Table 5-6](#) concerns natural variability in soil pH, Ca concentrations and studies that have used elevated N and S have been noted in that table under the “N and S Deposition/Additions” column. Soil chemistry indicators examined in recent literature include exchangeable base cations, soil pH, exchangeable acidity (hydrogen ions [H<sup>+</sup>] and Al), exchangeable Ca:Al ratio, base saturation, and Al concentrations. Biological endpoints evaluated included physiological responses of trees and other vegetation, lichens, soil biota, and fauna. Trees and other vegetation included sugar maple (*Acer saccharum*), red spruce (*Picea rubens*), yellow birch (*Betula alleghaniensis*), American beech (*Fagus grandifolia*), American basswood (*Tilia americana*), black cherry (*Prunus serotina*), eastern hophornbeam (*Ostrya virginiana*), white ash (*Fraxinus americana*), hickories (*Carya* spp.), northern red oak (*Quercus rubra*), and forest understory, grassland, and alpine plant species. [Table 5-1](#) provides a summary of the soil chemistry indicator-biological endpoint relationships that have been evaluated in the literature since the 2008 ISA. The 2008 ISA only considered changes in vegetation in the analysis of how acid deposition affected terrestrial ecosystems. More recent research has quantified effects on fauna (e.g., birds, snails) and soil biota ([Appendix 5.2.4](#); [Appendix 5.2.5](#)).

Together with the information available in the 2008 ISA, **this body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.** Further, **the body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.**



Al = aluminum; Ca = calcium; H = hydrogen; H<sub>2</sub>O = water; S = sulfur.

Source: [Fenn et al. \(2006\)](#).

**Figure 5-1** Diagram based on [Fenn et al. \(2006\)](#) showing indicators of forest physiological function, growth, and structure that are linked to biogeochemical cycles through processes that control rates of calcium supply. Calcium affects plant physiological processes that influence growth rates and the capacity of plants to resist environmental stresses, such as extremes of temperature, drought, insects, and diseases. Therefore, acidifying deposition, which can deplete soil calcium or interfere with calcium uptake through mobilization of soil aluminum, can affect forest health.

**Table 5-1 Relationships between soil chemistry indicators and biological endpoints that have been evaluated in the literature since the 2008 Integrated Science Assessment.**

Taxa	Exchangeable Base Cations	pH	Exchangeable Acidity	Exchangeable Ca:Al Ratio	Base Saturation	Exchangeable Al or Al Concentrations
Sugar maple	<a href="#">Beier et al. (2012)</a> ; <a href="#">Bilodeau-Gauthier et al. (2011)</a> ; <a href="#">Long et al. (2009)</a> ; <a href="#">Page and Mitchell (2008)</a> ; <a href="#">Sullivan et al. (2013)</a> ; <a href="#">Cleavitt et al. (2014)</a> ; <a href="#">Duchesne and Ouimet (2009)</a> ; <a href="#">Pitel and Yanai (2014)</a>	<a href="#">Long et al. (2009)</a> ; <a href="#">McEathron et al. (2013)</a> ; <a href="#">Sullivan et al. (2013)</a> ; <a href="#">Miller and Watmough (2009)</a>	<a href="#">Bilodeau-Gauthier et al. (2011)</a>	-	<a href="#">Bilodeau-Gauthier et al. (2011)</a> ; <a href="#">Sullivan et al. (2013)</a>	<a href="#">Bilodeau-Gauthier et al. (2011)</a>
Yellow birch	<a href="#">McEathron et al. (2013)</a>	-	-	-	-	-
American beech	<a href="#">Page and Mitchell (2008)</a> ; <a href="#">Duchesne and Ouimet (2009)</a>	-	-	-	-	-
American basswood	<a href="#">Page and Mitchell (2008)</a> ; <a href="#">Beier et al. (2012)</a>	-	-	-	-	-
Black cherry	-	-	-	<a href="#">Long et al. (2009)</a>	-	-
Eastern hophornbeam	<a href="#">Beier et al. (2012)</a>	-	-	-	-	-
Hickories	-	-	-	-	<a href="#">Elias et al. (2009)</a>	-

**Table 5-1 (Continued): Relationships between soil chemistry indicators and biological endpoints that have been evaluated in the literature since the 2008 Integrated Science Assessment.**

Taxa	Exchangeable Base Cations	pH	Exchangeable Acidity	Exchangeable Ca:Al Ratio	Base Saturation	Exchangeable Al or Al Concentrations
Northern red oak	-	-	-	-	-	<a href="#">Elias et al. (2009)</a>
Forest understory plant species	<a href="#">Horsley et al. (2008)</a>	<a href="#">Horsley et al. (2008)</a>	<a href="#">Horsley et al. (2008)</a>	-	-	<a href="#">Horsley et al. (2008)</a>
Grassland plant species	-	<a href="#">Pannek et al. (2015)</a>	-	-	-	-
Lichens	-	<a href="#">Cleavitt et al. (2011a)</a>	-	-	-	-
Soil biota	<a href="#">Sridevi et al. (2012);</a> <a href="#">Ohta et al. (2014)</a>	<a href="#">Chen et al. (2013);</a> <a href="#">Rousk et al. (2009);</a> <a href="#">Gilliam et al. (2011b);</a> <a href="#">Sridevi et al. (2012)</a>	-	-	-	<a href="#">Chen et al. (2013);</a> <a href="#">Rousk et al. (2009)</a>
Fauna	<a href="#">Beier et al. (2012);</a> <a href="#">Pabian and Brittingham (2012)</a>	<a href="#">Pabian and Brittingham (2012)</a>	-	-	-	-

Al = aluminum; Ca = calcium.

Note: Only soil chemistry indicators with a reported significant relationship (positive or negative) with a biological endpoint are indicated in this table. See [Table 5-6](#) for a listing of soil chemical indicators included in each study.

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## 5.2 Effects on Terrestrial Organisms and Ecosystems

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### 5.2.1 Trees and Forests

Both coniferous and deciduous forests throughout the eastern U.S. have been experiencing gradual losses of base cation nutrients from the soil due to accelerated leaching from acidifying deposition. This change in base cation nutrient availability can reduce the quality of forest nutrition over the long term in sensitive areas of low base cation soils. Evidence suggests that red spruce and sugar maple in some areas in the eastern U.S. have experienced declining health as a consequence of acidifying deposition.

The 2008 ISA reported several indicators of stress to forest trees (Table 3-3 in the 2008 ISA), including the percentage of dieback of canopy trees, dead tree basal area (as a percentage), crown vigor index, and fine twig dieback. Biological effects of acidification on terrestrial ecosystems were generally attributed to Al toxicity, decreased ability of plant roots to take up nutrient cations (due to leaching of base cations from soil and interference with uptake), and elevated leaching of  $\text{Ca}^{2+}$  from conifer needles. The Ca:Al ratio in soil solution is a chemical indicator of the negative impacts of soil acidification on terrestrial vegetation ([Cronan and Grigal, 1995](#)). As tree species have shown similar sensitivities to Ca:Al and the molar ratio of base cation (Bc):Al in soil solution (with Bc representing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ), the Bc:Al ratio was used to represent the Ca:Al ratio, and it is the most commonly used indicator in the simple mass balance (SMB) model to estimate critical acid loads in the European Union, Canada, and the U.S. ([McNulty et al., 2007](#); [Ouimet et al., 2006](#); [Spranger et al., 2004](#)).

[Sverdrup and Warfvinge \(1993\)](#), in a meta-analysis of laboratory, greenhouse, and field studies, reported that the critical soil solution Bc:Al ratios for a large variety of tree species ranged from 0.09 to 20.0, although the Bc:Al ratio range reported for tree species native to North America was more restricted at 0.09 to 2.0. This range is similar to that described by [Cronan and Grigal \(1995\)](#) for Ca:Al. In their meta-analysis of studies examining sensitivities to the soil solution Ca:Al ratio, plant toxicity or nutrient antagonism was reported to occur at Ca:Al ratios ranging from 0.2 to 2.5. The meta-analyses conducted by [Sverdrup and Warfvinge \(1993\)](#) explored the relationships between Bc:Al ratios in soil solution and the growth of different tree species. They reported the Bc:Al ratios at which growth was reduced by 20% relative to controls. A Bc:Al ratio of 1.0 is often applied to protect forested systems of Europe, particularly conifers ([Spranger et al., 2004](#)), and a Bc:Al ratio of 10.0 has been identified for forests

in North America, to protect deciduous forests ([McNulty et al., 2007](#); [Quimet et al., 2006](#)). The higher ratio (i.e., 10.0 vs. 1.0) provides a greater level of protection for a wider range of species and various biotic and abiotic conditions.

However, when using soil solution Bc:Al or Ca:Al ratios as the chemical indicators or criterion in the estimation of terrestrial acidification critical loads, several uncertainties must be considered. Many of these considerations have been addressed in the reviews conducted by [Cronan and Grigal \(1995\)](#) and [Vanguelova et al. \(2007\)](#). Although recognized as one of the best indicators of soil acidity risk in forest ecosystems, soil Ca:Al and Bc:Al ratios are variable and can change with soil conditions temporarily and spatially. Estimates of soil base cations and Al concentrations are also influenced by sampling and laboratory analysis methods, and there is still uncertainty regarding which forms of Al are phytotoxic. Soil solution Al occurs in many different ionic and complexed forms, depending on the soil pH and concentrations of soil ligands. In addition, uncertainties regarding the sensitivity of the biological receptor should also be considered. Critical Bc:Al and Ca:Al ratios are often based on seedling studies in controlled environments, and the relationships are less consistent for trees growing in the forest. Environmental and biological conditions, such as differences in tree age, soil horizon chemistry experienced by the roots, and root mycorrhizae are important to consider when comparing laboratory and field-based research studies. Recognizing these different sources of variability, [Cronan and Grigal \(1995\)](#) recommended applying a  $\pm 50\%$  uncertainty to their critical soil Ca:Al ratio of 1.0. Critical fine root Ca:Al ratios have also been suggested as indicators of stress in acidic forest soils ([Vanguelova et al., 2007](#); [Cronan and Grigal, 1995](#)). Fine root Ca and Al indicate what is absorbed by the tree, and there are often strong correlations between fine root and soil solution Ca:Al ratios. Similarly, studies have shown relationships between fine root Ca:Al ratio and metrics of root and above-ground tree health and productivity. However, similar to critical soil solution Ca:Al and Bc:Al ratios, fine root Ca:Al ratios also have sources of uncertainty that can be attributed to factors including soil water and chemistry variability, analysis methods and timing, fine root age, and differences in tree physiology. In addition, U.S. EPA is unaware of a method that uses fine root Ca:Al ratio as the chemical indicator within SMB calculations of critical loads.

The tree species most commonly studied in North America and used in the 2008 ISA to assess the impacts of acidification due to total nitrogen and sulfur deposition include red spruce and sugar maple, although other tree species like flowering dogwood (*Cornus florida*) can also be sensitive to conditions created by acidifying deposition. New information regarding the effects of acidifying deposition on the commonly studied sugar maple and red spruce, as well as other tree, understory, and grassland species is summarized below.

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### 5.2.1.1 Sugar Maple

Among broadleaf tree species in the northeastern U.S., sugar maple is the species most commonly associated with adverse acidification-related effects resulting from S and N deposition, although other base cation accumulating hardwoods may also be at risk ([Driscoll et al., 2001b](#)). Sugar maple is distributed from Missouri and Minnesota in the northcentral U.S. eastward to Maine and the central Appalachian Mountain region, and the species is a dominant component of the northern hardwood forest type ([Braun, 2001](#)). Within this range, soil acidification is widespread throughout the northeastern U.S. and within many portions of the Appalachian Mountains ([Warby et al., 2009](#)).

The 2008 ISA reported that acidifying deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple trees (Section 3.2.2.3 of 2008 ISA). Sugar maple decline has been noted to occur in some portions of the eastern U.S., on base cation-poor soils developed from parent material dominated by sandstone or other base cation-poor substrates. Sugar maple appears to be particularly sensitive to reduced Ca and magnesium (Mg) availability caused by acidifying deposition. Based on the results from a compilation of laboratory studies, sugar maple growth can be reduced by approximately 20% at a Bc:Al soil solution ratio of 0.6 ([Sverdrup and Warfvinge, 1993](#)).

The more recent literature on sugar maple is consistent with the 2008 ISA. In these studies, sugar maple was sensitive to soil conditions and chemistries associated with acidifying deposition ([Appendix 5.2.1.1.1](#)). Soil chemical indicators that were evaluated included exchangeable base cations, soil pH, exchangeable acidity ( $H^+$  and Al), exchangeable Ca:Al ratios, base saturation, and Al concentrations (Al form unspecified). Measured sugar maple responses included changes in basal area, growth, regeneration success, and foliar nutrient concentrations and chemistry ([Table 5-6](#)). In addition, several studies evaluated physiological mechanisms through Ca and Al addition that could explain the response of sugar maple to changes in soil chemistry induced by acidifying deposition ([Table 5-2](#)).

**Table 5-2 Summary of calcium addition studies in North America.**

Reference	Region	Species	Additions (Ca and/or Al)	Description
<a href="#">Battles et al. (2014)</a>	New Hampshire	Sugar maple, American beech, yellow birch, red spruce, and balsam fir	Approximately 1,000 kg Ca/ha (applied in 1999)	Ca additions resulted in the recovery of tree biomass increments, higher aboveground NPP, and increased photosynthetic surface area. Sugar maple exhibited the largest cumulative change in biomass, while American beech showed a negative cumulative change in biomass.
<a href="#">Boyce et al. (2013)</a>	New Hampshire, Vermont	Red spruce and balsam fir	Total of 38 g Ca/m <sup>2</sup> and/or 10.8 g Al/m <sup>2</sup>	Trends toward greater foliar Ca and Ca:Al ratios and lower Al concentrations across the treatment gradient. Ca availability appeared to enhance the ability of red spruce and balsam fir to repair oxidative stress damage.
<a href="#">Cleavitt et al. (2011b)</a>	New Hampshire	Sugar maple	Approximately 1,000 kg Ca/ha (applied in 1999)	Masting events were not influenced by the Ca treatment. Seeds from the Ca treated sites had lower concentrations of Al, K, and Mg and significantly higher concentrations of Si (but no differences in Ca concentrations). Seeds from the Ca treated sites had higher percentage of seedling emergence and higher seedling survival for the first 3 yr.
<a href="#">Halman et al. (2008)</a>	New Hampshire	Red spruce	Approximately 1,000 kg Ca/ha (applied in 1999)	Foliar Ca and total sugar concentrations were significantly higher in trees in the Ca addition watershed. Cold tolerance of foliage was significantly greater in trees in the Ca addition watershed.
<a href="#">Halman et al. (2013)</a>	New Hampshire	Sugar maple	Total of 38 g Ca/m <sup>2</sup> and/or 10.8 g Al/m <sup>2</sup>	Ca additions were found to increase C allocation to sugar maple growth. Al additions increased root Al concentrations, root cell membrane disturbance, and ascorbate peroxidase and glutathione reductase activity, and reduced foliar reflush following frost injury and the number of viable seeds.
<a href="#">Halman et al. (2015)</a>	New Hampshire	Sugar maple and American beech	Annual application of CaCl <sub>2</sub> (2.5 g/m <sup>2</sup> ) and AlCl <sub>3</sub> (0.9 g/m <sup>2</sup> ) from 1995–1999; Wollastonite (38 g/m <sup>2</sup> ) was applied in 1999 a single dose	The Al and Ca treatments did not affect beech foliar chemistry. Ca additions resulted in significantly higher Ca concentrations in both dominant and nondominant sugar maple trees. By 2008, the growth of American beech was higher than that of sugar maple on the control plots and Al treated plots, and nondominant sugar maple growth was greater than that of American beech and dominant sugar maple on the Ca treated plots. Increases in tree mortality on the Al treated plots may have released surviving American beech and increased their growth.

**Table 5-2 (Continued): Summary of calcium addition studies in North America.**

Reference	Region	Species	Additions (Ca and/or Al)	Description
<a href="#">Minocha et al. (2010)</a>	New Hampshire	Sugar maple, yellow birch, and American beech	Approximately 1,000 kg Ca/ha (applied in 1999)	Foliar soluble Ca increased significantly in all species at mid and high elevations at Ca supplemented watershed. Sensitivity to Ca limitation increased with elevation.
<a href="#">Moore et al. (2012)</a>	Quebec, Canada	Sugar maple	8 dolomite lime addition rates—0, 0.5, 1, 2, 5, 10, 20, and 50 megatonnes/ha (applied in 1994)	Foliar Ca and Mg concentrations were found to be higher for treated trees relative to the control trees. Mean crown dieback of trees decreased and seedling density increased with the lime rate. The stem basal area increment for maple trees and proportion of the sugar maple seedlings was increased with lime treatment.
<a href="#">Schaberg et al. (2011)</a>	New Hampshire	Red spruce	Approximately 1,000 kg Ca/ha (applied in 1999)	Trees from the Ca addition watershed had higher estimated levels of foliar biomass. Ca addition increased the stress tolerance of red spruce foliage during the cold season, resulting in greater crown mass.
<a href="#">Smith et al. (2009)</a>	New York, Vermont	Red spruce	Total of 160 kg Ca/yr (1992–1995)	Greater amounts of Ca were found in the wood from the high-Ca location than from the low-Ca location. Ca concentration was greater in wood formed in the 1970s than for wood formed in the 1980s, and Ca treatments resulted in increased concentration of Ca in both the 1970s and 1980s decadal bands of wood. Foliar concentrations of Ca oxalate were also higher on the high-Ca site.
<a href="#">Sridevi et al. (2012)</a>	New Hampshire	Soil microbes (bacteria)	Approximately 1,000 kg Ca/ha (applied in 1999)	Bacterial community structure in the Ca treated and nontreated reference soils was found to be significantly different, with differences among communities being more pronounced in the mineral soils.

Al = aluminum; AlCl<sub>3</sub> = aluminum chloride; C = carbon; Ca = calcium; CaCl<sub>2</sub> = calcium chloride; g = gram; ha = hectare; K = potassium; kg = kilograms; m = meter; Mg = magnesium; NPP = net primary production; Si = silicon; yr = year.

#### 5.2.1.1.1 Soil Chemical Indicators for Sugar Maple

##### Soil Exchangeable Base Cations

Sugar maple basal area and growth were responsive to soil exchangeable base cation concentrations in several studies in the northeastern U.S. In the Adirondack Mountains of New York, [Beier et al. \(2012\)](#) reported sugar maple basal area was positively correlated to forest floor and mineral soil (B-horizon) exchangeable soil Ca on sites that ranged in soil Ca from 1.83 to 53.89 cmol<sub>c</sub>/kg (in Oa-horizon) and 0.28 to 7.73 cmol<sub>c</sub>/kg in the B-horizon (see Figure 3-2 in the 2008 ISA for a description of soil horizons). Similar results were reported in Quebec, Canada by [Bilodeau-Gauthier et al. \(2011\)](#) who found that sugar maple basal area growth was positively correlated to concentrations of base cations (Ca, potassium [K], and Mg) in wood and mineral soil (B-horizon), and [Long et al. \(2009\)](#) who reported that sugar maple basal area increment (BAI) was positively correlated with exchangeable Ca and Mg in the upper B-horizon in the northeastern U.S. [Page and Mitchell \(2008\)](#) also found that the relative basal area of sugar maple was positively correlated with mineral soil (0–10 cm) exchangeable Ca in the Adirondack Mountains. In the same region, [Sullivan et al. \(2013\)](#) determined that sugar maple canopy vigor was positively correlated with soil exchangeable Ca and Mg, and mean growth rates (measured as BAI) were positively correlated with exchangeable Ca at the watershed level.

Relationships between soil exchangeable base cations and sugar maple regeneration (the growth and abundance of seedlings and saplings) have also been demonstrated. [Cleavitt et al. \(2014\)](#) evaluated sugar maple seedling survival and cause of death across 22 sites in New Hampshire that varied in soil Ca and topographic position. Soil Ca concentration exhibited a ninefold change across the study sites and was positively correlated to increases in sugar maple abundance and initial seedling densities. However, soil Ca concentration was not a significant predictor of 1st-year mortality, nor was it a factor that distinguished among the three main site types. In a study in Quebec, Canada, [Duchesne and Ouimet \(2009\)](#) explored relationships between soil chemistry and sugar maple in the sapling stratum and found that the basal area of sugar maple was positively correlated with soil exchangeable Ca and Mg.

[Pitel and Yanai \(2014\)](#) evaluated the abiotic and biotic factors influencing the mortality of dominant and codominant sugar maple trees in 47 stands in Massachusetts, Vermont, and New York that had experienced defoliation by native forest tent caterpillars (*Malacosoma disstria*) between 2002 and 2007. A total of 54 predictive variables (defoliation year, stand and site characteristics, and soil chemistry variables) were

evaluated through multiple linear regression followed by stepwise regression to produce the best predictive models of sugar maple mortality from 2006 to 2008. Mortality was highest in stands with the greatest amount of crown dieback the previous year, and drought, cold winter temperatures, concave micro-relief, and soil base cation availability were significant predictors of mortality. Concentrations of exchangeable Ca, Mg, and K in the upper B soil horizon were inversely correlated with sugar maple mortality, with exchangeable K showing the strongest relationship. Sites with above average sugar maple mortality (>3 or 4%) were found to occur on soils with low concentrations of exchangeable Ca (0.31–0.46 cmol<sub>e</sub>/kg), Mg (0.06–0.10 cmol<sub>e</sub>/kg), and K (0.03–0.05 cmol<sub>e</sub>/kg). There was also an interaction between defoliation and soil base cation availability: stands defoliated in 2005 that had low soil (A-horizon) Mg saturation suffered higher rates of mortality.

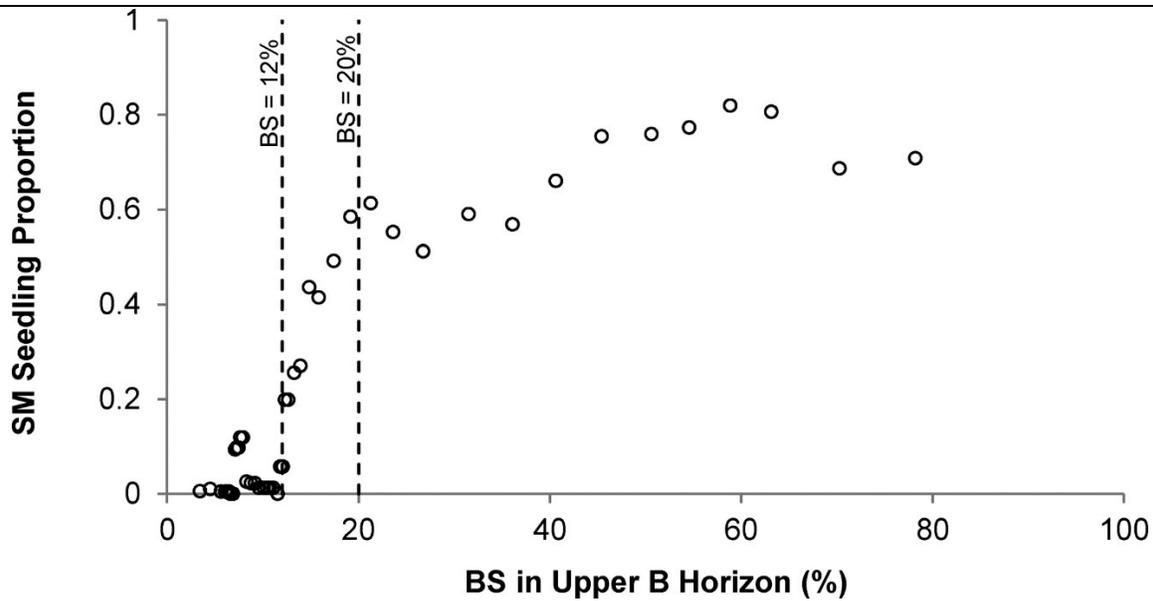
### **Soil Exchangeable Acidity and pH**

[Bilodeau-Gauthier et al. \(2011\)](#) found that sugar maple tree growth was negatively correlated to soil exchangeable acidity (H<sup>+</sup> and exchangeable Al), and through a multifactor analysis, showed that tree age and soil exchangeable Al accounted for 51% of the variation in sugar maple BAI. Positive correlations between mineral soil pH and sugar maple basal area growth have also been reported by [Long et al. \(2009\)](#) and [McEathron et al. \(2013\)](#). [Sullivan et al. \(2013\)](#) found that sugar maple canopy vigor was positively correlated with soil pH.

One study reported a relationship between sugar maple foliar chemistry and exchangeable soil chemistry. [Miller and Watmough \(2009\)](#), in their evaluation of hardwood plots along air-pollution (N, S, and ozone), soil-acidity, and climate gradients in Ontario, Canada, showed that foliar Ca and Mg content was positively correlated and foliar manganese (Mn) content was negatively correlated with soil A-horizon pH.

### **Soil Base Saturation**

An investigation of every relationship between sugar maple BAI and soil variables revealed that base saturation was the best predictor of BAI (nonlinear) and explained 43% of variance ([Bilodeau-Gauthier et al., 2011](#)). Similarly, [Sullivan et al. \(2013\)](#) found that soil base saturation was related to sugar maple regeneration and growth. Plots with lower soil base saturation did not have sugar maple regeneration; the proportion of sugar maple seedlings dropped substantially at base saturation levels less than 20% ([Figure 5-2](#)). Mean growth rates were positively correlated with soil base saturation at the watershed level.



BS = base saturation; SM = sugar maple.

Note: Plots were rank ordered based on soil base saturation, and a 5-plot rolling average was applied to both the soil base saturation and the seedling proportion data. Reference lines are added at base saturation values of 12 and 20%, indicating break points in the sugar maple seedling proportion-response function.

Source: Reprinted with permission from Sullivan, TJ; Lawrence, GB; Bailey, SW; McDonnell, TC; Beier, CM; Weathers, KC, McPherson, GT; Bishop, DA (2013) Effects of acidic deposition and soli acidification on sugar maple trees in the Adirondack Mountains, New York. Environmental Science and Technology 47(22): 12687–12694. Copyright (2020) American Chemical Society.

**Figure 5-2 Relationship between the proportion of seedlings that were sugar maple and soil base saturation in the upper B-horizon.**

### Soil Exchangeable Calcium:Aluminum Ratio

The relationship between sugar maple BAI and a soil exchangeable Ca:Al threshold of <0.03 was evaluated by [Long et al. \(2009\)](#) through an analysis of a regional network of 76 forest sites that spanned Pennsylvania, New Hampshire, New York, and Vermont. However, a repeated-measures analysis did not reveal statistically significant effects of the Ca:Al soil ratio threshold of <0.03 on BAI.

#### 5.2.1.1.2 Physiological Mechanisms for Sugar Maple

A number of studies were also conducted to determine the potential mechanisms underlying the sensitivity of sugar maple to the soil conditions created by acidifying deposition. These studies evaluated the influence of Ca additions on sugar maple physiology, growth, seeds, and seedlings ([Table 5-2](#)). In Hubbard Brook Experimental

Forest (HBEF), NH, one study involved the addition of a total of approximately 1,000 kg Ca/ha as pelletized wollastonite ( $\text{CaSiO}_3$ ) in October 1999 to a watershed ([Battles et al., 2014](#)). This treatment resulted in increases in: soil pH (in Oie-horizon) from 4.29 to 5.45; base saturation from 9.6 to 78.6% (in Oie layer), 56% (in Oa-horizon), and 14.3% (in upper mineral soil); and soil solution Ca:Al (inorganic monomeric Al) from 1.6 to 6.4 (in Oa-horizon) and from 0.97 to 3.8 (in the mineral soil). As part of this study, [Battles et al. \(2014\)](#) evaluated the effects of the Ca additions on tree growth and found that sugar maple in the treated watershed exhibited the largest increase in cumulative biomass relative to other species. Another study at the same experiment reported that sugar maple seedlings were 50% larger in the treated watershed and mycorrhizal colonization of seedlings was much higher in the treated watershed (22.47% of root length) as compared with the reference watershed [4.4%; [Juice et al. \(2006\)](#)]. Mycorrhizal colonization also increased in mature sugar maple in the treated watershed (56%) compared to the reference watershed [35%; [Juice et al. \(2006\)](#)]. In contrast to sugar maple, American beech showed a negative cumulative change in biomass. [Minocha et al. \(2010\)](#) examined the effects of the Ca addition treatment on foliar chemistry and found that sugar maple had increased foliar concentrations of Ca, which were accompanied by increases in soluble phosphorous (P), chlorophyll, and two amino acids (i.e., glutamate and glycine). The authors also reported decreases in known metabolic indicators of physiological stress (i.e., arginine and  $\gamma$ -aminobutyric acid, as well as putrescine, a diamine). Sugar maple also exhibited a decrease in foliar putrescine at higher elevations in the watershed, indicating possible remediation from Ca deficiency. [Cleavitt et al. \(2011b\)](#) evaluated sugar maple seed production, seed chemistry, seedling growth (lifestage), and seedling survival on the Ca treated watershed and found that seeds from the Ca treated sites had lower concentrations of Al, K, and Mg and significantly higher concentrations of silicon (Si) than seeds from the reference watershed. The percentage of seedling emergence was also higher, average lifestage was more significantly advanced, and seedling survival was greater on the Ca treated watershed.

In a second study (NuPert Study) conducted at HBEF, [Halman et al. \(2013\)](#) evaluated the impacts of Ca (380 kg/ha) and Al (108 kg/ha) additions on sugar maple physiology. The Ca additions increased the proportion of carbon allocated to sugar maple growth. In contrast, Al additions increased root Al concentrations and root cell membrane disturbance, increased ascorbate peroxidase (APX) and glutathione reductase (GR) activity, reduced foliar reflush following frost injury, and reduced the number of viable seeds. Ascorbate peroxidase and GR are antioxidant enzymes that target reactive oxygen species generated by environmental stresses, such as photo-oxidative stress damage at low temperatures. Elevated APX and GR activity are indicators of increased oxidative stress. Several years later, [Halman et al. \(2015\)](#) re-evaluated the NuPert study to determine the long-term and contrasting responses of sugar maple and American beech to

the Ca and Al treatments following a major ice storm in 1998. The Al and Ca treatments did not affect beech foliar chemistry. However, Ca additions significantly increased Ca concentrations in both dominant and nondominant sugar maple trees, relative to the trees treated with Al. Interestingly, for all treatments, foliar Al concentrations were higher in the nondominant than dominant sugar maple trees, and the opposite was found for foliar Ca concentrations. By 2008 (11 years after the ice storm), the growth of American beech was higher than that of sugar maple on the control plots and Al treated plots, and nondominant sugar maple growth was greater than that of American beech and dominant sugar maple on the Ca treated plots. These differential growth responses emerged within 2 to 11 years following the ice storm, depending on the treatment and species. Although plots were mainly composed of sugar maple, American beech experienced the greatest growth on Al treated plots. Increases in overstory tree mortality on the Al treated plots may have increased light availability, released surviving American beech, and increased beech growth.

[Moore et al. \(2012\)](#) evaluated soil chemistry and sugar maple status 15 years after treatment with dolomite lime (0 to 50 megatonnes/ha) to a hardwood forest in Quebec, Canada, and found results similar to those in HBEF. Foliar Ca and Mg concentrations were higher for treated trees relative to the control trees, and mean crown dieback of trees decreased quadratically with the lime addition rate, from 39% for the control trees to a value of 1 to 3% for the lime rates of 5 megatonnes/ha and higher. In addition, sugar maple BAI for the limed trees was nearly double that of the nonlimed trees. The lime application was also beneficial to the sugar maple regeneration. The overall sugar maple seedling density increased with the lime rate, doubling in the 50 megatonnes/ha (32 seedlings/m<sup>2</sup>) compared with the controls (16 seedlings/m<sup>2</sup>). The proportion of the sugar maple seedlings to all of the other species increased quadratically from 22% in controls to more than 55% in the 5 to 50 megatonnes/ha treatments. In contrast, the proportion of competitive species decreased quadratically with the lime rate, including American beech, for which the proportion in the treated plots (24%) was nearly half the proportion observed in the controls (46%).

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### **5.2.1.2 Red Spruce**

Red spruce is a conifer that occurs mainly in the northeastern U.S. and at scattered high-elevation sites (e.g., mountain and ridge tops) in the Appalachian Mountains. Red spruce dieback or decline has been observed across high elevation landscapes of the northeastern, and to a lesser extent, southeastern U.S. At high elevations in the Adirondack Mountains in New York and the Green Mountains in Vermont, more than 50% of the canopy red spruce trees died during the 1970s and 1980s. In the White

Mountains in New Hampshire, about 25% of the canopy spruce died during that same period ([DeHayes et al., 1999](#)). Dieback of red spruce has also been observed in mixed hardwood-conifer stands at relatively low elevations in the western Adirondack Mountains, an area that receives high inputs of acidifying deposition ([Shortle et al., 1997](#)); acidifying deposition has been implicated as a causal factor ([DeHayes et al., 1999](#)).

The 2008 ISA reported that changes in soil chemistry (e.g., depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water; see [Appendix 4.3.4](#) and [Appendix 4.3.5](#)) have contributed to high mortality rates and decreased growth of red spruce trees in some areas of the eastern U.S. over the past three decades. Studies evaluating the physiologic basis behind the responses of red spruce to acidifying deposition have attributed the reduced vigor of the species to increased sensitivity to frost injury and cold temperatures. The frequency of freezing injury to red spruce needles had increased during a period in the latter half of the 20th century that coincided with increased emissions of S and N oxides and increased acidifying deposition ([DeHayes et al., 1999](#)).

Since the 2008 ISA, research evaluating the sensitivity of red spruce to soil indicators of acidifying deposition have mainly focused on the potential mechanisms underlying the sensitivity of the species to acidic soil conditions. These studies have examined the physiological response of red spruce to Ca additions ([Table 5-2](#)).

In the HBEF study that involved the addition of approximately 1,000 kg Ca/ha, [Halman et al. \(2008\)](#) and [Schaberg et al. \(2011\)](#) evaluated the response of red spruce foliar chemistry. [Halman et al. \(2008\)](#) reported significantly higher foliar Ca and total sugar (fructose and glucose) in the Ca addition watershed than in trees in the reference watershed. Foliar APX activity was also higher in trees in the Ca addition watershed during winter. Cold tolerance of foliage was significantly greater in trees in the Ca addition watershed than in trees in the reference watershed. [Schaberg et al. \(2011\)](#) measured concentrations of foliar polyamines and free amino acids, foliar chlorophyll, and sapwood area (as a proxy for foliar biomass) in Ca treated and nontreated trees. Foliar polyamines (putrescine and spermidine) and free amino acids (alanine, gamma aminobutyric acid [GABA]) are putative stress protection compounds that may directly protect or provide other benefits to foliage that increase stress tolerance. The Ca additions increased November concentrations of alanine, GABA, putrescine, and spermidine relative to foliage from the reference watershed. Consistent with increased stress protection indicated by the elevated polyamine and free amino acids, foliage from the Ca addition watershed had higher total chlorophyll concentrations than foliage from the reference watershed. In contrast, foliage from the reference watershed had significantly

higher alanine:glutamic acid ratios, which have been attributed to cold sensitivity or damage in other species. In addition to concentration-based differences in foliar compounds, trees from the Ca addition watershed had higher estimated levels of foliar biomass than trees from the reference watershed. These findings suggested that Ca addition increased the stress tolerance and productive capacity of red spruce foliage during the cold season and resulted in greater crown mass compared to trees growing on nontreated soils.

Similar findings were reported by [Boyce et al. \(2013\)](#), who examined the influence of Ca and Al on the physiology of red spruce and balsam fir (*Abies balsamea*) in three different locations that varied in soil nutritional status. Processes known to be Ca sensitive (root and foliar cation concentrations, chlorophyll fluorescence, soluble sugar concentrations, and the activities of APX and GR in current-year foliage) were measured, and the results from the study suggest that Ca availability enhanced the ability of red spruce and balsam fir to repair oxidative stress damage, including photo-oxidation.

Concentrations of Ca in sapwood and accumulations of Ca oxalate in foliage have been used as markers of environmental change due to acidic deposition or forest management practices. [Smith et al. \(2009\)](#) compared the effects of different Ca fertilization treatments (approximately 178 kg Ca/ha/yr during 1992–1995) on Ca concentrations in wood and Ca and oxalate (Ox) concentrations in red spruce foliage at two locations with different initial concentrations of Ca in the soil (6.4 cmol/kg vs. 13.7 cmol/kg). Greater amounts of Ca were found in the wood from the high-Ca location than from the low-Ca location. Foliar concentrations of Ca oxalate were higher on the high-Ca site than on the low-Ca site and increased in response to Ca additions.

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### 5.2.1.3 Other Tree Species

In the 2008 ISA, there was some information regarding the effects of acidification on dogwood (*Cornus*) species. Loss of base cations, specifically Ca<sup>2+</sup>, had been implicated in increased susceptibility of flowering dogwood to dogwood anthracnose, its most destructive disease. Susceptibility to the disease and disease severity in stands appeared dependent on several factors, including acid deposition and various edaphic characteristics and meteorological conditions. Studies pointed to greater vulnerability of dogwoods to anthracnose under simulated acid rain treatments ([Britton et al., 1996](#)) and under Ca<sup>2+</sup> deficiency [[Holzmueller et al. \(2007\)](#); Section 3.2.2.3 of 2008 ISA].

Since the 2008 ISA, no further research on dogwood has been published. However, other tree species have been evaluated in studies relating soil chemistry to tree physiology, including red maple, white oak, yellow birch, white ash, American beech, black cherry,

northern red oak, hickories, American basswood, and eastern hophornbeam. These species were reported to vary in their sensitivities to soil conditions associated with acidifying deposition ([Table 5-6](#)).

In a recent study in West Virginia, [Thomas et al. \(2013\)](#) used dendroisotopic techniques to show the recovery of eastern redcedar (*Juniperus virginiana*) trees from decades of S pollution using an analysis of a tree ring chronology from 1909 to 2008. Growth, measured as BAI, in eastern redcedar old-growth stands (118–480 years old) increased significantly since 1970. A multivariate correlation analysis using historical climate variables, atmospheric CO<sub>2</sub> concentrations, and U.S. SO<sub>2</sub> and NO<sub>x</sub> emissions estimates showed that the growth of cedar trees over the 100-year chronology is explained best by increases in atmospheric CO<sub>2</sub> and NO<sub>x</sub> emissions, and decreases in SO<sub>2</sub> emissions. Through carbon isotope (<sup>13</sup>C) analyses, the researchers were able to show that the stomata of cedar may be more sensitive to SO<sub>2</sub> emissions than to increasing atmospheric CO<sub>2</sub>. A breakpoint in the 100-year δ<sup>13</sup>C tree ring chronology occurred around 1980, as SO<sub>2</sub> emissions declined, indicating a gradual increase in stomatal conductance and a concurrent increase in photosynthesis related to decreasing SO<sub>2</sub> emissions and increasing atmospheric CO<sub>2</sub>. After 1990, calculated stomatal conductance increased more than photosynthesis. These patterns in physiology led to changing trends in intrinsic water use efficiency (*i*WUE; the ratio of photosynthesis to water loss through stomatal conductance). The calculated *i*WUE generally increased from the 1940s to 1990 mainly because of SO<sub>2</sub> emission effects on stomatal conductance, and then *i*WUE began to decrease after 1990 because SO<sub>2</sub> emissions no longer constrained stomatal function. Through S isotope analysis (tree ring δ<sup>34</sup>S), the study showed a synchronous change in the sources of S used at the whole-tree level that indicated a reduced anthropogenic influence. The increase in growth and the δ<sup>13</sup>C and δ<sup>34</sup>S trends in the tree ring chronology of these *Juniperus* trees provide evidence for a distinct physiological response to changes in atmospheric SO<sub>2</sub> emissions since 1980. The authors attributed the changes since 1980 to an indirect effect of decreases in acid deposition. However, the exact mechanism is unclear because the 100-year chronology could only be correlated to estimated SO<sub>2</sub> emissions because acidifying deposition measurements were not available. Other researchers have pointed out that the trees in the [Thomas et al. \(2013\)](#) study were growing on a limestone outcrop that could be well buffered from soil acidification ([Schaberg et al., 2014](#)). Further, the rapid recovery of tree growth could also point to a direct effect of gaseous SO<sub>2</sub> rather than an indirect effect of soil acidification, which would have a longer response time to decreases in emissions. See [Appendix 3.2](#) for further discussion of direct gaseous SO<sub>2</sub> effects on vegetation.

**Soil Exchangeable Base Cations**

Several studies reported on the relationships between species-specific basal area and growth and soil exchangeable base cations. In the Adirondack Mountains, [McEathron et al. \(2013\)](#) evaluated the relationships between basal area and soil chemistry and reported that yellow birch basal area was positively correlated with mineral soil exchangeable Ca. Similarly, [Page and Mitchell \(2008\)](#) compared the basal areas of American basswood, American beech, and white ash with mineral soil (0–10 cm in depth) exchangeable Ca concentrations and found exchangeable Ca had a positive correlation with relative basal area of American basswood, a negative correlation with the relative basal area of American beech, and no correlation with relative basal area of white ash. The positive relationship between American basswood and soil exchangeable Ca is consistent with other studies. [Beier et al. \(2012\)](#), in their evaluation of vegetation communities across northern hardwood sites that ranged in exchangeable Ca concentrations from 1.83 to 53.89 cmol<sub>c</sub>/ha (in Oa-horizon) and 0.28 to 7.73 cmol<sub>c</sub>/ha (in B-horizon), reported that American basswood and eastern hophornbeam were only found on the sites with the highest exchangeable Ca concentrations. Similarly, negative relationships between American beech and soil exchangeable Ca have been reported elsewhere. [Duchesne and Ouimet \(2009\)](#) found that basal area of American beech in the sapling stratum in sugar maple-dominated forests was negatively correlated with exchangeable Ca and Mg. Soil concentrations of Ca and Mg on sites colonized by American beech were, on average, roughly half those on sites where American beech was absent, thereby suggesting that beech effectively colonizes sites with low base status. These findings are also consistent with the responses of American beech to the Ca addition studies described earlier ([Battles et al., 2014](#); [Moore et al., 2012](#)).

**Soil Base Saturation**

One study of 30 forest plots within Monongahela National Forest, WV reported on the relationship between soil base saturation and tree abundance. [Elias et al. \(2009\)](#) evaluated relationships between tree growth parameters and soil indicators of acidifying deposition and found that hickories were the only species (out of four within-species comparisons) to have significantly lower numbers on sites with base saturation below 20% (A-horizon) and 2.5% (B-horizon). They also found that the percentage of dead northern red oak was highest on sites with Al concentrations (A-horizon) above 43 cmol<sub>c</sub>/kg. The authors reported that sites in the year 2000 with subsurface base saturation above 10% had more unique species.

## Soil Exchangeable Calcium:Aluminum Ratio

A study of 76 hardwood stands across the northeastern U.S. noted the relationship between exchangeable Ca:Al ratios and BAI. [Long et al. \(2009\)](#) found that, unlike sugar maple, black cherry BAI was greater in stands with exchangeable Ca:Al ratios (B-horizon) below the <0.03 threshold adopted by the study.

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## 5.2.2 Forest Understory and Grassland Species

The 2008 ISA did not specifically assess the effect of acidification on forest understory species due to the lack of studies. Also, the 2008 ISA reported that grasslands were thought to be less sensitive to acidification than woodlands ([Köchy and Wilson, 2001](#); [Blake et al., 1999](#)), and grasslands with calcareous soils will be less sensitive than those with acidic soils ([Bobbink et al., 1998](#)).

Since the 2008 ISA, several studies have evaluated the relationships between soil chemistry indicators of acidification and forest understory and grassland species ([Table 5-6](#)).

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### 5.2.2.1 Soil Chemical Indicators for Forest Understory and Grassland Species

#### Soil pH, Exchangeable Base Cations, and Exchangeable Acidity

One study examined the relationship between soil chemistry indicators of acidification and forest understory species. [Horsley et al. \(2008\)](#) evaluated 35 soil chemistry, stand, and climatic variables as predictors of understory plant species composition in northern hardwood stands, and found that a base cation-acid cation nutrient gradient accounted for 71.9% (in New Hampshire and Vermont) and 63% (in Pennsylvania and New York) of the variation in the nonmetric multidimensional scaling ordination analyses of plant community composition. Soil Ca, Mg, and pH formed the base end and Al, Mn, K, soil acidity, and organic matter represented the acid end of the gradient. Based on results from McNemars' exact test, a total of 50 of the 234 understory species were associated with the base end of the base cation-acid cation nutrient gradient. These species have value as indicators of sites at the high end of the base cation nutrient gradient in northern hardwoods, sites that would be suitable for acid-sensitive species such as sugar maple.

In the U.K., [Stevens et al. \(2010b\)](#) used data from a national survey to evaluate the species richness of 68 grasslands along an N deposition gradient. Ellenberg R

(reaction-soil pH) and N (soil nutrient) scores and an index of soil acidity preference were used as the metrics to characterize the plant diversity responses to the soil chemistry conditions created by N deposition. Although the study did not find any significant relationships between the Ellenberg and soil acidity index values and N deposition, there was evidence that soil acidification was contributing to changes in species diversity and community composition. Soil acidification may have led to decreased nutrient availability and increased Al solubility, thus, masking the effects of increased soil N availability (see also [Appendix 6.3.5](#) for N discussion).

A similar analysis along an N deposition gradient (2.4 to 43.5 kg N/ha/yr) was conducted by [Pannek et al. \(2015\)](#) using a vegetation data set from 153 seminatural acidic grasslands in northwestern Europe. Species frequency in response to N and other factors including soil (0–10 cm) P, pH,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  and geographical, climatic, and management factors were evaluated. A second set of data from acidic grasslands in Germany (392 plots) and the Netherlands (144 plots) containing plots from different time periods were also included in the analyses to determine whether the results of the spatial gradient approach coincided with temporal changes in the abundance of species. Out of 44 species included in the study, 16 were found to be affected by N deposition, with 12 of them exhibiting a decreased abundance response. Increasing soil pH and P influenced 24 and 14 species, respectively, predominantly increasing abundance. Change of species over time was unrelated to their responses to pH. However, species were found to significantly decline over time in both Germany and the Netherlands in response to N deposition, soil P, and  $\text{NO}_3^-$ . These results show the influence of N deposition in a decline for many plant species in seminatural acidic grasslands, although impacts of N deposition on pH did not appear to be the mechanism of plant responses (see also [Appendix 6.2.5](#) for N discussion).

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### 5.2.3 Lichens

In the 2008 ISA it appeared that lichen populations were affected in areas with acidifying deposition ([Davies et al., 2007](#)). However, it was not clear whether effects were due to direct effects of  $\text{SO}_2$ , N effects, or acidifying deposition. See [Appendix 6.3.7](#) for a discussion of N deposition on lichens.

We have not identified any new studies published since the 2008 ISA that evaluated the relationships between conditions created by acidifying deposition and lichen physiology. However, in Acadia National Park, [Cleavitt et al. \(2011a\)](#) evaluated the interactions among N and S deposition, tree type, and epiphytic lichen and bryophyte diversity, biomass, and abundance to (1) document any differences in the depositional

environments (throughfall and cloud water) of red spruce and red maple (*Acer rubrum*) trees, (2) relate deposition differences to both chemistry of the bark and corresponding epiphyte biomass and composition on the bark, and (3) describe any species-specific relationships that emerged between the epiphytes and bark chemistry ([Table 5-6](#)). Throughfall N and S deposition were higher under spruce trees than under maple trees, and average S concentrations in cloud water were negatively correlated with bark Ca and bark Mg. Epiphytic lichen richness was higher on maple trees than spruce trees, and tree species differed in the number of rare epiphytic species. Several pollution-sensitive epiphytes were restricted to the maples: the cyanolichens *Leptogium cyanescens* (bipartite) and *Lobaria pulmonaria* (tripartite), the large ruffle lichen *Parmotrema crinitum*, and the moss *Zygodon viridissimus* var. *rupestris*. Cyanolichens only occurred on maple bark and did not occur on any bark with a pH below 5.02. Apparent overlap between the bark chemistry of spruce and maple, particularly for samples from higher on maple boles, suggest a reduction in the area of chemically suitable substratum for epiphytes.

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## 5.2.4 Soil Biota

Soil biota were not specifically addressed in the 2008 ISA. Since the 2008 ISA, several studies have evaluated the relationships between soil chemistry indicators of acidification and soil biota ([Table 5-6](#)). The effects of elevated N on soil biota is addressed throughout [Appendix 6](#) (see [Appendix 6.2.3](#), [Appendix 6.2.4](#), [Appendix 6.2.5](#), and [Appendix 6.3.5](#)).

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### 5.2.4.1 Soil Chemical Indicators for Soil Biota

#### Soil pH and Exchangeable Calcium:Aluminum Ratio

[Bardhan et al. \(2012\)](#) evaluated the relationships between soil chemistry and bacterial diversity in 30 plots along a soil chemistry and deposition gradient in high-elevation spruce-fir forests in the Great Smoky Mountain National Park (GSMNP). Modeled S deposition ranged from 6 to 41 kg S/ha/yr, measured soil pH ranged from 3.0 to 4.6, and measured CEC ranged from 1.3 to 23.1 cmol/kg (soil samples pooled from the O-, A-, and B-horizons). However, bacterial diversity and community composition did not change along the gradients of S deposition, soil pH, or exchangeable Ca:Al ratio.

## Soil pH and Aluminum Concentrations

[Chen et al. \(2013\)](#) evaluated the impacts of S additions on soil microbial and nematode communities in a grassland system of Inner Mongolia. Seven treatments of 28 to 166 mol H<sup>+</sup>/ha were applied in three doses in the form of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) from 2009 to 2010. The authors found that the proportions of soil bacteria, fungi, and nematodes were altered by the treatments, and the responses were related to soil pH and Al concentrations. Increases in fungal fatty acids (49% increase) and fungi:bacteria ratio (120% increase) and decreases in total and bacterial fatty acids (40–47% decrease) relative to the controls were attributed to soil pH and Al concentrations. High Al concentrations (51 to 83 mg/kg) were associated with decreases in total fatty acids and bacterial fatty acids and increases in fungal fatty acids. These results are consistent with a study of an agricultural soil gradient that showed that at soil pH below 4.5, microbes (bacteria and fungi) are decreased due to increased Al solubility ([Rousk et al., 2009](#)), and that fungi are often more dominant in acidic soils. [Chen et al. \(2013\)](#) also reported that acid additions also impacted the soil nematode community by initially increasing the total number of soil nematodes and then altering nematode community composition: bacterivorous and fungivorous nematodes increased, but plant-feeding and omnivorous and carnivorous nematodes decreased. The shifts in the nematode community were attributed to decreased soil pH and changes in soil moisture.

## Soil pH and Exchangeable Calcium

One study also investigated the influence of Ca addition (~1,000 kg Ca/ha/yr in 1999) on the soil bacterial community in a northeastern hardwood forest ([Sridevi et al., 2012](#)). The study detected 1,756 taxa spanning 42 phyla, 53 classes, 127 orders, and 154 families in the Ca treated and reference watersheds. Bacterial community structure was significantly different between the Ca treated and nontreated reference soils, with differences among communities being more pronounced in the mineral soils. Calcium additions resulted in significant changes in bacterial community composition in the organic and in the mineral soil horizons. The numbers of detectable taxa in families such as Acidobacteriaceae, Comamonadaceae, and Pseudomonadaceae were lower in the Ca amended soils, while Flavobacteriaceae and Geobacteraceae were higher. Analyses of relationships between soil chemistry and the bacterial communities indicated that only exchangeable Ca, pH, and P were significantly correlated with bacterial community structure.

## Soil pH

[Gilliam et al. \(2011b\)](#) evaluated the microbial community across a soil weathering gradient in a northern hardwood forest in West Virginia. Microbial community composition, characterized through phospholipid fatty acid (PLFA) analysis, varied among sites. Fungi were dominant at the most weathered, low  $\text{NO}_3^-$ -production site, while Gram-negative bacteria were significantly higher at the less weathered, moderate and high  $\text{NO}_3^-$ -production sites. Accordingly, the fungi:bacteria ratio increased in the direction of the low  $\text{NO}_3^-$ -production plots in ordination space. Correlations between the soil parameters and PLFA results suggest that low soil pH and  $\text{NO}_3^-$  concentrations supported fungal dominance, although other important factors including differences in plant community and clay and organic matter content may have also influenced the soil microbial community.

## Soil Exchangeable Calcium

A study in Japan evaluated the relationship between forest type and soil invertebrate communities in evergreen broad-leaved forests versus Japanese cedar (*Cryptomeria japonica*) plantation forests ([Ohta et al., 2014](#)). Exchangeable Ca was found to be significantly higher in soil from the Japanese cedar plantations than the evergreen forest. The invertebrate community composition also differed significantly between the two forest types and was best explained by exchangeable Ca concentrations. Two major taxa of soil crustaceans, Talitridae and *Ligidium japonicum*, were only found in the Japanese cedar plantations. In contrast, millipedes (Paradoxosomatidae) and beetles were relatively abundant in the evergreen plots.

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## 5.2.5 Fauna

Fauna were not specifically assessed in the 2008 ISA. Since the 2008 ISA, two studies were found that evaluated the relationships between soil chemistry indicators of acidifying deposition and fauna ([Table 5-6](#)).

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### 5.2.5.1 Soil Chemical Indicators for Fauna

## Soil Exchangeable Calcium

[Beier et al. \(2012\)](#) characterized the variation in gastropod, salamander, and vegetation communities among northern hardwood forests attributable to soil exchangeable Ca. The

sites represented the variability in soil Ca in the Adirondack Mountains, ranging from 1.83 to 53.89 cmol<sub>c</sub>/kg (Oa-horizon) and 0.28 to 7.73 cmol<sub>c</sub>/kg (B-horizon). Snail community richness and the abundance and live biomass of red-backed salamanders (*Plethodon cinereus*) were all positively correlated with soil Ca. Land snail species richness and abundance were positively correlated with Oa-horizon Ca and negatively correlated to SO<sub>4</sub><sup>2-</sup> deposition and site elevation (and NO<sub>3</sub><sup>-</sup> deposition for snail abundance). Salamander communities were dominated by mountain dusky salamanders (*Desmognathus ochrophaeus*) at Ca poor sites, with composition continuously shifting toward dominance by red-backed salamanders as Ca availability increased. Several known calciphilic species of snails (*Paravitrea multidentata*, *Gastrocopta pentodon*, and *Euconulus polygyrus*) were found only at the highest Ca sites. Some of the observations (e.g., decreasing snail abundance) were confounded by a strong positive correlation between elevation and estimated acid deposition. However, although the underlying mechanisms require further study, these findings indicate that Ca availability, which is shaped by geology and acidic deposition inputs, influences northern hardwood forest ecosystems at multiple trophic levels.

### **Soil Exchangeable Calcium and pH**

[Pabian and Brittingham \(2012\)](#) determined the relationships between soil (Oa-horizon) chemistry and forest bird community composition, abundance, and diversity, and evaluated potential mechanisms responsible for the relationships in oak and red maple-dominated forests in Pennsylvania. Mean soil (Oa-horizon) exchangeable Ca for the 14 forest sites ranged from 5.28 to 23.5 meq/100 g and pH ranged from 3.6 to 5.1. Bird community composition (species richness and species abundances) varied with soil Ca and pH, with 10 bird species having the highest abundances in forests with high-Ca soils, and 5 species having the highest abundances with low-Ca soils. Five species were classified as “generalists” because they had high abundances and were present at all forest sites. Bird species associated with low-Ca soils were associated with high densities of mountain laurel (*Kalmia latifolia*) and five tree species whose basal areas were explained by low soil pH and Ca. Bird species associated with high-Ca soils were associated with high densities of saplings and high basal areas of acid-sensitive tree species (17 species whose basal areas were, in part, explained by high Ca and soil pH). All environmental and soil variables explained 37.8% of the variation in bird species abundance data, with environmental variables explaining 36.0%, soils explaining 0.5%, and 1.3% being explained by both. Most (67%) of the variation in the bird abundance data explained by soils was also explained by the vegetation and invertebrate variables, thereby supporting the hypothesis that the environmental variables were responsible for the soil-bird relationships.

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## 5.3 Characteristics, Distribution, and Extent of Sensitive Ecosystems

In the 2008 ISA, it was known that geology (particularly surficial geology) is the principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition. Geologic formations with low base cation supply (e.g., sandstone, quartzite), due mainly to low weathering, generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been considered in numerous acidification studies ([Sullivan et al., 2007b](#); [Vertucci and Eilers, 1993](#); [Stauffer and Wittchen, 1991](#); [Stauffer, 1990](#); [Bricker and Rice, 1989](#)). Other factors contribute to the sensitivity of soils and surface waters to acidifying deposition, including topography, soil chemistry, land use, and hydrologic flowpath.

Forests of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and mountain top and ridge forest ecosystems in the southern Appalachians are the region's most sensitive to terrestrial acidification from atmospheric deposition (Section 3.2.4.2 of 2008 ISA). Recent decreases in acid deposition had been linked to improvements in surface water chemistry ([Appendix 7](#)). However, there remains widespread measurements of ongoing depletion of exchangeable base cations in forest soils in the northeastern U.S. ([Appendix 4.3.4](#)).

At the time of the 2008 ISA, there had been no systematic national survey to determine the extent and distribution of terrestrial ecosystem sensitivity to the effects of acidifying deposition. However, one preliminary national evaluation by [McNulty et al. \(2007\)](#) used a simple mass balance model and available national databases to estimate forest soil critical acidifying deposition loads (for wet and dry deposition of S and N) and exceedances. They found that approximately 15% of forest soils in the U.S. receive acidifying deposition that exceeds the estimated critical load of wet and dry deposition of S and N by more than 250 eq/ha/yr ([McNulty et al., 2007](#)). The areas where exceedances reach this level could be considered to represent those areas that are likely most sensitive to continued high levels of acidifying deposition.

Since the 2008 ISA, a series of studies have evaluated the characteristics, distribution, and/or sensitivity of ecosystems to acidifying N and S deposition. For descriptions of studies that characterized ecosystem sensitivity through critical load and critical load exceedance determinations, see [Appendix 5.5](#).

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## 5.4 Application of Terrestrial Acidification Models

The models that were used in recent studies to evaluate terrestrial acidification and its components included the simple mass balance [SMB; [Forsius et al. \(2010\)](#); [McNulty and Boggs \(2010\)](#); [Nasr et al. \(2010\)](#); [Whitfield and Watmough \(2012\)](#); [Duarte et al. \(2013\)](#); [Jung et al. \(2013\)](#); [Phelan et al. \(2014\)](#)], soil texture approximation [STA; [Whitfield et al. \(2010b\)](#)], MAGIC ([Sullivan et al., 2011a](#); [Whitfield et al., 2010a](#); [Whitfield et al., 2009](#)), ForSAFE-VEG ([McDonnell et al., 2014a](#); [Sverdrup et al., 2012](#)), and empirical models outlined by [Spranger et al. \(2004\)](#) and [Krzyzanowski \(2011\)](#). See [Appendix 4.5](#) for a review of models.

[Phelan et al. \(2014\)](#) applied the PROFILE model (see [Appendix 4.5.1.1](#)) to estimate BC<sub>w</sub> to support SMB critical load estimates for 51 hardwood forest sites in Pennsylvania. The rates of BC<sub>w</sub> ranged from 119 to 9,245 eq/ha/yr and were consistent with soil properties and regional geology. Critical loads ranged from 4 to 10,503 eq/ha/yr. The PROFILE model estimates by [Phelan et al. \(2014\)](#) were three times larger than those reported for the same sites by [McNulty et al. \(2007\)](#) who used the clay correlation-substrate method and SMB models to estimate BC<sub>w</sub> rates and critical loads, respectively. These PROFILE model results suggest that the hardwood sites in Pennsylvania may not be as sensitive to acidifying deposition as previously estimated by [McNulty et al. \(2007\)](#). It should be noted that BC<sub>w</sub> rates were not measured for these areas and may be a result of the different (empirical vs. mechanistic) approaches of each model. As the [Phelan et al. \(2014\)](#) study only tested and compared the PROFILE model in Pennsylvania, the researchers recommended applying PROFILE in different regions and ecosystems in the U.S. to gain a better understanding of the model performance and the degree to which BC<sub>w</sub> rates estimated by PROFILE differ from those estimated using the clay correlation-substrate model.

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## 5.5 Levels of Deposition at Which Effects Are Manifested

Since the 2008 ISA, several studies have evaluated the relationships between N and S deposition and the growth and physiology of terrestrial organisms and ecosystem function. In addition, numerous studies have used estimates of critical load exceedances caused by historic, current, and future N and S deposition levels to characterize the impacts of acidifying deposition. In this section, these relationships are described as (1) impacts of elevated N and S deposition, (2) impacts of ambient levels of N and S deposition, and (3) critical loads and exceedances.

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### 5.5.1 Impacts of Elevated Nitrogen and Sulfur Deposition

A number of studies published since the 2008 ISA have evaluated the impacts of elevated N and S deposition on trees, herbaceous species, and soil biota ([Table 5-3](#)). “Elevated” N and S deposition in this section refers to additions of N and S above ambient atmospheric deposition during the time of the specified study. As detailed in [Appendix 6](#), N deposition may lead to enrichment effects as well as acidification.

In Bear Brook Watershed, ME, [Bethers et al. \(2009\)](#) investigated the effects of chronically elevated N and S deposition (i.e., 25.2 kg N/ha/yr and 28.8 kg S/ha/yr additions since 1989) on growth, foliar nutrients, and photosynthetic capacity of sugar maple saplings. Sugar maple saplings in the treated watershed had higher foliar Al (+56%), N (+15%), P (+10%), and K (+15%) and lower foliar Ca (−25%) compared to the nontreated watershed, presumably through influences on soil chemistry. The treated saplings also had lower photosynthetic capacity, higher N:P ratios, negative correlations between leaf N and electron transport capacity, and reduced carboxylation capacity, which suggest nutrient imbalances induced by the elevated N and S deposition. However, sapling growth was unaffected by the treatments. In another study conducted in Quebec, Canada, [Moore and Houle \(2013\)](#) observed similar results in their evaluation of the effects of 8 years of NH<sub>4</sub>NO<sub>3</sub> additions (26 and 85 kg N/ha/yr applied from 2001–2008) on sugar maple physiology and soil chemistry. Foliar Ca in the high N treatment decreased by 79% compared to the control and reached 0.24%, the lowest foliar Ca concentration ever reported for sugar maple. The treatments did not significantly alter dieback rate or basal area growth. These results corresponded to changes in soil chemistry; the treatments significantly decreased exchangeable Ca, Mg, Mn, and K in at least one of the top organic soil layers. The largest differences were observed for exchangeable Ca between the control and the high N treatment, with the L and the H layers of the soil organic horizon showing exchangeable Ca decreases of 29 and 72%, respectively. These results suggest that increased N deposition can strongly affect Ca nutrition of sugar maple at sites with low base cation saturation; however, effects on tree growth have not been documented.

In West Virginia, [Jensen et al. \(2014\)](#) examined long-term impacts of relatively high N and S additions (22 years of 169 kg/ha/yr (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) on black cherry and yellow poplar (*Liriodendron tulipifera*) bole wood Ca, Mg, and Mn concentrations; tree growth; and basal area. Bole wood Ca concentrations were lower and Mn concentrations higher in both species on the treated versus nontreated watershed. Growth responses, measured through relative growth rates of cored trees and changes in basal area, were not conclusively affected by the treatment.

[Jung and Chang \(2012\)](#) evaluated the impacts of 4 years of elevated N and S deposition (30 kg N/ha/yr, 30 kg S/ha/yr, and 30 kg N/yr + 30 kg S/ha/yr additions from 2006 to 2009) on a forest composed of trembling aspen (*Populus tremuloides*), white spruce (*Picea glauca*), balsam fir, black spruce (*Picea mariana*), and paper birch (*Betula papyrifera*) in the Athabasca oil sands region of Alberta, Canada. None of the treatments influenced the growth of the understory plants or soil microbial biomass; understory and microbial community composition were not measured. However, N increased tree growth in the N and N + S treatments, indicating N limitation. Nitrogen and S additions decreased soil exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and these decreases were attributed to a combination of increased tree uptake to support greater growth and increased leaching with  $\text{SO}_4^{2-}$ .

[Guy et al. \(2013\)](#) conducted a greenhouse experiment to assess the potential effects of acidic deposition on the root system morphology of three endemic species that grow on sand dunes in the Athabasca oil sands region of Alberta, Canada: *Armeria maritima*, *Deschampsia mackenzieana*, and *Stellaria arenicola*. Plants were exposed to three pH treatments (pH 5.6, 5.0, and 4.2) together with additions of 2.61 to 4.67 mg/L of  $\text{SO}_4^{2-}$  and 1.95 to 3.51 mg/L  $\text{NO}_3^-$  for 55–60 days. There were no statistically significant differences in plant survival, root length, root surface area, or root tip numbers between acid treatments. Therefore, current rates of acidifying N and S deposition are not likely a threat to these species.

Since the 2008 ISA, three studies were identified on the impacts of N and/or S deposition on soil biota. [Payne et al. \(2010\)](#) examined the impacts of elevated  $\text{SO}_4^{2-}$  deposition on the microbial community in a Scottish peatland and showed that additions of 95 kg  $\text{SO}_4^{2-}$ /ha/yr applied over 18 months decreased the concentrations and percentages of live amoebae. Abundances of *Trinema lineare*, *Corythion dubium*, and *Euglypha rotunda* were also significantly reduced. These results suggest the potential importance of  $\text{SO}_4^{2-}$  deposition in influencing testate amoebae communities in the peatland soils. In another study, [Chen et al. \(2013\)](#) evaluated the impacts of S additions on soil microbial and nematode community composition in an Inner Mongolian grassland in China. Seven treatments of 28 to 166 mol  $\text{H}^+$ /ha were applied in three doses in the form of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) from 2009 to 2010. Fungal fatty acids were increased by 49% and fungi:bacteria ratio increased by up to 120% by the acid additions. Total and bacterial fatty acids were decreased by the S treatments by up to 47 and 40%, respectively. Acid additions also impacted the soil nematode community by initially increasing the total number of soil nematodes, then altering community composition; bacterivorous and fungivorous nematodes increased, while plant-feeding and omnivorous and carnivorous nematodes decreased. [Hu et al. \(2013\)](#) examined the impacts of N and S additions on soil microbial biomass and function in a boreal mixed-wood forest in the Athabasca oil sands region of

Alberta, Canada. Five years of N and S additions (30 kg N/ha/yr and/or 30 kg S/ha/yr) did not influence soil microbial biomass C and N. However, activities of some extracellular enzymes in the soil were decreased by the treatments, with greater  $\beta$ -glucosidase activity in the N + S treatment than in the S treatment and decreased soil arylsulfatase activity in the S addition treatment. Thus, the additions of N and/or S strongly affected soil microbial community functions and enzymatic activities without changing soil microbial biomass in this boreal forest.

**Table 5-3 Impacts of acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	Nitrogen and Sulfur Deposition/Additions	Description
<a href="#">Bardhan et al. (2012)</a>	Forest Great Smoky Mountain National Park, TN, NC	Soil microbes (bacteria)	6 to 41 kg S/ha/yr (modeled)	Soil analyses indicated only minor differences in bacterial diversity among sites; the bacterial community did not change along the gradients of S deposition.
<a href="#">Bethers et al. (2009)</a>	Forest Bear Brook watershed, ME	Sugar maple	Ambient: 8.4 kg N/ha/yr and 14.4 kg S/ha/yr; elevated: 25.2 kg N/ha/yr and 28.8 kg S/ha/yr	Treated watershed had a 56% increase in foliar Al, a 25% reduction in foliar Ca, N (+15%), P (+10%), and K (+15%). The treated saplings had lower photosynthetic capacity, high N:P ratios, and negative correlations between leaf N and electron transport capacity, which may indicate nutrient imbalance.
<a href="#">Boot et al. (2016)</a>	Loch Vale watershed in Rocky Mountain National Park, CO	Soil microbes	17 yr of 25 kg N/ha/yr (as NH <sub>4</sub> NO <sub>3</sub> ) addition	Long-term fertilization resulted in increased soil acidity and reduced soil C. Soil microbial biomass in the fertilized soils was also lower (22%), the microbial community was altered through reductions in vesicular arbuscular mycorrhizae and saprotrophic fungi, and activity of N degrading microbial enzymes was decreased.
<a href="#">Chen et al. (2013)</a>	Grassland Mongolia, China	Soil microbes, bacteria, fungi, and nematodes	Sulfuric acid (0, 2.76, 5.52, 8.28, 11.04, 13.8, and 16.56 mol H <sup>+</sup> /m <sup>2</sup> )	Fungal fatty acids were increased by 49% and fungi:bacteria ratio increased by up to 120% by the acid additions relative to the controls. Total and bacterial fatty acids were decreased by the S treatments by up to 47 and 40%, respectively. In the treatments, bacterivorous and fungivorous nematodes increased, while herbivorous and omnivorous + carnivorous nematodes decreased.

**Table 5-3 (Continued): Impacts of acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	Nitrogen and Sulfur Deposition/Additions	Description
<a href="#">Cleavitt et al. (2011a)</a>	Forest Acadia National Park, ME	Epiphytic lichens	12 to 18 kg S/ha/yr	Throughfall chemistry influenced bark pH and the suitability of tree boles as habitat for lichen; epiphytic lichen species richness and presence of pollution-sensitive epiphytes were greater on red maple trees, which have a higher pH in the bark relative to red spruce trees.
<a href="#">Dietze and Moorcroft (2011)</a>	Forest Eastern and central portions of the U.S.	267 tree species organized into 10 PFTs	6 to 16 kg/ha/yr as NO <sub>3</sub> <sup>-</sup> ; 4 to 30 kg/ha/yr as SO <sub>4</sub> <sup>2-</sup> (NADP wet)	Mean sensitivity by covariate and PFTs showed that overall tree mortality was most sensitive to atmospheric pollutants, with acid deposition (SO <sub>4</sub> <sup>2-</sup> ) showing the highest sensitivity and N deposition the third highest sensitivity. Stand DBH showed the second highest sensitivity.
<a href="#">Duarte et al. (2013)</a>	Forest Northeastern U.S.	21 tree species	256 to 920 eq/ha/yr of N; 242 to 1,154 eq/ha/yr of S (modeled)	Statistically significant negative correlations between critical load exceedance and growth (17 species), and crown density (4 species) were determined. Positive correlations between critical load exceedance and declining vigor (4 species), crown dieback (4 species), and crown transparency (7 species) were determined. Species that were most negatively affected by N and S deposition included balsam fir, red spruce, quaking aspen, and paper birch.
<a href="#">Jensen et al. (2014)</a>	Forest Fernow Experimental Forest, WV	Yellow poplar and black cherry	35.5 kg N/ha/yr; 40.5 kg S/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (addition)	Bole wood Ca concentrations were lower and Mn concentrations were higher in both species on the treated watershed. Growth responses were not conclusive and appeared to differ by species.

**Table 5-3 (Continued): Impacts of acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	Nitrogen and Sulfur Deposition/Additions	Description
<a href="#">Jung and Chang (2012)</a>	Forest Alberta, Canada	Trembling aspen, white spruce, balsam fir, black spruce, and paper birch	30 kg N/ha/yr, 30 kg S/ha/yr, and 30 kg N/yr + 30 kg S/ha/yr (additions)	Nitrogen addition increased tree growth in the N and N + S treatments. None of the treatments affected understory growth or soil microbial biomass. Annual leaching losses of SO <sub>4</sub> <sup>2-</sup> were increased by S and S + N additions. Leaching of base cations showed a similar trend to SO <sub>4</sub> <sup>2-</sup> leaching.
<a href="#">Miller and Watmough (2009)</a>	Forest Southern Ontario, Canada	Sugar maple	9 to 12.8 kg N/ha/yr; 7.6 to 14.8 kg S/ha/yr (ambient)	Sugar maple foliar S and N contents were positively correlated with modeled N and S deposition. Foliose lichen species richness was negatively correlated with modeled air pollution levels (S deposition, N deposition, and atmospheric ozone).
<a href="#">Pannek et al. (2015)</a>	Acidic grassland Atlantic biogeographic region of Europe	44 grassland species within the <i>Violion caninae</i> alliance	2.4 to 43.5 kg N/ha/yr (ambient)	Out of 44 species studied, 16 were affected by N deposition, with 12 of them exhibiting a negative response. Increasing soil pH and P influenced 24 and 14 species, respectively, predominantly positively. Species that were negatively affected by high N deposition and/or high soil P also showed a negative temporal trend characterized by short stature and slow growth.
<a href="#">Payne et al. (2010)</a>	Peatland Scotland	Soil microbes (testate amoebae)	Ambient: 5 kg SO <sub>4</sub> <sup>2-</sup> /ha/yr; elevated: 95 kg SO <sub>4</sub> <sup>2-</sup> /ha/yr	Analysis showed that the SO <sub>4</sub> <sup>2-</sup> treatment reduced the concentrations and percentages of live amoebae, suggesting a less active community as a result of the treatment. In addition, abundances of <i>Trinema lineare</i> , <i>Corythion dubium</i> , and <i>Euglypha rotunda</i> were significantly reduced.

**Table 5-3 (Continued): Impacts of acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	Nitrogen and Sulfur Deposition/Additions	Description
<a href="#">Quesnel and Cote (2009)</a>	Forest Boreal region of Canada	White spruce	NA	Meta-analysis of foliar results (nutrient concentrations) from 23 white spruce forests (natural and nonfertilized plantation forests) revealed that N deficiencies occurred in less than 10% of the sites. Base cation deficiencies identified were attributed to removals with harvest, higher requirements of white spruces for K and Ca, and nutrient deficiencies/imbbalances induced by N additions/deposition.
<a href="#">Rose et al. (2016)</a>	Open uplands, open lowlands, and woodlands U.K.	Vascular plants	NA	Changes in vegetation from 1993–2012 at a network of plots (504) within 12 Environmental Change Network (ECN) sites. Significant increases in species richness were detected at the network level. Increases in acid-sensitive species and comparatively little change in acid-tolerant species were noted. Changes are consistent with increases in pH observed and attributed to the large reductions in acid deposition. Increases in species diversity were also attributed to wetter summers and a reduction in soil N availability at some of the upland locations.
<a href="#">Soulé (2011)</a>	Forest Grandfather Mountain, NC	Red spruce	NA	Radial growth rates of red spruce increased through time, and growth rates were significantly correlated to temperature (positively), days with precipitation (negatively), atmospheric CO <sub>2</sub> (positively), and emissions of SO <sub>x</sub> and NO <sub>x</sub> (negatively).
<a href="#">Sullivan et al. (2013)</a>	Forest/Adirondack Mountains, NY	Sugar maple	750 to 1,120 eq/ha/yr as N + S (NADP wet, CASTNET dry)	Found that plots without sugar maple seedlings had higher rates of atmospheric N + S deposition.

**Table 5-3 (Continued): Impacts of acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	Nitrogen and Sulfur Deposition/Additions	Description
<a href="#">Thomas et al. (2013)</a>	Forest Appalachian Mountains, WV	Eastern redcedar	NA	Dendroisotopic techniques showed the recovery of eastern redcedar trees from decades of S pollution. Analysis provided evidence for a distinct physiological response to changes in atmospheric SO <sub>2</sub> emissions since 1980.
<a href="#">Cleavitt et al. (2015)</a>	Forest VT, NH, ME	Lichens	3 to 8 kg N/ha/yr and 4.5 to 5.2 kg S/ha/yr	Annual mean and cumulative N deposition were strongly correlated with decreases in lichen species richness, decreases in N sensitive species, and poorer thallus condition. Cumulative dry deposition of S had the best fit to decreases in thallus condition, poorer community-based S index values, and the absence of many S sensitive species.

Al = aluminum; C = carbon; Ca = calcium; CASTNET = Clean Air Status and Trends Network; CO<sub>2</sub> = carbon dioxide; DBH = diameter at breast height; eq = equivalents; H<sup>+</sup> = hydrogen ion; ha = hectare; K = potassium; kg = kilogram; L = liter; m = meter; mg = milligram; MN = manganese; mol = mole; N = nitrogen; NA = not applicable; Na<sub>2</sub>SO<sub>4</sub> = sodium sulfate; NADP = National Acid Deposition Program; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; NO<sub>x</sub> = the sum of nitric oxide and nitrogen dioxide; P = phosphorus; PFT = plant functional types; S = sulfur; SO<sub>2</sub> = sulfur dioxide; SO<sub>4</sub><sup>2-</sup> = sulfate; SO<sub>x</sub> = sulfur oxides; yr = year.

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## 5.5.2 Impacts of Ambient Deposition

Five studies that were published since the 2008 ISA have been identified that documented the impacts of ambient N and S deposition on terrestrial biological endpoints, including tree species, tree species grouped into plant functional types (PFTs), lichens, and soil biota ([Table 5-3](#)). “Ambient” N and S deposition in this section refers to the levels of atmospheric N and S deposition experienced during the time of the specified study.

[Dietze and Moorcroft \(2011\)](#) conducted a large-scale analysis of central and eastern U.S. that investigated 13 covariates (including climate, air pollutants [N deposition, acid deposition, and ozone averaged 1994–2005], topography, and stand characteristics) as predictors of individual tree mortality. Tree species (267 species) were grouped into 10 PFTs based on hardwoods/softwoods, latitude, successional phase (early, mid, and late successional), and hydrological soil status (i.e., hydric). The researchers found that tree mortality was most sensitive to stand characteristics and air pollutants. Nine PFTs had decreased mortality with increased N deposition, and only the northern mid successional hardwoods showing the opposite pattern (i.e., increased mortality with increased N deposition). Seven PFTs showed large increases in mortality with acid deposition (as  $\text{SO}_4^{2-}$ ), with only late successional conifers showing the inverse (i.e., a weak decline in mortality with increased acid deposition). Mean sensitivity by covariate and PFT showed that overall tree mortality was most sensitive to atmospheric pollutants, with acid deposition ( $\text{SO}_4^{2-}$ ) showing the highest sensitivity and N deposition the third highest sensitivity. Individual tree DBH showed the second highest sensitivity.

[Duarte et al. \(2013\)](#) evaluated the responses of tree species in 4,057 forest plots in the northeastern U.S. to the exceedance of critical loads of N and S deposition. Modeled S and N deposition ranged from 242 to 1,154 eq/ha/yr and 256 to 920 eq/ha/yr, respectively. Critical loads were exceeded in 45% (calculated using midpoint weathering rates) of the plots. See [Appendix 5.5.3](#) for a greater description of critical loads and exceedances from this study. Results from Spearman’s rank correlation analyses showed that the growth of 17 species and crown density of 4 species were negatively correlated with critical load exceedance ([Table 5-4](#)). Positive correlations between critical load exceedance and declining vigor (three species), crown dieback (four species), and crown transparency (seven species) were also found ([Table 5-5](#)). Crown dieback was considered the most reliable indicator of forest health. Based on this metric, balsam fir, red spruce, quaking aspen, red maple, and paper birch were identified as the species most negatively impacted by N and S deposition.

**Table 5-4 Results of Spearman’s rank correlation analysis comparing growth versus critical load exceedance by species for the forested plots in the northeastern U.S. [from [Duarte et al. \(2013\)](#)]. Modeled sulfur and nitrogen deposition on the plots ranged from 242 to 1,154 eq/ha/yr and 256 to 920 eq/ha/yr, respectively. Correlations shown here are significant at  $\alpha = 0.05$ .**

Species	Correlation Coefficient	Sample Size (n)
Black spruce ( <i>Picea mariana</i> )	-0.44	41
Balsam fir ( <i>Abies balsamea</i> )	-0.33	499
Chestnut oak ( <i>Quercus prinus</i> )	-0.28	238
Paper birch ( <i>Betula papyrifera</i> )	-0.27	574
Scarlet oak ( <i>Quercus coccinea</i> )	-0.26	170
Bigtooth aspen ( <i>Populus grandidentata</i> )	-0.25	280
Eastern white pine ( <i>Pinus alba</i> )	-0.19	1,464
Black oak ( <i>Quercus velutina</i> )	-0.18	257
White ash ( <i>Fraxinus americana</i> )	-0.18	1,256
Sweet birch ( <i>Betula lenta</i> )	-0.12	460
Yellow birch ( <i>Betula alleghaniensis</i> )	-0.12	669
Northern red oak ( <i>Quercus rubra</i> )	-0.11	1,533
Red maple ( <i>Acer rubrum</i> )	-0.11	3,861
Red spruce ( <i>Picea rubens</i> )	-0.09	616
American beech ( <i>Fagus grandifolia</i> )	-0.08	1,449
Black cherry ( <i>Prunus serotina</i> )	-0.07	1,026
Eastern hemlock ( <i>Tsuga canadensis</i> )	-0.07	1,055
Pignut hickory ( <i>Carya glabra</i> )	0.44	31
Norway spruce ( <i>Picea abies</i> )	0.38	148
Yellow poplar ( <i>Liriodendron tulipifera</i> )	0.35	47
White spruce ( <i>Picea glauca</i> )	0.24	97

eq = equivalents; ha = hectare; yr = year.

Source: [Duarte et al. \(2013\)](#).

**Table 5-5 Results of Spearman’s rank correlation analyses comparing tree vigor, crown density and dieback, and canopy transparency versus critical load exceedance by species for the forested plots in the northeastern U.S. [from [Duarte et al. \(2013\)](#)]. Modeled sulfur and nitrogen deposition on the plots ranged from 242 to 1,154 eq/ha/yr and 256 to 920 eq/ha/yr, respectively. Correlations shown here are significant at  $\alpha = 0.05$ .**

Species	Vigor		Crown Density		Crown Dieback		Canopy Transparency	
	Correlation Coefficient	Sample Size (n)						
American beech	0.13	433			0.12	502	0.30	502
Ash	0.22	189						
Balsam fir			-0.23	161	0.56	161	0.18	161
Black cherry	0.33	47						
Eastern hemlock			0.36	82	-0.24	148		
Fir							-0.36	33
Northern red oak							0.27	208
Paper birch			-0.29	125	0.13	300		
Quaking aspen			-0.56	61	0.44	61	0.40	61
Red maple			-0.16	337	0.10	767	0.19	767
Red spruce			0.20	115	0.43	168	0.61	168
Sugar maple	0.06	3,408			-0.04	3,466	0.12	3,467
White ash	-0.32	49						

eq = equivalents; ha = hectare; yr = year.

Source: [Duarte et al. \(2013\)](#).

[Sullivan et al. \(2013\)](#) evaluated relationships between deposition and sugar maple regeneration in the Adirondack Mountains. Total N and S deposition ranged between 750 and 1,120 eq/ha/yr, and plots that received higher rates of N (median of approximately 560 eq/ha/yr), S (median of approximately 480 eq/ha/yr), and N + S (median of approximately 1,040 eq/ha/yr) deposition had no sugar maple seedlings.

[Soulé \(2011\)](#) sampled red spruce trees within a high elevation red spruce-Fraser fir (*Abies fraseri*) forest on Grandfather Mountain, NC between 2006 and 2008, and used dendrochronology to evaluate the influences of climate (precipitation, temperature, and CO<sub>2</sub> concentrations) and emissions of SO<sub>x</sub> and NO<sub>x</sub> on growth. Radial growth rates of red spruce increased through time and were positively correlated to temperature and atmospheric CO<sub>2</sub> but were negatively correlated to emissions of SO<sub>x</sub> and NO<sub>x</sub> and number of days with precipitation in a year.

[Miller and Watmough \(2009\)](#) evaluated hardwood plots along air pollution (N, S, and ozone), soil acidity, and climate gradients in Ontario, Canada, and found that foliose lichen species richness was negatively correlated with modeled air pollution levels (S deposition, N deposition, and atmospheric ozone). In the same study, however, no relationship was seen in canopy condition and ground vegetation richness and diversity.

[Bardhan et al. \(2012\)](#) evaluated bacterial diversity along a soil and S deposition gradient in high elevation spruce-fir forests in GSMNP. Modeled S deposition ranged from 6 to 41 kg S/ha/yr. However, neither bacterial diversity nor community composition changed along the gradient of S deposition. The bacterial community on all sites was dominated by members of the phyla Actinobacteria, Acidobacteria, Planctomycetes, Proteobacteria, and Chloroflexi. Species from these phyla are often found in highly acidic environments such as acid-mine drainage and sphagnum bogs. Therefore, these analyses suggested that despite reductions in acid deposition, the soil conditions in these GSMNP sites were still acidic and had not yet reached a threshold suitable for nonacidophilic bacterial communities.

[Pannek et al. \(2015\)](#) used a data set from seminatural grasslands found on acidic soils along an N deposition gradient (2.4 to 43.5 kg N/ha/yr) in northwestern Europe to examine the response of species frequency to N and other factors including soil (0–10 cm) P, pH, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> and geographical, climatic, and management factors. Out of 44 studied species, 16 were affected by N deposition, with 12 of them exhibiting a negative response (see also [Appendix 6.2.5](#) and [Appendix 6.3.5](#)).

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### 5.5.3 Critical Loads and Exceedances

Since the 2008 ISA, critical load evaluations have been conducted in the northeastern forests of the U.S., hardwood forests in Pennsylvania, forests in western Canada, and arctic, subarctic, alpine, subalpine, and boreal systems. Studies also simulated target loads and critical loads and exceedances into the future under different deposition and climate scenarios and evaluated the sensitivity of critical load estimates to varying environmental conditions and forest management and uncertainties in critical load estimates. See [Appendix 4.6.2.1](#) for more information on critical loads based on soil acidification and [Appendix 6.5](#) for information on N critical loads in terrestrial systems.

[Duarte et al. \(2013\)](#) calculated critical loads of N and S for 4,057 forested plots in the northeastern U.S. using the steady-state SMB model (see also [Appendix 4.5.1.2](#)) and soil solution Bc:Al of 10.0 as the chemical indicator and threshold. In addition, the study evaluated the influence of three different BCw rates on critical loads: minimum, midpoint, and maximum. These BCw rates were determined using the clay correlation-substrate method and the range of U.S. Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS) Soil Survey Geographic Database (SSURGO) values for each soil series. Critical loads using the midpoint weathering rates were found to range from 11 to 6,540 eq/ha/yr (over 80% within the range of 850–2,050 eq/ha/yr), and in comparisons with deposition estimated using the ClimCalc model, were exceeded in 98% (calculated using minimum weathering rates), 45% (calculated using midpoint weathering rates), and 15% (calculated using maximum weathering rates) of plots. Similarly, [Phelan et al. \(2014\)](#) calculated critical loads of N and S deposition for 51 hardwood forests in Pennsylvania using the SMB model, soil solution Bc:Al of 10.0 as the chemical indicator, and the PROFILE model to estimate BCw rates. They found that critical loads ranged from 4 to 10,503 eq/ha/yr, and that critical loads at 53% of the sites were exceeded by the 2002 N and S deposition.

[Krzyzanowski \(2011\)](#) modeled deposition and soil acidification critical loads in northeastern British Columbia, Canada using empirical methods described in [Spranger et al. \(2004\)](#). Slow weathering of shale- and mudstone-derived feldspars, micas, and quartz placed the soils of the study area in the “high-sensitivity” class of critical loads. Soil acidification critical load was estimated to be 200 eq/ha/yr. Neither S nor N deposition exceeded this critical load. The combined S and N deposition at the dominant point of reception (i.e., near Blueberry River First Nation) was estimated to be 73.5 eq/ha/yr.

Estimates of S and N critical loads and exceedances for upland soils were generated for the Georgia Basin in British Columbia, Canada using the SMB model and zero base cation depletion as the chemical criterion and threshold ([Nasr et al., 2010](#)). The objective of the study was to evaluate critical load and exceedance calculations in the context of

sustainable forest and soil management policies by using “no further changes in soil base saturation” as the critical load criterion. Critical loads were found to range between 140 and 4,000 eq/ha/yr and were generally lowest on ridge tops and increased towards the valleys. Critical load exceedance ranged from 13% of the basin based on wet deposition fluxes to 32% under modeled total (wet and dry) deposition. With continued N and S deposition, significant portions of the basin were predicted to experience exceedance-enhanced base cation depletion rates greater than 200 eq/ha/yr.

[Forsius et al. \(2010\)](#) determined critical loads and exceedances for terrestrial ecosystems in the arctic and subarctic regions (with latitudes north of 60°) for 1990, 2000, 2010, and 2020 using the SMB model and two different chemical indicators (soil solution Al:Bc of 1.0 and ANCle of 0.0). The Al:Bc indicator was hypothesized to protect against fine root damage, and the ANCle indicator was hypothesized to preserve existing soil base cation pools. The 2020 deposition scenario was based on the maximum feasible reduction (MFR) emissions for 2020. Critical load estimates were generally comparable among the three main regions (northern Europe, Russia, and North America) and were influenced by the chemical indicator and associated threshold. The Al:Bc of 1.0 was less stringent than ANCle of 0.0, with the median critical loads for the two indicators being 700 and 300 eq/ha/yr, respectively. In North America, the lowest critical loads occurred in eastern Canada above latitudes of 60°. In general, low critical loads were found in areas with low weathering rates associated with coarse soils on acidic parent material. Critical loads in North America (above latitudes of 60°) were not exceeded by any of the deposition levels for any of the years: The lowest critical load was 130 eq/ha/yr, while the maximum rates of N and S deposition in North America were estimated to be 30 to 40 eq/ha/yr.

[Simkin et al. \(2016\)](#) quantified the effect of N deposition on species richness in the continental U.S. using data from over 15,000 plots. N deposition had a strong effect on species richness, but this effect differed between closed canopy and open ecosystems (i.e., forests and nonforest). In nonforested ecosystems (grasslands, deserts, shrublands, subalpine ecosystems), there was a positive relationship between N deposition and herbaceous species richness at low rates of N deposition, then a decrease in species richness with higher rates of N deposition over a threshold of 8.7 kg N/ha/yr. This study focused N enrichment, but highlighted interactions with soil acidification. Vegetation on acidic soils was more susceptible to species loss under elevated N. See [Appendix 6.2](#) and [Appendix 6.5.3](#) for more information on this study.

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### 5.5.3.1 Target and Future Critical Loads/Critical Load Exceedances

Target loads are generally defined as the deposition that is determined to provide a selected level of protection for or recovery of an ecosystem in a given future year. Target loads of S deposition were calculated for 44 watersheds and extrapolated to 1,320 acid-sensitive watersheds in the Adirondacks using MAGIC (see also [Appendix 4.5.1.4](#)) and different soil chemical indicator and thresholds of base saturation (5 and 10%), soil solution Bc:Al, and Ca:Al [1.0 and 10.0; [Sullivan et al. \(2011a\)](#)]. In a comparison of target loads (out to years 2050 and 2100) and the 2002 deposition, only 11.6 to 13.5% of the watersheds were simulated to be in exceedance of target loads to protect soil base saturation to 5%. For target loads to protect soils to a base saturation of 10%, 79.7 to 87.5% of the watersheds were in exceedance. For soil solution Bc:Al, 7.8 and 98.1% of watersheds were exceeded by the 2002 deposition for target loads to protect soil solution ratios of 1.0 and 10.0, respectively. For soil solution Ca:Al, 44.1 to 58.2% of watersheds experienced exceedances of target loads associated with a soil solution ratio of 1.0, and 98.1% of watersheds with target loads to protect Ca:Al ratios of 10.0 were exceeded. Further investigations revealed that 58.2, 85.7, and 93.6% of watersheds could not obtain threshold values of 10% base saturation, Bc:Al = 10, or Ca:Al = 10, respectively, even if acidic deposition was held at zero, thereby demonstrating that these chemical indicator threshold values were not useful for target load calculations using MAGIC in the Adirondack Mountains.

[Sverdrup et al. \(2012\)](#) and [McDonnell et al. \(2014a\)](#) used the ForSAFE-VEG model (see also [Appendix 4.5.1.3](#)) to evaluate potential long-term effects of climate change and atmospheric N deposition on alpine/subalpine ecosystems. Critical loads in both studies were defined as the amount of N deposition to protect against a change in plant biodiversity of 5 to 10 Mondrian (M) units (i.e., 5–10% change in plant species cover). [Sverdrup et al. \(2012\)](#) focused on a “generalized” alpine/subalpine site in the Rocky Mountain National Park, and simulated plant responses to a future climate (IPCC scenario A2) and four levels of N and S deposition (preindustrial background, Clean Air Act [CAA] controls, no CAA controls, and no CAA controls + high deposition). Soil base saturation decrease to less than 1% and soil solution Bc:Al were predicted to be less than 10.0 after year 2100, with the futures of no CAA emission controls and no CAA controls + high deposition (indicating soil acidification). Future plant species coverages were predicted to change in successively greater amounts in response to the altered climate, CAA emission controls, no CAA emission controls, and no CAA emission controls + high deposition. Critical loads of N deposition were calculated (based on a change of 5 M) to be 1 kg N/ha/yr. Critical loads related to S deposition were not discussed. All future N deposition scenarios (except preindustrial background N) were

simulated to result in critical load exceedance. [McDonnell et al. \(2014a\)](#) found similar results in their study that evaluated the response of plants on a site in the Loch Vale watershed, CO to 100 different scenario combinations of N deposition, precipitation, and temperature. The estimated critical load of N to protect against future (average of years 2010–2100) change in biodiversity (10 M) was estimated to be between 1.9 and 3.5 kg N/ha/yr, depending on the temperature increase scenario. Current deposition levels were found to exceed the critical load. Future increases in temperature were forecasted to substantially impact plant community composition beyond the predicted changes in response to N alone; N deposition was forecasted to result in approximately a 10- to 25-M change by 2100, whereas a +4.6°C increase in temperature was forecasted to result in approximately a 38- to 48-M change by 2100. In both studies, plant community response appeared to be attributed to N enrichment or eutrophication, as [McDonnell et al. \(2014a\)](#) stated that the critical load adopted in their study was much lower than critical loads to protect against  $\text{NO}_3^-$  leaching and soil acidification determined by other studies.

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### **5.5.3.2 Sensitivity of Critical Load Estimates to Forest Management and Environmental Stresses**

#### **Influences of Forest Management**

Removal of N and base cations with tree harvesting can be included in the calculation of critical loads. Several recent studies evaluated the amounts of base cations removed through different harvesting practices and determined that base cation removal can be substantial and contribute to site acidification.

[Duchesne and Houle \(2008\)](#) determined base cation budgets in a managed boreal balsam fir forest in Quebec, Canada according to six different scenarios, including two harvesting scenarios (whole-tree and stem-only harvesting), and three scenarios of mineral weathering. Whole-tree harvesting was found to remove twice as much Ca (1,358 vs. 664 mol/ha) and K (483 vs. 200 mol/ha) as stem only. In contrast to Ca and Mg, immobilization of K within tree biomass (69 mol/ha/yr) was the main pathway of K losses from the soil exchangeable reservoir, being five times higher than losses via soil leaching (14 mol/ha/yr). The amounts of K contained within the aboveground biomass and the exchangeable soil reservoir were 3.3 and 4.2 kmol/ha, respectively. Whole-tree harvesting was estimated to remove 44% of the K that was readily available for cycling in the short term.

Similar results were found by [Iwald et al. \(2013\)](#) in their evaluation of the removal of base cations with the harvesting of tree stumps and logging residues for biofuels in

Sweden. Their study evaluated three levels of harvesting intensity that varied in the amounts of stump and logging residues left on site (0–40%). Results from the study indicated that harvesting of stumps and logging residues constituted 13 to 24% and 27 to 45% of total (stumps + stem wood + logging residues) base cation extraction, respectively, depending on harvest intensity and tree species. The higher acidifying effect of logging residue removal was explained by the higher contents of base cations in needles and branches compared to stem wood. In a comparison between total net cation extraction by tree harvesting and maximum levels of current acid deposition, the acidifying effect of pine harvesting was found to be 57 to 108% of that of acid deposition, the acidifying effect of spruce harvesting was 114 to 263%, and the acidifying effect of birch harvesting was 60 to 171%.

In the northeastern U.S., [Lucas et al. \(2014\)](#) evaluated base cation extractions under three different management scenarios that varied in management intensity and conservation focus. The MaxGrowth management option, which involved site scarification, intensive fertilization (ammonium nitrate), and short rotation lengths (60–100 years), resulted in roughly 50 to 100% greater base cation removal than that associated with the other three management scenarios. Additionally, removal of treetops, branches, and stumps consistently resulted in removal rates of Ca, Mg, and K three to four times greater than conventional stem-only harvests.

[Johnson et al. \(2015a\)](#) used mass balance calculations to evaluate the impact of harvesting on ecosystem balances of Ca, Mg, K, and acidification of forest soils at 40 sites in Ireland. Three harvesting scenarios were evaluated: stem-only harvest (SOH), stem plus branch harvest (SBH), and whole-tree harvest (WTH). Mass balances for Ca, Mg, and K were determined based on the difference between long-term inputs (atmospheric deposition plus mineral weathering) and outputs (biomass removal plus leaching losses). Soil acidification was calculated using a simplified acidity balance of inputs (base cation and Na deposition and base cation weathering) and outputs (base cation uptake, S deposition, and Cl<sup>-</sup> deposition). Under the SOH and SBH management, inputs of Ca, Mg, and K were predicted to be sufficient to meet outputs. Atmospheric deposition was the most important source of Ca and Mg input. For K, inputs from soil weathering were as important as deposition. Under the WTH scenario, Ca output exceeded input at 19 of the 40 study sites. However, the differences were small relative to the sizes of the Ca pools; at the 19 sites, exchangeable pools could support Ca removal with WTH for a median of 220 years. Mg and K removal with WTH was balanced by inputs through deposition and soil weathering. In contrast, for soil acidification budgets, base cation removal with all scenarios of harvesting was much greater than that generated by soil weathering, suggesting that soils will become acidified over the long term. However, there was considerable uncertainty around the calculation of base cation fluxes.

For Ca balances, confidence intervals spanned positive and negative values at so many sites that it was not possible to predict the balance of Ca budgets. In addition, uncertainty in flux calculations was particularly important for K, as soil exchangeable pools were small and could be depleted within one or two rotations.

[Zetterberg et al. \(2014\)](#) evaluated the long-term effects of whole-tree harvest (WTH) on soil and stream water acidity in three forested catchments dominated by Norway spruce in Sweden. Potential influences of varying the amounts of logging residues, Ca concentrations in tree biomass, and site productivity on the model predictions were also evaluated through a sensitivity analysis. The MAGIC model was used to simulate changes in forest soil exchangeable Ca pools and stream water ANC from 1850 to 2100, with WTH occurring in 2020. Large depletions in soil Ca supply and a reversal of the positive trend in stream ANC were predicted for all three catchments sites after WTH. However, the magnitude of impact on stream ANC varied depending on site and the concentrations of mobile strong acid anions. Varying the tree biomass Ca concentrations was found to have the largest impacts on modeled soil and stream chemistry. Site productivity was the second most influential variable, and changing the amount of harvest residues left on site only marginally affected soil exchangeable Ca and stream water ANC. The results from this study suggest that future research should concentrate on minimizing uncertainties in tree biomass Ca concentrations and performing studies on biological feedback mechanisms that can increase Ca availability in the soils.

### **Influences of Environmental Stresses**

Climate and other environmental stresses may also directly or indirectly alter ecosystem parameters that are used in the SMB model to determine critical loads. The potential influences of climate were examined by [McNulty and Boggs \(2010\)](#) in their case-study evaluation of red spruce stands in western North Carolina that were experiencing low versus high rates of mortality associated with a pine beetle outbreak. There were positive relationships between site fertility (forest floor and soil measurements, foliar N concentrations, and Mg:N ratios) and red spruce mortality. Annual basal area growth of red spruce on more fertile plots was more sensitive to drought than on less fertile sites. Based on these observations, critical loads of acidity could change as a result of episodic stress (e.g., drought, insect infestations, frost injury, cold tolerance, etc.), and increased growth due to higher fertility and/or nutrient imbalances caused by acidifying deposition may make red spruce more susceptible to environmental stresses. Critical loads of N and S, therefore, might be lower when environmental stresses are present.

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### 5.5.3.3 Uncertainties in Critical Load Estimates

[Reinds and de Vries \(2010\)](#) evaluated the uncertainties in critical and target loads of S and N for 182 European forest soil plots using the Very Simple Dynamic (VSD) model (see also [Appendix 4.5.2.2](#)). Target loads were defined as the deposition that leads to a desired chemical state of the ecosystem in a given future year. The VSD model was calibrated using Bayesian prior probability functions for model parameters based on literature data, data from 200 Dutch forest sites and from simulated denitrification rates from a detailed ecosystem model, which improved the model fit to observed soil measurements. Critical loads determined by the calibrated model varied by chemical criterion. Minimum critical loads of N ranged between 181 (5th percentile) and 1,606 eq/ha/yr (95th percentile), maximum critical loads of N ranged between 502 (5th percentile) and 31,247 eq/ha/yr (95th percentile), and maximum critical loads of S ranged between 4 (5th percentile) and 9,670 eq/ha/yr (95th percentile), with the critical loads based on Al:Bc = 1 being higher than those determined using the ANC = 0 eq/ha/yr criterion. Uncertainty analysis also showed that the main drivers of uncertainty were largely dependent on the chemical criterion used in the critical and target load calculations. Base cation weathering, deposition, and the parameters describing the H-Al equilibrium in the soil solution were the main sources of uncertainty in the estimates of maximum critical loads for S ( $Cl_{max}[S]$ ) based on the Al:Bc criterion of 1.0, and uncertainty in  $Cl_{max}(S)$  based on ANC was completely determined by base cation inputs. The denitrification fraction was the most important source of uncertainty for the maximum critical loads of N ( $Cl_{max}[N]$ ). Calibration of VSD reduced the levels of uncertainty for all critical loads and criteria. After calibration, the coefficient of variation (CV) for  $Cl_{max}(S)$  was below 0.4 for almost all plots, and target loads were not needed in any of the simulations for 40% of the plots. According to the noncalibrated model, there was a positive probability for the need of a target load for almost all plots.

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## 5.6 Climate Modification of Ecosystem Response

The effect of acidifying deposition on terrestrial ecosystems can be modified by climate shifts in temperature and precipitation. [Appendix 13](#) provides an overview on this topic and [Appendix 4.7.1](#) provides information on climate modification of soil acidification.

Warmer temperatures increase decomposition and nitrification. Nitrification will also increase with increased N supply caused by increased weathering or decomposition ([Booth et al., 2005](#)). The process of nitrification generates protons that increase the rate of nitrate and base cation leaching to drainage waters ([Murdoch et al., 1998](#)). The combined increase of  $NO_3^-$  leaching and loss of base cations has the potential to magnify

acidification in forest soils ([Fernandez et al., 2003](#)). Soil weathering is typically the key buffer to acidic deposition ([Li and McNulty, 2007](#)), and while weathering is increased by both soil temperature and soil moisture ([Gwiazda and Broecker, 1994](#)), it is unclear whether any future change in the magnitude of temperature and precipitation will be enough to alter base cation supply or influence the acid-base balance of sensitive ecosystems. Furthermore, it is unclear whether increased supply of N in soils from either deposition, increased decomposition, or increased nitrogen fixation may negate the ameliorative effect of enhanced weathering. Some studies show that climate change will mitigate acidification with increased weathering ([Belyazid et al., 2011a](#)), while others show that climate change will aggravate acidification although increased nitrification outpaces enhanced weathering ([Wu and Driscoll, 2010](#)). In general, increased temperature and precipitation will likely enhance inputs of buffering agents from weathering and deposition, but also increase inputs of acidifying agents from deposition and enhanced N cycling. The relative sensitivity of these opposing processes to a given change in climate remains unresolved.

The mountainous regions of the Eastern U.S. are especially interesting to study because acidifying deposition and climate change interact in these areas. Recently, [Wason et al. \(2017\)](#) studied the responses of red spruce and balsam fir to acidic deposition and trends in climate on Whiteface Mountain in New York using tree ring analysis in forests plots along an elevational gradient. They found that both species increased growth with increased precipitation and pH. Red spruce growth appeared to increase growth with a warming climate and balsam fir did not. Despite the changes in growth due to precipitation chemistry and climate, the authors did not detect changes in the distribution in the spruce-fir forest and perhaps this is a longer-term process. The study demonstrated the complexity of forest response as multiple environmental factors change as these forests recover from acidifying deposition.

[Koo et al. \(2014\)](#) used the Annual Radial Model (ARIUM) to investigate projected climate change effects and changing air pollution on red spruce growth in the Great Smoky Mountain national park. The model estimated that high elevation (<1,700 m) red spruce growth would decline 10.8% when a climate change interacted with a 10% increase in air pollution. However, growth increased by 8.4% when air pollution decreased 10% in air pollution with climate change. In contrast, low elevation red spruce growth decreased with future climate change with decreased, increased and no change in air pollution.

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## 5.7 Summary

Since publication of the 2008 ISA, the overarching understanding of terrestrial acidification has not appreciably changed. More recent research has confirmed and strengthened this understanding and provided more quantitative information, especially across the regional landscape. A number of studies have evaluated the relationships between soil chemistry indicators of acidification and ecosystem biological endpoints (see [Table 5-6](#)). Soil chemistry indicators examined in recent literature include exchangeable base cations, soil pH, exchangeable acidity ( $H^+$  and Al), exchangeable Bc:Al ratio, base saturation, and Al concentrations. Biological endpoints included in the evaluations consisted of physiological and community responses of trees and other vegetation, lichens, soil biota, and fauna.

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### 5.7.1 Physiology and Growth

The physiological effects of acidification on terrestrial ecosystems in the U.S. were well characterized at the time of the 2008 ISA. Consistent and coherent evidence from multiple species and studies in 2008 showed that the biological effects of acidification on terrestrial ecosystems were generally attributable to physiological impairment caused by Al toxicity and decreased ability of plant roots to take up base cations (Section 3.2.2.3 of the 2008 ISA). Acid deposition can also leach membrane-associated stores of Ca from young red spruce needles, which affects membrane stability and freezing tolerance. New information since the 2008 ISA has supported these conclusions ([Appendix 5.2](#)), including further studies on the impact of acidifying deposition on sensitive tree species, such as sugar maple and red spruce. Much of the new evidence for the negative effects of acidifying deposition on these species comes from Ca addition experiments, in which the addition of Ca has alleviated many of the negative plant physiological and growth effects. Consistent with the findings of the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.**

In the 2008 ISA, acidifying deposition, in combination with other stressors, was found to be a likely contributor to physiological effects that led to the decline of sugar maple trees living at higher elevation in some portions of the eastern U.S. that have geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils. Studies since the 2008 ISA support these findings (see [Appendix 5.2.1.1](#)). For example, recent field studies demonstrated relationships between soil chemical indicator threshold values and tree responses. Substantial declines in sugar maple regeneration were found at

soil base saturation levels <20%, which is consistent the range reported in the 2008 ISA. In new studies, sugar maple showed positive growth and regeneration responses to increasing exchangeable base cations, base saturation and soil pH, and negative relationships with increasing exchangeable Al. Additional studies indicated that growth, regeneration and physiological responses of sugar maple to soil conditions created by acidifying N and S deposition were reversed or ameliorated by Ca additions. The responses to Ca additions included increased growth and regeneration, decreased crown dieback, increased foliar chlorophyll, and decreases in foliar metabolic indicators of physiological stress.

The 2008 ISA reported that changes in soil chemistry, such as depletion of soil base cations, increasing Al concentration, and leaching of base cations into drainage water, have contributed to physiological stress, high mortality rates, and decreasing growth trends of red spruce trees. New information since the 2008 ISA from Ca addition studies supports the conclusion that depletion of base cations contributed to these effects in trees ([Appendix 5.2.1.2](#)). Foliar biomass and physiological responses of red spruce to soil conditions created by acidifying N and S deposition were reversed or ameliorated by Ca additions. The responses included higher foliar antioxidant activity in the winter, significantly greater foliar cold tolerance, and higher levels of foliar metabolic compounds that indicate an increased tolerance of environmental stresses. ([Schaberg et al., 2011](#); [Halman et al., 2008](#)).

In the 2008 ISA, there was a limited amount of information on acidification effects on flowering dogwood. Since the 2008 ISA, no additional information on dogwood has been published; however, other tree species that have been evaluated in studies relating soil chemistry to tree physiology include yellow birch, white ash, American beech, black cherry, northern red oak, hickories, American basswood, and eastern hophornbeam. These species were reported to vary in their sensitivities to soil conditions associated with acidifying deposition. Data are insufficient to draw general conclusions for other species. New information was also published on the recovery of eastern redcedar since the 1980s as SO<sub>2</sub> emissions declined. However, it is unclear whether this recovery was from acid deposition, direct SO<sub>2</sub> effects, or a combination of each ([Appendix 5.2.1.3](#)).

New studies since the 2008 ISA have also added new information about acidifying deposition on forest understory vegetation, grasslands, lichen communities, and higher trophic-level organisms (snails and salamanders). These studies are not as numerous as those from the decades of tree research; however, results of these studies support the conclusions of the 2008 ISA regarding the effects of acid deposition on terrestrial ecosystems.

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## 5.7.2 Biodiversity

Consistent with the findings of the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between acidifying N and S deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.** The physiological effects of acidifying deposition can result in changes in species composition and biodiversity whereby sensitive species are replaced by more tolerant species. For example, sugar maple was found to have greater growth and seedling colonization with increasing soil cation availability, and American beech was more prevalent on soils with lower levels of base cations—locations where sugar maple does less well ([Appendix 5.2.1.3.1](#)). As noted above, studies have found increased regeneration of sugar maple with Ca additions and less regeneration with increasing exchangeable Al. Soil acid-base chemistry was found to be a predictor of understory species composition. Fifty understory species were associated with the basic end of a soil pH gradient, and these species could have value as indicators of sites with high base cation status and potentially suitable habitat for acid-sensitive species like sugar maple. In another set of studies, soil acid-base chemistry predicted and was correlated with soil biota diversity and community composition. Proportions of soil bacteria, fungi, and nematodes were found to be correlated to soil pH and Al concentrations. Fungi and nematodes were more abundant in acidic soils. Ca additions resulted in a change in soil bacterial community composition, and the bacterial community structure was found to be significantly correlated with soil exchangeable Ca, pH, and P ([Appendix 5.2.4](#)).

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## 5.7.3 National-Scale Sensitivity and Critical Loads

Sensitivity of soils to acidifying deposition is discussed in detail in [Appendix 4](#) and summarized in [Section IS.5.1](#). In general, surficial geology is the principal factor governing the sensitivity of terrestrial ecosystems soil to acidification from S and N deposition. Other factors contribute to the sensitivity of soils to acidifying deposition, including topography, soil chemistry, and land use. Forests of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and mountain top and ridge forest ecosystems in the southern Appalachians are the regions most sensitive to terrestrial acidification from atmospheric deposition (Section 3.2.4.2 of the 2008 ISA). Sensitive ecosystems can also be characterized by presence of acid-sensitive soils and plant species ([Appendix 5.3](#)).

Models used to determine critical loads of acidifying deposition included: SMB, STA, MAGIC, ForSAFE-VEG, and empirical models. Several models and extrapolation methods to estimate BCw rates were also investigated. The PROFILE model was

evaluated as a model to estimate soil BCw rates to support estimates of SMB critical loads in the U.S. In general, recently published models used soil solution Bc:Al of 10.0 as an indicator to estimate critical loads in North America. These models are described in more detail in [Appendix 4.5](#).

Sensitivities of ecosystems to ambient N and S deposition were also characterized through critical loads and exceedances ([Appendix 5.5](#)). Calculated critical loads for forest sites based on the soil solution Bc:Al of 10.0 in the northeastern U.S. ranged from 11 to 6,540 eq/ha/yr (eq quantifies the supply of H<sup>+</sup> ions available for acid-base reaction, allowing the acidifying effects of N and S deposition to be combined into the same unit), and 15–98% of these critical loads were exceeded by N and S deposition. In this region, correlation analyses showed that the growth of 17 species and crown density of 4 species were negatively correlated with critical load exceedance. In Pennsylvania, critical loads based on the soil solution Bc:Al of 10.0 for hardwood forests ranged from 4 to 10,503 eq/ha/yr and were exceeded by the 2002 N and S deposition in 53% of the plots. In comparison, critical loads for terrestrial ecosystems in the arctic and subarctic regions of North America were not exceeded by estimated deposition in the years 1900, 2000, 2010, and 2020. For these high latitude ecosystems, the lowest critical load was 130 eq/ha/yr, while the maximum N and S deposition was 30 to 40 eq/ha/yr.

In western Canada, critical loads ranged from 40 to 4,000 eq/ha/yr depending on the study and location. Several studies evaluated the influence of BCw rates, soil chemical indicators and thresholds, N retention, tree species-specific base cation uptake, and/or bulk (i.e., wet) versus total deposition on critical load estimates. All of these parameters were found to influence critical load and exceedance determinations, thereby demonstrating the uncertainties and sensitivities associated with critical load estimates.

**Table 5-6 Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Bardhan et al. (2012)</a>	Forest Great Smoky Mountain National Park, TN, NC	Soil microbes (bacteria)	6 to 41 kg S/ha/yr modeled deposition classes ( <a href="#">Weathers et al., 2006</a> )	Soil pH and exchangeable Ca and Al, CEC and base saturation (O-, A-, and B-horizons)	Only minor differences in bacterial diversity among sites; the bacterial community did not change along the gradients of S deposition, soil pH, or exchangeable Ca:Al ratio. High elevation sites remain acidic and have not yet reached a threshold suitable for nonacidophilic bacterial communities.
<a href="#">Beier et al. (2012)</a>	Forest Adirondack Mountains, NY (12 upland hardwood forests)	NA	14.57 to 19.7 kg/ha/yr as wet NO <sub>3</sub> <sup>-</sup> ; 17.44 to 29.09 kg/ha/yr as wet SO <sub>4</sub> <sup>2-</sup> ; modeled ( <a href="#">Ito et al., 2002</a> ) 1990–1999	Exchangeable Ca and pH (Oa- and B-horizons)	Increasing trends in snail community richness and abundance, live biomass of red-backed salamanders, and canopy tree basal area with increasing soil Ca. Land snail species richness and abundance were positively correlated with Oa-horizon Ca and negatively correlated to SO <sub>4</sub> <sup>2-</sup> deposition. Salamander communities changed continuously along the Ca gradient. Several known calciphilic species of snails and plants were found only at the highest Ca sites. The proportion of basal area attributed to standing dead trees decreased significantly with Oa-horizon Ca.
<a href="#">Bilodeau-Gauthier et al. (2011)</a>	Forest Quebec lakes network, Quebec, Canada (6 watersheds)	Sugar maple	NA	Soil pH, base saturation, exchangeable Ca:Al ratio, exchangeable Al, Ca, Mg, Mn, and K (forest floor and 0 to 15 cm of B-horizon)	Tree growth was positively correlated to concentrations of base cations (Ca, K, and Mg) in wood and soil, and negatively correlated to concentrations of acidic metals in wood (Al, Mn, and Cd) and soil (H <sup>+</sup> and exchangeable Al). Percentage base saturation was the best predictor of BAI (nonlinear) and explained 43% of variance. Multifactorial relationships indicated that tree age and soil exchangeable Al accounted for 51% and tree age and log of the ratio of base cations (Ca + Mg + K):Al in the soluble (water and acid soluble wood extracts) fractions accounted for 46% of the variation in sugar maple BAI.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Bondi et al. (2016)</a>	White, Green, and Adirondack Mountains (34 forest sites)	Red-backed salamander ( <i>Plethodon cinereus</i> )	NA	Soil pH (Oa-horizon—on 16 sites A-horizon). Soil pH range was 2.73–5.54.	Studied the relationships between soil pH (organic horizon) and the abundance and health of red-backed salamanders. No associations between soil pH and salamander metrics (abundance, body size, and body condition) were found, and the salamanders did not appear to select habitats based on soil pH. The strongest driver of the abundance of red-backed salamanders was the presence of dusky salamanders ( <i>Desmognathus</i> spp.).
<a href="#">Cai et al. (2017a)</a>	Semiarid grassland Inner Mongolia, China	Grasses ( <i>Agropyron cristatum</i> , <i>Stipa krylovii</i> ), forbs ( <i>Artemisia frigida</i> , <i>Potentilla tanacetifolia</i> , <i>Potentilla bifurca</i> )	0, 5, 10, and 15 g N/m <sup>2</sup> /yr and two water addition treatments	Soil pH and Al plant tissue Zn, Cu, Mn, and Fe concentrations	N additions resulted in decreased pH and increased soil available Fe, Mn, and Cu concentrations, with water additions partially counteracting the impacts of N. Nitrogen additions caused higher foliar Mn, Cu, and Zn and lower Fe concentrations, resulting in micronutrient imbalances. Similar to the soils, water additions partially offset the impacts of the N additions on foliar chemistry.
<a href="#">Chen et al. (2013)</a>	Grassland Mongolian steppe, China	Soil microbes (bacteria, fungi, and nematodes)	Seven treatments of S additions as sulfuric acid (0, 2.76, 5.52, 8.28, 11.04, 13.8, and 16.56 mol H <sup>+</sup> /m <sup>2</sup> ) as three additions (2009–2010)	Soil pH and extractable cations (Al, Ca, Mg, and NA; 0 to 15 cm)	Fungal fatty acids were increased by 49% and fungi:bacteria ratio increased by up to 120% by the H <sub>2</sub> SO <sub>4</sub> additions, relative to the controls. The H <sub>2</sub> SO <sub>4</sub> treatments decreased total and bacterial fatty acids by up to 47 and 40%, respectively. These responses were attributed to soil pH and Al <sup>3+</sup> concentrations. High Al <sup>3+</sup> concentrations (51 to 83 mg/kg) were associated with decreased total fatty acids and decreases in bacterial and increases in fungal fatty acids. Soil nematode numbers were initially increased by the H <sub>2</sub> SO <sub>4</sub> treatments followed by changes in the nematode community. The shifts in the nematode community were attributed to decreased soil pH and changes in soil moisture.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Chen et al. (2016)</a>	Alpine grasslands and global terrestrial biomes	Soil microbes (bacteria, fungi)	NA	Soil pH	Studied the relative importance of site, biotic, and climatic factors on soil microbial communities in two alpine grasslands in the Tibetan Plateau and across global terrestrial biomes. Microbial communities were characterized by phospholipid fatty acid (PFLA) and grouped as total microbial biomass, fungal biomass, arbuscular mycorrhizal fungi biomass, actinomycete biomass, and fungal:bacterial ratio. In the Tibetan grasslands, all measures of soil microbial communities were found to be negatively related to soil pH (soil pH ranged from ~6–10) and positively correlated with soil C:N ratio (C:N ratio range of 4–15). The fungal:bacterial ratio showed a positive relationship with pH at soil pHs that ranged from 7.5–10, and negative relationship with soil C:N. Across the global biomes, total microbial biomass was also found to be positively correlated with soil C:N and negatively correlated with soil pH. Soil variables (alone) accounted for 43.4% of the variation in total microbial biomass, while climatic and biotic variables (alone) only accounted for 4.5 and 0.2% of variation, respectively.
<a href="#">Cleavitt et al. (2014)</a>	Forest Hubbard Brook Experimental Forest, NH	Sugar maple	NA	Exchangeable Ca (top 5 cm of B-horizon)	Soil Ca concentration exhibited a 9x change across the study sites and was positively correlated to sugar maple abundance and initial seedling densities. However, soil Ca concentration was not a significant predictor of 1st-year mortality, nor was it a factor that distinguished among the three main site types.
<a href="#">Duchesne and Ouimet (2009)</a>	Forest Southern Quebec, Canada (426 monitoring plots)	Sugar maple and American beech	NA	Soil pH, exchangeable K, Ca, Mg, H, and Al (upper B-horizon)	The basal area of sugar maple in the sapling stratum was positively correlated with soil exchangeable Ca and Mg. Basal area of American beech in the sapling stratum was negatively correlated with exchangeable Ca and Mg. However, the basal area of sugar maple in the sapling stratum was positively correlated with both the relative basal area of dead sugar maple and sugar maple in the tree stratum. The basal area of American beech was also positively correlated with the relative basal area of American beech in the tree stratum.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Elias et al. (2009)</a>	Forest Monongahela National Forest, WV (FIA plots)	Hardwood and conifer tree species	NA	Soil pH, base saturation, exchangeable Ca:Al (A- and B-horizons)	The study authors found that hickories were the only species to be in significantly lower numbers on sites with base saturation below 20 (A-horizon) and 2.5% (B-horizon). Percentage of dead northern red oak was highest on sites with A-horizon Al concentrations above 43 cmol <sub>e</sub> /kg of soil. Soil exchangeable Ca:Al and sum of base cations in the B-horizon were highest in stands that experienced the lowest species turnover rates (1989–2000). Periodic mean annual volume increment (whole stand) was positively correlated with A-horizon base saturation (range of 5 to 77%), Ca concentrations, and exchangeable Ca:Al (range of 0.17 to 10.2) and B-horizon pH. The exchangeable Ca:Al of the A-horizon accounted for over 30% of the variation in the periodic mean annual volume increment.
<a href="#">Gilliam et al. (2011b)</a>	Forest Fernow Experimental Forest, WV	Soil microbes (bacteria and fungi)	NA	Soil pH (5 cm)	Fungi were dominant at the most weathered, low NO <sub>3</sub> <sup>-</sup> site, while Gram-negative bacteria were significantly higher at the less weathered, moderate and high NO <sub>3</sub> <sup>-</sup> sites. Accordingly, the fungi:bacteria ratio increased in the direction of the low NO <sub>3</sub> <sup>-</sup> plots in ordination space. Correlations between the soil parameters and PLFA results suggest that low soil pH and NO <sub>3</sub> <sup>-</sup> concentrations supported fungal dominance, although other factors including differences in plant community and clay and organic matter content may have also influenced the soil microbial community.
<a href="#">Horsley et al. (2008)</a>	Forest Pennsylvania, New York, New Hampshire, and Vermont (86 northern hardwood stands)	234 forest understory species	NA		The study authors found that a base cation-acid cation nutrient gradient accounted for 71.9% (in NH and VT) and 63% (in PA and NY) of the variation in the nonmetric multidimensional scaling ordination analyses of plant community composition. Sugar maple foliar Mg and Ca had the strongest association with the base end of the gradient. Exchangeable Al (in NH and VT) and foliar Mn (in PA and NY) were strongly associated with the acid end of the gradient. A total of 50 of the 234 understory species were associated with the base end of the base cation-acid cation nutrient gradient.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Huang et al. (2017)</a>	Forest Eastern China	Soil microbes (Archaeal diversity)	NA	Soil pH and Al concentrations	Studied influence of Al additions on the archaeal diversity in red soils. Three Al treatments of 0, 100, or 200 mg Al/kg soil (as AlCl <sub>3</sub> ·6H <sub>2</sub> O); pH maintained at pretreatment level. Al additions were found to increase the abundance but decrease the evenness of the Archaea. Abundances of Crenarchaeota increased while those of Euryarchaeota decreased in response to higher Al concentrations, suggesting that Crenarchaeota is more tolerant of Al than is Euryarchaeota
<a href="#">Kunito et al. (2016)</a>	Forest Japan (27 sites)	Soil microbes	NA	pH and Al (soluble and exchangeable) concentrations in 0–15 cm of soil	Evaluated the relationship between soil chemistry (Al concentrations and pH) and soil microbial biomass and enzymes involved with C, N, and P cycling ( $\beta$ -D-glucosidase, polyphenol oxidase, L-asparaginase, acid phosphatase). The researchers found that $\beta$ -D-glucosidase and polyphenol oxidase were reduced with higher amounts of soluble and exchangeable Al, acid phosphatase shared an inverse relationship with soil pH, and L-asparaginase increased as pH increased. Microbial biomass was also found to decrease as organically bound Al and Fe increased.
<a href="#">Li et al. (2016a)</a>	Natural steppe ecosystem Inner Mongolia, China	Soil microbes (bacteria)	<u>Elevated N</u> 5–15 g N/m <sup>2</sup> /yr as urea applied in May and June since 2005	Soil pH (0–15 cm)	Evaluated: (1) the impacts of N and water additions on soil microbial community (0–15 cm of soil), (2) the linkages between the variation in belowground bacterial community and aboveground vegetation community, and (3) relationships between soil/plant factors and soil microbial community. In general, bacterial alpha diversity was positively correlated with total N and pH and negatively correlated with soil C:N ratio and concentrations of NH <sub>4</sub> and NO <sub>3</sub> . Beta diversity of the bacterial community was significantly correlated with C/N ratio, inorganic N, and pH. The relative abundances of Proteobacteria, Firmicutes, TM7, and OD1 increased with N addition gradient. The relative abundances of Proteobacteria Firmicutes, TM7, and OD1 were positively correlated with inorganic N and negatively correlated with soil pH.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Long et al. (2009)</a>	Forest Pennsylvania, New York, New Hampshire, and Vermont (76 sites)	Sugar maple and black cherry	NA	Soil Ca:Al (threshold of 0.03; upper B-horizon)	Exchangeable Ca, Mg, and pH in upper B-horizon were positively correlated with sugar maple BAI growth in 1987–1996. Generally, in long-term trends (1937–1996), sugar maple in stands with below-threshold amounts of foliar Ca or Mg and above-threshold amounts of Mn had decreasing BAI trends, while stands with above-threshold Ca and Mg and below-threshold Mn showed a leveling off of the BAI. Black cherry consistently showed greater growth on stands with below-threshold foliar Ca and Mg compared with above-threshold stands. Black cherry BAI was also greater in stands with below-threshold Ca:Al molar ratios in the upper B-horizon.
<a href="#">Lucash et al. (2012)</a>	Forest 19 sites in northeastern U.S. (New York and New Hampshire)	Hardwood and conifer tree species	NA	Exchangeable Ca, Mg, and Al (Oie, Oa 0 to 10 cm, 10 to 30 cm, and 30 cm to top of C-horizon)	Concentrations of Ca and Mg in foliage were correlated with exchangeable Ca and Mg concentrations in the upper mineral soil; for most tree species they were also correlated to acid-extractable Ca and Mg in the parent material (C-horizon). Foliar Al was insensitive to soil Al concentrations.
<a href="#">Medeiros et al. (2016)</a>	Greenhouse study	Red maple and white oak	N and P treatments (control and low N/P—90% of control N/P levels), pH (4.5 and 6)	pH	Studied the influence of pH (simulated acid rain) on leaf, xylem, and hydraulic trait coordination responses of 1-yr-old red maple and white oak seedlings in a greenhouse study. The researchers found interactions between nutrient levels and pH; low pH reduced the ability of both species to adjust xylem traits and leaf water relations (i.e., hydraulic acclimation) in response to changes in nutrient availability.
<a href="#">McEathron et al. (2013)</a>	Forest Ha-De-Ron-Dah Wilderness Area in Adirondack Mountains, NY (seven subwatersheds)	Sugar maple, black cherry, American beech, red maple, and yellow birch	NA	Soil pH and exchangeable Ca and Al (0 to 10 cm mineral soil horizon)	Evaluated the relationships between species-specific basal area and soil and stream water chemistry. Sugar maple basal area was positively correlated with mineral soil pH, and yellow birch basal area was positively correlated with mineral soil exchangeable Ca. Sugar maple basal area was also negatively correlated with stream water DOC.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Mueller et al. (2016)</a>	Sugar maple dominated forests Michigan	Soil microbes	NA	Soil pH	Studied the relationships between soil bacterial and fungal community activity and soil pH and C:N gradients in the litter from sugar maple stands in Michigan. The proportion of active bacteria were found to increase along the soil pH gradient, but decreased along the soil C:N gradient. In contrast, no significant correlations were detected for the fungal community. Similarly, no significant correlations were between temperature and the fungal or bacterial communities.
<a href="#">Pabian and Brittingham (2012)</a>	Forest Pennsylvania (14 forest sites)	NA	NA	Exchangeable Ca and pH (Oa-horizon). Mean soil exchangeable Ca and pH for the 14 study sites ranged from 5.28 to 23.5 meq/100 g and 3.6 to 5.1, respectively.	Bird community composition (species richness and species abundances) varied with soil Ca and pH, with 10 bird species having the highest abundances in forests with high-Ca soils, and 5 species having the highest abundances with low-Ca soils. Bird species associated with low-Ca soils were associated with high densities of acid-loving mountain laurel ( <i>Kalmia latifolia</i> ) and five tree species with basal area explained by low soil pH and Ca, whereas bird species associated with high-Ca soils were associated with high densities of saplings and high basal area of acid-sensitive tree species.
<a href="#">Page and Mitchell (2008)</a>	Forest Adirondack Mountains, NY (11 sites)	Sugar maple, American beech, American basswood, and white ash	NA	Exchangeable Ca, exchangeable Ca:Al (forest floor and upper [0 to 10 cm] mineral soil)	Evaluated the relationships between exchangeable soil Ca concentrations and tree basal area. There were no observed trends relating total basal area to mineral soil (0 to 10 cm) exchangeable Ca concentrations; however, the relative basal areas of sugar maple and American basswood were positively correlated with mineral soil exchangeable Ca, and relative basal area of American beech was negatively correlated. Relative basal area of white ash was not correlated to soil exchangeable Ca.
<a href="#">Perakis et al. (2013)</a>	Forest Oregon (coastal range)	Douglas fir (plantations)	NA	None	Nitrate leaching (at 20 and 100 cm) increased, soil pH declined (from 5.8 to 4.2), and exchangeable soil Ca, Mg, and K decreased (10x declines) along the soil N gradient. Exchangeable Ca and Mg (in both 0 to 20 cm and 0 to 100 cm) and K (0 to 20 cm) declined with increasing nitrate leaching. Mean soil profile pH declined logarithmically with nitrate leaching at 20 and 100 cm. The sum of exchangeable Ca, Mg, and K was positively correlated with soil pH at 20 and 100 cm. Aboveground tree biomass contained an increasing percentage of total ecosystem Ca, Mg, and K as soil N increased.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Pitel and Yanai (2014)</a>	Forest Massachusetts, Vermont, and New York	Sugar maple	NA	Soil pH, exchangeable Ca:Al, Al, and cations (Ca, Mg, K), cation (Ca, Mg, K, and total) saturation, and effective CEC (A- and upper B-horizons)	Evaluated the mortality of dominant and codominant sugar maple in 47 stands that had experienced defoliation by native forest tent caterpillar ( <i>Malacosoma disstria</i> ). Mortality was found to be highest in stands with the greatest amount of crown dieback the previous year. Drought, cold winter temperatures, concave microrelief and soil base cation availability were also significant predictors of mortality. Concentrations of exchangeable Ca, Mg, and K in the upper B soil horizon were inversely correlated with sugar maple mortality, with exchangeable K having the strongest relationship with mortality. Site with above-average sugar maple mortality (>3 or 4%) occurred on soils with low concentrations of exchangeable Ca (0.31 to 0.46 cmol <sub>e</sub> /kg), Mg (0.06 to 0.10 cmol <sub>e</sub> /kg), and K (0.03 to 0.05 cmol <sub>e</sub> /kg). Stands defoliated in 2005 that had low Mg saturation (A-horizon) suffered higher rates of mortality, suggesting an interaction between low base cations and defoliation events.
<a href="#">Sridevi et al. (2012)</a>	Forest Hubbard Brook Experimental Forest, NH	Soil microbes (bacteria)	NA	Soil pH, exchangeable cations, Al, Fe, P, Mn, Zn, exchangeable acidity, and CEC (0 to 15 cm)	Ca additions of 1,000 kg Ca/ha applied in 1999. The bacterial community structure in the Ca treated and nontreated reference soils was found to be significantly different, with differences among communities being more pronounced in the mineral soils. Calcium additions resulted in a change in bacterial community composition of 23% in the organic and 22% in the mineral soil horizons. Numbers of detectable taxa in some families were lower in the Ca amended soils, while some families were higher. Analyses of relationships between soil chemistry and the bacterial communities indicated that only Ca, pH, and P were significantly correlated with bacterial community structure.
<a href="#">Stevens et al. (2010b)</a>	Grassland U.K. (68 sites)	Grassland species	6.2 to 36.3 kg N/ha/yr Centre for Ecology and Hydrology (CEH) National Atmospheric Deposition Model	Ellenberg R (reaction-soil pH) and N (soil nutrient) scores	Data from a national survey were used to evaluate species richness of 68 U.K. grasslands along an N deposition gradient. The results suggest that soil acidification (instead of eutrophication) was contributing to changes in species diversity and composition. Soil acidification may have led to reduced nutrient availability and increased Al solubility preventing the “fertilizing” effects of N addition from being apparent.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Sullivan et al. (2013)</a>	Forest Adirondack Mountains, NY (50 plots in 20 small watersheds with sugar maple overstory)	Sugar maple	75 to 112 meq/m <sup>2</sup> /yr as N + S NADP (wet deposition); CASTNET (dry deposition) 2000–2004 (average)	Soil pH, exchangeable Ca, exchangeable Mg, and base saturation (forest floor, A- and upper B- (0 to 10 cm) horizons)	The study found that plots with lower soil base saturation did not have sugar maple regeneration (these same plots also received higher N and S deposition levels); proportion of sugar maple seedlings dropped substantially at base saturation levels less than 20%. Canopy vigor was positively correlated with soil pH and exchangeable Ca and Mg. Mean growth rates (BAI) were positively correlated with exchangeable Ca and base saturation at the watershed level.
<a href="#">Tian et al. (2016b)</a>	Temperate steppe Inner Mongolia, China	Grassland species; <i>Stipa krylovii</i> and <i>Artemisia frigida</i>	<u>Elevated N</u> 9 yr of urea additions at 0, 1, 2, 4, 8, 16, 32, and 64 g N/m <sup>2</sup> /yr	Soil pH, exchangeable Mn and Al (three soil depths: 0–10, 10–20, 20–30 cm)	Long-term N additions increased total above-ground plant biomass but decreased species richness; N additions significantly reduced forb species richness, while the diversity of grass species was not affected. Soil chemistry was influenced by the N additions; soil pH was reduced and concentrations of exchangeable Mn, ferric Fe, and Al were increased. Foliar concentrations of Mn in both <i>A. frigida</i> and <i>S. krylovii</i> were increased by N additions. A greenhouse study showed that the biomass of <i>A. frigida</i> seedling shoots and roots were significantly reduced with MnCl <sub>2</sub> additions, but the treatments had no effect on <i>S. krylovii</i> seedlings.
<a href="#">Tu et al. (2016)</a>	Forest types across North America	Soil diazotrophs (N <sup>2</sup> fixing microbes)	NA	Soil pH (0–10 cm)	The soil diazotrophic community structure was found to differ significantly across the six forests; lower microbial spatial turnover and greater community diversity were found in rainforests relative to temperate forests. In addition, community diversity was strongly correlated with latitude, mean annual temperature, plant species richness, and total annual precipitation. Diazotrophic community diversity was weakly correlated with soil pH and moisture.
<a href="#">Ying et al. (2017)</a>	Grassland Inner Mongolia, China	Soil microbes (ammonia-oxidizing bacteria and Archaea)	<u>Elevated S</u> H <sub>2</sub> SO <sub>4</sub> additions started in 2009; 0, 2.76, 5.52, 8.28, 11.04, 13.80, 16.56 mol H/m <sup>2</sup>	Soil pH and NH <sub>4</sub> <sup>+</sup> -N and NO <sub>3</sub> <sup>-</sup> -N	Study evaluated the impacts of soil pH on the abundance and structure of soil ammonia-oxidizing bacteria (AOB) and Archaea (AOA) communities. Decreasing soil pH was found to be correlated with decreases in AOB abundance (pH range of 5.0–7.3) and increases in AOA (pH range of 5.3–7.3) abundance, except at the lowest pH (pH 5.0), which negatively influenced AOA abundance. Soil acidification did not significantly influence AOA or AOB community composition.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Yuan et al. (2016)</a>	Alpine tundra Niwoot Ridge, Colorado Rocky Mountain National Park	Soil bacteria	<u>Elevated N</u> 20 yr of N and P additions—0 and 20 g N/m <sup>2</sup> /yr and 0 and 2 g P/m <sup>2</sup> /yr (1993–1995), 0 and 10 g N/m <sup>2</sup> /yr and 2 g P/m <sup>2</sup> /yr (1996–1997), same application rates every 2 yr (1998–2009), 10 g N/m <sup>2</sup> /yr was added as Ca(NO <sub>3</sub> ) <sub>2</sub> to address soil acidification	Soil pH (0–10 cm)	Soil bacterial communities differed by plant community type, with bacterial alpha diversity being significantly correlated with plant richness and production of forbs. N additions also influenced soil bacteria, with bacterial communities treated with N (and N + P) being significantly different than those in the control and P treatments. Chloroflexi and Bacteroidetes responded positively to the additions of N, while Acidobacteria and Verrucomicrobia responded negatively to N. The N additions resulted in reduced soil pH; from wet to dry systems, the relative importance of N additions on soil pH increased. Of the soil variables, pH shared the strongest correlations with plant and bacterial diversity metrics. Structural equation modeling showed that the indirect effects (as opposed to direct effects) of N additions—changes in soil pH and plant communities—were the strongest determinants of soil bacterial community responses.
<a href="#">Zeng et al. (2016)</a>	Temperate steppe Inner Mongolia, China	Soil microbial communities	<u>Elevated N</u> 6 yr of NH <sub>4</sub> NO <sub>3</sub> additions at 0, 60, 120 and 240 kg N/ha/yr	Soil pH (0–10 cm and 10–20 cm)	Plant community biomass was found to significantly increase, species richness decrease, and N concentrations increase with N additions. Seven bacterial phyla (mainly rare phyla) in the 0–10-cm soil depth were significantly changed with N additions, while only 1 phylum in the 10–20-cm depth was affected by the additions of N. Hierarchical structural equation modeling revealed that changes in bacterial community composition were due to changes in soil pH and plant composition, while shifts in bacterial richness were attributed to NH <sub>4</sub> <sup>+</sup> concentrations.

**Table 5-6 (Continued): Mode of action for acidifying nitrogen and sulfur deposition.**

Reference	Ecosystem Type/Region	Species	N and S Deposition/ Additions	Soil Indicator	Description
<a href="#">Zhang et al. (2016b)</a>	Temperate steppe Inner Mongolia, China	57 vascular plant species	<u>Elevated N</u> 6 yr of NH <sub>4</sub> NO <sub>3</sub> additions at 0, 1, 2, 3, 5, 10, 15, 20, and 50 g N/m <sup>2</sup> /yr (2x and 12x per year)	Soil pH (0–10 cm)	N additions, at both frequencies, significantly decreased the number of new species gained and increased the number of old species lost. However, the number of new species gained was lower on the low frequency of N addition plots compared to the high frequency, while the number of old species lost was not affected by N addition frequencies. There was a negative correlation between the cumulative gain of new species and soil pH, NH <sub>4</sub> concentrations and community biomass accumulation, while cumulative loss of old species was positively correlated with these variables.
<a href="#">Basto et al. (2015b)</a>	Grassland Peak District National Park, U.K.	261 grassland species; seed bank	NA	Soil pH (gradient with soil pH range of 3.5 to 6.5)	Studied seed bank and seed germination, viability, and damage (through seed burial experiment conducted with <i>Scabiosa columbaria</i> , <i>Hypericum pulchrum</i> , and <i>Campanula rotundifolia</i> ) along a natural pH gradient from acidic to calcareous grasslands. Increasing soil pH was found to be correlated with decreases in total and grass seed abundance, declines in the persistence of <i>H. pulchrum</i> seed, and declines in damage to <i>C. rotundifolia</i> seed. Seed germination was not influenced by pH. In soil with pH higher than 5.6, indirect effects of pH (through increased fungal pathogens) appeared to decrease the persistence of the seed of all three grassland species. This study suggested that: acidic soils are associated with increased seed persistence; the longevity and size of grassland seed banks decline as soil pH increases; and that pH indirectly influences seed persistence.

Al = aluminum; BAI = basal area increment; Ca = calcium; CASTNET = Clean Air Status and Trends Network; Cd = cadmium; CEC = cation exchange capacity; CEH = Centre for Ecology and Hydrology; cm = centimeter; DOC = dissolved organic compound; Fe = iron; FIA = Forest Inventory and Analysis; g = grams; H<sup>+</sup> = hydrogen; ha = hectare; K = potassium; kg = kilograms; m = meter; meq = milliequivalent; mg = milligrams; Mg = magnesium; Mn = manganese; mol = mole; N = nitrogen; NA = not applicable; NADP = National Acid Deposition Program; P = phosphorus; PLFA = phospholipid fatty acid; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year; Zn = zinc.

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## APPENDIX 6 TERRESTRIAL ECOSYSTEMS: NITROGEN ENRICHMENT EFFECTS ON ECOLOGICAL PROCESSES

[Appendix 5](#) examined the biological effects of terrestrial acidification from nitrogen (N) and sulfur (S) deposition. This appendix characterizes the biological effects of terrestrial N enrichment that can be caused by atmospheric N deposition. Following an introduction ([Appendix 6.1](#)), this appendix is composed of five major sections: effects on physiology, growth, and productivity ([Appendix 6.2](#)); changes in biodiversity and community composition ([Appendix 6.3](#)); climate modifications of N enrichment effects ([Appendix 6.4](#)); critical loads ([Appendix 6.5](#)); and a summary ([Appendix 6.6](#)). The first two sections begin with an introduction ([Appendix 6.2.1](#) and [Appendix 6.3.1](#)) reviewing the previous causal determination and presenting the current causal determination. Following this introduction, an overview is presented of the mechanisms operating across ecosystems to link N enrichment to biological change ([Appendix 6.2.2](#) and [Appendix 6.3.2](#)). [Appendix 6.2](#), [Appendix 6.3](#), and [Appendix 6.5](#) are further divided into subsections based on ecosystem type (e.g., forests, grasslands, etc.) or functional group (e.g., lichens, trees, herbaceous plants). Finally, [Appendix 6.6](#) provides a summary of the new information generated since the *2008 ISA for Oxides of Nitrogen and Sulfur—Ecological Criteria* (hereafter referred to as the “2008 ISA”).

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### 6.1 Introduction

Nitrogen (N) is a key element required by all organisms in order to build amino acids and nucleic acids, the basic biochemical subunits needed to synthesize the proteins, enzymes, RNA, and DNA sustaining all biological processes. By the second half of the 19th century, before these biochemical pathways had been identified, it was already understood that N was a component of plant and animal tissues and a supply of N was essential for plant growth ([Galloway et al., 2004](#)). Indeed, the ability of added N to stimulate plant growth had been recognized by science (and commerce) for over a century ([Galloway et al., 2004](#); [Galloway and Cowling, 2002](#)) prior to the 2008 ISA. By 2008, it was already clear that N availability broadly limited productivity in terrestrial ecosystems.

By 2008, it was also clear N availability could alter the biodiversity of terrestrial ecosystems. Broadly, the effects of N deposition on the diversity of terrestrial ecosystems stem from four mechanisms [*sensu* [Bobbink et al. \(2010\)](#)]: (1) eutrophication, (2) acidification, (3) direct toxicity and damage, and (4) increased susceptibility to

secondary stress. Multiple mechanisms likely operate simultaneously to alter diversity within a particular community or ecosystem. As described in [Appendix 5](#), N deposition may lead to soil acidification, which can have negative effects on plants and microorganisms. Direct toxicity and damage from N deposition often come from an accumulation of  $\text{NH}_4^+$  in soils and plant tissues. Increased susceptibility to secondary stressors includes greater impacts of pathogens ([Bobbink et al., 2010](#)) and shifts in herbivory as a result of altered tissue chemistry ([Throop and Lerdau, 2004](#)). Among these four major mechanisms, eutrophication is perhaps the most complex because it can change the physiology of individual organisms, alter the relative growth and abundance of species, transform relationships between species, and indirectly affect the availability of other essential resources such as light, water, and nutrients [[Suding et al. \(2005\)](#); [Clark et al. \(2007\)](#); [Hautier et al. \(2009\)](#); see also [Appendix 4](#)]. These can lead to biodiversity shifts, including community compositional changes, the loss of species, and decline in species richness.

Since the 2008 ISA, the effects of N deposition on terrestrial ecological processes and biodiversity have continued to be widely studied. With the increasing volume of research, a number of new studies have been conducted using meta-analysis to synthesize published observations or using continental or global data sets to understand broad-scale patterns. New studies have provided a more detailed understanding of how N influences terrestrial ecosystem growth and productivity; community composition and biodiversity; and sensitive organisms and ecosystems. Further, a large body of work has been published on critical loads (CLs) for N since 2008. Together with the information available in the 2008 ISA, **this body of evidence is sufficient to infer a causal relationship between N deposition and (1) the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems; and (2) the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.**

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## 6.2 Linking Nitrogen Deposition to Changes in Physiology, Growth, and Productivity in Terrestrial Ecosystems

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### 6.2.1 Introduction

In the 2008 ISA, evidence was sufficient to infer a causal relationship between N deposition and the alteration of the terrestrial carbon (C) and N biogeochemical cycles. These effects included not only changes in soil C and N pools and fluxes (described in

[Appendix 4](#)), but also significant alterations of plant and microbial growth and physiology. The 2008 ISA built upon the conclusions of the 1993 Oxides of Nitrogen Air Quality Criteria Document. By 1993, a series of hypotheses regarding the effects of chronic N deposition on northern temperate forests had already been developed from early field observations ([Aber et al., 1989](#)). Briefly, N deposition was expected to increase tree growth in most forests, but once plant demand for N had been satisfied (biological and physical sinks had reached “N saturation”), further N deposition could lead to nitrification, soil cation leaching, acidification, nutrient deficiencies, and decreased tree growth [[Aber et al. \(1989\)](#)]; described in [Appendix 4](#) and [Appendix 5](#)]. A revised form of these N saturation hypotheses ([Aber et al., 1998](#)) provided much of the conceptual foundation in the 2008 ISA for understanding how N deposition influenced plant physiology, growth, and ecosystem productivity.

The effects of N deposition on terrestrial ecological processes have been widely studied since 2008. Research on N deposition has continued in North America and Europe, with other areas receiving less attention [e.g., temperate forests in Asia and the Southern Hemisphere ([Gilliam, 2016](#))]. A significant new body of research has developed in the boreal, arid, and subtropical ecosystems of Asia, particularly in China [e.g., [Du and Fang \(2014\)](#); [Du et al. \(2014b\)](#); [Du et al. \(2014a\)](#); [Sun et al. \(2014\)](#); [Zhang et al. \(2015e\)](#)]. New meta-analyses have provided a more detailed understanding of how added N affects productivity responses in different biomes ([LeBauer and Treseder, 2008](#)), growth among plant functional types ([Xia and Wan, 2008](#)), growth of individual plant parts ([Xia and Wan, 2008](#)), root growth ([Li et al., 2015](#)), and ecosystem C storage ([Liu and Greaver, 2009](#)), while other broad-scale analyses have examined changes in plant N concentrations ([Xia and Wan, 2008](#)), microbial biomass ([Treseder, 2008](#)), and belowground C cycling ([Liu and Greaver, 2010](#)). This expanded body of research has created a better understanding of how N influences processes at molecular to global scales. Together with the information available in the 2008 ISA, this body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.

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## 6.2.2 Mechanisms Operating across Terrestrial Ecosystems

The 2008 ISA evaluated a large number of studies assessing how N deposition has changed terrestrial C cycling and found an array of ecological responses. The most extensive evidence of the effect of N deposition on C cycling was available for forests in North America and Europe. In experimental N addition studies, moderate to high additions of N led to either no significant change in tree growth rates or transient growth increases (generally at deposition rates lower than 10 kg N/ha/yr), followed by increased

mortality, especially at higher rates of N addition. This group of studies showed coherence in effects and indicated the presence of a biological gradient in responses with increasing N deposition.

Some of the broad-scale changes caused by N additions to terrestrial ecosystems have been quantified by meta-analysis, a data synthesis tool that started to become common in ecological research beginning in the late 1990s ([Gurevitch et al., 2001](#)). Using this tool to understand the effects of N additions on herbaceous plant communities, ([Gough et al., 2000](#)) found that N additions stimulated aboveground plant productivity by an average of 53%. In a broader synthesis, [Elser et al. \(2007\)](#) conducted a meta-analysis of N addition effects on plant community productivity and observed average increases in productivity of 20–30% in grasslands, forests, tundra, and wetlands. In addition to changes in plant growth, [Koricheva et al. \(1998\)](#) identified via meta-analysis that added N could alter the chemistry of plant tissues, including increasing tissue concentrations of N and free amino acids, while decreasing concentrations of starch and C based secondary compounds (important for defense against herbivores), including phenylpropanoid compounds. In a meta-analysis of the belowground effects of N, [Treseder \(2004\)](#) found N additions decreased both the abundance of mycorrhizal fungi and the percentage of plant roots colonized by mycorrhizal fungi. In addition, multiple lines of evidence showed that N deposition increases the performance of insect herbivores, and potentially, insect populations ([Throop and Lerdau, 2004](#)). In a synthesis of 500 observations of the effect of N on litter decomposition rates, [Knorr et al. \(2005\)](#) found that added N stimulated decomposition at sites with low rates of ambient N deposition (<5 kg N/ha/yr), but slowed decomposition at sites with moderate rates of N deposition [5–10 kg N/ha/yr; [Knorr et al. \(2005\)](#)] and that N additions at rates from 2 to 20 times ambient N deposition inhibited decomposition by 8 to 16%.

These changes can cause a cascade of ecological consequences. For instance, the inhibition of decomposition can increase soil C content, but the accumulation of plant litter on the soil surface can inhibit the establishment of some plant species ([Patterson et al., 2012](#); [Cleavitt et al., 2011b](#); [Xiong and Nilsson, 1999](#); [Facelli and Pickett, 1991](#)). In the western U.S., [Fenn et al. \(2003a\)](#) suggested greater plant growth caused by N deposition could increase plant litter accumulation, in turn increasing the susceptibility of forests and other wildlands to severe wildfires. Nitrogen deposition also affects the patterns of C allocation because most of the additional plant growth occurs aboveground. This increases the shoot-to-root ratio, which can be detrimental to plants because of decreased resistance to environmental stressors, such as drought and wind ([Braun et al., 2003](#); [Krupa, 2003](#); [Minnich et al., 1995](#); [Fangmeier et al., 1994](#)). Thus, it was recognized in the 2008 ISA that the effects of N deposition on biological and ecological processes in

terrestrial ecosystems were pervasive, complex, and difficult to fully understand and predict.

Although evidence showed plant productivity responses to N deposition as of the 2008 ISA, the extent to which N increased forest C content in C budget measurements (quantified input and output of C to the ecosystem) was uncertain. A prominently reported estimate of >600 kg C sequestered per kg of N deposited to forests, which was based on a regional gradient technique ([Magnani et al., 2007](#)), was widely criticized. Subsequent reassessments of these data suggested that forest C sequestration was an order of magnitude lower ([Sutton et al., 2008](#)). [Liu and Greaver \(2009\)](#) found in a meta-analysis that N additions ranging from 25.5 to 200 kg N/ha/yr increased forest ecosystem C content (+6%).

In addition, fewer studies had examined the effects of N deposition on the eutrophication of nonforested ecosystems. [Mack et al. \(2004\)](#) examined C and N pools in a long-term N addition experiment at the Arctic Long-Term Ecological Research site near Toolik Lake, AK. Plant growth increased as a result of N additions, but the N additions enhanced decomposition of belowground C pools in deep soil layers more than it increased primary production, leading to a substantial net loss of C from this ecosystem. More broadly, [Liu and Greaver \(2009\)](#) conducted a meta-analysis of 16 observations from nine publications to evaluate the relationship between N addition (16 to 320 kg N/ha/yr) and C sequestration in nonforest ecosystems and did not find a significant effect on net ecosystem exchange (NEE, kg C/ha/yr).

[Xia and Wan \(2008\)](#) identified nearly 1,600 observations of plant biomass growth in response to N additions, excluding agricultural and horticultural species ([Figure 6-1A](#)). Overall, plant biomass increased by 54%, with a larger gain in seeded plants (+55%) than spore plants (+21%; not shown). Among the seeded plants, grasses showed the largest biomass response, followed by trees, forbs, and shrubs. Annual herbs (+92%) showed a stronger response than perennial herbs (+56%). Overall, biomass responses to N increased linearly with mean annual precipitation (MAP). The studies included in the analysis had addition rates ranging from 10 kg N/ha/yr to 1,000 kg N/ha/yr. When the N additions were divided into low (<100 kg N/ha/yr) and high (>100 kg N/ha/yr) groups, there were only a few differences among functional groups. The response of woody species was lower than for herbaceous species at the low addition rate (+25 vs. +51%), but the groups had similar responses at the high N addition rate. Among herbaceous plants, both legumes and nonlegumes had positive responses to low rates of N additions (19 and 23%, respectively), while the high rate of N additions increased nonlegume biomass (+43%) but did not significantly affect legume growth. The authors also examined how these responses varied in response to the rate of N additions. The N

addition studies were divided into 50 kg N/ha/yr increments from 0 to 300 kg N/ha/yr, but aside from increasingly positive growth responses for trees and woody plants with greater N additions, there were few apparent trends, and sample sizes were inconsistent.

In their analysis, [Xia and Wan \(2008\)](#) separated plant growth data into aboveground (887 observations) and belowground (340 observations) components. Across almost all functional groups, there were greater increases in biomass in aboveground than belowground components ([Figure 6-1A](#); see also [Appendix 4](#)). In a subsequent meta-analysis of plant C pools, [Lu et al. \(2011b\)](#) also found that N additions to plants in nonagricultural systems stimulated shoot C by 28.5% (n = 146) and root C by 20% (n = 77). These results indirectly suggest that plant C allocation changes in response to N addition. These changes were also shown by a more direct analysis of a much smaller meta-analysis data set (n = 15) in which [Li et al. \(2015\)](#) observed a significant 11% decrease in the root:shoot biomass ratio. Together, these results provide further support to the conclusion in the 2008 ISA that N additions can alter plant C allocation and result in elevated shoot:root ratios. Further, [Lu et al. \(2011b\)](#) analyzed the response of some individual plant parts to added N and observed a 1.6% increase in leaf C mass.

Belowground processes are important components of terrestrial ecosystems. As detailed in [Appendix 5](#), soils are often the largest ecosystem pools of both C and N; soil respiration can be the largest ecosystem efflux of CO<sub>2</sub>; and soils can be important sources and sinks for the greenhouse gases N<sub>2</sub>O and CH<sub>4</sub>. Biologically, the large C fluxes plants allocate belowground for root exudation, the growth and maintenance of roots, and the support of mycorrhizal fungi help support complex belowground food webs. Less information is available about belowground responses to N additions than aboveground responses. However, [Li et al. \(2015\)](#) recently conducted a meta-analysis of how root traits respond to N additions. Notably, [Li et al. \(2015\)](#) found that although total root biomass increased (+20%; n = 74), fine root biomass declined (-13%; [Figure 6-2B](#)). This discrepancy is apparently accounted for by an increase in the biomass of coarse roots (+57%; n = 7), which are typically structural and conductive tissues. Morphological traits of fine roots, such as length (n = 25), diameter (n = 10), and specific root length (n = 22), were unaffected by N additions. Fine root turnover rate was 21% higher (n = 12), but fine root production was not significantly affected by the N additions [n = 22; [Li et al. \(2015\)](#)].

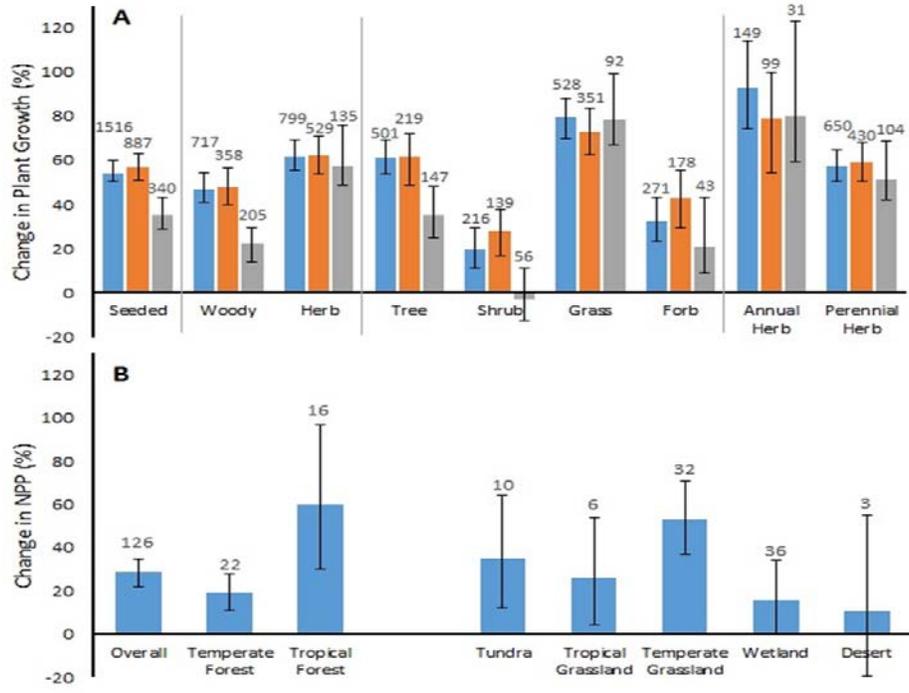
Aboveground net primary productivity (NPP), which measures aboveground plant growth at the community scale, was less responsive on average (+29%) than individual plant growth to N additions [[LeBauer and Treseder \(2008\)](#); [Figure 6-1B](#) and [Figure 6-2A](#)]. Consistent with the plant functional group analysis conducted by [Xia and Wan \(2008\)](#), [LeBauer and Treseder \(2008\)](#) observed a large stimulation of aboveground NPP in

grass-dominated ecosystems such as temperate grasslands (+53%), tropical grasslands (+26%), and tundra (+35%), whereas NPP increased only 19% in temperate forests. There were also significant NPP increases in tropical forests and wetlands. Added N did not significantly increase NPP in deserts, but the analysis only included three observations.

More recently, [Tian et al. \(2016a\)](#) synthesized aboveground NPP data from studies that had experimentally added N at more than one rate in order to examine how plant growth responses per unit N changed with increasing levels of N. Their metric, termed “N response efficiency” [ $100 \times (\text{ANPP}_{\text{treatment}} - \text{ANPP}_{\text{control}}) / \text{ANPP}_{\text{control}} / \text{N addition rate}$ ] did not significantly differ across the three ecosystem types (wetlands, forests, grasslands), with an average increase of 3 to 4% in NPP per g of added N. The N response efficiency decreased with N addition rates above 50 kg N/ha/yr, consistent with a saturating response to N.

[Liu and Greaver \(2009\)](#) had smaller data sets, with 16 observations of net ecosystem exchange (NEE; all in nonforested systems) and 17 observations of ecosystem C content ([Figure 6-2](#)). There were no significant effects of added N on NEE overall or within the individual biomes included in the analysis (grasslands, wetlands, tundra). However, added N did increase forest ecosystem C content by 6%. Belowground NPP responses have not been synthesized, at least in part, because data are lacking ([LeBauer and Treseder, 2008](#)).

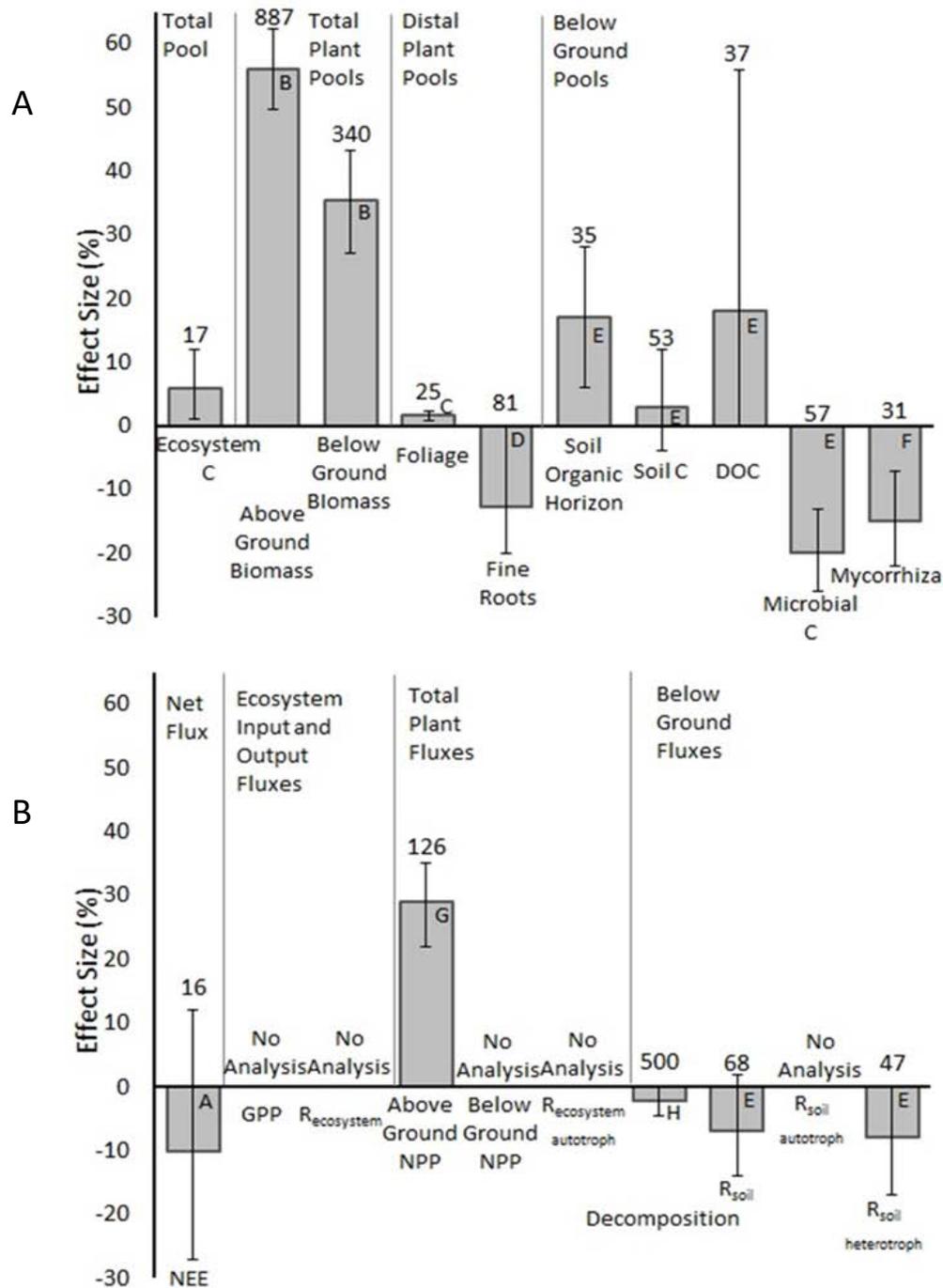
In terms of altered physiology, there is also widespread evidence that N additions increase plant tissue N concentrations. The meta-analysis by [Xia and Wan \(2008\)](#) included changes in plant N concentrations overall, aboveground, and belowground. Overall, N additions increased plant N concentrations by an average of 28.5% ([Xia and Wan, 2008](#)). Although there was significant variation among plant functional groups, the average increase in tissue N concentration among seeded plants was much more similar across functional groups than the biomass growth response, ranging only from +24 to +35% once legumes (+7%) and the two broader functional groups containing legumes (forbs, +14%; perennial herbs: +22%) were excluded. Likewise, belowground and aboveground plant tissues had a similar change in N concentration, in contrast to the varying biomass growth responses to N ([Xia and Wan, 2008](#)). [Li et al. \(2015\)](#) also observed that N additions significantly increased root N concentrations in a root trait meta-analysis (+18%;  $n = 84$ ). Because of these increased N concentrations, N additions can significantly decrease plant C:N ratios ([Yue et al., 2017](#)).



NPP = net primary productivity.

Notes: (A) Mean change in plant biomass growth in response to N additions redrawn from [Xia and Wan \(2008\)](#), with blue bars representing the overall response, orange bars representing aboveground growth, and grey bars representing belowground growth. Vertical grey lines identify different ways the data were parsed (i.e., all seeded plants; woody vs. herbaceous plants, etc.). (B) Mean change in aboveground net primary productivity data from [LeBauer and Treseder \(2008\)](#). Error bars represent the 95% confidence interval. Numbers above the error bars indicate the number of observations included in the analysis.

**Figure 6-1 Effects of nitrogen additions on plant growth and net primary productivity.**



DOC = dissolved organic carbon; NEE = net ecosystem exchange; NPP = net primary production; GPP = gross primary production; R<sub>ecosystem</sub> = ecosystem respiration; R<sub>ecosystem autotroph</sub> = plant respiration; R<sub>soil</sub> = soil respiration; R<sub>soil heterotroph</sub> = heterotroph soil respiration.

Notes: mean effect sizes from meta-analyses of N addition experiments on ecosystem, plant, and soil pools ([a] top panel) and fluxes ([b] bottom panel). Error bars represent 95% confidence intervals. Numbers above the bars are the sample sizes for each analysis. Letter with each bar denote the data source. No Analysis denotes a pool or flux that has not yet been meta-analyzed.

Data sources: (A) [Liu and Greaver \(2009\)](#); (B) [Xia and Wan \(2008\)](#); (C) [Lu et al. \(2011b\)](#); (D) [Li et al. \(2015\)](#); (E) [Liu and Greaver \(2010\)](#); (F) [Treseder \(2004\)](#); (G) [LeBauer and Treseder \(2008\)](#); (H) [Knorr et al. \(2005\)](#).

**Figure 6-2 Effects of added nitrogen on ecosystem carbon pools and fluxes.**

The 2008 ISA linked enhanced terrestrial productivity to increases in photosynthesis and gross primary productivity. Gross primary productivity (GPP) can increase as a result of either a greater amount of photosynthetic tissue (more light absorption) or a higher rate of photosynthesis per leaf. There is a strong mechanistic and conceptual link between greater foliar N concentrations, higher leaf concentrations of the C assimilating enzyme rubisco ([Evans, 1989](#)), and greater maximum rates of leaf-level photosynthesis in vascular plants ([Wright et al., 2004](#)). Consequently, the increase in foliar N caused by N additions has been linked to increases in the leaf-level rate of photosynthesis for decades [e.g., [Teskey et al. \(1994\)](#) and references therein]. Alternately, evidence cited in the 2008 ISA suggests that much of the increased foliar N observed when N is added may be physiologically inactive because it manifests as an increase in storage compounds such as free amino acids ([Bauer et al., 2004](#)). While increases in photosynthesis in response to N additions have been observed in trees, grasses, and shrubs, these increases have not been consistent [e.g., [Gulmon and Chu \(1981\)](#); [Lajtha and Whitford \(1989\)](#); [Newman et al. \(2003\)](#); [Chen et al. \(2005b\)](#); [Elvir et al. \(2006\)](#); [Talhelm et al. \(2011\)](#); [Pivovarov et al. \(2016\)](#)] and there does not appear to be a meta-analysis or other synthesis on the response of leaf-level photosynthesis or GPP ([Figure 6-2B](#)) to N additions. Similarly, there is a strong fundamental relationship between tissue N concentration and respiration rates in plants ([Reich et al., 2008](#); [Reich et al., 2006](#); [Ryan et al., 1996](#)), such that this relationship is used to model respiration rates [e.g., [Amthor \(2000\)](#); [Hanson et al. \(2004\)](#)]. However, there is evidence that this relationship can breakdown in N addition studies [e.g., [Schaberg et al. \(1997\)](#); [Drake et al. \(2008\)](#); [Burton et al. \(2012\)](#)], and there are currently no broad analyses on the effects of N additions on ecosystem or plant-scale autotrophic respiration ([Figure 6-2B](#)).

The 2008 ISA noted some observations of decreased microbial biomass as a result of added N, particularly for mycorrhizal fungi [[Treseder \(2004\)](#); [Figure 6-2B](#)]. Since 2008, however, it has become increasingly clear that N deposition can greatly impact microbial communities, often including a decrease in microbial biomass. Meta-analyses conducted across all ecosystem types have found that N additions can decrease microbial biomass ([Treseder, 2008](#)), microbial biomass C ([Liu and Greaver, 2010](#)), and microbial biomass N ([Lu et al., 2011b](#)) and that the effects of added N on microbial biomass increase with the duration of N additions and the total amount of N added ([Treseder, 2008](#)). These changes are noteworthy given the diverse role of microorganisms in nutrient cycling, greenhouse gas fluxes, and other ecosystem services. Although N additions frequently decrease microbial biomass, the results are not always consistent ([Liu and Greaver, 2010](#); [Treseder, 2008](#)). The effects of N were not significant at the level of individual microbial domains (bacteria, fungi), although there were trends toward increasing negative effects of N additions on fungal biomass as duration and cumulative N load increased ([Treseder, 2008](#)). In a meta-analysis, [Carey et al. \(2016\)](#) observed that N additions increased the

abundance of ammonia-oxidizing bacteria across nonagricultural ecosystems, but did not affect the abundance of ammonia-oxidizing archaea. Recently, [Li et al. \(2015\)](#) provided a new meta-analysis of N addition effects on mycorrhizal colonization of fine root tips and observed an overall 17% decline (n = 21). While this reinforces the conclusions of an earlier meta-analysis by [Treseder \(2004\)](#), there are important qualifiers to this finding: the sample only included observations from forests and grasslands in temperate and subtropical climates; significant decreases were only observed in temperate and forested ecosystems, after more than 3 years of N additions, or at N addition rates >100 kg N/ha/yr ([Li et al., 2015](#)).

Changes in mycorrhizae in turn can affect plant productivity. Mycorrhizal fungi provide benefits to plants, yet also carry costs. In exchange for nutrients and water from the fungus, the plant provides C from photosynthesis ([Högberg et al., 2010](#); [Rillig, 2004](#)). In many cases, this tradeoff works to the plant's advantage. For instance, [Van der Heijden et al. \(1998\)](#) observed higher biomass for most of the individual plant species in their study when inoculated with arbuscular mycorrhizae versus when mycorrhizae were absent. They suggested the mycorrhizal acquisition of a limiting nutrient, in this case phosphorus (P), for the plant in exchange for C explained this finding. However, under conditions in which the nutrient limitation of the plant is relieved (e.g., high N availability), mycorrhizae may no longer be as needed by the plant for nutrient acquisition, yet concomitantly still impose a C cost. In this case, the tradeoff is no longer as beneficial to the plant. With increased N availability, plants that make fewer mycorrhizal associations can benefit both from the physiological advantages accompanying an alleviation of N limitation (e.g., increases in photosynthesis, changes in plant chemistry) and from incurring a lower C cost for mycorrhizae ([Johnson et al., 2008](#)). Indeed, shifts in C allocation away from mycorrhizae may be a mechanism to support increased plant productivity in situations where plants do not show gains in photosynthesis [e.g., [Talhelm et al. \(2011\)](#)].

There are numerous mechanisms through which N deposition could impact microbial biomass, including changes in soil chemistry, changes in the rates of aboveground and belowground plant C inputs (including litter production, root exudates, and C supplied to mycorrhizal fungi), and changes in plant tissue chemistry ([Treseder, 2008](#)). Nitrogen additions can change the chemistry of litter inputs by altering the tissue composition of plant species ([Throop and Lerdau, 2004](#)) or by changing the composition of plant communities contributing to the ecosystem flux of plant litter [e.g., [Manning et al. \(2008\)](#)]. Within a particular species, N additions can cause changes in both of the dominant forms of plant litter: leaf litter and fine roots [e.g., [Xia et al. \(2015\)](#)]. These changes can be relatively direct, such as increases in tissue concentrations of inorganic and organic forms of N [e.g., [Koricheva et al. \(1998\)](#); [Bauer et al. \(2004\)](#)]. While leaf

litter N concentrations are not as widely measured as green leaf N, increases in leaf litter N concentrations due to added N are also likely to be widespread because increased N availability often either decreases or has no effect on the fraction of N plants absorb from leaves during senescence ([Aerts, 1996](#)). Other changes in litter chemistry, such as increases in condensed tannins, soluble phenolics, and nonstructural carbohydrates ([Xia et al., 2015](#)), likely involve more complex biological mechanisms. In a meta-analysis of plant biochemistry data, [Liu et al. \(2016a\)](#) observed different effects of added N on trees and herbs. For the live tissues of trees, N additions decreased concentrations of lignin, cellulose, and nonstructural carbohydrates, and increased the concentration of protein. In the live tissues of herbs, added N decreased the concentrations of nonstructural carbohydrates and hemicellulose, but increased lignin, cellulose, and protein concentrations. These changes have implications for herbivores and detritivores, as well plant growth dynamics.

In a litter decomposition meta-analysis, [Knorr et al. \(2005\)](#) observed that the effects of added N also differed based on the length of the study and the initial litter lignin content. Added N stimulated decomposition in studies lasting less than 2 years, but reduced decomposition in studies lasting more than 2 years. High-lignin litter decomposed more slowly than low-lignin litter. Because lignin concentrations tend to increase during litter decomposition, both of these results were considered to be consistent with earlier evidence that increased N supplies stimulate microbial activity responsible for the decomposition of labile litter constituents, while suppressing the microbial production of extracellular enzymes responsible for the degradation of lignin [[Knorr et al. \(2005\)](#); see also [Appendix 4](#)]. In a meta-analysis of biochemistry data for decomposing litter, [Liu et al. \(2016a\)](#) observed that N additions increased the concentration of lignin in decomposing litter for herbs and shrubs, but did not have a significant effect on decomposing tree litter. In comparison, N additions decreased cellulose concentrations in decomposing tree litter, but did not significantly affect cellulose concentrations in decomposing herb litter. In another meta-analysis, [Liu and Greaver \(2010\)](#) found that although N additions increased aboveground litter production (+20%; n = 37; not shown) across all biomes and N addition rates, there were no significant overall changes in either total soil respiration ([Figure 6-2B](#)) or heterotrophic soil respiration ([Figure 6-2B](#)). In fact, both forms of soil respiration tended to decline. Currently, no similar cross-biome analysis has been conducted for changes in autotrophic soil respiration (respiration from roots and mycorrhizal fungi), but [Janssens et al. \(2010\)](#) noted in a meta-analysis that autotrophic respiration was suppressed by N additions in forests.

Because some biogeochemical processes involve specific chemical forms of N (e.g., denitrification, ammonium toxicity; see [Appendix 4](#)), there is the potential that biological responses to N deposition (or N addition) could depend on whether the

dominant form of deposited N is oxidized ( $\text{NO}_y$ ) or reduced ( $\text{NH}_x$ ). A number of studies have specifically addressed this issue, either by conducting experiments directly testing additions of different forms of N or indirectly through syntheses comparing the effects of  $\text{NO}_y$  and  $\text{NH}_x$  in different experiments. Different responses to individual forms of N have been observed for some endpoints, such as increases in dissolved organic C, decreases in ecosystem N retention, increases in soil  $\text{N}_2\text{O}$  emissions, plant growth, and defense against pathogens [[Liu and Greaver \(2009\)](#); [Liu and Greaver \(2010\)](#); [Templer et al. \(2012\)](#); [Verhoeven et al. \(2011\)](#); [Yue et al. \(2016\)](#); [Mur et al. \(2016\)](#); see also [Table 4-13](#)]. By contrast, other studies have failed to observe a difference between the effects of N forms. One direct test occurred in the Front Range of the Rocky Mountains in Colorado, where [Ramirez et al. \(2010a\)](#) investigated whether soil microbes respond differently to additions of  $\text{NH}_4^+$  versus  $\text{NO}_3^-$  and found that the total amount of N added was correlated with a decrease in soil respiration, not the form of the N ( $\text{NH}_4^+$  vs.  $\text{NO}_3^-$ ). A more comprehensive understanding is available by reviewing the results of meta-analyses comparing the responses of N addition experiments conducted with different forms of N ([Table 6-1](#)). With notable exceptions, most often differences in the effect of the form of N were not observed in these meta-analyses. Moreover, studies finding differences tended to occur where sample sizes were small [e.g., belowground C pools in [Yue et al. \(2016\)](#)].

**Table 6-1 The effects of different forms of inorganic nitrogen on biological endpoints according to meta-analyses.**

See [Table 4-13](#) for the effects of different forms of inorganic nitrogen on biogeochemical processes and indicators.

Reference	Endpoint	Effect of NO <sub>y</sub> vs. NH <sub>x</sub> Forms
<a href="#">Yue et al. (2016)</a>	Aboveground plant C pool	Not significant
<a href="#">LeBauer and Treseder (2008)</a>	Aboveground plant productivity	Not significant
<a href="#">Yue et al. (2016)</a>	Aboveground plant productivity	Not significant
<a href="#">Treseder (2008)</a>	Bacteria biomass	Not significant
<a href="#">Yue et al. (2016)</a>	Belowground plant C pool	Increase with NH <sub>4</sub> <sup>+</sup>
<a href="#">Liu and Greaver (2009)</a>	Ecosystem C content	Not significant
<a href="#">Liu and Greaver (2010)</a>	Fine root litter production	Not significant
<a href="#">Treseder (2008)</a>	Fungal biomass	Not significant
<a href="#">Liu and Greaver (2010)</a>	Leaf litter production	Insufficient data
<a href="#">Yue et al. (2016)</a>	Leaf litter production	Insufficient data
<a href="#">Knorr et al. (2005)</a>	Litter decomposition	Not significant
<a href="#">Yue et al. (2016)</a>	Litter decomposition	Not significant
<a href="#">Treseder (2008)</a>	Microbial biomass	Not significant
<a href="#">Liu and Greaver (2010)</a>	Microbial biomass C	Decrease with NH <sub>4</sub> <sup>+</sup>
<a href="#">Yue et al. (2016)</a>	Microbial biomass C	Not significant
<a href="#">Treseder (2004)</a>	Mycorrhizal abundance	Not significant

C = carbon; <sup>15</sup>N = tracer isotope of nitrogen; N<sub>2</sub>O = nitrous oxide; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NH<sub>x</sub> = sum of reduced forms of N; NO<sub>3</sub><sup>-</sup> = nitrate; NO<sub>y</sub> = the sum of oxidized forms of nitrogen.

Notes: References ordered by endpoint. Only statistically significant differences between the effects of forms of N listed as increases or decreases.

Before the 2008 ISA, neither terrestrial N cycling nor anthropogenic N deposition had been widely incorporated into Earth systems models (ESMs) used to understand and forecast global climate and biogeochemical cycling. [Thornton et al. \(2007\)](#) made the first effort to understand how both coupled C and N cycling and anthropogenic N deposition would impact ESM predictions for terrestrial C uptake by inserting a new land biogeochemistry model into a coupled climate system model. In the resulting model

output, N limitation greatly decreased the amount of terrestrial C uptake predicted from future increases in atmospheric CO<sub>2</sub> and decreased the sensitivity of terrestrial C sequestration to increases in temperature and precipitation ([Thornton et al., 2007](#)). Including N deposition within the model directly increased terrestrial C uptake and also indirectly increased terrestrial C uptake by removing some of the N limitation predicted to occur under increased atmospheric CO<sub>2</sub> ([Thornton et al., 2007](#)). Subsequently, efforts to model biogeochemical processes at regional and global scales have expanded ([Thomas et al., 2015](#); [Zaehle and Dalmonech, 2011](#)). Although the integration of terrestrial N cycling into ESMs remains relatively weak, more ESMs are incorporating the coupling of terrestrial C and N cycling as overall model development and sophistication advances ([Thomas et al., 2015](#); [Arora et al., 2013](#); [Zaehle and Dalmonech, 2011](#); [Bonan and Levis, 2010](#); [Gerber et al., 2010](#)). Consistent with the findings of [Thornton et al. \(2007\)](#), inclusion of coupled C-N cycling in ESMs has two primary effects: decreasing the stimulatory effects of elevated atmospheric CO<sub>2</sub> on terrestrial productivity and decreasing the sensitivity of terrestrial C sequestration to climate warming because increased soil N mineralization stimulates plant productivity ([Arora et al., 2013](#); [Zaehle and Dalmonech, 2011](#); [Zhang et al., 2011b](#); [Arneeth et al., 2010](#); [Bonan and Levis, 2010](#); [Gerber et al., 2010](#); [Yang et al., 2010](#); [Zaehle et al., 2010](#); [Thornton et al., 2009](#)). However, the ESMs that do include basic terrestrial C-N coupling lack more recently identified interactions such as plant organic N uptake, soil priming (root exudation), and the suppression of litter decomposition at high soil N availability, all of which could increase terrestrial C uptake to varying extents ([Thomas et al., 2015](#); [Zaehle and Dalmonech, 2011](#)). In addition, the interactions between and the net effects of N, precipitation, and temperature on ecosystem C response in soils are unknown in many cases (see [Appendix 13.1.2.1](#)).

In the few ESMs that have directly included the effects of N deposition, the additional N increased terrestrial C uptake and increased the extent to which elevated atmospheric CO<sub>2</sub> stimulates terrestrial C uptake ([Devaraju et al., 2016](#); [Bonan and Levis, 2010](#); [Yang et al., 2010](#)). In addition, N deposition in the Northern Hemisphere (particularly in the U.S.) apparently compounded the increase in C sequestration caused by the regrowth of secondary forests during the late 20th century following agricultural abandonment and timber harvest ([Gerber et al., 2013](#); [Yang et al., 2010](#)). However, ESMs that do not include potential N saturation may overestimate the effect of N deposition on terrestrial C uptake in regions experiencing high N deposition rates ([Lu et al., 2016](#)). In addition, it should be noted that although N deposition and the overall anthropogenic production of reactive N increases terrestrial C sequestration, they are not the only influence of anthropogenic N on global climate. It is difficult to quantify the overall climate impact of anthropogenic N [e.g., [Pinder et al. \(2013\)](#)] because reactive N can change the planetary albedo by enhancing aerosol formation, stimulate the production of biogenic greenhouse gases, alter the production and destruction of methane and tropospheric ozone in the

atmosphere, and indirectly decrease terrestrial productivity due to the phytotoxic effects of ozone ([Lu and Tian, 2013](#); [Pinder et al., 2013](#); [Pinder et al., 2012](#); [Arneeth et al., 2010](#); [Zaehle et al., 2010](#)). Many of these effects are discussed further in the atmospheric chemistry and terrestrial biogeochemistry portions of this ISA (see [Appendix 2](#) and [Appendix 4](#)).

In addition to the global-scale analyses conducted using ESMs, biogeochemical process models have been used to assess the impact of N deposition on terrestrial productivity and C sequestration at national and regional scales. [Tian et al. \(2012\)](#) used the Dynamic Land Ecosystem Model (DLEM) to model the influence of climate, tropospheric ozone, fertilizer use, land use/land cover change, atmospheric CO<sub>2</sub>, and N deposition on terrestrial C storage over the 20th century in the southeastern U.S. (encompassing Texas and Oklahoma to Florida and Virginia). Terrestrial C storage increased from 1951–2007, with the model identifying atmospheric CO<sub>2</sub> and N deposition as the environmental factors responsible for the increase in C sequestration ([Tian et al., 2012](#)). In China, a series of papers has been published using biogeochemical process models to identify how this same set of environmental factors influenced terrestrial C cycling in that country. Rates of N deposition in China grew rapidly during the late 20th century and were considerably higher than in the U.S. by the early 21st century, with nationwide average rates of approximately 20 kg N/ha/yr and rates in southeast China averaging 35–40 kg N/ha/yr ([Lu and Tian, 2013](#); [Lu et al., 2012](#)). [Tian et al. \(2011\)](#) applied the Terrestrial Ecosystem Model and the DLEM model to China using data from 1961–2005. In both models, China was a C sink during this time period, with the combination of N deposition and agricultural fertilizer use accounting for 61% of the increase in C sequestration. Notably, the responsiveness of terrestrial C sequestration to N deposition has declined since the 1980s as N deposition in China increased, providing evidence that terrestrial ecosystems are becoming less N limited in China ([Tian et al., 2011](#)). [Lu et al. \(2012\)](#) conducted a similar analysis, using DLEM to understand how multifactor environmental change influenced terrestrial C sequestration in China from 1901–2005. Like [Tian et al. \(2011\)](#), [Lu et al. \(2012\)](#) observed that N deposition increased terrestrial C sequestration in China throughout much of the late 20th century, but that the responsiveness of terrestrial C sequestration to N deposition has declined since the 1980s. Moreover, [Lu et al. \(2012\)](#) reported that all areas of China, aside from some shrublands and portions of western China, are becoming N saturated.

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## 6.2.3 Forests

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### 6.2.3.1 Aboveground Processes

The 2008 ISA noted a wide range of forest productivity responses to added N. Responses to low levels of N were often positive because N availability tends to limit growth in terrestrial ecosystems ([LeBauer and Treseder, 2008](#)). However, forest productivity responses to higher rates of N addition were neutral or negative [e.g., [Magill et al. \(2004\)](#)]. The effects of N deposition were variable across species. Conifer species, particularly at high elevations, were more likely to exhibit negative growth responses or mortality in response to added N. Conifer species were less likely to demonstrate increased growth in response to additional N and more often exhibited decreased growth and increased mortality [e.g., [McNulty et al. \(2005\)](#); [Beier et al. \(1998\)](#); [Boxman et al. \(1998a\)](#)]. Differences between broadleaf and conifer species were especially clear in long-term N addition experiments: [Elvir et al. \(2003\)](#) observed increased sugar maple (*Acer saccharum*) basal area growth in response to long-term (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (25 kg N/ha/yr for 10 years) additions, but red spruce (*Picea rubens*) growth was unchanged. At Harvard Forest, oak (*Quercus velutina*, *Q. rubra*) increased growth in response to chronic N additions (50 or 150 kg N/ha/yr for 15 years), while red pine (*Pinus resinosa*) growth slowed and mortality increased ([Magill et al., 2004](#)). Most empirical observations of the effects on atmospheric N deposition on forest productivity came from chronic N addition experiments in temperate forests in the U.S. [e.g., [Aber et al. \(1995\)](#); [McNulty et al. \(1996\)](#); [Elvir et al. \(2003\)](#); [Magill et al. \(2004\)](#); [Pregitzer et al. \(2008\)](#)] and temperate and boreal forests in Europe ([Hyvönen et al., 2008](#); [Högberg et al., 2006](#); [Beier et al., 1998](#); [Boxman et al., 1998a](#)). Empirical analyses of the effects of atmospheric N deposition on forest productivity in the U.S. were lacking.

Research published since 2008 has reinforced many of the ideas in the 2008 ISA. There is considerable evidence from deposition gradient studies, forest modeling, and long-term N addition experiments that N deposition broadly stimulates tree growth and the productivity of forested ecosystems, but that effects vary by species. Using forest inventory data collected between 2000 and 2016, [Horn et al. \(2018\)](#) found N deposition coincided with a small overall increase in tree growth and mortality. The particular response though varied greatly between species. The study analyzed results for 94 tree species, but ultimately focused on a subset of 71. Of the 71 species, 39 exhibited a significant relationship between growth and N deposition. Twenty of the 39 had increasing growth with greater N deposition across the full depositional range experienced by that species. Seventeen displayed increasing growth at lower levels of N

deposition but decreasing growth at higher levels. Two species (yellow birch [*Betula alleghaniensis*] and eastern hemlock [*Tsuga canadensis*]) declined in growth consistently with increasing N deposition. Mortality also varied between species, with 3 species increasing in survival, 25 species increasing in survival at lower N deposition before decreasing in survival at higher levels, and 6 species consistently declining in survival ([Horn et al., 2018](#)).

Similarly, other studies have shown variation in tree growth and mortality with N deposition. [Thomas et al. \(2010\)](#) assessed tree species response to N deposition using forest inventory data from the early 1980s through the mid-1990s. Of the 23 species surveyed, N deposition accelerated growth in 11 species, including 3 of the 4 most abundant species (red maple [*Acer rubrum*], sugar maple, and northern red oak [*Quercus rubra*]). Negative effects on growth were seen in three species, all of which were evergreen conifers (red pine [*Pinus resinosa*], red spruce, northern white cedar [*Thuja occidentalis*]). All five of the arbuscular mycorrhizal tree species included in the analysis exhibited increased growth. Eight species exhibited higher mortality rates with increasing N deposition in the [Thomas et al. \(2010\)](#) analysis, notably several oak species, including northern red oak. Only three species showed increased survival. Additionally, [Xia and Wan \(2008\)](#) observed positive effects of added N on growth for both broadleaf and coniferous trees in a meta-analysis, with broadleaf trees (+73%) more responsive than conifers (+37%).

Examining forest stand-level responses, [Hember et al. \(2017\)](#) concluded N deposition had increased forest stand growth in one of the five Canadian ecozones (Montane Cordillera), decreased it in another (Boreal Plain), and did not significantly affect stand growth in the remaining three (Pacific Maritime, Boreal Shield, and Atlantic Maritime). They similarly found differences in forest stand mortality, with N deposition decreasing mortality in three of the five ecozones (Pacific Maritime, Montane Cordillera, and Boreal Plain) and no significant effect in the remaining two. In an analysis of forest inventory data from across the entire eastern U.S. from the 1970s through early 2000s, [Dietze and Moorcroft \(2011\)](#), as noted in [Appendix 5](#), found N deposition was linked to decreased tree mortality in 9 of 10 plant functional types and increased mortality only in the northern midsuccessional hardwoods functional type. Across a smaller gradient within the Adirondacks, [Bedison and McNeil \(2009\)](#) found a significant positive overall effect of N deposition on tree growth from 1984–2004, but positive growth effects only for red maple, balsam fir (*Abies balsamea*), and red spruce at the species level. Thus, it appears from these inventory analyses that while tree growth has generally been enhanced by N deposition over the last several decades, individual species have exhibited variable responses to N deposition in mortality and growth.

Variation has also been shown in tree responses to experimental N additions. Overstory sugar maple trees increased growth in response to added N in Michigan [Pregitzer et al. (2008); N added at 30 kg N/ha/yr] and Maine [Elvir et al. (2003); 25 kg N/ha/yr], but mature sugar maple and red maple did not respond in the Catskills [Lovett et al. (2013); 50 kg N/ha/yr]. Northern red oak increased growth at Harvard Forest [Frey et al. (2014); 50 and 150 kg N/ha/yr] but showed no growth response at two sites in New York state [Wallace et al. (2007); 75 kg N/ha/yr, Lovett et al. (2013); 50 kg N/ha/yr], with increased mortality at one of the New York sites (Wallace et al., 2007). Red pine at Harvard Forest exhibited decreased growth and higher mortality in response to chronic N additions [Frey et al. (2014); 50 and 150 kg N/ha/yr], while red spruce showed no growth response in Maine [Elvir et al. (2003); 25 kg N/ha/yr]. A 13-year study in a young forest in West Virginia included the two species with the most positive growth responses in the Thomas et al. (2010) analysis and found that N addition (35 kg N/ha/yr of  $[\text{NH}_4]_2\text{SO}_4$ ) generally decreased growth of black cherry (*Prunus serotina*) and tulip poplar (*Liriodendron tulipifera*), although these changes were not statistically significant (May et al., 2005).

Notably, N additions in these studies often exceeded levels observed in forest inventory studies (Horn et al., 2018; Thomas et al., 2010). For instance, Horn et al. (2018) found growth in black cherry increased with N deposition up to just over 15 kgN/ha/yr, before declining with increases in deposition beyond that. Thus, the N addition of 35 kg N/ha/yr in (May et al., 2005) far exceeded the point of maximum growth for black cherry. Tulip poplar consistently increased in growth with N deposition according to Horn et al. (2018), but, even in this case, the 35 kg N/ha/yr added by May et al. (2005) exceeded the maximum amount of deposition (almost 34 kg N/ha/yr) experienced by tulip poplar in the Horn et al. (2018) study. This could help explain some of the differences in tree growth and mortality responses between experimental N addition and forest inventory studies.

Other studies have also observed similarly mixed results on tree growth and mortality in U.S. forests. At the same sites in Michigan where long-term N additions increased growth of mature sugar maple (Pregitzer et al., 2008), N additions decreased the growth and survival of sugar maple saplings (Talhelm et al., 2013; Patterson et al., 2012). Notably, this negative effect occurred without increase in overstory leaf area that would reduce light availability or a decrease in soil pH (Talhelm et al., 2013). More recently, Ibanez et al. (2016) observed that although small overstory trees (5–10 cm diameter at breast height) at these sites were growing faster, they were also experiencing increased mortality. As with sugar maple saplings in Michigan, N deposition appears to be decreasing growth among northern red oak saplings in the Chicago area, potentially contributing to the inability of this species to regenerate in that region (Bassirrad et al., 2015). In Vermont, 2 years of N addition at 150 kg N/ha/yr increased growth in four hardwood species (including sugar maple and northern red oak), decreased growth in one

conifer, and had no effect on two other hardwoods ([Finzi, 2009](#)). [Allen et al. \(2010\)](#) reported higher mortality and a decrease in ectomycorrhizal root tips ([Table 6-2](#)), with N addition (100 kg N/ha/yr) in ectomycorrhizal piñon pine in New Mexico, while no change in the mortality of arbuscular mycorrhizal juniper. [Allison et al. \(2010\)](#) observed a 2.5-fold increase in aboveground net primary productivity in response to several years of N additions (100 kg N/ha/yr) in central Alaska in a recently burned boreal forest. At two mixed conifer forests in the Sierra Nevada, 2 years of N additions (12 or 24 kg N/ha/yr) had a positive effect on herb community biomass at one site (24 kg N/ha/yr) and a negative effect at the other site (12 kg N/ha/yr); shrub biomass was unaffected ([Hurteau and North, 2008](#)). Modeling 50 years into the future based on these results, a lower rate of N deposition (12 kg N/ha/yr) was expected to increase herb biomass, while the high rate of N deposition (24 kg N/ha/yr) led only to a small increase in shrub biomass. In combination with a wetter precipitation regime, both N deposition rates were predicted to increase shrub and herb biomass ([Hurteau et al., 2009](#)). In a greenhouse study, N additions of up to 120 kg N/ha/yr had no effect on the N fixing tree black locust (*Robinia pseudoacacia*) when grown in a monoculture or in competition with the sawtooth oak (*Quercus acutissima*), but N additions increased the height and total biomass of the sawtooth oak when grown in competition with black locust ([Luo et al., 2014](#)).

**Table 6-2 Growth, productivity, and carbon cycle responses of ectomycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Högberg et al. (2010)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	100	2	<sup>13</sup> C labeling of EM biomarker PLFA 18:2ω6,9	Decrease
<a href="#">Näsholm et al. (2013)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	100	0 (2 weeks)	<sup>13</sup> C labeling of EM biomarker PLFA 18:2ω6,9	Not significant
<a href="#">Parrent and Vilgalys (2009)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	1	Ectomycorrhizal 18S RNA expression	Not significant
<a href="#">Högberg et al. (2011)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	120	20; 15-yr recovery	Ectomycorrhizal biomarker 18:2ω6,9	Not significant
<a href="#">Högberg et al. (2011)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	30, 70	35	Ectomycorrhizal biomarker 18:2ω6,9	Decrease
<a href="#">Näsholm et al. (2013)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	100	0 (2 weeks)	Fine root chitin concentration	Not significant
<a href="#">Kjøller et al. (2012)</a>	Denmark	Norway spruce ( <i>Picea abies</i> )	Ambient	27–43	n/a	Mycelium production	Decrease
<a href="#">Bahr et al. (2013)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Ambient	0.9–24.6	n/a	Mycelium production	Decrease
<a href="#">Bahr et al. (2015)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	200 (once)	1	Mycelium production	Decrease
<a href="#">Hasselquist et al. (2012)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	20, 100	6	Mycorrhizal respiration	<u>Low dose</u> : increase <u>High dose</u> : decrease

**Table 6-2 (Continued): Growth, productivity, and carbon cycle responses of ectomycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Vallack et al. (2012)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	100	2	Mycorrhizal respiration	Decrease
<a href="#">Allen et al. (2010)</a>	New Mexico	Piñon pine ( <i>Pinus edulis</i> ) and one-seeded juniper ( <i>Juniperus monospermum</i> )	Addition	100	7+	Mycorrhizal root tip colonization (by ectomycorrhizal and arbuscular mycorrhizae)	Decrease in ectomycorrhizal root tips; no change in arbuscular mycorrhizal root tips
<a href="#">Pritchard et al. (2014)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	6	Mycorrhizal root tip production	Decrease
<a href="#">Pritchard et al. (2014)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	6	Mycorrhizal root tip survival (deep soil)	Increase
<a href="#">Kou et al. (2017)</a>	China (sub-tropical)	Slash pine ( <i>Pinus elliotii</i> )	Addition	40, 120	2	Mycorrhizal (ectomycorrhizal) survival	Increase at both low and high additions, except for deeper soil and dichotomous mycorrhizae
<a href="#">Parrent and Vilgalys (2009)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	1	Root ammonium transport gene expression	Not significant
<a href="#">Garcia et al. (2008)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	2	Root colonization (%)	Increase
<a href="#">Diaz et al. (2010)</a>	Spain	Aleppo pine ( <i>Pinus halepensis</i> )	Addition	35, 60, 120 mg/plant	1	Root colonization (%)	Decrease
<a href="#">Kjøller et al. (2012)</a>	Denmark	Norway spruce ( <i>Picea abies</i> )	Ambient	27–43	n/a	Root colonization (%)	Decrease
<a href="#">Kou et al. (2015)</a>	China	Slash pine ( <i>Pinus elliotii</i> )	Addition	40, 120	2	Root colonization (%)	<u>Low dose</u> : not significant <u>High dose</u> : increase

**Table 6-2 (Continued): Growth, productivity, and carbon cycle responses of ectomycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Parrent and Vilgalys (2009)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	112	1	Root monosaccharide transport gene expression	Not significant
<a href="#">Allison et al. (2008)</a>	Alaska	Black spruce ( <i>Picea mariana</i> )	Addition	140	5	Sporocarp abundance	Decrease
<a href="#">Allen et al. (2010)</a>	New Mexico	Piñon pine ( <i>Pinus edulis</i> ) and one-seeded juniper ( <i>Juniperus monospermum</i> )	Addition	100	7+	Sporocarp abundance	Decrease
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Sporocarp abundance	Decrease
<a href="#">Hasselquist et al. (2012)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	20, 100	6	Sporocarp abundance	<u>Low dose</u> : not significant <u>High dose</u> : decrease
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	110	20, 15-yr recovery	Sporocarp abundance	Not significant
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	20, 100	6	Sporocarp abundance	<u>Low dose</u> : not significant <u>High dose</u> : decrease
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	35, 70	40, 2-yr recovery for 70-kg treatment	Sporocarp abundance	Decrease

EM = ectomycorrhizal fungi; ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; PLFA = phospholipid fatty acids; RNA = ribonucleic acid; yr = year.

Notes: single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

A number of studies on the effects on N deposition or chronic N additions have been conducted in temperate and boreal forests in Europe, and these studies have more consistently found positive effects of N on tree growth [e.g., [Solberg et al. \(2009\)](#); [Ferretti et al. \(2014\)](#); [Nair et al. \(2016\)](#)]. [Ferretti et al. \(2014\)](#) observed a positive relationship between N deposition and tree growth across 26 forest plots in Italy. A positive effect of N deposition on tree growth was also found on 135 Swiss long-term observation plots for mature beech and spruce from the mid-1980s through late 2000s ([Braun et al., 2010](#)). Further N additions decreased tree growth at three of seven experimental sites, yet these changes were linked to P deficiencies ([Braun et al., 2010](#)). [Eastaugh et al. \(2011\)](#) took a more complex approach to understand growth trends of Norway spruce (*Picea abies*) in the Austrian National Forest Inventory from 1960–2008. Using the Biome-BGC model to isolate growth trends from variation in climate, the authors found a positive relationship between tree growth and N deposition. Using data from long-term N addition experiments in Norway spruce and Scots pine (*Pinus sylvestris*) forests throughout Sweden and Finland, [Hyvönen et al. \(2008\)](#) found increased tree growth at 11 of 12 sites. The effects of added N on forest productivity appear to persist for decades and carry over through major ecosystem disturbances. [From et al. \(2015\)](#) studied young Norway spruce and Scots pine forests planted in the late 1990s after the original forests were clear-cut. The original forests had received N additions of 150 kg N/ha/yr (as  $\text{NH}_4\text{NO}_3$ ) either twice (in 1977 and 1985), once (1985), or never. Tree height growth of the young forests was positively related to the amount of previous N additions, with significantly greater height growth in the forests that had received two N additions. Foliar N concentrations were also significantly higher in the forests that had received N additions ([From et al., 2015](#)). Biomass of understory shrubs and bryophytes decreased in response to N additions (100 kg N/ha/yr for 6 years) on boreal forest islands in Sweden, although one of three shrub species increased in growth ([Wardle et al., 2016](#)).

The 2008 ISA tied greater tree growth and forest productivity to increases in foliar N, photosynthesis, and gross primary productivity. In addition, foliar N was identified as a sensitive indicator of changes in forest N availability ([Aber et al., 1989](#)). Since the 2008 ISA, increases in foliar N continue to have been linked to N deposition in forests in the U.S., Europe, and Asia in pollution gradient studies ([Sardans et al., 2016](#); [Talhelm et al., 2012](#); [Jones et al., 2011](#); [Cox et al., 2010](#); [Thimonier et al., 2010](#); [Fenn et al., 2008](#)) and N addition experiments ([Du, 2017](#); [Fusaro et al., 2017](#); [Gilliam et al., 2016a](#); [Wardle et al., 2016](#); [Fowler et al., 2015](#); [Du and Fang, 2014](#); [Lovett et al., 2013](#); [Talhelm et al., 2013](#); [Lovett and Goodale, 2011](#); [Talhelm et al., 2011](#); [Allen et al., 2010](#); [Braun et al., 2010](#)). For instance, [Cox et al. \(2010\)](#) observed a 40% increase in foliar N (from 15 mg/g to 21 mg/g) in Scots pine forests in Germany and the U.K. along an N deposition gradient of 4.6 to 28 kg N/ha/yr. In addition to trees, forest bryophytes and lichens also show increased tissue N concentrations when exposed to additional N ([Maaroufi et al., 2016](#);

[McMurray et al., 2015](#); [McMurray et al., 2013](#); [Gundale et al., 2011](#); [Fenn et al., 2008](#); [Glavich and Geiser, 2008](#)). Increased foliar N is not universally observed in N addition studies [e.g., [Lovett et al. \(2013\)](#); [Zhang et al. \(2015c\)](#); [Zhang et al. \(2017\)](#)] or along N deposition gradients ([Watmough and Meadows, 2014](#)), but a meta-analysis found that N additions generally increase foliar N in trees ([Lu et al., 2011b](#)).

Although there are clear links between N deposition and increased foliar N and between higher foliar N and increased photosynthesis, there is only limited evidence that chronic N deposition directly increases leaf-level photosynthesis in forests. For instance, in long-term simulated N deposition experiments in Massachusetts and Maine, only one of four species exhibited increased photosynthesis with N additions ([Elvir et al., 2006](#); [Bauer et al., 2004](#)). Research on photosynthesis since the 2008 ISA has been similarly mixed. [Talhelm et al. \(2011\)](#) did not observe a significant increase in either photosynthesis or canopy leaf area in mature sugar maple trees at four sites in Michigan in response to N additions (30 kg N/ha/yr as NaNO<sub>3</sub> for 14 years). Using a canopy-applied N treatment at two Swiss forests, [Wortman et al. \(2012\)](#) found that N additions improved photosynthetic processes in oak at one site, but did not significantly influence photosynthetic parameters in spruce or beech at the other site. In Swedish boreal forests, higher tissue N concentrations resulting from N additions (20 or 100 kg N/ha/yr for 4 years) increased the amount of <sup>13</sup>CO<sub>2</sub> assimilated into shrub (*Vaccinium*) foliage but decreased the amount of C assimilated by bryophytes ([Hasselquist et al., 2016](#)). At a broader scale, [Fleischer et al. \(2013\)](#) analyzed the effect of N deposition on photosynthesis using observations from 80 forest eddy covariance C flux measurement sites predominantly located in the eastern U.S. and western Europe. In this data set, canopy photosynthetic capacity was positively correlated to N deposition for conifer forests when N deposition was below an observed critical load of approximately 8 kg N/ha/yr ([Fleischer et al., 2013](#)). Most of the stimulus provided by N deposition occurred in boreal forests, with little to no influence of N deposition in broadleaf forests or forests in the temperate climate zones ([Fleischer et al., 2013](#)). [Leonardi et al. \(2012\)](#) compiled a global data set of published tree ring <sup>13</sup>C chronologies and found that the rate of N deposition had a significant linear effect on intrinsic water-use efficiency (iWUE) and <sup>13</sup>C discrimination ( $\Delta^{13}\text{C}$ ) in conifers and a quadratic effect in angiosperms. This change in <sup>13</sup>C discrimination suggests that the additional N either stimulated photosynthesis or stimulated growth to the extent that the trees became more water limited.

The apparent contradiction between the wide observations that N deposition can increase both tree growth and foliar N concentrations and the inconsistent effects of N deposition on leaf-level photosynthesis could be explained by two other physiological responses to N. First, plants can store excess N in foliage as free amino acids and other

physiologically inactive forms of N ([Bauer et al., 2004](#)). Increases in foliar amino acid concentrations, particularly arginine, have been observed in forests in chronic N addition experiments ([Bauer et al., 2004](#)) and along N deposition gradients ([Braun et al., 2010](#)). In these cases, the added foliar N would have no impact on photosynthesis. Second, plants can respond to added N by altering C allocation. As noted in the 2008 ISA, higher N availability often causes trees to allocate less photosynthate to roots and belowground processes and more toward aboveground growth ([Vicca et al., 2012](#); [Högberg et al., 2010](#); [Janssens et al., 2010](#); [Litton et al., 2007](#); [Aerts and Chapin, 1999](#); [Minnich et al., 1995](#)). Research since the 2008 ISA has provided further evidence that N deposition is likely capable of causing such a shift in forests. In a greenhouse experiment, N additions (2, 5, and 10 kg N/ha/yr) resulted in more biomass allocated to leaves than to roots at all four N addition levels for oak and black locust trees. At the same Michigan sites where [Talhelm et al. \(2011\)](#) observed that chronic N additions had no effect on leaf-level photosynthesis or stand leaf area, the combination of increased aboveground growth, no change in root production or respiration, and decreased mycorrhizal abundance led the authors to conclude that a change in C allocation away from mycorrhizae was the likely cause for enhanced tree growth. More broadly, [Vicca et al. \(2012\)](#) found that across 49 forest sites, higher site fertility increased both the fraction of biomass that was allocated aboveground and the fraction of photosynthate that was allocated toward biomass production. The increase in C allocated to biomass production was thought to most likely result from less C being allocated to root symbionts such as mycorrhizae ([Vicca et al., 2012](#)). Likewise, [Janssens et al. \(2010\)](#) conducted a meta-analysis of 20 forest N addition experiments and found that N additions decreased the fraction of C allocated to belowground processes but did not affect root biomass. As an example of this, [Högberg et al. \(2010\)](#) conducted a short-term (~2 hour)  $^{13}\text{CO}_2$  canopy labeling experiment in a young Scots pine forest in northern Sweden to determine how N additions (two 100 kg N/ha additions over 2 years) altered the allocation of recent photosynthate belowground. In the 3 weeks following the canopy labeling, the total soil respiratory efflux of the  $^{13}\text{C}$  label was 62% lower in the plots that had received the N additions. Other observed physiological responses to N include delayed bud burst ([De Barba et al., 2016](#)), decreased tree ring width, and increased xylem conduit density ([Borghetti et al., 2017](#)).

The effects of N addition on forest productivity have the potential to be moderated by increases in herbivory, particularly among insects ([Throop and Lerdau, 2004](#)). For instance, [Andersen et al. \(2010\)](#) observed that N additions increased foliar N and photosynthetic rates within a tropical forest in Panama, but that tree growth rates were unaffected because of increased herbivory. At Harvard Forest in Massachusetts, northern red oak regeneration declined with N additions [50 and 100 kg N/ha/yr; [Bogdziewicz et al. \(2017\)](#)]. Acorn production increased, but so did weevil infestation of the acorns, and

germination rates declined. In a Pennsylvania common garden experiment with northern red oak, saplings receiving N additions (200 kg N/ha/yr) tended to have greater herbivore damage, but the effects of N addition on herbivory and the link between herbivory and decreased growth both varied by the type of herbivore, the tree lineage (breeding family), and the study location ([Cha et al., 2010](#)). Similarly, [Jones et al. \(2008\)](#) and [Jones et al. \(2011\)](#) observed that the most abundant herbivore of bracken fern (*Pteridium aquilinum*) and a beetle herbivore of California black oak (*Quercus kelloggii*) were increased by N addition at a heavily polluted site, but not at a drier, less polluted site. However, there was a positive correlation between leaf NO<sub>3</sub><sup>-</sup> concentrations and the abundance of several groups of black oak herbivores.

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### 6.2.3.2 Belowground Processes

The 2008 ISA analysis of how belowground processes in forests reacted to N deposition focused on fine root dynamics, aboveground litter inputs, decomposition, soil respiration, and soil C. [Johnson \(2001\)](#) had found a significant increase in forest soil C in response to N additions as part of a meta-analysis, but only a single long-term N addition field study had observed a significant increase in forest soil C [[Pregitzer et al. \(2008\)](#); see [Appendix 4](#)]. For fine roots, [Nadelhoffer \(2000\)](#) hypothesized that N deposition would decrease biomass, but stimulate turnover and production. The 2008 ISA found little evidence with which to evaluate this hypothesis. There was more available research on N effects on decomposition and soil respiration. As noted earlier, [Knorr et al. \(2005\)](#) observed in a meta-analysis that N additions increased decomposition at sites receiving low rates of ambient N deposition (<5 kg N/ha/yr), but N additions suppressed decomposition at sites receiving moderate rates of N deposition (5–10 kg N/ha/yr).

Research completed since the 2008 ISA has advanced our understanding of how N affects belowground processes in forests. In two meta-analyses, [Liu and Greaver \(2010\)](#) did not find a consistent effect of N additions on forest fine root production, while [Li et al. \(2015\)](#) observed a decrease (–13.5%) in forest fine root biomass. Broadly, some of the results discussed in the 2008 ISA that appeared inconsistent at the time were likely a reflection of how N additions interacted with other ecological processes. In young, rapidly expanding forests, N addition may increase root biomass as a consequence of an overall enhancement of plant growth ([Janssens et al., 2010](#)). For instance, N additions (150 kg N/ha/yr for 3 years) to a young bamboo forest increased fine root growth by >30%, even though this forest already received high rates of atmospheric N deposition [95 kg N/ha/yr of wet deposition; [Tu et al. \(2015\)](#)]. However, as noted in the “Aboveground Processes” section ([Appendix 6.2.3.1](#)), increases in N deposition tend to decrease the proportion of C allocated to roots relative to aboveground growth ([Li et al.,](#)

[2015](#); [Vicca et al., 2012](#); [Janssens et al., 2010](#); [Litton et al., 2007](#); [Minnich et al., 1995](#)). Thus, in more mature forests, root biomass and production are not consistently affected by N deposition. For instance, there were no effects of chronic N additions on fine root biomass in four mature hardwood forests in Michigan [30 kg N/ha/yr for over 15 years; [Burton et al. \(2012\)](#)], and in two mature mixed oak (*Quercus*) stands at Harvard Forest [50 or 150 kg N/ha/yr for over 20 years; [Frey et al. \(2014\)](#)]. Likewise, N addition (50 kg N/ha/yr) did not cause significant changes in root biomass in a tropical forest in Puerto Rico ([Cusack et al., 2010](#)). Root turnover did not respond to N addition (30 kg N/ha/yr for 3 years) across 13 successional (20–40 years old) and mature (>90 years old) hardwood stands in central New Hampshire ([Kang et al., 2016](#)). In contrast with the mixed oak stands, fine root biomass decreased in two red pine stands at Harvard Forest [50 or 150 kg N/ha/yr for over 10 years; [Frey et al. \(2014\)](#)], and root biomass also decreased with N additions (50 or 150 kg N/ha/yr for 3 years) in a subtropical, broadleaf forest in China ([Peng et al., 2017](#)).

Observations of how other belowground processes respond to N additions provide further evidence of an increase in the ratio of tree C allocated to aboveground growth and productivity versus the C allocated belowground. In a meta-analysis of forest soil respiration responses to N addition, [Janssens et al. \(2010\)](#) noted that N additions decreased soil respiration overall, with a portion of this effect caused by a decrease in autotrophic respiration. Within forests, autotrophic respiration may make up more than 50% of total soil respiration ([Hasselquist et al., 2012](#)). Much of this autotrophic respiration is mycorrhizal respiration, with the C allocated to and respired by mycorrhizae estimated to account for 9 to 34% of forest soil respiration ([Hasselquist et al., 2012](#); [Heinemeyer et al., 2007](#)).

Mycorrhizal fungi have long been observed to be sensitive to increased forest N availability, particularly ectomycorrhizae because these fungi have direct roles in plant N acquisition, and their production of aboveground fruiting bodies (sporocarps) makes it easier to observe changes in abundance ([Treseder, 2004](#); [Lilleskov et al., 2002](#); [Wallenda and Kottke, 1998](#)). As noted in [Appendix 4](#), when N supply increases, C allocation to ectomycorrhizal fungi decreases, and their abundance and activity decline. In a meta-analysis, [Li et al. \(2015\)](#) found that N additions decreased mycorrhizal colonization of fine root tips by 19% (n = 12). In contrast to the widespread increases in aboveground tree growth, studies of ectomycorrhizal growth and productivity responses to added N have documented nearly universally negative or neutral effects on metrics such as mycorrhizal root colonization, sporocarp abundance, and the abundance of the fungal lipid biomarker 18:2 $\omega$ 6,9 in the soil ([Table 6-2](#)). Although this research is consistent, these studies have limitations because nearly all of this research has been conducted on conifer species and most of the negative effects occur in studies using unrealistically high

rates of N addition (>100 kg N/ha/yr). However, two studies of ectomycorrhizae in Norway spruce forests in Europe have documented significant declines along gradients of ambient N deposition ([Bahr et al., 2013](#); [Kjøller et al., 2012](#)). In particular, ([Kjøller et al., 2012](#)) observed an 80 and 90% decrease in ectomycorrhizal root tip abundance and mycelial production, respectively, across a canopy throughfall N deposition gradient of 27 to 43 kg N/ha/yr in Denmark. [Morrison et al. \(2016\)](#) also observed a decline in the relative abundance of ectomycorrhizal fungal DNA within the soil of the N addition (50 or 150 kg N/ha/yr for 25 years) plots at the oak (*Quercus*)-dominated Harvard Forest in Massachusetts.

Given these decreases in ectomycorrhizal growth and productivity in response to added N, it is not surprising that the amount of C allocated belowground by plants to mycorrhizae can be sensitive to N availability. [Högberg \(2012\)](#) twice added N (100 kg N/ha) over a period of two growing seasons to boreal Scots pine forests in Sweden as part of a short (~2 hour) <sup>13</sup>C canopy labeling experiment. In the 5 weeks following the labeling, 48% less of the <sup>13</sup>C label was found in an ectomycorrhizal fungal lipid biomarker in the soil of the N amended plots. [Hasselquist et al. \(2012\)](#) found that in Scots pine forests in northern Sweden, 6 years of N additions at a rate of 100 kg N/ha/yr decreased respiration from ectomycorrhizae by 40%, but N additions at a rate of 20 kg N/ha/yr increased this respiration by 120%. However, the low N addition did not change the fractional contribution of ectomycorrhizae to total soil respiration. The low N addition treatment also had no effect on ectomycorrhizal sporocarp production, but the high N addition treatment nearly eliminated sporocarp production [99% decrease; [Hasselquist et al. \(2012\)](#)]. The availability of N also appears to influence the transfer of N from mycorrhizal fungi to plants. In a boreal Scots pine forest in Sweden, [Näsholm et al. \(2013\)](#) observed that a single N dose (100 kg N/ha) shifted the dominant sink for a <sup>15</sup>N tracer added 2 weeks later from the cytoplasm of ectomycorrhizal fungi and other soil microorganisms to the pine foliage.

Although ectomycorrhizae are important in many high latitude and temperate ecosystems, particularly forests, most species of terrestrial plants form arbuscular mycorrhizae ([Rillig, 2004](#)). The impact of N deposition on arbuscular mycorrhizae has received less research attention, perhaps partly because these fungi are best known for their role in plant P acquisition ([Rillig, 2004](#)). Arbuscular mycorrhizae community composition and production can be sensitive to added N [[Egerton-Warburton and Allen \(2000\)](#); [van Diepen et al. \(2010\)](#); [Table 6-3](#)], but these effects may not be consistent. [van Diepen et al. \(2010\)](#) reviewed eight previous studies of how intraradical (within root) and extraradical arbuscular mycorrhizal biomass responded to N additions, predominantly in forests, and found inconsistent effects. Intraradical biomass significantly declined in response to N in three studies and increased in two studies, including in the work of

[Garcia et al. \(2008\)](#). In comparison, extraradical biomass was either unresponsive or declined ([van Diepen et al., 2010](#)). Aside from the work of [Garcia et al. \(2008\)](#), other researchers since 2008 have found either neutral or negative effects on metrics of arbuscular mycorrhizal biomass and abundance ([Table 6-3](#)). Observations of decreased arbuscular mycorrhizal biomass span from a subtropical broadleaf evergreen forest in China that experienced a single year of N additions [25 or 50 kg N/ha/yr; [Shi et al. \(2016a\)](#)] to a subalpine Englemann spruce (*Picea engelmannii*) forest in Rocky Mountain National Park that had received more than 15 years of N additions [25 kg N/ha/yr; [Boot et al. \(2016\)](#)].

Notably, the arbuscular mycorrhizal species studied by [Garcia et al. \(2008\)](#) were all understory or subdominant canopy species growing beneath ectomycorrhizal loblolly pines. The increased growth of these larger trees in response to added N may have imposed other resource limitations on the arbuscular mycorrhizal plant species. In general, the response of arbuscular mycorrhizae to N additions may depend upon the relative availability of P or other nutrients. [Johnson et al. \(2003\)](#) found N additions decreased arbuscular mycorrhizae when the soil N:P ratio was low (i.e., P-rich soils), while increasing arbuscular mycorrhizae under high soil N:P (i.e., P-poor soils). Where P is more limiting, plants may allocate more carbon to arbuscular mycorrhizae in order to acquire it ([Egerton-Warburton et al., 2007](#); [Johnson et al., 2003](#)). Thus, the varying availability of soil P may explain in part the seemingly inconsistent response of arbuscular mycorrhizae to N additions.

**Table 6-3 Growth, productivity, and carbon cycle responses of arbuscular mycorrhizal fungi to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">van Diepen et al. (2010)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	13	Extraradical biomass production	Decrease
<a href="#">van Diepen et al. (2010)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	13	Extraradical biomass (16:1ω5c abundance)	Decrease
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Hyphal length	Decrease
<a href="#">van Diepen et al. (2010)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	13	Intraradical biomass (16:1ω5c abundance)	Decrease
<a href="#">Garcia et al. (2008)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	100	1-2	Root colonization (%)	Increase
<a href="#">Mandyam and Jumpponen (2008)</a>	Kansas	C3 and C4 grasses	Addition	100	3	Root colonization (%)	Not significant
<a href="#">Van der Heijden et al. (2008)</a>	Holland	Dune grasses	Addition	100	1	Root colonization (%)	Decrease
<a href="#">Camenzind et al. (2014)</a>	Ecuador	Evergreen tropical forest	Addition	50	3	Root colonization (%)	Decrease
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Root colonization (%)	Not significant
<a href="#">Garcia et al. (2008)</a>	North Carolina	Loblolly pine ( <i>Pinus taeda</i> )	Addition	100	1-2	Soil glomalin content	Not significant

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Aside from mycorrhizal respiration, the other dominant component of autotrophic soil respiration is root respiration. Although [Janssens et al. \(2010\)](#) observed a decrease in autotrophic soil respiration in the presence of N, this decrease was not apparently related to changes in root respiration. In a long-term N addition experiment (30 kg N/ha/yr for +15 years) in four northern hardwoods forests, [Burton et al. \(2012\)](#) found that although root N concentration was a strong predictor of the root respiration rate and N additions had increased root N concentrations, N additions had not increased root respiration because the added N changed the relationship between root N and respiration. [Drake et al. \(2008\)](#) made a similar observation in loblolly pine forests in North Carolina: N additions (100 kg N/ha/yr for 2 years) increased fine root N concentrations but did not impact fine root respiration rates, resulting in an altered tissue N respiration relationship. [Frey et al. \(2014\)](#) also reported that root respiration was unresponsive to long-term N additions (50 or 150 kg N/ha/yr) in oak forests and pine forests in Massachusetts. However, [Hasselquist et al. \(2012\)](#) found that a relatively modest N addition rate (20 kg N/ha/yr for 6 years) increased both root and mycorrhizal respiration in a boreal forest in Sweden that received relatively low rates of ambient N deposition (<5 kg N/ha/yr). Thus, it appears that C allocation to mycorrhizae is more sensitive to N availability than C allocation to root respiration.

In a meta-analysis of the effects of N additions on microbial biomass, [Treseder \(2008\)](#) found that changes in soil respiration were significantly and positively correlated with the response of microbial biomass. Mycorrhizal fungi are major components of forest soil microbial communities, with [Högberg et al. \(2010\)](#) estimating that ectomycorrhizal mycelium made up 39% of total soil microbial biomass in a Swedish boreal forest. At Harvard Forest, [Morrison et al. \(2016\)](#) observed that 59–72% of all fungal operational taxonomic units (OTUs) belonged to ectomycorrhizal fungi. Given the widespread negative effects of added N on mycorrhizal fungi, the results of Treseder's meta-analysis and the broadly negative or neutral effects of N additions on microbial biomass in the studies published since 2008 are unsurprising ([Table 6-4](#)).

**Table 6-4 Abundance and carbon cycle responses of forest soil microorganisms and soil invertebrates to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Treseder (2008)</a>	Meta-analysis	Mostly boreal and temperate forests	Addition	1–600	0.5–57	Bacterial biomass	Not significant
<a href="#">Zhao et al. (2014a)</a>	China (Tibetan plateau)	Spruce-fir ( <i>Picea asperata</i> , <i>Abies faxoniana</i> )	Addition	250	4	Bacterial biomass	Decrease
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Bacterial biomass	Not significant
<a href="#">Treseder (2008)</a>	Meta-analysis	Mostly boreal and temperate forests	Addition	1–600	0.5–57	Fungal biomass	Not significant
<a href="#">Zhao et al. (2014a)</a>	China (Tibetan plateau)	Spruce-fir ( <i>Picea asperata</i> , <i>Abies faxoniana</i> )	Addition	250	4	Fungal biomass	Decrease
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal biomass	Not significant
<a href="#">Enowashu et al. (2009)</a>	Germany	Norway spruce ( <i>Picea abies</i> )	Subtraction	9.7 (–21)	16 (recovery)	Fungal biomass (ergosterol)	Increase
<a href="#">Bebber et al. (2011)</a>	U.K.	Broadleaf temperate forest ( <i>Fraxinus-Acer, Fagus</i> )	Addition	2.8	1	Fungal mycelium growth	Not significant

**Table 6-4 (Continued): Abundance and carbon cycle responses of forest soil microorganisms and invertebrates to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">van Diepen et al. (2017)</a>	Massachusetts (Harvard Forest)	Temperate, mixed hardwood forest ( <i>Quercus velutina</i> , <i>Quercus rubra</i> )	Addition	50, 150	28	Fungal mycelium growth	Not significant overall; varied by fungal isolate
<a href="#">Allison et al. (2008)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> )	Addition	140	5	Fungal sporocarp biomass	Decrease
<a href="#">Lin et al. (2017)</a>	China	Subtropical deciduous and coniferous forests	Addition	47	10 mo	Invertebrate density (pre-dominantly Collembola and Acari) on decomposing litter	Increase on coniferous litter; not significant on deciduous litter
<a href="#">Allison et al. (2008)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> )	Addition	140	5	Microbial biomass	Not significant
<a href="#">Treseder (2008)</a>	Meta-analysis	Mostly boreal and temperate forests	Addition	1–600	0.5–57	Microbial biomass	Decrease
<a href="#">Keeler et al. (2009)</a>	Minnesota (Cedar Creek)	Temperate forests ( <i>Quercus ellipsoidalis</i> , <i>Pinus strobus</i> ) and grassland	Addition	100	5	Microbial biomass	Not significant
<a href="#">van Diepen et al. (2010)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	12	Microbial biomass	Decrease
<a href="#">Hobbie et al. (2012)</a>	Minnesota (Cedar Creek)	Oak and pine forests ( <i>Quercus ellipsoidalis</i> , <i>Pinus strobus</i> )	Addition	100	5	Microbial biomass	Not significant

**Table 6-4 (Continued): Abundance and carbon cycle responses of forest soil microorganisms and invertebrates to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Zhao et al. (2014a)</a>	China (Tibetan plateau)	Spruce-fir ( <i>Picea asperata</i> , <i>Abies faxoniana</i> )	Addition	250	4	Microbial biomass	Decrease
<a href="#">Allison et al. (2010)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> )	Addition	114	7	Microbial biomass C	Decrease
<a href="#">Wang et al. (2015b)</a>	China (southern)	Subtropical pine forest ( <i>Pinus massoniana</i> )	Addition	50, 100	8	Microbial biomass C	Low dose: increase High dose: not significant
<a href="#">Wang et al. (2015b)</a>	China (southern)	Subtropical pine-broadleaf forest ( <i>Pinus massoniana</i> )	Addition	50, 100	8	Microbial biomass C	Not significant
<a href="#">Wang et al. (2015b)</a>	China (southern)	Subtropical broadleaf forests	Addition	50, 100, 150	8	Microbial biomass C	Low, mid dose: not significant High dose: decrease
<a href="#">Peng et al. (2017)</a>	China (Sichuan Province)	Mid-subtropical, evergreen, broadleaf forest	Addition	50, 150	2+	Microbial biomass C	Decrease
<a href="#">Lin et al. (2017)</a>	China	Subtropical deciduous and coniferous forests	Addition	47	10 mo	Microbial biomass on decomposing litter	Not significant
<a href="#">Kang et al. (2016)</a>	New Hampshire	Northern hardwood forests ( <i>Acer saccharum</i> , <i>Fagus grandifolia</i> )	Addition	30	2,3	Microbial respiration	Not significant

**Table 6-4 (Continued): Abundance and carbon cycle responses of forest soil microorganisms and invertebrates to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Saprobic fungal sporocarp abundance	Increase and decrease (N × yr)
<a href="#">van Diepen et al. (2010)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	12	Saprotrophic fungal biomass	Not significant

C = carbon; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

However, forest soil microbial communities are taxonomically and functionally diverse (see [Appendix 6.3.3.3](#)) and have exhibited varying responses to added N ([Zhang et al., 2015c](#); [Treseder, 2008](#)). For instance, [Wang et al. \(2015b\)](#) added N (50, 100, or 150 kg N/ha/yr for 9 years) to pine, broadleaf, and mixed pine-broadleaf forests in southern China; the 50 kg N treatment increased microbial biomass C in the pine forests and the 150 kg N treatment decreased microbial biomass C in the broadleaf forests, but there were no other significant treatment effects. Elsewhere in China, a single year of N additions (25 or 50 kg N/ha/yr) in a subtropical broadleaf evergreen and temperate broadleaf deciduous forest had no effect on total microbial biomass in either forest, but decreased the abundance of Gram-negative bacteria, actinomycetes, and saprotrophic fungi in the subtropical evergreen forest ([Shi et al., 2016a](#)). The addition of 100 kg N/ha/yr to a regenerating Alaskan boreal forest decreased the microbial biomass and the C:N ratio of microbial biomass ([Allison et al., 2010](#); [Allison et al., 2008](#)), while N additions (50 kg N/ha/yr) in Indiana mixed hardwood forests decreased microbial biomass without affecting the microbial C:N ratio ([Midgley and Phillips, 2016](#)). In Sweden, the addition of 100 kg N/ha/yr to boreal forests for 6 years decreased bacterial biomass, but did not significantly affect fungal biomass ([Wardle et al., 2016](#)). The opposite result was observed in pine and hardwood stands at Harvard Forest and in subalpine spruce-fir forests in Rocky Mountain National Park (RMNP). There, N additions decreased fungal biomass, but bacterial biomass was unaffected [50 and 150 kg N/ha/yr for 14 years at Harvard Forest; 25 kg N/ha/yr for 17 years in RMNP; [Boot et al. \(2016\)](#)]. In Michigan, long-term (+15 years) N additions (30 kg N/ha/yr) to northern hardwood forests decreased the abundance of actinobacteria in the surface mineral soil, but not in the soil organic horizon ([Eisenlord and Zak, 2010](#)). Relative to mycorrhizal

fungi, there is less information available regarding the growth and biomass responses of individual domains and other taxonomic groupings within microbial communities ([Table 6-4](#)). Of this finer scale information, most observations are for fungi (sometimes including mycorrhizal fungi), with positive, neutral, and negative effects of added N.

Atmospheric N deposition may affect forest microbial communities and litter decomposition by altering litter chemistry through shifts in forest community composition, increasing litter N concentrations, or changing the secondary chemistry of litter. The two dominant forms of forest plant litter, leaves and fine roots, can each be altered by N additions ([Xia et al., 2015](#)). As noted in the aboveground processes section of this appendix, there is abundant evidence that N deposition can increase foliar N concentrations in trees and there is also a large body of research that the increase in foliar N concentrations will result in increased leaf litter N concentrations ([Aerts, 1996](#)). Since the 2008 ISA, there have been new observations of increased leaf litter N concentrations both in long-term N addition experiments ([van Diepen et al., 2015](#); [Xia et al., 2015](#); [Zak et al., 2008](#)) and along an N deposition gradient [6.8–11.8 kg N/ha/yr; [Talhelm et al. \(2012\)](#)]. Increases in leaf litter N concentrations with greater N deposition are not universal [e.g., [Watmough and Meadows \(2014\)](#)], but in a meta-analysis, [van Diepen et al. \(2015\)](#) observed a >20% increase in tree leaf litter N concentrations in response to N additions. Other changes in forest litter chemistry likely involve changes in more complex physiological and biogeochemical mechanisms ([Du and Fang, 2014](#)). In an old growth boreal forest in China, N additions (20, 50, or 100 kg N/ha/yr for 3 years) decreased leaf litter P concentrations, an effect that could have been caused by changes in either physiological or biogeochemical processes ([Du and Fang, 2014](#)). In a meta-analysis, [van Diepen et al. \(2015\)](#) found that simulated N deposition significantly decreased leaf litter concentrations of P, calcium, manganese, aluminum, and zinc, but did not find significant changes in concentrations of potassium (K), magnesium, boron, iron, or copper. It is not entirely understood how all of these changes in elemental composition impact the composition and function of soil microbial communities, but manganese and calcium are needed for the production of extracellular enzymes that degrade lignin ([van Diepen et al., 2015](#)).

There is a large volume of research about how major biochemical constituents of plant litter such as lignin, cellulose, condensed tannins, and phenolics impact leaf litter decomposition, but less information about how N additions change the abundance of these compounds. [Xia et al. \(2015\)](#) researched the effects of long-term N additions (30 kg N/ha/yr for +15 years) on sugar maple leaf litter and fine root chemistry in four mature northern hardwood forests in Michigan. The N additions increased concentrations of condensed tannins in leaf litter and in fine roots. At three of the four sites, N additions increased the fraction of nonstructural cell wall material and decreased both cellulose and

lignin in leaf litter. On an ecosystem basis, N additions decreased total annual litter (leaf + fine root) fluxes of condensed tannins and soluble protein and increased the fluxes of nonstructural carbohydrates (sugars + starch) and N (Xia et al., 2015). Based on broad decomposition chemistry patterns observed elsewhere, these changes in litter chemistry were expected to increase initial rates of litter decomposition, which contrasts with the decrease in litter turnover rates observed at these sites (Xia et al., 2015). However, changes in tissue chemistry are not ubiquitous; for example, Griepentrog et al. (2015) observed that the abundance and composition of fatty acids in leaf and root tissues in spruce and beech trees in Switzerland were not influenced by added N (70 kg N/ha/yr). Further, while N additions can change plant tissue chemistry, links between litter chemistry and microbial abundance and microbial function are complex [e.g., Baumann et al. (2009)].

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### 6.2.3.3 Forest Lichens

Lichens are widely used as indicators of N deposition impacts on ecosystems, particularly in forests. However, lichens also are important for ecosystem function. For insects, birds, and mammals, lichens represent camouflage, building materials for nests, and a source of food (Brodo et al., 2001). Lichens absorb N, sulfur (S), and other elements from atmospheric deposition and throughfall, and lichens that host cyanobacteria can add significantly to ecosystem N inputs, providing N to other plants (Kobylinski and Fredeen, 2015). In addition, lichens also have a role in hydrologic cycling, have many traditional human uses, and have high potential for pharmaceutical use (McCune and Geiser, 1997). Lichens are symbioses comprised of fungi (mycobiont) and a green alga and/or cyanobacterium [photobiont; Palmqvist (2000); Sundberg et al. (2001)]. Much of the lichen biomass is comprised of fungal (mycobiont) tissue, but the photobiont synthesizes organic compounds, supplying the energy and structural C needed for growth of the lichen. Both the photobiont and the mycobiont require N for growth (Palmqvist, 2000), but the supply of C and N must be coordinated for the development of lichen thalli (Sundberg et al., 2001). Lichens with a cyanobacterial photobiont are N fixing, but those with a green algal photobiont depend on atmospheric deposition for N.

Lichens can be classified based on their response to N pollution. Lichens occurring in areas that receive high N deposition are considered nitrophytic or eutrophic; lichens common in areas receiving low N input are designated acidophytic or oligotrophic (Gai-Oliveira et al., 2005; van Herk, 2001). Atmospheric N deposition can impact lichens through changes in physiological function caused by an increased supply of N or by altering the pH of tree bark hosting the lichen (Jovan, 2008). Although lichens with a green algal photobiont depend on atmospheric deposition as a source of N, these lichens

can also be negatively impacted by N deposition via the accumulation of toxic concentrations of  $\text{NH}_4^+$  within the thallus. Cyanobacteria can grow on either  $\text{NO}_3^-$  or  $\text{NH}_4^+$  sources when administered at nontoxic concentrations, but more rapid growth has been observed with  $\text{NH}_4^+$  than  $\text{NO}_3^-$  (Von Rückert and Giani, 2004). Ammonium is more easily assimilated by lichens; both  $\text{NO}_3^-$  and nitrite must first be reduced to  $\text{NH}_4^+$  before assimilation can occur (Von Rückert and Giani, 2004). The 2008 ISA noted that lichens with a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens (Dahlman et al., 2002; Hallingbäck and Kellner, 1992; Hallingbäck, 1991). In part, the sensitivity of lichens to increasing N deposition is a function of the mechanisms with which that lichen can respond to high N supply, such as decreasing N uptake or assimilating N into nontoxic forms such as arginine (Gaio-Oliveira et al., 2005; Dahlman et al., 2002).

Since the 2008 ISA, new research on the impact of N deposition on the growth and physiology of forest lichens has both confirmed that lichen abundance is sensitive to N deposition and provided further insight on the growth and physiological changes that occur when lichens are exposed to exogenous N (Table 6-5). For example, previous research had suggested that lichens were most sensitive to N as ammonia (Sheppard et al., 2011; Jovan, 2008). However, a study of lichen communities on California black oak (*Quercus kelloggii*) forests at 22 sites in the Los Angeles Basin in California, Jovan et al. (2012) found that the abundance of eutrophic lichen species was only weakly related to gaseous  $\text{NH}_3$  concentrations. Instead, the strongest N pollution-related predictor of eutrophic lichen abundance was total N deposition (as canopy throughfall). Further, at the relatively neutral bark pH levels in the Los Angeles Basin, there was no influence of pH on the abundance of eutrophic lichen species. The abundance of eutrophic lichens was also best correlated with total throughfall N deposition in southeastern Alaska (Schirokauer et al., 2014a). This research provides strong evidence that total N deposition, not the deposition of a particular form of N, is the primary driver of changes in the growth, physiology, and composition of epiphytic lichens.

Increases in lichen thalli N concentrations in response to added N have been widely observed in the U.S. and Europe (Table 6-5), even at relatively low rates of atmospheric N deposition. For instance, McMurray et al. (2013) measured throughfall N deposition and sampled lichen thalli N concentrations at sites near the Bridger-Teton National Forest Wilderness that were at increasing distances downwind of a major oil and natural gas production field. Although the observed rates of N deposition were only 0.8 to 4.1 kg N/ha/yr along this gradient, thalli N concentrations in *Usnea lapponica* approximately doubled from ~1.2 to 2.4%. In southeastern Alaska, Schirokauer et al. (2014a) found increases in thalli N concentrations along an even smaller range of N

deposition (0.05 to 1.05 kg N/ha/yr), a pollution gradient attributed to cruise ship emissions.

In southern California, [Riddell et al. \(2008\)](#) transplanted thalli from the oligotrophic lichen *Ramalina menziesii* from relatively unpolluted sites into fumigation chambers under moderate and high HNO<sub>3</sub> concentrations (19.9–25 µg/m<sup>3</sup> and 26.4–35.3 µg/m<sup>3</sup>, respectively). The HNO<sub>3</sub> fumigation caused significant declines in chlorophyll content and C exchange capacity compared to thalli in control chambers. This research was later expanded to six species known to vary in sensitivity to N pollution ([Riddell et al., 2012](#)). Fumigation with HNO<sub>3</sub> (daily peaks near 50 ppb) decreased chlorophyll content, chlorophyll fluorescence, gross photosynthesis, and dark respiration in three of the five N sensitive species; while only photosynthesis declined in the other two N sensitive species. Four of the N sensitive species were tested for fumigation effects on cell membrane ion leakage; overall ion leakage, and specifically K<sup>+</sup> ion leakage, were increased by HNO<sub>3</sub> fumigation in all species.

Johansson and colleagues conducted a series of experiments in Sweden intended to understand the physiological responses of epiphytic lichens to added N ([Johansson et al., 2012](#); [Johansson et al., 2011](#); [Johansson et al., 2010](#)). In a whole-tree N addition experiment in a spruce forest in boreal Sweden, low rates of N addition (6, 12.5 kg N/ha/yr for 3 years) increased total lichen abundance, but higher N addition rates (25, 50 kg N/ha/yr) decreased total lichen abundance ([Johansson et al., 2012](#)). However, there was considerable variation among lichen species in the N addition treatment rate that resulted in optimal growth. For two of the lichen species in that experiment, *Alectoria sarmentosa* and *Platismatia glauca*, [Johansson et al. \(2010\)](#) quantified physiological responses to N additions. Thalli N concentrations increased in both species at the two highest N addition rates (25, 50 kg N/ha/yr). There was a significant positive relationship between cumulative N dose and chlorophyll content, but the N additions did not affect thalli P concentrations. In a separate experiment with a single much higher N addition rate (300 kg N/ha/yr for one season), [Johansson et al. \(2011\)](#) examined the physiological and growth responses of three lichen species. All three lichen species exhibited increased tissue N concentrations, increased chlorophyll concentrations, increased photosynthesis, and increased growth of the photobiont. However, mycobiont growth decreased in two species and was unchanged in the third. Total biomass changes among the three species were positive, neutral, and negative.

**Table 6-5 Growth and physiology responses of forest epiphytic lichens to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Nybakken et al. (2009)</a>	Sweden and Norway	Boreal forests	Addition	50	1	C-based secondary compounds	<u>Three species</u> : not significant <u>One species</u> : decrease
<a href="#">Riddell et al. (2008)</a>	California (Los Angeles basin)	Oak forests ( <i>Quercus douglasii</i> )	HNO <sub>3</sub> gas fumigation	0, 15, 30 mg/m <sup>3</sup>	0.08	Chlorophyll content	Decrease
<a href="#">Nybakken et al. (2009)</a>	Sweden and Norway	Boreal forest	Addition	50	1	Chlorophyll content	<u>Three species</u> : increase <u>One species</u> : not significant
<a href="#">Johansson et al. (2010)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	3	Chlorophyll content	Increase
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Chlorophyll content	Increase
<a href="#">Asplund et al. (2010)</a>	Sweden and Norway	Boreal forests	Addition	50	1	Gastropod feeding preference	<u>Three of four lichen species</u> : decrease <u>One species</u> : increase
<a href="#">Strengbom and Nordin (2008)</a>	Sweden	Boreal forest	Addition	150 (twice)	Additions 22 and 30 yr prior to surveys	Lichen abundance	Decrease
<a href="#">Johansson et al. (2012)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	4	Lichen abundance	<u>Six and 12.5 doses</u> : increase <u>25 and 50 doses</u> : decrease
<a href="#">Will-Wolf et al. (2015)</a>	Northeastern U.S.	Forests	Ambient	Not stated	n/a	Lichen abundance	Decrease

**Table 6-5 (Continued): Growth and physiology responses of forest epiphytic lichens to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Riddell et al. (2008)</a>	California (Los Angeles Basin)	Oak forests ( <i>Quercus douglasii</i> )	HNO <sub>3</sub> gas fumigation	0, 15, 30 mg/m <sup>3</sup>	0.08	Membrane ion leakage	Increase
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Mycobiont growth	<u>One species:</u> decrease <u>Two species:</u> not significant
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Photobiont growth	Increase
<a href="#">Riddell et al. (2008)</a>	California (Los Angeles Basin)	Oak forests ( <i>Quercus douglasii</i> )	HNO <sub>3</sub> gas fumigation	0, 15, 30 mg/m <sup>3</sup>	0.08	Photosynthesis	Decrease
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Photosynthesis	Increase
<a href="#">Riddell et al. (2008)</a>	California (Los Angeles Basin)	Oak forests ( <i>Quercus douglasii</i> )	HNO <sub>3</sub> gas fumigation	0, 15, 30 mg/m <sup>3</sup>	0.08	Respiration	Decrease
<a href="#">Johansson et al. (2010)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	3	Thalli N %	<u>Six and 12.5 doses:</u> not significant <u>25 and 50 doses:</u> increase
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Thalli N %	Increase
<a href="#">McMurray et al. (2013)</a>	Wyoming	Conifer forests	Ambient	0.8–4.1	n/a	Thalli N %	Increase
<a href="#">Root et al. (2013)</a>	Western North America	Forests	Ambient	0.1–39.3	n/a	Thalli N %	Increase
<a href="#">Boltersdorf et al. (2014)</a>	Germany	Forests	Ambient	2.2–9.5	n/a	Thalli N %	Increase
<a href="#">Schirokauer et al. (2014a)</a>	Alaska (southeast)	Conifer forests	Ambient	0.05–1.05	n/a	Thalli N %	Increase
<a href="#">McMurray et al. (2015)</a>	Idaho, Wyoming, Montana	Conifer forests	Ambient	0.5–4.3	n/a	Thalli N %	Increase

**Table 6-5 (Continued): Growth and physiology responses of forest epiphytic lichens to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Johansson et al. (2010)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	3	Thalli P %	Not significant
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Thalli P %	<u>Two species:</u> increase <u>One species:</u> not significant
<a href="#">Nybakken et al. (2009)</a>	Sweden and Norway	Boreal forest	Addition	50	1	Thallus growth	<u>Three species:</u> increase <u>One species:</u> not significant
<a href="#">Johansson et al. (2011)</a>	Sweden	Boreal forest	Addition	300	1	Thallus growth	<u>One species:</u> increase <u>One species:</u> not significant <u>One species:</u> decrease

C = carbon; ha = hectare; HNO<sub>3</sub> = nitric acid; kg = kilogram; m = meter; mg = milligram; N = nitrogen; n/a = not applicable; P = phosphorus; yr = year.

Notes: single studies are reported more than once if multiple endpoints were measured. References are ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

In another experiment in Scandinavia, lichens collected from Sweden and Norway were exposed to added N (50 kg N/ha/yr for one season) to understand whether this addition altered the concentrations of the C based secondary compounds (CBSCs) thought to protect lichens from herbivores and whether it affected feeding preferences of gastropod herbivores ([Asplund et al., 2010](#); [Nybakken et al., 2009](#)). The N additions decreased the concentrations of CBSCs in one species, but had no effect on the other three lichen species ([Nybakken et al., 2009](#)). The gastropod herbivores preferred to feed on lichens from the control treatment for three of the four species, while preferring the thalli from the N addition treatment for the fourth lichen species ([Asplund et al., 2010](#)). Notably, the species exhibiting the decrease in CBSCs was not the species that was preferable to herbivores in the N addition treatment. Together, these results suggest that N deposition may alter lichen community composition by shifting herbivore feeding preferences.

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#### 6.2.3.4 Net Ecosystem Production and Carbon Sequestration Response

The 2008 ISA concluded that N deposited onto terrestrial ecosystems increased net primary productivity (NPP) and ecosystem C storage (kg C/ha). However, the extent to which this additional N stimulates forest C sequestration was a topic of debate [e.g., [Nadelhoffer et al. \(1999b\)](#); [Magnani et al. \(2007\)](#); [De Schrijver et al. \(2008\)](#); [de Vries et al. \(2008\)](#); [Sutton et al. \(2008\)](#)]. [Magnani et al. \(2007\)](#) correlated net ecosystem production (NEP; kg C/ha/yr) with estimated rates of N deposition for 20 forested sites in North America and Europe, which resulted in an estimate of 725 kg C sequestered per kg of added N (i.e., kg C/kg N). However, this estimate was widely criticized and a reanalysis of these data produced an estimate of C sequestration more than an order of magnitude lower [68 kg C/kg N; [Sutton et al. \(2008\)](#)].

Since the 2008 ISA, several new syntheses and a number of field experiments and modeling studies have provided further evidence that N deposition increases NPP, NEP, and ecosystem C content, and that have more tightly constrained estimates of the response of plant, soil, and ecosystem C content to N deposition. [Nave et al. \(2009b\)](#) estimated that up to 15% of the N needed to support NPP in a northern Michigan aspen forest was supplied by atmospheric N deposition. In China, N additions of 20, 50, or 100 kg N/ha/yr to an old growth boreal forest stimulated aboveground tree productivity by 5, 7, and 23% during the second and third years of the experiment ([Du and Fang, 2014](#)). [Chen et al. \(2011\)](#) found that a Douglas fir stand in the Pacific Northwest increased NEP by 2,500 kg/ha (+83%) in the first year after receiving 200 kg N/ha of urea, both from decreased respiration (930 kg/ha) and increased gross primary production (157 kg/ha). Increases in ecosystem C content have been noted in long-term N addition experiments in Massachusetts ([Frey et al., 2014](#)), Michigan ([Pregitzer et al., 2008](#)), and New York ([Lovett et al., 2013](#)). Using a process model that neglected changes in stand ontogeny, disturbances, and shifts in forest management, [de Vries and Posch \(2011\)](#) concluded that N deposition was a dominant determinant of European forest productivity throughout the 20th century.

Since the 2008 ISA, a variety of techniques have been used to quantify the C sequestration response of forests to N deposition, particularly in Europe ([Frey et al., 2014](#)). Using a <sup>15</sup>N-labeling technique, [Gundale et al. \(2014\)](#) observed a linear relationship between C sequestration and N additions of up to 50 kg N/ha/yr that had a slope of 16 kg C/kg N in a Swedish boreal forest. [Hyvönen et al. \(2008\)](#) synthesized soil and plant C sequestration data from 15 long-term (14–30 year) N addition experiments in boreal (*Picea abies*, *Pinus sylvestris*) forests in Sweden and Finland and estimated that C sequestration averaged 23 kg C/kg N for *Picea* and 30 kg C/kg N for *Pinus*, with an

additional 11 kg C/kg N within the soil. Also in Sweden, [Eliasson and Ågren \(2011\)](#) applied an ecosystem model to Scots pine (*Pinus sylvestris*) forests and estimated that ecosystem C stocks increased by 24,123 kg/ha in response to a cumulative 224 kg N/ha added over a century (108 kg C/kg N). Based on the stimulation of photosynthesis and assumptions about the fraction of photosynthate that is ultimately transformed into tree biomass, [Fleischer et al. \(2013\)](#) estimated that N deposition stimulates C sequestration by 25 kg C/kg N.

Forest inventory studies typically make use of one or more decades of tree growth data from national or continental monitoring networks and relate the variation in this growth to differences in N deposition and other environmental factors. Across western and northern Europe, [Solberg et al. \(2009\)](#) found that variation in tree volume increment was positively related to N deposition and summer temperature, particularly for pine (*Pinus*) and spruce (*Picea*), with similar, but weaker, relationships for beech (*Fagus*) and oak (*Quercus*). The overall model estimated C sequestration was 19 kg C/kg N. [Eastaugh et al. \(2011\)](#) analyzed Norway spruce (*Picea abies*) growth data from the Austrian National Forest Inventory and estimated that N deposition sequestered 21.6 kg C/kg N in aboveground tree biomass during the latter half of the 21st century. [Etzold et al. \(2014\)](#) and [Ferretti et al. \(2014\)](#) took similar approaches with 18 inventory plots in Switzerland and 25 inventory plots in Italy, respectively. Both studies found a positive relationship between N deposition and NPP, but the authors were unable to isolate NPP effects from other environmental factors.

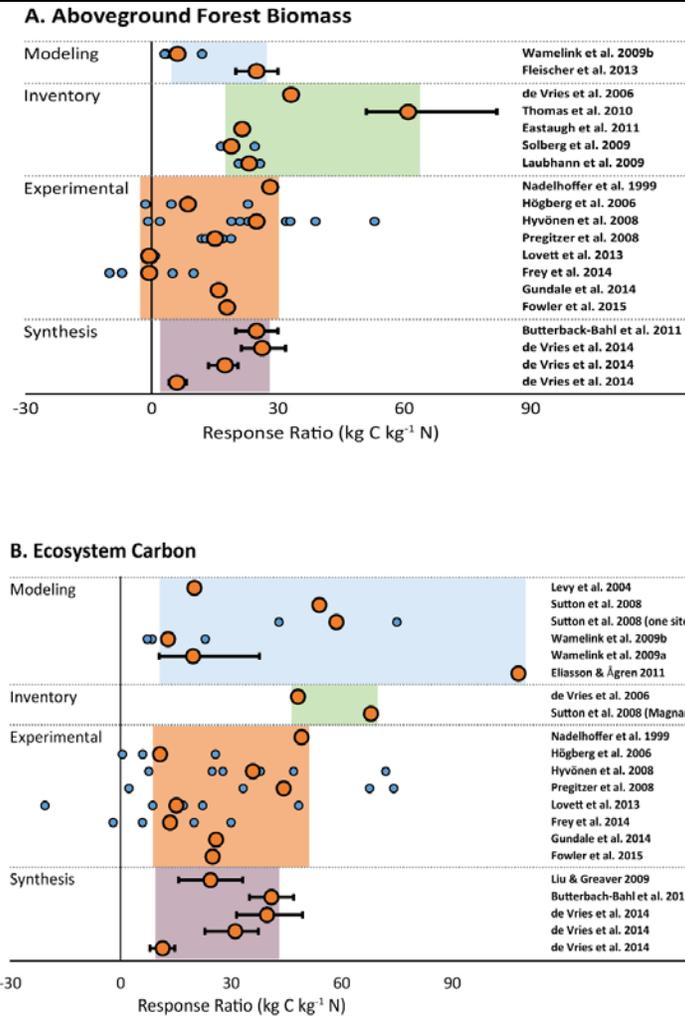
Within the U.S., the analysis of forest inventory data in the northeastern U.S. by [Thomas et al. \(2010\)](#) estimated that N deposition increased aboveground tree biomass at 61 kg C/kg N; a rough estimate including belowground C increased this to 73 kg C/kg N. [Pinder et al. \(2012\)](#) modified the estimates of [Thomas et al. \(2010\)](#), using alternate values for N deposition, more complex belowground biomass estimates, and changes in soil C pools, to produce an enhancement of 65 kg C/kg N. One criticism of the inventory and modeling studies is that they match variation in growth only to current levels of N deposition and neglect the potential effects of previous N deposition at that site. Thus, the influence of current N deposition may be exaggerated ([Högberg, 2012](#)). In addition, estimates of tree growth and biomass production typically rely on the application of equations that predict tree biomass based on measurements of tree stem diameter, either alone or in combination with tree height measurements. [Ibanez et al. \(2016\)](#) observed that at the sites in Michigan where N additions had increased tree growth ([Pregitzer et al., 2008](#)), the N additions had also altered the allometric patterns of sugar maple tree growth so that at a given tree stem diameter at breast height (1.4 m), the trees receiving N additions were taller than those in the control plots. This meant that stemwood biomass equations underestimated tree size for trees receiving N additions ([Ibanez et al., 2016](#)). If

these results apply in other environments and with other tree species, this implies that allometric biomass equations may be underestimating tree biomass in regions experiencing high rates of atmospheric N deposition and that estimates of C sequestration due to tree growth increases [e.g., [Thomas et al. \(2010\)](#)] may be too low.

In the long-term N addition experiment at Harvard Forest ([Frey et al., 2014](#)), the C response to N deposition ranged from  $-2$  to  $30$  kg C/kg N among the four treatment types ( $50$  or  $150$  kg N/ha/yr; *Pinus* or *Quercus* forests) and the amount of C sequestered in the soil was equal to or greater than the amount of C sequestered in trees. Similar results showing more C sequestration in the soil than in trees were found in N addition experiments at four Michigan forests [ $23$  kg C/kg N soil vs.  $17$  kg C/kg N tree; [Pregitzer et al. \(2008\)](#)] and in the Catskills ([Lovett et al., 2013](#)). Several syntheses of forest C sequestration changes in response to N deposition have been conducted ([Tian et al., 2016a](#); [Frey et al., 2014](#); [Pinder et al., 2013](#); [Pinder et al., 2012](#); [Butterbach-Bahl et al., 2011](#); [Janssens et al., 2010](#); [Liu and Greaver, 2009](#)), producing estimates of  $12$ – $41$  kg C/kg N. Often these synthesis studies are meta-analyses; however, [de Vries et al. \(2014a\)](#) took a novel approach of combining estimates of ecosystem N retention with N allocation and C:N ratios to develop stoichiometric estimates of N deposition for tropical, temperate, and boreal ecosystems. Although this approach involves a number of important assumptions about biogeochemistry and tree physiology, estimates for tree and soil C sequestration response rates were similar to values from other syntheses ([Figure 6-3](#)). In their study of aboveground NPP responses per unit of added N, [Tian et al. \(2016a\)](#) found that the average forest response was a  $3.75\%$  increase in NPP per g of N.

Variation in these estimates is likely influenced by the research approach. For instance, the model used by [Eliasson and Ågren \(2011\)](#) predicted almost no N losses from the forests due to leaching or denitrification, which are both widely reported at high rates of N deposition. However, environmental and ontological factors also appear to influence the sensitivity of forest C sequestration to N deposition. Using the G'DAY model, [Dezi et al. \(2010\)](#) found recent forest harvests, shifts in plant C allocation away from roots, and canopy N uptake all increased the C sequestration response to N deposition. Among the 15 experiments synthesized by [Hyvönen et al. \(2008\)](#), the amount of C sequestered ranged from  $-0.8$  to  $61$  kg C/kg N, with greater increases in kg C/kg N at lower N doses. The amount of additional tree C sequestered was small in plots that had low soil O-horizon C:N ratios (near 25) and the amount of C sequestered by added N increased with O-horizon C:N until C:N reached 35. Among *Picea* forests, young stands were more responsive than old stands, but no such effect was apparent for *Pinus*. In addition, C sequestration increased more in plots simultaneously supplied with K and P ([Hyvönen et al., 2008](#)). [Janssens et al. \(2010\)](#) acknowledged the role of stand age in altering the

dynamic of C cycling, explicitly removing young, rapidly expanding forests from some portions of the meta-analysis.



C = carbon; kg = kilogram; N = nitrogen.

Notes: Studies are grouped by research approaches, including process modeling, forest inventory analyses, long-term N addition experiments, or data syntheses. The citations to the right represent studies that quantified at least one of three aspects of forest C sequestration responses to N (forest biomass, soil C, or ecosystem C). The large orange circles represent the mean response for each study and the smaller blue circles represent individual estimates (replicate plots, study sites, or model simulations). The colored boxes bound the range of mean responses.

Data sources: [Nadelhoffer et al. \(1999b\)](#); [Levy et al. \(2005\)](#); [de Vries et al. \(2006\)](#); [Högberg et al. \(2006\)](#); [Hyvönen et al. \(2008\)](#); [Pregitzer et al. \(2008\)](#); [Sutton et al. \(2008\)](#); [Laubhann et al. \(2009\)](#); [Liu and Greaver \(2009\)](#); [Solberg et al. \(2009\)](#); [Wamelink et al. \(2009a\)](#); [Wamelink et al. \(2009b\)](#); [Thomas et al. \(2010\)](#); [Butterbach-Bahl et al. \(2011\)](#); [Eastaugh et al. \(2011\)](#); [Eliasson and Ågren \(2011\)](#); [Fleischer et al. \(2013\)](#); [Lovett et al. \(2013\)](#); [de Vries et al. \(2014a\)](#); [Gundale et al. \(2014\)](#); [Frey et al. \(2014\)](#); [Fowler et al. \(2015\)](#).

**Figure 6-3** Studies reporting the response of forest (A) aboveground biomass carbon sequestration and (B) ecosystem carbon sequestration to nitrogen deposition or long-term nitrogen additions.

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## 6.2.4 Arctic and Alpine Tundra and Grasslands

Tundra areas in the U.S. are concentrated in high-elevation alpine areas in the western U.S. and high-latitude areas in Alaska. Although alpine ecosystems are limited in their spatial extent, these ecosystems are important components of many national parks (e.g., Rocky Mountain, Yosemite, Sequoia-Kings Canyon, Mount Rainier) and other Class I areas within these regions. Nitrogen deposition rates in Arctic tundra areas are generally low, but there is a distinct impact of anthropogenic pollution on N cycling that could increase with further industrial development at high latitudes ([Holtgrieve et al., 2011](#)). In addition, although baseline rates of N deposition in Arctic deposition tend to be low, isolated precipitation events carrying air masses from industrialized or agricultural regions can result in high rates of deposition ([Kuhnel et al., 2011](#)). In Svalbard (north of Norway), 10% of precipitation events were responsible for 93% of all N deposited in snow or rain ([Kuhnel et al., 2011](#)).

For Arctic tundra ecosystems, the 2008 ISA identified a single N addition experiment and cited two studies from the 1980s on the effects of decreased N availability. The two studies on plants grown under conditions of low N availability found that tundra plants responded by increasing root growth ([Bloom et al., 1985](#)) or increasing N use efficiency ([Chapin, 1980](#)). The N addition (50 or 100 kg N/ha/yr) experiment began in 1981 and caused changes in plant community composition ([Shaver et al., 2001](#)) and increases in aboveground plant growth, but losses in soil C pools that resulted in decreased ecosystem C content ([Mack et al., 2004](#)).

The 2008 ISA reported that alpine plant species are often sensitive to N enrichment because many are adapted to low nutrient availability ([Bowman et al., 2006](#)) and that N deposition may increase alpine plant productivity and alter plant community composition ([Neff et al., 2002](#); [Seastedt and Vaccaro, 2001](#); [Bowman et al., 1995](#)). Some alpine plants in the southern Rocky Mountains exhibit greater growth in response to increased N, but this species-specific growth response to N deposition is one of the mechanisms that can change community composition ([Bowman et al., 1993](#)). Many of the dominant plant species do not respond to additional N supply with increased production. Rather, many subdominant species increase in abundance when the N supply is increased ([Fenn et al., 2003a](#)). The 2008 ISA also noted that the effects of N deposition can be spatially heterogeneous in alpine tundra ecosystems, with areas that accumulate wind-blown snow receiving higher rates of winter N deposition ([Bowman and Steltzer, 1998](#)). Further, the 2008 ISA also cited evidence that chronic N additions to alpine ecosystems can accelerate the decomposition of some soil C fractions, while preserving other C fractions ([Neff et al., 2002](#)).

Research since 2008 on the effects of added N on alpine and Arctic ecosystems has included broad syntheses, a number of experiments in both Europe and Asia, and additional research in North America. [Bouskill et al. \(2014\)](#) conducted a meta-analysis of high-latitude N addition experiments and compared these results with model simulations from the Community Land Model (CLM), the land component of the Community ESM (CESM). [Bouskill et al. \(2014\)](#) identified 37 N addition field experiments from 14 sites in North America and Europe. In this synthesis, N additions significantly stimulated gross primary production (GPP;  $+44 \pm 7\%$ , mean  $\pm$  standard error), while soil respiration declined by  $12 \pm 7\%$ . Total aboveground plant biomass was not significantly affected by N additions (increase of  $15 \pm 22\%$ ), but vascular plant biomass increased by  $33 \pm 8\%$ . Notably, the modeled responses produced from CLM matched observations only for two parameters: soil organic matter and GPP. These matches occurred only under the lowest rates of N addition ( $<1$  kg N/ha/yr), suggesting that N cycling processes or parameters are not well characterized in tundra ecosystems.

Three multiyear experiments span the period before and after the 2008 ISA was published ([Table 6-6](#)). In a subalpine shrub heathland in Scotland, [Britton and Fisher \(2007\)](#) examined the effects on plant communities of burning, clipping, and N additions of 0, 10, 20, or 50 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$  for 5 years. Since the 2008 ISA was published, [Britton et al. \(2008\)](#) observed that N additions increased shoot N concentration in the dominant shrub *Calluna vulgaris*, with significant increases only at the two highest levels of N addition. In assessing plant growth, [Britton and Fisher \(2008\)](#) found increased growth of the dominant alpine shrub *Calluna vulgaris* and of *Vaccinium vitis-idaea* with N additions of 20 and 50 kg N/ha/yr, but no effect with 10 kg N/ha/yr or with N at any level on three other shrub species. Notably, in a greenhouse study with *Calluna vulgaris* plants from four different geographic populations, [Meyer-Gruenefeldt et al. \(2016\)](#) observed that N additions (35 kg N/ha/yr for 2 years) increased aboveground biomass in all populations, but that responses varied by factor of two between populations. Belowground biomass was unresponsive to N addition in the greenhouse study, resulting in decreased root:shoot ratios and potentially making the plants more susceptible to drought. In a second study within Scotland, [Britton and Fisher \(2010\)](#) found that N additions of 7.5, 12.5, and 22.5 kg N/ha/yr increased thallus N concentration in three of four alpine lichen species, but decreased growth of two species and did not significantly affect growth in three other species.

**Table 6-6 Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Kelley and Epstein (2009)</a>	Alaska	Tundra meadow ( <i>Dryas integrifolia</i> , <i>Eriophorum vaginatum</i> , <i>Carex</i> spp.)	Addition	100	3	Aboveground plant biomass	Not significant
<a href="#">Volk et al. (2011)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	5, 10, 25, 50	4	Aboveground plant biomass	<u>Low dose</u> : not significant <u>Other doses</u> : increase
<a href="#">Bassin et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Carex sempervirens</i> )	Addition	50	2	Aboveground plant biomass	Increase
<a href="#">Blanke et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>F. violacea</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Aboveground plant biomass	Increase
<a href="#">Blanke et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Festuca violacea</i> , <i>Leontodon helveticus</i> , <i>Carex sempervirens</i> , <i>Trifolium alpinum</i> )	Addition	50	1	Aboveground plant biomass	<u>Festuca</u> : increase <u>Leontodon</u> , <u>Carex</u> , <u>Trifolium</u> : not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Bowman et al. (2012)</a>	Colorado (Rocky Mountain National. Park)	Dry sedge meadow ( <i>Kobresia myosuroides</i> , <i>Carex rupestris</i> )	Addition	5, 10, 30	4	Aboveground plant biomass	Not significant
<a href="#">Onipchenko et al. (2012)</a>	Russia (Caucasus Mountains)	Lichen heath ( <i>Cetraria islandica</i> )	Addition	90	5	Aboveground plant biomass	Increase
<a href="#">Onipchenko et al. (2012)</a>	Russia (Caucasus Mountains)	Alpine grassland ( <i>Festuca varia</i> )	Addition	90	5	Aboveground plant biomass	Not significant
<a href="#">Onipchenko et al. (2012)</a>	Russia (Caucasus Mountains)	Alpine meadow ( <i>Geranium gymnocaulon</i> )	Addition	90	5	Aboveground plant biomass	Not significant
<a href="#">Onipchenko et al. (2012)</a>	Russia (Caucasus Mountains)	Alpine snowbeds ( <i>Sibbaldia procumbens</i> )	Addition	90	5	Aboveground plant biomass	Not significant
<a href="#">Bouskill et al. (2014)</a>	North America and Europe	Arctic and high latitude	Addition	Average: 72 range: 1–100	Meta-analysis	Aboveground plant biomass	Not significant
<a href="#">Gill (2014)</a>	Utah	Subalpine meadow ( <i>Achnatherum lettermanii</i> , <i>Artemisia michauxiana</i> )	Addition	70	3	Aboveground plant biomass	Increase
<a href="#">Volk et al. (2014)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	5, 10, 25, 50	7	Aboveground plant biomass	Increase

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Zamin et al. (2014)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Vaccinium vitis-idaea</i> , <i>Rhododendron subarcticum</i> , <i>Andromeda polifolia</i> )	Addition	10, 100	8	Aboveground plant biomass	<u>Low dose</u> : not significant <u>High dose</u> : decrease
<a href="#">Farrer et al. (2015)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	229	7	Aboveground plant biomass	<u>Deschampsia</u> : increase <u>Geum</u> : decrease
<a href="#">Song and Yu (2015)</a>	China (Tibetan Plateau)	Alpine meadow ( <i>Kobresia humilis</i> , <i>Elymus nutans</i> , <i>Stipa aliena</i> , <i>Festuca ovina</i> )	Addition	3.75, 15, 75	8	Aboveground plant biomass	<u>Low and mid dose</u> : not significant <u>High dose</u> : increase
<a href="#">Blanke et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>F. violacea</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Aboveground plant biomass (functional group)	<u>Grasses</u> : increase <u>Forbs, sedges, legumes</u> : not significant
<a href="#">Bassin et al. (2013)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Arnica montana</i> , <i>Gentiana acaulis</i> )	Addition	5, 10, 25, 50	7	Aboveground plant biomass (functional group)	<u>Sedge, grass</u> : increase <u>Forbs, legumes</u> : not significant
<a href="#">Bouskill et al. (2014)</a>	North America and Europe	Arctic and high latitude	Addition	Average: 72 range: 1–100	Meta-analysis	Aboveground plant biomass (vascular)	Increase

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Zamin and Grogan (2012)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Betula glandulosa</i> , <i>Vaccinium vitis-idaea</i> , <i>Rhododendron subarcticum</i> )	Addition	10, 100	7	Aboveground plant growth ( <i>Betula</i> )	<u>Low dose</u> : not significant <u>High dose</u> : increase
<a href="#">Blanke et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Festuca violacea</i> , <i>Leontodon helveticus</i> , <i>Carex sempervirens</i> , <i>Trifolium alpinum</i> )	Addition	50	1	Belowground plant biomass	<u>Festuca</u> : increase <u>Leontodon</u> : decrease <u>Carex, Trifolium</u> : not significant
<a href="#">Volk et al. (2014)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	10, 50	7	Belowground plant biomass	Increase
<a href="#">Arens et al. (2008)</a>	Greenland	Dwarf shrub/herb tundra ( <i>Salix arctica</i> , <i>Carex rupestris</i> , <i>Dryas integrifolia</i> )	Addition	5, 10, 50	3	Belowground respiration	<u>Low and high dose</u> : not significant <u>Mid dose</u> : increase
<a href="#">Armitage et al. (2011)</a>	U.K.	Bryophyte heathlands ( <i>Ranacomitrium lanuginosum</i> )	Ambient	Reciprocal transplant (7.2 with 8.2–32.9)	2	Bryophyte biomass ( <i>R. lanuginosum</i> )	Decrease

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Bryophyte cover	Decrease
<a href="#">Armitage et al. (2012)</a>	Europe (North Atlantic)	Alpine heathlands ( <i>Ranacomitrium lanuginosum</i> )	Ambient	0.6–39.6	n/a	Bryophyte cover ( <i>R. lanuginosum</i> )	Decrease
<a href="#">Armitage et al. (2011)</a>	U.K.	Bryophyte heathlands ( <i>Ranicomitrium lanuginosum</i> )	Ambient	Reciprocal transplant (7.2 with 8.2–32.9)	2	Bryophyte growth ( <i>R. lanuginosum</i> )	Increase
<a href="#">Armitage et al. (2012)</a>	Europe (North Atlantic)	Alpine heathlands ( <i>Ranicomitrium lanuginosum</i> )	Ambient	0.6–39.6	n/a	Bryophyte growth ( <i>R. lanuginosum</i> )	Increase
<a href="#">Armitage et al. (2011)</a>	U.K.	Bryophyte heathlands ( <i>Ranicomitrium lanuginosum</i> )	Ambient	Reciprocal transplant (7.2 with 8.2–32.9)	2	Bryophyte tissue N % ( <i>R. lanuginosum</i> )	Increase
<a href="#">Armitage et al. (2012)</a>	Europe (North Atlantic)	Alpine heathlands ( <i>Ranicomitrium lanuginosum</i> )	Ambient	0.6–39.6	n/a	Bryophyte tissue N % ( <i>R. lanuginosum</i> )	Increase
<a href="#">Armitage et al. (2012)</a>	Europe (North Atlantic)	Alpine heathlands ( <i>Ranicomitrium lanuginosum</i> )	Ambient	0.6–39.6	n/a	Bryophyte tissue P % ( <i>R. lanuginosum</i> )	Increase
<a href="#">Wang et al. (2017a)</a>	China (Tibetan Plateau)	Alpine shrubland ( <i>Sibiraea angustata</i> )	Addition	20, 50, 100	1.5	Ecosystem C pools (shrubs, grass, litter and soil)	Increase; linear increase with N

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Arens et al. (2008)</a>	Greenland	Dwarf shrub/herb tundra ( <i>Salix arctica</i> , <i>Carex rupestris</i> , <i>Dryas integrifolia</i> )	Addition	5, 10, 50	3	Ecosystem respiration	Increase
<a href="#">Volk et al. (2011)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	10, 50	4	Ecosystem respiration	Not significant
<a href="#">Liu et al. (2017b)</a>	China (Tibetan Plateau)	Alpine meadow	Addition	50	2	Flowering height of three perennial forb species	Increase in flowering height in two of the species; not significant for the remaining species
<a href="#">Yuan et al. (2016)</a>	Colorado (Niwot Ridge)	Alpine meadow	Addition	50–200 (varied over the 20 yr duration; averaged ca. 85)	20	Foliage biomass (total-graminoid and forb; graminoid only; and forb only)	Not significant for total and forb only biomass; graminoid biomass increased in moist and wet meadow type, but not dry meadow type
<a href="#">Bassin et al. (2009)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Foliar N %	<u>Six species:</u> increase <u>Two species:</u> not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Kelley and Epstein (2009)</a>	Alaska	Tundra meadow ( <i>Dryas integrifolia</i> , <i>Eriophorum vaginatum</i> , <i>Carex</i> spp.)	Addition	100	3	Foliar N %	Increase
<a href="#">Bishop et al. (2010)</a>	Washington (Mount. St. Helens)	Primary successional alpine meadow ( <i>Agrostis pallens</i> , <i>Lupinus lepidus</i> )	Addition	78	4	Foliar N %	<i>Agrostis</i> : increase <i>Lupinus</i> : decrease
<a href="#">Bowman et al. (2012)</a>	Colorado (Rocky Mountain National Park)	Dry sedge meadow ( <i>Kobresia myosuroides</i> , <i>Carex rupestris</i> )	Addition	5, 10, 30	4	Foliar N %	Not significant
<a href="#">Bassin et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Carex sempervirens</i> )	Addition	50	2	Foliar N % ( <i>C. sempervirens</i> )	Increase
<a href="#">Britton et al. (2008)</a>	Scotland	Shrub heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 50	5	Foliar N % ( <i>Calluna vulgaris</i> )	<u>Low dose</u> : not significant <u>Mid and high dose</u> : increase
<a href="#">Southon et al. (2013)</a>	U.K.	Heathlands ( <i>Calluna vulgaris</i> )	Ambient	5.9–32.4	n/a	Foliar N % ( <i>Calluna vulgaris</i> )	Not significant
<a href="#">Blanke et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>F. violacea</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Foliar N % (functional group)	<u>Grasses</u> : increase <u>Forbs, sedges</u> : not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Arens et al. (2008)</a>	Greenland	Dwarf shrub/herb tundra ( <i>Salix arctica</i> , <i>Carex rupestris</i> , <i>Dryas integrifolia</i> )	Addition	5, 10, 50	3	Gross ecosystem production	Increase
<a href="#">Volk et al. (2011)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	10, 50	4	Gross primary production	Not significant
<a href="#">Bouskill et al. (2014)</a>	North America and Europe	Arctic and high latitude	Addition	Average: 72 range: 1–100	Meta-analysis	Gross primary productivity	Increase
<a href="#">Aerts (2009)</a>	Sweden	Tundra meadow ( <i>Betula nana</i> )	Addition	75	10	Inflorescence production	Decrease
<a href="#">Zamin and Grogan (2012)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Betula glandulosa</i> )	Addition	10, 100	7	Inflorescence production	Not significant
<a href="#">Bassin et al. (2009)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Leaf chlorophyll concentration	<u>Nine species:</u> increase <u>One species:</u> not significant
<a href="#">Bassin et al. (2012)</a>	Switzerland	Subalpine grassland ( <i>Carex sempervirens</i> )	Addition	50	2	Leaf length ( <i>C. sempervirens</i> )	Increase
<a href="#">Bassin et al. (2009)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Leaf mass (per leaf)	<u>Three species:</u> increase <u>Seven species:</u> not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Aerts (2009)</a>	Sweden	Tundra meadow ( <i>Empetrum hermaphroditum</i> , <i>Andromeda polifolia</i> , <i>Betula nana</i> , <i>Eriophorum vaginatum</i> )	Addition	75	10	Leaf production	<i>Andromeda</i> : increase <i>Other three species</i> : not significant
<a href="#">Aerts (2009)</a>	Sweden	Tundra meadow ( <i>Empetrum hermaphroditum</i> , <i>Andromeda polifolia</i> , <i>Eriophorum vaginatum</i> )	Addition	75	10	Leaf survival	<i>Andromeda</i> and <i>Eriophorum</i> : decrease <i>Empetrum</i> : not significant
<a href="#">Arens et al. (2008)</a>	Greenland	Dwarf shrub/herb tundra ( <i>Salix arctica</i> , <i>Carex rupestris</i> , <i>Dryas integrifolia</i> )	Addition	5, 10, 50	3	Net ecosystem exchange	<i>Low dose</i> : not significant <i>Mid and high dose</i> : decrease
<a href="#">Volk et al. (2011)</a>	Switzerland	Subalpine grassland ( <i>Nardus stricta</i> , <i>Carex sempervirens</i> , <i>Festuca</i> spp.)	Addition	10, 50	4	Net ecosystem production	<i>Low dose</i> : not significant <i>High dose</i> : decrease
<a href="#">Farrer et al. (2015)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	229	7	Net primary productivity	Not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Liu et al. (2017b)</a>	China (Tibetan Plateau)	Alpine meadow	Addition	50	2	Phenology of three perennial forb species—first and last flowering time	Delay in first flowering time for two of the species, not significant for the remaining species; delay in last fruiting time for two of the species, moved-up last fruiting time in the remaining species
<a href="#">Liu et al. (2017b)</a>	China (Tibetan Plateau)	Alpine meadow	Addition	50	2	Phenology of three perennial forb species—first and last fruiting time	Delay in first fruiting time for one of the species, not significant for the others; delay in last fruiting time for one of the species, not significant for the others
<a href="#">Liu et al. (2017a)</a>	China (Tibetan Plateau)	Alpine meadow	Addition	50	1–2	Phenological traits of six species (two graminoids and four forbs)	Change in fruiting date in one of the 2 yr; not significant for the remaining traits (flowering date, flowering duration, fruiting duration, and growing duration) or years

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Yin et al. (2017)</a>	China (Tibetan Plateau)	Alpine meadow	Addition	75	8	Phenological traits of six species (two grasses, one sedge, and three forbs)	Change depended upon form of N added and species; NH <sub>4</sub> <sup>+</sup> modified reproductive phenology of three species; NO <sub>3</sub> <sup>-</sup> delayed senescence for <i>Elymus nutans</i> ; effects of NH <sub>4</sub> NO <sub>3</sub> were not significant
<a href="#">Field et al. (2017)</a>	Wales	Shrub heathland ( <i>Calluna</i> spp.)	Addition	10, 20, 40, 120	10–25	Plant biomass C	Increase
<a href="#">Wang et al. (2017a)</a>	China (Tibetan Plateau)	Alpine shrubland ( <i>Sibiraea angustata</i> )	Addition	20, 50, 100	1.5	Plant biomass (total shrub and grass biomass)	Increase; linear increase with N mainly due to increased root biomass in shrubs and grasses
<a href="#">Bishop et al. (2010)</a>	Washington (Mt. St. Helens)	Primary successional alpine meadow	Addition	78	5	Plant cover	Increase
<a href="#">Bishop et al. (2010)</a>	Washington (Mt. St. Helens)	Primary successional alpine meadow	Addition	78	5	Plant cover (functional group)	<u>Forbs</u> : increase <u>Graminoids</u> : not significant <u>Legumes</u> : decrease
<a href="#">Armitage et al. (2014)</a>	Europe (North Atlantic)	Alpine heathlands	Ambient	0.6–39.6	n/a	Plant cover (functional group)	<u>Shrubs</u> : decrease <u>Forbs</u> : not significant <u>Graminoids</u> : increase

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Field et al. (2017)</a>	Wales	Shrub heathland ( <i>Calluna</i> spp.)	Addition	10, 20, 40, 120	10–25	Plant height	Increase
<a href="#">Field et al. (2017)</a>	Wales	Shrub heathland ( <i>Calluna</i> spp.)	Addition	10, 20, 40, 120	10–25	Plant litterfall	Increase
<a href="#">Farrer et al. (2013)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Geum rossii</i> )	Addition	288	11	Plant nonstructural carbohydrate pools	Decrease
<a href="#">Wang et al. (2017a)</a>	China (Tibetan Plateau)	Alpine shrubland ( <i>Sibiraea angustata</i> )	Addition	20, 50, 100	1.5	Plant root:shoot ratio	Increase
<a href="#">Churchland et al. (2010)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Betula glandulosa</i> , <i>Vaccinium vitis-idaea</i> , <i>Rhododendron subarcticum</i> )	Addition	100	1	Plant tissue N %	Increase
<a href="#">Britton and Fisher (2008)</a>	Scotland	Shrub heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 50	5	Shoot growth ( <i>Calluna vulgaris</i> )	<u>Low dose:</u> not significant <u>Mid and high dose:</u> increase
<a href="#">Britton and Fisher (2008)</a>	Scotland	Shrub heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 50	5	Shoot growth ( <i>Empetrum hermaphroditum</i> , <i>Arctostaphylos uva-ursi</i> , <i>Vaccinium myrtillus</i> )	Not significant

**Table 6-6 (Continued): Alpine and Arctic tundra plant productivity and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate kg N/ha/yr	Duration yr	Endpoint	Effect of Additional Nitrogen
<a href="#">Britton and Fisher (2008)</a>	Scotland	Shrub heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 50	5	Shoot growth ( <i>Vaccinium vitis-idaea</i> )	<u>Low dose:</u> not significant <u>Mid and high dose:</u> increase
<a href="#">Bassin et al. (2009)</a>	Switzerland	Subalpine grassland ( <i>Festuca rubra</i> , <i>Nardus stricta</i> , <i>Carex sempervirens</i> )	Addition	50	3	Specific leaf area	<u>One species:</u> increase <u>Two species:</u> decrease <u>Eight species:</u> not significant
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Vascular plant cover	Increase

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; NEE = net ecosystem exchange; yr = year.

Notes: single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

In subalpine tundra in Sweden, a long-term experiment was started in 1989 to understand how alleviating nutrient limitations altered ecological processes, including productivity, decomposition, and the development of plant communities ([Wardle et al., 2013](#); [Nilsson et al., 2002](#)). The experimental design included six treatments, including additions of  $\text{NO}_3^-$  and  $\text{NH}_4\text{NO}_3$  at rates of 50 kg N/ha/yr. After the first 9 years, there were negative effects of both  $\text{NO}_3^-$  and  $\text{NH}_4\text{NO}_3$  on the percentage cover of the dominant ericaceous shrub *Empetrum hermaphroditum*, but increased cover of two ericaceous *Vaccinium* shrub species ([Nilsson et al., 2002](#)). An even stronger positive response was exhibited by the bunchgrass *Deschampsia flexuosa*, which became the dominant plant in plots receiving N additions. The N additions also had varying effects on the cover of the dominant bryophyte species. *Dicranum* spp. decreased in cover in response to added N and *Pleurozium schreberi* disappeared entirely from some N addition plots, while *Polia* spp., *Bryum* spp., and *Barbilophozia lycopodioides* were not significantly affected by N additions. The dominant lichen, *Cladina* spp., decreased in response to added N ([Nilsson et al., 2002](#)). The N addition treatments did not impact vascular plant diversity, but moss species richness was decreased by  $\text{NH}_4\text{NO}_3$  and lichen species richness was decreased by  $\text{NO}_3^-$ . Decomposition of pine needles in litterbags was followed for 4 years, but no significant effects of the N addition treatments were observed ([Nilsson et al., 2002](#)). In 2010, [Wardle et al. \(2013\)](#) reassessed the changes in plant cover caused by the N addition treatments. The N addition treatments increased cover of vascular plants, but decreased bryophyte cover and lichen cover. Specifically, N additions repeatedly increased cover of *Deschampsia* and decreased cover of *Empetrum*, although these changes were not always significant. Within the soil microbial community,  $\text{NH}_4\text{NO}_3$  additions decreased the abundance of fungal phospholipid fatty acids (PLFAs; a marker of microbial abundance), while bacterial PLFAs were increased by  $\text{NO}_3^-$  additions. However,  $\text{NO}_3^-$  and  $\text{NH}_4\text{NO}_3$  each decreased the fungal-to-bacterial PLFA ratio in the soil. Humus mass and C content were increased by  $\text{NH}_4\text{NO}_3$  additions, but not significantly affected by  $\text{NO}_3^-$ .

Also spanning the period before and after the 2008 ISA was a 7-year N deposition study in a subalpine grassland in the Swiss Alps, with rates of N addition of 0, 5, 10, 25, or 50 kg N/ha/yr (as  $\text{NH}_4\text{NO}_3$ ). The initial analysis of the first 3 years of data found that N additions increased aboveground plant productivity ([Bassin et al., 2007](#)). Among functional groups, sedge growth was consistently stimulated, forb growth increased strongly in the first year of the experiment, and grasses and legumes were unresponsive to N. Species richness was not influenced by the N additions, but N did alter the relative abundance of the 11 most frequently occurring species. A subsequent analysis of this experiment ([Bassin et al., 2009](#)) focused on the physiological responses of these 11 species to the 50 kg N/ha/yr treatment. The N addition treatment increased leaf concentrations of N and chlorophyll in 9 of the 11 species. Notably, the species exhibiting the largest growth response (*Carex sempervirens*) also showed the largest

increase in foliar concentrations of N and chlorophyll. Four years into the experiment, [Volk et al. \(2011\)](#) measured changes in ecosystem C fluxes in response to the 10 and 50 kg N/ha/yr treatments. Although aboveground plant growth increased, there were no significant changes in gross primary productivity or ecosystem respiration. Net ecosystem production was unaffected by the lower rate of N addition but declined with the 50 kg N/ha/yr treatment, which suggests decreases in belowground C pools.

[Bassin et al. \(2013\)](#) and [Volk et al. \(2014\)](#) reassessed this Swiss Alps grassland N addition experiment after 7 years when the experiment concluded. [Volk et al. \(2014\)](#) observed that N additions had a strong positive effect on aboveground productivity, ranging from a 31% stimulation caused by 5 kg N/ha/yr to a 60% increase caused by 50 kg N/ha/yr. Effects on belowground biomass were smaller, ranging from a 19% increase for the 5 kg N treatment to a 24% increase for the 50 kg N treatment. Thus, N additions increased the ratio of shoot-to-root biomass ([Volk et al., 2014](#)). This is consistent with a <sup>15</sup>N tracer study at the site, in which the N addition treatment increased the proportion of the <sup>15</sup>N tracer found in aboveground biomass ([Bassin et al., 2015](#)). However, the stimulation of plant N pools was relatively similar among aboveground biomass (+31%), roots (+31%), necromass (+41%), and litter [+30%; [Bassin et al. \(2015\)](#)]. Among functional groups, the longer term results were both similar and different from the results observed after the initial 3 years ([Bassin et al., 2013](#)). The effects of N addition on sedge biomass increased through time, with the highest rate of N addition (50 kg N/ha/yr) increasing sedge biomass by 360%. In this same treatment, grass biomass increased by 14%, forb biomass was unchanged, and legume biomass decreased by 43%. Unsurprisingly, these changes resulted in more sedge-dominated plant communities. Two aspects of this community change are notable: (1) changes were largely complete after 4–5 years, and (2) the lowest rate of N addition (5 kg N/ha/yr) was sufficient to cause significant changes ([Bassin et al., 2013](#)). This experiment also included an ozone fumigation treatment, but there were no interactions between ozone and added N for productivity or community composition ([Volk et al., 2014](#); [Bassin et al., 2013](#); [Bassin et al., 2007](#)) and few N × ozone interactions for leaf physiological traits ([Bassin et al., 2009](#)). Two related studies on alpine grasslands have also been conducted in the Swiss Alps by members of the same research group. At 10 sites, [Bassin et al. \(2012\)](#) found that grassland aboveground productivity increased 30% with 2 years of NH<sub>4</sub>NO<sub>3</sub> additions of 50 kg N/ha/yr. [Blanke et al. \(2012\)](#) planted seedlings of four local plant species into intact grass/soil monoliths excavated from the same Swiss alpine grassland site as [Bassin et al. \(2013\)](#), [Bassin et al. \(2009\)](#), and [Bassin et al. \(2007\)](#). Nitrogen addition (50 kg N/ha/yr) treatments increased overall biomass of the unplanted vegetation in the monoliths. Among the planted species, N additions increased biomass of the grass and decreased biomass of the forb but had no effect on the sedge or legume. Roots of the

grass, forb, and legume were colonized by arbuscular mycorrhizal fungi; N addition increased mycorrhizal root colonization in the grass ([Blanke et al., 2012](#)).

As in other environments, the plant growth response to N additions in alpine and Arctic ecosystems varies among taxonomic groups. For example, in the Swiss subalpine grassland experiment, [Bassin et al. \(2013\)](#) noted that within plant communities, sedge (Cyperaceae) species tended to show especially strong positive responses to N additions. As discussed in [Appendix 5](#), [Bowman et al. \(2012\)](#) found N additions of 5, 10, and 30 kg N/ha/yr increased cover of the sedge *Carex rupestris* from 34 to 125% within a dry meadow in Rocky Mountain National Park in Colorado. In the northern Caucasus Mountains of Russia, [Onipchenko et al. \(2012\)](#) examined the response of four different alpine plant communities to 90 kg N/ha/yr for 5 years. The N additions increased vascular plant biomass in a lichen heath community, but not in grassland, meadow, or snowbed communities. Within these communities, the response of individual plant functional groups to N varied. The N additions increased sedge biomass in the lichen heath, increased forbs and sedges in the meadow, increased grasses in the grassland, and decreased legumes in the lichen heath and meadow. Shrubs were not significantly affected by N additions.

This variation among plant species was also observed in long-term N addition experiments in moist alpine meadows at the Niwot Ridge Long-Term Ecological Research site in Colorado. In two long-term experiments lasting for 7 and 11 years, average N additions of 229 and 288 kg N/ha/yr (far exceeding background deposition of 4–6 kg N/ha/yr) increased growth of the grass *Deschampsia cespitosa*, but decreased growth of the perennial forb *Geum rossii* ([Farrer et al., 2015](#); [Farrer et al., 2013](#)). The decrease in *Geum* abundance was not necessarily due to competitive exclusion: *Geum* decreased even in study plots where *Deschampsia* had been removed ([Farrer et al., 2013](#)). Instead, *Geum* showed effects of physiological stress with N additions, with less C allocation to storage organs and lower concentrations of nonstructural carbohydrates ([Farrer et al., 2013](#)). In wet, moist, and dry alpine meadows at Niwot Ridge, two decades of N additions (averaging ~85 kg N/ha/yr) did not alter total aboveground biomass, but significantly increased graminoid abundance in the moist and wet meadows ([Yuan et al., 2016](#)).

In addition to the research on alpine tundra in Colorado, there have been several other recent publications on the effect of N additions on plant productivity in tundra ecosystems in North America. Additions of 70 kg N/ha/yr for 3 years to plots in a central Utah alpine meadow increased aboveground plant production by 10–20%, but did not significantly impact soil respiration or soil C content ([Gill, 2014](#)). Given the large contribution of root and mycorrhizal respiration to soil respiration, these results suggest a

change in C allocation toward aboveground growth. In shrub tundra in the Northwest Territories of Canada, 8 years of N additions of 10 kg N/ha/yr had no effect on overall aboveground plant biomass or the biomass of the dominant plant (*Betula*), but each of these metrics was increased by N additions at a rate of 100 kg N/ha/yr ([Zamin et al., 2014](#); [Zamin and Grogan, 2012](#)). Inflorescence production in *Betula* was unaffected at both N addition rates. Elsewhere in the Northwest Territories, [Churchland et al. \(2010\)](#) observed that a single year of N additions (100 kg N/ha/yr) increased foliar N concentrations in shrub tundra plants. In an Alaskan tundra meadow, [Kelley and Epstein \(2009\)](#) found that N additions (100 kg N/ha/yr for 3 years) increased foliar N concentrations but had no effect on aboveground plant growth. Together, the results of these studies in North America are consistent with the overall body N addition research in tundra ecosystems ([Table 6-6](#)).

The influence of N additions on tundra plant biomass and productivity has also been assessed in other areas of the world since 2008. In particular, numerous N addition experiments have been conducted in alpine grasslands within the Tibetan Plateau region of China ([Fu and Shen, 2016](#)). Although the effects of added N on plant growth clearly vary by functional type ([Fu and Shen, 2016](#)), differences between functional groups are not necessarily consistent between ecosystems. For instance, while ([Fu and Shen, 2016](#)) found that added N increased sedge biomass and decreased forb biomass in their meta-analysis of 51 Tibetan plateau studies, 4 years of  $\text{NH}_4\text{NO}_3$  additions at rates of 10, 20, 40, and 80 kg N/ha/yr caused significant increases in aboveground plant biomass and cover of grasses and forbs and either decreases or no change in sedges ([Zong et al., 2016](#)). Species-specific changes in cover and foliar N concentration on the Tibetan Plateau were observed even in studies using very high N addition rates [50, 150, or 300 kg N/ha/yr for 3 years; [Xiong et al. \(2016\)](#)]. Also on the Tibetan Plateau, 100 kg N/ha/yr over 2 years increased leaf litter N concentrations in three herbaceous species, but also changed the biochemical composition of leaf litter by increasing the concentration of cellulose and decreasing the concentration of lignin in a forb (*Gentiana straminea*) and decreasing the concentration of hemicellulose in a sedge [*Kobresia humilis*; [Zhu et al. \(2016b\)](#)]. While higher leaf litter concentrations of these structural biochemicals were linked to slower decomposition overall within this experiment, N additions did not significantly alter decomposition. As in other terrestrial ecosystems, increases in plant biomass on the Tibetan Plateau appear to be more dependent on the amount of N added (3.75 or 15 vs. 75 kg N/ha/yr) than the form of N added [ $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ; [Song and Yu \(2015\)](#)].

In an Arctic shrub ecosystem in Greenland, [Arens et al. \(2008\)](#) studied the effects of N additions at 5, 10, and 50 kg N/ha/yr over 3 years on ecosystem C fluxes and community composition. Net ecosystem productivity (NPP), gross primary production (GPP), and

ecosystem respiration (ER) all increased in response to N additions, but these responses were saturated beyond 10 kg N/ha/yr. The smallest rate of N addition caused both GPP and ER to nearly double. However, soil respiration was not significantly affected by the N addition treatments. Dominant vascular plant cover was highest in the 10 kg N/ha/yr treatment. Nitrogen additions increased the cover of subdominant vascular plants from 3% in control plots to 8% in the highest N treatment. There were also other changes in the cover of plant functional groups, including a 41% increase in deciduous shrubs in the lowest N addition plots, a doubling of graminoid biomass in the moderate N treatment relative to control, and large increases in forb biomass in the moderate and high N addition treatment.

As in forests, lichens are an important component of plant communities and a significant contributor to ecosystem function in Arctic and alpine tundra ecosystems. Since 2008, there have been numerous observations of how lichens respond to added N in these systems ([Table 6-7](#)), and these responses are broadly similar to those observed in forests. [Britton and Fisher \(2010\)](#) observed increased tissue N concentrations in three of four lichen species from Scottish heathlands over the course of a growing season with N additions of 2.5 to 22.5 kg N/ha/yr. [Hogan et al. \(2010b\)](#) collected lichens from 27 heathland sites in the U.K. along a wet N deposition gradient (2–33 kg N/ha/yr) and observed increased thalli N concentrations, decreased thalli P concentrations, and increased phosphomonoesterase activity, an enzyme important for P acquisition. [Hogan et al. \(2010a\)](#) found similar results in an N addition study. [Armitage et al. \(2014\)](#) observed a decline in lichen cover in alpine heathland sites across an N deposition gradient of 0.6 to 39.6 kg N/ha/yr in the North Atlantic region of Europe. Similarly, there were decreases in lichen biomass or lichen cover with additional N in studies in Scotland ([Britton and Fisher, 2010](#)), Sweden ([Wardle et al., 2013](#)), Alaska ([Kelley and Epstein, 2009](#)), and Canada ([Zamin et al., 2014](#)).

**Table 6-7 Alpine and Arctic tundra lichen growth and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Zamin et al. (2014)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Vaccinium vitis-idaea</i> , <i>Rhododendron subarcticum</i> , <i>Andromeda polifolia</i> )	Addition	10, 100	8	Lichen biomass	<u>Low dose</u> : not significant <u>High dose</u> : decrease
<a href="#">Kelley and Epstein (2009)</a>	Alaska	Tundra meadow ( <i>Dryas integrifolia</i> , <i>Eriophorum vaginatum</i> , <i>Carex</i> spp.)	Addition	100	3	Lichen cover	Decrease
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Lichen cover	Decrease
<a href="#">Armitage et al. (2014)</a>	Europe (North Atlantic)	Alpine heathlands	Ambient	0.6–39.6	n/a	Lichen cover	Decrease
<a href="#">Britton and Fisher (2010)</a>	Scotland	Heathlands ( <i>Calluna vulgaris</i> )	Addition	2.5, 7.5, 12.5, 22.5	0.25	Lichen thalli mass	<u>Three species</u> : not significant <u>Two species</u> : decrease
<a href="#">Hogan et al. (2010a)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Addition	8, 24, 56	4	Phosphomono-esterase activity	Increase
<a href="#">Hogan et al. (2010b)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Ambient	2.32–32.8	n/a	Phosphomono-esterase activity	Increase

**Table 6-7 (Continued): Alpine and Arctic tundra lichen growth and physiology responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Britton and Fisher (2010)</a>	Scotland	Heathlands ( <i>Calluna vulgaris</i> )	Addition	2.5, 7.5, 12.5, 22.5	0.25	Thalli N %	<u>Three species:</u> increase <u>One species:</u> not significant
<a href="#">Hogan et al. (2010a)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Addition	8, 24, 56	4	Thalli N %	Increase
<a href="#">Hogan et al. (2010b)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Ambient	2.32–32.8	n/a	Thalli N %	Increase
<a href="#">Hogan et al. (2010b)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Ambient	2.32–32.8	n/a	Thalli N %	Increase
<a href="#">Hogan et al. (2010b)</a>	U.K.	Heathland lichen ( <i>Cladonia portentosa</i> )	Ambient	2.32–32.8	n/a	Thalli P %	Decrease

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; P = phosphorus; yr = year.

Notes: single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Because of the often sparse cover of vascular plants in tundra ecosystems, bryophytes are often relatively larger components of plant communities than in other terrestrial systems. As with lichens, bryophyte physiology and growth in tundra ecosystems can be impacted by added N. [Armitage et al. \(2012\)](#) conducted an analysis of the tissue chemistry, growth, and cover of the bryophyte *Racomitrium lanuginosum* in alpine heathlands at 36 sites in Great Britain, Iceland, the Faroe Islands, and Norway. Estimated N deposition at these sites ranged from ~1 kg N/ha/yr to nearly 40 kg N/ha/yr. Among environmental variables that included temperature, precipitation, and grazing, N deposition was the largest influence on tissue N and P concentrations. Notably, tissue N concentration increased rapidly with N deposition rates up to 5 kg N/ha/yr, then increased at a slower rate with higher levels of N deposition. Tissue N concentration was positively related to moss shoot growth, but also positively related to shoot turnover and negatively related to moss mat depth. These effects were nonlinear and especially pronounced at high tissue N concentrations. Among other plant functional types at these sites, shrub growth decreased with greater N deposition, graminoid growth increased, and forbs were not significantly affected ([Armitage et al., 2014](#)). In related work using a subset of these sites, [Armitage et al. \(2011\)](#) conducted a 2-year transplant experiment that moved *Racomitrium* between 10 sites receiving higher N deposition (8.2–32.9 kg N/ha/yr) and a lower N site (7.2 kg N/ha/yr). When the authors transplanted *Racomitrium* from elevated N deposition sites to low N deposition sites and vice versa, tissue N concentration remained higher in the plants from higher N sites, whereas moss moved from lower N to higher N sites increased tissue N to nearly match levels in the moss natural to the site. [Armitage et al. \(2011\)](#) also observed that moss at high N sites had higher shoot growth, whereas moss transplanted to lower N sites increased in biomass due to decreasing tissue C:N and slowing decomposition ([Armitage et al., 2011](#)).

In high-latitude and high-elevation ecosystems, such as tundra, heathlands, and boreal forests, plants in the Ericaceae family are often abundant. Notable members of the Ericaceae family include blueberries and cranberries (both *Vaccinium*). Ericaceous plants uniquely host ericoid mycorrhizae, which are distinct from ectomycorrhizae and arbuscular mycorrhizae. Ericoid fungi are recognized for their ability to decompose large organic molecules and absorb organic forms of soil N ([Read et al., 2004](#)). This specialization in organic N uptake could make these mycorrhizae more sensitive to increased inorganic N availability. However, only a relatively small number of N addition studies have quantified changes in mycorrhizal growth or physiology in ecosystems supporting plants that host ericoid mycorrhizae ([Table 6-8](#)). [Ishida and Nordin \(2010\)](#) added 12.5 or 50 kg N/ha/yr for 4 or 12 years to boreal forests in Sweden and observed no change in the percentage of *Vaccinium myrtillus* roots colonized by ericoid mycorrhizae, the number of ericoid fungal species per root tip, or ericoid community composition, and observed mixed effects on ericoid species richness. [Dean et al. \(2014\)](#)

studied the response of root-associated fungi in alpine tundra in Colorado to 8 years of N additions (29 kg N/ha/yr). Ericoid fungi abundance decreased and the overall community composition of root-associated fungi changed, including a reduction in diversity and richness. Further research is needed to understand the response of ericoid mycorrhizae to added N.

Although [Bouskill et al. \(2014\)](#) observed that N additions increased fungal biomass in a meta-analysis of high-latitude N addition experiments, other studies of fungal biomass in tundra ecosystems have found negative ([Xiong et al., 2016](#); [Farrer et al., 2013](#); [Wardle et al., 2013](#)) or neutral responses ([Sundqvist et al., 2014](#)). [Bouskill et al. \(2014\)](#) did not find a significant effect of added N on total microbial biomass in their meta-analysis, with individual studies reporting a negative effect ([Farrer et al., 2015](#)), positive effect ([Xiong et al., 2016](#); [Zong et al., 2016](#)), or no effect ([Zong et al., 2016](#); [Churchland et al., 2010](#)). In a meta-analysis, [Treseder \(2008\)](#) found that N additions decreased bacterial biomass in tundra ecosystems, but this analysis included only two studies. Of the four subsequent studies of bacterial biomass, N additions had no effect in two, a positive effect in one, and a negative effect in a fourth ([Table 6-9](#)). Notably, [Bouskill et al. \(2014\)](#) observed that microbial biomass responses were positive under relatively low rates of N addition, but became negative as N addition rates exceeded ~50 kg N/ha/yr. Belowground respiration showed a similar response, but lower threshold (~25 kg N/ha/yr) at which the response switched from positive to negative.

To examine the influence of added N on organisms at higher trophic levels, [Bishop et al. \(2010\)](#) studied the effects of N additions (78 kg N/ha/yr for 5 years) on plant and arthropod communities in alpine meadows that were primary successional ecosystems on recently formed volcanic substrates on Mount St. Helens in Washington. The N additions increased foliar N concentration in the dominant graminoid but decreased foliar N concentration in the dominant legume. The N additions also increased both plant species diversity and plant cover, although in the final year of the experiment, increased browsing by small mammals negated the effect of the N additions. There was no effect on total arthropod abundance (individuals per m<sup>2</sup>), but the number of Orthoptera approximately doubled. Overall, total arthropod abundance was strongly positively related to both plant diversity and plant cover, with arthropod abundance among individual orders both positively and negatively related to plant diversity and plant cover.

**Table 6-8 Growth and biodiversity responses of ericoid mycorrhizal fungi to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Ishida and Nordin (2010)</a>	Sweden	<i>Vaccinium myrtillus</i> roots in <i>Picea abies</i> forests and <i>Pinus sylvestris</i> forest	Addition	12.5, 50	12 ( <i>Picea</i> ), 4 ( <i>Pinus</i> )	Ericoid community composition	Not significant
<a href="#">Dean et al. (2014)</a>	Colorado (Niwot Ridge)	Alpine tundra ( <i>Geum rossii</i> )	Addition	28.8	8	Ericoid fungal abundance	Decrease
<a href="#">Ishida and Nordin (2010)</a>	Sweden	<i>Vaccinium myrtillus</i> roots in <i>Picea abies</i> forests and <i>Pinus sylvestris</i> forests	Addition	12.5, 50	12 ( <i>Picea</i> ), 4 ( <i>Pinus</i> )	Ericoid species per root tip	Not significant
<a href="#">Ishida and Nordin (2010)</a>	Sweden	<i>Vaccinium myrtillus</i> roots in <i>Picea abies</i> forests and <i>Pinus sylvestris</i> forests	Addition	12.5, 50	12 ( <i>Picea</i> ), 4 ( <i>Pinus</i> )	Ericoid species richness	<i>Pinus</i> : increase <i>Picea</i> : not significant
<a href="#">Ishida and Nordin (2010)</a>	Sweden	<i>Vaccinium myrtillus</i> roots in <i>Picea abies</i> forests and <i>Pinus sylvestris</i> forests	Addition	12.5, 50	12 ( <i>Picea</i> ), 4 ( <i>Pinus</i> )	Root colonization (%)	Not significant
<a href="#">Dean et al. (2014)</a>	Colorado (Niwot Ridge)	Alpine tundra ( <i>Geum rossii</i> , <i>Deschampsia cespitosa</i> )	Addition	28.8	8	Root-associated fungal community composition	Change
<a href="#">Dean et al. (2014)</a>	Colorado (Niwot Ridge)	Alpine tundra ( <i>Geum rossii</i> , <i>Deschampsia cespitosa</i> )	Addition	28.8	8	Root-associated fungal diversity and richness	<i>Deschampsia</i> : decrease <i>Geum</i> : increase

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

**Table 6-9 Alpine and Arctic tundra microbial biomass responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Treseder (2008)</a>	Tundra	Meta-analysis	Addition		Various	Bacterial biomass	Decrease
<a href="#">Farrer et al. (2013)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	288	11	Bacterial biomass	Decrease
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Bacterial biomass	Not significant
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra heath ( <i>Vaccinium vitis-idaea</i> , <i>Vaccinium uliginosum</i> , <i>Betula nana</i> )	Addition	100	3	Bacterial biomass	Not significant
<a href="#">Farrer et al. (2013)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	288	11	Fungal biomass	Decrease
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Fungal biomass	Decrease
<a href="#">Bouskill et al. (2014)</a>	North America and Europe	Arctic and high-latitude meta-analysis	Addition	Average: 72; range: 1–100	Various	Fungal biomass	Increase
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Anthoxanthum alpinum</i> )	Addition	100	3	Fungal biomass	Not significant

**Table 6-9 (Continued): Alpine and Arctic tundra microbial biomass responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Bouskill et al. (2014)</a>	North America and Europe	Arctic and high-latitude meta-analysis	Addition	Average: 72; range: 1–100	Various	Microbial biomass	Not significant
<a href="#">Farrer et al. (2015)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	229	7	Microbial biomass	Decrease
<a href="#">Churchland et al. (2010)</a>	Northwest Territories (Canada)	Shrub tundra ( <i>Betula glandulosa</i> , <i>Vaccinium vitis-idaea</i> , <i>Rhododendron subarcticum</i> )	Addition	100	1	Microbial biomass C	Not significant
<a href="#">Fu and Shen (2017)</a>	Tibetan Plateau	Meta-analysis	Addition	10–350	0–8	Microbial biomass C	Not significant

C = carbon; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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## 6.2.5 Grasslands

The 2008 ISA contained limited information regarding the effects of N deposition on productivity and related aspects of eutrophication in grasslands. That assessment included the work of ([Neff et al., 2002](#)), who examined the long-term effects (+10 years) of N deposition (10 kg N/ha/yr) in an alpine meadow, where N additions stimulated aboveground NPP by 47%. Factors affecting productivity in grasslands are similar in many ways to forests, with N availability limiting primary production. Grasslands dominate largely in places where forests cannot grow because of low moisture availability, high disturbance rates (such as from fire or grazing), and/or cold temperatures and shorter growing seasons [such as at high latitudes and elevations; [Chapin et al. \(2002\)](#); [Knapp et al. \(1998\)](#)]. However, because of the commonality of N limitation to primary production ([Vitousek and Howarth, 1991](#)), many of the processes that occur when N is added to forests also occur when N is deposited onto grasslands. These include increases in primary production and foliar N, increases in allocation to aboveground biomass (increased shoot:root ratio), decreased levels of light reaching the ground surface, elevated litter inputs, and changes in the soil biota ([Aerts and Chapin, 1999](#); [Knapp et al., 1998](#)), which are described further below.

Since the 2008 ISA, further advancements in our understanding of the effects of N deposition on grasslands have occurred. A meta-analysis estimated that N additions increased grassland aboveground NPP by 53% ([LeBauer and Treseder, 2008](#)). Increased plant growth, NPP, or plant biomass in response to added N has been observed in prairies in Wyoming, Kansas, and Minnesota ([Henry et al., 2015](#); [Farrior et al., 2013](#); [Isbell et al., 2013a](#); [Hillerislambers et al., 2009](#); [Johnson et al., 2008](#)), in temperate grasslands in Ontario ([Vankoughnett and Henry, 2014](#); [Hutchison and Henry, 2010](#)) and Michigan ([Grman and Robinson, 2013](#)), in Mediterranean grasslands in California ([Tulloss and Cadenasso, 2016](#); [Borer et al., 2014](#); [Vallano et al., 2012](#)), and steppe grasslands of China ([Li et al., 2017a](#)). Although the response to N enrichment is variable among species in many terrestrial ecosystems, the comparatively rapid turnover rate of plant biomass in grasslands means that wide differences in the response of individual species to N deposition are frequently observed even in short-term studies ([Tulloss and Cadenasso, 2016](#); [Hautier et al., 2014](#); [Vankoughnett and Henry, 2014](#); [Grman and Robinson, 2013](#); [Isbell et al., 2013a](#); [Bradford et al., 2012](#); [Vallano et al., 2012](#); [Skogen et al., 2011](#)). Three new syntheses of grassland responses to N additions or N deposition have been published since the 2008 ISA. [Stevens et al. \(2015\)](#) used data from a network of 42 grassland sites on four continents and found that estimated rates of atmospheric N deposition were the strongest predictor of aboveground NPP in these ecosystems. On average, aboveground

NPP increased 3% for every 1 kg N/ha/yr increase in N deposition, and N deposition explained 16% of the variance in productivity in these systems ([Stevens et al., 2015](#)), implying that much of the variation in NPP was not understood. [Yue et al. \(2016\)](#) conducted a meta-analysis of N addition studies and found a 50.4% stimulation of grassland aboveground NPP, similar to the estimate of [LeBauer and Treseder \(2008\)](#). Aboveground plant C was stimulated by an average of 30.5% in the [Yue et al. \(2016\)](#) analysis.

The belowground productivity responses to N appear to be more mixed. [Yue et al. \(2016\)](#) found a 28% increase in belowground plant C; whereas [Li et al. \(2015\)](#) did not observe a significant change in grassland fine root biomass. Belowground net primary productivity in an experimental grassland declined with N additions when summed over a 9-year period, along with the ratio of belowground-to-aboveground net primary productivity ([Xu et al., 2017b](#)). In a controlled pot experiment, [Wang et al. \(2017b\)](#) found that both fine root production and turnover rates increased in a temperate grass species (*Bothriochloa ischaemum*) with N additions. The net result was lower standing root biomass.

The differences in how individual plant species respond to added N may in part be due to variation in functional traits, including the ability to change plant C allocation. In a common garden experiment, [Johnson et al. \(2008\)](#) grew plants that were among the most positively and negatively responsive to long-term N additions at the Cedar Creek and Konza Prairie LTER sites. The plants that were most positively affected by N additions allocated more biomass to shoots than roots and formed fewer associations with mycorrhizal fungi. Likewise, [Grman and Robinson \(2013\)](#) also found that N additions increased aboveground biomass and decreased the relative allocation of C to mycorrhizae. Of the two grass species studied, the species that more strongly decreased allocation to mycorrhizae as N availability increased also showed a greater aboveground biomass response to added N. [Bradford et al. \(2012\)](#) documented a somewhat different functional response, finding that increasing rates of N additions favored the species that showed greater leaf trait plasticity in response to the N additions. Earlier studies suggested leaf plasticity was an important determinant of plant growth responses to added N, and that the ability of a species to upregulate production if nutrients were abundant was an advantage ([Knops and Reinhart, 2000](#)). [Hillerislambers et al. \(2009\)](#) observed that N amendments (40 kg N/ha/yr) had similar effects on grasses within the same functional groups: C3 grasses tended to increase aboveground biomass and decrease seed production, while C4 grasses increased seed production and decreased aboveground biomass. In a survey of 44 species in 153 acidic grassland sites across northern and western Europe, [Pannek et al. \(2015\)](#) found that species with high relative growth rates tended to show beneficial responses to N deposition.

In multiyear studies, responses to N enrichment often varied through time. For instance, over a 7-year period of N addition, [Henry et al. \(2015\)](#) found that the stimulation of aboveground biomass ranged approximately 10 to nearly 100%. Working at a long-term biodiversity and N deposition experiment at Cedar Creek in Minnesota that used seven different N addition rates from 10 to 270 kg N/ha/yr, [Isbell et al. \(2013a\)](#) initially observed that N additions increased grassland productivity, with higher rates of N addition causing greater increases in productivity. Although N additions continued to stimulate productivity, productivity decreased in plots that lost the most species over time. In a large synthesis, [Hautier et al. \(2014\)](#) used data from studies of 41 experimental grassland communities on 5 continents and found grassland communities had greater annual variability in plant productivity (less stability) as the N input rate increased. Under ambient conditions, annual variability in plant productivity is limited by asynchronous productivity among different species, wherein slower growth by some species is balanced by more rapid growth of neighboring species. In these unmanipulated systems, the stability of plant productivity is positively associated with plant diversity ([Hautier et al., 2014](#); [Tilman et al., 2001](#); [Tilman et al., 1997](#)). With added N, the increase in annual variability in productivity could not be linked to a loss of species richness but was instead caused by a decrease in the asynchrony of productivity among individual plant species. In a more recent experiment in China, [Zhang et al. \(2016a\)](#) observed that N additions (10–500 kg N/ha/yr for 6 years) created a series of changes: decreased plant species richness, decreased asynchrony among plant species, increased aboveground productivity, and decreased stability (more annual variability) in aboveground productivity.

Nitrogen enrichment can also cause variation in plant chemistry, particularly increases in tissue N concentrations ([Lu et al., 2017](#); [Reich et al., 2003](#)). [Bradford et al. \(2012\)](#) conducted a greenhouse experiment with several grass and forb species and observed increases in shoot N concentrations, but root C:N and root mass N were not consistently affected by N additions. In a greenhouse experiment conducted by [Jamieson et al. \(2012\)](#), N addition had no effect on the concentration of a defensive compound in shoots, whereas concentrations decreased in flowers by ~35%. As in other terrestrial ecosystems, these increases in shoot N concentrations can lead to an increase in leaf-level photosynthesis if other resources are not limiting [e.g., [Lee et al. \(2001\)](#); [Reich et al. \(2003\)](#)]. However, such increases in photosynthesis vary among species and can vary temporally ([Reich et al., 2003](#); [Lee et al., 2001](#)). Within a U.K. grassland exposed to N additions of 35 or 140 kg N/ha/yr for 11 years, [Arróniz-Crespo et al. \(2008\)](#) observed decreases in cover of two bryophyte species as well as a decrease in chlorophyll fluorescence in both species (despite an increase in chlorophyll content in one species). Both bryophyte species exhibited increased activity of an enzyme involved in P acquisition (phosphomonoesterase) and decreased nitrate reductase enzyme activity, but

only one of the two bryophyte species exhibited increased tissue N concentrations and N:P ratios.

Several experiments in Ontario, Canada have examined the response of old field grasslands to the interaction between N additions and climate change in the form of altered snowpack, soil freezing, or warming. [Vankoughnett and Henry \(2014\)](#) found that N additions of 20 or 60 kg N/ha/yr increased aboveground production, but this increase varied by species. In the first year of the experiment, plant production showed a stronger response to N in plots where snow had been experimentally removed, but this interaction did not occur in subsequent years. Although the extent of the effect varied by year, [Henry et al. \(2015\)](#) found that 7 years of N additions at a rate of 60 kg N/ha/yr increased aboveground biomass and showed no interaction with experimental warming.

Effects of water availability were also observed in grassland studies by [Friedrich et al. \(2012\)](#), [Jamieson et al. \(2013\)](#), and [Farrior et al. \(2013\)](#). In a greenhouse experiment with a grass native to German grasslands, [Friedrich et al. \(2012\)](#) found that N additions of 48 kg N/ha/yr increased aboveground biomass by 500%. However, plants receiving N were more likely to suffer dieback when N additions were combined with drought. Nitrogen enrichment in a Wyoming prairie increased the production of a defensive chemical compound in an invasive plant by 37% under ambient conditions, but decreased the production of this compound by 25% when water availability was reduced ([Jamieson et al., 2013](#)). At Cedar Creek in Minnesota, [Farrior et al. \(2013\)](#) found complex responses to changes in N and water availability: N enrichment increased shoot biomass regardless of water availability, fine root biomass declined when availability of both water and N was high, and higher water availability increased fine root biomass only at low rates of N addition.

There has been less research on the effects on N enrichment on belowground C cycling in grasslands than in forests ([Yue et al., 2016](#); [Li et al., 2015](#); [Liu and Greaver, 2010](#)). In a meta-analysis, [Liu and Greaver \(2010\)](#) found that N additions to grasslands increased aboveground litter inputs, but did not significantly affect soil respiration, microbial respiration, or soil C. In part, the lack of an overall effect on these processes could be due to the combination of high variability among grasslands and the small sample sizes for the meta-analysis, as only approximately six studies were available for the [Liu and Greaver \(2010\)](#) analysis. However, a more recent meta-analysis of N addition experiments by [Yue et al. \(2016\)](#) that had larger sample sizes found somewhat similar results: belowground plant C was stimulated by 24.2%, but there were no significant effects on soil respiration, microbial respiration, litter decomposition rates, or soil organic C. Meta-analyses of changes in microbial biomass have produced inconsistent results: [Yue et al. \(2016\)](#) did not find a significant effect of added N, [Liu and Greaver \(2010\)](#)

found a negative effect, and [Geisseler et al. \(2016\)](#) observed a negative effect only with at least 5 years of N additions.

The conflicting meta-analytic results for changes in grassland soil microbial biomass could be caused by differences in analyses or data sets, or could reflect ecological complexities that require more nuanced understanding, such as the influence of P availability, varying responses among microbial taxa, or measurement techniques ([Johnson et al., 2008](#)). For instance, at Jasper Ridge in the San Francisco Bay area, [Liang et al. \(2015\)](#) did not find any significant changes in fungal lipid biomass caused by N additions (70 kg N/ha/yr), yet did observe changes in the abundance of individual amino sugars that indicated decreases in total microbial biomass and fungal biomass, and increases in bacterial biomass. In measuring the abundance of nitrite-oxidizing bacteria at Jasper Ridge, [Le Roux et al. \(2016\)](#) observed that N additions increased the abundance of *Nitrobacter*, but did not affect *Nitrospira*. In the over 150-year Park Grass Experiment, [Zhalnina et al. \(2015\)](#) observed that NaNO<sub>3</sub> additions had no effect on bacterial and archaeal biomass as assessed by 16S ribosomal RNA abundance, but (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> additions decreased bacterial and archaeal biomass. [Li et al. \(2015\)](#) found no effect of N additions on fine root biomass or mycorrhizal colonization of root tips in a meta-analysis of grassland experiments, but sample sizes were small (four biomass studies, nine mycorrhizal studies).

A number of studies have examined the effects of N additions on mycorrhizal abundance in grasslands ([Table 6-3](#)). Grassland plants predominantly host arbuscular mycorrhizal fungal associations. Like arbuscular mycorrhizal responses observed in forests [e.g., [van Diepen et al. \(2010\)](#)], arbuscular mycorrhizal responses to added N in grasslands have been inconsistent, with a similar number of studies showing no response ([Liang et al., 2015](#); [Chen et al., 2014](#); [Mandyam and Jumpponen, 2008](#)) versus showing a negative effect on colonization or growth [e.g., [Van der Heijden et al. \(2008\)](#); [Johnson et al. \(2008\)](#); [Chen et al. \(2014\)](#)].

Most studies of grassland soil microbial responses to N deposition ([Table 6-10](#)) have focused on free-living soil heterotrophs or mycorrhizal fungi, but [Weese et al. \(2015\)](#) examined the response of N fixing rhizobial bacteria in clover (*Trifolium*) as part of a 22-year chronic N addition (123 kg N/ha/yr as NH<sub>4</sub>NO<sub>3</sub>) experiment in a Michigan grassland. Clover inoculated with rhizobial bacteria from soil or bacterial strains that were collected from the long-term N addition experiment exhibited lower chlorophyll content and decreased plant biomass, including fewer leaves and stolons. These patterns were consistent across all three clover species used in the experiment. Notably, these changes did not result from a shift in the community composition of the rhizobial bacteria, but instead resulted from the evolution of new strains of the bacteria *Rhizobium*

*leguminosarum* that were less symbiotic and less cooperative in the exchange of C for N. A similar change toward less mutualistic interactions in response to N additions have been observed for mycorrhizae in grasslands ([Johnson, 1993](#)). It is unclear whether these evolutionary changes are reversible, and if so, how long this reversion would take ([Weese et al., 2015](#)).

[Zehnder and Hunter \(2008\)](#) performed a plant density manipulation experiment to examine the effect of N deposition on the interaction between a host plant from the southeastern U.S., *Asclepias tuberosa*, and its herbivore, *Aphis nerii*. Added N increased aphid population growth, plant foliar N concentrations, and plant biomass. In southern California coastal grasslands, [Borer et al. \(2014\)](#) observed that N additions (40 or 100 kg N/ha/yr as Ca[NO<sub>3</sub>]<sub>2</sub>) increased plant biomass, but only in the absence of herbivores (pocket gophers, *Thomomys bottae*).

**Table 6-10 Grassland microbial biomass responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Eisenhauer et al. (2012)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Amoeba and flagellate abundance	Not significant
<a href="#">Kastl et al. (2015)</a>	Germany (greenhouse)	Temperate grasses ( <i>Dactylis glomerata</i> , <i>Festuca rubra</i> )	Addition	50, 100, 200	0.12	Archaeal and bacterial <i>amoA</i> (NH <sub>3</sub> monooxygenase) gene abundance	<u>Archaea</u> : not significant <u>Bacteria</u> : increase
<a href="#">Wei et al. (2013)</a>	China	Steppe grassland	Addition	5.6, 11.2, 22.4, 39.2, 56	4	Bacterial biomass	<u>Lowest dose</u> : not significant <u>Other doses</u> : decrease
<a href="#">Liang et al. (2015)</a>	California (northern)	Annual grassland ( <i>Avena barbata</i> , <i>A. fatua</i> )	Addition	70	9	Bacterial biomass	Not significant
<a href="#">Wei et al. (2013)</a>	China	Steppe grassland	Addition	5.6, 11.2, 22.4, 39.2, 56	4	Fungal biomass	<u>Three lowest doses</u> : not significant <u>Two highest doses</u> : decrease
<a href="#">Liang et al. (2015)</a>	California (northern)	Annual grassland ( <i>Avena barbata</i> , <i>A. fatua</i> )	Addition	70	9	Fungal biomass	Not significant

**Table 6-10 (Continued): Grassland microbial biomass responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Ramirez et al. (2010b)</a>	Minnesota (Cedar Creek)	Temperate grasslands	Addition	30, 60, 100, 160, 280, 500, 800	27	Microbial biomass	Not significant
<a href="#">Eisenhauer et al. (2013)</a>	Minnesota (Cedar Creek)	Prairie	Addition	40	14	Microbial biomass	Not significant
<a href="#">Wei et al. (2013)</a>	China	Steppe grassland	Addition	5.6, 11.2, 22.4, 39.2, 56	4	Microbial biomass	<u>Lowest dose:</u> not significant <u>Other doses:</u> decrease
<a href="#">Liang et al. (2015)</a>	California (northern)	Annual grassland ( <i>Avena barbata</i> , <i>A. fatua</i> )	Addition	70	9	Microbial biomass	Not significant
<a href="#">Li et al. (2017a)</a>	China (Inner Mongolia)	Steppe grassland	Addition	50, 100, 150	8	Microbial biomass C	Decrease
<a href="#">Liang et al. (2015)</a>	California (northern)	Annual grassland ( <i>Avena barbata</i> , <i>A. fatua</i> )	Addition	70	9	Saprotrophic fungal biomass	Not significant

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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## 6.2.6 Arid and Semiarid Ecosystems

Large portions of the western U.S. are covered by arid and semiarid ecosystems. While many of these ecosystems receive little anthropogenic N deposition compared to the eastern U.S., some areas downwind of agricultural and metropolitan centers receive high levels of atmospheric N deposition ([Fenn et al., 2003b](#)). In addition, the unique nutrient cycling processes in these systems can intensify the influence of N deposition on ecosystem processes ([Homyak et al. \(2014\)](#); see [Appendix 4](#)).

The lack of moisture in arid and semiarid climates changes the nature of how N deposition impacts biological communities in these ecosystems compared to more mesic ecosystems such as tallgrass prairies and forests. First, the strong moisture constraint on productivity limits the influence of increased N availability on plant communities [e.g., [Rao and Allen \(2010\)](#)], with shifts in community composition less likely to occur without sufficient moisture [e.g., [Concilio and Loik \(2013\)](#)]. Second, the lack of strong biological demand for N during periods of moisture limitation, combined with infrequent soil leaching and runoff events, leads to the accumulation of inorganic N in surface soils, intensifying the effects of N deposition on soil N concentrations when moisture is available [e.g., [Homyak et al. \(2014\)](#)]. Broadly, soil base saturation and pH increase as the climate becomes more arid ([Schlesinger, 2005](#)), buffering dryland ecosystems from the acidification-driven losses in biodiversity that are observed along N deposition gradients [e.g., [Simkin et al. \(2016\)](#)]. Finally, the patchy vegetation that often develops in deserts tends to create isolated islands of fertility, wherein nutrients (including N) are concentrated beneath shrub canopies ([Titus et al., 2002](#); [Schlesinger and Pilmanis, 1998](#)). Under these circumstances, anthropogenic N deposition can increase N availability in the interspaces between shrubs, allowing the growth of annual grasses and forbs, which can grow and reproduce during the brief seasonal periods with adequate moisture availability ([Brooks, 2003](#)). In particular, there have been numerous observations from semiarid and arid ecosystems that N deposition can increase the productivity and dominance of invasive grasses [e.g., [Padgett and Allen \(1999\)](#); [Brooks \(2003\)](#); [Fenn et al. \(2003a\)](#)]. This phenomenon provides a more continuous fuel bed for wildfires, increasing the potential for fire ([Rao et al., 2010](#)) and shifting plant community composition away from species that are not fire adapted ([Padgett and Allen, 1999](#); [Allen et al., 1998](#)).

There was already a large amount of information available on how N deposition impacted arid and semiarid ecosystems at the time of the 2008 ISA, especially in areas around southern California downwind of Los Angeles, where dry N deposition can be >30 kg N/ha/yr ([Bytnerowicz and Fenn, 1996](#)). In particular, the 2008 ISA described results from several N deposition studies in this region that showed increased biomass of

invasive species, high mortality of native shrubs in heavily polluted areas, and increased fire risk ([Padgett and Allen, 1999](#); [Allen et al., 1998](#)). These experiments were primarily conducted in coastal sage scrub (CSS) ecosystems or in the Mojave Desert.

The amount of land area covered by CSS in southern California has greatly declined in the past 60 years due to changes in land use, grazing, and increased wildfire frequency ([Allen et al., 1998](#)). In addition, native CSS vegetation has been replaced in many areas by annual grasses from the Mediterranean region ([Padgett et al., 1999](#); [Padgett and Allen, 1999](#); [Allen et al., 1998](#)). In the mid-1990s, N deposition had been implicated as a contributor to this ecosystem alteration because it decreased the growth of native shrubs and increased the growth of invasive grasses, with the secondary effect of increasing fire frequency ([Padgett et al., 1999](#); [Padgett and Allen, 1999](#); [Allen et al., 1998](#)). There was also evidence that the N assisted conversion from CSS to invasive annual grasses had altered the hydrology of these ecosystems ([Wood et al., 2006](#)). The loss of native vegetation in the CSS and chaparral ecosystems in southern California is particularly notable because these ecosystems are unique within the U.S., are limited in their spatial extent, and are important global and national hotspots for biodiversity.

At the time of the 2008 ISA, similar effects of N deposition on plant communities had also been observed farther east in the Mojave Desert. [Brooks \(2003\)](#) documented that  $\text{NH}_4\text{NO}_3$  additions (32 kg N/ha/yr) increased the biomass of invasive annual grasses and forbs by more than 50%. The increased growth of the invasive plants suppressed the growth of native annual plants. In particular, N additions stimulated the growth of *Bromus madritensis* beneath the dominant native shrub *Larrea tridentata*, while the invasive grasses in the genus *Schismus* and the invasive forb *Erodium cicutarium* had enhanced growth in the interspaces between shrubs. This spatial nature of these effects is important because as in the CSS, the spatially continuous fuel beds created by high grass biomass have been associated with increased fire frequency in the Mojave Desert ([Brooks et al., 2004](#); [Brooks and Esque, 2002](#); [Brooks, 1999](#)). This effect is stronger at higher elevation, likely because the higher precipitation stimulates grass productivity. Fire was relatively rare in the Mojave Desert until the 1980s ([Syphard et al., 2017](#)), but now fire occurs frequently in areas that have experienced invasion of exotic grasses ([Brooks, 1999](#)). The comparatively unresponsive nature of native Mojave vegetation to N deposition was also observed elsewhere. For instance, 3 years of N additions [40 kg N/ha/yr as  $\text{Ca}(\text{NO}_3)_2$ ] had almost no impact on leaf-level photosynthetic or hydraulic performance in *Larrea tridentata* growing north of Las Vegas, NV ([Barker et al., 2006](#)).

At the time of the 2008 ISA, N deposition effects on belowground processes in arid and semiarid lands were not well understood. In a Chihuahuan Desert grassland in New

Mexico, 10 years of N additions (10 kg N/ha/yr) increased the activity of extracellular glucosidase enzymes important in the breakdown of carbohydrates, but decreased the activity of extracellular aminopeptidase enzymes important in the decomposition of proteins and peptides ([Stursova et al., 2006](#)). In contrast, there were no differences in C mineralization (decomposition) in soils collected at a similar southern California gradient of CSS sites [4 to 23 kg N/ha/yr; [Vourlitis and Zorba \(2007\)](#)]. Along a CSS N deposition gradient in the Los Angeles area, arbuscular mycorrhizal fungi associated with the dominant sagebrush shrub declined with increasing N pollution and also in response to N additions (60 kg N/ha/yr; 4–5 years) at a relatively unpolluted site ([Sigüenza et al., 2006](#)). Evidence is conflicting about whether these changes in mycorrhizal colonization influenced the plant growth response to N deposition. An earlier study suggested that differences in mycorrhizal colonization were not responsible for the effects of N deposition on CSS plant growth in this region ([Yoshida and Allen, 2001](#)). [Sigüenza et al. \(2006\)](#) found that sagebrush inoculated with arbuscular mycorrhizae from a high N deposition site grew more slowly than those with inoculum from a low N deposition site. Grasses in semiarid ecosystems in New Mexico and Colorado grew slower when inoculated with mycorrhizae from sites that had received N additions than from sites without N additions ([Corkidi et al., 2002](#)).

Research published since 2008 has continued to concentrate on CSS and Mojave Desert ecosystems in the southern California, but new studies in southern California chaparral ecosystems, the Sonoran Desert of Arizona, and elsewhere have also been published. Most studies investigating the effects of N deposition in arid and semiarid environments published since the 2008 ISA have further emphasized that the impacts of increased N are heavily dependent on water availability ([Valliere and Allen, 2016a](#); [Rao et al., 2015](#); [Homyak et al., 2014](#); [Newingham et al., 2012](#); [Ochoa-Hueso and Manrique, 2010](#); [Rao and Allen, 2010](#)). The high dependence on precipitation is consistent with ecosystem models for C cycling in desert systems ([Shen et al., 2008](#)).

For instance, [Rao and Allen \(2010\)](#) investigated how productivity in Joshua Tree National Park annuals is altered by increasing N supply under a range of water availabilities ([Table 6-11](#)). Using a 5-year field N addition experiment and N additions of up to 30 kg N/ha/yr, the authors observed the greatest production of invasive grasses and native forbs under the highest soil N and highest watering regime. Similarly, [Newingham et al. \(2012\)](#) found that N additions of 10 or 40 kg N/ha/yr as  $\text{Ca}(\text{NO}_3)_2$  in the Mojave Desert increased branch production in creosote (*Larrea tridentata*) only during a wet year, whereas the addition of water and N significantly increased the amount of rodent herbivory.

**Table 6-11 Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Rao and Allen (2010)</a>	Garden (California, Mojave)	Invasive grass ( <i>Bromus madritensis</i> ), native forb ( <i>Amsinckia tessellata</i> )	Addition	5, 30	1	Aboveground plant biomass	<u>Forb</u> : increase <u>Grass</u> : increase
<a href="#">Wang et al. (2015a)</a>	China (north, Jilin)	Arid grassland ( <i>Leymus chinensis</i> )	Addition	100	4	Ecosystem respiration	Increase
<a href="#">Zhang et al. (2015a)</a>	Beijing, China	Shrubland ( <i>Vitex negundo</i> )	Addition	20, 50, 100	1	Foliar N %	<u>Low dose</u> : not significant <u>Mid dose</u> : increase in one of four species <u>High dose</u> : increase in 3/4 species
<a href="#">Zhang et al. (2015a)</a>	Beijing, China	Shrubland ( <i>Spirea trilobata</i> )	Addition	20, 50, 100	1	Foliar N %	Not significant
<a href="#">Rao and Allen (2010)</a>	California (Mojave)	<i>Larrea tridentata</i> or <i>Juniperus californica</i> , <i>Pinus monophylla</i>	Addition	2, 5, 30	5	Grass and forb biomass	Increase
<a href="#">Wang et al. (2015a)</a>	China (north, Jilin)	Arid grassland ( <i>Leymus chinensis</i> )	Addition	100	4	Gross ecosystem production	Increase
<a href="#">Pasquini and Vourlitis (2010)</a>	California (southern; three sites)	Chaparral ( <i>Adenostoma fasciculatum</i> , <i>Ceanothus</i> spp.)	Ambient	8.1, 11.9, 18.4	n/a	Growth rate per shrub	Increase

**Table 6-11 (Continued): Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Hall et al. (2011)</a>	Phoenix, AZ	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia</i> spp.)	Addition	60	5	Herbaceous annual plant production	Increase
<a href="#">Allen et al. (2009)</a>	California (Joshua Tree NP; four sites)	Creosote bush scrub ( <i>Larrea tridentata</i> ); pinyon-juniper woodland ( <i>Pinus monophylla</i> , <i>Juniperus californica</i> )	Addition	5, 30	2	Invasive grass biomass	<u>Low dose</u> : not significant <u>High dose</u> : increase at 3/4 sites
<a href="#">Newingham et al. (2012)</a>	Nevada (Mojave)	Creosote bush ( <i>Larrea tridentata</i> )	Addition	10, 40	6	<i>Larrea</i> branch elongation	Not significant
<a href="#">Newingham et al. (2012)</a>	Nevada (Mojave)	Creosote bush ( <i>Larrea tridentata</i> )	Addition	10, 40	6	<i>Larrea</i> branch number	Increase
<a href="#">Newingham et al. (2012)</a>	Nevada (Mojave)	Creosote bush ( <i>Larrea tridentata</i> )	Addition	10, 40	6	<i>Larrea</i> leaf production	Not significant
<a href="#">Newingham et al. (2012)</a>	Nevada (Mojave)	Creosote bush ( <i>Larrea tridentata</i> )	Addition	10, 40	6	<i>Larrea</i> seed production	Not significant
<a href="#">Zhang et al. (2015a)</a>	China (north, Songnen)	Shrubland ( <i>Vitex negundo</i> )	Addition	20, 50, 100	1	Leaf litter N %	<u>Low dose</u> : not significant <u>Mid dose</u> : increase in one of four species <u>High dose</u> : increase
<a href="#">Zhang et al. (2015a)</a>	China (north, Songnen)	Shrubland ( <i>Spirea trilobata</i> )	Addition	20, 50, 100	1	Leaf litter N %	Not significant

**Table 6-11 (Continued): Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Allen et al. (2009)</a>	California (Joshua tree NP; four sites)	Creosote bush scrub ( <i>Larrea tridentata</i> ); pinyon-juniper woodland ( <i>Pinus monophylla</i> , <i>Juniperus californica</i> )	Addition	5, 30	2	Native and exotic plant cover	<u>Low dose</u> : not significant <u>High dose</u> : not significant at three sites, increased native cover at one site
<a href="#">Wang et al. (2015a)</a>	China (north, Jilin)	Arid grassland ( <i>Leymus chinensis</i> )	Addition	100	4	Net ecosystem exchange	Increase
<a href="#">Belnap et al. (2008)</a>	Utah (Canyonlands NP)	Biological soil crusts	Addition	Not stated	1	Photosynthetic pigments	Decrease
<a href="#">Sun et al. (2014)</a>	China (north, Songnen)	Shrubland ( <i>Leymus chinensis</i> , <i>Artemisia scoparia</i> )	Addition	23, 46, 69, 92	3	Plant aboveground biomass	<u>Low dose</u> : not significant <u>Other doses</u> : increase
<a href="#">Wang et al. (2015a)</a>	China (north, Jilin)	Arid grassland ( <i>Leymus chinensis</i> )	Addition	100	4	Plant aboveground biomass	Increase
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant aboveground biomass	Increase
<a href="#">Collins et al. (2017)</a>	New Mexico	Grassland ( <i>Bouteloua eriopoda</i> , <i>Bouteloua gracilis</i> )	Addition	20	1 to 7	Plant aboveground biomass for grass and forbs	Increase in grass biomass in 1 yr (the year following a fire); not significant in the other years or for forb biomass
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant belowground biomass	Increase

**Table 6-11 (Continued): Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Rao et al. (2009)</a>	California (Joshua Tree NP)	Creosote bush ( <i>Larrea tridentata</i> ) or pinyon-juniper woodland ( <i>Pinus monophylla</i> , <i>Juniperus californica</i> )	Ambient	2.7–14.4	n/a	Plant biomass	Not significant
<a href="#">Ochoa-Hueso and Stevens (2015)</a>	Spain	Shrubland ( <i>Quercus coccifera</i> , <i>Rosmarinus officinalis</i> , <i>Lithodara fruticosa</i> )	Addition	10, 20, 50	3	Plant biomass	Not significant
<a href="#">Rao et al. (2015)</a>	California (Mojave)	Desert wash, desert scrub, desert succulent cover types	Ambient	0.4–15.3	n/a	Plant biomass	Not significant; precipitation was main driver of biomass
<a href="#">McHugh et al. (2017)</a>	Utah	Semiarid grassland	Addition	2, 5, 8	2	Plant cover	Not significant
<a href="#">Vourlitis (2017)</a>	California (southern)	Shrubland (coastal sage scrub)	Addition	50	13	Plant cover (total)	Not significant for most of the 13 yr; increase in the 7th and 8th yr of experiment
<a href="#">Regus et al. (2017)</a>	California	Desert, shrubland	Addition	1.8–8.7+	8 weeks	Plant growth due to rhizobia nodules on native legume ( <i>Acmispon strigosus</i> )	Decrease
<a href="#">Hall et al. (2011)</a>	Phoenix, AZ	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia</i> spp.)	Addition	60	5	Shrub biomass production	Not significant

**Table 6-11 (Continued): Arid and semiarid ecosystem plant productivity and physiology responses to nitrogen added in experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Pasquini and Vourlitis (2010)</a>	California (southern; three sites)	Chaparral ( <i>Adenostoma fasciculatum</i> , <i>Ceanothus</i> spp.)	Ambient	8.1, 11.9, 18.4	n/a	Shrub density (plants/ha)	Decrease
<a href="#">Sinsabaugh et al. (2015)</a>	Nevada (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Addition	7, 15	1	Shrub foliar element % (including N, P)	Not significant
<a href="#">Hall et al. (2011)</a>	Phoenix, AZ	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia</i> spp.)	Addition	60	5	Shrub foliar N %	<i>Larrea</i> and herbs: increase <i>Ambrosia</i> : not significant
<a href="#">Wissinger et al. (2014)</a>	California (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Ambient	2–12	n/a	Shrub foliar N %	Not significant
<a href="#">Wissinger et al. (2014)</a>	California (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Ambient	2–12	n/a	Shrub seed production	Increase

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; NP = national park; P = phosphorus; yr = year.

Notes: single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

A similar interaction between N and water was found in the Sonoran Desert. Herbaceous annual biomass increased with added N (60 kg N/ha/yr) during above-normal rainfall seasons, but not in low precipitation years ([Hall et al., 2011](#)). In contrast, no increases in productivity were observed in the dominant shrub *Larrea tridentata*, even during above-normal rainfall ([Hall et al., 2011](#)). Ecosystem modeling for this same study system, however, conducted by [Shen et al. \(2008\)](#) suggested observed rates of N deposition in the Phoenix region would increase *Larrea* productivity by more than an order of magnitude in wet years. Mosses in this region also appear to be influenced by N deposition, with lower moss abundance and higher tissue N concentrations at urban study sites that receive higher N deposition ([Ball and Guevara, 2015](#)).

As in other terrestrial ecosystems (see [Appendix 6.2.2](#), [Appendix 6.2.3.1](#)), increases in foliar N concentrations in ecosystems receiving chronic N additions are not necessarily associated with changes in leaf physiological function in semiarid plants. With the exception of the N fixing *Ceanothus*, shrubs in a chaparral ecosystem and a CSS ecosystem in southern California increased foliar N concentrations in response to long-term N additions (50 kg N/ha/yr for 10 years), but none of the four shrub species (*Artemisia californica*, *Salvia mellifera*, *Adenostoma fasciculatum*, *Ceanothus greggii*) increased leaf-level photosynthesis ([Pivovarov et al., 2016](#)). Several species in this study had higher dry season predawn water potential, indicating relative improvements in water availability. However, wet season water potential (predawn and midday) were unresponsive to N additions and only *Artemisia* exhibited changes in plant hydraulic function (increased stomatal conductance and sapwood conductivity and decreased wood density) that would indicate the shrubs were benefitting from greater water availability. In contrast, *Adenostoma* wood xylem became more prone to cavitation ([Pivovarov et al., 2016](#)). The limited aboveground physiological responses of the dominant shrubs in these ecosystems is consistent with the idea that other resources (e.g., water) are often more limiting to plant productivity than N in arid and semiarid ecosystems.

Other studies document the overall effect of N deposition on vegetation communities, including the occurrence of fire. At Joshua Tree National Park in the Mojave desert of California, non-native grass biomass increased significantly at three of the four study sites receiving 30 kg N/ha/yr for 2 years, but saw no change with 5 kg N/ha/yr of added N ([Allen et al., 2009](#)). Native species showed no clear response to N addition, but these plants made up a small fraction of community biomass. [Rao et al. \(2015\)](#) tried to model the effects of N deposition on the biomass of invasive annual grasses and the occurrence of wildfire in the Mojave Desert of California but were unable to effectively disentangle the effects of N deposition on fire from factors such as precipitation, distance from roads, and firefighting resources. However, in an earlier modeling study of Mojave Desert vegetation, [Rao et al. \(2010\)](#) did conclude that increases in precipitation and N deposition

raise fire risks by stimulating greater vegetation biomass, and thus fuel loads. In a study covering California deserts stretching from the Mexican border into the Great Basin, the stimulatory effect of N deposition on the growth of annual grasses was one of the largest contributors to the occurrence of large fires (>20 ha) across four semiarid ecoregions, including the Mojave Desert ([Syphard et al., 2017](#)). Additionally, [Wissinger et al. \(2014\)](#) observed higher seed production in areas of the Mojave with higher atmospheric N deposition (up to 16 kg N/ha/yr).

In arid ecosystems with low vascular plant cover, soil crusts with photoautotrophs such as cyanobacteria, green algae, bryophytes, and lichens can be important ecosystem components and large contributors to biogeochemical cycles. In the Mojave Desert, [Stark et al. \(2011\)](#) investigated the effects of 10 or 40 kg N/ha/yr N addition on the dominant biological soil-crust moss (*Syntrichia caninervis*) for a period of 5 years. Interestingly, the lower rate of N application had negative effects on the amount dead chlorotic tissue in shoots and crust regeneration, while higher rates of N addition only negatively impacted apical meristem growth. In Spain, the abundance of most pigments associated with cyanobacteria and green algae in soil crusts within Mediterranean ecosystems did not significantly vary with N deposition along a gradient, but the cyanobacterial pigment echinenone was negatively correlated with N deposition [4.3–7.3 kg N/ha/yr; [Ochoa-Hueso et al. \(2016\)](#)]. In China, [Zhou et al. \(2016\)](#) observed that high N addition rates (50 kg N/ha/yr for 4 years) decreased total chlorophyll and chlorophyll *b* content in soil crusts dominated by cyanobacteria. Lower N addition rates (3–15 kg N/ha/yr), however, did not affect cyanobacteria chlorophyll, and lichen chlorophyll was unaffected by the N addition treatments. Cyanobacteria soluble sugar concentrations, an osmolyte produced as a response to stress, increased at the second highest N dose, but other osmolytes (proline, soluble protein) and lichens were unaffected ([Zhou et al., 2016](#)).

There are very few field studies of how N enrichment impacts belowground C cycling in arid systems ([Liu and Greaver, 2010](#)). In a meta-analysis of these studies, [Liu and Greaver \(2010\)](#) found no consistent effect of N enrichment on soil respiration. [Verburg et al. \(2013\)](#) quantified the effects of increased summer precipitation and N deposition on fine root dynamics in a Mojave Desert ecosystem during a 2-year field experiment. Increased summer precipitation and 40 kg N/ha/yr N additions did not have an overall significant effect on any of the measured root parameters. Within the Sonoran Desert near Phoenix, [Marusenko et al. \(2015\)](#) observed that N additions (60 kg N/ha/yr for 8 years) increased the abundance of the *amoA* gene, which is needed for ammonia oxidation, in both archaea and bacteria. There was no increase in ammonia-oxidizing bacteria or archaea along a narrow N deposition gradient (4.3–7.3 kg N/ha/yr) in Mediterranean shrublands and grasslands in Spain, and overall bacterial abundance was negatively related to N deposition ([Ochoa-Hueso et al., 2016](#)). [Sinsabaugh et al. \(2015\)](#) conducted a

meta-analysis of soil microbial responses to N additions (5 to 560 kg N/ha/yr; 0.3 to 10 years) in arid ecosystems and identified only 8 studies of various microbial biomass responses and 10 studies of various microbial metabolic responses. Broadly, both metrics increased with the addition of low amounts of N, but responses became negative once threshold N addition rates (kg N/ha/yr: 88 for biomass, 70 for metabolism) or cumulative loads (kg N/ha: 159 for biomass, 114 for metabolism) had been reached.

In a greenhouse study with California sagebrush (*Artemisia californica*) seedlings, [Valliere and Allen \(2016a\)](#) observed that the effects of added N on root colonization by arbuscular mycorrhizal fungi depended both on whether the soil inoculum came from a high or low N deposition site and whether the seedlings were stressed by drought; root colonization was generally lower with soil inoculum from the high N deposition site, except when N was added under well-watered conditions. Notably, the same was also true for root colonization by nonmycorrhizal fungi ([Valliere and Allen, 2016a](#)). A related greenhouse study grew a non-native grass and two non-native forbs from CSS ecosystems in two trials using either sterile soils or soil inoculated from plots receiving N additions or control plots ([Valliere and Allen, 2016b](#)). This study found that N additions (57 kg N/ha/yr) had no effect on arbuscular mycorrhizal root colonization in one forb (*Hirschfeldia incana*), increased arbuscular mycorrhizal colonization in only the second trial for the other forb (*Centaurea melitensis*), and increased arbuscular mycorrhizal colonization in the second trial for the grass (*Bromus diandrus*) when it was inoculated with soil from N addition plots ([Valliere and Allen, 2016b](#)). Although there were differences in mycorrhizal colonization between the species and soil types, no direct link was observed between colonization and the plant growth response to added N; while not always significant, added N increased aboveground biomass in all plants and in all soil types. The effect of added N was larger in the second trial and in inoculated soils, but there was little difference in aboveground growth of the non-native plants between the N addition inoculum and the control soil inoculum ([Valliere and Allen, 2016b](#)). However, [Valliere and Allen \(2016a\)](#) only observed positive sagebrush seedling growth responses to added N in soils with high N deposition site inoculum, whereas sterile and low N deposition inoculum were unresponsive to added N. Thus, evidence is still mixed that soil microbial communities at sites that have experienced N additions can themselves change the growth response of plants to added N in arid and semiarid ecosystems.

[Vourlitis \(2012\)](#) measured the aboveground biomass and litter production of a post-fire chaparral and a mature CSS stand in southern California over an 8-year period. Nitrogen additions decreased NPP in the chaparral during the first 3 years of the study, but these additions increased NPP during the last 3 years of the experiment. In the CSS, the effect of added N positively correlated with precipitation and was only significant in the high rainfall years. The authors suggested N enrichment (50 kg N/ha/yr) may increase the

productivity, but temporal patterns may take years to emerge and be dependent on water availability. In contrast, shorter experiments conducted by [Vourlitis and Fernandez \(2012\)](#) and [Vourlitis et al. \(2009\)](#) in chaparral and CSS ecosystems in southern California found 4 years of dry season N addition at 50 kg N/ha/yr increased litter N and plant tissue, but had no effect on ecosystem productivity or ecosystem N storage. Another study using the same N deposition gradient in the CSS as [Padgett and Allen \(1999\)](#) found lower soil C content at high deposition sites ([Liu and Crowley, 2009](#)). Further, experimental N additions [50 kg N/ha/yr as Ca(NO<sub>3</sub>)<sub>2</sub>] decreased soil C content at the low deposition site. However, there were no clear changes in microbial community composition along the deposition gradient or as a result of the N additions.

A study by [Vourlitis and Pasquini \(2008\)](#) analyzed pre- and post-fire nutrient and soil dynamics of three southern California chaparral stands exposed to varying levels of N deposition and determined that periodic fire may not reduce N enrichment from decades of N deposition. In a subsequent study, ([Pasquini and Vourlitis, 2010](#)) exposed chaparral stands to different levels of N deposition over the first 3 years of post-fire succession. High N deposition was associated with a lower relative abundance of *A. fasciculatum* and a higher relative abundance of other shrub and herbaceous species. However, overall aboveground net productivity was not related to N deposition.

Numerous studies were also conducted on dryland ecosystems outside of the U.S., including in China. Many of these Chinese N addition experiments have been conducted in semiarid steppe ecosystems, particularly within the Inner Mongolia region. In these experiments, N additions increased plant productivity ([Zeng et al., 2016](#); [Zhang et al., 2015d](#); [Li et al., 2014](#); [Sun et al., 2014](#)), with a larger stimulation of aboveground growth than belowground growth ([Wang et al., 2015a](#); [Zhang et al., 2015d](#); [Li et al., 2014](#)). In one of these experiments, 4 years of N additions (50 kg N/ha/yr as urea) increased NEE (+53.8%), ER (+47.6%), and GEP (+47.9%) in the last 3 years of the experiment ([Wang et al., 2015a](#)). The N additions increased foliar N concentrations ([Zeng et al., 2016](#); [Zhang et al., 2015a](#)), but [Zhang et al. \(2015a\)](#) also observed that the N additions decreased the amount of N resorbed during leaf senescence in seven perennial grass, sedge, and shrub species. Effects on microbial biomass in these Chinese N addition experiments have been both positive ([Shi et al., 2016b](#); [Sun et al., 2014](#)) and negative ([Li et al., 2016a](#)).

[Huang et al. \(2015\)](#) conducted a 3-year N × water experiment focused on soil microbial community composition and function in a desert steppe ecosystem in northwestern China that receives 25 kg N/ha/yr of ambient deposition. The N addition treatment (50 kg N/ha/yr as NH<sub>4</sub>NO<sub>3</sub>) did not have consistent effects, increasing microbial respiration in the spaces between shrubs in the first year, while decreasing microbial

respiration and microbial biomass C beneath the shrubs in the abnormally dry second year. The N addition effects differed between inter-plant spaces and beneath shrub sites. In the inter-plant spaces, N additions tended to increase overall microbial abundance, with significant increases in bacteria and total microbial PLFA biomass in all 3 years and an increase in actinobacteria in the last 2 years of the experiment. Beneath the shrubs, N additions decreased bacterial biomass, fungal biomass, and total PLFA in 2 years and decreased actinobacterial biomass in all 3 years ([Table 6-12](#)).

[Zhang et al. \(2015e\)](#) studied how N added (eight levels from 10 to 500 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$ ) frequently (12 doses/yr) or infrequently (2 doses/yr) over 5 years influenced plant productivity in a steppe grassland in the Inner Mongolia region of China. The higher doses of N increased aboveground NPP regardless of how frequently the N was added. However, the authors pointed to a group of similar studies that had shown small frequent N doses caused more, less, or similar growth responses relative to large infrequent N doses. As in other semiarid systems, the authors noted greater productivity responses to N in years with higher precipitation. Although the N additions increased ecosystem aboveground NPP, some individual species were less productive with added N ([Zhang et al., 2015e](#)).

**Table 6-12 Arid and semiarid microbial biomass responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Treseder (2008)</a>	Desert	Meta-analysis	Addition	50–500	0.4–2	Microbial biomass	Increase
<a href="#">Sinsabaugh et al. (2015)</a>	Global	Arid lands meta-analysis	Addition	5–560	0.3–10	Microbial biomass	<u>Low dose:</u> increase <u>High dose:</u> decrease
<a href="#">Sinsabaugh et al. (2015)</a>	Nevada (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Addition	7, 15	1	Microbial biomass	Not significant
<a href="#">Sun et al. (2014)</a>	China (north, Songnen)	Shrubland ( <i>Leymus chinensis</i> , <i>Artemisia scoparia</i> )	Addition	23, 46, 69, 92	3	Microbial biomass C	<u>Highest dose:</u> increase <u>Other doses:</u> not significant
<a href="#">Huang et al. (2015)</a>	China	Desert shrubs ( <i>Haloxylon ammodendron</i> )	Addition	50	3	Microbial biomass C	Not significant
<a href="#">Sinsabaugh et al. (2015)</a>	Global	Arid lands meta-analysis	Addition	5–560	0.3–10	Microbial metabolism	<u>Low dose:</u> increase <u>High dose:</u> decrease
<a href="#">Regus et al. (2017)</a>	California	Desert, shrubland	Addition	1.8–8.7+	8 weeks	Nodule formation by rhizobia on native legume ( <i>Acmispon strigosus</i> )	Decrease

C = carbon; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints or ecosystems were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

In a greenhouse study of plants collected from a semiarid ecosystem in Spain, [Ochoa-Hueso and Manrique \(2010\)](#) found that grass biomass was relatively unresponsive to N enrichment of up to 50 kg N/ha, even when provided with increased water. However, forb biomass and community biomass approximately tripled when both water and N were enriched. In a related field experiment in central Spain, [Ochoa-Hueso and Stevens \(2015\)](#) added N (10, 20, or 50 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$ ) to a semiarid shrubland ecosystem for 6 years. The effects on plant productivity varied by time. After 2.5 years, N additions decreased the biomass of the dominant forb species. After 5.5 years, N additions increased the biomass of plants in the Cruciferae family, but only in areas where sufficient soil P was available. The authors noted that each of the biomass assessments occurred in years with above-average precipitation. In year 4 of the experiment, [Ochoa-Hueso et al. \(2014\)](#) surveyed soil fauna (largely arthropods) and observed that the moderate dose (20 kg N/ha/yr) significantly increased the total abundance of soil fauna (organisms/g of soil), principally by increasing Collembola populations. This increase was not significant at other doses and was attributed to soil acidification. At the highest dose, soil Pauropoda increased ([Ochoa-Hueso et al., 2014](#)).

Elsewhere in Spain, [Taboada et al. \(2016\)](#) conducted a series of experiments to understand how N deposition influenced herbivorous heather beetles (*Lochmaea suturalis*) and their predators (beetles and Arachnids) in a semiarid *Calluna vulgaris* heathland. In food-choice lab experiments, beetle larvae caused significantly greater shoot weight loss in plants that had experienced high N addition rates (20, 50, or 56 kg N/ha/yr) than the low N addition rate (10 kg N/ha/yr) or control, but N addition had no influence on shoot consumption by adult beetles. [Taboada et al. \(2016\)](#) suggested that this was evidence that the larvae could detect differences in tissue N and preferred to feed on high-N shoots. The number of herbaceous heather beetle larvae was greater in plots that had received long-term N additions (56 kg N/ha/yr for 10 years) than in the control or short-term (2 year) N addition plots. In contrast, the number of predaceous Arachnids was unaffected by N additions and the number of predatory beetles was greater in the control plots, particularly in recently burned plots ([Taboada et al., 2016](#)).

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## 6.3 Relationships between Nitrogen Deposition and Terrestrial Species Composition, Species Richness, and Biodiversity

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### 6.3.1 Introduction

Given the role of N in biogeochemical cycling ([Appendix 4](#)), soil acidification ([Appendix 5](#)), and the growth and physiology of terrestrial organisms ([Appendix 6.2](#)), it is unsurprising that N availability can influence community composition and biodiversity. In the 2008 ISA, the evidence was sufficient to infer a causal relationship between N deposition on the alteration of terrestrial species composition, richness, and biodiversity. In the 2008 ISA, the most sensitive terrestrial taxa were lichens. Empirical evidence indicated that lichen composition and richness in the U.S. are adversely affected by deposition levels as low as 3 kg N/ha/yr. Alpine ecosystems were also found to be sensitive to N deposition. Changes in individual species were estimated to occur at deposition levels near 4 kg N/ha/yr, and modeling indicated that deposition levels near 10 kg N/ha/yr alter plant community assemblages.

Since 2008, many studies have examined the relationship between N and terrestrial community composition and species richness. The effects of N deposition on diversity have been observed in all major biomes ([Bobbink et al., 2010](#)), and these effects have been particularly well studied in the temperate ecosystems prevalent across much of the U.S. ([Murphy and Romanuk, 2016](#)). Changes in biological communities have been found across a wide range of taxonomic and functional classifications, including trees, shrubs, grasses, forbs, bryophytes, fungi (including mycorrhizae), bacteria, and arthropods. Among these effects, N deposition has been identified as a threat to 12 terrestrial plant or animal species that are listed or candidates for protection under the federal Endangered Species Act ([Hernández et al., 2016](#)).

A number of global, continental, and regional syntheses have compiled information about changes in biodiversity as a result of N deposition. Some of these studies predate the 2008 ISA and served as part of the basis for the conclusions in that assessment [e.g., [Vitousek et al. \(1997\)](#); [Wallenda and Kottke \(1998\)](#); [Gough et al. \(2000\)](#); [Bobbink et al. \(2003\)](#); [Matson et al. \(2002\)](#); [Pennings et al. \(2005\)](#); [Stevens et al. \(2004\)](#); [Suding et al. \(2005\)](#); [Phoenix et al. \(2006\)](#)]. More recent assessments have reinforced the conclusion that N deposition is a major cause of species loss in ecosystems around the world [e.g., [Bobbink et al. \(2010\)](#); [De Schrijver et al. \(2011\)](#); [Pardo et al. \(2011a\)](#); [Phoenix et al. \(2012\)](#); [van Den Berg et al. \(2016\)](#)]. Further, these new assessments have provided a more detailed understanding of both sensitive and heavily impacted species,

ecosystems, and biomes and have created a more precise understanding of the mechanisms linking species loss to N deposition. This new research, combined with information from the 2008 ISA, creates a body of evidence sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.

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### 6.3.2 Mechanisms Operating across Terrestrial Ecosystems

Given the complexities of N effects, it is difficult to develop mechanistic models that can accurately predict shifts in the composition of ecological communities as a result of N deposition. Consequently, assessments of how N deposition alters species diversity, species richness, and changes in community composition predominately rely on experimental manipulations and empirical relationships developed across large spatial and temporal scales [e.g., [Suding et al. \(2005\)](#); [Clark et al. \(2007\)](#); [Verheyen et al. \(2012\)](#); [Simkin et al. \(2016\)](#)].

Much of the ecological theory regarding the loss of species richness with N enrichment has been developed from observations of changes in plant species abundance in grasslands and other nonforest ecosystems [e.g., [Gough et al. \(2000\)](#); [Suding et al. \(2005\)](#); [Pennings et al. \(2005\)](#); [Farrer and Suding \(2016\)](#)]. Many investigators have found a unimodal relationship between plant species richness and aboveground primary productivity, such that there is a negative relationship between productivity and local-scale plant species richness in terrestrial ecosystems that takes effect once an initial threshold for minimum productivity has been reached ([Suding et al., 2005](#); [Gough et al., 2000](#); [Gross et al., 2000](#); [Grime, 1973](#)). In a synthesis of long-term (>4 years) N addition experiments (90–130 kg N/ha/yr) in open-canopy ecosystems (grasslands, tundra, etc.), [Gough et al. \(2000\)](#) found that as the relative stimulation of aboveground primary productivity by N additions increased, there was a greater relative loss of species richness. Thus, there was a direct linkage between the stimulation of productivity by added N and the loss of plant species richness.

Variation among plants in the magnitude of growth responses to added N can have critical and asymmetric effects on community composition because small differences in plant height can cause substantial differences in the amount of light absorbed by plant foliage ([Farrer and Suding, 2016](#)). There are a number of potential causes for the variation in plant response to added N within communities. Two meta-analyses published in 2005 synthesized data from nonforested N addition experiments across North America to understand the role of plant functional traits versus random effects in determining changes in community diversity ([Pennings et al., 2005](#); [Suding et al., 2005](#)). The

random-loss hypothesis of biodiversity decline suggests that rare species are most likely to disappear as increased competition for resources such as light eliminates less successful individuals, whereas the functional trait hypothesis predicts that organisms will become more or less successful when N is added depending upon particular traits. These mechanisms could operate simultaneously ([Suding et al., 2005](#)). In this synthesis, N additions increased primary production and decreased species richness in all terrestrial ecosystems ([Suding et al., 2005](#)). There was also support for random loss of species: the rarest species had a >60% chance of disappearance, while the chance of disappearance for the most abundant species was 10%. This suggests ecosystems with many rare species that experience increases in competition after N additions are especially sensitive to species loss.

There was also support for the functional trait hypothesis: N fixing forbs, species shorter in stature, and perennial plants were more likely to be lost, although there was variation among the sites in which traits made species the most sensitive to N additions. [Pennings et al. \(2005\)](#) took a somewhat different approach by following the fate of 20 individual species across experiments. They noted consistent responses in 10 of the 20 species, but for all but two species, these responses were dependent on the combination of site productivity, species richness, functional traits, and initial abundance ([Pennings et al., 2005](#)). In a related synthesis of these data to understand the environmental and experimental factors associated with the loss of species richness, [Clark et al. \(2007\)](#) observed that several individual factors were almost equally correlated to the loss of species richness, including aboveground plant production ( $r = -0.50$ ), lower soil cation exchange capacity ( $r = 0.48$ ), and length of the experiment ( $r = -0.57$ ). Overall, a full multifactor structural equation model indicated that increased risk of species loss among the study sites was tied to lower average annual minimum temperature, low soil cation exchange capacity, and larger productivity responses to N additions ([Clark et al., 2007](#)). This suggests that high latitude or high elevation ecosystems, those with low cation exchange capacity (often associated with traits such as sandy soils, low pH, low organic matter content, and highly weathered soils), and productivity that is strongly limited to N, would be the most sensitive to plant species loss—traits common in alpine and Arctic tundra, among other ecosystems.

More recently, [De Schrijver et al. \(2011\)](#) conducted a meta-analysis of plant species richness responses in N addition experiments conducted in forests (understory plants only), heathlands, grasslands, tundra, and wetlands. Additions of N increased graminoid biomass, decreased bryophyte biomass, and decreased the biomass of understory plants in forests. The addition of N decreased species richness when analyzed across experiments; within individual ecosystems the effect was only significant in grasslands and heathlands,

while other ecosystems had negative effects but small sample sizes. The loss of species richness increased with higher cumulative N loads.

The alteration of species interaction by added N occurs via several mechanisms. In addition to altered interactions between species within the same trophic level (e.g., competition between plant species), an increased supply of N can change interactions across trophic levels. These trophic shifts can include changes in the plant-fungal symbioses that occur in mycorrhizae ([Appendix 6.2.3.2](#) and [Appendix 6.3.3.3](#)), the photobiont-mycobiont relationships in lichens ([Appendix 6.2.3.3](#) and [Appendix 6.3.7](#)), and more complex changes in food webs that can occur as a consequence of decreases in plant C allocation to belowground processes ([Appendix 6.2.3.2](#)) and chemical changes in the plant tissues and litter that are consumed by herbivores and detritivores ([Appendix 6.2.3.1](#), [Appendix 6.3.3.4](#)). Changes at higher trophic levels can feed back to affect the productivity and diversity of primary producers. For instance, in a greenhouse experiment conducted by [Farrer and Suding \(2016\)](#) using plants and soils from three long-term N addition experiments (prairie, alpine tundra, arid grassland), mesocosms inoculated with microorganisms collected from soils that had received the long-term N additions were significantly more productive and less diverse than mesocosms inoculated by microorganisms from soils that had not received added N; these effects occurred regardless of whether the mesocosms received N additions. [Valliere and Allen \(2016a\)](#) conducted a similar experiment with California sagebrush (*Artemisia californica*) and observed that plant productivity was greater under low N deposition conditions when plants were grown with inoculum from low deposition sites and greater under high N deposition conditions with inoculum from high deposition sites. These types of interactions complicate predictions of species loss from N deposition.

A new analysis by [Simkin et al. \(2016\)](#) has dramatically increased our understanding of how N deposition is altering plant biodiversity in the continental U.S. They gathered data on herbaceous species richness from more than 15,000 study plots in a variety of habitats. N deposition had a strong effect on species richness, but this effect differed between closed canopy and open ecosystems (i.e., forests and nonforest). In nonforested ecosystems (grasslands, deserts, shrublands, subalpine ecosystems), there was a positive relationship between N deposition and herbaceous species richness at low rates of N deposition, then a decrease in species richness with higher rates of N deposition over a threshold of 8.7 kg N/ha/yr. The effect was notably stronger at low pH (i.e., more acidic). In forests, the relationship between N deposition and herbaceous species richness was similar, but more complex. In acidic soils, the relationship was similar to open canopy systems. In neutral or basic soils, the relationship between N deposition and species richness was consistently positive. Overall, these national-scale results are consistent with the relationship between productivity and species richness suggested by ecological theory

[e.g., [Suding et al. \(2005\)](#); [Clark et al. \(2007\)](#)] and provide evidence that vegetation on acidic soils is more susceptible to species loss under elevated N.

There are few direct analyses comparing the impacts of oxidized and reduced forms of N deposition on biodiversity. Because  $\text{NO}_3^-$  tends to be more readily lost to both leaching and denitrification than  $\text{NH}_4^+$  ([Brady and Weil, 1999](#)), it is possible that this form of N is less likely to accumulate in the soil and cause fewer changes in plant and microbial communities. The meta-analyses literature referenced previously ([Table 6-1](#)) tended to find no difference in the effects of individual forms of N on ecological and biogeochemical endpoints, such as plant productivity or microbial biomass. This is suggestive that plant diversity is also not affected, yet a number of individual studies have observed differential effects on diversity of  $\text{NH}_4^+$  versus  $\text{NO}_3^-$  additions [e.g., [Kleijn et al. \(2008\)](#); [Dias et al. \(2014\)](#)]. For example, in a nutrient-poor, Mediterranean site, an  $\text{NH}_4^+$  addition (40 kg N/ha/yr) increased plant richness, while the addition of a half  $\text{NH}_4^+$  and half  $\text{NO}_3^-$  mixture (for a total of 40 kg N/ha/yr also) did not. In the U.K., [van Den Berg et al. \(2016\)](#) observed that once an overall negative effect of N deposition on plant species richness had been accounted for, the  $\text{NH}_x:\text{NO}_y$  ratio decreased species richness in grasslands, but increased species richness in woodlands. By contrast, [Jovan et al. \(2012\)](#) observed that lichen communities in the Los Angeles basin were best predicted by total N deposition (as throughfall) than the deposition or gaseous concentrations of any particular form of N. The national-scale analysis of herbaceous species richness completed by [Simkin et al. \(2016\)](#) only evaluated total N deposition, not individual forms of deposition.

Future effects of N deposition on biodiversity will depend in part on not only N emissions, but also on the rate at which populations and communities respond to increases or decreases in emission rates and the pace at which total cumulative N deposition increases. Compared to the number of N addition studies, there have been relatively few studies of recovery following the cessation of N additions or decreases in N deposition, and nearly all of these have been in Europe ([Stevens, 2016](#)). In a review of these recovery studies, [Stevens \(2016\)](#) found that soil nitrate and ammonium concentrations recovered to levels observed in untreated controls within 1 to 3 years, but that soil processes such as N mineralization and litter decomposition were slower to recover. For instance, differences in decomposition and soil  $\text{N}_2\text{O}$  emissions persisted 4 and 7 years, respectively, after installation of a roof system to decrease atmospheric deposition to European forests ([Borken and Beese, 2002](#); [Boxman et al., 1998b](#)). Although there were observations that plant physiological processes recovered in less than 2 years, grassland plant communities were slower to recover and still differed from controls 11 to 20 years after the cessation of N additions ([Isbell et al., 2013b](#); [Stevens et al., 2012](#)). [Stevens \(2016\)](#) observed a wide range of recovery times for mycorrhizal community composition and abundance, with some recovery observed in as few as

4 years ([Emmett et al., 1998](#)) and differences persisting for as long as 28 or 48 years ([Strengbom et al., 2001](#)). Based on the slow pace at which plant community composition recovered following observed or experimental decreases in deposition elsewhere in Europe, [Stevens et al. \(2016\)](#) predicted that despite future decreases in reactive N emissions, habitat suitability would decline in 2020 and 2030 for a majority of plant species within grasslands, heathlands and bogs, and deciduous forests in Great Britain due to the cumulative effects of N deposition. Plant communities in these ecosystems were predicted to become more eutrophic: favoring grasses, decreasing the abundance of forbs and lichens, and having mixed species-specific effects on bryophytes and other plant groups ([Stevens et al., 2016](#)).

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### 6.3.3 Forests

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#### 6.3.3.1 Overstory Trees

The 2008 ISA reported that there was very little information on the effect of N deposition on the biodiversity of overstory trees in the U.S. However, the altered growth rates caused by N enrichment have the potential to affect forest structure and biodiversity. The life span of many trees is 100 years or more; therefore, it is difficult to observe how changes in growth or mortality affect biodiversity within established forests. The 2008 ISA cited evidence for boreal forest encroachment into grasslands under increased N deposition ([Köchy and Wilson, 2001](#)). Since the 2008 ISA, little new direct information is available on the effect of N deposition on the biodiversity of overstory trees in the U.S. or Europe. In subtropical forests in China along a rural to urban N deposition gradient of 30 to 43 kg N/ha/yr across four sites, [Huang et al. \(2012\)](#) found a decrease in tree diversity with increasing N deposition, but there were also differences in management regimes, elevation, and dominant vegetation among the study sites. There is widespread evidence of species-specific effects of N deposition on tree growth and mortality in the U.S. [e.g., [Thomas et al. \(2010\)](#); [Dietze and Moorcroft \(2011\)](#); [Horn et al. \(2018\)](#)]. Further, [Horn et al. \(2018\)](#) concluded that species with positive versus negative responses in growth or survival co-occurred in places in the U.S. This implies overstory tree community composition does shift with N deposition, but this information has not yet been transformed into a quantitative assessment of changes in tree community composition. A broad-scale analysis of changes in overstory community composition as a result of N deposition remains a research need.

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### 6.3.3.2 Understory Plants

Compared to overstory trees, there was more information available in the 2008 ISA regarding the effects of N deposition on understory plants. A major influence on the 2008 ISA was a review by [Gilliam \(2006\)](#), who identified nine studies on N deposition effects on forest understory plant communities, all within the U.S. and Europe. All of the North American studies cited by [Gilliam \(2006\)](#) were N addition experiments within temperate forests in the northeastern U.S.; two of these studies found no significant changes in community composition ([Gilliam et al., 2006](#); [Gilliam et al., 1994](#)). Notably, research by [Gilliam et al. \(2016b\)](#) has subsequently reported decreases in understory species richness, community evenness, and diversity, and changes in community composition at one of the northeastern temperate forest sites where understory community composition had earlier been unaffected by chronic N additions ([Gilliam et al., 2006](#); [Gilliam et al., 1994](#)). In particular, the change in understory community composition caused by N additions included a large increase in the cover of blackberry (*Rubus* spp.) shrubs ([Gilliam et al., 2016b](#); [Walter et al., 2016](#)), but more broadly included an increase in nitrophilous species and a loss of more N efficient (oligotrophic) species ([Gilliam et al., 2016b](#)). In Sweden, shifts in understory plant community composition were documented along two forest N deposition gradients that ranged from 6 to 20 kg N/ha/yr ([Brunet et al., 1998](#)) and from 3 to 12 kg N/ha/yr ([Strengbom et al., 2001](#)).

Many of the mechanisms through which N additions alter plant community composition and species richness in other terrestrial ecosystems also function in forest understory environments, including shifts in mycorrhizal communities, competitive exclusion, increases in herbivory, and species-specific growth responses to increased N availability ([Gilliam, 2006](#)). However, resource heterogeneity in forests can be especially high, and limited light availability can constrain the effects of competitive exclusion ([Simkin et al., 2016](#)). Since the 2008 ISA, a number of new studies of N addition and ambient deposition effects on understory plant diversity have been conducted in temperate and boreal forests in the U.S. and Europe, as well as in subtropical forests in China ([Table 6-13](#)). In a national-scale analysis of herbaceous species richness, [Simkin et al. \(2016\)](#) found that the effect of N deposition on forest understory species richness was highly dependent on soil pH. At all soil pH values, low rates of N deposition (~5 kg N/ha/yr) had neutral or positive effects on species richness. At a low pH (4.5), species richness declined at N deposition rates >11.6 kg N/ha/yr, but among neutral and basic soils there was no point in the data set at which N deposition had a negative effect on species richness (the analysis included deposition values up to ~20 kg N/ha/yr). In a study that synthesized data from >1,200 forest understory vegetation plots in northern and central Europe, [Verheyen et al. \(2012\)](#) did not find a significant effect of increasing N deposition (8.3 to 35.7 kg N/ha/yr) on species richness. Although understory plant

species richness did not change, community composition shifted significantly away from light-demanding species and toward nutrient-demanding species. [van Dobben and de Vries \(2010\)](#) found a similar result in 366 plots in managed forests throughout western and northern Europe and in a smaller network of 197 plots within the Netherlands: N deposition was not a significant influence on plant species richness or diversity and only a minor influence on community composition via a shift toward more nitrophilic species. Soil, elevation, climate, and overstory tree composition were much more important determinants of community composition at this scale ([van Dobben and de Vries, 2010](#)). In a study of forest understory vegetation plots at 28 sites across Europe, [Dirnböck et al. \(2014\)](#) also found that although understory plant species richness was not affected by N deposition, plant communities became more strongly dominated by both more nutrient-demanding species and more shade-tolerant species as N deposition rates increased beyond identified critical loads.

There is also evidence for shifts in plant communities across local and regional N deposition gradients. In a survey of 260 sessile oak (*Quercus petraea*) forests in Ireland, [Wilkins and Aherne \(2016\)](#) observed that N deposition was negatively correlated with plant species richness and had a significant influence on community composition. Community composition and species richness were also significantly influenced by soil pH (positive effect on species richness) and atmospheric NH<sub>3</sub> concentrations (negative effect). Ten species were positively associated with total N deposition and atmospheric NH<sub>3</sub>, while 10 other species had negative associations with these N variables; each group included shrubs, trees, ferns, and bryophytes ([Wilkins and Aherne, 2016](#)). The authors suggested that focusing on a single forest type allowed them to better isolate the effect of N deposition relative to studies of broader forest communities in Europe ([Wilkins and Aherne, 2016](#)). In a survey of woodlands across the U.K., [van Den Berg et al. \(2016\)](#) observed a negative effect of N deposition on plant species richness. [Huang et al. \(2012\)](#) observed that understory plant species richness was negatively correlated with N deposition along a rural to urban gradient (30 to 40 kg N/ha/yr) of four subtropical forests in China. At a network of 40 sugar maple forest monitoring sites in Ontario, [McDonough and Watmough \(2015\)](#) observed that most of the variability in understory plant community composition could be explained by climate and soil factors, but that N deposition (8 to 12.9 kg N/ha/yr) explained a statistically significant portion of the variability. However, there was no effect on understory species richness over this relatively narrow range of N deposition.

**Table 6-13 Forest plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Huang et al. (2012)</a>	China (southern tropical)	Moist subtropical evergreen broadleaf forests	Ambient	30.1–43.1	n/a	Overstory species richness	Decrease
<a href="#">Walter et al. (2016)</a>	West Virginia	Blackberry and berries in the <i>Rubus</i> genus	Addition	35	18	Relative cover of <i>Rubus</i> spp.	Increase, when N addition accompanied by greater forest canopy openness
<a href="#">Talhelm et al. (2013)</a>	Michigan (four sites)	Northern hardwood ( <i>Acer saccharum</i> )	Addition	30	+10	Tree sapling community composition	Not significant
<a href="#">Talhelm et al. (2013)</a>	Michigan (four sites)	Northern hardwood ( <i>Acer saccharum</i> )	Addition	30	+10	Tree sapling species richness	Not significant
<a href="#">Strengbom and Nordin (2008)</a>	Sweden	Scots pine, Norway spruce, birch ( <i>Pinus sylvestris</i> , <i>Picea abies</i> , <i>Betula</i> )	Addition	150 (twice)	Additions 22 and 30 yr prior to surveys	Understory community composition	Change
<a href="#">Verheyen et al. (2012)</a>	Central and northern Europe	Temperate deciduous forests	Ambient	8.3–35.7	n/a	Understory community composition	Change
<a href="#">Hedwall et al. (2013)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Ambient	4.4–16.1	n/a	Understory community composition	Change

**Table 6-13 (Continued): Forest plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Dirnböck et al. (2014)</a>	Europe	Boreal, temperate, and Mediterranean forests	Ambient	0.6–20.2	n/a	Understory community composition	Change
<a href="#">McDonough and Watmough (2015)</a>	Ontario, Canada	Northern hardwood ( <i>Acer saccharum</i> )	Ambient	8.3–12.9	n/a	Understory community composition	Change
<a href="#">Chapman et al. (2016)</a>	Pennsylvania	Mixed oak ( <i>Quercus</i> )	Addition	100, 200	4	Understory community composition	Not significant
<a href="#">Du (2017)</a>	China (northeastern)	Boreal forest ( <i>Larix gmelinii</i> )	Addition	20, 50, 100	3	Understory community composition	Change
<a href="#">Gilliam et al. (2016b)</a>	West Virginia	Mixed temperate hardwood forest	Addition	35	25	Understory herbaceous cover and species diversity	Increase in understory herbaceous cover; decrease in species diversity
<a href="#">Talhelm et al. (2013)</a>	Michigan (four sites)	Northern hardwood ( <i>Acer saccharum</i> )	Addition	30	+10	Understory plant community composition	Change
<a href="#">Strengbom and Nordin (2008)</a>	Sweden	Scots pine, Norway spruce, birch ( <i>Pinus sylvestris</i> , <i>Picea abies</i> , <i>Betula</i> )	Addition	150 (twice)	Additions 22 and 30 yr prior to surveys	Understory species diversity	Decrease
<a href="#">Jones and Chapman (2011)</a>	Pennsylvania	Mixed oak ( <i>Quercus</i> )	Addition	13	1	Understory species diversity	Not significant
<a href="#">Talhelm et al. (2013)</a>	Michigan (four sites)	Northern hardwood ( <i>Acer saccharum</i> )	Addition	30	+10	Understory species diversity	Not significant

**Table 6-13 (Continued): Forest plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Lu et al. (2010)</a>	China (southern tropical)	Evergreen tropical moist forest	Addition	50, 100, 150 (35 ambient)	6	Understory species richness	Decrease
<a href="#">Jones and Chapman (2011)</a>	Pennsylvania	Mixed oak ( <i>Quercus</i> )	Addition	13	1	Understory species richness	Not significant
<a href="#">Lu et al. (2011c)</a>	China (southern tropical)	Pine and broadleaf ( <i>Pinus massoniana</i> , <i>Schima superba</i> )	Addition	50, 100 (40 ambient)	6	Understory species richness	Not significant
<a href="#">Huang et al. (2012)</a>	China (southern tropical)	Moist subtropical evergreen broadleaf forests	Ambient	30.1–43.1	n/a	Understory species richness	Decrease
<a href="#">Verheyen et al. (2012)</a>	Central and northern Europe	Temperate deciduous forests	Ambient	8.3–35.7	n/a	Understory species richness	Not significant
<a href="#">Talhelm et al. (2013)</a>	Michigan (four sites)	Northern hardwood ( <i>Acer saccharum</i> )	Addition	30	+10	Understory species richness	Not significant
<a href="#">Dirnböck et al. (2014)</a>	Europe	Boreal, temperate, and Mediterranean forests	Ambient	0.6–20.2	n/a	Understory species richness	Not significant
<a href="#">McDonough and Watmough (2015)</a>	Ontario, Canada	Northern hardwood ( <i>Acer saccharum</i> )	Ambient	8.3–12.9	n/a	Understory species richness	Not significant
<a href="#">Chapman et al. (2016)</a>	Pennsylvania	Mixed oak ( <i>Quercus</i> )	Addition	100, 200	4	Understory species richness	Not significant
<a href="#">Simkin et al. (2016)</a>	Contiguous U.S.	Forests	Ambient	1.3–17.9	n/a	Understory species richness	<u>Low soil pH:</u> decrease <u>High soil pH:</u> increase

**Table 6-13 (Continued): Forest plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Du (2017)</a>	China (northeastern)	Boreal forest ( <i>Larix gmelinii</i> )	Addition	20, 50, 100	3	Understory species richness	Not significant

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Understory plant species richness was also not affected in several N addition studies in temperate forests in the U.S. ([Chapman et al., 2016](#); [Talhelm et al., 2013](#); [Jones and Chapman, 2011](#)). In an oak forest in the Philadelphia, PA area, [Jones and Chapman \(2011\)](#) found that native understory plant diversity and richness were negatively correlated with soil inorganic N, but not significantly impacted by N additions (13 kg N/ha/yr). In a follow up at the same site, [Chapman et al. \(2016\)](#) used higher rates of N additions (100 or 200 kg N/ha/yr as NH<sub>4</sub>NO<sub>3</sub> for 4 years). Changes in total, native, or invasive species cover were not detected, but N additions increased invasive species richness in some years. In Michigan, [Talhelm et al. \(2013\)](#) found that although N additions did not alter understory plant species richness, community composition was altered. Tree sapling communities were apparently more resistant, as neither species richness nor community composition changed in response to N additions ([Talhelm et al., 2013](#)).

The effects of N additions on forest understory plant communities can be long lasting. [Strengbom and Nordin \(2008\)](#) found significant differences in understory plant communities in recently harvested regenerating Swedish forests as a result of two single additions of 150 kg N/ha 22 and 30 years earlier. The forests that received N decades earlier had denser understory vegetation, much less shrub cover, and much more herb and graminoid cover. The abundance of individual species, including ground-dwelling bryophytes and lichens, differed by as much as 20 times due to the N additions ([Strengbom and Nordin, 2008](#)). In a related study, [Hedwall et al. \(2013\)](#) found that the amount of change in understory plant community composition in regenerating forests caused by N additions was negatively correlated with the rate of N deposition along a Swedish deposition gradient of 4.4 to 16.1 kg N/ha/yr. [Wardle et al. \(2016\)](#) observed that 6 years of N additions (100 kg N/ha/yr) decreased species richness and altered community composition in boreal forest understory communities dominated by Ericaceous shrubs and bryophytes.

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### 6.3.3.3 Microbial Diversity

There is an ongoing debate about how to define a microbial species, so taxonomists often use measures of similarity in genetic material to classify microbial diversity ([Fraser et al., 2009](#)). This can lead to discussion of biodiversity changes in terms of taxonomic community shifts or taxonomic richness. For instance, [Turlapati et al. \(2013\)](#) measured microbial diversity in surface soils at Harvard Forest by clustering operational taxonomic units (OTUs) based on 97% sequence similarity from 16S rRNA pyrosequencing.

Soils contain a high amount of microbial diversity ([Lynch et al., 2012](#)), but this diversity is not evenly distributed among phylogenetic groups. In the Harvard Forest study, [Turlapati et al. \(2013\)](#) observed that 2% of the OTUs contained >50% of the total sequences, while 80% of the OTUs were infrequently observed and contained only about 10% of total sequences. This suggests that many individual soil microbes are either from the same or closely related taxonomic groups, while concomitantly there are a large number of relatively rare taxonomic groups. Reanalyzing these data with a more detailed oligotype sequence clustering approach, [Turlapati et al. \(2015\)](#) found a more even distribution of taxonomic groups, but 2% of oligotypes still represented ~38% of the total number of sequences. In an oligotype analysis of soil fungal communities at the same site, [Morrison et al. \(2016\)](#) observed a similar distribution of fungal populations: the Basidiomycota phylum comprised 63–71% of all sequences, while the Ascomycota phylum averaged 26%, and the ectomycorrhizal genus *Russula* made up 40–50% of all sequences across plots. A shotgun metagenomics assessment of microbial communities in four northern hardwood forests in Michigan documented that taxonomic classification of the metagenomics hits via the RDP databased within MG-RAST were heavily dominated by bacteria (98% of reads), with much smaller contributions of fungi (1%) and archaea [0.03%; [Freedman et al. \(2016\)](#)]. However, annotation databases are biased toward culturable bacteria and there is transcriptomic evidence that metagenomic approaches greatly underrepresent the fungal contribution to soil metabolic function ([Freedman et al., 2016](#)).

Much of the available information about changes in microbial community composition published since 2008 has been about changes in fungal communities, including mycorrhizal species. Of the studies identified for this assessment that quantified the compositional response of forest fungal communities to N additions, one study had site-specific results, but N additions changed community composition in five of the remaining seven studies ([Table 6-14](#)). Among studies of ectomycorrhizal fungi community composition, N caused changes in six out of seven studies, including in four studies along ambient N deposition gradients ([Table 6-15](#)). As with lichens and plants, the sensitivity of ectomycorrhizal fungi appears to vary taxonomically, with these taxonomic differences apparently related to differences in functional traits such as organic N acquisition ([Lilleskov et al., 2011](#)). At Harvard Forest, [Morrison et al. \(2016\)](#) observed that N additions (50 or 150 kg N/ha/yr) decreased the relative abundance of the ectomycorrhizal genus *Cenococcum* and increased the ectomycorrhizal genera *Scleroderma* and *Rhizoscyphus*. *Scleroderma* is thought to be important in organic P acquisition, and *Rhizoscyphus* has proteolytic, cellulolytic, and partial lignin degradation capabilities, but less is known about *Cenococcum*. The overall abundance of the genus *Russula* did not change as a result of N additions, but the *Russula* species (*R. vinacea*)

that was the single most abundant OTU in the data set increased from 10% relative abundance to 28–37% in the N addition plots, while the other *Russula* decreased.

Shifts in ectomycorrhizal composition have also been observed along N depositional gradients. [Kjøller et al. \(2012\)](#) observed changes in the ectomycorrhizal community composition and a loss of ectomycorrhizal species richness across an N deposition gradient in Denmark from 27 to 43 kg N/ha/yr at the edge of a spruce forest. In Scotland, [Jarvis et al. \(2013\)](#) analyzed ectomycorrhizal fungal communities from 15 seminatural Scots pine forests and found changes in abundance of *Cortinarius* spp. at higher N deposition (9.8 kg N/ha/yr). In red spruce-dominated forests in the northeastern U.S., [Lilleskov et al. \(2008\)](#) observed changes in ectomycorrhizal communities over a much lower N deposition gradient, ranging from 2.8 to 7.9 kg N/ha/yr of wet deposition. Nitrogen deposition was positively related to fine root N concentrations, and those root N concentrations had positive relationships with the abundance of three of the ectomycorrhizal fungal morphotypes, negative relationships with three morphotypes, and ambiguous relationships with three other morphotypes. In Scots pine (*Pinus sylvestris*) forests in Germany and the U.K. arrayed along an N deposition gradient ranging from 4.6 to 28.6 kg N/ha/yr, [Cox et al. \(2010\)](#) used DNA extracted from fine roots and group sequences at 97% similarity to assess changes in ectomycorrhizal community composition. Similar to the results in the [Lilleskov et al. \(2008\)](#) study, N deposition was positively correlated to foliar N concentrations and foliar N was linked to shifts in mycorrhizal community structure. In particular, foliar N concentrations were significantly negatively correlated with ectomycorrhizal richness. Of the 35 taxa that occurred widely across the gradient, 11 showed significant responses to increased N availability: 6 taxa increased and 5 taxa decreased with greater N availability ([Cox et al., 2010](#)). Thus, the effects of N deposition on ectomycorrhizal community composition observed by [Lilleskov et al. \(2008\)](#) and [Cox et al. \(2010\)](#) were indirect.

**Table 6-14 Forest microbial biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Actinobacterial community composition	<u>Three sites</u> : change <u>One site</u> : not significant
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Actinobacterial gene diversity	<u>Two sites</u> : decrease <u>Two sites</u> : not significant
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Actinobacterial gene functional richness	<u>Two sites</u> : decrease <u>Two sites</u> : not significant
<a href="#">Krumins et al. (2009)</a>	Florida and New Jersey	Scrub oak forests ( <i>Quercus myrtifolia</i> , <i>Q. ilicifolia</i> )	Addition	35, 70	1	Bacterial community composition	Not significant
<a href="#">Turlapati et al. (2013)</a>	Massachusetts (Harvard Forest)	Temperate oak forest ( <i>Quercus rubra</i> , <i>Q. velutina</i> )	Addition	50, 150	22	Bacterial community composition	Change
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Bacterial community composition	Not significant

**Table 6-14 (Continued): Forest microbial biodiversity responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Turlapati et al. (2015)</a>	Massachusetts (Harvard Forest)	Temperate oak forest ( <i>Quercus rubra</i> , <i>Q. velutina</i> )	Addition	50, 150	22	Bacterial community composition	Change
<a href="#">Turlapati et al. (2013)</a>	Massachusetts (Harvard Forest)	Temperate oak forest ( <i>Quercus rubra</i> , <i>Q. velutina</i> )	Addition	50, 150	22	Bacterial richness	Increase
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Bacterial richness	Not significant
<a href="#">Zechmeister-Boltenstern et al. (2011)</a>	Europe	Conifer and broadleaf forests	Ambient	2–40	n/a	Bacterial/fungi ratio	Increase
<a href="#">Allison et al. (2008)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> )	Addition	140	5	Fungal community composition	Change
<a href="#">Krumins et al. (2009)</a>	Florida and New Jersey	Scrub oak forests ( <i>Quercus myrtifolia</i> , <i>Q. ilicifolia</i> )	Addition	35, 70	1	Fungal community composition	Not significant
<a href="#">Allison et al. (2010)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> , <i>Festuca altaica</i> )	Addition	114	7	Fungal community composition	Change
<a href="#">Edwards et al. (2011)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	14	Fungal community composition	Not significant

**Table 6-14 (Continued): Forest microbial biodiversity responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal community composition	<u>Two sites</u> : change <u>Two sites</u> : not significant
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal community composition	Change
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Fungal community composition (saprobic fungi)	Change
<a href="#">Allison et al. (2008)</a>	Alaska	Boreal forest ( <i>Picea mariana</i> )	Addition	140	5	Fungal diversity	Not significant
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal gene diversity	<u>Two sites</u> : decrease <u>Two sites</u> : not significant
<a href="#">Eisenlord et al. (2013)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal gene functional richness	<u>Two sites</u> : decrease <u>Two sites</u> : not significant
<a href="#">Krumins et al. (2009)</a>	Florida and New Jersey	Scrub oak forests ( <i>Quercus myrtifolia</i> , <i>Q. ilicifolia</i> )	Addition	35, 70	1	Fungal morphotype richness	Not significant
<a href="#">Hesse et al. (2015)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	16	Fungal richness	Not significant

**Table 6-14 (Continued): Forest microbial biodiversity responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Fungal richness (saprobic fungi)	Decrease
<a href="#">van Diepen et al. (2010)</a>	Michigan (MI gradient)	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	12	Microbial community composition	Change
<a href="#">Zechmeister-Boltenstern et al. (2011)</a>	Europe	Conifer and broadleaf forests	Ambient	2–40	n/a	Microbial community composition	Change
<a href="#">Hobbie et al. (2012)</a>	Minnesota (Cedar Creek)	Oak and pine forests ( <i>Quercus ellipsoidalis</i> , <i>Pinus strobus</i> )	Addition	100	5	Microbial community composition	Change
<a href="#">Zhao et al. (2014a)</a>	China (Tibetan Plateau)	Spruce-fir ( <i>Picea asperata</i> , <i>Abies faxoniana</i> )	Addition	250	4	Microbial community composition	Change

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

**Table 6-15 Ectomycorrhizal biodiversity responses to nitrogen added via atmospheric deposition or experimental N additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Avis et al. (2008)</a>	Illinois	Oak ( <i>Quercus alba</i> , <i>Q. rubra</i> )	Addition	21	4	Community composition	Change
<a href="#">Lilleskov et al. (2008)</a>	Northeastern U.S.	Red spruce ( <i>Picea rubens</i> )	Ambient	2.8–7.9 (wet only)	n/a	Community composition	Change (indirect)
<a href="#">Wright et al. (2009)</a>	British Columbia, Canada	Western hemlock ( <i>Tsuga heterophylla</i> )	Addition	300 (once)	7-yr recovery	Community composition	Not significant
<a href="#">Cox et al. (2010)</a>	Germany, U.K.	Scots pine ( <i>Pinus sylvestris</i> )	Ambient	4.6–28.6	n/a	Community composition	Change (indirect)
<a href="#">Kjøller et al. (2012)</a>	Denmark	Norway spruce ( <i>Picea abies</i> )	Ambient	27–43	n/a	Community composition	Change
<a href="#">Jarvis et al. (2013)</a>	Scotland, U.K.	Scots pine ( <i>Pinus sylvestris</i> )	Ambient	3.1–9.9	n/a	Community composition	Change
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Community composition (sporocarps)	Change
<a href="#">Suz et al. (2014)</a>	Europe (nine countries)	Oak ( <i>Quercus robur</i> , <i>Q. petraea</i> )	Ambient	5.1–35.5	n/a	Community evenness	Decrease
<a href="#">Krumins et al. (2009)</a>	Florida and New Jersey	Scrub oak forest ( <i>Quercus myrtifolia</i> , <i>Q. ilicifolia</i> )	Addition	35, 70	1	Morphotype richness	Not significant

**Table 6-15 (Continued): Ectomycorrhizal biodiversity responses to nitrogen added via atmospheric deposition or experimental N additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Avis et al. (2008)</a>	Illinois	Oak ( <i>Quercus alba</i> , <i>Q. rubra</i> )	Addition	21	4	Species richness	Decrease
<a href="#">Wright et al. (2009)</a>	British Columbia, Canada	Western hemlock ( <i>Tsuga heterophylla</i> )	Addition	300 (once)	7-yr recovery	Species richness	Not significant
<a href="#">Kjøller et al. (2012)</a>	Denmark	Norway spruce ( <i>Picea abies</i> )	Ambient	27–43	n/a	Species richness	Decrease
<a href="#">Jarvis et al. (2013)</a>	Scotland, U.K.	Scots pine ( <i>Pinus sylvestris</i> )	Ambient	3.1–9.9	n/a	Species richness	Not significant
<a href="#">Suz et al. (2014)</a>	Europe (nine countries)	Oak ( <i>Quercus robur</i> , <i>Q. petraea</i> )	Ambient	5.1–35.5	n/a	Species richness	Decrease
<a href="#">Gillet et al. (2010)</a>	Switzerland	Norway spruce ( <i>Picea abies</i> )	Addition	150	12	Sporocarp richness	Decrease
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	35, 70	40, 2-yr recovery for 70 kg treatment	Sporocarp richness	Decrease
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	110	20; 15-yr recovery	Sporocarp richness	Not significant
<a href="#">Hasselquist and Högberg (2014)</a>	Sweden	Scots pine ( <i>Pinus sylvestris</i> )	Addition	20, 100	6	Sporocarp richness	Not significant at 20; decrease at 100

**Table 6-15 (Continued): Ectomycorrhizal biodiversity responses to nitrogen added via atmospheric deposition or experimental N additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Cox et al. (2010)</a>	Germany, U.K.	Scots pine ( <i>Pinus sylvestris</i> )	Ambient	4.6–28.6	n/a	Taxonomic richness	Decrease (indirect)

Ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Although shifts in fungal community composition are widely reported, these shifts are not necessarily consistent, even in similar ecosystems. [Allison et al. \(2010\)](#) conducted an N addition experiment in a recently burned boreal forest in Alaska. In that site, the forest microbial community was dominated by fungi in the Ascomycota, and N additions increased their abundance. In contrast, [Allison et al. \(2008\)](#) conducted a similar experiment in a mature boreal forest in Alaska and observed that the microbial community was dominated by Basidiomycota, and N additions did not change the overall abundance of fungi in this phylum. However, in both ecosystems, N additions greatly changed the relative abundance of individual taxa (orders and families) within these phyla ([Allison et al., 2010](#); [Allison et al., 2008](#)). Individual components of microbial communities also appear to react to N additions at different speeds. In a long-term forest N addition in Switzerland, [Gillet et al. \(2010\)](#) observed that both ectomycorrhizal and saprotrophic fungal communities responded to an increase in soil N input, but the ectomycorrhizal community rapidly decreased in species richness, whereas the saprotrophic community was less affected. The response was highly species specific, especially for the saprotrophic community. At Harvard Forest, [Frey et al. \(2004\)](#) found fungal biomass was reduced in fertilized versus control plots, and this was accompanied by a decrease in phenol oxidase activity, an enzyme produced by saprophytic, white-rot fungi to decompose lignin. Among fungal saprotrophs at Harvard Forest, [Morrison et al. \(2016\)](#) found that high rates of N addition (150 kg N/ha/yr for 25 years) decreased the abundance of the saprotrophic basidiomycete genus *Agaricus*, which has lignolytic abilities, and increased the abundance of two saprophytic ascomycete genera (*Hypocrea*, *Phialophora*) that are cellulolytic. These changes in the fungal community at Harvard Forest are consistent with observations elsewhere ([Freedman et al., 2016](#); [Edwards et al., 2011](#)) that N additions can stimulate cellulose decomposition and inhibit fungal decomposition of lignin (see [Appendix 4](#)).

Decreases in taxonomic richness among fungi appear to be less common than changes in community composition. Taxonomic richness is often used as a measure of biodiversity for microbial communities since it can be difficult to define species as noted previously. Only three studies of taxonomic richness in overall fungal communities were identified for this assessment ([Table 6-14](#)). One study saw changes at two of four study sites ([Eisenlord et al., 2013](#)); there was no effect in another study ([Krumins et al., 2009](#)); and [Morrison et al. \(2016\)](#) observed a shift in composition under a very high dose (150 kg N/ha/yr), but not a more moderate dose (50 kg N/ha/yr). Of the 11 identified ectomycorrhizal richness studies, decreases were observed in 6 studies ([Table 6-15](#)).

Compared to ectomycorrhizal fungi, there is also less information about how N additions alter arbuscular mycorrhizal and bacterial community composition ([Table 6-14](#), [Table 6-16](#)). Two studies on arbuscular mycorrhizae were identified, one in Ecuador

([Camenzind et al., 2014](#)) that observed no effect of added N (50 kg N/ha/yr for 3 years) on community composition and another in northern hardwood forests in Michigan where the effect of added N (30 kg N/ha/yr for +12 years) on community composition was dependent on the measurement technique ([van Diepen et al., 2013](#); [van Diepen et al., 2011](#)). At the Harvard Forest long-term N addition study in Massachusetts (50 and 150 kg N/ha/yr), [Turlapati et al. \(2013\)](#) and [Turlapati et al. \(2015\)](#) used molecular techniques to assess changes in bacterial community composition. Using a 97% sequence identity approach to clustering OTUs, [Turlapati et al. \(2013\)](#) found the chronic N additions caused major changes in the bacterial phyla of Acidobacteria, Proteobacteria, and Verrucomicrobia. Using the more detailed oligotype sequence clustering approach, [Turlapati et al. \(2015\)](#) observed five genera that exclusively appeared in N treated soils (*Aquabacterium*, *Nitrosospira*, *Yersinia*, *Legionella*, and *Niabella*) and eight genera that were present only in the control plots (*Comamonas*, *Microbacterium*, *Mycetocola*, *Brochothrix*, *Flavobacterium*, *Pedobacter*, *Sphingobacterium*, and *Terrimonas*). However, the N addition treatments also caused shifts in community structure within most genera. As with [Fierer et al. \(2012\)](#), microbial communities in the mineral soil were less affected by the N additions than communities in the organic soil.

Shifts in microbial community composition can alter ecosystem processes and plant community diversity, in addition to affecting plant productivity as noted previously ([Appendix 6.2.3](#)). Lower microbial diversity has been linked to slower decomposition of plant litter and can affect, for example, ecosystem C and nutrient cycling ([Bardgett and van der Putten, 2014](#); [Handa et al., 2014](#)). In a global scale study, [Delgado-Baquerizo et al. \(2016\)](#) found a positive correlation between microbial diversity and a broad suite of ecosystem services and functions. Mycorrhizal diversity has been shown experimentally to affect plant diversity. For instance, [Van der Heijden et al. \(1998\)](#) concluded that plant species composition fluctuated greatly under low arbuscular mycorrhizal diversity, whereas it increased and exhibited greater stability alongside higher mycorrhizal diversity. Specifically on N effects, [Van der Heijden et al. \(2008\)](#) observed smaller impacts on plant community composition from N additions (100 kg N/ha/yr) when plant mesocosms were inoculated with arbuscular mycorrhizal fungi than in those without fungal inoculum. Plant communities in the inoculated mesocosms had greater evenness among functional groups. Altogether, these studies suggest microbial, including mycorrhizal, diversity have a positive effect on ecosystem processes and plant community diversity. This implies that N induced decreases in microbial diversity may in turn negatively affect these endpoints.

**Table 6-16 Arbuscular mycorrhizal responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">van Diepen et al. (2011)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	13	Community composition	Change
<a href="#">van Diepen et al. (2013)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	14	Community composition	Not significant
<a href="#">Camenzind et al. (2014)</a>	Ecuador	Evergreen tropical forest	Addition	50	3	Community composition	Not significant
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Plant-associated microbial phylotype diversity	Not significant
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Plant-associated microbial phylotype richness	Not significant
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Soil microbial phylotype diversity	Not significant
<a href="#">Chen et al. (2014)</a>	China	Steppe grassland	Addition	100	6	Soil microbial phylotype richness	Decrease
<a href="#">van Diepen et al. (2011)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	13	Taxonomic diversity	<u>Three sites:</u> not significant <u>One site:</u> decrease

**Table 6-16 (Continued): Arbuscular mycorrhizal responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">van Diepen et al. (2013)</a>	Michigan (four sites)	Sugar maple ( <i>Acer saccharum</i> )	Addition	30	14	Taxonomic richness	Decrease
<a href="#">Camenzind et al. (2014)</a>	Ecuador	Evergreen tropical forest	Addition	50	3	Taxonomic richness	Decrease

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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### 6.3.3.4 Arthropod and Other Invertebrate Diversity

Arthropods can be key components of forest productivity and nutrient cycling because they can feed on living plant tissues, plant litter, or on litter-degrading fungi, and arthropod communities can be directly or indirectly altered by changes in plant productivity and chemistry ([Gan et al., 2014](#); [Throop and Lerdau, 2004](#)). Consequently, recent research has quantified the response of arthropods to added N ([Table 6-17](#)). Both before and after the 2008 ISA, Jones and colleagues published a series of studies on how N air pollution altered plant-associated insect communities in mixed conifer forests outside Los Angeles, CA ([Jones et al., 2011](#); [Jones et al., 2008](#); [Jones and Paine, 2006](#); [Jones et al., 2004](#)). [Jones et al. \(2004\)](#) observed significantly higher tree mortality and bark beetle activity at a high versus a low N pollution site. Moreover, experimental N additions at the low pollution site increased mortality and bark beetle activity relative to unfertilized control plots. In contrast, the opposite occurred at the high pollution site, with the control plots exhibiting higher tree mortality and beetle activity. The authors suggested this could be because N deposition already exceeded biological demand at the high pollution site, with additional N no longer increasing tree mortality. [Jones et al. \(2008\)](#) found that insect herbivore communities on California black oak (*Quercus kelloggii*) trees did not change in response to several years of N additions (150 kg N/ha/yr) at a relatively unpolluted and dry site, but were altered by N additions at a wetter site that received more ambient N deposition. [Jones et al. \(2011\)](#) found a similar response for insect herbivore communities associated with bracken fern plants at these sites, with no change in insect taxonomic richness at the dry and low-deposition site and increased richness at the wetter, higher deposition site. Notably, as with plant productivity responses in grassland and arid environments, the effects of added N on insect abundance and diversity appeared to be strongly dependent on climate ([Jones et al., 2011](#)).

[Gan et al. \(2013\)](#) and [Gan et al. \(2014\)](#) quantified changes in the abundance and community composition of soil microarthropods and trophic position of soil-dwelling oribatid mites at the same four northern hardwoods forests in which [Talhelm et al. \(2013\)](#) quantified changes in understory plant composition. The overall abundance of microarthropods declined by approximately 45% in response to N additions, a change that was attributed to changes in soil food webs as a consequence of previously documented decreases in litter decomposition ([Zak et al., 2008](#)), decreases in mycorrhizal productivity ([van Diepen et al., 2010](#)), and shifts in the microbial community composition ([van Diepen et al., 2013](#); [Edwards et al., 2011](#); [van Diepen et al., 2011](#)). More specifically, [Gan et al. \(2013\)](#) observed decreases in two orders of detritivores

(Oribatida, Collembola) and one order of predaceous mites (Mesostigmata), with the largest decline in the oribatid mites. The decrease in oribatid mites did not affect species richness or their trophic position, but did cause a shift in the community composition ([Gan et al., 2014, 2013](#)).

Lastly, in addition to arthropods, other soil invertebrates, such as earthworms or nematodes, can be affected by N additions ([Table 6-17](#)). [Romanowicz and Zak \(2017\)](#), for example, observed that the abundance of middens created by the non-native earthworm species *Lumbricus terrestris* was 363% higher in plots receiving N additions at one of the four sites in the study. Many northern temperate forests in the U.S. have no native earthworms and the spread of these non-native worms can cause decreases in soil C storage, a redistribution of soil C and N as earthworms consume the soil organic horizon, shifts in soil food webs, and changes in understory plant communities ([Bohlen et al., 2004](#)).

**Table 6-17 Arthropod and other invertebrate responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Zehnder and Hunter (2008)</a>	Georgia	Milkweed ( <i>Asclepias tuberosa</i> )	Addition	25, 40	0.1	Aphid carrying capacity	Increase
<a href="#">Zehnder and Hunter (2008)</a>	Georgia	Milkweed ( <i>Asclepias tuberosa</i> )	Addition	25, 40	0.1	Aphid population growth rate	Increase
<a href="#">Cha et al. (2010)</a>	Pennsylvania	Northern red oak ( <i>Quercus rubra</i> )	Addition	200	1	Chewing insect herbivory	Increase
<a href="#">Romanowicz and Zak (2017)</a>	Michigan	Northern hardwood forests ( <i>Acer saccharum</i> )	Addition	30	22	Earthworm abundance ( <i>Lumbricus terrestris middens</i> )	Increase in one of two sites where <i>L. terrestris</i> was present
<a href="#">Payne et al. (2012)</a>	U.K.	Heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 40, 80, 120	11, 21	Enchytraeid worm abundance	Not significant
<a href="#">Cha et al. (2010)</a>	Pennsylvania	Northern red oak ( <i>Quercus rubra</i> )	Addition	200	1	Galling insect herbivory	Not significant
<a href="#">Wissinger et al. (2014)</a>	California (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Ambient	2–12	n/a	Harvester ant ( <i>Messor pergandei</i> ) nest density	Increase

**Table 6-17 (Continued): Arthropod and other invertebrate responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Wissinger et al. (2014)</a>	California (Mojave)	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia dumosa</i> )	Ambient	2–12	n/a	Harvester ant ( <i>Messor pergandei</i> ) nest size	Decrease
<a href="#">Jones et al. (2011)</a>	California (southern CA, two sites)	Bracken fern ( <i>Pteridium aquilinum</i> ) in mixed conifer forests	Addition	150	3	Insect herbivore abundance	<u>Low dep site:</u> not significant <u>High dep site:</u> decrease
<a href="#">Jones et al. (2008)</a>	California (southern CA, two sites)	California black oak ( <i>Quercus kelloggii</i> ) in mixed conifer forests	Addition	150	3–4	Insect herbivore community composition	<u>Low dep site:</u> not significant <u>High dep site:</u> change
<a href="#">Jones et al. (2011)</a>	California (southern CA, two sites)	Bracken fern ( <i>Pteridium aquilinum</i> ) in mixed conifer forests	Addition	150	3	Insect herbivore taxonomic richness	<u>Low dep site:</u> not significant <u>High dep site:</u> increase
<a href="#">Eisenhauer et al. (2013)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Mesofauna abundance (arthropods—five orders)	Not significant
<a href="#">Eisenhauer et al. (2013)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Mesofauna diversity (arthropods—five orders)	Not significant

**Table 6-17 (Continued): Arthropod and other invertebrate responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Eisenhauer et al. (2012)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Microarthropod richness	Decrease
<a href="#">Eisenhauer et al. (2013)</a>	Minnesota (Cedar Creek)	Prairie	Addition	40	14	Nematode abundance	<u>Three guilds</u> : not significant <u>One guild</u> : increase <u>One guild</u> : decrease
<a href="#">Cesarz et al. (2015)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Nematode community composition	Change
<a href="#">Eisenhauer et al. (2013)</a>	Minnesota (Cedar Creek)	Prairie C3 and C4 grasses, forbs, legumes	Addition	40	14	Nematode richness	Not significant
<a href="#">Bishop et al. (2010)</a>	Washington (Mt. St. Helens)	Primary successional alpine meadow	Addition	78	5	Orthoptera abundance	Increase
<a href="#">Gan et al. (2013)</a>	Michigan (four sites)	Northern hardwoods forests ( <i>Acer saccharum</i> )	Addition	30	18	Soil oribatid mite abundance	Decrease
<a href="#">Gan et al. (2013)</a>	Michigan (four sites)	Northern hardwoods forests ( <i>Acer saccharum</i> )	Addition	30	18	Soil oribatid mite community composition	Change
<a href="#">Gan et al. (2013)</a>	Michigan (four sites)	Northern hardwoods forests ( <i>Acer saccharum</i> )	Addition	30	18	Soil oribatid mite species richness	Not significant

**Table 6-17 (Continued): Arthropod and other invertebrate responses to experimental nitrogen additions.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Gan et al. (2014)</a>	Michigan (four sites)	Northern hardwoods forests ( <i>Acer saccharum</i> )	Addition	30	18	Soil oribatid mite trophic position	Not significant
<a href="#">Bishop et al. (2010)</a>	Washington (Mt. St. Helens)	Primary successional alpine meadow	Addition	78	3	Total arthropod abundance	Not significant

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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### 6.3.4 Alpine and Arctic Tundra

There was consistent and coherent evidence in the 2008 ISA indicating that alpine plant communities are among the terrestrial communities most sensitive to atmospheric N deposition. The previous assessment identified a number of factors that made these ecosystems sensitive to N deposition, including low rates of primary production, short growing seasons, low temperature, and low rates of N mineralization ([Bowman and Fisk, 2001](#); [Bowman and Steltzer, 1998](#); [Fisk et al., 1998](#); [Bowman, 1994](#); [Bowman et al., 1993](#)). Alpine plants are broadly N limited, and increased N inputs have been observed to cause changes in alpine growth and species composition ([Bowman et al., 2006](#); [Bowman and Steltzer, 1998](#); [Vitousek et al., 1997](#)). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this was also thought to contribute to their N sensitivity.

Many of the alpine tundra ecosystems in the U.S. are found in the western U.S., particularly in the Rocky Mountains, Cascade Mountains, and the Sierra Nevada. Atmospheric deposition tends to be low in the western U.S., but alpine sites can be affected by relatively low or moderate levels of N deposition because of their high sensitivity. In several studies, the capacity of Colorado Rocky Mountain alpine catchments to sequester N was exceeded at input levels of 10 kg N/ha/yr or less [e.g., [Baron et al. \(1994\)](#)]. Similarly, relatively low N addition rates can cause shifts in alpine plant communities. [Bowman et al. \(2006\)](#) estimated that changes in the abundance of *Carex rupestris* occurred at deposition rates of 4 kg N/ha/yr and changes in alpine tundra community composition occurred at deposition rates of approximately 10 kg N/ha/yr. In Europe, critical loads for alpine plant communities were estimated to be between 5 and 15 kg N/ha/yr ([Bobbink et al., 2003](#)).

Since 2008, there was further research in the U.S. on the effects of added N on plant communities in Colorado at the Niwot Ridge Long-Term Ecological Research Site and in Rocky Mountain National Park (RMNP), as well as on Mount St. Helens in Washington ([Table 6-18](#)). In RMNP, [Bowman et al. \(2012\)](#) conducted a 4-year study in a dry alpine meadow ecosystem where N was added at rates of 5, 10, and 30 kg N/ha/yr, while ambient N deposition was 4 kg N/ha/yr. No shifts in species richness or diversity were observed in response to the N additions; however, *Carex rupestris* increased in cover from 34 to 125% in response to the treatments ([Bowman et al., 2014](#)). More broadly, as noted in [Appendix 5](#), [McDonnell et al. \(2014a\)](#) used the ForSAFE-VEG model to assess changes in vegetation cover in subalpine ecosystems in RMNP since 1900 and forecast the changes through the end of the 21st century as a result of N deposition and climate change scenarios. Based on the model output, plant community composition changed by

10% over the past 100 years as a result of increases in N deposition, with increases in graminoid species and decreases in forb species. Over the next 100 years, forecasted changes in N deposition and climate factors are predicted to increase tree cover. At Niwot Ridge, two decades of N additions (averaging ~75 kg N/ha/yr) generally decreased plant species richness across a wet-to-dry gradient of alpine meadows, with a significant decrease in the moist meadow type ([Yuan et al., 2016](#)). Plant diversity increased with N additions (78 kg N/ha/yr for 5 years) on Mount St. Helens, but this plant community was growing on very N poor soils formed following the volcanic eruption there in 1980 ([Bishop et al., 2010](#)).

Internationally, plant diversity research has been conducted in Arctic ecosystems in Scandinavia and North Atlantic Europe (Greenland, Iceland, northern Great Britain, etc.) and in alpine ecosystems in Switzerland and China. In a subalpine grassland in the Swiss Alps, [Bassin et al. \(2013\)](#) observed that 7 years of N additions of 5 to 50 kg N/ha/yr decreased plant diversity and changed plant community composition. [Arens et al. \(2008\)](#) found no effects of N additions (5, 10, or 50 kg N/ha/yr) on plant community composition over 3 years in dwarf shrub/herb tundra ecosystems in Greenland. In Sweden, [Sundqvist et al. \(2014\)](#) did not observe any change in plant species diversity or plant species richness as a result of 3 years of N additions (100 kg N/ha/yr) to a tundra heath and a tundra meadow. Elsewhere in Sweden, [Wardle et al. \(2013\)](#) found that two decades of N additions (50 kg N/ha/yr) to a tundra meadow decreased both plant species richness and plant community diversity.

**Table 6-18 Alpine and Arctic tundra plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Arens et al. (2008)</a>	Greenland	Dwarf shrub/herb tundra ( <i>Salix arctica</i> , <i>Carex rupestris</i> , <i>Dryas integrifolia</i> )	Addition	5, 10, 50	3	Plant community composition	Not significant
<a href="#">Bassin et al. (2013)</a>	Switzerland	Subalpine grassland	Addition	5, 10, 25, 50	7	Plant community composition	Change
<a href="#">Armitage et al. (2014)</a>	Europe (North Atlantic)	Alpine heathlands	Ambient	0.6–39.6	n/a	Plant community composition	Change
<a href="#">Song and Yu (2015)</a>	China (Tibetan Plateau)	Alpine meadow ( <i>Kobresia humilis</i> , <i>Elymus nutans</i> , <i>Stipa aliena</i> , <i>Festuca ovina</i> )	Addition	3.75, 15, 75	8	Plant community composition	Change
<a href="#">Bishop et al. (2010)</a>	Washington (Mt. St. Helens)	Primary successional alpine meadow	Addition	78	5	Plant species diversity	Increase
<a href="#">Bowman et al. (2012)</a>	Colorado (Rocky Mountain National Park)	Dry sedge meadow ( <i>Kobresia myosuroides</i> , <i>Carex rupestris</i> )	Addition	5, 10, 30	4	Plant species diversity	Not significant
<a href="#">Bassin et al. (2013)</a>	Switzerland	Subalpine grassland	Addition	5, 10, 25, 50	7	Plant species diversity	Decrease
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Anthoxanthum alpinum</i> )	Addition	100	3	Plant species diversity	Not significant
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra heath ( <i>Vaccinium vitis-idaea</i> , <i>Vaccinium uliginosum</i> , <i>Betula nana</i> )	Addition	100	3	Plant species diversity	Not significant

**Table 6-18 (Continued): Alpine and Arctic tundra plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Farrer et al. (2015)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	229	7	Plant species diversity	Decrease
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Plant species diversity (vascular)	Decrease
<a href="#">Song and Yu (2015)</a>	China (Tibetan Plateau)	Alpine meadow ( <i>Kobresia humilis</i> , <i>Elymus nutans</i> , <i>Stipa aliena</i> , <i>Festuca ovina</i> )	Addition	3.75, 15, 75	8	Plant species evenness	Not significant
<a href="#">Bowman et al. (2012)</a>	Colorado (Rocky Mountain National Park)	Dry sedge meadow ( <i>Kobresia myosuroides</i> , <i>Carex rupestris</i> )	Addition	5, 10, 30	4	Plant species richness	Not significant
<a href="#">Armitage et al. (2014)</a>	Europe (North Atlantic)	Alpine heathlands	Ambient	0.6–39.6	n/a	Plant species richness	Decrease
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Anthoxanthum alpinum</i> )	Addition	100	3	Plant species richness	Not significant
<a href="#">Sundqvist et al. (2014)</a>	Sweden	Tundra heath ( <i>Vaccinium vitis-idaea</i> , <i>Vaccinium uliginosum</i> , <i>Betula nana</i> )	Addition	100	3	Plant species richness	Not significant
<a href="#">Song and Yu (2015)</a>	China (Tibetan Plateau)	Alpine meadow ( <i>Kobresia humilis</i> , <i>Elymus nutans</i> , <i>Stipa aliena</i> , <i>Festuca ovina</i> )	Addition	3.75, 15, 75	8	Plant species richness	Low and mid dose: not significant High dose: decrease

**Table 6-18 (Continued): Alpine and Arctic tundra plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Yuan et al. (2016)</a>	Colorado (Niwot Ridge)	Alpine meadow	Addition	50–200 (varied over the 20 yr duration; averaged ca. 85)	20	Plant species richness	Not significant in dry and wet meadow type; decrease in moist meadow type
<a href="#">Southon et al. (2013)</a>	U.K.	Heathlands ( <i>Calluna vulgaris</i> )	Ambient	5.9–32.4	n/a	Plant species richness (vascular)	Decrease
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Plant species richness (vascular)	Decrease

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Because of the similarities in soil and plant community properties, heathlands are discussed in this alpine and arctic tundra section. [Southon et al. \(2013\)](#) quantified plant species richness at heathland sites in the U.K. along an N deposition gradient (5.9–32.4 kg N/ha/yr) and observed declines in both vascular plant species richness and bryophyte species richness. Similarly, [Armitage et al. \(2014\)](#) observed changes in plant community composition and decreases in plant species richness in alpine heathlands along an N deposition gradient of 0.6 to 39.6 kg N/ha/yr across the northern U.K., Iceland, Norway, and the Faroe Islands. Three studies quantified changes in lichen species richness in alpine tundra ecosystems along atmospheric N deposition gradients in northern Europe; two observed significant declines with increases in N deposition. At 15 of the U.K. alpine tundra sites surveyed by [Armitage et al. \(2014\)](#), [Mitchell et al. \(2016\)](#) sampled soil microarthropods (oribatid, prostigmatid, and mesostigmatid mites, and Collembola). Across the gradient of sites, there was no direct influence of N deposition on microarthropod community structure or the species richness, community composition, or density for Collembola or any of the three groups of mites. However, N deposition indirectly affected microarthropod communities by altering variables such as graminoid cover, moss depth, moss cover, and plant biomass C:N ratio, all of which significantly influenced microarthropod communities ([Mitchell et al., 2016](#)).

There has been a considerable amount of new research on the effects on added N plant diversity in alpine meadows within the Tibetan Plateau region of China. In a meta-analysis of N addition studies in this region, [Fu and Shen \(2016\)](#) found that N additions decreased both plant species richness and plant diversity. [Song and Yu \(2015\)](#) examined how different rates (3.75, 15, or 75 kg N/ha/yr) and chemical forms of N ( $[\text{NH}_4]_2\text{SO}_4$ ,  $\text{NaNO}_3$ , or  $\text{NH}_4\text{NO}_3$ ) additions over 8 years influenced plant diversity and the stability of plant communities in alpine plant communities on the Tibetan Plateau in China. Throughout the experiment, there were no effects of N form. The highest rate of N addition decreased community stability (mean biomass/mean temporal standard deviation), species richness, and the dominance of community composition by individual species; other rates of N did not affect these metrics. Broadly, added N also increased the temporal synchrony of species cover, meaning that there were stronger correlations among species and functional groups in year-to-year variation in cover. This suggests that N additions can decrease compensatory effects within plant communities, wherein one species or functional group increases in cover during periods when others are exhibiting decreased growth. Instead, the high N treatment increased the abundance of both of the two dominant grass species. [Song and Yu \(2015\)](#) suggested that the reduction in compensatory growth could result from decreased competition for N. As expected, there was a strong correlation between log-transformed species variance in abundance and log-transformed mean abundance, meaning that more abundant species were also more variable in their abundance; this relationship was not affected by N additions. Notably,

there was no relationship between community stability and species richness. Although this is unusual among studies of community stability and richness [e.g., [Tilman \(1996\)](#); [Steiner et al. \(2005\)](#); [Tilman et al. \(2006\)](#); [Loreau and de Mazancourt \(2013\)](#)], the high rate of N addition caused the loss of only 2 of 20 species within these communities; neither was a dominant species in the community. In comparison, 4 years of N additions (100 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$ ) had no effect on plant species richness or diversity in a less diverse (10–14 species) alpine meadow community on the Tibetan Plateau ([Zong et al., 2016](#)).

Among studies of microbial diversity ([Table 6-19](#)), three studies ([Yuan et al., 2016](#); [Farrer et al., 2013](#); [Nemergut et al., 2008](#)) investigated the effect of N additions in the Rocky Mountains. [Farrer et al. \(2013\)](#) asked whether soil microbial changes were related to the demonstrated decline in the abundance of the plant *Geum rossii* under increased N deposition. Microbial community composition changed, but the influence of this change on *G. rossii* was unclear. However, there was evidence that N additions imposed a stronger physiological C limitation on *G. rossii*. [Nemergut et al. \(2008\)](#) also found shifts in fungal and bacterial soil communities with chronic N additions (10 to 25 kg N/ha/yr for >10 years). The fungal community shifted in response to N amendments, with a decrease in the relative abundance of basidiomycetes. Bacterial community composition also shifted in the N amended soil, with increases in the relative abundance of sequences related to the Bacteroidetes and Gemmatimonadetes, and decreases in the relative abundance of the Verrucomicrobia. [Yuan et al. \(2016\)](#) observed changes in bacterial community composition after 20 years of N additions, with N additions increasing the abundance of the phyla Chloroflexi and Bacteroidetes and N additions decreasing Acidobacteria and Verrucomicrobia. Notably, forb biomass (but not grass biomass) was positively correlated with bacterial diversity and bacterial richness covaried with plant richness. Structural equation modeling revealed that the effects of N additions on bacterial community composition were primarily indirect effects occurring via changes in soil pH and forb biomass rather than direct effects of N availability ([Yuan et al., 2016](#)).

**Table 6-19 Alpine and Arctic tundra microbial diversity responses to nitrogen added via experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Payne et al. (2012)</a>	U.K.	Heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 40, 80, 120	11, 21	Amoeba community composition	Change
<a href="#">Payne et al. (2012)</a>	U.K.	Heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 40, 80, 120	11, 21	Amoeba species diversity	Decrease
<a href="#">Payne et al. (2012)</a>	U.K.	Heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 40, 80, 120	11, 21	Amoeba species richness	Not significant
<a href="#">Payne et al. (2012)</a>	U.K.	Heathland ( <i>Calluna vulgaris</i> )	Addition	10, 20, 40, 80, 120	11, 21	Amoeba species richness	Not significant
<a href="#">Yuan et al. (2016)</a>	Colorado (Niwot Ridge)	Alpine meadow	Addition	50–200 (varied over the 20 yr duration; averaged ca. 85)	20	Bacterial phylotype richness	Not significant in dry and wet meadow type; decrease in moist meadow type
<a href="#">Nemergut et al. (2008)</a>	Colorado (Niwot Ridge)	Dry alpine meadow ( <i>Kobresia myosuroides</i> )	Addition	11.5	10	Fungal community composition	Change
<a href="#">Nemergut et al. (2008)</a>	Colorado (Niwot Ridge)	Dry alpine meadow ( <i>Kobresia myosuroides</i> )	Addition	11.5	10	Microbial community composition	Change

**Table 6-19 (Continued): Alpine and Arctic tundra microbial diversity responses to nitrogen added via experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Farrer et al. (2013)</a>	Colorado (Niwot Ridge)	Moist alpine meadow ( <i>Deschampsia cespitosa</i> , <i>Geum rossii</i> )	Addition	288	11	Microbial community composition	Change
<a href="#">Wardle et al. (2013)</a>	Sweden	Tundra meadow ( <i>Deschampsia flexuosa</i> , <i>Empetrum hermaphroditum</i> , <i>Vaccinium</i> spp.)	Addition	50	21	Microbial community composition	Change

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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### 6.3.5 Grasslands

In the 2008 ISA, there was consistent and coherent evidence suggesting that N additions reduced plant biodiversity in grasslands in the U.S. and Europe. In the U.S., [Clark and Tilman \(2008\)](#) evaluated the effects of chronic N addition over 23 years in Minnesota prairie grasslands and found species numbers declined at the lowest addition level (10 kg N/ha/yr added to 6 kg N/ha/yr of ambient deposition). In the San Francisco Bay area of California, exotic nitrophilous grasses displaced native grass species, likely due to greater N availability from deposition—at the time approximately 10 to 15 kg N/ha/yr—and from the cessation of grazing, which previously exported N out of the ecosystem ([Fenn et al., 2003b](#); [Weiss, 1999](#)).

In Europe, there were observations of N deposition-related declines in grassland plant diversity in a variety of environments, including calcareous, neutral, and acidic soils, species-rich heaths, and montane-subalpine grasslands ([Stevens et al., 2004](#); [Bobbink et al., 1998](#); [Bobbink et al., 1992](#)). In a transect of 68 acidic grasslands across Great Britain that covered a broad range of ambient N deposition (5 to 35 kg N/ha/yr), chronic N deposition significantly decreased plant species richness ([Stevens et al., 2004](#)). Species richness declined as a linear function of the rate of inorganic N deposition, with a reduction of one species per 4-m<sup>2</sup> quadrant for every 2.5 kg N/ha/yr of chronic N deposition ([Stevens et al., 2004](#)).

Although only a few studies had examined low levels of N inputs to grasslands in the U.S. as of 2008, there were many that added higher levels of N ([Clark et al., 2007](#); [Bradley et al., 2006](#); [Suding et al., 2005](#); [Gough et al., 2000](#)) and examined how N enrichment interacted with other factors such as fire, elevated atmospheric CO<sub>2</sub>, species diversity, and climate change ([Zavaleta et al., 2003](#); [Reich et al., 2001](#); [Collins et al., 1998](#)). These studies were not necessarily designed to simulate N deposition, rather their focus was on nutrient limitation and what happened following the alleviation of this limitation. Recent gradient studies and studies using low level N addition rates verify that the direction of effect between low and high N input rates are similar. This suggests that although the magnitude of effect depends on the level of input, the direction of effect does not, and that nutrient enrichment in grasslands follows a general response. This response includes increases in aboveground production, decreases in light availability at the soil surface, changes in soil fauna, and increases in litter buildup, all of which can lead to competitive displacement of slower growing and shorter plant species from either shading and/or reduced recruitment and regrowth ([Hautier et al., 2009](#); [Bobbink et al., 1998](#); [Tilman, 1993, 1987](#)).

In total, before 2008, large-scale biodiversity assessments across gradients of atmospheric N deposition were restricted to Europe ([Stevens et al., 2004](#)). Although there was wide evidence in the U.S. linking the composition of plant and microbial communities to N availability, most of these experiments had been conducted using N addition rates considerably exceeding observed atmospheric N deposition rates in the U.S. [e.g., [Suding et al. \(2005\)](#); [Bradley et al. \(2006\)](#)]. Experiments demonstrating the sensitivity of grassland community composition to lower rates of N deposition were more limited, with evidence for Mediterranean grasslands ([Weiss, 1999](#)) and a northern prairie ecosystem ([Clark and Tilman, 2008](#)).

Since the 2008 ISA, research on the effects of anthropogenic N on biodiversity in grassland ecosystems has expanded to include a wider range of organisms and ecosystems and a further understanding of how added N (particularly at more realistic N input rates) alters biodiversity, including the species and functional groups most susceptible to increased N availability. Much of this new research has been conducted in the U.S. (particularly at Cedar Creek in Minnesota) and in western Europe, but China has also emerged as a center for research on the effects of excess N on grasslands.

As noted earlier, [Simkin et al. \(2016\)](#) quantified the effect of N deposition on species richness in the continental U.S. using data from over 15,000 plots, including grassland ecosystems. While Europe has several large-scale continental studies on the effects from N deposition ([Stevens et al., 2010a](#); [Stevens et al., 2004](#)), this is the first study of its size in the U.S. and provides a unique insight on the impacts from N deposition on U.S. grassland ecosystems. In their analysis, [Simkin et al. \(2016\)](#) observed that at very low rates of N deposition, increases in N deposition were associated with higher plant species richness in open canopy ecosystems (e.g., grasslands, shrublands, and woodlands), but species richness declined at N deposition rates above 8.7 kg N/ha/yr (5th–95th percentile: 6.4–11.3 kg N/ha/yr). Levels causing a decline in species richness are common across much of the eastern and central U.S. and also occur near urban and intensive agricultural areas in the West. Evidence of increases at low N input rates had not been observed across N deposition gradients in Europe, likely due to higher historical deposition rates. [Simkin et al. \(2016\)](#) also reported that the loss of species was strongly contingent on soil pH, with more losses occurring in more acidic soils. Notably, the authors reported that approximately 40% of grassland plots used for the study received N deposition at rates above the threshold for declines in species richness.

A number of studies in Europe have built upon the work of [Stevens et al. \(2004\)](#) in documenting N deposition impacts on grassland plant communities over long time periods and/or large geographic areas, with these studies consistently indicating changes in plant community composition and decreases in diversity as a result of N deposition

(see also [Appendix 5](#) for discussion). Changes in grassland plant diversity in the U.K. from N deposition have been particularly well documented. [Stevens et al. \(2010b\)](#) and [Maskell et al. \(2010\)](#) built on the work of [Stevens et al. \(2004\)](#) in the U.K., trying to identify whether changes in plant community composition caused by N deposition were the result of acidification or eutrophication. [Stevens et al. \(2010b\)](#) worked from the same 68 acidic grasslands in Great Britain as [Stevens et al. \(2004\)](#), but included more detailed information about soil pH and the sensitivity of individual plant species to pH and N availability. Based on these data, [Stevens et al. \(2010b\)](#) observed that N deposition mostly caused a shift toward more acid-tolerant species rather than nitrophilic species, suggesting that acidification is the primary impact of N deposition on acidic grassland plant communities. A broader analysis by [Maskell et al. \(2010\)](#), which expanded the work of [Stevens et al. \(2004\)](#) and [Stevens et al. \(2010b\)](#) beyond acidic grasslands to also include calcareous grasslands, heathlands, and mesotrophic grasslands—and also included direct soil measurements at a subset of these sites—also found that the primary link between N deposition and species loss was acidification in acidic grasslands and heathlands. However, eutrophication was the primary link between species loss and N deposition in calcareous grasslands ([Maskell et al., 2010](#)). Notably, species losses along the deposition gradient were smaller in calcareous ecosystems than in acidic ecosystems. In a similar assessment, [van Den Berg et al. \(2016\)](#) observed negative effects of N deposition on plant species richness in ecosystems across the U.K. (woodlands, heaths, bogs, and grasslands), with the exception of a positive effect of deposition on species richness in calcareous grasslands. [Henrys et al. \(2011\)](#) used data from two national observation networks over Great Britain and found clear negative trends in plant species prevalence to increasing N in all acidic grassland habitats. [Field et al. \(2014\)](#) also expanded on the work of [Stevens et al. \(2004\)](#) by surveying a broader range of ecosystem types across the U.K.: acidic grasslands, bogs, upland and lowland heaths, and sand dunes. Higher N deposition was associated with decreases in species richness and changes in community composition across all ecosystem types. Among functional groups, N deposition decreased the diversity of mosses, lichens, forbs, and graminoids, but generally increased the cover of graminoids ([Field et al., 2014](#)). [van Den Berg et al. \(2016\)](#) found that N deposition increased the ratio of grass-to-forb species in some U.K. ecosystems (heathlands, bogs, acidic grasslands), but had the opposite effect in calcareous grasslands.

Similar results were observed at broader scales in Europe. Several studies surveyed 153 acidic grassland sites across northern and western Europe ([Pannek et al., 2015](#); [Stevens et al., 2011a](#); [Stevens et al., 2011b, 2010a](#)). These sites spanned a deposition gradient of 2 to 44 kg N/ha/yr, but the decreases in plant species richness were not linear and the highest rate of species loss occurred at deposition rates <20 kg N/ha/yr ([Stevens et al., 2010a](#)). Across the gradient, most of the decline in species richness was caused by

a loss of forb species, but grass and bryophyte species also declined ([Stevens et al., 2010a](#)). As a fraction of total species richness, grass species richness increased and forb species richness declined with increasing N deposition ([Stevens et al., 2011b](#)). Notably, these changes occurred without consistent effects of N deposition on soil  $\text{NO}_3^-$ , soil  $\text{NH}_4^+$ , or tissue N concentrations in broadly sampled forb (*Galium saxatile*) and grass (*Agrostis capillaris*) species, but both soil C:N and the foliar N concentration of a bryophyte (*Rhytidiadelphus squarrosus*) were positively correlated with N deposition ([Stevens et al., 2011b](#)). [Stevens et al. \(2011b\)](#) were able to explain 24% of the total variation in plant species composition using climate, soil, and atmospheric deposition metrics. Among this 24% of the total variation, soil variables (pH, aluminum concentrations, C and N content) explained 38% of the variation and deposition represented about 10% of this variation ([Stevens et al., 2011a](#)). This influence of deposition on community composition was notably weaker than the relationship to changes in species richness. A survey of 44 species in these grasslands found that the presence of 16 species responded to N deposition, with 12 of these 16 species responding negatively ([Pannek et al., 2015](#)). In the Atlantic region of France, [Gaudnik et al. \(2011\)](#) observed that N deposition was one of the primary determinants of community composition in acidic grasslands, even though the observed range of N deposition was much smaller than in [Stevens et al. \(2004\)](#). [Dupre et al. \(2010\)](#) examined plant community composition change in acidic grasslands in north-central Europe and the U.K. over 70 years, dating back to 1939. Vegetation communities were differentiated predominately according to soil pH, soil N availability, cumulative N deposition and S deposition, and sampling date. Plot species richness declined through time for both vascular plants and bryophytes, with cumulative N deposition identified as the primary determinant of species loss.

While these N deposition gradient studies have provided strong documentation that anthropogenic N pollution is altering biodiversity in grasslands in North America and in Europe, experimental N addition studies have provided new information about the mechanisms linking N deposition to shifts in community composition. For instance, using grassland mesocosms in Switzerland receiving 150 to 200 kg N/ha/yr, [Hautier et al. \(2009\)](#) conducted a unique experiment to understand the role of light competition in the loss of species under conditions of high N availability. The addition of N increased aboveground productivity and decreased both light availability near the ground surface and species richness. An experimental increase in light availability caused by the use of plant growth lights beneath the grassland canopy further increased productivity, but also prevented the loss of plant species richness. Similarly, light competition was a mechanism behind the negative effects of N deposition on species richness in grassland sites in Israel ([Demalach et al., 2017](#)).

At Cedar Creek in Minnesota, [Reich \(2009\)](#) conducted a 10-year experiment where grassland assemblages of 16 perennial species were grown under factorial combinations of ambient and elevated CO<sub>2</sub> and ambient and elevated N. Increased N (40 kg N/ha/yr) reduced species at both ambient and elevated CO<sub>2</sub>, by 16 and 8%, respectively. The reduced losses of biodiversity at higher CO<sub>2</sub> levels remains an active area of research but is thought to be caused by greater soil water availability at higher CO<sub>2</sub> levels (from reduced stomatal conductance) that reduced the competitive displacement with N addition. An even longer experiment, 25 years, conducted at Cedar Creek and analyzed by [Isbell et al. \(2013a\)](#) also demonstrated that N enrichment decreased the number of plant species, and that over time, this effect became increasingly negative at all rates of N addition. Moreover, species losses were nonrandom, with initially dominant native perennial grasses becoming less dominant and then lost, and non-native perennial C3 grasses becoming increasingly dominant. Plot composition changed from a high-diversity, native-dominated state (C4 grasses) to a low-diversity, non-native dominated state (C3 grasses). Several earlier studies at this site also reported this general effect ([Clark and Tilman, 2008](#); [Tilman, 1987](#)). Nine native species were particularly susceptible to becoming locally extinct under chronic nutrient enrichment, including initially dominant and initially rare species. All of the findings from this seminal experiment in Cedar Creek, MN, are representative of terrestrial eutrophication, as opposed to acidification, because these soils were limed to maintain a constant pH ([Tilman, 1987](#)). However, there were no lime additions in the experiment conducted at this site by [Reich \(2009\)](#), indicating that both terrestrial eutrophication and acidification could be occurring in that experiment.

[Lan et al. \(2015\)](#) examined how N deposition altered spatial patterns in biodiversity and species-area relationships by measuring plant species loss and species richness in a grassland in Inner Mongolia in 14 different plot sizes ranging from 1 to 25 m<sup>2</sup>. The experiment included five levels of N addition between 17.5 and 280 kg N/ha/yr (NH<sub>4</sub>NO<sub>3</sub>) for 10 years. Except for the 17.5 kg N/ha/yr treatment, N additions decreased species richness. The absolute number of species lost versus the control group increased rapidly as plot size increased from 1 to 8 m<sup>2</sup>, but then stayed the same (high N doses) or decreased (low N doses). However, the proportional loss of species decreased as plot size increased, which allowed for predictions of critical loads for species loss at different plots sizes: 11.4 kg N/ha/yr at 5 m<sup>2</sup> and 17.4 kg N/ha/yr at 25 m<sup>2</sup>. A previous study at these sites using 0.5-m<sup>2</sup> plots found a critical load of 8.5 kg N/ha/yr, indicating that species loss as a consequence of N additions is sensitive to survey design.

Ecological theory suggests that plant diversity can be maintained by several factors, including disturbance [e.g., [Hobbs and Huenneke \(1996\)](#); [Mack et al. \(2000\)](#); [Davis et al. \(2000\)](#)]. Among grasslands, the managed reintroduction of some disturbances has been

proposed as a way of maintaining plant diversity in eutrophic ecosystems. In a California serpentine grassland, [Pasari et al. \(2014\)](#) examined the interactive effects of grazing and simulated N deposition (80 kg N/ha total over 4 years) on native and exotic species dynamics. With N additions, grazing helped maintain native species richness. High grazing intensity decreased exotic plant cover, but only under ambient conditions ([Pasari et al., 2014](#)). In a southern California coastal grassland, [Borer et al. \(2014\)](#) conducted several nutrient enrichment experiments, two of which involved the addition of N (40 and 100 kg N/ha/yr). At the higher N level, species richness (forbs primarily) was reduced by one species per 0.5 m<sup>2</sup> after 2 years. However, unlike in the work of [Pasari et al. \(2014\)](#), this change in diversity was not affected by the presence of pocket gophers (*Thomomys bottae*), a keystone herbivore that eliminated the effect of N on plant productivity. In an annually burned Kansas tallgrass prairie, [McLaughlan et al. \(2014\)](#) analyzed a 27-year record of plant community composition and N cycling. Despite rates of N deposition (average 7 kg N/ha/yr) persistently within the range of critical loads for temperate grasslands in the region, there was no evidence for increases in plant N concentrations, decreases in forb diversity, or shifts in the relative abundance of dominant grass species. The authors suggested that losses of N through frequent burning or grazing are sufficient to prevent grassland eutrophication at low rates of N deposition.

There is also new evidence that N additions can alter flowering, seed production, and seed abundance in grasslands. In Minnesota, [Hillerislambers et al. \(2009\)](#) developed a statistical model to determine the effects of multiple global change factors, including N deposition, on inflorescence mass. The effects of N deposition on seed production were similar within functional groups and negatively correlated with aboveground productivity: C3 grasses increased aboveground biomass and decreased seed production, while C4 grasses decreased aboveground biomass and increased seed production. In a greenhouse study of California oak savannah annual grasses, N additions (28 kg N/ha/yr for 1 year) increased seed production (g/plant) by an invasive grass ([Tulloss and Cadenasso, 2016](#)). In addition to seed production, the abundance of seed in soil seed banks is important because seed banks help in revegetation following disturbances and help maintain plant diversity, especially in small and isolated ecosystems ([Piessens et al., 2004](#)). However, N impacts on grassland seed banks are not necessarily directly related to changes in plant cover or flowering. [Basto et al. \(2015a\)](#) found that 13 years of simulated N deposition at rates of 35 or 140 kg N/ha/yr decreased cover and flowering in only one species (*Potentilla erecta*) in an acidic grassland in England, but total seed bank abundance declined by 34 and 61% in the low and high N treatments, respectively. Further, seed bank species richness declined by 29 and 41% in these treatments. Among taxa, there were decreases of >50% in the seed bank abundance of forbs, sedges, and grasses with the high N dose, but only a significant decrease (34%) in grass seed bank abundance at the lower N dose. Seed banks were quantified again 4 years after the

cessation of N additions but did not significantly recover in any metric of abundance, richness, or composition.

The Park Grass Experiment in England is the longest ecological experiment in the world and has examined the effect of various soil amendments, including N (96 kg N/ha/yr) as  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NaNO}_3$ , on grassland productivity and composition since 1856. [Zhalnina et al. \(2015\)](#) conducted 16S ribosomal RNA sequencing of soil samples from this experiment to assess bacterial and archaeal community composition ([Table 6-20](#)). Soil nitrate concentrations were positively correlated with the abundance of Thaumarchaeota and Nitrospirae DNA, whereas total soil N was negatively correlated with Firmicutes, Verrucomicrobia, and Chloroflexi. Multivariate analyses of community composition found that the primary determinants of microbial community composition were soil pH and C:N. Soil C:N was negatively correlated with Thaumarchaeota, Nitrospirae, and Gemmatimonadetes, but positively correlated with Acidobacteria and Chlamydiae. Changes in soil pH were a much larger control on microbial abundance, with significant correlations with 17 of the 37 most abundant soil microbial genera. The two different forms of N had different effects on pH, and unsurprisingly, different effects on microbial community composition. Amendments of  $(\text{NH}_4)_2\text{SO}_4$  decreased the phyla Verrucomicrobia and Chloroflexi and the genera *Bradyrhizobium*, *Paenibacillus*, and *Geobacter*, while  $\text{NaNO}_3$  increased the abundance of the phyla Thaumarchaeota and Nitrospirae and the genera *Geobacter*, *Candidatus*, *Nitrososphaera*, *Nitrospira*, and *Methylibium*. In comparison, 27 years of N additions at Cedar Creek in Minnesota changed bacterial composition ([Fierer et al., 2012](#); [Ramirez et al., 2010b](#)) but had no effect on bacterial diversity [[Fierer et al. \(2012\)](#); [Table 6-20](#)].

**Table 6-20 Grassland microbial diversity responses to nitrogen added via experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Ramirez et al. (2010b)</a>	Minnesota (Cedar Creek)	Temperate grassland	Addition	30, 60, 100, 160, 280, 500, 800	27	Bacterial community composition	Change
<a href="#">Fierer et al. (2012)</a>	Minnesota (Cedar Creek)	Temperate grassland	Addition	34, 272	27	Bacterial community composition	<u>Low dose</u> : not significant <u>High dose</u> : change
<a href="#">Fierer et al. (2012)</a>	Minnesota (Cedar Creek)	Temperate grassland	Addition	34, 272	27	Bacterial diversity	Not significant
<a href="#">Wang et al. (2017d)</a>	China (Inner Mongolia)	Steppe grassland	Addition	50, 100, 150	8+	Ratio of fungal to bacterial abundances	Declined
<a href="#">Zhalnina et al. (2015)</a>	U.K.	Temperate grassland	Addition	96	153	Microbial community composition	Change
<a href="#">Daebeler et al. (2017)</a>	Iceland	Subarctic grassland	Addition	100	5	Microbial community composition (archaeal ammonia-oxidizing communities)	Not significant

**Table 6-20 (Continued): Grassland microbial diversity responses to nitrogen added via experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Wang et al. (2017d)</a>	China (Inner Mongolia)	Steppe grassland	Addition	50, 100, 150	8+	Microbial composition (relative abundance of different microbial groups)	Change; Actinomycetes, Gram-negative bacteria, and arbuscular mycorrhizae declined; Gram-positive bacteria increased; no significant change in saprophytic fungi

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Relative to forests, there is comparably little information on how N additions shift the composition of mycorrhizal communities in grasslands ([Table 6-16](#)). In a steppe grassland in China, [Chen et al. \(2014\)](#) observed that 6 years of N additions (100 kg N/ha/yr) decreased the richness of arbuscular mycorrhizal phylotypes found in the soil, but did not affect the diversity of soil phylotypes or alter the richness or diversity of phylotypes observed in plant roots.

As with that of forests, some information is also available regarding the effects of N additions on grassland soil fauna ([Table 6-17](#)). In particular, several studies have been conducted on soil fauna and their role in soil food webs at Cedar Creek in Minnesota ([Cesarz et al., 2015](#); [Eisenhauer et al., 2013](#); [Eisenhauer et al., 2012](#)). [Eisenhauer et al. \(2012\)](#) observed that the N deposition treatment at Cedar Creek (40 kg N/ha/yr) significantly altered the abundance of 5 of 14 groups of soil biota. Simulated N deposition decreased predaceous nematode abundance by 62% but increased fungal feeding nematodes by 206%. Nematode taxon richness and microarthropod taxon richness declined by 7 and 15% under added N ([Eisenhauer et al., 2012](#)). A more detailed analysis by [Cesarz et al. \(2015\)](#) found that N enrichment increased the density of the plant-feeding Longidoridae nematode family by 148% and increased the density of a rapidly growing guild of fungal-feeding nematodes, while a slower-growing guild of predaceous nematodes declined ([Cesarz et al., 2015](#)). Overall, N additions increased nematode community composition toward nematode guilds favored by decomposition pathways dominated by fungi and away from bacterial-dominated decomposition pathways ([Cesarz et al., 2015](#); [Eisenhauer et al., 2012](#)). However, while simulated N deposition had significant effects on soil food webs, these influences were weaker than the direct effects caused by differences in plant diversity ([Eisenhauer et al., 2013](#)).

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### 6.3.6 Arid and Semiarid Ecosystems

As of the 2008 ISA, there was consistent and coherent evidence of altered plant communities in N addition experiments in arid and semiarid ecosystems, particularly within CSS and chaparral ecosystems along the southern California coast and in portions of the Mojave Desert near large population centers. There was further additional evidence about shifts in plant and microbial community composition from N addition experiments in the Mojave, Chihuahuan, Sonoran, and Great Basin Deserts. Although many of these ecosystems are relatively remote and lightly impacted by anthropogenic N deposition, the 2008 ISA noted that deposition to some arid and semiarid ecosystems can be high downwind of major urban and agricultural areas, reaching more than 30 kg N/ha/yr in areas of southern California ([Fenn et al., 2003b](#)). Like other terrestrial ecosystems, there was widespread evidence that N additions altered plant communities by causing a

differential stimulation of growth among plant species ([Báez et al., 2007](#); [Inouye, 2006](#)), such as by favoring rapidly growing nitrophilous species ([Fenn et al., 2003b](#)). In addition to these effects on plant communities, [Egerton-Warburton and Allen \(2000\)](#) found a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along an N deposition gradient among CSS ecosystems in southern California (2 to 57  $\mu\text{g N/g}$  as soil  $\text{NO}_3^-$ ). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by exotic annual grasslands.

There are two ecological interactions that are particularly important controlling how N deposition influences plant community composition in arid and semiarid ecosystems: (1) the strong dependence of biological responses on an adequate water supply and (2) the ability of N deposition to promote the growth of exotic plants [particularly annual grasses; [Brooks \(2003\)](#)], which can dramatically alter the fire cycle by providing a more spatially continuous fuel supply ([Brooks et al., 2004](#)). The fire cycle impacts of increased invasive grass biomass were particularly apparent in southern California in CSS ecosystems near the coast and in Mojave Desert ecosystems inland ([Brooks et al., 2004](#); [Brooks and Esque, 2002](#); [Cione et al., 2002](#); [Yoshida and Allen, 2001](#); [Brooks, 1999](#); [Eliason and Allen, 1997](#)). Fire was relatively rare in the Mojave Desert until the past two decades, but fire now occurs frequently in areas that have experienced invasion of exotic grasses ([Brooks, 1999](#)). These interactions are apparent in an  $\text{NH}_4\text{NO}_3$  addition (32 kg N/ha/yr) study in the Mojave Desert of southern California conducted by [Brooks \(2003\)](#). In the second and wetter year of the experiment, N additions decreased species richness among native annual plants ([Brooks, 2003](#)). Overall, N additions increased the growth of the invasive grass compact brome (*Bromus madritensis*) beneath the dominant native shrub creosote bush (*Larrea tridentata*) and increased the growth of invasive grasses in the genus *Schismus* and the invasive forb *Erodium cicutarium* in the interspaces between *Larrea* shrubs, creating a more continuous fuel bed.

Since the 2008 ISA, a number of new N addition experiments and ambient N deposition gradient studies on shifts in plant community composition and diversity have been conducted, primarily in California and in arid portions of China ([Table 6-21](#)). Broadly, while some of these studies found decreases in plant species richness [e.g., [Allen et al. \(2009\)](#); [Sun et al. \(2014\)](#)], there were more frequent observations of changes in plant community composition. This disparity may be a function of both the relative brevity of these experiments (mostly 2 to 4 years) and the strong moisture limitation that constrains biological responses to added N in these ecosystems.

**Table 6-21 Arid and semiarid ecosystem plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Rao et al. (2009)</a>	California (Joshua Tree NP)	Creosote bush ( <i>Larrea tridentata</i> ) or pinyon-juniper woodland ( <i>Pinus monophylla</i> , <i>Juniperus californica</i> )	Ambient	2.7–14.4	n/a	Invasive annual grass cover	Increase
<a href="#">Allen et al. (2009)</a>	California (Joshua Tree NP; four sites)	Creosote Bush ( <i>Larrea tridentata</i> ) scrub; pinyon-juniper woodland ( <i>Pinus monophylla</i> , <i>Juniperus californica</i> )	Addition	5, 30	2	Native plant species richness	<u>Low dose</u> : not significant <u>High dose</u> : not significant at two sites, increase at one site, decrease at one site
<a href="#">Vourlitis (2017)</a>	California (southern, coastal)	Coastal sage scrub ( <i>Artemisia californica</i> , <i>Salvia mellifera</i> )	Addition	50	13	Native and exotic plant species cover	Increase in the native shrub <i>Artemisia californica</i> in the 4th and 5–9th yr of the 13-yr experiment; decrease in the native shrub <i>Salvia mellifera</i> in the 4th and 11–13th yr; increase in the exotic plant <i>Brassica nigra</i> in the 11–13th yr
<a href="#">Vourlitis and Pasquini (2009)</a>	California (southern coastal)	Coastal sage scrub ( <i>Artemisia californica</i> , <i>Salvia mellifera</i> )	Addition	50	5	Plant community composition	Change
<a href="#">Vourlitis and Pasquini (2009)</a>	California (southern coastal)	Chaparral ( <i>Adenostoma fasciculatum</i> , <i>Ceanothus greggii</i> )	Addition	50	5	Plant community composition	Not significant

**Table 6-21 (Continued): Arid and semiarid ecosystem plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Pasquini and Vourlitis (2010)</a>	California (southern; three sites)	Chaparral ( <i>Adenostoma fasciculatum</i> , <i>Ceanothus</i> spp.)	Ambient	8.1, 11.9, 18.4	n/a	Plant community composition	Change
<a href="#">Concilio and Loik (2013)</a>	California (Great Basin)	Cheatgrass ( <i>Bromus tectorum</i> ) in sagebrush ( <i>Artemisia tridentata</i> ) steppe	Addition	50	4	Plant community composition	Not significant
<a href="#">Cox et al. (2014)</a>	California (southern coastal)	Coastal sage scrub	Ambient	5.7–23.8	n/a	Plant community composition	More invasive grasses when N deposition >11 kg N/ha/yr
<a href="#">Ochoa-Hueso and Stevens (2015)</a>	Spain	Shrubland ( <i>Quercus coccifera</i> , <i>Rosmarinus officinalis</i> , <i>Lithodora fruticosa</i> )	Addition	10, 20, 50	3	Plant community composition	Change
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant community composition	Change
<a href="#">Collins et al. (2017)</a>	New Mexico	Grassland ( <i>Bouteloua eriopoda</i> , <i>Bouteloua gracilis</i> )	Addition	20	1 to 7	Plant community composition	Change in 3 of the 4 yr following fire; not significant in 2 yr preceding fire and last year of the experiment
<a href="#">McHugh et al. (2017)</a>	Utah	Semiarid grassland	Addition	2, 5, 8	2	Plant community composition	Not significant
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant community evenness	Not significant
<a href="#">Zhang et al. (2014)</a>	China (north, Inner Mongolia)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Stipa grandis</i> )	Addition (2 or 12 additions/yr)	10, 20, 30, 50, 100, 150, 200, 500	5	Plant species diversity	Decrease (stronger decrease with two additions/yr)

**Table 6-21 (Continued): Arid and semiarid ecosystem plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Ochoa-Hueso and Stevens (2015)</a>	Spain	Shrubland ( <i>Quercus coccifera</i> , <i>Rosmarinus officinalis</i> , <i>Lithodora fruticosa</i> )	Addition	10, 20, 50	3	Plant species diversity	Not significant
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant species diversity	Decrease
<a href="#">Vourlitis and Pasquini (2009)</a>	California (southern coastal)	Coastal sage scrub ( <i>Artemisia californica</i> , <i>Salvia mellifera</i> )	Addition	50	5	Plant species richness	Not significant
<a href="#">Vourlitis and Pasquini (2009)</a>	California (southern coastal)	Chaparral ( <i>Adenostoma fasciculatum</i> , <i>Ceanothus greggii</i> )	Addition	50	5	Plant species richness	Not significant
<a href="#">Concilio and Loik (2013)</a>	California (Great Basin)	Cheatgrass ( <i>Bromus tectorum</i> ) in sagebrush ( <i>Artemisia tridentata</i> ) steppe	Addition	50	4	Plant species richness	Not significant
<a href="#">Sun et al. (2014)</a>	China (north, Songnen)	Shrubland ( <i>Leymus chinensis</i> , <i>Artemisia scoparia</i> )	Addition	23, 46, 69, 92	3	Plant species richness	<u>Low dose</u> : not significant <u>Other doses</u> : decrease
<a href="#">Zhang et al. (2014)</a>	China (north, Inner Mongolia)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Stipa grandis</i> )	Addition (2 or 12 additions/yr)	10, 20, 30, 50, 100, 150, 200, 500	5	Plant species richness	Decrease (stronger decrease with two additions/yr)
<a href="#">Zhang et al. (2015b)</a>	China (north, Songnen)	Alkaline grassland ( <i>Leymus chinensis</i> , <i>Kalimeris integrifolia</i> )	Addition	100	4	Plant species richness	Decrease
<a href="#">McHugh et al. (2017)</a>	Utah	Semiarid grassland	Addition	2, 5, 8	2	Plant species richness	Not significant

**Table 6-21 (Continued): Arid and semiarid ecosystem plant diversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Vourlitis (2017)</a>	California (southern, coastal)	Coastal sage scrub ( <i>Artemisia californica</i> , <i>Salvia mellifera</i> )	Addition	50	13	Plant species richness	Decrease in the last 3 yr of the 13-yr experiment; not significant for previous years
<a href="#">Collins et al. (2017)</a>	New Mexico	Grassland ( <i>Bouteloua eriopoda</i> , <i>Bouteloua gracilis</i> )	Addition	20	1 to 7	Plant species richness for grasses and forbs	Not significant

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; NP = national park; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Within southern California, there was a continued research focus on how N deposition alters the abundance of invasive annual plants (particularly grasses) in CSS, chaparral, and Mojave Desert ecosystems ([Cox et al., 2014](#); [Pasquini and Vourlitis, 2010](#); [Allen et al., 2009](#); [Rao et al., 2009](#); [Vourlitis and Pasquini, 2009](#); [Talluto and Suding, 2008](#)). Among inland ecosystems, [Allen et al. \(2009\)](#) added N (5 and 30 kg N/ha/yr for 2 years) to four sites at Joshua Tree National Park (JOTR) in California and found that the effects of added N on native plant diversity depended on the abundance of invasive grasses. At one site where invasive grass biomass (primarily *Bromus madritensis*) was high and responded positively to added N, N additions decreased native forb species richness; at a site where invasive grasses were a small component of the plant community, N additions increased native forb cover and species richness. Given that [Rao et al. \(2009\)](#) found greater invasive annual grass cover at sites with higher N deposition across a 16-site N deposition gradient in the JOTR area, the results of [Allen et al. \(2009\)](#) imply that N deposition may be decreasing native forb richness across broad areas in the JOTR area.

Near the southern California coast, [Vourlitis and Pasquini \(2009\)](#) investigated the effects of dry-season N addition in chaparral (dominated by the shrubs *Adenostoma fasciculatum* and *Ceanothus greggii*) and CSS (dominated by the shrubs *Artemisia californica* and *Salvia mellifera*) stands over a 5-year period. The additional N (50 kg N/ha/yr) significantly altered the community composition of CSS, but not chaparral. The differences in CSS community composition were due to changes in the relative abundance of dominant shrubs, not herbaceous plant species. This is not necessarily consistent with previous research, including observations that although both native shrubs and invasive annual plants can exhibit faster growth rates with added N, high N availability can cause mortality in native shrubs ([Allen et al., 1998](#)). [Talluto and Suding \(2008\)](#) revisited 232 plots in southern California that had been dominated by CSS vegetation during a 1930s vegetation survey and found that CSS cover had declined by 49%, and only 15% of the 1930s CSS plots lacked invasive annual grasses. At a landscape scale, the conversion of CSS to invasive-dominated land was positively related to N deposition rates and fire frequency, which itself has been linked to N deposition. In another landscape-level analysis of vegetation change since the 1930s, [Cox et al. \(2014\)](#) observed that CSS converted to non-native grasslands when N deposition was greater than 11 kg N/ha/yr, more consistent with the previous results. Also in southern California, [Pasquini and Vourlitis \(2010\)](#) found evidence that N deposition caused changes in chaparral plant community composition in recently burned ecosystems, but the influence of N deposition in this study was confounded by changes in other environmental factors across the three-site N deposition gradient (8.1 to 18.4 kg N/ha/yr) used for this research.

Elsewhere in California, [Concilio and Loik \(2013\)](#) studied the effects of added N (50 kg N/ha/yr for 4 years) on sagebrush steppe ecosystems in the eastern Sierra Nevada where the invasive annual grass *Bromus tectorum* was beginning to establish. Although N addition treatments increased plant available N and total N, no changes were observed in cover, community composition, or richness of native or invasive species. *Bromus tectorum* cover was inversely related to native forb species richness, but increased N deposition did not affect plant diversity. However, [Concilio and Loik \(2013\)](#) cautioned that precipitation was below average during the study and N additions may have different effects when moisture availability is greater.

Several notable N addition studies have been conducted in the arid steppe grassland and shrubland ecosystems in northern and western China. [Zhang et al. \(2014\)](#) studied whether the frequency of additions (12 doses/year vs. 2 doses/year) altered the effect of added N on plant diversity in a steppe grassland in the Inner Mongolia region of China (eight levels from 10 to 500 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$  for 5 years). Species richness declined by about 50% as N addition rates increased; plant diversity also decreased more with higher N addition rates. [Zhang et al. \(2014\)](#) noted that the declines in diversity and richness were smaller with the smaller frequent N doses than with the large infrequent doses and suggested that this implied that some N addition studies may be overestimating the negative effects on plant biodiversity. However, at the lower N addition rates (10, 20, and 30 kg N/ha/yr) that are more relevant to N deposition levels in the U.S., the effects of dose frequency were not consistently observed; species richness was sometimes (nonsignificantly) higher with the large infrequent doses at these N addition rates. The frequency of N additions did not impact the rate of species loss in perennial forbs but did affect the rate of species loss in grasses and annual and biennial forbs. Notably, N additions were associated with significant decreases in soil temperature, soil moisture, and soil pH and increases in  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . All of these soil changes were correlated with each other and the proportional changes in each of these variables were correlated with the proportional loss in species richness. Among these soil traits, higher N addition frequency increased  $\text{NH}_4^+$ , but had no other significant effects. In subsequent research at these sites, [Zhang et al. \(2016b\)](#) observed that the lower plant species richness in the low frequency N addition plots relative to the high frequency plots was not caused by differences in the rate of species loss, but instead resulted from slower colonization by new species in the plots that received large infrequent N additions. In another experiment in semiarid Chinese steppe grasslands, [Li et al. \(2016a\)](#) observed that N additions (50, 100, 150 kg N/ha/yr for 8 years) decreased species richness, decreased diversity, and altered community composition for both plant and bacterial communities and that changes in plant and microbial communities were significantly correlated. [Li et al. \(2016a\)](#) also observed that N additions decreased both plant and microbial species

richness and altered microbial community composition in a semiarid Chinese steppe grassland.

A recent study by [Tian et al. \(2016b\)](#) examined how N addition at several rates affected grassland structure and function in the temperate steppe of China (20, 40, 80, 160, 320 kg N/ha/yr). They found that N addition led to increases in aboveground biomass and to shifts in relative abundance from forbs to grasses even at the lowest input rate, as reported in other studies. However, they reported a novel mechanism related to manganese (Mn) toxicity to explain reductions in forb diversity that had not been demonstrated before, but had been reported in forestry literature ([St.Clair et al., 2008](#); [St.Clair and Lynch, 2005](#)). They reported that forbs were much more prone to Mn toxicity than grasses following N addition because of physiological differences in root enzymes associated with metal uptake. Manganese accumulated more in forbs than grasses, leading to decreased forb photosynthetic rates and shifts in relative abundances towards grasses. It is unknown whether this mechanism is operating in other grassland systems.

In an arid steppe grassland in northeastern China, [Sun et al. \(2014\)](#) observed that N additions of 23, 46, 69, and 92 kg N/ha/yr (3 years, as urea) caused proportional decreases in forb species richness, but found added N caused soil bacterial communities to become more diverse except at the highest N dose ([Table 6-22](#)). [Huang et al. \(2015\)](#) conducted a 3-year N × water experiment focused on soil microbial community composition in a desert steppe ecosystem in northwestern China that receives 25 kg N/ha/yr of ambient deposition. The N addition treatment (50 kg N/ha/yr as NH<sub>4</sub>NO<sub>3</sub>) effects on microbial composition differed between inter-plant and beneath shrub sites. In the interspaces, N additions increased the portion of bacteria in total microbial biomass in all 3 years and increased actinobacteria in the last 2 years of the experiment. Beneath the shrubs, N additions broadly suppressed microorganisms in all domains. In the Sonoran Desert near Phoenix, [Marusenko et al. \(2015\)](#) found that although N additions (60 kg N/ha/yr for 8 years) increased the abundance of the *amoA* gene (needed for ammonia oxidation) in both archaea and bacteria, the community composition of ammonia-oxidizing microorganisms was unaffected.

In Mediterranean shrublands in Spain, N additions (10, 20, and 50 kg N/ha/yr for 4 years) increased the abundance of Collembola, which were a dominant component (44%) of the soil fauna. The N additions did not significantly affect soil fauna richness or diversity, but there was a significant negative relationship between richness and soil C:N ratio and a positive relationship between diversity and soil pH ([Ochoa-Hueso et al., 2014](#)).

**Table 6-22 Arid and semiarid ecosystem microbial diversity responses to nitrogen added via experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Marusenko et al. (2015)</a>	Phoenix, AZ	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia</i> spp.)	Addition	60	8	Archaeal and bacterial <i>amoA</i> (NH <sub>3</sub> mono-oxygenase) community composition	Not significant
<a href="#">Marusenko et al. (2015)</a>	Phoenix, AZ	Creosote and bursage shrublands ( <i>Larrea tridentata</i> , <i>Ambrosia</i> spp.)	Addition	60	8	Archaeal and bacterial <i>amoA</i> (NH <sub>3</sub> mono-oxygenase) gene abundance	Increase
<a href="#">Huang et al. (2015)</a>	China	Desert shrubs ( <i>Haloxylon ammodendron</i> )	Addition	50	3	Microbial community composition	Change
<a href="#">McHugh et al. (2017)</a>	Utah	Semiarid grassland	Addition	2, 5, 8	2	Microbial community composition	Not significant
<a href="#">McHugh et al. (2017)</a>	Utah	Semiarid grassland	Addition	2, 5, 8	2	Microbial diversity	Not significant
<a href="#">Sun et al. (2014)</a>	China (north, Songnen)	Shrubland ( <i>Leymus chinensis</i> , <i>Artemisia scoparia</i> )	Addition	23, 46, 69, 92	3	Soil bacterial community composition	Change
<a href="#">Sun et al. (2014)</a>	China (north, Songnen)	Shrubland ( <i>Leymus chinensis</i> , <i>Artemisia scoparia</i> )	Addition	23, 46, 69, 92	3	Soil bacterial diversity	Increase

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

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### 6.3.7 Lichens

In the 2008 ISA, there was consistent and coherent evidence indicating that lichen communities were affected by current levels of N deposition. Lichen community composition is highly sensitive to atmospheric pollution from N and S ([Jovan, 2008](#)). Based on the widely recognized sensitivity of lichen species to air pollution, [Geiser and Neitlich \(2007\)](#) developed a model to assess local air quality in Pacific Northwest forests based on lichen community composition. In addition to being good subjects for biomonitoring, lichens constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife ([McCune and Geiser, 1997](#)). The composition of the lichen community is important because individual species have different physical and physiological traits, and thus make particular contributions to the provisioning of ecosystem services.

Lichens containing a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens ([Hallingbäck and Kellner, 1992](#); [Hallingbäck, 1991](#)). In central Europe, [Hauck and Wirth \(2010\)](#) analyzed 514 lichen species and found that shade-adapted lichen species are nearly universally intolerant of high rates of N deposition. Nearly all of these shade-tolerant and pollution-sensitive species are crustose lichens ([Hauck and Wirth, 2010](#)). The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr ([Bobbink et al., 1998](#)). In Sweden, the probability of occurrence for three genera of hair lichens (*Alectoria*, *Bryoria*, *Usnea*) on Norway spruce (*Picea abies*) in forest inventory plots peaked at 3–6 kg N/ha/yr of deposition and then rapidly declined; N deposition was the strongest or second-strongest environmental predictor of lichen occurrence ([Esseen et al., 2016](#)). In the U.S., lichen species are negatively affected by N inputs as low as 3 to 8 kg N/ha/yr ([Fenn et al., 2003a](#)).

In the San Bernardino Mountains, CA, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared ([Fenn et al., 2003a](#); [Nash and Sigal, 1999](#)). In mixed conifer forests in California, the critical load for lichen communities has been estimated at 3.1 kg N/ha/yr ([Fenn et al., 2008](#)). Compared to California, air pollution has historically been less problematic in the Pacific Northwest and this region still has large populations of pollution-sensitive lichens ([Jovan, 2008](#); [Fenn et al., 2003a](#)). [Jovan \(2008\)](#) reported that hotspots for lichen diversity in the U.S. include Klamath-Siskiyou region along the Oregon-California border, the Okanogan highlands region in northeastern Washington, and the Blue Mountains in eastern Oregon—all areas that are relatively distant from large human population centers and industrial centers. However, lichen

communities in the Pacific Northwest are beginning to show evidence of changes in response to increased N pollution, including decreased distribution of sensitive lichen taxa and their replacement with nitrophilous species ([Geiser and Neitlich, 2007](#)).

Research on lichens since 2008 continues to indicate that lichen communities change in response to increased atmospheric N, in both U.S. and Europe. Unlike most other N deposition biodiversity studies, lichen research has been dominated by studies using measurements along ambient N deposition gradients rather than using experimental N additions ([Table 6-23](#)). Within the U.S., there are numerous examples of shifts in lichen community composition along gradients of atmospheric N deposition. Lichen community composition has been quantified in many parts of the U.S. as part of the U.S. Department of Agriculture Forest Service’s Forest Inventory and Analysis (FIA) program. [Jovan \(2008\)](#) reported the results from surveys of almost 800 plots conducted from 1998 to 2003 in California, Washington, and Oregon, documenting clear shifts in lichen community composition in forests in and around areas of intensive agricultural and industrial production in the Central Valley of California, the Willamette Valley in Oregon, and the Puget Trough (Seattle/Tacoma/Olympia) in Washington. In the northeastern U.S., [Will-Wolf et al. \(2015\)](#) analyzed approximately 600 plots of survey data collected in the 1990s and 2000s as part of the FIA program and from other sources. These data showed strong relationships between total N deposition and decreased lichen abundance, reduced species richness, and altered community composition, but the high overlap between N deposition and acidifying deposition in this region made it difficult to discern the primary influence on lichen biodiversity.

**Table 6-23 Lichen biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr or as Otherwise Noted)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Jovan (2008)</a>	California, Oregon, Washington	Forest	Ambient	0.5–21	n/a	Community composition	Change
<a href="#">Rogers et al. (2009)</a>	Utah and Idaho	Aspen forests ( <i>Populus tremuloides</i> )	Ambient (NH <sub>3</sub> gas)	7.3–92.2 µm/m <sup>3</sup>	n/a	Community composition	Change

**Table 6-23 (Continued): Lichen biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr or as Otherwise Noted)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">Geiser et al. (2010)</a>	Oregon and Washington	Conifer forests	Ambient	0.8–8	n/a	Community composition	Change
<a href="#">Johansson et al. (2012)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	4	Community composition	Change
<a href="#">Jovan et al. (2012)</a>	California (Los Angeles Basin)	Oak forests ( <i>Quercus kelloggii</i> )	Ambient	6.1–71.1	n/a	Community composition	Change
<a href="#">Gibson et al. (2013)</a>	Nova Scotia (Canada)	Northern hardwood forests ( <i>Acer saccharum</i> , <i>Betula alleghaniensis</i> )	Ambient (NO <sub>2</sub> gas)	0.01–0.35 ppb	n/a	Community composition	Change
<a href="#">Schirokauer et al. (2014b)</a>	Alaska (southeast)	Conifer forests	Ambient	0.05–1.05	n/a	Community composition	Change
<a href="#">McMurray et al. (2015)</a>	Idaho, Wyoming, Montana	Conifer forests	Ambient	0.5–4.3	n/a	Community composition	Change
<a href="#">Johansson et al. (2012)</a>	Sweden	Norway spruce ( <i>Picea abies</i> )	Addition	6, 12.5, 25, 50	4	Species richness	<u>6 and 12.5 doses:</u> increase <u>25 and 50 doses:</u> decrease
<a href="#">Gibson et al. (2013)</a>	Nova Scotia (Canada)	Northern hardwood forests ( <i>Acer saccharum</i> , <i>Betula alleghaniensis</i> )	Ambient (NO <sub>2</sub> gas)	0.01–0.35 ppb	n/a	Species richness	Decrease
<a href="#">Southon et al. (2013)</a>	U.K.	Heathlands ( <i>Calluna vulgaris</i> )	Ambient	5.9–32.4	n/a	Species richness	Decrease
<a href="#">Armitage et al. (2014)</a>	Europe (North Atlantic)	Alpine heathlands	Ambient	0.6–39.6	n/a	Species richness	Not significant
<a href="#">Field et al. (2014)</a>	U.K.	Heathlands	Ambient	5.4–32.4	n/a	Species richness	Decrease

**Table 6-23 (Continued): Lichen biodiversity responses to nitrogen added via atmospheric deposition or experimental treatments.**

Reference	Study Location	Vegetation	Ambient Deposition or Addition	Nitrogen Addition Rate (kg N/ha/yr or as Otherwise Noted)	Duration (yr)	Endpoint	Effect of Additional Nitrogen
<a href="#">McDonough and Watmough (2015)</a>	Ontario, Canada	Sugar maple forests ( <i>Acer saccharum</i> )	Ambient	8.3–12.9	n/a	Species richness	Not significant
<a href="#">Will-Wolf et al. (2015)</a>	North-eastern U.S.	Forests	Ambient	Not stated	n/a	Species richness	Decrease

ha = hectare; kg = kilogram; N = nitrogen; n/a = not applicable; NH<sub>3</sub> = ammonia; NO<sub>2</sub> = nitrogen dioxide; ppb = parts per billion; yr = year.

Notes: Single studies are reported more than once if multiple endpoints were measured. References ordered by endpoint. Only statistically significant effects are listed as increases or decreases.

Other surveys of lichen community composition in the U.S. also documented changes even at relatively low rates of N deposition. For instance, lichen community composition in southeastern Alaska shifted toward more eutrophic species along an N deposition gradient of 0.05 to 1.05 kg N/ha/yr ([Schirokauer et al., 2014b](#)). In the northern Rockies, [McMurray et al. \(2015\)](#) observed a shift in lichen community composition at deposition rates greater than 4.0 kg N/ha/yr. In montane aspen forests in the Utah-Idaho border region, [Rogers et al. \(2009\)](#) observed a shift in lichen community composition away from nitrophilous species along a NH<sub>3</sub> concentration gradient away from urban and agricultural sources. In the Los Angeles Basin area of California, [Jovan et al. \(2012\)](#) documented increases in the abundance of eutrophic lichen species along a gradient of N deposition. In coniferous forests in the Pacific Northwest, shifts in lichen community composition and declines in oligotrophic lichen species were observed as N deposition increased to levels from 3 to 9 kg N/ha/yr range ([Geiser et al., 2010](#); [Glavich and Geiser, 2008](#)).

Outside of the U.S., changes in lichen community composition have been observed in Canada and in Europe. In the U.K., [Southon et al. \(2013\)](#) and [Field et al. \(2014\)](#) observed decreased lichen species richness in over 50 heathland survey locations along an N deposition gradient of 5.4 to 32.4 kg N/ha/yr. However, [Armitage et al. \(2014\)](#) did not find a significant change in lichen species richness along an N deposition gradient of 0.6 to 39.4 kg N/ha/yr in alpine heathlands in the North Atlantic region of Europe. In Sweden, [Johansson et al. \(2012\)](#) found additions of 6 kg N/ha/yr, applied directly onto trees in a liquid spray, in old growth boreal spruce forests changed the species composition of epiphytic lichen communities and reduced species richness. [Gibson et al. \(2013\)](#) also noted that in Cape Breton Highlands National Park in Nova Scotia, the

number of pollutant-intolerant lichen species decreased from 10 to 5 when median summer and winter atmospheric NO<sub>2</sub> concentrations increased above 0.46 and 0.15 ppb, respectively. [McDonough and Watmough \(2015\)](#) were unable to detect an influence of modeled N deposition (ranging from ca. 8 to 13 kg N/ha/yr) on epiphytic foliose lichen species richness across a network of 70 sugar maple forest monitoring plots in southern Ontario, Canada. The lack of a relationship, however, may have been caused by already low lichen richness across much of the region, due to prior and current deposition from industrial and agricultural sources ([McDonough and Watmough, 2015](#)).

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### 6.3.8 Most Sensitive Ecosystems

The 2008 ISA reported that the most responsive ecosystems to N enrichment from atmospheric N deposition were those that receive high levels of N loading, are N limited, or contain species that have evolved in nutrient-poor environments. Species adapted to low N supply are readily outcompeted by species that have higher N demand when the availability of N is increased ([Krupa, 2003](#); [Tilman and Wedin, 1991](#); [Aerts et al., 1990](#)). As a consequence, some native species can be eliminated by N deposition ([Stevens et al., 2004](#); [Falkengren-Grerup, 1989, 1986](#); [Roelofs, 1986](#); [Ellenberg, 1985](#)).

Unlike the case of acidifying deposition where ecosystem sensitivity is tied principally to underlying geology, most terrestrial ecosystems are N limited and, therefore, sensitive to perturbation caused by N additions ([LeBauer and Treseder, 2008](#)). Consequently, little was known in the 2008 ISA about the full extent and distribution of the terrestrial ecosystems in the U.S. most sensitive to adverse impacts caused by atmospheric N deposition. Effects were most likely to occur where areas of relatively high atmospheric N deposition intersect with N limited plant communities. The factors governing the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the rates of N deposition, degree of N limitation, ecosystem productivity, elevation, species composition, length of growing season, and soil N retention capacity. Thus, ecosystems such as alpine tundra, which are typically strongly N limited, contain vegetation adapted to low N availability, often have thin soils with limited N retention capacity, and have short growing seasons, can be particularly sensitive to N deposition. Similarly, the ability of atmospheric N deposition to override the natural spatial heterogeneity in N availability in arid ecosystems, such as the Mojave Desert and CSS ecosystems in southern California, makes these ecosystems more prone to wildfires and sensitive to N deposition.

In the 2008 ISA, effects on individual plant species had not been well studied in the U.S. More was known about the sensitivity of particular plant communities, based largely on results obtained in more extensive studies conducted in Europe, which included

hardwood forests, alpine meadows, arid and semiarid lands, and grassland ecosystems. Among communities sensitive to N deposition, lichens and ectomycorrhizal fungi have particularly low thresholds for effects (see [Appendix 6.5.1](#) and [Appendix 6.5.2](#)). Thus, the ecosystems containing a large number and/or diversity of these organisms, such as temperate and boreal forests and alpine tundras, could be considered particularly sensitive to N deposition. More broadly, there has been substantial work on critical loads for N in U.S. ecoregions since the 2008 ISA (see [Appendix 6.5](#)), creating an improved understanding of which processes, taxa, and regions are sensitive to N deposition impacts.

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## 6.4 Climate Modification of Ecosystem Nitrogen Response

Biotic responses to N deposition can be modified by climatic shifts in temperature and precipitation. [Appendix 13](#) provides an overview of this topic, whereas this section describes in brief some of the climate modifications specific to the N response of terrestrial ecosystems, particularly plant productivity and diversity. Shifts in temperature and precipitation can alter the effects of N deposition on these two endpoints, as well as the N response of microbial communities.

Temperature and precipitation can interact with N to affect plant productivity. As noted in [Appendix 6.2](#), [Xia and Wan \(2008\)](#) identified almost 1,600 observations of plant biomass growth in response to N additions, excluding agricultural and horticultural species ([Figure 6-1A](#)). They found that biomass responses to N increased linearly with mean annual precipitation (MAP). [LeBauer and Treseder \(2008\)](#) had a considerably smaller data set ( $n = 126$ ) than [Xia and Wan \(2008\)](#) and did not find that MAP, mean annual temperature (MAT), or latitude had significant overall influences on responsiveness of NPP to added N. However, within individual biomes, forest and tundra NPP responses to N increased with MAT, and forests also became more responsive with greater MAP. In general, as precipitation increases, water limitation to plant productivity is relieved, allowing vegetation to be more responsive to changes in N.

As also described in [Appendix 6.2](#), [Tian et al. \(2016a\)](#) developed a “N response efficiency” metric ( $100 \times (\text{ANPP}_{\text{treatment}} - \text{ANPP}_{\text{control}}) / \text{ANPP}_{\text{control}} / \text{N addition rate}$ ) in order to examine how plant growth responses per unit N changed with increasing levels of N. They found N response efficiency significantly changed with environmental factors. Response efficiency decreased with soil pH and total soil N concentration and increased with soil C:N ratios and with precipitation until annual precipitation reached 800 mm/year. The N response efficiency also peaked with moderate annual temperatures ( $\sim 8^\circ\text{C}$ ) and declined under cooler or warmer conditions ([Tian et al., 2016a](#)).

Not surprisingly, climate modification of plant productivity responses can be particularly pronounced in drier ecosystems. In the Sonoran Desert near Phoenix, [Hall et al. \(2011\)](#) added 60 kg N/ha/yr and found little or no increase in production among herbaceous annuals in low precipitation years, moderate N responses with average rainfall, and strong increases in biomass with added N during above-normal rainfall seasons. [Vourlitis \(2012\)](#) measured aboveground biomass and litter production in a mature CSS stand in southern California over an 8-year period. The effect of added N positively correlated with precipitation and was only significant in the high rainfall years. Similarly, [Zhang et al. \(2015e\)](#) observed greater plant productivity responses to N in years with higher precipitation in a steppe grassland in Inner Mongolia.

In addition to shifts in plant productivity, plant diversity can also be affected by the interactions of temperature, precipitation, and N ([Porter et al., 2013](#)). In their national-scale analysis of herbaceous species richness, [Simkin et al. \(2016\)](#) found that temperature and precipitation could moderate N effects in some instances. They did not observe a significant interaction between N and temperature or precipitation on plant species richness for closed canopy systems (deciduous, evergreen, and mixed forests), but did in open canopy systems (grasslands, shrublands, and woodlands). In these open canopy ecosystems, they found that N had a more negative effect on species richness at lower temperatures. This finding is consistent with [Clark et al. \(2007\)](#) who also found a small increase in the risk of species loss with lower annual minimum temperatures, among other factors. Even though the overall effects within closed systems were not significant, [Simkin et al. \(2016\)](#) also analyzed smaller regional forest gradients dominated by maple-birch (*Acer-Betula*), white oak (*Quercus alba*), or Douglas fir (*Pseudotsuga menziesii*) trees. At this scale, the threshold for negative deposition effects tended to be lower (7.5–9.5 kg N/ha/yr), and the negative effects of N deposition on species richness were greatest when temperature and precipitation were high.

Some studies have explored these interactive effects under future climatic and N scenarios. In ForSAFE-VEG model projections of plant community composition in three French forests, two N reduction scenarios—the maximum feasible N emission reductions scenario and the current European legislation scenario for reactive N emissions rates—resulted in gradual shifts over the next 90 years back toward the plant community composition observed at the beginning of the 20th century ([Rizzetto et al., 2016](#)). Notably, the recovery of these plant communities occurred only if climatic factors were held constant at current levels. In another modeling study, [Phelan et al. \(2016\)](#) made a similar observation for understory plant community composition in northern hardwood forests at Bear Brook Watershed in Maine and Hubbard Brook in New Hampshire: the simulated plant community composition returned toward preindustrial conditions over the

next century only in a scenario in which N deposition rates returned to background and climate was kept stable.

Finally, in addition to plant responses, climatic factors also can modify the N response of microbial communities and other soil biota. For instance, N deposition has been shown to alter the soil microbial community responsible for a step in nitrification, particularly at ambient temperature and precipitation ([Horz et al., 2004](#)). The N effect was then reduced when temperature and precipitation were increased ([Horz et al., 2004](#)). Similarly, N additions and lower precipitation interacted to shift microbial community composition in forests soils in northeastern China ([Wang et al., 2014c](#)) and in grassland soils in Inner Mongolia ([Li et al., 2016a](#)). [Jarvis et al. \(2013\)](#) found that both changes in precipitation and nitrogen were associated with shifts in ectomycorrhizal species composition in European Scots pine (*Pinus sylvestris*) stands, although their observational study did not allow them to test the interactive effects. In a Minnesota grassland, [Eisenhauer et al. \(2012\)](#) observed a decline in several categories of biota within a soil food web (numbers of nematode predators, microarthropod herbivores, and taxa richness of nematodes and microarthropods) under increased N, and a decrease in ciliate protists under high N and drought. The authors suggested the impact of drought may have been limited by the soil food web's prior adaption to dry conditions because the study was conducted on a sandy outwash soil, which dries out quickly in the summer. These studies on disparate biota and ecosystems suggest climatic factors, namely temperature and precipitation, can interact with N to affect soil biotic communities. In general, the functional implications to terrestrial ecosystems of these combined climate-and-N induced shifts in soil biota remain unclear, although there are notable exceptions [e.g., nitrification; [Horz et al. \(2004\)](#)].

Overall, studies investigating the interactive effects of climatic factors and N have been limited to date ([Porter et al., 2013](#)). Despite this, evidence suggests climatic shifts in temperature and/or precipitation can alter the effects of N on plant productivity and diversity, and soil microbial communities and other soil biota.

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## 6.5 Critical Loads

As discussed elsewhere in this ISA (e.g., [Appendix 1](#), [Appendix 4](#), [Appendix 5](#)), critical loads (CLs) are a determination of how much atmospheric deposition can be tolerated by an environmental system before a significant change occurs. Most commonly, this approach defines a level of deposition associated with an adverse geochemical or biological response within an ecoregion. As of the 2008 ISA, most of the CLs developed for North American ecosystems were for aquatic ecosystems (lakes and streams) in

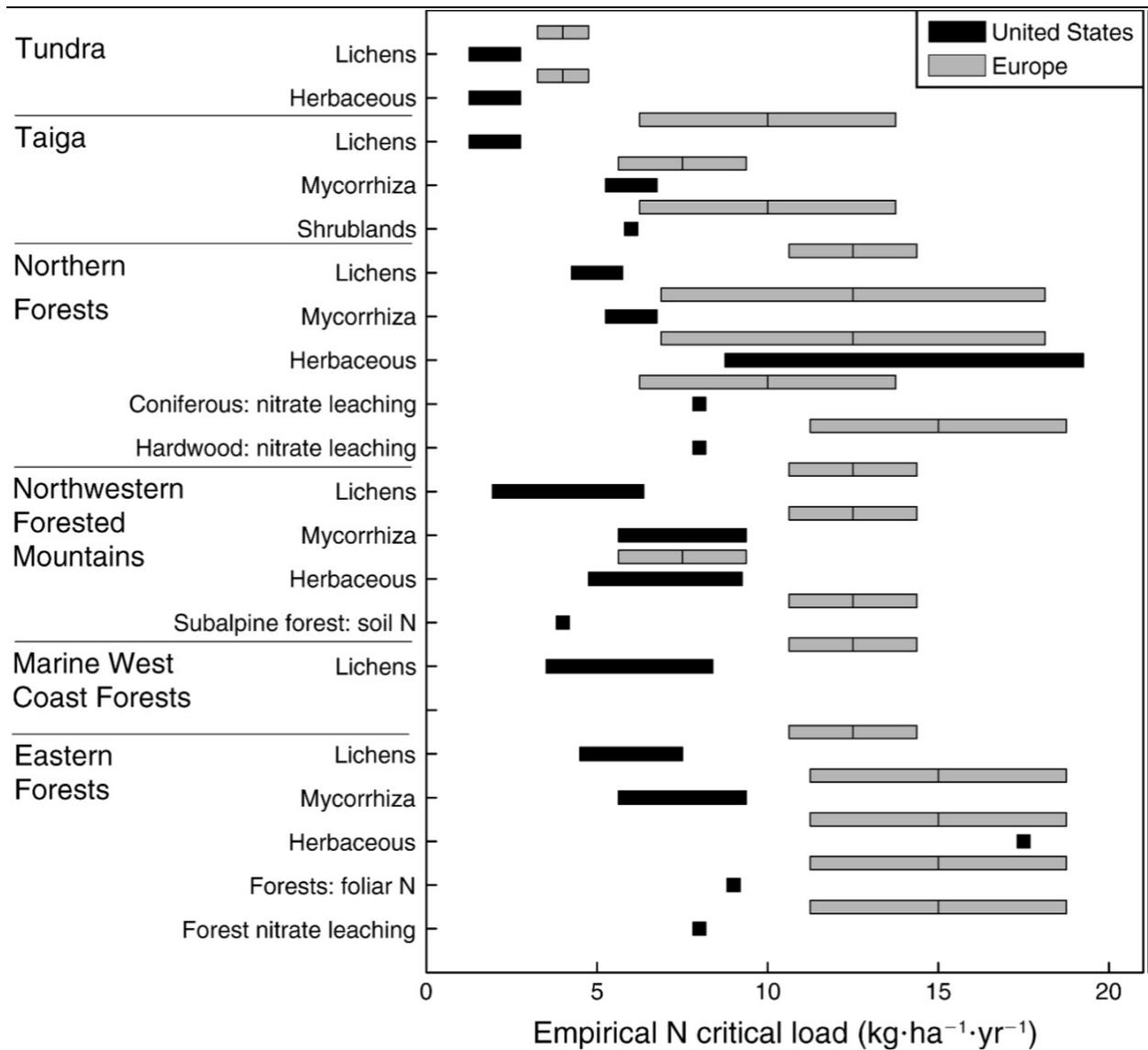
Canada and the northeastern U.S. Among terrestrial ecosystems in North America, the 2008 ISA identified efforts to develop empirical CLs for western ecosystems in the U.S., particularly alpine and arid ecosystems. The reported effect levels ranged from 4 to 5 kg N/ha/yr for changes in the abundance of individual sensitive alpine plant species, to 20 kg N/ha/yr for community level changes in alpine plant communities. [Clark and Tilman \(2008\)](#) calculated the CL for the onset of reduced relative species numbers in grasslands to be 5.3 kg N/ha/yr with a 95% inverse prediction interval of 1.3–9.8 kg N/ha/yr. A CL of 3.1 kg N/ha/yr was considered protective of lichen communities in the western U.S. ([Fenn et al., 2008](#)). However, as of 2008, there was no published CL assessment that spanned the U.S.

A large body of work has been published on CLs for N since the 2008 ISA. Most notably, the U.S. Department of Agriculture (USDA)-Forest Service (FS) created a detailed national assessment of empirically developed CLs for the U.S. ([Pardo et al., 2011c](#)), which has also been summarized into a refereed manuscript ([Pardo et al., 2011a](#)). This national CL document, *Assessment of Nitrogen Deposition Effects and Empirical Critical Loads* ([Pardo et al., 2011c](#)), reports CLs for various biological and biogeochemical endpoints in 15 terrestrial ecoregions. Additionally, in some cases, more recent CLs have been published, often falling into the range of CLs identified by the USDA-FS assessment [[Pardo et al. \(2011c\)](#); summarized in [Appendix 6.6.3](#)].

As with many published CL estimates, most of the CLs reported in the USDA-FS assessment were empirically derived, based on ecological changes observed along atmospheric N deposition gradients or in response to experimental N additions at rates near ambient deposition. Consequently, the links between N deposition and the measured response variable are direct for empirically derived CLs, and full process-level knowledge is not required. There can be a few potential sources of uncertainty with empirically derived CLs, however. The lack of a full process-based understanding can make it difficult to extrapolate observed results across space and time. Spatially, variation in biological and biogeochemical processes imposed by climate, geology, biota, and other environmental factors may alter the observed deposition-response relationship. This is particularly problematic in areas where N deposition has received sparse research attention. [Pardo et al. \(2011c\)](#) reported that for some ecoregions, a single study or very few studies were available. If the variability of ecosystem response to N deposition across an ecoregion is not available, the estimated CL for N may be relevant for only a single ecosystem type or a single subregion within the ecoregion. Whereas atmospheric deposition responds dynamically to shifts in emissions and weather patterns, ecological processes react to environmental stress at a variety of timescales. Because ecological changes can be dependent on a series of underlying processes, there can be a time lag between deposition and ecological responses. Finally, reference plots at the low end of

the deposition gradient may already have been altered from a “pristine” condition, which can bias CL estimates upwards. This shift from a background state can be particularly problematic for highly sensitive indicators, as well as in regions such as the northeastern U.S. that have long and geographically extensive histories of elevated N deposition. In the USDA-FS assessment, [Pardo et al. \(2011c\)](#) reported CLs that tended to be higher in regions experiencing greater rates of N deposition.

Because environmental factors are large influences on both biogeochemical cycling and biological processes ([Pardo et al., 2011c](#)), the discussion of terrestrial biological CLs in this ISA focuses largely on research conducted in North America. Notably, [Pardo et al. \(2011c\)](#) reported that CLs developed for Europe and China both tended to be higher than those reported in the U.S., likely because of the higher rates of N deposition in these regions ([Figure 6-4](#)). Further, because a large portion of the variation in CLs is a function of particular ecological receptors ([Pardo et al., 2011c](#)), the analysis of CL research presented here compares observations for key receptors (e.g., mycorrhizal fungi, lichens, herbaceous plants) across ecoregions, focusing on the estimates created by [Pardo et al. \(2011c\)](#) and other CL research published since 2008.



Source: [Pardo et al. \(2011a\)](#).

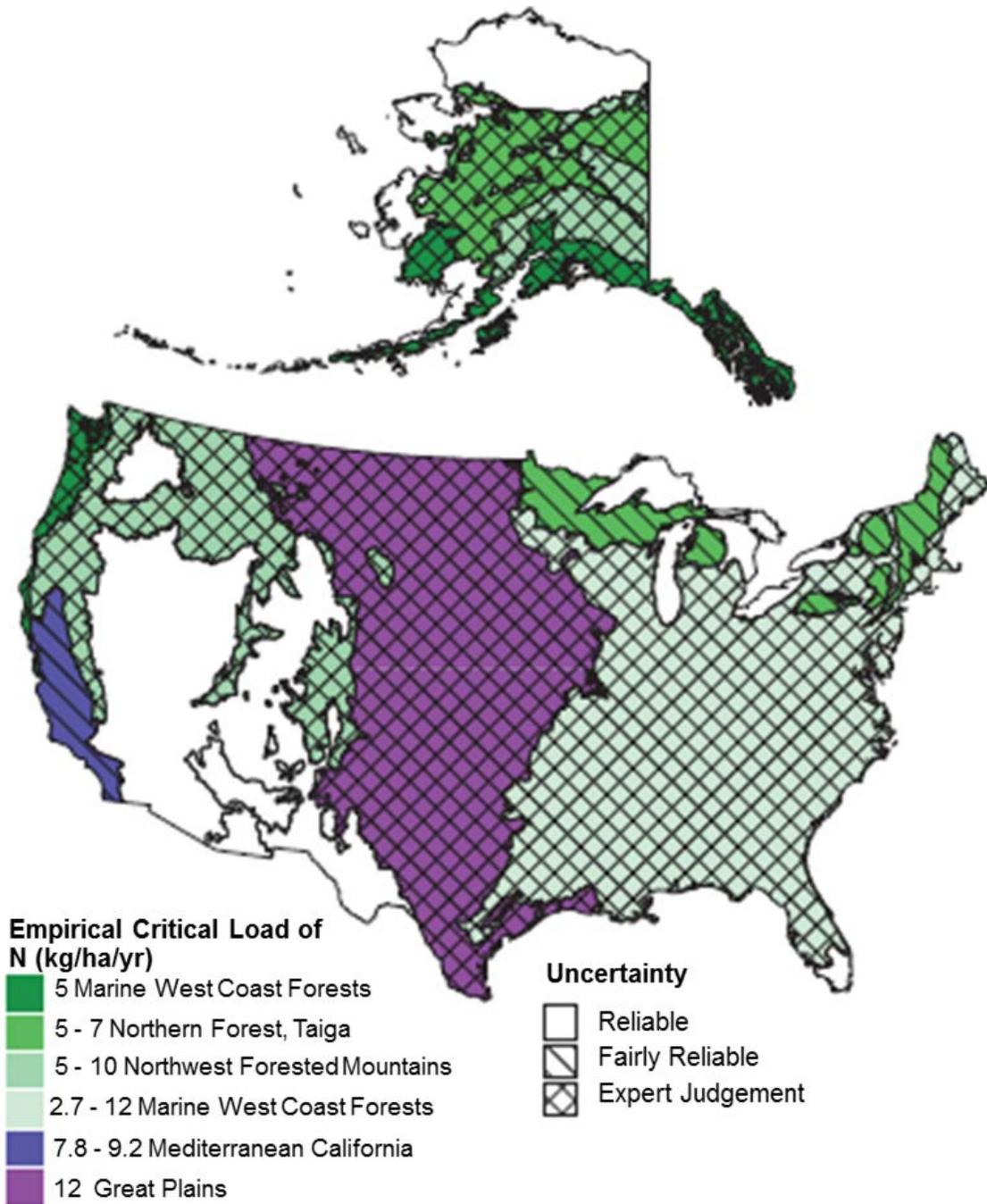
**Figure 6-4 Comparison of European and U.S. empirical critical loads for nitrogen from [Pardo et al. \(2011a\)](#).**

### 6.5.1 Mycorrhizal Fungi

Mycorrhizal fungi are symbiotic organisms hosted on the roots of many plant species, with important roles in plant nutrient acquisition, belowground C cycling, and as food sources for other organisms. As noted in [Appendix 6.2](#) and [Appendix 6.3](#), mycorrhizal fungi can be sensitive to added N, responding through changes in physiology and growth

([Table 6-2](#), [Table 6-3](#), and [Table 6-8](#)), as well as shifts in species richness and community composition ([Table 6-15](#) and [Table 6-16](#)).

Nitrogen CLs for mycorrhizal fungi range between 5 and 12 kg N/ha/yr in the U.S. ([Figure 6-5](#); [Table 6-24](#)) according to studies assessed in [Pardo et al. \(2011c\)](#) and one additional study conducted in a southern California CSS ecosystem ([Allen et al., 2016](#)). [Pardo et al. \(2011c\)](#) documented that N deposition in the range of 5 to 10 kg N/ha/yr can significantly alter ectomycorrhizal fungi community composition and decrease species richness in N limited conifer forests. Similarly, N deposition levels of 7.8 to 12 kg N/ha/yr can lead to arbuscular mycorrhizal community changes in CSS ecosystems in California and grasslands in the Midwest (see Mediterranean California and Great Plains ecoregions in [Figure 6-5](#)), due to declines in spore abundance and root colonization, and changes in community function. Based on additional analysis, [Pardo et al. \(2011c\)](#) suggested the threshold for N effects on mycorrhizae are even lower because high background deposition precludes consideration of sites receiving deposition at or near preindustrial levels. The provisional expert judgment was that CLs for mycorrhizal diversity for sensitive ecosystem types are 5 to 10 kg N/ha/yr ([Table 6-24](#)). [Pardo et al. \(2011c\)](#) indicated there is high uncertainty in this estimate because few studies had been conducted at low rates of N deposition. Since the publication of the USDA-FS assessment, there has been one additional study on CLs for mycorrhizae in the U.S. In that study, [Allen et al. \(2016\)](#) estimated an N deposition CL of 10–11 kg N/ha/yr for mycorrhizal biodiversity in southern California CSS ecosystems.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: The range of CLs reported for mycorrhizal fungi is shown for each ecoregion. The hatch marks indicate increasing level of uncertainty: no hatch marks for the most certain "reliable" category, single hatching for the "fairly reliable" category, and double hatching for the "expert judgment" category. The color sequence moves from green toward blue and violet as the CL increases. As the range of the CL gets broader, the saturation of the color decreases. White areas lack data for CL determination for mycorrhizal fungi.

Source: [Pardo et al. \(2011c\)](#).

**Figure 6-5** Map of critical loads for mycorrhizal fungi by ecoregion in the U.S.

**Table 6-24 Mycorrhizal critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Species	Reference
California coastal sage scrub	10–11	Rapid decline in mycorrhizal biodiversity	Arbuscular mycorrhizal fungi	<a href="#">Allen et al. (2016)</a>
Sensitive ecosystem types in the U.S.	5–10	Diversity	Mycorrhizal	<a href="#">Pardo et al. (2011c)</a>
Scots pine forest in Scotland	5–10	Community composition	Ectomycorrhizal fungi	<a href="#">Jarvis et al. (2013)</a>

ha = hectare; kg = kilogram; N = nitrogen; yr = year.

## 6.5.2 Lichens and Bryophytes

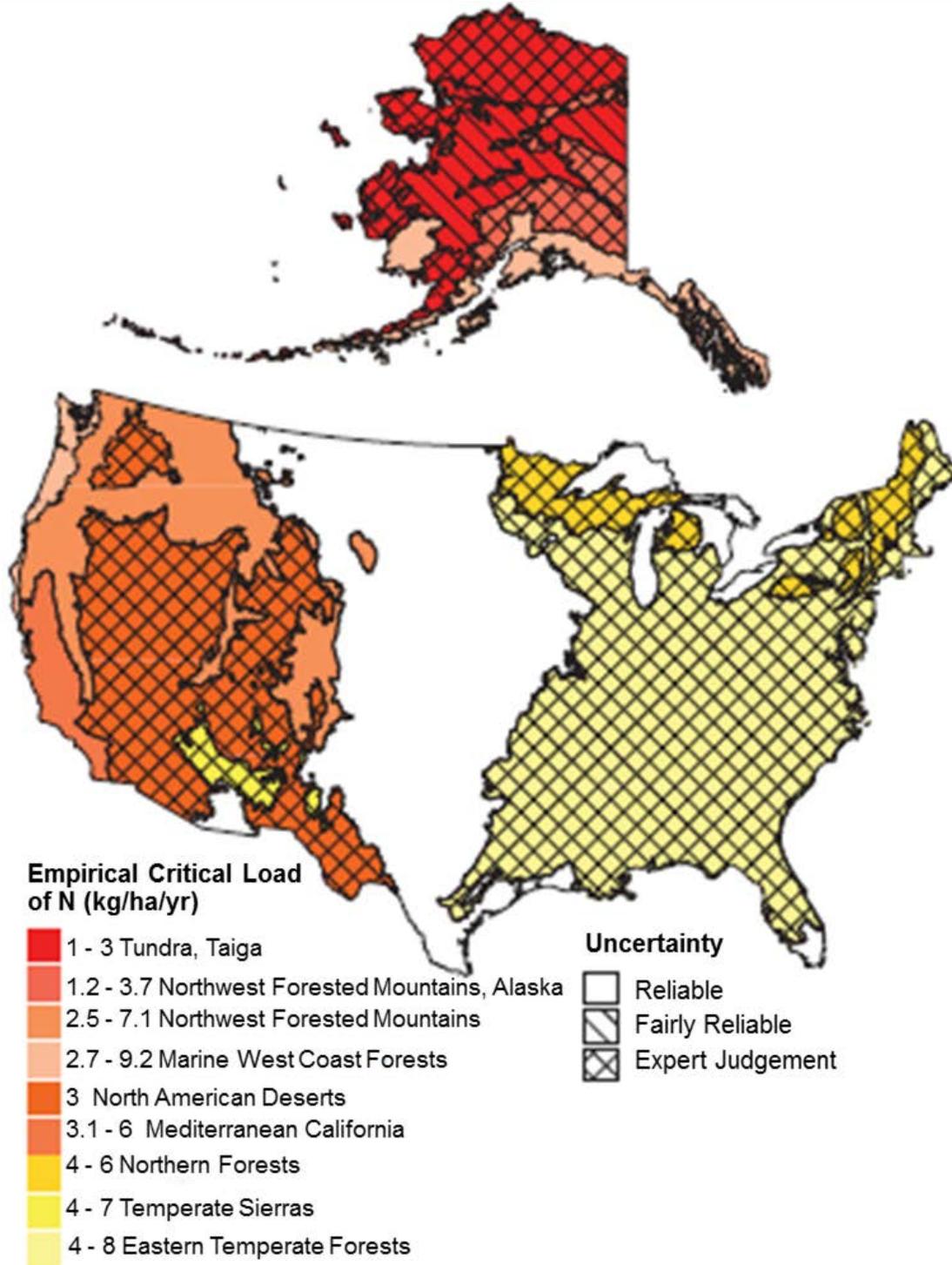
Lichens are symbioses between fungi and algae or cyanobacteria and are important components of plant communities in forests, tundra, and some arid ecosystems. Lichens contribute to ecosystem function by providing food and habitat for wildlife and affecting nutrient and hydrologic cycling. Like mycorrhizae, the growth, physiology, and community composition of lichens is sensitive to atmospheric N deposition ([Table 6-5](#), [Table 6-7](#), and [Table 6-23](#)). The 2008 ISA documented observations that N deposition altered lichen community composition at deposition rates of 3 to 8 kg N/ha/yr ([Fenn et al., 2003a](#)). In the San Bernardino Mountains in southern California, up to 50% of lichen species that occurred in the region in the early 1900s had disappeared by the 1990s ([Fenn et al., 2003a](#); [Nash and Sigal, 1999](#)). The CL has been calculated for lichen communities in mixed conifer forests in California at 3.1 kg N/ha/yr ([Fenn et al., 2008](#)). In the Pacific Northwest, lichen communities have shown evidence of changes in response to increased N pollution, including decreases in the distribution of sensitive lichen taxa and the replacement of these taxa with nitrophilous species ([Geiser and Neitlich, 2007](#)).

Since the 2008 ISA, it has become clear that although simple N deposition CL estimates for changes in lichen community composition can be constructed ([McMurray et al., 2013](#); [Fenn et al., 2008](#)), accounting for the effects of climate and other environmental factors can improve lichen CL estimates ([Blett et al., 2014](#); [Pardo et al., 2011c](#); [Geiser et al., 2010](#)), providing more refined estimates of CL variability and exceedance. As noted in [Appendix 6.2.3.3](#), changes in lichen growth are best correlated with integrated measures

of total N deposition, rather than with the deposition of a single chemical species such as  $\text{HNO}_3$  or  $\text{NH}_4^+$ . Lichen responses to N deposition such as increases in thalli N concentration and shifts in community composition have been most tightly correlated with colocated canopy throughfall measurements of  $\text{N-NO}_3^- + \text{N-NH}_4^+$  ([McMurray et al., 2013](#); [Root et al., 2013](#); [Jovan et al., 2012](#); [Fenn et al., 2007](#)) and ambient N concentrations in fine particulates of  $[\text{NH}_4]_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  ([Root et al., 2015](#); [Geiser et al., 2010](#)).

Lichen community composition and lichen thallus N concentrations shift continuously with all increments of N addition and the response is generally unimodal. In the latter case, the fastest rate of change occurs with the earliest increments of N addition and slows as only tolerant species are left in the community. As N deposition increases, dominance of lichen communities shifts from oligotrophic to eutrophic species (i.e., the number of oligotrophs decrease and the number of eutrophs increase). At very high deposition levels, total biodiversity decreases.

Critical loads for lichen range between 0.26 to 10.2 kg N/ha/yr based on [Pardo et al. \(2011c\)](#) and a number of studies for lichens published since 2008 ([Figure 6-6](#), [Table 6-25](#)). In the USDA-FS CL assessment, [Pardo et al. \(2011c\)](#) documented CLs for lichens of 1 to 9.2 kg N/ha/yr for Level 1 ecoregions. These CLs were predominantly based on the shift in community composition toward eutrophic lichen species and away from oligotrophs. The certainty associated with the lichen CL estimates for each ecoregion varied considerably, in part because of differences in sampling scheme and intensity. There were highly reliable CL estimates in the Pacific Northwest and California, where sampling intensity was high and the linkages between N deposition and lichen community composition have been well documented. Assessments in the eastern U.S. are more problematic due to historical and contemporary S emissions and acidifying deposition. Historical information necessary to identify a “pristine” or “clean” state has been lacking, making it difficult to determine the CL, and the resulting confidence associated with the CL was low.



CL = critical loads; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: The range of critical loads reported for lichens is shown for each ecoregion. The hatch marks indicate increasing level of uncertainty: no hatch marks for the most certain "reliable" category, single hatching for the "fairly reliable" category, and double hatching for the "expert judgment" category. White areas lack data for CL determination for lichens.

Source: [Pardo et al. \(2011c\)](#).

**Figure 6-6** Map of critical loads for lichens by ecoregion in the U.S.

**Table 6-25 Lichen critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Chaparral and oak woodland	5.5	Shift to nitrophyte dominance in the lichen community	California	Epiphytic lichens	<a href="#">Pardo et al. (2011c)</a> <a href="#">Fenn et al. (2010)</a>
Forest	0.26 to 0.33 kg inorganic N/ha/yr and 0.044–0.055 mg/L of ammonium wet deposition	Declines in presence and abundance of sensitive lichen communities	Western Oregon and Washington	Lichens	<a href="#">Glavich and Geiser (2008)</a>
Forest	<4.1	Poorer thallus condition	Wind River Range, WY, including the Class I Bridger Wilderness	Epiphytic lichens	<a href="#">McMurray et al. (2013)</a>
Forest	4–6 for total N deposition	Decreases in lichen species richness and N sensitive species, and poorer thallus condition	Northeastern U.S. Class I areas	Epiphytic lichens	<a href="#">Cleavitt et al. (2015)</a>
Forest	4	Degradation to lichen communities	Northern Rocky Mountains	Epiphytic lichens	<a href="#">McMurray et al. (2015)</a>
Forest	1.54 and 2.51 kg N/ha/yr of through-fall dissolved inorganic N deposition	Lichen communities and lichen N concentration	Pacific Northwest	Epiphytic lichens	<a href="#">Root et al. (2015)</a>
Mixed conifer forests	3.1	Enhanced lichen tissue N concentrations	California	Epiphytic lichens	<a href="#">Fenn et al. (2008)</a> <a href="#">Fenn et al. (2010)</a>
Mixed conifer forests	5.2	Lichen community shifted from acidophyte dominance to neutrophyte dominance	California	Epiphytic lichens	<a href="#">Fenn et al. (2008)</a> <a href="#">Fenn et al. (2010)</a>

**Table 6-25 (Continued): Lichen critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Mixed conifer forests	10.2	Lichen species classified as acidophytes were extirpated	California	Epiphytic lichens	<a href="#">Fenn et al. (2008)</a> <a href="#">Fenn et al. (2010)</a>
Temperate forest	3–9	Sensitive species declines of 20–40%	Western Oregon and Washington	Epiphytic lichens	<a href="#">Geiser et al. (2010)</a>
Various	1–9.2	Lichen health and community composition	U.S. (national)	Epiphytic lichens	<a href="#">Pardo et al. (2011c)</a>

CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

In addition to the USDA-FS assessment by [Pardo et al. \(2011c\)](#), there have been a number of N deposition CL studies for lichens published since 2008, including research in the northeastern U.S. ([Cleavitt et al., 2015](#)), California ([Fenn et al., 2010](#); [Fenn et al., 2008](#)), the Pacific Northwest ([Root et al., 2015](#); [Geiser et al., 2010](#); [Glavich and Geiser, 2008](#)), and the Rocky Mountains ([McMurray et al., 2013](#)). In the northeastern U.S., [Cleavitt et al. \(2015\)](#) studied four Class I areas and found annual mean and cumulative deposition of N were strongly negatively correlated with lichen species richness, the abundance of N sensitive species, and thallus condition. The work by [Cleavitt et al. \(2015\)](#) supported the CL of 4–6 kg N/ha/yr of total N deposition for epiphytic lichens in the Northern Forests Ecoregion created by [Pardo et al. \(2011c\)](#).

Based on sampling in mixed conifer forests in the Sierra Nevada and San Bernardino Mountains in California, [Fenn et al. \(2008\)](#) developed a CL estimate of 3.1 kg N/ha/yr for throughfall N deposition based on increases in thallus N concentration for the lichen *Letharia vulpina*. Above this CL, there were shifts in lichen community composition away from acidophytic lichen species and toward lichen species considered to be neutrophytic and nitrophytic. [Fenn et al. \(2010\)](#) later applied these and other previously published CL values for lichens in California to estimate that 53 and 41% of the chaparral and oak woodland ecosystems in the state received N deposition in excess of the lichen CL of 5.5 kg N/ha/yr.

In the Wind River Range in western Wyoming, [McMurray et al. \(2013\)](#) developed a lichen CL based on study sites adjacent to the Bridger Wilderness, a Class I area downwind of an area experiencing oil and gas production. Above a threshold of 4.0 kg N/ha/yr of throughfall N deposition, [McMurray et al. \(2013\)](#) observed a degradation of lichen communities in this area that included necrotic and bleached thalli and decreased growth.

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### 6.5.3 Herbaceous and Shrub Species

Herbaceous species and shrubs are found in grasslands, shrublands, forests, deserts, and wetlands, and comprise the majority of the roughly 26,600 vascular plant species found in North America north of Mexico ([NRCS, 2009](#)). In forests, herbaceous-layer (understory) vegetation can be important contributors to ecosystem processes such as litter production and N cycling ([Talhelm et al., 2013](#)), and can comprise up to 90% of forest plant biodiversity, including endangered or threatened species ([Gilliam, 2007](#)). As described in [Appendix 6.3.3.2](#), there is abundant evidence that forest understory vegetation composition can be sensitive to N deposition ([Table 6-13](#)).

Critical loads for herbaceous and shrub species range between 0.9 to 33 kg N/ha/yr based on studies published since 2008 ([Table 6-26](#)). In the USDA-FS assessment, [Pardo et al. \(2011c\)](#) reported N deposition CLs of 1 to 33 kg N/ha/yr for herbaceous species and shrubs across all ecoregions ([Figure 6-7](#); [Table 6-26](#)). The lowest CL was for tundra (1–3 kg N/ha/yr), while the highest was for the Mediterranean California ecoregion, specifically a mixed conifer forest ecosystem in the San Bernardino Mountains ([Pardo et al., 2011c](#)).

Among the new research published since the USDA-FS assessment was completed, [Simkin et al. \(2016\)](#) examined the influence of N deposition on species richness of grasses and forbs in over 15,000 plots located across the continental U.S. Notably, they found different relationships between N deposition and species richness in open canopy and closed canopy ecosystems, likely a function of different species loss mechanisms ([Appendix 6.3.2](#)) operating in these systems. In open canopy systems (e.g., grasslands, shrublands, and woodlands), N deposition above an average of 8.7 kg N/ha/yr led to a reduction in species richness (5th–95th percentile: 6.4–11.3 kg N/ha/yr). These rates of N deposition are common across much of the eastern and central U.S., as well as areas in the western U.S. that are downwind of major urban and agricultural areas ([Figure 6-8](#)). Average CLs for grasses and forbs did not differ widely among the grassland, shrubland, and woodland ecosystems (8.9, 8.5, and 8.5 kg N/ha/yr). The calculated CL for closed canopy systems was considerably higher: 13.4 kg N/ha/yr (5th–95th percentile: 6.8–22.2 kg N/ha/yr). At higher levels of N input, processes such as competitive exclusion and soil acidification occur, decreasing species richness. There are two important observations from this analysis. First, increases in N deposition below the CL levels could increase species richness, particularly in open canopy ecosystems. Second, the effects of N deposition on species richness were often pH dependent (see [Appendix 6.3.2](#)). [Simkin et al. \(2016\)](#) also developed more localized CL estimates. In forests, these ranged from a low of 7.9 kg N/ha/yr in open canopy eastern forests to a high of 15.3 kg N/ha/yr in northwestern forested mountains. In the Great Plains region, [Simkin et al. \(2016\)](#) estimated CLs for grasses and forbs of 8.3–9.8 kg N/ha/yr in the open canopy systems to 11.3–19.6 kg N/ha/yr in closed canopy systems. In arid ecosystems, [Simkin et al. \(2016\)](#) estimated a CL of 8.3–9.9 kg N/ha/yr for open canopy ecosystems and 13.5–17 kg N/ha/yr for closed canopy ecosystems.

**Table 6-26 Herbaceous and shrub critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Alpine tundra	3.0	Protection of natural community cover	Rocky Mountain National Park	Alpine grasses and forbs	<a href="#">Bowman et al. (2012)</a>
Alpine and subalpine ground vegetation	1 to 2	ForSAFE-VEG modeled changes in alpine and subalpine plant community (modeled from 1750 to 2500)	Northern and central Rocky Mountains	Alpine and subalpine ground vegetation, including two tree species (Engelmann spruce and white spruce [ <i>Picea engelmannii</i> and <i>Picea glauca</i> ])	<a href="#">Sverdrup et al. (2012)</a>
Desert	2.1 and 3.6	Exponential increase in the probability of biomass (simulated using the DayCent model) exceeding the fire threshold of 1,000 kg/ha	Southern CA Joshua Tree National Park	Creosote bush ( <i>Larrea tridentata</i> ) other shrubs, forbs, and grasses; two tree species included (California juniper and single leaf pinyon [ <i>Juniperus californica</i> and <i>Pinus monophylla</i> ])	<a href="#">Rao et al. (2010)</a>
North American desert	Open: 8.3–9.9 (mean = 9.2, n = 240) Closed: 13.5–17.0 (mean = 16.5, n = 32)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Semiarid coastal sage scrub	<11	Conversion to exotic grasslands	Riverside County, CA	Various	<a href="#">Cox et al. (2014)</a>
Forest	16.8	Plant biodiversity loss as predicted by SMART2	Netherlands	EUNIS classes	<a href="#">de Vries et al. (2010)</a>
Beech and fir/spruce forest	5–11	Plant biodiversity loss predicted by ForSAFE-VEG	Aeshau, Switzerland	Forest understory plants	<a href="#">Belyazid et al. (2011b)</a>

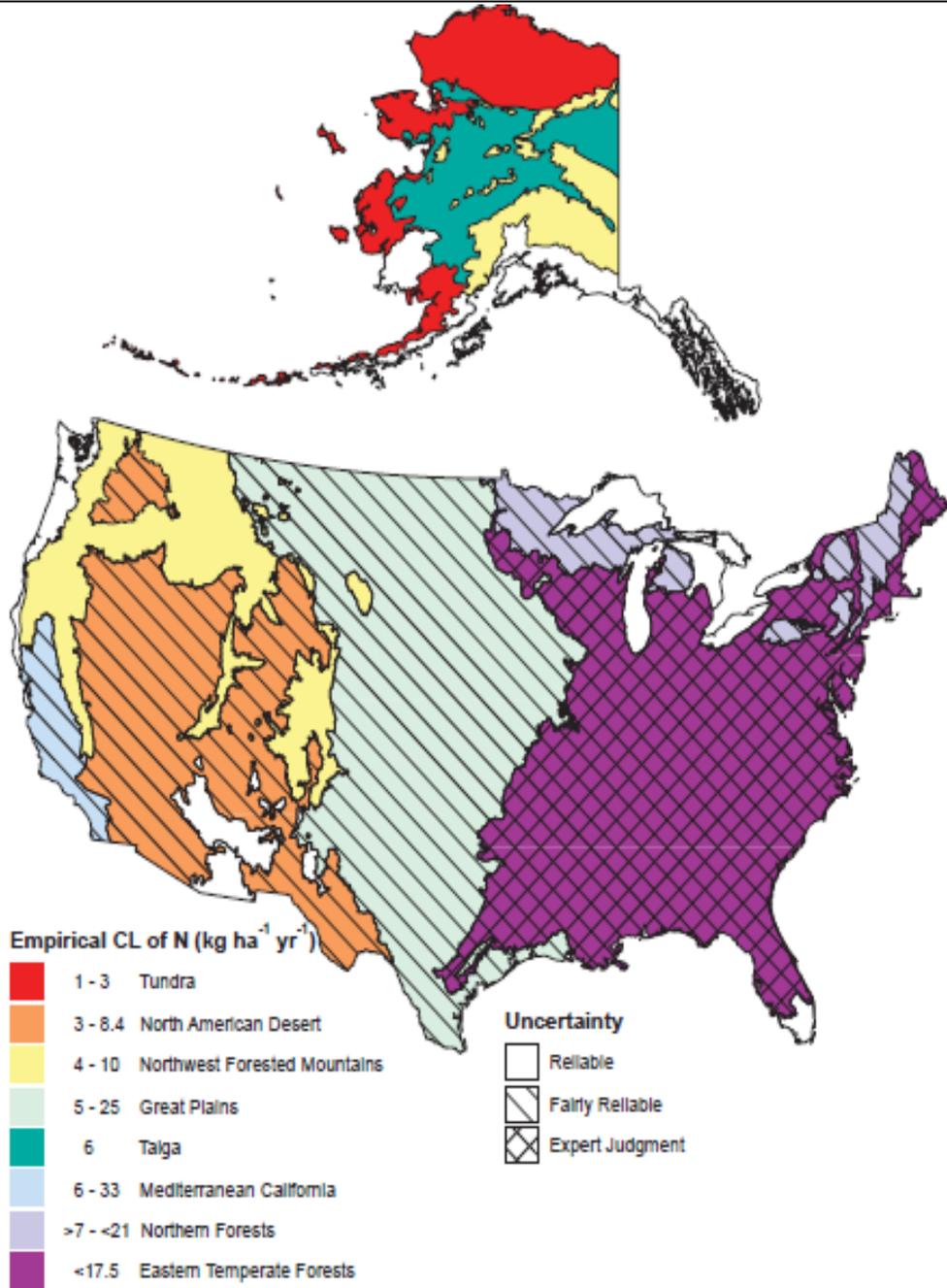
**Table 6-26 (Continued): Herbaceous and shrub critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Boreal forests	0.9–7.8	Plant biodiversity loss predicted by ForSAFE-VEG	Sweden	Forest understory plants	<a href="#">de Vries et al. (2010)</a>
Subalpine vegetation	1.9–3.5	ForSAFE-VEG modeled changes in subalpine plant community between 2010 and 2100	Rocky Mountain National Park	Subalpine plant community, consisting primarily of forest understory plants and one additional tree species (subalpine fir [ <i>Abies lasiocarpa</i> ])	<a href="#">McDonnell et al. (2014a)</a>
Pine forest	4–6	Plant biodiversity loss predicted by ForSAFE-VEG	Söstared, Sweden	Forest understory plants	<a href="#">Belyazid et al. (2011b)</a>
Spruce forest	10–16	Plant biodiversity loss predicted by ForSAFE-VEG	Bachtel, Switzerland	Forest understory plants	<a href="#">Belyazid et al. (2011b)</a>
Spruce forest	1–2	Plant biodiversity loss predicted by ForSAFE-VEG	Högbränna, Sweden	Forest understory plants	<a href="#">Belyazid et al. (2011b)</a>
Eastern temperate forests	Open: 6.6–9.7 (mean = 7.9, n = 947) Closed: 7.8–19.3 (mean = 12.5, n = 7,378)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Marine West Coast forests	Open: no data Closed: 10.4–15.0 (mean = 12.8, n = 24)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Northern forests	Open: 8.0–9.8 (mean = 8.9, n = 75) Closed: 8.0–18.9 (mean = 13.8, n = 1,955)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>

**Table 6-26 (Continued): Herbaceous and shrub critical loads.**

Type of Ecosystem	Critical Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Northwestern forested mountains	Open: 8.0–10.2 (mean = 9.1, n = 1,429)  Closed: 10.8–19.6 (mean = 15.3, n = 2,113)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Temperate sierras	Open: 8.6–8.7 (mean = 8.65, n = 3)  Closed: 14.8–14.8 (mean = 14.8, n = 42)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Dry and neutral grasslands	8.0	Plant biodiversity loss as predicted by SMART2	Netherlands	Dry and neutral grasslands	<a href="#">de Vries et al. (2010)</a>
Semidry calcareous grasslands	12.4	Plant biodiversity loss as predicted by SMART2	Netherlands	Semidry calcareous grasslands	<a href="#">de Vries et al. (2010)</a>
Moist and wet oligotrophic grasslands	12.6	Plant biodiversity loss as predicted by SMART2	Netherlands	Moist and wet oligotrophic grasslands	<a href="#">de Vries et al. (2010)</a>
Great Plains	Open: 8.3–9.8 (mean = 9.3, n = 618)  Closed: 11.3–19.6 (mean = 16.6, n = 274)	Decreasing species richness grasses and forbs	Ecoregion	Various	<a href="#">Simkin et al. (2016)</a>
Various	1–33	Change in plant community composition; other various effects	U.S. (national)	Various	<a href="#">Pardo et al. (2011c)</a>

EUNIS = European Nature Information System; ForSAFE-VEG = a dynamic forest ecosystem model; ha = hectare; kg = kilogram; N = nitrogen; SMART2 = a simple soil acidification and nutrient-cycling model; yr = year.

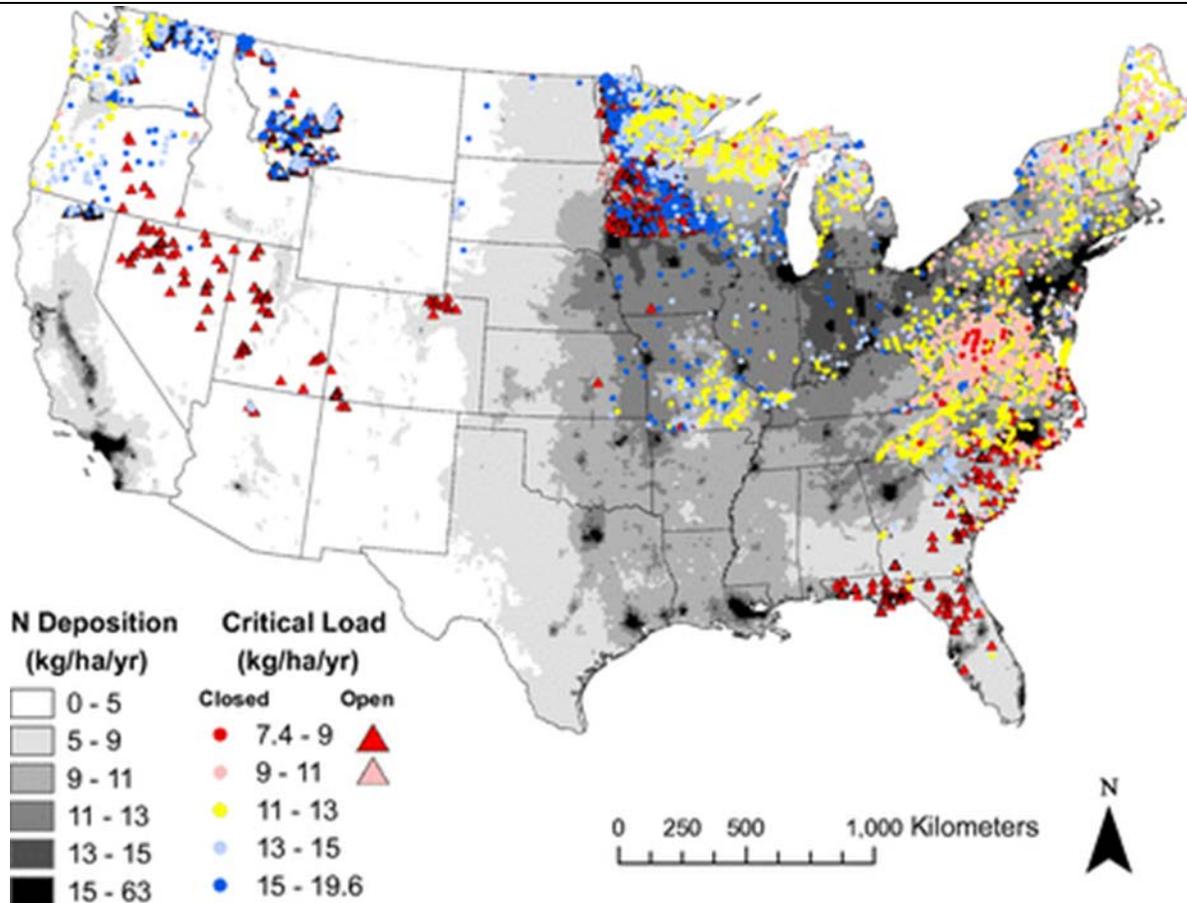


CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: The range of CLs reported for herbaceous plants and shrubs is shown for each ecoregion. The hatch marks indicate increasing level of uncertainty: no hatch marks for the most certain "reliable" category, single hatching for the "fairly reliable" category, and double hatching for the "expert judgment" category. White areas lack data for CL determination for herbaceous species and shrubs.

Source: [Pardo et al. \(2011c\)](#).

**Figure 6-7** Map of critical loads for herbaceous plants and shrubs by ecoregion in the U.S.



ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: The 3,317 open sites (combined grassland, shrubland, and woodland vegetation types) are portrayed with triangles, and the 11,819 closed canopy sites (deciduous, evergreen, and mixed forests) are portrayed with circles. Background deposition values are the average of 27 years of wet deposition (NADP 1985–2011) plus the average of 10 years of dry deposition (from Community Multiscale Air Quality model, 2002–2011). Other variation in CLs is due to the other predictor variables (soil pH, temperature, and precipitation).

Source: [Simkin et al. \(2016\)](#).

**Figure 6-8 Nitrogen deposition (gray scale) and critical loads for nitrogen deposition based on total graminoid plus forb species richness (colored symbols).**

Within the Colorado Rocky Mountains, there were several efforts to develop CLs based on both empirical and modeled data. In the Rocky Mountain National Park, [Bowman et al. \(2012\)](#) calculated an empirical CL of 3 kg N/ha/yr to protect natural community cover based on large increases in the abundance of the sedge *Carex rupestris* to additional N deposition. [McDonnell et al. \(2014a\)](#) applied the ForSAFE-VEG model to develop a long-term CL estimate aimed at avoiding future (2010–2100) changes (of more than 10%) in subalpine plant biodiversity in Rocky Mountain National Park. The estimated

CL to protect future plant diversity was 1.9–3.5 kg N/ha/yr, a value already exceeded in the study area. [Sverdrup et al. \(2012\)](#) also used the ForSAFE-VEG model to understand how long-term CLs would be influenced by climate change, but worked from a synthetic alpine and subalpine vegetation data set developed from observations at national parks in the northern and central Rocky Mountains region of the U.S. They determined CL values of 1 to 2 kg N/ha/yr to protect against a future change in plant diversity of 5–20%.

Notably, CLs protecting against future biodiversity changes may not be comparable directly to other CLs protective against current changes to herbaceous and shrub biodiversity ([Table 6-26](#)). Critical loads are expressed on an annual basis, and CLs protective of future biodiversity may be lower generally than shorter-term CLs to avoid the accumulating effects of deposition over longer periods of time. Consideration of future temperature increases, among other factors, however, may complicate this relationship. In their simulations, [McDonnell et al. \(2014a\)](#) concluded that where the CL was between 1.9 and 3.5 kg N/ha/yr depended upon future temperatures. Higher simulated temperatures resulted in CL values higher in the range, closer to 3.5 kg N/ha/yr. They attributed this to the increased N uptake of the vegetation with higher temperatures, allowing an increase in deposition while protecting against shifts in plant diversity. Thus, among other factors, comparison of CLs protecting against future versus current changes likely requires a consideration of the underlying assumptions about future conditions.

In addition to the CL estimates for plant species richness ([Simkin et al., 2016](#)), two other CL estimates have been developed for arid and semiarid ecosystems. [Pardo et al. \(2011c\)](#) determined a CL of 3–8.4 kg N/ha/yr for North American deserts based on a decrease in native forbs. [Rao et al. \(2010\)](#) developed unique CL estimates for the rate of N deposition that would increase the probability of vegetation productivity in two arid ecosystems within Joshua Tree National Park in southern California exceeding a wildfire risk threshold. To do this, [Rao et al. \(2010\)](#) applied the DayCent model. The risk of exceeding the wildfire risk threshold of 1,000 kg of biomass/ha increased rapidly above CLs of 2.1 and 3.6 kg N/ha/yr for the two ecosystem types. The risk of exceeding the threshold increased until N deposition levels reached 5.5 and 8.8 kg N/ha/yr for the two ecosystem types. Notably, contemporary rates of N deposition at the study sites were 3 to 8 kg N/ha/yr, and up to 16 kg N/ha/yr has been observed in areas adjacent to these desert ecosystems and downwind from or near urban areas ([Fenn et al., 2010](#)). In southern California, [Cox et al. \(2014\)](#) modeled the influence of environmental factors such as climate, land use, and N deposition on the conversion of CSS ecosystems to exotic annual grasslands from 1930 to 2009. Here, conversion of CSS to exotic grasslands was more likely to occur if N deposition exceeded 11 kg N/ha/yr. This CL estimate was similar to a CL of 10 kg N/ha/yr for CSS developed by [Pardo et al. \(2011c\)](#).

## 6.5.4 Trees

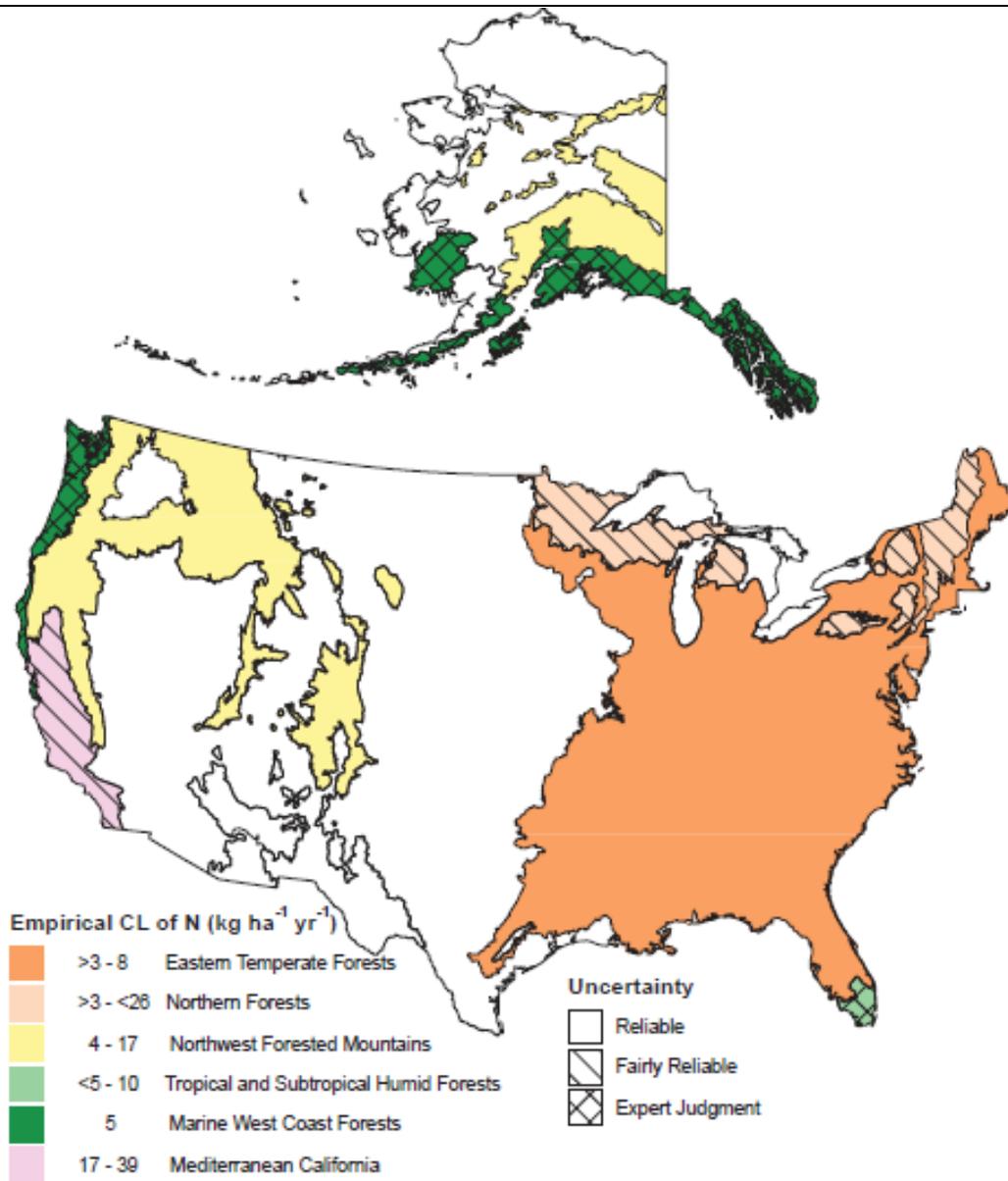
As noted in [Appendix 6.3.3.1](#), there are relatively few direct observations of overstory tree community composition change, likely because it is difficult to observe changes for long-lived organisms in slowly developing communities. However, there is more abundant evidence of changes in tree growth, mortality, and physiology ([Appendix 6.2.3.1](#)). Notably, CLs for trees due to N + S deposition are presented in [Appendix 5](#).

Nitrogen CLs for trees range between >3 to 39 kg N/ha/yr based on studies compiled in [Pardo et al. \(2011c\)](#) and one other study published since 2008 ([Table 6-27](#)). In the USDA-FS assessment, [Pardo et al. \(2011c\)](#) reported that N CLs for forest ecosystems ranged from >3 to 39 kg N/ha/yr ([Figure 6-9](#)). Estimates of 3–26 kg N/ha/yr for declining forest growth and increased mortality were based on the forest inventory data analysis conducted by [Thomas et al. \(2010\)](#) and a chronic N addition experiment conducted in red spruce forests in the northeastern U.S. ([McNulty et al., 2005](#)). In California mixed conifers, [Pardo et al. \(2011c\)](#) reported a CL of 17 kg N/ha/yr for decreased fine root biomass and 39 kg N/ha/yr for forest sustainability, both developed from observations reported by [Fenn et al. \(2008\)](#). In one additional study subsequent to the USDA-FS assessment, [Fleischer et al. \(2013\)](#) reported that greater rates of N deposition increased canopy photosynthetic capacity in evergreen needleleaf forests below a CL threshold of 8 kg N/ha/yr.

**Table 6-27 Tree critical loads.**

Type of Ecosystem	Critical Load kg N/ha/yr	Biological and Chemical Effects	Study Site	Study Species	Reference
Evergreen forest	~8	Saturation of photosynthetic capacity of the canopy	32 forest sites around the globe	Conifer	<a href="#">Fleischer et al. (2013)</a>
Various forests	>3–39	Tree growth and survival; other various effects	U.S. (national)	Various	<a href="#">Pardo et al. (2011c)</a>

ha = hectare; kg = kilogram; N = nitrogen; yr = year.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: The range of CLs reported for forest ecosystems is shown for each ecoregion; this map does not include the responses of mycorrhizal fungi, lichens, or understory herbaceous plants already represented. The hatch marks indicate increasing level of uncertainty: no hatch marks for the most certain "reliable" category, single hatching for the "fairly reliable" category, and double hatching for the "expert judgment" category. White areas lack data for CL determination for forest ecosystems.

Source: [Pardo et al. \(2011c\)](#).

**Figure 6-9** Map of critical loads for forest ecosystems by ecoregion in the U.S.

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## 6.5.5 Critical Loads Exceedance Studies

In the USDA-FS assessment of N deposition CLs, [Pardo et al. \(2011c\)](#) evaluated the CL exceedances for mycorrhizal fungi, lichens and bryophytes, herbaceous plants and shrubs, and forests using N deposition estimates produced by the Community Multiscale Air Quality (CMAQ) model v.4.3. This CMAQ model used data reported in 2001 for the simulations of wet plus dry N deposition. [Pardo et al. \(2011c\)](#) concluded that large parts of the eastern U.S., as well as localized areas in the West, experience rates of N deposition that exceed the CL for sensitive ecosystem components. In this assessment, [Pardo et al. \(2011c\)](#) determined that the resources most threatened by elevated N deposition included freshwater diatoms, lichens, bryophytes, and herbaceous plants.

In addition to [Pardo et al. \(2011c\)](#), several studies have quantified N deposition CL exceedance at the regional scale for herbaceous plants. In the [Simkin et al. \(2016\)](#) analysis of herbaceous species richness in over 15,000 plots over the continental U.S., approximately 41% of grassland plots were experiencing N deposition in exceedance of the CL for plant species richness. [Clark et al. \(2013\)](#) used 26 years (1985–2010) of N deposition data with ecosystem-specific functional responses from local field experiments and a national CLs database to generate estimates of herbaceous species loss. In scenarios using the low end of the CL range, N deposition exceeded CLs over 0.38, 6.5, 13.1, 88.6, and 222.1 million ha for the Mediterranean California, North American Desert, Northwestern Forested Mountains, Great Plains, and Eastern Forests ecoregions, respectively, with corresponding species losses ranging from <1 to 30%. When scenarios assumed less sensitivity (using a common CL of 10 kg N/ha/yr, and the high end of the CL range) minimal losses were estimated. The large range in projected impacts among scenarios highlights the uncertainty in current CLs estimates for plant diversity in the U.S.

[McLauchlan et al. \(2014\)](#) analyzed a 27-year record of ecophysiological, community, and ecosystem metrics for an annually burned Kansas tallgrass prairie. Despite observed rates of atmospheric N deposition (7 kg N/ha/yr from 2002 to 2009) that exceed the minimum estimated CL for herbaceous plants in tallgrass prairie of the Great Plains of North America [5–15 kg N/ha/yr; [Pardo et al. \(2011c\)](#)], there were no observations of plant community composition change or effects on plant physiology that signaled an obvious influence of N deposition: plant N concentrations and plant N availability did not increase, aboveground NPP was unchanged, forb diversity did not decline, and the relative abundance of dominant grasses did not shift toward more eutrophic species. Thus, current rates of N deposition do not appear to be altering ecosystem function in this grassland, even though these rates exceed minimum CLs. The authors offered a couple of potential explanations for this lack of response, including sequestration of the additional

N into soil organic matter pools and offsetting removal of N by biomass burning and/or grazing.

Finally, [Clark et al. \(2018\)](#) estimated CL exceedance areas for the conterminous U.S. over a more than 200 year period. In this study, they examined six CL types, with three N CLs germane to terrestrial ecosystems: (1) changes in forest tree health, (2) changes in lichen communities, and (3) changes in herbaceous and shrub plant community composition. Overall, this analysis showed terrestrial N CLs have been exceeded for many decades in areas across the U.S. Minimum values for these CLs were already exceeded by 1855 for the first two CLs, and the latter CL was exceeded between 1935 and 1955. Exceedance areas peaked in 1995 for changes in lichen communities and plant community composition at 3.47 and 2.87 million km<sup>2</sup>, respectively, before declining marginally by 2006. The minimum forest tree health CL was exceeded in 2.41 million km<sup>2</sup> by 1855 and did not change much over time, primarily because the relatively low CL compared to deposition values in the Eastern Temperate and Northern Forests ecoregions.

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## 6.6 Summary

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### 6.6.1 Physiology, Growth, and Productivity Summary

At the time of the 2008 ISA, there was evidence sufficient to infer a causal relationship between N deposition and the alteration of the biogeochemical cycling of C in terrestrial ecosystems. This evidence included observations that added N increased plant productivity across a broad range of terrestrial ecosystems. The 2008 ISA, however, made no explicit statement regarding the effects of N deposition on physiology, growth, and productivity.

Since the 2008 ISA, a more complete understanding of how N deposition effects terrestrial organisms and ecosystems has been developed, the effects of N deposition in terrestrial ecosystems in North America and Europe have been more widely documented, and a significant new body of research has observed N deposition impacts in Asia (particularly China). These efforts have provided further evidence that added N alters plant physiological processes, stimulates the growth of most plants, and broadly increases productivity ([Liu and Greaver, 2010](#); [LeBauer and Treseder, 2008](#); [Xia and Wan, 2008](#)). Moreover, studies have shown species-specific effects of N deposition on tree growth and mortality ([Horn et al., 2018](#); [Dietze and Moorcroft, 2011](#); [Thomas et al., 2010](#)). There is also widespread evidence that N additions affect soil microbial physiology and biomass (see [Appendix 4](#) for soil extracellular enzyme responses), particularly by decreasing the abundance of symbiotic mycorrhizal fungi ([Li et al., 2015](#); [Treseder, 2008](#)). There have also been numerous observations that additional N can alter arthropod performance and abundance among both detritivores and herbivores [[Throop and Lerdau \(2004\)](#); [Table 6-17](#)]. Thus, it is apparent that plants, microorganisms, and ecosystem-scale productivity are sensitive to N availability. **This body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems.**

Although plants are broadly sensitive to added N, it is clear that the effects of N on plant growth and productivity vary considerably among plant tissues ([Li et al., 2015](#); [Xia and Wan, 2008](#)), individual species and functional types ([Xia and Wan, 2008](#)), and biomes ([LeBauer and Treseder, 2008](#)). In a meta-analysis of 1,600 observations, short-lived plant functional types tended to have stronger relative responses than long-lived plants; herbaceous plants responded more than woody plants, and annual herbs responded more than perennial herbs [[Xia and Wan \(2008\)](#); [Figure 6-1](#)]. Shrubs were notably less

responsive than trees ([Figure 6-1](#)), potentially because of the prevalence of shrubs in more arid environments; overall, biomass responses increased linearly with mean annual precipitation ([Xia and Wan, 2008](#)). There is also now more consistent and widespread evidence that N additions increase aboveground biomass more than belowground biomass, raising the shoot:root ratio among plants ([Li et al., 2015](#); [Lu et al., 2011b](#)).

The increase in aboveground growth of individual plant species is the best documented response of plants to N, with fewer studies documenting belowground growth responses and more complex physiological and ecosystem-scale responses (e.g., [Figure 6-1](#) and [Figure 6-2](#)). [LeBauer and Treseder \(2008\)](#) found that N additions stimulated aboveground productivity, but the relative stimulation was smaller than the response of individual plants identified by [Xia and Wan \(2008\)](#). Belowground net primary productivity responses to added N have not yet been synthesized because of lack of data ([LeBauer and Treseder, 2008](#)). [Liu and Greaver \(2009\)](#) did not find a significant effect on net ecosystem exchange, but forest ecosystem C content was increased by 6%.

In the 2008 ISA, the increase in plant growth and terrestrial productivity was attributed to increases in foliar N content and related increases in photosynthesis. As noted earlier, increases in plant N concentrations are widespread ([Koricheva et al., 1998](#)), particularly in the foliage. [Koricheva et al. \(1998\)](#) had previously quantified increases in foliar N concentrations among woody plants; [Xia and Wan \(2008\)](#) expanded this analysis to other plant functional groups, with an overall stimulation of +28.5%. Aside from smaller responses among legumes and broader functional groups containing legumes, there was a relatively narrow range of responses across functional groups (+24–34%). Root N concentrations show similar responses ([Li et al., 2015](#); [Xia and Wan, 2008](#)). Given the mechanistic and empirical relationships between greater foliar N concentrations, higher leaf concentrations of the C assimilating enzyme RuBisCo ([Evans, 1989](#)), and greater maximum rates of leaf-level photosynthesis in vascular plants ([Wright et al., 2004](#)), the increases in foliar N observed with greater N supply have been linked to higher rates of leaf-level photosynthesis [e.g., [Teskey et al. \(1994\)](#)]. Alternately, there was evidence in the 2008 ISA that much of the additional foliar N could be physiologically inactive ([Bauer et al., 2004](#)), consistent with the significant increase in free amino acids observed by [Koricheva et al. \(1998\)](#). Increases in photosynthesis following N additions have been observed across a variety of plant functional types, but higher rates of photosynthesis have not been universally observed in long-term experiments [e.g., [Gulmon and Chu \(1981\)](#); [Lajtha and Whitford \(1989\)](#); [Newman et al. \(2003\)](#); [Chen et al. \(2005b\)](#); [Elvir et al. \(2006\)](#); [Talhelm et al. \(2011\)](#)] and there have not been any broad syntheses or meta-analyses of either leaf-level photosynthesis or gross primary productivity. There is a similar mechanistic and empirical relationship between tissue N concentrations and respiration rates, but this relationship has shifted in long-term N addition studies,

providing further evidence that much of the additional tissue N is physiologically inactive [e.g., [Drake et al. \(2008\)](#); [Burton et al. \(2012\)](#)].

Decreases in the quantity of C allocated belowground to roots, mycorrhizae, and root exudation could provide a mechanism that increases aboveground plant growth in plants and ecosystems that do not show gains in photosynthesis [e.g., [Talhelm et al. \(2011\)](#)]. Plants provide mycorrhizal fungal symbionts with C in exchange for nutrients, and the abundance of mycorrhizal fungi and the rates at which these fungi colonize roots declines when N is added to terrestrial ecosystems ([Treseder, 2004](#)), a finding that has since been corroborated ([Li et al., 2015](#); [Treseder, 2008](#)). The decrease is particularly well documented for ectomycorrhizal fungi ([Table 6-2](#)), but can also occur with arbuscular mycorrhizal fungi [[van Diepen et al. \(2010\)](#); [Table 6-3](#)].

Nitrogen deposition can affect the physiology and abundance of soil microorganisms through decreases in soil pH, increases in inorganic N availability, changes in soil food webs, and shifts in the quantity and quality of available C ([Xia et al., 2015](#); [Manning et al., 2008](#); [Treseder, 2008](#); [Koricheva et al., 1998](#)). There were some observations in the 2008 ISA that added N decreased microbial biomass. There is now more abundant evidence that N deposition can affect microbial communities. In meta-analyses, N additions have been shown to decrease microbial biomass ([Treseder, 2008](#)), microbial biomass C ([Liu and Greaver, 2010](#)), and microbial biomass N ([Lu et al., 2011b](#)). In a meta-analysis, [Treseder \(2008\)](#) found that the negative effects of added N on microbial biomass increased in magnitude with the duration of the N additions and the cumulative amount of added N. Notably, these observations of soil microbial biomass would include the hyphal biomass of mycorrhizal fungi. There are fewer observations of N addition effects at the level of individual microbial domains (e.g., bacteria, fungi), functional groups (e.g., saprotrophic vs. mycorrhizal fungi), or other higher level taxonomic groups, and aside from the aforementioned decreases in mycorrhizal fungi, effects at these scales appear to be less consistent ([Table 6-4](#)).

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## 6.6.2 Biodiversity Summary

The 2008 ISA found evidence sufficient to infer a causal relationship between deposition and the alteration of species richness, species composition, and biodiversity in terrestrial ecosystems. Since 2008, there is now more widespread documentation of decreases in lichen species richness as the result of N deposition in the U.S. [e.g., [Jovan \(2008\)](#); [Geiser et al. \(2010\)](#)], and there are now direct observations that: (1) N deposition in the U.S. is altering herbaceous plant species richness across a broad range of ecosystems, including forests, grasslands, arid and semiarid ecosystems, and alpine tundra

[e.g., [Simkin et al. \(2016\)](#)], and (2) N deposition in the U.S. is changing mycorrhizal community composition [e.g., [Lilleskov et al. \(2008\)](#); [Allen et al. \(2016\)](#)]. Further, based on changes in mortality and growth rates of overstory tree species, there is also now indirect evidence that N deposition is altering overstory tree community composition [e.g., [Thomas et al. \(2010\)](#); [Dietze and Moorcroft \(2011\)](#); [Horn et al. \(2018\)](#)]. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems.**

In forests, research since 2008 has provided evidence of altered understory plant, soil microbial, arbuscular and ectomycorrhizal, and arthropod communities. Three new assessments using forest inventory plots from the eastern U.S. have observed effects on growth and mortality that likely impact forest overstory tree composition [e.g., [Thomas et al. \(2010\)](#); [Dietze and Moorcroft \(2011\)](#); [Horn et al. \(2018\)](#)]. However, these data sets and analyses have not directly been applied to assess changes in forest overstory composition either in North America or Europe. Evidence for altered forest understory plant communities (also known as herbaceous layer or groundcover vegetation) come from both the 2008 ISA and the literature published since 2008. [Gilliam \(2006\)](#) reviewed nine studies on the effects of N deposition on forest understory plant communities in North America and Europe, including two European studies that documented shifts in understory plant community composition along N deposition gradients ([Strengbom et al., 2001](#); [Brunet et al., 1998](#)). In a new analysis of understory plant community composition, [Simkin et al. \(2016\)](#) observed that N deposition increased herbaceous plant species richness where soil pH was neutral or basic, but that N deposition above 11.6 kg N/ha/yr decreased herbaceous species richness on acidic soils. Similar studies of plant community composition have been conducted across N deposition gradients in Europe, with both [Verheyen et al. \(2012\)](#) and [Dirnböck et al. \(2014\)](#) finding shifts in plant community composition toward more nutrient-demanding and shade-tolerant plant species, but no loss of species richness. For soil microbial communities, [Zechmeister-Boltenstern et al. \(2011\)](#) observed shifts in soil microbial community composition along an N deposition gradient in Europe and multiple N addition studies identified since 2008 have observed changes in microbial community composition [e.g., [van Diepen et al. \(2010\)](#); [Hobbie et al. \(2012\)](#); [Zhao et al. \(2014a\)](#)]. Among studies of how N affects forest ectomycorrhizal community composition, there were changes in six out of seven studies identified ([Table 6-15](#)). This included four studies where shifts in community composition could be directly or indirectly linked to N deposition gradients in the U.S. or Europe.

Since 2008, new studies have quantified the impact of N additions on species richness, species diversity, and community composition among vascular plants, bryophytes, lichens, and soil microorganisms in alpine and Arctic tundra ecosystems in North

America, Europe, and Asia. Within the U.S., several N addition studies have documented changes in plant community composition, including experiments in Colorado ([Farrer et al., 2015](#); [Bowman et al., 2012](#)) and Washington ([Bishop et al., 2010](#)). In the North Atlantic region of Europe, [Armitage et al. \(2014\)](#) observed shifts in community composition and decreases in plant species richness among alpine heathlands located along an N deposition gradient. Similarly, [Southon et al. \(2013\)](#) found decreasing vascular plant species richness with increasing N deposition in heathlands in the U.K. [Arens et al. \(2008\)](#) did not observe changes in community composition as a result of N additions in Greenland, but shifts in plant community composition were observed in longer (7 to 8 years) experiments in tundra ecosystems in China ([Song and Yu, 2015](#)), Switzerland ([Bassin et al., 2013](#)), and Sweden ([Wardle et al., 2013](#)). Shifts in microbial community composition were observed in several N addition experiments, including in the U.S. in Colorado ([Farrer et al., 2013](#); [Nemergut et al., 2008](#)).

New research on lichens has added further evidence that lichen communities in the U.S. and Europe are sensitive to current levels of atmospheric N deposition. Shifts in lichen community composition attributable to atmospheric N pollution have been observed in forests throughout the West Coast ([Jovan et al., 2012](#); [Geiser et al., 2010](#); [Jovan, 2008](#)), in the Rocky Mountains ([McMurray et al., 2015](#); [Rogers et al., 2009](#)), and in southeastern Alaska ([Schirokauer et al., 2014b](#)). Outside of the U.S., changes in lichen community composition have been observed with increased atmospheric NO<sub>2</sub> concentrations in Nova Scotia, Canada ([Gibson et al., 2013](#)) and experimental N additions in Sweden ([Johansson et al., 2012](#)).

Since 2008, there have been direct observations of reduced species richness along atmospheric N deposition gradients for grasslands in the U.S. ([Simkin et al., 2016](#)) and in Europe ([Pannek et al., 2015](#); [Field et al., 2014](#); [Gaudnik et al., 2011](#); [Stevens et al., 2011a](#); [Stevens et al., 2011b](#); [Dupre et al., 2010](#); [Stevens et al., 2010b](#); [Stevens et al., 2010a](#)). Studies in both the U.S. and in Europe have found that the effects of N deposition on grassland communities are often dependent on soil pH [e.g., [Stevens et al. \(2010b\)](#); [Stevens et al. \(2011a\)](#); [Maskell et al. \(2010\)](#); [Simkin et al. \(2016\)](#)]. Information about changes in mycorrhizal communities in grasslands was limited and provided mixed results ([Chen et al., 2014](#)); while of the five studies identified investigating compositional changes to soil microbial communities in grasslands, four observed shifts in composition ([Table 6-20](#)).

Research since 2008 from N deposition gradient studies and N addition experiments in U.S. arid and semiarid regions has been dominated by research from southern California, which has provided evidence that higher N availability alters plant community composition through an increase in invasive annual plants ([Cox et al., 2014](#); [Allen et al.,](#)

[2009](#); [Rao et al., 2009](#)). Many of these studies documented changes in plant community composition, with fewer observations of plant species loss. Evidence for shifts in plant community composition is particularly strong for CSS and chaparral ecosystems near the southern California coast and in areas of the Mojave Desert downwind of major southern California population centers. An important effect of N deposition in arid ecosystems is an increase in N availability in the interspaces between shrubs, allowing the growth of annual grasses and forbs, which can grow and reproduce during the brief seasonal periods with adequate moisture availability ([Brooks, 2003](#)). This phenomenon provides a more continuous fuel bed for wildfires, increasing fire frequency and shifting plant community composition away from species that are not fire-adapted ([Padgett and Allen, 1999](#); [Allen et al., 1998](#)). Relative to plants, there are fewer studies of N effects on microbial biodiversity in arid and semiarid ecosystems, with these studies showing mixed results ([Table 6-22](#)).

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### 6.6.3 Critical Loads Summary

The 2008 ISA documented efforts to develop CLs in the U.S. However, the CLs for terrestrial ecosystems available in 2008 were for a subset of western ecosystems. There were no published assessments of N deposition CLs spanning ecosystems across the U.S. Since the 2008 ISA, there has been substantial work on CLs for N for U.S. ecoregions. A large body of work has been published on CLs for N since the 2008 ISA. Notably, the USDA-FS published *Assessment of Nitrogen Deposition Effects and Empirical Critical Loads* ([Pardo et al., 2011c](#)), which reports CLs for various biological and biogeochemical endpoints in terrestrial ecoregions (Omernick Level 1) in the U.S.

Most of the published CLs included in the [Pardo et al. \(2011c\)](#) assessment or published subsequently have covered lichens, mycorrhizae, and herbaceous and understory plant species. There are still relatively few observations of CLs for overstory tree species. There do not appear to have been any CLs published for birds, mammals, or arthropods in terrestrial ecosystems. In general, CLs were higher in regions that experienced greater rates of ambient N deposition. In part, these higher critical loads may represent previous ecological change caused by historical N deposition. This pattern would explain why the empirical CL is often above ambient deposition even as that deposition increases in the same ecosystem type across a region ([Pardo et al., 2011c](#)). The CLs published since the publication of the USDA-FS assessment by [Pardo et al. \(2011c\)](#) often fall into the range of CLs identified by [Pardo et al. \(2011c\)](#), particularly if these CLs assess similar ecological endpoints. The new information is presented in tandem with the CLs by [Pardo et al. \(2011c\)](#) in [Table 6-28](#). Notably, the CLs reported for [Pardo et al. \(2011c\)](#) are a

range for the entire Level 1 ecoregion, whereas the new CL estimates are either for the entire ecoregion or specific ecosystems within each respective ecoregion.

**Table 6-28 Critical loads for nitrogen by [Pardo et al. \(2011c\)](#) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	<a href="#">Pardo et al. (2011c)</a>		New Critical Load Information				Reference
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	
<i>Mycorrhizal fungi</i>							
Mediterranean California	7.8	9.2	10–11	California coastal sage scrub	Rapid decline in mycorrhizal biodiversity	Arbuscular mycorrhizal fungi	<a href="#">Allen et al. (2016)</a>
North American deserts	n/a	n/a	n/a				
Southern semiarid highlands	n/a	n/a	n/a				
Eastern temperate forests	5	12	n/a				
Marine West Coast forests	5	n/a	n/a				
Northern forests	5	7	n/a				
Northwest forested mountains	5	10	n/a				
Temperate sierras	n/a	n/a	n/a				
Great Plains	12	n/a	n/a				
<i>Lichens</i>							
Mediterranean California	3.1	6	n/a				

**Table 6-28 (Continued): Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	<a href="#">Pardo et al. (2011c)</a>		New Critical Load Information				
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	Reference
North American deserts	3	n/a	n/a				
Southern semiarid highlands	n/a	n/a	n/a				
Eastern temperate forests	4	8	n/a				
Marine West Coast forests	2.7	9.2	1.54 and 2.51	Pacific Northwest	Lichen communities and lichen N concentration	Epiphytic lichens	<a href="#">Root et al. (2015)</a>
			4	Northern Rocky Mountains	Degradation to lichen communities	Epiphytic lichens	<a href="#">McMurray et al. (2015)</a>
Northern forests	4	6	4–6	Northeastern U.S. Class I areas	Decreases in species richness and N sensitive species, and poorer thallus condition	Epiphytic lichens	<a href="#">Cleavitt et al. (2015)</a>
Northwest forested mountains	1.2 (2.5 if Alaska excluded))	7.1	<4.1	Wind River Range, WY, including the Class I Bridger Wilderness	Poorer thallus condition	Epiphytic lichens	<a href="#">McMurray et al. (2013)</a>
Temperate sierras	4	7	n/a				
Great Plains	n/a	n/a	n/a				
<i>Herb and shrub</i>							
Mediterranean California	6	33	<11 kg N/ha/yr	Semiarid coastal sage scrub, CA	Conversion to exotic grasslands	Shrubs, grasses, and forbs	<a href="#">Cox et al. (2014)</a>

**Table 6-28 (Continued): Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	<a href="#">Pardo et al. (2011c)</a>		New Critical Load Information				
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	Reference
North American deserts	3	8.4	Open: 8.3–9.9 (mean = 9.2, n = 240) Closed: 13.5–17.0 (mean = 16.5, n = 32)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
			2.1 and 3.6	Southern California Joshua Tree National Park	Exponential increase in the probability of biomass (simulated using the DayCent model) exceeding the fire threshold of 1,000 kg/ha	Creosote bush ( <i>Larrea tridentata</i> ) other shrubs, forbs, and grasses; two tree species included (California juniper and single leaf pinyon [ <i>Juniperus californica</i> and <i>Pinus monophylla</i> ])	<a href="#">Rao et al. (2010)</a>
Southern semiarid highlands	n/a	n/a	n/a				
Eastern temperate forests	n/a	17.5	Open: 6.6–9.7 (mean = 7.9, n = 947) Closed: 7.8–19.3 (mean = 12.5, n = 7,378)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
Marine West Coast forests	n/a	n/a	Open: No data Closed: 10.4–15.0 (mean = 12.8, n = 24)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>

**Table 6-28 (Continued): Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	Pardo et al. (2011c)		New Critical Load Information				
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	Reference
Northern forests	7	21	Open: 8.0–9.8 (mean = 8.9, n = 75)  Closed: 8.0–18.9 (mean = 13.8, n = 1,955)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
Northwest forested mountains	4	10	Open: 8.0–10.2 (mean = 9.1, n = 1,429)  Closed: 10.8–19.6 (mean = 15.3, n = 2,113)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
			1.9–3	Subalpine	ForSAFE-VEG modeled changes in subalpine plant community between 2010 and 2100	Subalpine plant community, consisting primarily of forest understory plants and one additional tree species (subalpine fir [ <i>Abies lasiocarpa</i> ])	<a href="#">McDonnell et al. (2014a)</a>
			3.0	Alpine	Protection of natural community cover	Grasses and forbs	<a href="#">Bowman et al. (2012)</a>
			1–2	Alpine and subalpine	ForSAFE-VEG modeled changes in alpine and subalpine plant community (modeled from 1750 to 2500)	Alpine and subalpine ground vegetation, including two tree species (Engelmann spruce and white spruce [ <i>Picea engelmannii</i> and <i>Picea glauca</i> ])	<a href="#">Sverdrup et al. (2012)</a>

**Table 6-28 (Continued): Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	<a href="#">Pardo et al. (2011c)</a>		New Critical Load Information				
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	Reference
Temperate sierras	n/a	n/a	Open: 8.6–8.7 (mean = 8.65, n = 3)  Closed: 14.8–14.8 (mean = 14.8, n = 42)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
Great Plains	5	25	Open: 8.3–9.8 (mean = 9.3, n = 618)  Closed: 11.3–19.6 (mean = 16.6, n = 274)	Ecoregion	Decreasing species richness	Grasses and forbs	<a href="#">Simkin et al. (2016)</a>
<i>Forest</i>							
n/a	n/a	n/a	8	32 forest sites around the globe	Saturation of photosynthetic capacity of the canopy	Conifer	<a href="#">Fleischer et al. (2013)</a>
Mediterranean California	17	39	n/a				
North American deserts	n/a	n/a	n/a				
Southern semiarid highlands	n/a	n/a	n/a				
Eastern temperate forests	>3	8 <sup>b</sup>	n/a				
Marine West Coast forests	5	n/a	n/a				
Northern forests	>3	26	n/a				
Northwest forested mountains	4	17	n/a				

**Table 6-28 (Continued): Critical loads for nitrogen by Pardo et al. (2011c) and more recent critical load information.<sup>a</sup>**

Ecoregion (Level 1)	<a href="#">Pardo et al. (2011c)</a>		New Critical Load Information				
	Lower Critical Load (kg N/ha/yr)	Upper Critical Load (kg N/ha/yr)	Critical Load (kg N/ha/yr)	Type of Ecosystem	Biological and Chemical Effects	Study Species	Reference
Temperate sierras	n/a	n/a	n/a				
Great Plains	n/a	n/a	n/a				

ForSAFE-VEG = a dynamic forest ecosystem model; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

<sup>a</sup>The critical loads (CLs) reported for [Pardo et al. \(2011c\)](#) are for Level 1 Ecoregions, whereas the new CL information may be for more specific ecosystems within each respective Ecoregion (e.g., California coastal sage scrub within the Mediterranean California Ecoregion; this is noted in the 5th column of the table entitled "Type of Ecosystem").

<sup>b</sup>Critical load for increased NO<sub>3</sub><sup>-</sup> loading to surface waters only; not specific to trees.

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## APPENDIX 7 AQUATIC BIOGEOCHEMISTRY

This appendix summarizes recent advancements in understanding the effects of nitrogen (N) and sulfur (S) deposition on aquatic biogeochemical processes and cycles. Freshwater systems of the U.S. include lakes (lentic systems), rivers and streams (lotic systems), and wetlands. The latter, including bogs, fens, marshes, and swamps, are discussed in [Appendix 11](#) and [Appendix 12](#). The freshwater section ([Appendix 7.1](#)) is further subdivided into N and S sources ([Appendix 7.1.1](#)); ecosystem processes, effects, and indicators ([Appendix 7.1.2](#)); monitoring ([Appendix 7.1.3](#)); modeling ([Appendix 7.1.4](#)); national scale sensitivity and chemical recovery ([Appendix 7.1.5](#)); water quality criteria ([Appendix 7.1.6](#)); and a summary ([Appendix 7.1.7](#)).

[Appendix 7.2](#) is an overview of the complex biogeochemical processes affected by N loading to estuaries (where fresh water from rivers meets the salt water of oceans) and other near-coastal areas such as lagoons and open ocean areas near coastlines. Inputs of N, including atmospheric deposition ([Appendix 7.2.1](#)), to the highly variable estuarine environment ([Appendix 7.2.2](#)), and factors such as dissolved oxygen (DO; [Appendix 7.2.3](#)) and pH ([Appendix 7.2.4](#)) affect N cycling. Key processes and indicators of N cycling are discussed in [Appendix 7.2.5](#) and [Appendix 7.2.6](#) followed by monitoring ([Appendix 7.2.7](#)), modeling ([Appendix 7.2.8](#)), national scale sensitivity ([Appendix 7.2.9](#)), water quality criteria ([Appendix 7.2.10](#)), and a summary ([Appendix 7.2.11](#)).

Biological effects and indicators linked to altered aquatic biogeochemistry are discussed in [Appendix 8](#) (Biological Effects of Freshwater Acidification), [Appendix 9](#) (Biological Effects of Freshwater Nitrogen Enrichment), [Appendix 10](#) (Biological Effects of Nitrogen Enrichment in Estuaries and Near-Coastal Systems), and [Appendix 12](#) (Non-Acidifying Effects of Sulfur).

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### 7.1 Biogeochemistry of Nitrogen and Sulfur in Freshwater Systems

As described in the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria* (hereafter referred to as the 2008 ISA), the most common and well-documented aquatic effects are acidification and eutrophication, which may occur simultaneously in some water bodies. Since the 2008 ISA, there have been additional estimates of the proportion of total N loading in freshwater systems attributed to atmospheric deposition and refinements in spatial and temporal trends of N and S deposition across the U.S. Chemical indicators of N deposition identified by the 2008

ISA were nitrate ( $\text{NO}_3^-$ ) and dissolved inorganic nitrogen (DIN) concentrations in surface waters. Surface water chemistry indicative of acidic conditions and acidification effects includes concentrations of sulfate ( $\text{SO}_4^{2-}$ ),  $\text{NO}_3^-$ , inorganic aluminum (Al), calcium (Ca), sum and surplus of base cations, acid neutralizing capacity (ANC), and surface water pH. Continued monitoring of these indicators provides some evidence of chemical recovery from acidification in some U.S. surface waters. A number of studies since 2008 have focused on improving understanding of aquatic acidification and eutrophication processes mediated by N. Many of these have focused on pathways of pollutant and other constituent movement within ecosystems, including monitoring studies of various kinds. **The body of evidence is sufficient to infer a causal relationship between N and S deposition and the alteration of freshwater biogeochemistry**, which is consistent with the conclusions of the 2008 ISA.

Acidification of freshwater ecosystems occurs in response to either S or N deposition alone or in combination. This is because both N and S deposition can act as acidifying agents. Acidifying deposition effects on biogeochemical processes in soils ([Appendix 4](#)) have significant ramifications for the water chemistry and biological functioning of associated surface waters. Surface water chemistry integrates direct air-to-water deposition with deposition impacts on soil chemistry of hydrologically connected terrestrial ecosystems within the watershed. Deposited N and S interact with the soils and sediments of terrestrial and aquatic ecosystems via oxidation and reduction reactions as well as biological uptake and microbially mediated processes.

Acidification of fresh water may occur as a chronic or an episodic condition ([Appendix 8.2](#)). The 2008 ISA defined chronic acidification by reference to annual average conditions, often quantified as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic acidification refers to conditions during rainstorms or snowmelt when water has a relatively short residence time in soil before entering surface water. During these stormflow events, proportionately more water drains through upper soil horizons, providing less neutralization of atmospheric acidity compared with flow through deeper soil horizons. Episodes of acidification are typified by lower pH, lower ANC, and higher inorganic Al concentration in surface water than during baseflow conditions. The short-term change in chemical conditions may be toxic or lethal to aquatic biota ([Appendix 8](#)). These conditions are caused partly by acidifying deposition ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) and partly by natural processes, including base cation dilution and flushing of organic acids into drainage water. It is known that the biota in many streams/lakes are impacted when the ANC is consistently below 50  $\mu\text{eq/L}$ . For this reason, the U.S. EPA National Lakes Assessment used an ANC threshold of  $>50 \mu\text{eq/L}$  as indicative of nonacidified water bodies ([U.S. EPA, 2009b](#)).

In aquatic systems, N is a nutrient that stimulates growth of primary producers (algae and/or aquatic plants). Even small inputs of N in low nutrient water bodies such as remote headwater and lower order streams and alpine lakes can increase nutrient availability, alter the balance of N and phosphorus (P) nutrients, affect biogeochemical processing of N and increase the productivity of photosynthesizing organisms, resulting in an increase in pool of fixed carbon (C). Nutrient enrichment leads to changes in aquatic assemblages and biodiversity in freshwater ([Appendix 9](#)) and coastal regions ([Appendix 10](#)). The freshwater ecosystems in the U.S. most likely to be sensitive to nutrient enrichment from N deposition are headwater streams, lower order streams, and alpine lakes which have very low nutrients and productivity and are far from local pollution sources [[Appendix 9.1.1.2](#); [U.S. EPA \(2008a\)](#)]. High-elevation lakes in the western U.S. are naturally oligotrophic and are considered among the aquatic ecosystems most sensitive to N deposition ([Williams et al., 2017b](#)). A portion of these lakes and streams in the western U.S. are in Class I wilderness areas ([Williams et al., 2017b](#); [Clow et al., 2015](#); [Nanus et al., 2012](#)). In higher order streams, N deposition typically mixes with N derived from other nonatmospheric sources, including urban/suburban point and nonpoint sources, industrial sources, and agricultural sources. The long-held paradigm that fresh waters are typically P limited has been replaced by an understanding that both N and P can limit primary production, and that nutrient limitation can be a dynamic and transient process ([Paerl et al., 2016b](#); [Paerl et al., 2014](#); [Conley et al., 2009](#); [Paerl, 2009](#)). Although over-enrichment with P is not specifically addressed in this assessment, recent trends in increased atmospheric deposition of P ([Appendix 9.1.1.2](#)) have ramifications for nutrient stoichiometry.

The geochemical processes and associated chemical indicators discussed in this appendix can be considered to indicate or suggest eutrophication or acidification. Some of the biogeochemical alterations associated with N and S deposition link directly to the biological effects discussed in subsequent appendices. Others do not cause direct biological effects but are precursory steps to changes in soil or water chemistry that can lead to biological effects. [Table 7-1](#) summarizes the key freshwater indicators for N driven nutrient enrichment and acidification and the section of the ISA that discusses each endpoint.

A separate appendix addresses the biogeochemistry of terrestrial responses to nutrient and acidic additions ([Appendix 4](#)). Aquatic and terrestrial systems are interconnected and many of the biogeochemical processes discussed herein bridge the transitions between these two environmental compartments.

**Table 7-1 Summary of key freshwater indicators of eutrophication and acidification.**

Endpoint	N Driven Nutrient Enrichment	Acidification	Section of ISA That Discusses Endpoint
<b>Chemical indicator</b>			
Water NO <sub>3</sub> <sup>-</sup> concentration	X	X	<a href="#">7.1.2.1</a>
Water SO <sub>4</sub> <sup>2-</sup> concentration		X	<a href="#">7.1.2.2</a>
Water pH		X	<a href="#">7.1.2.5</a>
Water ANC		X	<a href="#">7.1.2.6</a>
Water base cation surplus		X	<a href="#">7.1.2.7</a>
Water inorganic Al concentration		X	<a href="#">7.1.2.8</a>
<b>Biological indicator</b>			
Diatoms	X		<a href="#">9.2.1</a>
Nutrient ratios	X		<a href="#">9.2.2</a>
Phytoplankton biomass shift	X		<a href="#">9.2.3</a>
Periphyton/microbial biomass	X		<a href="#">9.2.4</a>
Chlorophyll a	X		<a href="#">9.2.5</a>

## 7.1.1 Nitrogen and Sulfur Sources

In fresh water, both S and N can contribute to acidification while nutrient enrichment effects are associated with N. Long-range atmospheric transport of N and S can affect remote freshwater catchments far from pollutant sources. Major sources of N and S and deposition trends are discussed in [Appendix 2](#).

### 7.1.1.1 Nitrogen Sources

Since the 2008 ISA, additional analyses have refined the understanding of N sources and deposition trends ([Appendix 2](#)) to freshwater systems. [Sobota et al. \(2013\)](#) synthesized data on N inputs to lands and waterways throughout the U.S. They found that human-caused N inputs are ubiquitous but spatially heterogeneous. The highest N loads

generally occurred in the Midwest, Mid-Atlantic region, central and southern California, and portions of the Columbia River Valley. Synthetic fertilizer was estimated to be the single largest source of human-caused N inputs to 41% of the water resource units analyzed, followed by atmospheric deposition (33%) and biological N fixation (22%). A tool for calculating net anthropogenic nitrogen inputs (NANI) was developed for watersheds across the contiguous U.S. at the county level ([Hong et al., 2013, 2011](#)). The NANI Calculator Toolbox takes into consideration fertilizer N application, agricultural N fixation, net food and feed imports, and atmospheric sources of N. Unlike S, geological sources of N are rare.

In a U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) report on occurrence and distribution of nutrients in streams and groundwater (based on water quality assessments conducted from 1992 to 2001), atmospheric deposition was identified as the largest nonpoint source of N in the less developed watersheds (areas dominated by forest or rangeland with  $\leq 5\%$  urban and  $\leq 25\%$  agricultural land) in the eastern part of the country where deposition rates have historically been highest, in areas near the Great Lakes, and the mountainous west ([Dubrovsky et al., 2010](#)). Atmospheric sources have been shown to be quantitatively important ( $>33\%$  of total input) to Lake Tahoe, CA/NV ([Sahoo et al., 2013](#); [Dolislager et al., 2012](#)), Flathead Lake, MT ([Ellis et al., 2015](#)), and Nine Mile Run in Pittsburgh, PA ([Divers et al., 2014](#)). Even in lowland lakes, N from atmospheric sources has been shown to contribute appreciably to the total input of N. In a study of nutrient sources to Saginaw Bay, MI, N deposition was estimated to comprise 10 to 11% of the total N input from 1987 to 2002 ([He et al., 2014](#)).

Nitrogen is deposited in various reduced and oxidized forms, including organic N, and, in wet or dry forms as well ([Appendix 2](#)). Oxidized N is emitted into the atmosphere mainly from motor vehicles, electricity generating units, and industry. Reduced N is emitted mainly from agricultural sources such as livestock and fertilizer applications. Direct deposition of N to open water surfaces constitutes an appreciable source of N to relatively large freshwater lakes and rivers, estuaries, and coastal marine waters ([Appendix 7.2.1](#)). Alternatively, N can be deposited in the watershed of receiving waters and then move through soils before entering surface waters. Atmospheric deposition of reduced N has increased relative to oxidized N in parts of the U.S. including the East and Midwest in the last few decades, shifting from a  $\text{NO}_3^-$  dominated to an ammonium ( $\text{NH}_4^+$ ) dominated condition, and this trend is expected to continue under existing emissions controls ([Li et al., 2016d](#); [Pinder et al., 2008](#); [U.S. EPA, 2008a](#)). Since the 2008 ISA, there is a greater understanding of the potential ecological changes associated with the increase in deposition of reduced N relative to oxidized N in terrestrial, freshwater and coastal systems ([Section IS. 2.2.5](#)).

[Table 7-2](#) summarizes key studies that have quantified total N loading in freshwater systems from atmospheric deposition. In the 2008 ISA, the difficulty in determining the percentage of atmospheric N in lowland waters was noted because there are so many other point and nonpoint sources of N to drainage waters in these areas ([U.S. EPA, 2008a](#)). As described in the 2008 ISA, a large fraction of atmospheric N deposition is retained in most forested ecosystems with less retention in urban, suburban, and agricultural lands ([U.S. EPA, 2008a](#)). The atmospheric fraction that does leach to streams can make a substantial contribution to total N inputs to downstream waters, especially in the eastern U.S. ([Driscoll et al., 2003d](#)). Apportionment of N sources to identify the contribution of atmospherically derived N was described in a few studies in the 2008 ISA ([U.S. EPA, 2008a](#)). In Spatially Referenced Regressions on Watershed Attributes (SPARROW) modeling studies, approximately 70% of the N in headwater streams in the northeastern U.S. was judged to be from N deposition ([Alexander et al., 2007](#); [Moore et al., 2004a](#); [Alexander et al., 2002](#)).

Several new studies published since the 2008 ISA further quantified N sources, including atmospheric contribution, to lakes and streams ([Table 7-2](#)). [Sebestyen et al. \(2008\)](#) showed the dominant direct role of atmospheric  $\text{NO}_3^-$  in snowmelt runoff at Sleepers River, VT. At peak flow, 48% of  $\text{NO}_3^-$  was from atmospheric sources in this forested watershed. In the Uinta Mountains, UT, at least 70% of  $\text{NO}_3^-$  was atmospherically deposited to high alpine lakes from distant anthropogenic sources ([Hundey et al., 2016](#)). Approximately 60% of the reactive N was from agriculture, based on isotopic analysis and modeling of snow, inflow and lake  $\text{NO}_3^-$ . The authors suggested these findings are widely applicable to other western U.S. alpine sites based on comparison of isotope and precipitation data in the region.

Additional information is available since the 2008 ISA on atmospheric contributions of reduced versus oxidized N to lakes. In Lake Tahoe, where a total maximum daily load (TMDL) allocation was adopted in 2011 by California and Nevada to reduce nutrient loading, atmospheric N represented approximately 57% of the total N loading to the lake ([Sahoo et al., 2013](#)). In this large alpine lake in the Sierra Nevada mountain range, an estimated 185 metric tons of N was directly deposited from the atmosphere, with  $\text{NH}_4^+$  as the dominant component and nitric acid plus  $\text{NO}_3^-$  representing a smaller, but not insignificant, proportion of total N ([Dolislager et al., 2012](#)). In Flathead Lake, MT, atmospheric loading of  $\text{NH}_4^+$  averaged 44% of the total load between 1985 and 2004 and was the primary form of N in atmospheric deposition ([Ellis et al., 2013](#)). There was an increase in atmospheric loading of  $\text{NO}_3^-$  + nitrite ( $\text{NO}_2^-$ ; +48%) and  $\text{NH}_4^+$  (+198%) and decrease in total P loading (-135%)

**Table 7-2 Summary of recent studies quantifying nitrogen deposition contribution to total nitrogen loading in freshwater systems.**

Region	Total N Loading Due to Atmospheric Deposition	Method	Reference
Lake Tahoe, CA	Approximately 57%, NH <sub>3</sub> as the dominant component and nitric acid and NO <sub>3</sub> <sup>-</sup> representing a smaller but not insignificant proportion of total N.	Field data and Lake Tahoe watershed model	<a href="#">Sahoo et al. (2013)</a> <a href="#">Dolislager et al. (2012)</a>
Flathead Lake, MT	Atmospheric loading of NH <sub>4</sub> <sup>+</sup> averaged 44% of total load between 1985 and 2004 and was the primary form of N in deposition.	Field data and statistical analysis, linear regression	<a href="#">Ellis et al. (2013)</a>
Unita Mountains, UT	At least 70% of NO <sub>3</sub> <sup>-</sup> in the high alpine lakes is from atmospheric deposition. Most reactive N originates from agricultural activities (approximately 60%).	Isotopic analysis and bayesian-based stable isotope mixing model	<a href="#">Hundey et al. (2016)</a>
Saginaw Bay, MI	N deposition was estimated to be 10 to 11% of total N from 1987–2002.	Multiple databases of land use/cover, hydrography, animal production, fertilizers, combined wastewater overflows	<a href="#">He et al. (2014)</a>
St. Lawrence River, Quebec City	Atmospheric N contributed about 0 to 4% of total N load in the summer; in the spring, this source represented 4 to 11% of total N.	Isotopic analysis	<a href="#">Thibodeau et al. (2013)</a>
Quinnipiac River, CT	Atmospherically deposited NO <sub>3</sub> <sup>-</sup> represented <6% of N loading; however, during storm events, atmospheric deposition represented up to 50% of stream NO <sub>3</sub> <sup>-</sup> but varied widely by site.	Stable isotope ratios	<a href="#">Anisfeld et al. (2007)</a>
Baltimore Long-Term Ecological Research site	Atmospheric contributions ranged from 5 to 94% during storm flow conditions and represented approximately 50% of the highest NO <sub>3</sub> <sup>-</sup> loads during storms.	N watershed mass balances and stable isotopes	<a href="#">Kaushal et al. (2011)</a>
Tributary to Teff Run, MD	Contributions of atmospheric N to surface water in an Appalachian Mountain stream were most evident during hydrological episodes, but baseflow accounted for much of the NO <sub>3</sub> <sup>-</sup> loss in stream water.	Isotopic analysis	<a href="#">Sabo et al. (2016)</a>
Nine Mile Run in Pittsburgh, PA	34% of NO <sub>3</sub> <sup>-</sup> in stream water was atmospheric in origin during storm events while 94% of stream water NO <sub>3</sub> <sup>-</sup> was from sewage sources during baseflow conditions.	Stable isotope ratios	<a href="#">Divers et al. (2014)</a>
Suburban watershed (Lisha)	About 40% or more of NO <sub>3</sub> <sup>-</sup> in stream water in a suburban watershed during storm runoff was attributed to direct NO <sub>3</sub> <sup>-</sup> deposition.	Stable isotope ratios	<a href="#">Burns et al. (2009)</a>

**Table 7-2 (Continued): Summary of recent studies quantifying nitrogen deposition contribution to total nitrogen loading in freshwater systems.**

Region	Total N Loading Due to Atmospheric Deposition	Method	Reference
Kill) in eastern New York			
Sleepers River watershed, northeastern Vermont	In this forested watershed 48% of $\text{NO}_3^-$ was from atmospheric sources at peak flow. More than half of the $\text{NO}_3^-$ in soil and shallow groundwater after the start of snowmelt originated directly from atmospheric deposition.	Isotopic tracers and mixing analysis Stable isotope ratios, hydrochemistry, end-member mixing analyses	<a href="#">Sebestyen et al. (2008)</a>
<b>Key pre-2008 literature</b>			
16 northeastern watersheds	Approximately 70% of the N in headwater streams was from N deposition and the net transport of N from headwater streams was between 40 and 65% of total N.	SPARROW	<a href="#">Alexander et al. (2002)</a> ; <a href="#">Alexander et al. (2007)</a>
16 large northeastern river basins	N deposition contributes approximately 31% of the total N load to large river basins, although this fraction varies regionally. Values for watersheds in northern New England were substantially higher and atmospheric deposition dominated.		<a href="#">Boyer et al. (2002)</a>
Eight watersheds in New York and New England	Atmospheric deposition was second largest N input for the eight watersheds (11 to 36% of total) with four watersheds ranging from 34 to 36%.	PnET-BGC and WATERS N	<a href="#">Driscoll et al. (2003d)</a>

N = nitrogen;  $\text{NH}_3$  = ammonia;  $\text{NH}_4^+$  = ammonium;  $\text{NO}_3^-$  = nitrate; SPARROW = Spatially Referenced Regressions on Watershed Attributes.

In the studies reviewed in the 2008 ISA, the role of atmospheric deposition in downstream urban and residential water bodies was rarely addressed ([U.S. EPA, 2008a](#)). New studies using stable isotope ratios to quantify N loading in streams have characterized the contributions of atmospheric N in these systems. Several of these studies have shown shifts to higher atmospheric N contributions during storm events. In the Quinnipiac River in Connecticut which drains into Long Island Sound, atmospherically deposited  $\text{NO}_3^-$  averaged <6% of average N loading during baseflow conditions; however, during storm events, atmospheric deposition represented up to 50% of stream  $\text{NO}_3^-$ , although the amount varied widely by site ([Anisfeld et al., 2007](#)). In the St. Lawrence River outlet at Quebec City, Canada, isotopic analysis of N inputs indicated that atmospheric N contributed about 0 to 4% of total N load in the summer, while in the spring this source was 4 to 11% of total N ([Thibodeau et al., 2013](#)). In forested, agricultural and urban watersheds at the Baltimore Long-Term Ecological Research site,

atmospheric N contributions ranged from 5 to 94% during storm flow conditions and represented approximately 50% of peak storm  $\text{NO}_3^-$  ([Kaushal et al., 2011](#)). In Nine Mile Run in Pittsburgh, PA, 34% of  $\text{NO}_3^-$  in stream water was atmospheric in origin during storm events, whereas during baseflow conditions 94% of stream water  $\text{NO}_3^-$  was from storm drain and wastewater treatment sources ([Divers et al., 2014](#)). In another study in Pennsylvania, stream water from Spring Creek was monitored at sites from upstream to downstream during storm flow events to assess changes in N sources ([Buda and DeWalle, 2009](#)). For the forested upstream site, the atmospheric contribution varied by storm size. In the downstream urbanized watershed, atmospheric  $\text{NO}_3^-$  was an important N source at peak flow, especially during short-duration storms when overland flow was prevalent.

[Burns et al. \(2009\)](#) applied dual isotope analysis of  $\text{NO}_3^-$  to determine the dominant sources and processes that affect  $\text{NO}_3^-$  concentrations in six streams on different land uses in New York. The dual isotope data revealed varying sources and processes that affect  $\text{NO}_3^-$  concentration among the six stream watersheds. Atmospheric  $\text{NO}_3^-$  was about half of stream  $\text{NO}_3^-$  during storms because of rapid shunting of runoff through storm drains. The suburban watershed that had no septic or wastewater influence showed  $\text{NO}_3^-$  concentrations only slightly higher than those observed in two forested watersheds. Overall, these studies appear to have characterized relatively well the atmospheric contribution of N to water bodies that have multiple sources of N. Results show substantial variability, with atmospheric sources typically being most pronounced during high-flow conditions.

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#### 7.1.1.2 Sulfur Sources

The 2008 ISA reported that there were both depositional and geological sources of  $\text{SO}_4^{2-}$  to aquatic ecosystems.  $\text{SO}_x$  deposition to ecosystems is primarily in the chemical form  $\text{SO}_4^{2-}$ , which is a moderately mobile anion in the soil solution and surface water of many glaciated acid-sensitive watersheds in the northeastern U.S. Note that  $\text{SO}_4^{2-}$  is less mobile in unglaciated watersheds of the southeastern U.S. ([Rice et al., 2014](#)). Other major sources of  $\text{SO}_4^{2-}$  in ecosystems include mineralization of S from organic matter and weathering of geologic sources of S, including pyrite minerals. Anthropogenic soil and rock disturbance in the form of road cuts or mine tailings can increase geological contributions of  $\text{SO}_4^{2-}$  to soil or surface water by exposing S bearing minerals to oxygen ( $\text{O}_2$ ), promoting mineral oxidation and the release of  $\text{SO}_4^{2-}$ . Acid mine drainage is one result of this process and is prevalent in many parts of the Appalachian Mountain region. New published evidence regarding the influence of geologic sources of S or acid mine drainage on stream chemistry has not been reviewed for this ISA.

The 2008 ISA described how SO<sub>x</sub> deposition causes the release of S from terrestrial to aquatic ecosystems via SO<sub>4</sub><sup>2-</sup> leaching, and other changes in surface water chemistry caused by increasing SO<sub>4</sub><sup>2-</sup> concentrations. At that time, acidification of surface waters at most locations in the U.S. where acidification has been documented in response to deposition was caused mainly by SO<sub>4</sub><sup>2-</sup> ([Driscoll et al., 2001b](#); [Sullivan, 2000](#)). This was partly due to the mobility of SO<sub>4</sub><sup>2-</sup> in many (especially northeastern) waters draining from terrestrial ecosystems to aquatic ecosystems. It was also known that the mobility of SO<sub>4</sub><sup>2-</sup> varies geographically, with S adsorption on soils most significant in regions that were unglaciated during the most recent glaciation. This includes many acid-sensitive watersheds in the southeastern U.S. In the most recently glaciated Northeast and upper Midwest, a substantial component of the atmospherically deposited S accumulates in organic pools in soil, although microbial mineralization can transform this organic S back into more mobile SO<sub>4</sub><sup>2-</sup>.

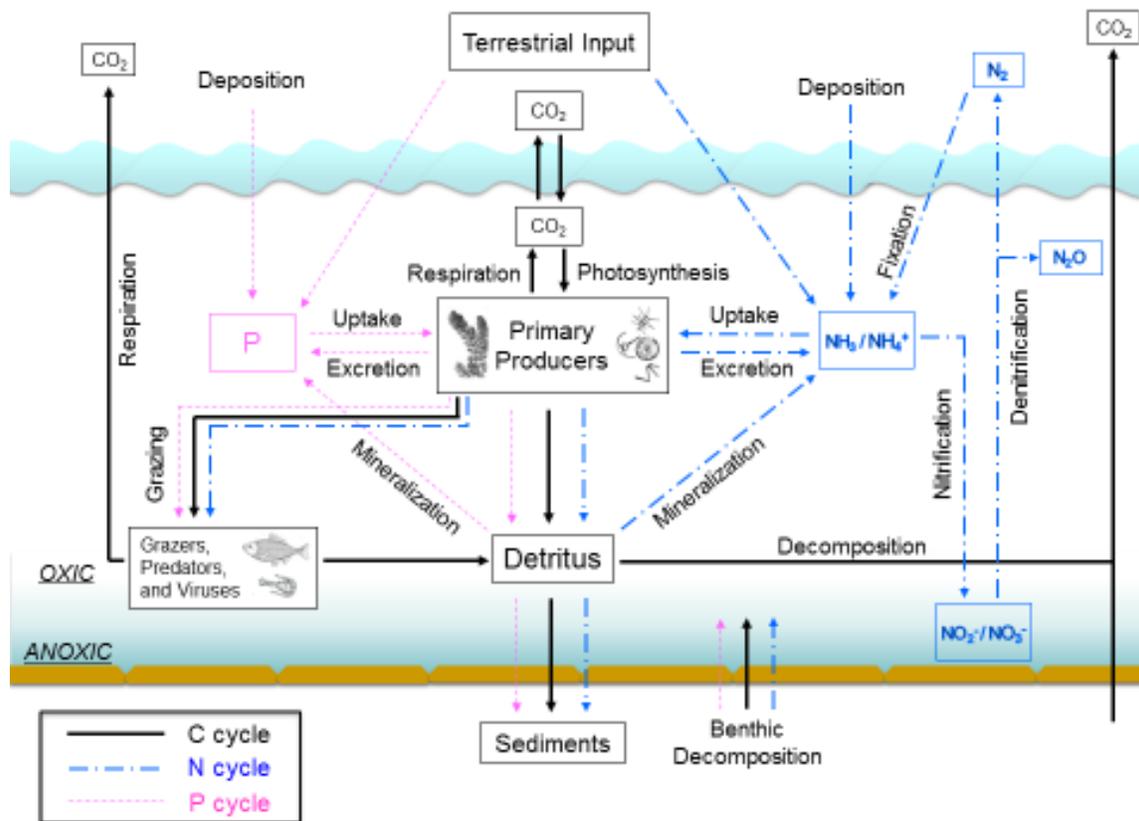
A mass balance study by [Mitchell et al. \(2011\)](#) of 15 watersheds located in the northeastern U.S. and southeastern Canada suggested substantial sources of SO<sub>4</sub><sup>2-</sup> in watershed soils. The internal S sources were attributed mainly to mineralization of S stored in soils in response to decades of atmospheric S deposition. In a study of 16 lakes from the original Adirondack Long-Term Monitoring program from 1984 to 2010 [Mitchell et al. \(2013\)](#) observed discrepancies in the calculated S mass balances that were associated with discharge. These results suggested that internal S sources have become more important to the watershed S budget as atmospheric S deposition has decreased. Declines in lake SO<sub>4</sub><sup>2-</sup> concentrations have been observed in locations where S deposition has decreased significantly, such as in the Adirondack Mountains [[Mitchell et al. \(2013\)](#); [Appendix 7.1.5.1](#)].

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## 7.1.2 Ecosystem Processes, Effects, and Indicators

New information on biogeochemical indicators and processes of eutrophication and acidification are presented in the following sections, along with summaries of information from the 2008 ISA. These processes may occur either in sequence or simultaneously in a given geographic area. Impacts of N and S deposition on aquatic ecosystems can be described by changes in acid-base chemical indicators including SO<sub>4</sub><sup>2-</sup> concentration, NO<sub>3</sub><sup>-</sup> concentration, DIN concentration, inorganic Al concentration, base cation concentrations, base cation surplus (BCS), pH, and ANC. Surface water NO<sub>3</sub><sup>-</sup> concentration can reflect both eutrophication and acidification. Water pH and the concentrations of ANC, SO<sub>4</sub><sup>2-</sup>, and inorganic Al are commonly used indicators of the likelihood of surface water acidification ([U.S. EPA, 2008a](#)). As reported in the 2008 ISA and summarized in [Figure 7-1](#), the biogeochemical cycles of N, P, and C are linked in

freshwater ecosystems. Nitrogen deposition can alter the pools and fluxes of the C, N, and P cycles, including nitrification and denitrification. Sulfur deposition adds  $\text{SO}_4^{2-}$  directly to soil solutions and to surface waters with effects on ecosystems ([Appendix 12](#)), but many ecological effects are mediated through the indirect effects of  $\text{SO}_4^{2-}$  on the exchange of acidic and basic cations on soils. The chemical indicators of deposition discussed below also link to biological effects of acidifying deposition ([Appendix 8](#)) and freshwater N enrichment ([Appendix 9](#)).



C = carbon;  $\text{CO}_2$  = carbon dioxide; N = nitrogen; P = phosphorus.  
 Modified from [U.S. EPA \(2008a\)](#).

**Figure 7-1 Nitrogen cycle in freshwater ecosystem.**

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### 7.1.2.1 Nitrogen in Surface Waters

As reviewed in the 2008 ISA and supported by more recent studies, the fate and transport of deposited N is influenced by characteristics of the catchment and the receiving waters. Retention of N varies among watershed types such that similar amounts of deposition can result in different rates of N leaching, depending on catchment characteristics [[Appendix 9.1.1.2](#); [Bergström \(2010\)](#)]. In most surface waters of the U.S., dissolved inorganic N (DIN, the sum of the concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and nitrite) is overwhelmingly dominated by  $\text{NO}_3^-$ . As summarized in the 2008 ISA, high concentrations of  $\text{NO}_3^-$  in lakes and streams, indicative of terrestrial ecosystem N saturation, have been found at a variety of locations throughout the U.S. Surface water  $\text{NO}_3^-$  is a chemical indicator for both eutrophication and acidification. Nitrate contributes to the acidity of many lakes and streams in the eastern U.S. that have been affected by acidifying deposition, especially during spring snowmelt and under high-flow conditions.

In the 2008 ISA, a study evaluating the relationship between wet deposition and DIN concentration in 4,296 lakes across Canada, Europe, and the U.S. showed a significant correlation between increases in N wet deposition and increases in lake DIN concentration ([Bergström and Jansson, 2006](#)). More recent studies from some regions of the U.S. [e.g., [Eshleman et al. \(2013\)](#); [Driscoll et al. \(2016\)](#); [Strock et al. \(2014\)](#); [Eshleman and Sabo \(2016\)](#); [Appendix 7.1.5.1](#)] showed recent declines in concentrations of  $\text{NO}_3^-$  in surface waters that are consistent with declines in N deposition. Using the Lake Multi-Scaled Geospatial and Temporal Database of the Northeast Lakes of the U.S. (LAGOS-NE) containing water quality data from 2,913 lakes, [Oliver et al. \(2017\)](#) identified atmospheric deposition as the main driver of declines in total N (TN) deposition and lake TN:total P (TP) ratios from 1990 to 2011.

Reactive N can be taken up by terrestrial and aquatic biota or stored in soils and/or sediments, be re-emitted back to the atmosphere by the microbial process of denitrification ([Appendix 7.1.2.3](#)), or carried downstream in a dissolved state, most typically as  $\text{NO}_3^-$ , because much of the deposited  $\text{NH}_4^+$  is either taken up by biota or nitrified to  $\text{NO}_3^-$ . Typically, a rather large percentage of the N deposition to a given watershed is taken up or stored and is not denitrified or made available for leaching to surface waters. On average, for a large watershed with mixed land use, it has been estimated that roughly 75% of N inputs are retained in the watershed and 25% are exported downstream regardless of the dominant N input, including deposition ([Howarth et al., 2012](#); [Howarth et al., 1996a](#)). This stored N does not contribute directly to water acidification or eutrophication and represents a significant portion of the incoming N deposition to forested ecosystems in the U.S. The portion of the N deposition that is not

retained or lost to denitrification can contribute to water acidification or eutrophication, both on a chronic and especially an episodic basis.

It was well understood at the time of the 2008 ISA that streams and their associated sediments can transform nutrients, store them for the short term, or serve as a sink for N loss from the watershed through denitrification. It is important to consider the balance between how much and how long streams retain elements versus transport them downstream. This balance is key to modeling watershed nutrient export. Headwater streams can play disproportionately large roles in N transformation and N cycling in aquatic ecosystems, and they are important to predicting effects of N loading on downstream ecosystems. Atmospheric deposition may represent a significant source of N to some headwater streams [[Lawrence et al. \(2015b\)](#); [Table 7-2](#)], which often have increased water residence time and solute retention due to increased interactions between surface and groundwater in the hyporheic zone.

The majority of atmospherically deposited N is either denitrified or accumulates in watershed soils, vegetation, or groundwater ([Galloway et al., 2008](#)). The relative partitioning of N loss via denitrification versus watershed storage is poorly known ([Galloway et al., 2004](#)). Watershed denitrification hot spots and hot-moments tend to occur in areas characterized by wet conditions, including wetlands and riparian zones. Such ecosystems can be highly efficient in removing N from surface waters via denitrification ([Galloway et al., 2003](#)). Nitrogen in fresh waters is also controlled by hydrological conditions. For example, [Lusardi et al. \(2016\)](#) showed that spring-fed rivers of northern California had higher  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations and cooler temperatures than rivers that were fed more by runoff. Recent studies have added more quantitative context to hydrologic processes that control nutrient cycling, including hydrologic exchange between the streams and the groundwater. This hyporheic exchange can contribute to N retention in streams because it promotes denitrification associated with anoxic flow paths through organic stream bottom substrates. For example, [Hall et al. \(2009b\)](#) observed in a tracer study in the Sawtooth Mountains of Idaho that assimilation and hydrologic storage can be important for retaining N at the watershed scale. The study stream was not solely a conduit for nutrients at high flow. It had as high an uptake velocity for N during the snowmelt high flow as during summer baseflow.

Influence of beaver and human-made dams on  $\text{NO}_3^-$  uptake in a small headwater stream in the Rocky Mountains was investigated by [Hubbard et al. \(2010\)](#). Dams influenced stream water geochemistry because a portion of the stream water flow was diverted into the more reactive hyporheic zone. Highly oxic and anoxic regions of the streambed developed around the more permanent structures. This enhanced N cycling in the hyporheic zone and increased the potential for denitrification and  $\text{NO}_3^-$  uptake. In parts of

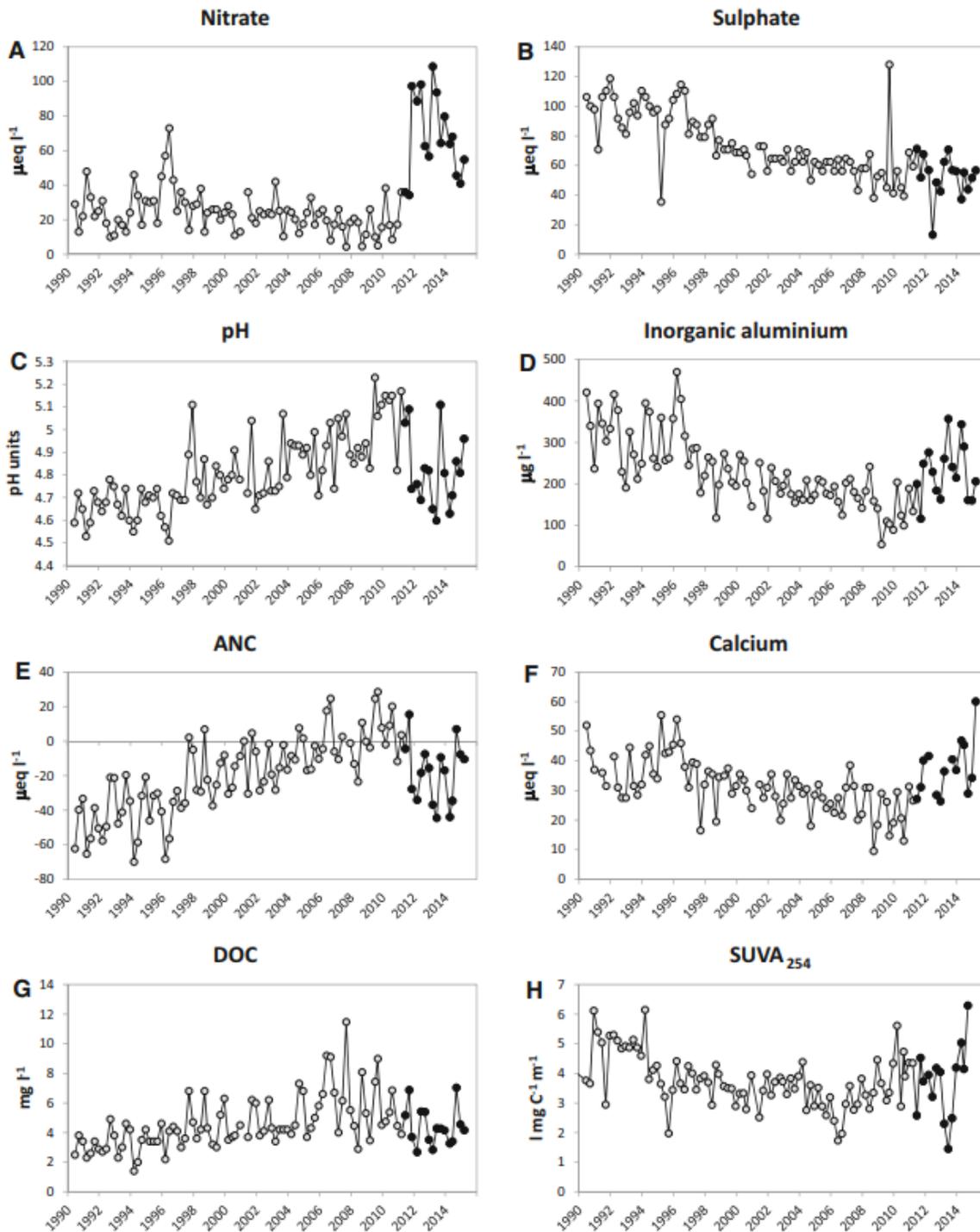
the western U.S. Rocky Mountains, there was a strong positive correlation between surface water  $\text{NO}_3^-$  concentration and atmospheric N deposition ([Elser et al., 2009b](#); [Bergström and Jansson, 2006](#)). Such a correlation does not always occur elsewhere because nonatmospheric watershed sources of N are often larger than atmospheric sources, depending mainly on land use. Analysis of increasing  $\text{NO}_3^-$  trends over three decades in streams draining into Lake Ontario, Canada, [Eimers and Watmough \(2016\)](#) suggested that tributary loading, rather than atmospheric deposition, may have played a dominant role in causing the recent observed increase in  $\text{NO}_3^-$  concentrations in the waters of Lake Ontario. The authors pointed to an observed trend in Ontario towards more annual grain crop production that required more N fertilizer addition and less reliance on perennial crops. This shift in crops could be contributing to the observed increase in  $\text{NO}_3^-$  concentration in the lake.

Studies have been conducted in recent years to elucidate processes affecting surface water  $\text{NO}_3^-$  concentrations, including experimental studies, isotopic analyses, monitoring, and observational studies. The concentration of  $\text{NO}_3^-$  may vary widely between baseflow and peak flow conditions ([Table 7-2](#)). Seasonality in surface water chemistry can be caused, in part, by differential hydrologic flows from watershed seeps and glaciers. These flows can influence  $\text{NO}_3^-$  leaching to surface waters. [O'Driscoll and DeWalle \(2010\)](#) showed that seeps are generally  $\text{NO}_3^-$  sinks with  $\text{NO}_3^-$  concentrations decreasing downslope from seep locations in Baldwin Creek in southwestern Pennsylvania. During cold and wet periods, however, the seeps frequently acted as  $\text{NO}_3^-$  sources to the stream. Locations where upwelling groundwater saturates the surface for most of the year and excess groundwater can be delivered to the stream channel via surface flow paths may provide seasonally linked water quality functions that can modify the effects of N deposition.

Changes in the amount of  $\text{NO}_3^-$  leaching and disruption of N cycling can occur with events in the watershed, including wildfire and timber extraction. Human activities have contributed to greater frequency and magnitude of wildfire in many parts of the U.S., which is well known to increase  $\text{NO}_3^-$  leaching. The area impacted by fire has increased in response to climate change, past fire suppression, and increased human presence in forested ecosystems ([Bladon et al., 2014](#)). Extreme events have the potential to delay ecosystem recovery from past water acidification. [Evans et al. \(2017\)](#) assessed the role of wildfire in regulating the chemistry of a mountain lake in a moorland catchment in the U.K. affected by a large fire. The lake had been subjected to more than two decades of ecosystem monitoring prior to the fire. The most pronounced change in lake chemistry was a substantial increase in lake  $\text{NO}_3^-$  concentration to peak values of 111  $\mu\text{eq/L}$  (1.55 mg/L) 2 years after the fire. Past N deposition may have been high enough to make the catchment more susceptible to  $\text{NO}_3^-$  leaching and accompanying reacidification in

response to the fire ([Figure 7-2](#)). The increase in the concentration of this mobile acid anion increased lake acidity and the concentration of inorganic Al. These changes represented a reversal in the ongoing documented recovery from past acidification. Forest disturbance, including clear-cut logging, also contributes to increased leaching of inorganic N, with potential impacts on downstream nutrient concentrations and acid-base chemistry. [Schelker et al. \(2016\)](#) evaluated N dynamics in Sweden over a 10-year period after tree harvesting. DIN leaching in first order streams increased substantially (~15 times) subsequent to logging. In the larger streams,  $\text{NO}_3^-$  leaching was seasonal and increased in response to logging in the mid-sized, but not the largest, streams. Thus, the increased mobilization of  $\text{NO}_3^-$  in first-order streams caused by logging can affect some downstream locations at certain times.

Nitrogen deposition to snow and glaciers is an important source of N to alpine lakes and streams which are fed by meltwaters. Since the 2008 ISA, several studies indicate that glacial meltwater has higher  $\text{NO}_3^-$  than snowmelt water in some regions of the U.S. This may influence interpretation of biological data from high elevation lakes and streams [[Baron et al. \(2009\)](#); [Saros et al. \(2010\)](#); [Slemmons et al. \(2015\)](#); [Slemmons et al. \(2013\)](#); [Appendix 9.3.2.1](#)]. In two sets of high-elevation lakes in the U.S. Rocky Mountains—those fed by snowpack melt alone and those fed by both glacial and snowpack meltwaters—the  $\text{NO}_3^-$  concentrations in the glacially influenced lakes were one to two orders of magnitude higher than in the lakes that were fed only by snowmelt ([Saros et al., 2010](#)). The higher concentration of  $\text{NO}_3^-$  in glacial meltwater relative to seasonal snowpack meltwater was attributed, at least in part, to reduced contact with watershed soils where microbial communities could rapidly assimilate the available N. This contrasts with snowmelt watersheds where the meltwater typically percolates through soils before reaching the streams ([Saros et al., 2010](#)). [Williams et al. \(2007\)](#) found that, in the Colorado Front Range, rock/glacier outflow had  $\text{NO}_3^-$  concentrations of 69  $\mu\text{eq/L}$  compared to snow with 7  $\mu\text{eq/L}$ . In two proximal lakes in the central Rocky Mountains,  $\text{NO}_3^-$  concentration from glacier-fed Jasper Lake, was 2  $\mu\text{eq/L}$  compared to the snowpack-fed Lake Albino where  $\text{NO}_3^-$  concentration was only 0.03  $\mu\text{eq/L}$  ([Slemmons et al., 2015](#)). In contrast, in the Northern Cascade Mountains, WA, differences in  $\text{NO}_3^-$  concentration between glacier-fed and snowpack-fed lakes were much smaller and not statistically significant in some years ([Williams et al., 2016b](#)).



Notes: Samples collected before the May 2011 fire are denoted by grey circles, and those from after the fire by black circles.  
 Source: [Evans et al. \(2017\)](#).

**Figure 7-2** Quarterly measured concentrations of a range of water chemistry variables at Blue Lough from 1990 to 2014.

Advances in isotopic analyses have improved techniques for investigating the role of  $\text{NO}_3^-$  in N cycling. [Curtis et al. \(2012\)](#) used the dual isotope technique at four moorland watersheds in Great Britain to investigate  $\text{NO}_3^-$  production in surface waters. An estimated 79–98% of the annual median  $\text{NO}_3^-$  had been microbially produced, indicating that both reduced and oxidized N deposition may cycle through the microbial flora and contribute similarly to  $\text{NO}_3^-$  leaching. This is important because atmospheric deposition of  $\text{NH}_4^+$  has been increasing in many areas of the eastern U.S. while deposition of oxidized N forms ( $\text{NO}_y$ ) has decreased ([Appendix 2](#)). [Goodale et al. \(2009\)](#) characterized the amount, form, isotopic composition ( $^{15}\text{N}$  and  $^{18}\text{O}$ ), and seasonality of stream N in forested subwatersheds of the Susquehanna River. Atmospheric deposition contributed substantial N to this river, which provides two-thirds of the annual N load to Chesapeake Bay. Retention of atmospherically deposited N in the watershed was estimated to be higher than 95%. Nevertheless, stream  $\text{NO}_3^-$  patterns exhibited substantial seasonality. Peak values of  $\text{NO}_3^-$  (14–96  $\mu\text{eq/L}$ ) were reached during summer. Lowest values (<1  $\mu\text{eq/L}$ ) occurred in October. The summer's increase in net soil nitrification and in-stream heterotrophic N uptake in response to litterfall during autumn were identified as likely important drivers of the observed  $\text{NO}_3^-$  seasonality. Other studies that included mixed land uses found far lower N retention at larger spatial scales, including the Susquehanna River ([Howarth et al., 2006](#); [Boyer et al., 2002](#)). Using stable isotope analysis, atmospheric deposition was identified as an important source of stream  $\text{NO}_3^-$  concentration at a low  $\text{NO}_3^-$  site at Fernow Experimental Forest, WV ([Rose et al., 2015b](#)). Based on more than 30 years of monitoring data, three hardwood watersheds appeared to be less responsive to changes in N deposition than the one study watershed that had coniferous vegetation. The percentage of stream  $\text{NO}_3^-$  concentration contributed by atmospheric deposition in the study watersheds increased during high-flow periods.

Watershed N budgets and empirical models can be useful for assessing the relative magnitude and sources of N inputs and losses to watersheds via riverine export. A variety of computational approaches can be used. [Alexander et al. \(2002\)](#) compared predictions of total N and stream N transport of six watershed models and showed that models with greater precision were those that had the most detailed descriptions of N sources, water N attenuation, and water flow paths. [Han and Allan \(2008\)](#) compared N budget estimation approaches for 18 catchments located in the vicinity of Lake Michigan. The most robust model suggested that riverine N export constituted about 21% of N inputs. Using a larger data set, [Howarth et al. \(2012\)](#) estimated that 25% of N inputs are exported from the watershed on average. The improved ability to predict N export using methods that incorporated description of agricultural N sources was particularly noticeable when applied to watersheds that had pronounced diversity of land use and geology ([Han and Allan, 2008](#)). Comparisons of watershed N budgets across the U.S. indicates that there is geographic variation in the proportion of N inputs that are exported, and the scaling of

export with runoff indicates that drier conditions may lead to lower proportions of N inputs that are exported by rivers ([Sobota et al., 2009](#)).

Overall, some studies show recent declines in concentrations of  $\text{NO}_3^-$  and TN in surface waters that are consistent with declines in N deposition. Advances in isotopic analysis have allowed for greater characterization of how  $\text{NO}_3^-$  in surface waters affects N cycling and has led to improved understanding of how factors such as seasonality and contribution of snowmelt affect  $\text{NO}_3^-$  concentrations.

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### 7.1.2.2 Sulfate in Surface Waters

Measurements of  $\text{SO}_4^{2-}$  concentration in surface waters provide important information regarding the probable extent of cation leaching in soils and how  $\text{SO}_4^{2-}$  concentrations relate to ambient and past levels of atmospheric S deposition. The 2008 ISA documented widespread declines in surface water  $\text{SO}_4^{2-}$  concentration in response to decreasing S deposition over previous decades. Assessments of acidifying deposition effects reported in the 2008 ISA dating from the 1980s showed  $\text{SO}_4^{2-}$  to be the primary strong acid anion in most, but not all, acid-sensitive waters in the U.S. ([Webb et al., 2004](#); [Driscoll et al., 2001b](#); [Driscoll et al., 1988](#); [Driscoll and Newton, 1985](#)). At the time of the 2008 ISA, available data indicated that before the peak of S emissions in the 1970s and 1980s,  $\text{SO}_4^{2-}$  concentrations in surface waters increased in response to S deposition. After the emissions peak, there were decreasing regional trends in  $\text{SO}_4^{2-}$  surface water concentrations in the 1980s, 1990s, and thereafter, particularly in the Northeast. In some regions, especially the Blue Ridge Mountains region in Virginia, surface water  $\text{SO}_4^{2-}$  remained relatively stable even as emissions declined, due to changes in S adsorption on soils and the release of historically deposited S from soils into surface water. The rate of surface water response was variable by watershed, and some model results suggested that chemical recovery may be delayed as adsorption decreases and accumulated S leaches from watersheds, even as emissions and deposition decline. Recent studies on  $\text{SO}_4^{2-}$  concentration in surface waters continue to show evidence of chemical recovery consistent with reductions in S deposition ([Appendix 7.1.5.1](#)).

Drought has been shown in some situations, where geological S sources are prevalent, to be a partial cause of lake acidification. This was documented at lakes in the Murry-Darling Basin in Australia by [Li et al. \(2017b\)](#). Pyritic sediment rewetting after the drought (2007–2010) caused an extreme decrease in the water pH around the lake margins from above 7 to near 3.

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### 7.1.2.3 Nitrogen Transformations

Nitrogen in surface waters can undergo various chemical transformations in the water column ([Appendix 7.1.2.3.1](#)) and sediments ([Appendix 7.1.2.3.2](#)). It was well known at the time of the 2008 ISA that nitrification and denitrification are quantitatively important portions of the N cycle and that these processes can be influenced by atmospheric inputs of oxidized and reduced N. Nitrification can be important even when N deposition is low. More recent research has further substantiated earlier findings and provided additional quantitative context. At some locations, new research suggests that denitrification may play a larger role than was previously recognized in removing oxidized N from the watershed.

#### 7.1.2.3.1 Water Column Transformations

Much of the deposited  $\text{NH}_4^+$  is either taken up by vegetation or nitrified to  $\text{NO}_3^-$ , which is more mobile in soils than  $\text{NH}_4^+$ . The  $\text{NO}_3^-$ , in turn, can be leached to drainage water or denitrified and released back to the atmosphere as gaseous  $\text{N}_2\text{O}$  or  $\text{N}_2$ . During the nitrification process,  $\text{NH}_4^+$  is oxidized to  $\text{NO}_3^-$  and the  $\text{NO}_3^-$  that is produced can contribute to acidification of soil and drainage waters. The 2008 ISA concluded that nitrification in soil solution is stimulated at soil C:N ratios less than about 20 to 25 ([U.S. EPA, 2008a](#); [Aber et al., 2003](#)). Since the 2008 ISA, additional isotope, modeling, observational, and experiment studies have further characterized denitrification processes.

Only a small portion of the N added to the land surface by human activities is carried by stream flow to estuaries and the ocean ([Boyer et al., 2002](#); [Howarth et al., 1996a](#)). Streams have been shown to provide an important ecosystem service by acting as N sinks ([Mulholland et al., 2008](#)). Denitrification is a critical process that removes N from stream water. Changes in  $\text{N}_2$  concentration over space or time have been used to estimate the denitrification rate at the scale of stream reaches ([McCutchan et al., 2003](#); [Laursen and Seitzinger, 2002](#)) to large river basins ([Mulholland et al., 2008](#); [Alexander et al., 2000](#)).

Nitrous oxide ( $\text{N}_2\text{O}$ ), which is emitted to the atmosphere during the process of denitrification, is a potent greenhouse gas. [Beaulieu et al. \(2011\)](#) presented results of  $^{15}\text{N}$  tracer addition to 72 headwater streams draining multiple land uses across the U.S. Denitrification in the streams produced  $\text{N}_2\text{O}$  at rates that increased with stream  $\text{NO}_3^-$  concentration. The study streams were mostly sources of  $\text{N}_2\text{O}$  to the atmosphere. Results of this study reiterated previous findings that suggested that the process of denitrification may be quantitatively important. In another isotopic study, [Mulholland et al. \(2009\)](#) measured denitrification rates using  $^{15}\text{N}$  tracer addition to 49 streams, including

reference, agricultural-impacted, and suburban/urban streams. The fraction of total  $\text{NO}_3^-$  removed from stream water by denitrification ranged from 0.5 to 100%, with a median of 16%. Removal was related to  $\text{NH}_4^+$  concentration and the ecosystem respiration rate. Although the areal denitrification rate increased with increasing  $\text{NO}_3^-$  concentration, the efficiency of  $\text{NO}_3^-$  removal from water via denitrification declined. This resulted in a smaller proportion of stream water  $\text{NO}_3^-$  load removed over a given length of stream at higher N loading.

Freshwater nutrient cycling studies have also focused some attention on N fixation. In Waco Reservoir, TX, [Scott et al. \(2008\)](#) measured N fixation over a 19-month period and linked those data with nutrient-loading estimates derived from a physically based watershed model. Readily available topographic, soil, land cover, effluent discharge, and climate data were used in the Soil and Water Assessment Tool (SWAT) model in order to derive estimates of nutrient loading from the watershed to the reservoir. Results suggested that human activities in the watershed can exert significant control over planktonic N fixation.

#### **7.1.2.3.2 Sediment Nitrogen Transformations**

The deposition and transport of N derived from human sources is partially ameliorated by bacterially mediated denitrification in sediments. The conversion of  $\text{NO}_3^-$  to  $\text{N}_2$  gas permanently removes N from the watershed ([Seitzinger et al., 2006](#); [Galloway et al., 2003](#)). It has been estimated that denitrification in lakes may remove up to about 30% of the inputs to surface waters ([McCrackin and Elser, 2012](#); [Harrison et al., 2009](#); [Wollheim et al., 2008](#)).

Residence time of water in the sediments and hydraulics can be important controls on nutrient uptake in headwater streams. [Drummond et al. \(2016\)](#) characterized water transient storage zones and their effects on nutrient uptake in the sediments of two headwater streams in Spain. These zones represented regions of slow-moving water and temporary water retention in stream sediments. Modeled exchange between the water column and retention zones explained more than 40% of the variation in  $\text{NH}_4^+$  uptake.

A study by [Bellinger et al. \(2014\)](#) provided additional evidence that bacterially mediated denitrification in lake sediments can partly ameliorate the effects of N loading from the atmosphere by permanently removing some of the N inputs. [McCrackin and Elser \(2012\)](#) also measured denitrification in sediments, in this case from lakes in the Colorado Rocky Mountains. The study lakes received either elevated (357–571 eq N/ha/yr) or low (<142 eq N/ha/yr) inputs of atmospheric N deposition. The  $\text{NO}_3^-$ -N concentration was significantly higher in high-deposition lakes (0.1582 mg/L) compared to low deposition

lakes (0.0462 mg/L). The researchers concluded that the sampled lakes were capable of removing a significant portion of N inputs via denitrification in the lake sediment. They found no difference between high- and low-deposition lakes in the extent to which chronic N loading has altered sediment denitrification capacity. The abundance of denitrifying bacteria in this study was largely related to light availability. An earlier study by [McCrackin and Elser \(2010\)](#) measured rates of denitrification and N<sub>2</sub>O production during denitrification in the sediments of 32 Norwegian lakes at the high and the low ends of a gradient of atmospheric N deposition. They also found that denitrification varied with N loading. The findings also suggested that lake sediments may be an important source of N<sub>2</sub>O emissions, which play a role in climate warming, particularly in areas that are subject to elevated N deposition levels. Results of new research by [McCrackin and Elser \(2012\)](#) support growing evidence that lake sediments can play important roles in N removal, although it appears that recent levels of N deposition have not altered the abundance of denitrifying bacteria or saturated the capacity for sediment denitrification in Rocky Mountain lakes.

Organic matter can also influence the rate of denitrification in sediments. [Fork and Heffernan \(2014\)](#) investigated how DOC derived from terrestrial ecosystems affects the rate of denitrification in river sediments. They examined the extent to which higher concentrations of DOC in black water rivers stimulate or inhibit denitrification. Results supported the hypothesis that terrestrially derived DOC might indirectly inhibit denitrification via a decrease in autochthonous production. Therefore, changes in DOC concentration might change the ability of inland waterways to remove reactive N from the aquatic ecosystem.

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#### **7.1.2.4 Sulfur Transformations**

Studies of S cycling reported in the 2008 ISA emphasized the importance of S adsorption and desorption and their interactions with soil pH ([Appendix 4](#)). The importance of S adsorption on soils in the southern Appalachian Mountains was further confirmed by S budget studies reported by [Rice et al. \(2014\)](#). In addition, internal watershed sources of SO<sub>4</sub><sup>2-</sup> (e.g., S mineralized from soil organic matter), which were previously relatively minor sources to surface water in the northeastern U.S., have become proportionately more important as S deposition has declined ([Appendix 4](#)).

Both chronic and episodic leaching of SO<sub>4</sub><sup>2-</sup> from terrestrial ecosystems influence surface water acidification. The literature reviewed in the 2008 ISA did not fully address how terrestrial S cycling affects water sulfate concentrations. More recently, [Rice et al. \(2014\)](#) calculated SO<sub>4</sub><sup>2-</sup> mass balances for 27 watersheds in the Appalachian Mountain region.

Results suggested that many watersheds where  $\text{SO}_4^{2-}$  inputs are currently retained will begin releasing more  $\text{SO}_4^{2-}$  to drainage water in the near future. [Dewalle et al. \(2016\)](#) evaluated Appalachian forested watersheds and estimated the lag times between changes in S deposition and consequent watershed responses. Lag times were generally consistent and significant for S in the forest basins that demonstrated relatively high soil S retention and high N retention. [Strock et al. \(2016\)](#) investigated the effects of extreme (wet or dry) weather on the chemistry of 84 lakes across the northeastern U.S. The average differences in lake water  $\text{SO}_4^{2-}$  concentrations were about 2–3  $\mu\text{eq/L}$  higher in 2001 (dry year) as compared with the average observed during the entire study period 1990–2010. This has implications for S cycling as the climate changes.

Some of the  $\text{SO}_4^{2-}$  leached from soil, as well as the  $\text{SO}_x$  deposited directly into surface water, is reduced and retained in aquatic sediments as hydrogen sulfide, especially in wetlands. However, S stored in reduced form in sediments can be subsequently reoxidized and become available for down-gradient transport as  $\text{SO}_4^{2-}$  during periods of high discharge, particularly during hydrologic events that follow periods of drought. The leaching of  $\text{SO}_4^{2-}$  then can contribute to a variety of ecological effects ([Appendix 8](#) and [Appendix 12](#)). When  $\text{SO}_4^{2-}$  is released from catchment soils to drainage water, it is accompanied by an equivalent amount of cationic counter-charge in the form of acidic ( $\text{H}^+$ ,  $\text{Al}^{3+}$ ) or basic ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) cations ([U.S. EPA, 2008a](#)), affecting the concentrations of parameters addressed in the following sections of this report.

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### 7.1.2.5 Surface Water pH

Surface water pH is commonly used as an indicator of acidification. This was the case in the 2008 ISA, and nothing has changed in that regard in more recent years. It correlates with other biologically important components of surface water acid-base chemistry, including estimates of organic acidity and concentrations of inorganic Al and  $\text{Ca}^{2+}$ . Low pH can have direct toxic effects on aquatic species [[Driscoll et al. \(2001b\)](#); [U.S. EPA \(2008a\)](#); [Appendix 8.3](#)] and this was widely understood at the time of the 2008 ISA. Low pH can disturb normal ion osmoregulation in aquatic biota. Threshold pH levels for adverse biological effects are described in [Appendix 8](#) and [Table 8-2](#). A pH value of 6.0 is often considered the level below which biota are at increased risk from acidification, but some waters can have pH below this threshold in the absence of acidic deposition. This is most commonly caused by relatively high levels of natural organic acidity. Below pH 5.5, inorganic Al often becomes the greatest threat to aquatic biota, especially in low-DOC waters. In the 2008 ISA, increasing trends in pH in surface waters in the northeastern U.S. were common through the 1990s up to 2004 and have continued in

more recent times at many locations ([Appendix 7.1.5.1](#)). Rates of change have generally been relatively small.

Surface water pH (as well as other parameters) is sensitive to hydrological conditions at the time of sampling. [Burns et al. \(2008b\)](#) sampled 12 Catskill mountain streams within the Neversink River watershed in New York for stream chemistry. The measured pH values in 2003 were generally lower than those in 1987 and this was attributed to higher stream flow during the summer of 2003, rather than to chronic acidification during the intervening period. There were no significant differences in biota observed between 1987 and 2003. Although surface water pH is a common alternative to ANC as an indicator of acidification, at pH values above about 6.0, pH is of less value as an indicator of either sensitivity to acidification or level of effect. In addition, pH measurements (especially at these higher values) are sensitive to levels of dissolved CO<sub>2</sub> in the water, which is influenced by plant root respiration.

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#### **7.1.2.6 Surface Water Acid Neutralizing Capacity**

The most widely used measure of surface water acidification, and subsequent recovery under reduced acid deposition, is ANC. Most aquatic critical load (CL) studies conducted in the U.S. have used surface water ANC as the principal metric of water quality change in response to changes in acidic deposition ([Appendix 7.1.5.2](#)). It is typically either determined by Gran titration in a laboratory (titrated ANC) or calculated from the charge balance (calculated ANC or CALK). Titrated ANC is useful because it reflects the ANC of the complete chemical system, which is typically decreased by acidic deposition in acid-sensitive landscapes. The ANC is associated with the surface water constituents that directly cause or reduce acidity-related stress, in particular pH, Ca<sup>2+</sup>, and inorganic Al concentrations. The ANC is generally a more stable measurement than pH because ANC is insensitive to changes in CO<sub>2</sub> and it reflects sensitivity and effects of acidification in a linear fashion across the full range of ANC values. Therefore, ANC is usually the preferred indicator for assessment of surface water acidification and recovery. Both titrated and calculated ANC values are commonly determined in studies aimed at resource characterization or long-term monitoring. Models simulate calculated ANC. The two measures can differ greatly, depending mainly on the amount of organic acidity and dissolved Al in the water. The BCS ([Lawrence et al., 2007](#)) is an alternate index to ANC that integrates acid-base status and accounts for the influence of natural organic acidity.

As described in the 2008 ISA, ANC is typically used as the primary chemical indicator for assessing past effects of acidifying deposition on aquatic biota and the recovery expected from decreasing acidic atmospheric deposition ([Sullivan et al., 2006a](#); [Aber et](#)

[al., 2003](#); [Bulger et al., 2000](#)). Notably, the ANC level that reflects recovery of pH or inorganic Al may differ between the acidification and recovery phases [[Hesthagen et al. \(2008\)](#); [Appendix 7.1.5.1](#)]. In general, ANC measures over the past two to three decades in the northeastern U.S. suggest rather modest increases in ANC in many surface waters in response to large decreases in acidic deposition and surface water  $\text{SO}_4^{2-}$  concentration ([Appendix 7.1.5.1](#)).

Information on biological indicators of acidification such as fish species richness that are associated with changes in ANC are presented in [Appendix 8](#). There is often a positive relationship between ANC and number of fish species, at least for ANC values between about 0 and 50 to 100  $\mu\text{eq/L}$  ([Cosby et al., 2006](#); [Sullivan et al., 2006a](#); [Bulger et al., 1999](#)). Lakes and streams having ANC  $<0$   $\mu\text{eq/L}$  generally do not support fish. Loss of fish species seems to occur with decreases in ANC below a threshold of approximately 50 to 100  $\mu\text{eq/L}$  ([Sullivan et al., 2006a](#)).

Sensitive water bodies can be defined as those that have ANC of 100  $\mu\text{eq/L}$  or less. Sensitivity increases with further decreases in ANC. Al mobilization is largely confined, however, to waters that have pH less than about 5.5, which corresponds with ANC in the range of about 10 to 30  $\mu\text{eq/L}$  in low-DOC to moderate-DOC (less than about 400  $\mu\text{M}$ ) waters in the Northeast. Therefore, inorganic Al is not a useful indicator of acidification or chemical recovery in waters that have ANC higher than about 10–30  $\mu\text{eq/L}$ . Thus, evaluation of improvement in biologically relevant water chemistry in response to decreases in acidic deposition should perhaps include assessment of response using both the ANC and inorganic Al metrics.

[Povak et al. \(2013\)](#) reported the ANC of over 900 streams in the southern Appalachian Mountains, and estimated ANC at other stream segments throughout the region using observed relationships between ANC and watershed characteristics. Low stream ANC was commonly found at locations that exhibited siliciclastic geology; cool, short, and moist growing seasons; high clay soil content; low soil pH; and small forested watersheds.

[Sullivan \(2017\)](#) constructed a map of surface water ANC across the U.S. that included nearly 20,000 unique locations sampled between 1980 and 2011 ([Figure 8-11](#)). Samples expected to be strongly influenced by acid mine drainage, sea salt spray, or road salt application were excluded. He found 6,065 sites that had ANC  $<100$   $\mu\text{eq/L}$ . Waters having ANC  $\leq 0$   $\mu\text{eq/L}$  were mostly restricted to northern New York, New England, the Appalachian Mountain chain, upper Midwest, and Florida. In addition, low, but positive, ANC values were found in high-elevation portions of the West and parts of Arkansas and the Gulf states. These spatial patterns in surface water ANC are thought to mainly reflect the influence of soil base cation supply on ANC.

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### 7.1.2.7 Base Cation Concentrations

Quantitatively, the most important component of the overall surface water acidification and chemical recovery response to atmospherically deposited S and N (and associated  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations) has been a change in base cation supply ([Charles and Christie, 1991](#)). As stated in the 2008 ISA, decreases in base cation concentrations in surface waters in the eastern U.S. over the past two to three decades have been ubiquitous and closely tied to trends in  $\text{SO}_4^{2-}$  concentrations in surface waters. In most regions, rates of decrease for base cations have been like those for  $\text{SO}_4^{2-}$  plus  $\text{NO}_3^-$ , with the exception of streams in western Virginia and in Shenandoah National Park, which are strongly affected by  $\text{SO}_4^{2-}$  adsorption on soils. The 2008 ISA concluded that acidifying deposition has been an important cause of decreasing amounts of exchangeable base cations on soils. This influences base cation leaching to surface waters and soil buffering of deposition acidity. Surface water base cation concentrations increase with acidification and generally decrease under reduced levels of acidic deposition. However, in some watersheds that have acidified, concentrations of  $\text{Ca}^{2+}$  and other base cations have become substantially reduced from likely preindustrial levels, in response to depletion by many years of acidic deposition. This base cation depletion constrains surface water ANC and pH recovery, as described in the 2008 ISA. Recent results have further corroborated these earlier findings. More recent studies have included experiments (liming), modeling, and gradient studies with geographical focus on the Adirondack Mountains, southern Appalachian Mountains, Rocky Mountains, and the Hubbard Brook Experimental Forest (HBEF) in New Hampshire.

Base cations are contributed to soils and surface waters through weathering and atmospheric base cation deposition ([Appendix 4](#)). Estimates of base cation weathering ( $\text{BC}_w$ ) largely control simulated base cation concentrations in drainage water and are needed for evaluating CLs of surface water acidity using steady-state models ([Appendix 8](#)). [McDonnell et al. \(2012\)](#) developed an approach for regionalizing  $\text{BC}_w$  using regionally specific empirical relationships. The dynamic model MAGIC was used to calibrate  $\text{BC}_w$  in 92 watersheds distributed across the southern Appalachian Mountains. About one-third of the study region had  $\text{BC}_w$  estimates that were less than 1,000 eq/ha/year, with lowest values for watersheds located in national parks and wilderness areas.

Base cation surplus is defined as the difference between the summed concentrations of base cations (Ca, Mg, Na, K) and strongly acidic inorganic anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , chloride), minus an estimate of the strongly acidic organic anions estimated from dissolved organic C and an assumed charge density. These strongly acidic organic anions are dissociated at low pH, and function essentially as mineral acid anions in terms of their

effect on ANC. The BCS is an alternative statistic to ANC for use mainly in waters that have appreciable natural organic acidity.

In high-elevation portions of three watersheds in the southern Appalachian Mountains, [Knoepp et al. \(2016\)](#) found that stream acid-base chemistry was related to the concentrations of N and Al in the soil O-horizon and to the total amount of C and Ca in the soil. Each watershed contained four to six first-order catchments with moderate to high levels of acid sensitivity (ANC 11–50  $\mu\text{eq/L}$ ). Differences across catchments in stream ANC, pH, and the ratio of Ca:Al concentrations were also significantly correlated with watershed vegetation, as reflected in basal area, tree height, and diameter at breast height.

In the Muskoka River Watershed in Ontario, Canada, further improvement in lake ANC and pH might be limited by Ca depletion, which can be made worse by tree harvesting ([Reid and Watmough, 2016](#)). More than 60% of the tree Ca is commonly found in the bark and boles, which are largely removed from the watershed during timber extraction. The authors estimated that timber harvesting at planned levels will cause approximately a 30% increase in the number of sampled lakes that decline to Ca levels below 1 mg/L.

Changes in acidic deposition exert complex effects on the concentration of Ca in surface waters. During the early phases of soil and water acidification, acidic deposition increases the leaching of Ca from soil to drainage water. This Ca leaching causes increased concentrations of Ca in streams and lakes. In base-poor watersheds having thin soils, the rate of Ca leaching can exceed the resupply via weathering and atmospheric input. Over time, soil base saturation decreases, and the concentration of Ca in runoff decreases, perhaps to levels lower than what existed prior to the advent of acidic deposition. Decreases in acidic deposition will further accentuate this Ca depletion. Decline in lake water Ca concentration has severe consequences for some species of zooplankton, especially *Daphnia* species that have high Ca requirements. [Jeziorski et al. \(2008\)](#) documented major reductions in abundance of Ca rich *Daphnia* spp., keystone herbivores in pelagic food webs, in association with decreases in the concentration of Ca in lake water. They reported that a high proportion of Canadian Shield lakes had Ca concentration near or below the threshold level (1.5 mg/L) for decreased survival and fecundity in laboratory studies. Ecological impacts of these changes on food webs may be substantial.

Increased atmospheric transport of dust enriched with nutrients, metals, and base cations to alpine watersheds in the western U.S. has been shown to alter lake biogeochemical processes. [Ballantyne et al. \(2011\)](#) examined temporal trends in dust deposition from sediment cores collected from two lakes in Colorado with distinct physical and chemical properties. Recent increases in dust deposition and its enrichment in various elements,

including Ca, has contributed base cations to drainage water and altered the biogeochemistry of the two study lakes.

Liming studies confirm ecosystem responses when depleted base cation pools in soils are restored by addition of base cations experimentally or for management purposes. In a base cation addition study (45,000 kg of calcium silicate [wollastonite,  $\text{CaSiO}_3$ ]) in HBEF, increases in the concentrations of Ca and decreases in the concentrations of  $\text{H}^+$  and inorganic Al in stream water were observed and stream ANC increased ([Cho et al., 2012](#)). By the end of 2010, an estimated 3 to 5% of added Ca was exported in stream water and the Ca retained in the watershed was detected in lower soil horizons or taken up by vegetation ([Shao et al., 2016](#); [Johnson et al., 2014](#)). Exchangeable Ca increased significantly and exchangeable Al decreased significantly in the organic and upper mineral soils over the years following wollastonite addition ([Johnson et al., 2014](#)).

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#### **7.1.2.8 Surface Water Aluminum**

As stated in the 2008 ISA, the concentration of dissolved inorganic monomeric Al in surface waters is an especially useful indicator of acidifying deposition effects because (1) it is toxic to many species of aquatic biota ([Appendix 8](#)) and (2) it generally does not leach from soils to surface waters in the absence of input of strong acids [e.g., sulfuric acid, nitric acid, strong organic acid anions; [Driscoll et al. \(1988\)](#); [Lawrence et al. \(2007\)](#)]. It has well-documented effects on aquatic biota at specific thresholds ([Appendix 8](#)). In the 2008 ISA, limited data suggested that some acid-sensitive surface waters in regions of the northeastern U.S. have elevated inorganic Al concentrations, which have been induced by years of acidifying deposition and pose threats to aquatic life. Since the 2008 ISA, several monitoring studies have reported decreases in inorganic Al suggestive of chemical recovery of surface waters [[Warby et al. \(2008\)](#); [Strock et al. \(2014\)](#); [Driscoll et al. \(2016\)](#); [Baldigo et al. \(2016\)](#); [Appendix 7.1.5.1](#)].

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#### **7.1.2.9 Surface Water Dissolved Organic Carbon Concentration**

An especially important, and relatively new, area of research focus in the context of recovery from surface water acidification has been the observed increase in DOC or total organic carbon (TOC) concentration in many surface waters recovering from acidification. This has implications with respect to water toxicity and cycling of C, Al, and N. Changes in lake DOC are important because DOC helps to regulate biological, chemical, and physical lake characteristics by adding C, changing pH, affecting nutrient cycling, and changing the availability of toxic metals, including Al. Lake DOC regulates

UV light penetration into the water column and the amount and depth of photosynthetically active radiation (PAR), which affects the lake mixing depth, especially in small lakes. Increased DOC contributes to shallower mixing depth and greater fluctuation in diel temperature and may affect lake nutrient status ([Gerson et al., 2016](#)). Increases over the past two to three decades in lake DOC in the northeastern U.S. have likely been part of the chemical recovery from previous lake acidification ([SanClements et al., 2012](#); [Monteith et al., 2007](#)) and/or caused or exacerbated by changes in climate, including precipitation patterns ([Couture et al., 2012](#); [Weyhenmeyer and Karlsson, 2009](#)).

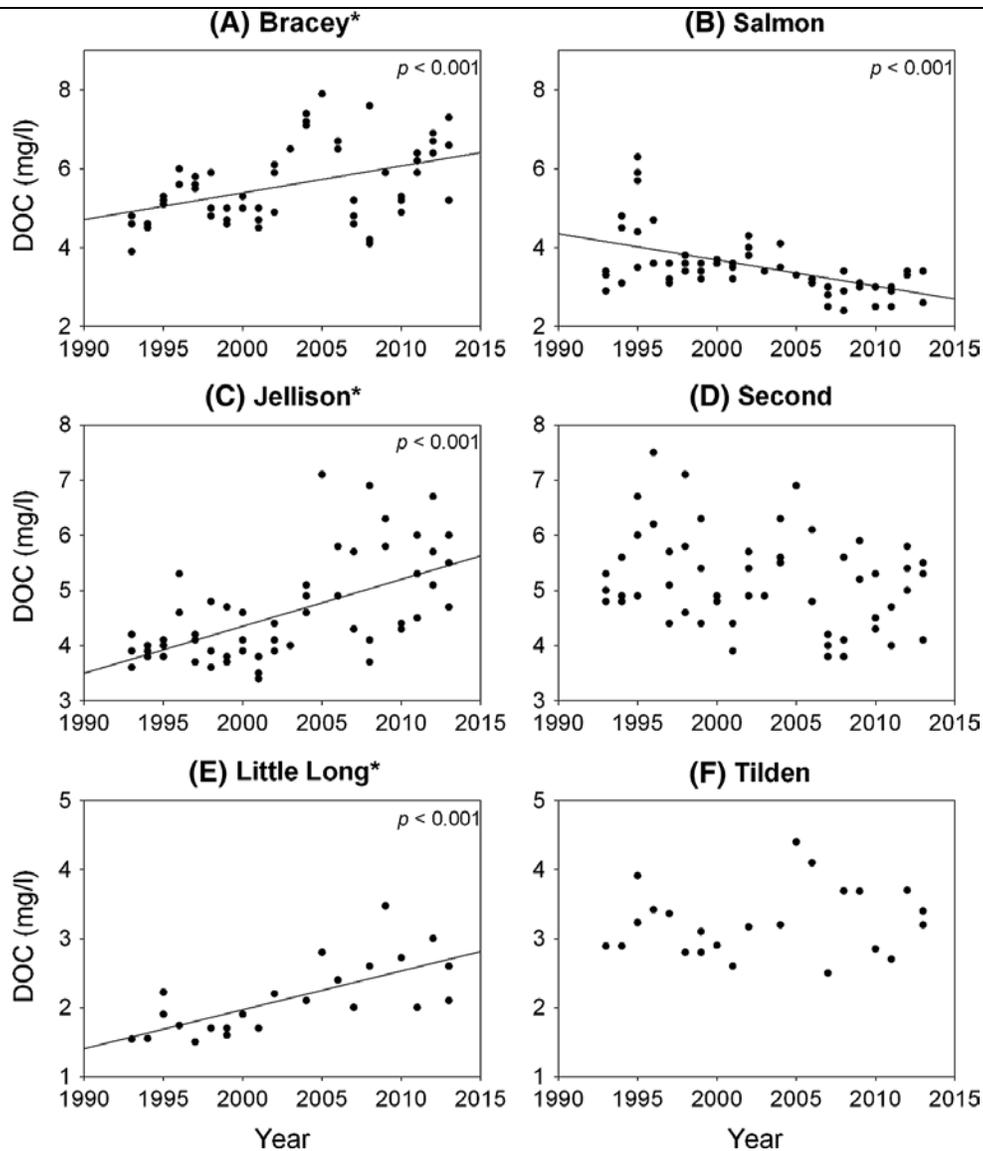
The 2008 ISA reported widely observed increased concentrations of DOC or TOC in surface waters across North America and Europe and that these increases were at least partly related to changes in atmospheric deposition of S and N. Thus, it has been recognized for well over a decade that surface water organic carbon concentrations have decreased to some extent in many water bodies that previously experienced water acidification. Therefore, DOC concentration would likely increase with recovery. More recent research on this topic has been diverse and has included experiments, observation, isotope studies, and synthesis and integration work. Overall, they illustrate relatively large increases in DOC with acidification recovery in some aquatic systems. This response constrains the level of ANC, and especially pH, recovery, but decreases the toxicity of dissolved Al by converting some of it from inorganic to organic forms ([Lawrence et al., 2013](#)). As a result of this widely observed pattern, surface water DOC concentration has become an important focus of water acidification and recovery research ([Appendix 7.1.5.1](#)).

DOC is comprised of a diverse mix of organic matter and functional groups. [Wood et al. \(2011\)](#) noted that dark, aromatic-rich organic matter with relatively high humic content and of allochthonous origin may be more effective in ameliorating metal bioavailability and toxicity than other organic materials. In addition, part of the protection provided by DOC may involve physiological mechanisms other than metal complexation ([Wood et al., 2011](#)). Soil mechanisms that contribute to higher DOC in surface waters are discussed in [Appendix 4](#). At the Niwot Ridge Long-Term Ecological Research site in Colorado, [Miller and Mcknight \(2015\)](#) reported downstream transport of dissolved organic matter (DOM) that had been produced in alpine lakes during low-flow periods.

Recent research suggested that increases in lake DOC may have changed key functions of affected lakes, causing decreased vertical distribution of phytoplankton and changes in phytoplankton species composition. This was investigated by [Brown et al. \(2017\)](#), who demonstrated that increases in lake DOC can potentially change the thermal structure of lakes, but that effects are variable. They analyzed fossil diatom remains in sediment cores collected from three pairs of small remote Maine lakes. Each pair consisted of one lake

that showed recent increases in DOC since the early 1990s and a similar lake that did not show increasing DOC. The focus was on changes in the relative abundances of diatom taxa that were known to reflect effects on thermal stratification, specifically *Discostella stelligera* and *Aulacoseira* spp. [Saros et al. \(2012\)](#) had constructed a diatom inference model for reconstructing past lake mixing depth based on the relative abundance of *D. stelligera*, which prefers shallower mixing depth. [Stone et al. \(2016\)](#) expanded this model and included species of *Aulacoseira*. [Brown et al. \(2017\)](#) hypothesized that those lakes that had experienced recent DOC increases (shown in [Figure 7-3](#)) would show increased diatom turnover and increases in the relative abundance of *D. stelligera* and *Aulacoseira* spp. since the 1990s. The three study lakes that had no increase in DOC also showed minimal change in the identified sensitive taxa. The three lakes that experienced recent increases in DOC showed variable diatom responses. Results were interpreted as being indicative of the potential of DOC to change the physical and biological structure of lakes that have experienced past or ongoing chemical recovery from prior lake acidification. The largest changes in diatom taxa occurred in two of the lakes that had experienced recent increases in DOC.

DOC effects on N cycling have been further elucidated since the 2008 ISA. [Rodriguez-Cardona et al. \(2016\)](#) and [Wymore et al. \(2016\)](#) suggested greater  $\text{NO}_3^-$  removal from drainage water under conditions of relatively high DOC and high ratio of  $\text{DOC}:\text{NO}_3^-$  concentration. Results of the study of [Fork and Heffernan \(2014\)](#) further suggested that the indirect effects of DOC on light will be important in determining how N cycling responds to increasing concentrations of DOC in surface waters. Under conditions of increased DOC, the quality of DOM may change, as may its binding with dissolved Al ([Fakhraei and Driscoll, 2015](#)). Dynamics of DOC may also have consequences for eutrophication of downstream ecosystems, but interactions appear to be complex.



Notes: Linear regression lines are shown for significant trends ( $p < 0.05$ ). Asterisk indicates lakes with a significant DOC increase. Source: [Brown et al. \(2017\)](#).

**Figure 7-3 Dissolved organic carbon (DOC) concentrations from 1993 to 2013 for Bracey Pond (a), Salmon Pond (b), Jellison Pond (c), Second Pond (d), Little Long Pond (e), and Tilden Pond (f) in Maine.**

Short-term studies to characterize acid-base chemistry have provided information on surface water quality and biogeochemistry of organic materials. [Kang and Mitchell \(2013\)](#) studied spatial and temporal variation in the quantity and quality of DOC, N, and S in Adirondack Mountain surface waters over a 14-month period. This investigation

included the sampling of two upland streams, two wetland-influenced streams, and one lake outlet (Arbutus Lake). The DOC and dissolved organic N (DON) concentrations increased as water was transported through wetland areas. Results highlighted the value of applying multiple approaches for understanding the biogeochemistry of DOM. The acid-base chemistry of DOC has been further investigated in several other studies. [Porcal et al. \(2009\)](#) confirmed that DOC concentrations in lakes and streams throughout much of Europe and North America have increased over the last three decades. Possible reasons for this change proposed by [Porcal et al. \(2009\)](#) included increased atmospheric CO<sub>2</sub> concentration, climate warming, decreased S deposition (and associated changes in water pH and ionic strength), and hydrologic changes caused by drought and precipitation. Any changes in DOC concentration or properties will impact the acid-base chemistry of surface waters and perhaps the composition of aquatic biota. In a laboratory study, [Al-Reasi et al. \(2013\)](#) performed titrations for a range of freshwater DOM isolates. In general, the proton site density ( $L_T$ ) exhibited maxima near proton binding constants ( $pK_a$ ) values of 3.5 and 10, reflecting the presence of both strong and weak organic acids. The Proton Binding Index parameter was described to summarize the chemical reactivity of DOM based on the  $pK_a$  values and the  $L_T$ . Results of this study provided a rationale for describing the protection provided by DOM against metal, including inorganic Al, toxicity. Recent additional research has also focused on improving scientific understanding of variation in the importance of organic versus mineral acids in controlling the acidity of soil water and surface water. [Chapman et al. \(2008\)](#) analyzed seasonality in soil water and surface water chemistry in two U.K. headwater watersheds. Strong seasonal patterns were observed for both ANC and DOC. Acidic deposition-controlled acidity during winter, whereas organic acids were more important during summer. The observed increase in DOC concentration in drainage water over the previous two decades was attributed mainly to climate warming, increased CO<sub>2</sub>, and/or decreased acidic deposition.

[SanClements et al. \(2012\)](#) used a chemical signature of terrestrial DOM to investigate the extent to which increased DOC concentrations in surface water since about 1993 in the northeastern U.S. have been driven by decreasing acidic deposition and increasing solubility of soil organic matter. They used fluorescence spectroscopy to characterize the quality of DOM in stored samples that had been collected from nine acid-sensitive lakes in Maine. Decreases in lake water SO<sub>4</sub><sup>2-</sup> concentration were associated with increases in DOC concentration and a shift during ecosystem recovery from microbial to terrestrially derived DOM. Changes in the quality or quantity of DOM can affect aquatic ecosystem functions. Dissolved organic matter is important for providing food for microbes, attenuating light, buffering pH, binding Al, and controlling the cycling of nutrients ([SanClements et al., 2012](#)).

The amount and composition of DOC mobilized from upland soils to surface waters is an important link in the global C cycle. The relationship between ultraviolet (UV) absorbance and DOC concentration has been shown to reflect the aromaticity of the DOC. [Dawson et al. \(2009\)](#) reported a change in correspondence between UV absorbance and DOC concentration over a period of 22 years at two moorland watersheds in Scotland. The DOC concentration has increased over time, while the proportion of hydrophobic DOC has decreased. A model analysis by [Dawson et al. \(2009\)](#) suggested that S deposition was the only factor that could reasonably explain the observed long-term DOC trend at both sites.

[Valinia et al. \(2015\)](#) used visible near-infrared spectroscopy of lake sediments to reconstruct the reference condition TOC in Swedish lakes. Long-term monitoring data were used to simulate recent changes in TOC and then analyzed using two empirical models. The first predicted historical TOC trends between reference conditions in the year 1860 and peak acidification in approximately the year 1980. The second model predicted TOC between 1988 and 2012 in conjunction with partial chemical recovery from acidification. The models were driven by lake and watershed area, the number of wetlands, historical S deposition, and current water chemistry. The researchers estimated that the present-day TOC concentrations are similar to reconstructed reference conditions in Swedish lakes. Thus, it was deemed unlikely that the TOC concentrations in Swedish lakes will continue to increase with continued controls on acidic deposition.

In a monitoring study from the Czech Republic, [Hruška et al. \(2009\)](#) reported high DOC in two watersheds: 18.8 mg/L and 20.2 mg/L at the acidic and base-rich watersheds, respectively. Between 1993 and 2007, the concentrations of DOC in stream water increased by about 65% at both streams. Increases in stream water DOC were associated with small increases in stream pH, but large decreases in ionic strength due to declining acidic deposition. Although neither of the catchments showed changes in soil water pH, DOC concentrations in soil water tripled. [Hruška et al. \(2009\)](#) concluded that the change in ionic strength of soil water and stream water, rather than acidity, was the major cause of increased stream water DOC. Changes in temperature, precipitation, and discharge during the study suggested that climate change may be an additional important control of DOC dynamics. The role of ionic strength in modifying temporal patterns of surface water DOC in the U.S. has not been studied at the time of this writing. [Evans et al. \(2017\)](#) also documented decreased lake DOC in response to reacidification of a moorland lake catchment in the U.K. In addition, the quality of the DOC changed towards higher levels of aromatic organic compounds and an increase in particulate organic C.

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### 7.1.2.10 Climate Modification of Ecosystem Response to Nitrogen and Sulfur

Surface water chemistry and chemical recovery ([Appendix 7.1.5.1](#)) of fresh waters are occurring within the context of projected changes in annual mean temperature and magnitude of precipitation associated with climate change ([Greaver et al., 2016](#)). In acid sensitive regions, altered hydrologic regimes are likely to affect weathering rate of base cations, lake water levels, and organic matter inputs to catchments ([Adrian et al., 2009](#); [Porcal et al., 2009](#)). Projected shifts in runoff, timing, and quantity of flushing will alter the frequency and duration of episodic events and the concentrations of nutrients and chemical indicators in surface waters ([Adrian et al., 2009](#); [Whitehead et al., 2009](#)). Extreme weather years (wet or dry) can shift water chemistry responses such as DOC and  $\text{SO}_4^{2-}$  concentrations ([Strock et al., 2016](#)). Increased loading of DOC to surface waters, attributed in part to increasing temperatures and changes in precipitation, may affect biogeochemical processes and nutrient availability ([Daggett et al., 2015](#); [Zhang et al., 2010](#); [Weyhenmeyer and Karlsson, 2009](#)). [Appendix 13](#) includes a more detailed discussion of how climate (e.g., temperature and precipitation) modifies ecosystem response to acidification.

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### 7.1.3 Freshwater Monitoring and Databases

Long-term monitoring of surface water chemistry over time has enabled a greater understanding of ecosystem response to deposition of N and S, including chemical and biological responses. Monitoring data inform determination and quantification of temporal trends and many monitoring studies for acidification have been ongoing for one or two decades, in some cases longer. Such data were available and incorporated into the 2008 ISA. Since that time, nearly a decade's worth of additional data have been added to some of these databases. This is noteworthy because short-term temporal variability can mask small changes that are part of a long-term trend. The availability of these additional data facilitates trend detection now, compared with 2008. A number of monitoring studies have been conducted or continued in recent years that document nutrient dynamics in water bodies in response to N inputs. Recent evidence that P deposition is increasing ([Appendix 9.1.1.4](#)) may contribute to total nutrient loading and affect shifts in lake nutrient status.

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### 7.1.3.1 Acidification

A number of freshwater monitoring studies have been conducted using data collected over the previous one to three decades that have documented ecosystem chemical damage and recovery ([Appendix 7.1.5.1](#)) caused by acidifying deposition of S and/or N. Many of these studies have been conducted in the U.S., especially in the Northeast and the southern Appalachian Mountains ([Table 7-3](#)), including a number of studies since 2008. Two surface water chemistry monitoring programs that have been especially useful to inform the assessment of aquatic ecosystem responses to changes in acidic atmospheric deposition have been Temporally Integrated Monitoring of Ecosystems [TIME; [Stoddard et al. \(1996\)](#)] which is no longer operating, and the U.S. EPA Long-Term Monitoring (LTM) project ([Stoddard et al., 1998](#); [Ford et al., 1993](#)). These U.S. EPA monitoring efforts focus on portions of the U.S. most affected by the acidifying influence of S and N deposition, including lakes in the Adirondack Mountains of New York and in New England, and streams in the Northern Appalachian Plateau and the Blue Ridge physiographic provinces in Virginia and West Virginia. Both projects are operated cooperatively with numerous collaborators in state agencies, academic institutions, and various federal agencies.

The Adirondack Lakes Survey Corporation (ALSC) has been monitoring Adirondack lakes for about 30 years. This work has mainly focused on acid-base chemistry but has also involved some fish monitoring and measurement of parameters relevant to nutrient enrichment. Monitoring data have shown some chemical recovery from lake acidification, reflected in increased pH and ANC and decreased inorganic Al concentrations ([Appendix 7.1.5.1](#)). HBEF in NH also has several decades of monitoring data. The central and southern Appalachian Mountains region is important because (1) it contains an abundance of low-ANC streams situated on base-poor geology, (2) atmospheric S and N deposition have been high, (3) S adsorption on soils complicates acidification/recovery responses, and (4) much of the acid-sensitive landscape is managed as national park and wilderness area. New studies have been conducted of stream acid-base chemistry throughout this region in West Virginia, Maryland, Virginia, and Tennessee. More recent monitoring studies are highlighted below and in [Table 7-3](#).

Since the early 2000s, U.S. EPA, together with states, tribes, other entities, and individuals, have collaborated on a series of statistically representative surveys (National Aquatic Resource Surveys [NARS]) of the nation's waters, including surveys of lakes ([U.S. EPA, 2016h](#), [2009b](#)), streams ([U.S. EPA, 2016i](#)), wetlands ([U.S. EPA, 2016j](#)), and coastal waters ([U.S. EPA, 2016g](#)). Based on standard sampling and analysis protocols and consistent quality assurance, these surveys periodically assess the magnitude and spatial extent of water quality issues and concerns across the U.S.

**Table 7-3 Monitoring and resurvey results of aquatic acidification and/or chemical recovery since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Process	Acidification Indicator	Nutrient Enrichment Indicator	Type of Ecosystem	Region	Time Period	Ambient N/S Deposition kg/ha/yr	Effect of Deposition	Publication
Chemical recovery	pH, ANC, SO <sub>4</sub> <sup>2-</sup> , DOC	N/Ap	12 streams	Adirondack Mts.	1980s–2008	Variable	On average, pH increased by 0.28; ANC increased 13 µeq/L; rate of decrease in stream SO <sub>4</sub> <sup>2-</sup> concentration was 2 µmol/L/yr between 1999 and 2008 at a high-DOC stream and 0.73 µmol/L/yr at a low-DOC stream.	<a href="#">Lawrence et al. (2011)</a>
Chemical recovery	pH, ANC, SO <sub>4</sub> <sup>2-</sup> , DOC, NO <sub>3</sub> <sup>-</sup> , Al <sub>i</sub>	NO <sub>3</sub> <sup>-</sup>	48 lakes (16 lakes that were part of the original ALTM monitoring project and addition of new lakes in 1992)	Adirondack Mts.	1982–2015		All study lakes showed significant decreases in the concentration of SO <sub>4</sub> <sup>2-</sup> in lake water consistent with reductions in S deposition. Concentration of NO <sub>3</sub> <sup>-</sup> declined at variable rates in 33 of the 48 study lakes. Widespread increases in ANC in 42 of the 48 study lakes and in lab pH in 33 of the 48 study lakes. Al <sub>i</sub> decreased in 45 of the 48 lakes. Dissolved organic C increased in 29 of the 48 lakes. Most of the 48 ALTM lakes showed significant decreases in the concentrations of base cations. Eleven of the 16 original ALTM lakes showed increases in lake ANC between 1982 and 2013.	<a href="#">Driscoll et al. (2016)</a>

**Table 7-3 (Continued): Monitoring and resurvey results of aquatic acidification and/or chemical recovery since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria.**

Process	Acidification Indicator	Nutrient Enrichment Indicator	Type of Ecosystem	Region	Time Period	Ambient N/S Deposition kg/ha/yr	Effect of Deposition	Publication
Chemical recovery	ANC, DOC	NO <sub>3</sub> <sup>-</sup>	TIME lakes	Adirondack Mts.	1991–2007	Variable	Percentage acidic lakes decreased from 15.5 to 8.3%; calculated ANC increased at more than twice the rate as Gran ANC, which was attributed to increase in DOC.	<a href="#">Waller et al. (2012)</a>
Chemical recovery	SO <sub>4</sub> <sup>2-</sup> , DOC	N/Ap	Nine lakes	Maine	1993–2009	Wet S = 6.2 (1980) to 1.5 (2010) N = 3	Decreases in lake SO <sub>4</sub> <sup>2-</sup> correlated with increases in DOC and a shift from microbial to terrestrially derived organic matter.	<a href="#">SanClements et al. (2012)</a>
Chemical recovery	NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Lakes	Adirondack Mts. and New England	2000–2010	N/Av	Lake NO <sub>3</sub> <sup>-</sup> concentrations declined at rate of -0.05 µeq/L/yr and there was a shift to nontoxic (organic) Al.	<a href="#">Strock et al. (2014)</a>
Chemical recovery	Al <sub>i</sub>	N/Ap	Resurvey of 113 lakes	Northeastern U.S.	1986–2001	N/Av	In 2001, only 7 lakes, representing 130 lakes in population, had Al <sub>i</sub> >2 µmol/L (toxic threshold to brook trout), compared with 20 sampled lakes (representing 449 lakes in population) in 1986.	<a href="#">Warby et al. (2008)</a>

**Table 7-3 (Continued): Monitoring and resurvey results of aquatic acidification and/or chemical recovery since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria.**

Process	Acidification Indicator	Nutrient Enrichment Indicator	Type of Ecosystem	Region	Time Period	Ambient N/S Deposition kg/ha/yr	Effect of Deposition	Publication
Chemical recovery	SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , ANC	NO <sub>3</sub> <sup>-</sup>	Two streams	Western MD	1990–2005	N/Av	Concentrations of SO <sub>4</sub> <sup>2-</sup> in stream water decreased at a rate of about 3 µeq/L/yr in response to 34% reduction in wet S deposition. Trends in stream NO <sub>3</sub> <sup>-</sup> appeared to be related to watershed factors, especially forest disturbance. Rate of ANC increase during the period 1996–2005 was about half the rate of the entire study period, suggesting that chemical recovery may be slowing or coming to an end.	<a href="#">Eshleman et al. (2008)</a>
Chemical recovery	Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Two streams (manipulated and control)	Bear Brook, ME	1988–2006	Wet S = 6 (1987) to 2.3 (2006)	Concentrations of Ca and Mg in stream water decreased more than SO <sub>4</sub> <sup>2-</sup> concentration, causing stream acidification in control stream.	<a href="#">Navrátil et al. (2010)</a>
Chemical recovery	ANC	N/Av	64 streams	Western Virginia	1987–2011	Wet S = 9 (1980) to 3.7 (2010) Wet N = 4.7 (1980) to 3.0 (2010)	At most sites underlain by base-poor bedrock, ANC decreased despite reductions in S deposition. This response was related to depletion of base cations.	<a href="#">Robison et al. (2013)</a>
S adsorption	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Stream watershed	Noland Divide, GSMNP, TN	1991–2006	S = 28	Sulfur adsorption on soil is important on average. During large precipitation events, SO <sub>4</sub> <sup>2-</sup> was more mobile and caused stream acidification.	<a href="#">Cai et al. (2010)</a>

**Table 7-3 (Continued): Monitoring and resurvey results of aquatic acidification and/or chemical recovery since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria.**

Process	Acidification Indicator	Nutrient Enrichment Indicator	Type of Ecosystem	Region	Time Period	Ambient N/S Deposition kg/ha/yr	Effect of Deposition	Publication
Pyrite weathering	SO <sub>4</sub> <sup>2-</sup>	N/Ap	High elevation lakes	Colorado	1985–2008	N/Av	Lake SO <sub>4</sub> <sup>2-</sup> concentration decreased at a rate of –0.12 to –0.27 µeq/L/yr. Climate warming appears to have affected pyrite weathering and lake SO <sub>4</sub> <sup>2-</sup> concentration.	<a href="#">Mast et al. (2011)</a>
ANC production	Alkalinity, Ca <sup>2+</sup>	N/Ap	Streams and rivers	Eastern U.S.	Varies, at least 25 yr of monitoring data per site	Varies	Acidifying deposition is one contributor along with carbonate lithology and watershed topography to significantly increasing alkalinity trends (in 64% of 97 river and stream sites). Most rapid rates of alkalization occurred at sites with the highest elevation and greatest inputs of acidifying deposition.	<a href="#">Kaushal et al. (2013)</a>
ANC production	Alkalinity, SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	N/Ap	Rivers	U.S.	Varies, average monitoring data spanned 50 yrs (range 27 to 65 yr)	Varies	Increasing alkalinity observed in 14 of 23 rivers attributed to recovery from acidification, agricultural processes and changing land uses.	<a href="#">Stets et al. (2014)</a>

In the most recent U.S. EPA National Lakes Assessment, based on lake surveys conducted in 2012, more than 1,000 lakes, ponds, and reservoirs (representing approximately 100,000 water bodies) were sampled for their water quality and biological and habitat conditions using generally comparable field and laboratory protocols ([U.S. EPA, 2016h](#)). Inclusion criteria were water bodies >1 hectare, at least 1 m deep, a minimum of 0.1-hectare open water and minimum water residence time of 1 week. Chemical indicators in the lake surveys included acidification. This survey updated the previous National Lakes Assessment ([U.S. EPA, 2009b](#)). In the earlier National Lakes Assessment that was conducted in 2007 ([U.S. EPA, 2009b](#)), ANC and pH were among the chosen chemical indicators used to assess biological integrity. However, due to logistical considerations, included sites were restricted to lakes larger than 10 acres (4 ha). This constraint eliminated from consideration many of the most acid-sensitive and acid-impacted lakes. In the more recent 2012 lakes survey, the size criterion for inclusion was decreased to lakes >1 hectare ([U.S. EPA, 2016h](#)).

The U.S. EPA also conducted a National Rivers and Streams Assessment (NRSA) during the period 2008–2009 ([U.S. EPA, 2016i](#)). Nearly 2,000 perennial river and stream sites were sampled, representing nearly 1.2 million miles of stream reach. Stream size ranged from very small headwaters to very large rivers. The NRSA reported four chemical stressors: total N, total P, salinity, and acidification along with biological indicators including benthic macroinvertebrates and fish. In the 2012 survey, 97% of lakes were classified in the least disturbed condition for acidification. During the period 2008–2009 ([U.S. EPA, 2016i](#)) acidification was found to be a problem in less than 1% of the stream and river length in the U.S. ([U.S. EPA, 2016i](#)). These results emphasize the finding that acidification impacts are largely confined to relatively small areas of high sensitivity and/or to relatively small lakes and tributary streams.

The U.S. Geological Survey (USGS) has operated several long-term monitoring efforts, including the National Ambient Water Quality Assessment (NAWQA) program that was created in 1991 to assess the nation's water quality in 51 study units defined primarily by major drainage divides. These units comprise approximately 50% of the conterminous U.S. Major objectives of the NAWQA program have been to determine the condition of the nation's streams, rivers, and groundwater; whether these conditions are changing over time; and how these conditions are affected by natural features and human activities. The major priority of the NAWQA program since its inception has been the study of watersheds that have experienced impacts from agriculture and various forms of development. The location of sites, sampling frequency, and types of measurements all reflect this priority. The NAWQA data set has also been used to develop predictive models for occurrence of macroinvertebrates and fish in U.S. streams and identify the relative importance of factors, including nutrients, in species distributions ([Carlisle and](#)

[Meador, 2007](#); [Carlisle et al., 2007](#); [Meador and Carlisle, 2007](#)). Additional USGS monitoring programs have included the Hydrologic Benchmark Network (discontinued in 1997), the New York District of the USGS for the water supply watershed for New York City (in the Catskill Mountain region), and a monitoring project conducted by USGS in the Adirondack Mountains at Buck Creek, NY.

Studies by [Kaushal et al. \(2013\)](#) and [Stets et al. \(2014\)](#) assessed changes in, and controls on, carbonate alkalinity of rivers in the U.S. Alkalinity was defined (in equivalent concentrations, expressed as  $\mu\text{eq/L}$ ) as:

$$[\text{ALK}] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Equation 7-1

which is mathematically equivalent to ANC defined as the difference between the equivalent sum of the base cations and the mineral acid anions ([Charles and Christie, 1991](#)). [Kaushal et al. \(2013\)](#) reported trends in alkalinity in 97 rivers and streams in the eastern U.S. They found significant increases in alkalinity, a product of chemical weathering, at 62 (64%) of the study sites, with no sites showing significant decreases. Trends of increasing alkalinity were weakly related to the presence of carbonate lithology in the watershed, acidic deposition, and topography. The authors interpreted the generally increasing alkalinity as reflective of human impacts on weathering rates. The role of temperature in modifying weathering rates was not assessed.

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### 7.1.3.2 Eutrophication

A number of monitoring studies have been conducted or continued in recent years that have documented the effects of N input on the  $\text{NO}_3^-$  flux and/or trophic state of fresh waters. Monitoring studies linked to eutrophication response and published since the 2008 ISA are highlighted in this section. In the most recent National Lakes Assessment, about one-third of the lakes in the continental U.S. were judged to have excess N, suggesting that N nutrient pollution is a widespread concern across the country ([U.S. EPA, 2016h](#)). Chemical indicators in the lake surveys included DO, N, and P. Benthic macroinvertebrates, chlorophyll *a*, and zooplankton were the biological indicators assessed by the sampling protocols. Algal toxin (microcystin) and cyanobacteria were also evaluated in the water bodies. Lakes that had high levels of N were 1.6 times as likely to have a degraded benthic macroinvertebrate community. Increases in both cyanobacteria (8.3% increase) and microcystin toxin (9.5% increase) were reported in the most recent lake sampling compared to the previous National Lakes Survey conducted in 2007 ([U.S. EPA, 2016h, 2009b](#)). In the NRSA, 41% of the nation's river and stream miles were rated poor for N compared to least-disturbed reference conditions ([U.S. EPA,](#)

[2016i](#)). Streams in the Plains and Lowlands were most impacted by N, followed by the mountainous areas east of the Mississippi River (Eastern Highlands).

Since the 2008 ISA, surface water chemistry data from long-term monitoring by federal, state, and local agencies as well as university research groups and nonprofits has been combined into publicly available metadatabases. The Lake Multi-Scaled Geospatial and Temporal Database of the Northeast Lakes of the U.S. (LAGOS-NE) is an integrated database that includes lake surface water chemistry data from a 17-state region ([Soranno et al., 2015](#)). A Georeferenced Lake Nutrient Chemistry (GLNC) database containing N and P water chemistry from 1964–2015 from 3,602 western U.S. mountain lakes has combined data from the National Park Service (NPS), U.S. Fish and Wildlife Service (USFS), the U.S. EPA National Lakes Assessments, and academic researchers for assessing nutrient deposition effects in the region ([Williams et al., 2017b](#)). These databases have been used to assess temporal and spatial trends of lake nutrient chemistry in response to environmental stressors including atmospheric deposition.

Research published since the 2008 ISA and described in detail in [Appendix 9.1.1.4](#) provided evidence suggesting that predominantly dry deposition of fine (<10 µm) and coarse (<100 µm) particulates containing P “dust” plays a role in the enrichment effects of N deposition to fresh waters and their catchments. Among the large natural P emission sources are soils, vegetation, and biomass combustion ash. Other notable sources include industry, agriculture, and mining. Although P is not a criteria pollutant, inputs of P may contribute to eutrophication and affect shifts in lake trophic status from P to N limitation or to colimitation. Data from the U.S. EPA National Lakes surveys and National Rivers and Streams surveys were analyzed by [Stoddard et al. \(2016\)](#) to determine whether total P (TP) concentrations changed between 2000 and 2014. They found increases in TP continentally and especially at sites that exhibited low disturbance ([Appendix 9.1.1.2](#)). In addition, they observed that TN was strongly correlated with TP in lakes and streams on a national scale. Although the authors determined that TP was increasing at “minimally disturbed sites,” they observed that TN was not increasing at those sites. A 5-year, Community Atmospheric Model (CAM<sub>4</sub>) simulation by [Brahney et al. \(2015\)](#) suggested that P deposition may play a large role in alpine lake trophic status and that TP deposition may have increased globally by 1.4 times the preindustrial deposition rate. A global-scale analysis by [Tipping et al. \(2014\)](#) suggested that oligotrophic lakes are most likely to experience effects of atmospheric P deposition, with implications for changes in productivity in response to anthropogenically emitted N.

Regional monitoring data have been used to infer the N saturation status of watersheds in forested ecosystems based on NO<sub>3</sub><sup>-</sup> leaching to surface waters. [Yanai et al. \(2013\)](#) conducted a detailed time-series analysis of precipitation and stream chemistry data

(1965–2007) to examine the N budget of a forested reference watershed at HBEF in New Hampshire. They found that decreases in stream  $\text{NO}_3^-$  preceded decreases in atmospheric N deposition. [Eshleman et al. \(2013\)](#) evaluated changes in the concentrations of  $\text{NO}_3^-$  in streams impacted by atmospheric N deposition in the Appalachian Mountains during the period 1986–2009. Long-term monitoring of nutrient dynamics has also been conducted in the western U.S. [Mast et al. \(2014\)](#) measured long-term changes in stream  $\text{NO}_3^-$  concentration over three decades at the Loch Vale watershed in Rocky Mountain National Park. During the last 15 years, surface waters in the Green Lakes Valley at the Niwot Ridge Long-Term Ecological Research site in Colorado have been subjects of a wide variety of monitoring and process studies that focused on surface waters as integrators of changes in environmental conditions and the response to external stressors, including atmospheric deposition and climate change ([Miller and Mcknight, 2015](#); [Elser et al., 2009b](#); [Elser et al., 2009a](#); [Gardner et al., 2008](#)).

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#### 7.1.4 Models

Models used to assess the effects of N and S deposition on U.S. ecosystems were described in the 2008 ISA (Annex A) and [Appendix 4](#) of this ISA. The most frequently used ecosystem models for aquatic systems situated in small watersheds have included the Model of Acidification of Groundwater in Catchments (MAGIC) and the Photosynthesis and Evapotranspiration-Biogeochemical (PnET/BGC) model [[U.S. EPA \(2008a\)](#); [Appendix 4.5](#)]. The ForSAFE model [Wallman et al. \(2005\)](#) has also been applied widely, especially in Europe, and has been linked with a terrestrial plant biodiversity model, VEG, and recently applied at several locations in the U.S. [[McDonnell et al. \(2014a\)](#); [Phelan et al. \(2016\)](#); [Appendix 4.5.1.4](#)]. The Very Simple Dynamic (VSD) soil acidification model is used in Europe to simulate acidification effects in soils when observed data are sparse ([Appendix 4.5.1.3](#)). It has not been used widely in the U.S. Three other models, SPARROW, Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N), and the Surface Water Assessment Tool (SWAT) have been used to evaluate N loading to large river systems. Another model that has been applied to analysis of nutrient enrichment in aquatic systems is AQUATOX ([Carleton et al., 2009](#)), which simulates nutrient dynamics and effects on aquatic biota. Such models were earlier summarized in Table A-8 in the 2008 ISA ([U.S. EPA, 2008a](#)).

In the 2008 secondary NAAQS review for oxides of N and S, an aquatic acidification index (AAI) was developed to relate (1) atmospheric concentrations of  $\text{SO}_x$  and  $\text{NO}_y + \text{NH}_y$  to N and S deposition levels using transference ratios ([Appendix 2](#)) and (2) to relate deposition to ANC values, using a modified Steady-State Water Chemistry

(SSWC) model ([Appendix 4](#)) and water chemistry data for over 6,000 sites in the U.S. The ANC values were grouped by site into ecoregions and evaluated by considering the distribution of predicted ANC values ([Scheffe et al., 2014](#)).

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#### **7.1.4.1 Updates to Key Previously Identified Models**

[Zanchi et al. \(2016\)](#) developed an approach to include lateral flow in ForSAFE. Results were assessed by comparison with research values at the Vindela Research forest in northern Sweden. Simulation of both saturated and unsaturated soil zones improved agreement between measured and modeled water flows. This model improvement will likely enhance the ability to simulate the export of elements from soil to drainage water using ForSAFE. In 2011, The SPARROW modeling group published a new set of regional models as a special issue ([Preston et al., 2011](#)). Other models have been used for assessing nutrient loading to freshwater systems. SWAT has been adopted as part of U.S. EPA's Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) platform in support of TMDL model development ([Gassman et al., 2007](#)).

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#### **7.1.4.2 New Models (Published since 2008)**

Several new freshwater acidification or eutrophication models have been developed and published since 2008. The Watershed Analysis Risk Management Framework (WARMF) is a model for evaluating point and nonpoint pollution, including N fate and transport ([Dayyani et al., 2013](#); [Herr and Chen, 2012](#)). A new national water quality modeling system (Hydrologic and Water Quality System [HAWQS]) is under development by Texas A&M University and U.S. Department of Agriculture (USDA) for U.S. EPA's Office of Water (<https://epahawqs.tamu.edu/>). The model is intended to assist resource managers and policy makers in evaluating the effectiveness of water pollution control efforts. HAWQS will support application of SWAT and SPARROW and will include simulations of nutrients and other pollutants. [Table 7-4](#) summarizes recent process-based model estimates of surface water acidification and chemical recovery in the U.S.

**Table 7-4 Recent process-based model estimates of surface water acidification and chemical recovery in the U.S.**

Model	Nutrient Enrichment	Acidification	Type of Ecosystem	Region	Model Application and Findings	Publication
PnET-BGC		X	30 watersheds in Great Smoky Mts. NP	Southern Appalachian Mtns.	Stream recovery has been limited.	<a href="#">Fakhraei et al. (2016)</a>
PnET-BGC		X	44 representative watersheds	Adirondack Mtns.	Larger historical lake acidification in lakes having lower ambient ANC.	<a href="#">Zhai et al. (2008)</a>
MAGIC		X	66 stream watersheds	Southern Blue Ridge Mtns.	All modeled streams had preindustrial ANC >30 µeq/L. Median stream lost about 25 µeq/L of ANC between 1860 and 2005.	<a href="#">Sullivan et al. (2011b)</a>
PnET-BGC		X	128 acid-impaired lakes	Adirondack Mtns.	Of 128 acid-impaired lakes that were modeled, 97 had ambient ANC below target of 20 µeq/L and 83 were below target of 11 µeq/L. TMDL corresponding to a moderate emissions control scenario (60% decrease in S deposition) was 7.9 meq/m <sup>2</sup> /yr.	<a href="#">Fakhraei et al. (2014)</a>
PnET-BGC		X	Streams, watershed	HBEF, NH	Simulations under changing climate reflected later snowpack development, earlier spring snowmelt, greater ET, and slight increase in water yield. Net soil mineralization and nitrification caused simulated soil and water acidification.	<a href="#">Pourmokhtarian et al. (2012)</a>
PnET-BGC, SAFE, VSD, MAGIC			Inter-model comparison	HBEF, NH	Hindcast and forecast projections were qualitatively similar, but temporal patterns of simulated change in chemistry differed substantially among models.	<a href="#">Tominaga et al. (2010)</a>

**Table 7-4 (Continued): Recent process-based model estimates of surface water acidification and chemical recovery in the U.S.**

Model	Nutrient Enrichment	Acidification	Type of Ecosystem	Region	Model Application and Findings	Publication
PnET-BGC		X	Three multipollutant scenarios	Adirondack Mtns.	Predicted ANC recovery closely related to percentage of watershed in conifers, elevation, and lake area.	<a href="#">Wu and Driscoll (2009)</a>

ANC = acid neutralizing capacity; ET = evapotranspiration; HBEF = Hubbard Brook Experimental Forest; L = liter; m = meter;  $\mu\text{eq}$  = microequivalent; meq = milliequivalent; MAGIC = Model of Acidification of Groundwater in Catchments; PnET-BGC = Photosynthesis and Evapo Transpiration-Biogeochemical; S = sulfur; SAFE = Soil Acidification in Forest Ecosystems; TMDL = total maximum daily load; VSD = Very Simple Dynamic; yr = year.

### 7.1.5 National-Scale Sensitivity and Response

The 2008 ISA documented that by the end of the 1980s, the regions of the U.S. with many acid-sensitive waters and ecosystems were well recognized. These acid-sensitive ecosystems are mostly located in upland mountainous terrain in the eastern and western U.S. and are underlain by bedrock that is resistant to weathering, such as granite or quartzite sandstone. However, a similar map for areas sensitive to the eutrophication effects of N were not available. There is strong evidence demonstrating that biogeochemical sensitivity to deposition-driven eutrophication and acidification is the result of historical loading, geologic/soil conditions (e.g., mineral weathering and S adsorption), and nonanthropogenic sources of N and S loading to the system. There is no single deposition level applicable to all ecosystems in the U.S. that can describe the onset of eutrophication or acidification. There are new publications that address recovery of freshwater ecosystems at either the national scale or in specific regions. National scale sensitivity of freshwater systems to N-nutrient effects is discussed in [Appendix 9.1.1.2](#).

#### 7.1.5.1 Chemical Recovery

Chemical recovery of previously acidified surface water is required to support biological recovery. An aquatic ecosystem in chemical recovery will have trends in water quality indicators ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , pH, ANC, inorganic monomeric Al) towards inferred preindustrial values (see [Integrated Synthesis](#)). Preindustrial water quality indicator values are inferred from models, paleolimnology samples, or historical samples of biological communities. Preindustrial water quality varied across the conterminous U.S. in response to variation in climate, geology, and biological communities. In general,

biological recovery has lagged chemical recovery in previously acid-impacted and more recently recovering surface waters ([Appendix 8](#)).

Surface water  $\text{NO}_3^-$  is a chemical indicator for both eutrophication and acidification. Several studies since the 2008 ISA have documented decreased surface water  $\text{NO}_3^-$  concentration attributed to decreases in atmospheric deposition. [Eshleman et al. \(2013\)](#) evaluated changes in the long-term concentration of  $\text{NO}_3^-$  in surface waters impacted by atmospheric N deposition in the Appalachian Mountains during the period 1986–2009. Regional  $\text{NO}_x$  emissions progressively decreased during the study period. Decreases in the annual surface water  $\text{NO}_3^-$  concentration and the  $\text{NO}_3^-$  yield were observed over the study period, which corresponded to generally comparable declines in annual wet N deposition. [Eshleman and Sabo \(2016\)](#) evaluated changes in  $\text{NO}_3^-$  concentration over time in tributary streams of the upper Potomac River. The basin-wide decrease, based on results at the Washington, D.C. station was  $-0.023$  mg N/L/year over 26 years (total change of  $-0.59$  mg N/L). They attributed observed decreases in discharge-weighted annual mean  $\text{NO}_3^-$  concentrations across the basin (mean decrease was 37%) largely to decreases in atmospheric N deposition. [Mast et al. \(2014\)](#) measured long-term changes in stream  $\text{NO}_3^-$  concentration over three decades at the Loch Vale watershed in Rocky Mountain National Park. The concentrations of  $\text{NO}_3^-$  in stream water increased during the early 1990s, peaked in the mid-2000s, and then declined by more than 40%. The recent decreases in stream  $\text{NO}_3^-$  corresponded with decreases in  $\text{NO}_x$  emissions and N deposition. As was found by [Eshleman et al. \(2013\)](#) in Maryland, similarities in the timing and magnitude of  $\text{NO}_3^-$  concentrations in stream water and N deposition suggested that stream chemistry is responding to changes in atmospheric deposition of N. However, the response was complicated in this case by a drought in the early 2000s that enhanced N export for several years. In the Adirondack region concentration of  $\text{NO}_3^-$  declined at variable rates in 33 of the 48 study lakes since 1992 ([Driscoll et al., 2016](#)). [Strock et al. \(2014\)](#) analyzed recent trends in lake chemistry using long-term data from lakes in the Adirondack Mountains and New England. Lake  $\text{NO}_3^-$  concentration showed no trend prior to 2000. During the 2000s, the wet deposition of  $\text{NO}_3^-$  declined more than 50%, and lake  $\text{NO}_3^-$  concentration declined subsequent to 2000 at a rate of  $-0.05$   $\mu\text{eq/L/yr}$ . TN declined in surface waters at a rate of 1.1% per year from 1990 to 2011 in an analysis of lake data from 17 states in the Midwest and northeastern U.S. ([Oliver et al., 2017](#)). Random forest analysis of the data showed atmospheric deposition was the top driver of observed declines in TN.

Evidence of chemical recovery from acidification has been provided by monitoring efforts spanning several decades ([Appendix 7.1.3](#)) and the use of models to hindcast and forecast the acid-base chemistry and N response in soils and surface waters ([Appendix 7.1.4](#)). Model projections of past and future changes in surface water

chemistry in response to changes in acidic deposition using the MAGIC and PnET-BGC models are summarized in [Table 7-5](#).

**Table 7-5 Model projections of surface water sulfate and associated acid neutralizing capacity, shown as changes between dates, for Adirondack and Shenandoah streams.**

Region	Water Bodies	Dates	Model	Pollution Scenario	Change in Median Surface Water SO <sub>4</sub> <sup>2-</sup> µeq/L	Change in Median Surface Water ANC µeq/L	Reference
<b>Hindcasts</b>							
Adirondacks, NY	38 lakes	1850 to 2003	PnET-BGC		+72.9	-39.9	<a href="#">Zhai et al. (2008)</a>
Adirondacks, NY	37 lakes	1850 to 1984	PnET-BGC		+107	-77.8	<a href="#">Chen et al. (2005a)</a>
Adirondacks, NY	44 potentially acid-sensitive lakes	1850 to 1990	MAGIC		+77.8	-38.3	<a href="#">Sullivan et al. (2006a)</a>
			PnET-BGC		+57.3	-29.5	
Adirondacks, NY	141 TMDL lakes	1850 to 2010	PnET-BGC		+65.2	-39.4	<a href="#">Fakhraei et al. (2014)</a>
<b>Forward projections</b>							
Shenandoah NP, VA	Five streams on siliciclastic bedrock	1990 to 2040	MAGIC	Constant deposition	+13	-11.6	<a href="#">Sullivan et al. (2008)</a>
				Mild reduction	-21	+6.2	
				Medium reduction	-23	+7.2	
				Strong reduction	-40	+24.2	
				Very strong reduction	-44	+27.2	

**Table 7-5 (Continued): Model projections of surface water sulfate and associated acid neutralizing capacity, shown as changes between dates, for Adirondack and Shenandoah streams.**

Region	Water Bodies	Dates	Model	Pollution Scenario	Change in Median Surface Water SO <sub>4</sub> <sup>2-</sup> µeq/L	Change in Median Surface Water ANC µeq/L	Reference
Shenandoah NP, VA	Four streams on granitic bedrock	1990 to 2040	MAGIC	Constant deposition	+22	-8	<a href="#">Sullivan et al. (2008)</a>
				Mild reduction	+11	-5	
				Medium reduction	+11	-5	
				Strong reduction	+3	-2	
				Very strong reduction	+2	-2	
Shenandoah NP, VA	Five streams on basaltic bedrock	1990 to 2040	MAGIC	Constant deposition	+33	-5	<a href="#">Sullivan et al. (2008)</a>
				Mild reduction	+12	0	
				Medium reduction	+11	+1	
				Strong reduction	-4	+5	
				Very strong reduction	-9	+6	
Adirondacks, NY	44 potentially acid-sensitive lakes	1990 to 2050	MAGIC	Current and expected controls	-42.4	+5.89	<a href="#">Sullivan et al. (2006a)</a>
				Moderate emissions controls	-58.9	+18.6	
				Aggressive emissions controls	-64.6	+22.6	

**Table 7-5 (Continued): Model projections of surface water sulfate and associated acid neutralizing capacity, shown as changes between dates, for Adirondack and Shenandoah streams.**

Region	Water Bodies	Dates	Model	Pollution Scenario	Change in Median Surface Water SO <sub>4</sub> <sup>2-</sup> µeq/L	Change in Median Surface Water ANC µeq/L	Reference
Adirondacks, NY	44 potentially acid-sensitive lakes	1990 to 2050	MAGIC	Current and expected controls	-18	-3.7	<a href="#">Sullivan et al. (2006a)</a>
				Moderate emissions controls	-32.2	+1.8	
				Aggressive emissions controls	-38.3	+9.3	

ANC = acid neutralizing capacity; L = liter; µeq = microequivalent; MAGIC = Model of Acidification of Groundwater in Catchments; PnET-BGC = Photosynthesis and Evapo Transpiration-Biogeochemical; SO<sub>4</sub><sup>2-</sup> = sulfate.

Source: [U.S. EPA \(2008a\)](#).

As reported in the 2008 ISA, lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations. Since about 1990, the ANC values of many previously acidified lakes and streams have shown some increases, but such increases have been relatively modest in most cases. [Kahl et al. \(2004\)](#) summarized 20 years of chemical monitoring data from regional U.S. EPA programs in the northern and eastern U.S. Surface water chemistry improved over the 20-year period in many lakes and streams; moderate, but significant increases in ANC and pH were observed. [Stets et al. \(2014\)](#) found widespread increasing alkalinity concentrations at 14 of 23 sites across the conterminous U.S. over the last half of the 20th century and the early 21st century. Results showing decreases in NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations and cation:alkalinity ratios at many sites were consistent with recovery from water acidification. Agricultural lime contributed alkalinity at some locations. These findings are important because large rivers constitute important pathways for transport of nutrients and other constituents to coastal waters and may influence coastal acidification and Ca supply.

Trends in surface water chemistry, including evidence for chemical recovery, are reported in several acid-sensitive regions of the U.S. where long-term monitoring programs have been in place several decades. These include the Adirondacks and the northeastern U.S. (see [Appendix 16](#)). In some portions of the Appalachian Mountains, chemical recovery of

surface waters has not always followed decreases in deposition due to high S absorption in watershed soils ([Appendix 16 Smoky Mountains Case Study](#)).

A long-term delay in surface water recovery from past acidification has been noted by [Likens et al. \(1996\)](#) at HBEF. This delay was attributed mainly to changes in base cation concentration. Similarly, based on an analysis of Adirondack lakes, [Lawrence et al. \(2013\)](#) concluded that chemical recovery processes in response to decreases in acidic deposition are complex and require evaluation of multiple chemical metrics in addition to ANC, including DOC, inorganic Al, and BCS. As an example of the complexity, the lower threshold of ANC required to protect brown trout in Norway against acidification damage was earlier estimated to be 20 µeq/L ([Lien et al., 1996](#)). This critical ANC limit may be lower in humic lakes (~8 µeq/L) because about one-third of the organic acid anions may act essentially as strong acid anions ([Lydersen et al., 2004](#); [Driscoll et al., 1994](#)). Inclusion of strong organic acids in the ANC calculation can be useful because the relationships between pH, inorganic Al, and ANC may have changed in response to increased concentrations of DOC and TOC. This is particularly true in lakes having higher DOC and TOC compared with clear water lakes. [Hesthagen et al. \(2008\)](#) estimated that threshold ANC values to prevent damage to brown trout had increased by 1995 to 48 µeq/L. The authors suggested that the higher ANC threshold for 1995 was attributable to lower pH and higher inorganic Al at a given ANC level.

#### 7.1.5.1.1 Adirondacks

At the time of the 2008 ISA, several studies reported chemical recovery from acidification in Adirondacks lakes ([Driscoll et al., 2007a](#); [Momen et al., 2006](#); [Driscoll et al., 2003c](#)) based on long-term monitoring efforts in the region ([Appendix 7.1.3.1](#)). [Driscoll et al. \(2003c\)](#) evaluated changes from 1982 to 2000 in the original 16 Adirondack LTM lakes and from 1992 to 2000 in the complete set of 48 Adirondack LTM lakes. They found that nearly all study lakes showed marked decreases in  $\text{SO}_4^{2-}$  concentration and several lakes showed declines in  $\text{NO}_3^-$  concentration. They found that 7 of the 16 original monitoring lakes showed statistically significant increases in ANC, with a mean rate of increase of 0.78 µeq/L/year. In a study of 30 of the 48 lakes studied by [Driscoll et al. \(2003c\)](#), pH increased in 25 lakes and ANC increased in 12 of the 30 lakes ([Momen et al., 2006](#)). Concentrations of dissolved  $\text{NO}_3^-$  were inversely correlated with concentrations of chlorophyll *a* in 11 lakes. Chlorophyll *a* increased in concentration in 9 lakes. The increase in pH observed in most of these lakes may have stimulated productivity so that N assimilation by plankton increased, indicating recovery from acidification to eutrophication, rather than to preindustrial conditions.

Monitoring data since the 2008 ISA continues to show chemical recovery in the Adirondack region. As described in the Adirondacks case study ([Appendix 16](#)), significant decreases in lake  $\text{SO}_4^{2-}$  concentrations ( $-2.14 \mu\text{mol/L/year}$ ) corresponding to significant declines in total S deposition were observed in monitoring data from 1984 to 2010 ([Mitchell et al., 2013](#)). Surface water ANC and pH recovery has been documented by [Lawrence et al. \(2013\)](#) and [Lawrence et al. \(2011\)](#) in studies of Adirondack streams and lakes. On average, the pH increased by only 0.28 pH units and ANC by  $13 \mu\text{eq/L}$  in 12 streams that were monitored over a period of 23 years. During that period, there was an approximate 50% reduction in atmospheric deposition of S in the Adirondack region. The percentage of Adirondack lakes that were acidic decreased from an estimated 15.5 to 8.3% using data from the TIME monitoring program ([Waller et al., 2012](#)). Decreases in lake water  $\text{SO}_4^{2-}$ , and to a lesser extent  $\text{NO}_3^-$ , concentrations generally were accompanied by increases in lake ANC. [Driscoll et al. \(2016\)](#) observed increases in ANC and pH and marked decreases in dissolved inorganic Al in 45 of 48 study lakes in the Adirondack region from 1982 to 2015, corresponding to decreases in acidifying deposition. Changes were most pronounced in the acid-sensitive thin-till drainage lakes. In another Adirondack long-term study that focused on 43 lakes sampled by the Adirondack Lakes Survey Corporation during three time periods (1984–1987, 1994–2005, and 2008–2012), the average concentration of inorganic Al decreased from  $2.2 \mu\text{M}$  (a level above that generally considered toxic to brook trout,  $2 \mu\text{M}$ ) to  $0.66 \mu\text{M}$  ([Baldigo et al., 2016](#)).

Interpretation of long-term trends in Adirondack surface water chemistry, as summarized above, has also been augmented by results of repeated surveys of the chemistry of lakes initially surveyed several decades previously. [Warby et al. \(2008\)](#) resurveyed 113 lakes throughout the Northeast in 2001 that had previously been sampled by the U.S. EPA in 1986 to assess chemical recovery from lake acidification. Decreases in total Al and inorganic Al concentrations were widespread and were largest in the Adirondack Mountains ( $-2.59$  to  $-4.60 \mu\text{mol/L}$ ). In 2001, only 7 study lakes (representing 130 lakes in the population) had inorganic Al concentrations above a toxic limit of  $2 \mu\text{mol/L}$ , compared with 20 sampled lakes (representing 449 lakes in the population) in 1986. Thus, it was estimated that in 2001 more than 300 northeastern lakes no longer had summer inorganic Al concentrations at levels considered harmful to aquatic biota. [Michelena et al. \(2016\)](#) reported changes in the water chemistry of 30 Adirondack lakes in response to reductions in acidic deposition from 1994 to 2012. The water quality of the study lakes generally improved during the study period, but the responses were sporadic and complex. Lake pH values increased until about 2002 and then fluctuated. Inorganic Al concentrations generally decreased throughout the period of record. During the early years of monitoring, the average pH increased dramatically from about 5.5 to 6.0. This increase was followed by a period of reacidification for about 5 years, followed by another period of increased pH.

This 5-year cycle was then repeated to a muted extent, even though acidic deposition continued to decline.

Chemical recovery from surface water acidification in the Adirondack Mountains has been accompanied by increasing concentrations of DOC, including organic acids, which have complicated and restricted recovery from acidification (Section DOC). Long-term monitoring of 48 Adirondack lakes by [Driscoll et al. \(2016\)](#) showed patterns of increasing DOC in 29 study lakes concurrent with decreases in acidic deposition. [Lawrence et al. \(2013\)](#) evaluated long-term changes in DOC and BCS (which reflects the calculated ANC and includes an adjustment for strong organic acid anions). Increases in DOC concentration from 1994 to 2011 contributed to organic complexation of Al. This reduced the fraction of monomeric Al that was in the inorganic (and potentially toxic) form from 57% in 1994 to 23% in 2011. Thus, the higher DOC found during latter sampling increased the organic acidity of the lake water and limited ANC recovery, but at the same time it decreased the toxicity of dissolved Al to aquatic biota. Similarly, [Strock et al. \(2014\)](#) reported trends in recovery from toxic Al levels caused by acidification of surface waters. They analyzed recent trends in lake chemistry using long-term data from lakes in the Adirondack Mountains and New England. During the 2000s, the wet deposition of  $\text{NO}_3^-$  declined more than 50%. The lake  $\text{NO}_3^-$  concentration, which showed no trend prior to 2000, declined subsequent to 2000 at a rate of  $-0.05 \mu\text{eq/L/year}$ . There was a shift to nontoxic (organic) forms of Al. Despite the Al recovery, both the ANC and pH in the study lakes failed to show evidence of appreciable chemical recovery; rather, the lakes continued to exhibit variable trends in ANC and pH.

The PnET-BGC model has been applied in the Adirondack region to assess chemical recovery. Model results from [Fakhraei et al. \(2014\)](#) suggested that ambient ANC values were below the target value of  $20 \mu\text{eq/L}$  in 97 of the 128 lakes that were judged to be acid impaired under Section 303(d) of the Clean Water Act (CWA); 83 lakes had ANC below the target value of  $11 \mu\text{eq/L}$ . A moderate emissions control scenario (60% decrease from the ambient atmospheric S deposition) was projected to recover the ANC of lakes by  $0.18$  and  $0.05 \mu\text{eq/L/year}$  on average during the periods 2022 to 2050 and 2050 to 2200, respectively. Model results suggested that controlling S deposition to Adirondack lake watersheds was more effective as a means to recover acidic lakes than was controlling N deposition in this region. [Wu and Driscoll \(2009\)](#) applied the PnET-BGC model to predict the responses of lake ANC during the period 2001 to 2050. Based on three multipollutant scenarios, predicted ANC recovery was associated with higher elevation, smaller lake area, and higher percentage of watershed area in coniferous vegetation. The variables lake depth and the square of the lake elevation explained 40% of the variation in predicted lake water ANC.

### 7.1.5.1.2

#### Northeast

The Northeast U.S. also has several decades of monitoring data, especially for HBEF ([Appendix 7.1.3.1](#)). [Strock et al. \(2016\)](#) documented decreases in water transparency and increases in DOC in lakes in Acadia National Park in Maine over a period of 14 years (1995–2008). Larger transparency decreases were noted in clear water lakes (–0.3 m/year) compared with the brown water lakes (–0.1 m/year). In the Catskill Mountains, NY, 23 years of stream water chemistry data showed significant decreasing  $\text{SO}_4^{2-}$  (mean trend of –2.5  $\mu\text{eq/L/year}$ ), while no significant trends were observed for  $\text{NO}_3^-$  ([Mchale et al., 2017](#)). A decreasing trend in inorganic Al and increasing trends in pH and ANC were evident under both low- and high-flow conditions. [Fuss et al. \(2015\)](#) examined long-term trends in soil solutions and surface waters from the early 1980s to 2011 at the HBEF in New Hampshire. They found that rates of annual average ANC increase during the period 1982–2011 were similar to what was observed during snowmelt, although the ANC during snowmelt was 10  $\mu\text{eq/L}$  lower than annual averages. In a summary of 20 years of data at Bear Brook, [Norton et al. \(2010\)](#) observed decreases in pH, base cation concentrations, and ANC, and increases in inorganic Al concentration in the East Bear reference watershed. These observations indicate that under ambient deposition conditions acidification continues even though S deposition and stream  $\text{SO}_4^{2-}$  concentrations have declined. [Laudon and Norton \(2010\)](#) analyzed 212 hydrological episodes in Bear Brook using the ANC Dilution Model (ADM) of [Laudon and Bishop \(1999\)](#). The results showed that 18 years of experimental addition of N and S to the West Bear Brook watershed had not altered the most important natural causes of episodic stream acidification: base cation dilution, processes associated with deposition of marine sea salts, and contributions of organic acidity during rain and snowmelt events. The results further indicated that the contributions of  $\text{SO}_4^{2-}$  to the observed ANC decreases in West Bear Brook during episodes increased steadily since the beginning of experimental watershed treatment. In contrast, the role of  $\text{NO}_3^-$  in episodic acidification events remained relatively constant after an early increase. Model stimulations at HBEF using the PnET-BGC model showed later development of snowpack, earlier snowmelt, higher evapotranspiration, and increased water yield expected with current and projected trends of increasing temperature will increase net soil N mineralization and nitrification ([Pourmokhtarian et al., 2012](#)). This could contribute to acidification of soil and stream water. In a model study comparison, [Tominaga et al. \(2010\)](#) noted that hindcast (1850–1992) and forecast (2005–2100) projections were qualitatively similar across MAGIC, PnET-BGC, SAFE, and VSD watershed acidification models at HBEF, although projected stream ANC and soil base saturation differed substantially through time.

#### 7.1.5.1.3 West

Surface water acidification, and presumably also chemical recovery, have been limited in the western U.S. Although acidification sensitivity has been shown to be high at many locations, acidic deposition levels have also mostly been lower. [Mast et al. \(2011\)](#) examined trends in precipitation chemistry and other factors that influence long-term changes in chemistry of high-elevation lakes in three Colorado wilderness areas during the years 1985 through 2008. Sulfate concentrations in precipitation decreased at rates of  $-0.15$  to  $-0.55$   $\mu\text{eq/L/year}$  at 10 monitoring stations in Colorado. In lakes where  $\text{SO}_4^{2-}$  was primarily derived from atmospheric sources, the lake  $\text{SO}_4^{2-}$  concentrations decreased by  $-0.12$  to  $-0.27$   $\mu\text{eq/L/year}$ . In lakes where  $\text{SO}_4^{2-}$  likely originated primarily from watershed weathering, the  $\text{SO}_4^{2-}$  concentrations in lake water increased, rather than decreased, from 1985 to 2008.

#### 7.1.5.1.4 Appalachians

Not all acid-sensitive regions of the U.S. have shown improvements in surface water quality with decreasing deposition trends. Monitoring data from the Great Smoky Mountains NP ([Appendix 16](#)) indicate that the high S absorption in watershed soils in this region delay recovery from previous stream acidification ([Cai et al., 2010](#)). The majority (about 61%) of the net  $\text{SO}_4^{2-}$  entering the study watershed was retained. However, during large precipitation events,  $\text{SO}_4^{2-}$  in wet deposition moved more directly and rapidly to streams, contributing to episodic stream acidification. [Cai et al. \(2010\)](#) concluded that base cation depletion from soils could limit chemical recovery from acidification of streams in the study watershed. Stream chemistry from 1993–2014 at 42 monitoring sites in the park did not show substantial changes over the recent period of long-term monitoring ([Fakhraei et al., 2016](#)). An empirical modeling study by [Robinson et al. \(2008\)](#) of baseflow water chemistry at 90 streams in Great Smoky Mountains National Park during the years 1993–2002 indicated significant decreasing trends in stream pH and  $\text{SO}_4^{2-}$  at lower elevation sites over time, but no long-term trends in stream  $\text{NO}_3^-$  or ANC. An estimated 30% of the sample sites were simulated to decrease pH to less than 6 within 10 years. The models explained 71% of the variability in pH and 86% of the variability in ANC. Soil retention of  $\text{SO}_4^{2-}$  and assimilation of  $\text{NO}_3^-$  into plants were important biogeochemical processes regulating stream chemistry. The stream pH at base flow has not yet shown signs of recovery in response to recent decreases in acidic deposition. The model developed for elevations between 305 and 1,070 m predicted that median pH values will decrease below 6 within 34 years if the observed statistical trends continue. The state of Tennessee currently lists streams within the park with mean pH below 6 as impaired under the Clean Water Act

Section 303d ([Appendix 16](#), Southeast case study), so the model by [Robinson et al. \(2008\)](#) indicated biologically significant ongoing acidification.

[Singh et al. \(2016\)](#) assessed DOC trends in a forested stream at the Coweeta Hydrologic Laboratory in the southeastern U.S. over a period of 25 years. Concentrations and fluxes of DOC decreased by 34 and 56%, respectively, between 1988 and 2001, corresponding with the stream acidification phase. During the period 1997 to 2012, DOC concentration increased in association with increases in precipitation and the number and intensity of short-duration storms during the early part of the growing season.

Several model applications have been conducted in the southern Appalachian Mountains to simulate stream chemistry and critical or target loads. These studies have employed the MAGIC, PnET-BGC, and SSWC models. Results of these studies have reinforced the widespread acid sensitivity of this region and the importance of S adsorption and base cation depletion to stream responses to changes in levels of acidic deposition. Critical and target loads ([Section IS.2.2.3](#)) for resource recovery/protection were quantified [[McDonnell et al. \(2012\)](#); [McDonnell et al. \(2010\)](#); [McDonnell et al. \(2013\)](#); [McDonnell et al. \(2014b\)](#); [Sullivan et al. \(2011c\)](#); [Fakhraei et al. \(2016\)](#); [Appendix 8.5.4](#)]. An important outcome of critical load modeling studies in the Appalachian Mountains is the suggestion that complete stream acid base chemistry recovery may not be possible ([Appendix 8.5.4](#)). [Sullivan et al. \(2011b\)](#) applied the MAGIC model to estimate the S target load for protecting aquatic resources in 66 stream watersheds in the Southern Blue Ridge province of the Appalachian Mountains at different points in the future. For some of the modeled sites, if S deposition was decreased to zero and maintained at that level throughout the simulation, one or more of the selected critical ANC levels (0, 20, 50, 100  $\mu\text{eq/L}$ ) could not be achieved by 2100. This was likely largely due to the simulation result suggesting that many of the streams did not exhibit such a high ANC during preindustrial times, in the absence of acidic deposition. For other sites with large watershed acid buffering capacity, even very high-sustained S deposition would not reduce stream ANC below thresholds associated with biological harm.

Monitoring studies suggested that the rate of stream ANC recovery in this region may be slow in the Southeast and that base cation depletion in soils contributed in the last two decades to further aquatic acidification despite reductions in S deposition ([Robison et al., 2013](#); [Cai et al., 2010](#)). [Rice et al. \(2014\)](#) examined the source-sink behavior of  $\text{SO}_4^{2-}$  in 27 unglaciated forested watersheds across a latitudinal gradient from Pennsylvania to Georgia and found that many of the watersheds still retain  $\text{SO}_4^{2-}$  under conditions of decreased S deposition. The specific years when the watersheds will likely cross over from retaining to releasing  $\text{SO}_4^{2-}$  varied from north to south, with the south generally showing later cross-over dates. [Eshleman et al. \(2008\)](#) used data from two long-term monitoring

stations in western Maryland to assess the recovery of stream water ANC due to declines in acidic deposition. Stream water  $\text{SO}_4^{2-}$  concentration declined at the two study sites between 1990 and 2005 by about  $3 \mu\text{eq/L/year}$  in response to a 34% reduction in wet atmospheric S deposition. However, trends in  $\text{NO}_3^-$  concentration were more strongly related to watershed factors, especially forest disturbance. Although ANC increased throughout the study, the rate of increase in later years (1996–2005) was only about half as large as the rate of increase in ANC over the entire study period. This result might suggest a slowing of chemical recovery from previous acidification ([Eshleman et al., 2008](#)). This supposition was further substantiated by [Robison et al. \(2013\)](#), who analyzed the chemistry of stream samples collected quarterly from 1987 to 2011 at 64 sites in the southern Appalachian Mountains of western Virginia. At most of the study streams, the pH increased over time. However, at most sites underlain by base-poor bedrock, ANC decreased even though S deposition decreased. These decreases in stream ANC were associated with depletion of base cations in watershed soils.

Stream acid-base chemistry from 1999 to 2014 in a group of 40 stream reaches in the Upper Savage River watershed in western Maryland showed statistically significant decreases in stream concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  that were qualitatively and quantitatively consistent with decreases in wet S and N deposition ([Kline et al., 2016](#)). Stream ANC increased by significant amounts in 10–20% of the monitored streams, but the magnitude of recovery was too small compared with natural variability to detect a regional ANC recovery. The percentage of streams having  $\text{ANC} \leq 0 \mu\text{eq/L}$  decreased from about 7% in 1999 to 0 in 2014. The percentages of streams having ANC values less than  $50 \mu\text{eq/L}$  and less than  $100 \mu\text{eq/L}$  also decreased markedly between 1999 and 2014. Concentrations of base cations (Ca, Mg, K) decreased, moderating regional ANC recovery.

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### 7.1.5.2 Critical Loads

A critical load (CL) is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge [[Nilsson and Grennfelt \(1988\)](#); [Spranger et al. \(2004\)](#); [Section IS. 2.2.3](#)]. These CLs can be used as early warning signals to indicate likely ecosystem sensitivity to change in N or S. Empirical CLs are developed from observational data while steady-state and dynamic models develop relationships between deposition, water quality measurements and biogeochemistry for watersheds.

For acidification, CLs from empirical data as well as modeling approaches are available for acid-sensitive regions of the U.S. ([Appendix 8.5.3](#)). Generalized empirical estimates are based on acidification or increased surface water  $\text{NO}_3^-$  leaching. Empirical CLs to protect

against aquatic acidification in U.S. ecosystems are summarized in [Table 8-7](#). Both steady-state ([Appendix 8.5.4.1.2.1](#)) and dynamic models ([Appendix 8.5.4.1.2.2](#)) have been used to quantify relationships between deposition and biogeochemistry for watersheds in order to develop CL estimates to protect against acidification or promote recovery of acid-base chemistry. Recent CL modeling studies in the U.S. to protect against aquatic acidification are summarized in [Table 8-8](#). Most aquatic CL studies conducted in the U.S. have used surface water ANC as the principal metric of water quality change in response to changes in acidic deposition, although ANC should not necessarily be used as the only environmental predictor of biological harm on which to base CLs. Other potentially useful variables include water pH, inorganic Al, and BCS. Since the 2008 ISA, dynamic modeling of CLs in the U.S. to achieve various ANC targets has been focused mostly on the Adirondack and Appalachian Mountains. The CL can be calculated to represent the individual or combined deposition load of S and/or N to which a stream and its watershed could be subjected and still have a surface water ANC within a targeted range.

For nutrient enrichment, diatoms are among the most sensitive aquatic organisms, thereby providing a basis for assessing aquatic ecosystem protection against nutrient enrichment across ecosystems. The lake water  $\text{NO}_3^-$  concentration has been identified as a useful chemical criterion indicative of biological change in the diatom community. Recently, [Williams et al. \(2017b\)](#) used phytoplankton biomass N to P limitation shifts as the basis for CL calculations. Critical loads ([Section IS.2.2.3](#)) for nutrient enrichment are described in [Appendix 9.5](#) and summarized in [Table 9-4](#).

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## 7.1.6 Water Quality Criteria

The term “water quality criteria” is used in two sections of the Clean Water Act: Section 304(a)(1) and Section 303(c)(2). The term has a different impact in each section. In Section 304, the term refers to a scientific assessment of ecological and human health effects that U.S. EPA recommends to states and authorized tribes for establishing water quality standards that ultimately provide a basis for controlling discharges or releases of pollutants or related parameters. Ambient water quality criteria associated with specific water body uses, when adopted as state or tribal water quality standards under Section 303 of the CWA, define the level of a pollutant (or, in the case of nutrients, a condition) necessary to protect designated uses in specific water bodies.

U.S. EPA develops Water Quality Criteria (WQC) using existing scientific knowledge to determine when water is unsafe for people and wildlife. These criteria are developed as recommendations. State and tribal governments may adopt these criteria or use them as guidance in developing their own. U.S. EPA bases aquatic life criteria on how much of a

chemical can be present in surface water before it is likely to harm plant and animal life. WQC are determined to protect aquatic life, biology, human health, microbial/recreational, and sediment condition. For aquatic life, the criteria are designed to protect both freshwater and marine organisms from short-term and long-term exposure to pollutants. Biological criteria indicate the health of water bodies based on how many and what kinds of organisms are present. More details about the scientific basis for these criteria may be found at <https://www.epa.gov/wqc/basic-information-water-quality-criteria>.

The U.S. EPA is working with the states to develop numeric nutrient criteria to better define levels of N and P that affect U.S. waters. The numeric values include both causative (N and P) and response (chlorophyll *a*, turbidity) variables. The U.S. EPA's National Nutrient Program recommended nutrient criteria for rivers and streams in 14 ecoregions of the U.S. (based on Omernik Level III ecoregions) to use as starting points for states to develop their own criteria ([U.S. EPA, 1998b](#)).

WQC indicators related to N are available for 10 states to date ([Table 7-6](#)) including Oregon, California, Arizona, Colorado, Montana, Utah, and Mississippi which have numeric nutrient criteria. These criteria may include a variety of N species and chlorophyll *a* ([Table 7-6](#)). For Washington and Louisiana, which lack explicit numeric nutrient criteria, U.S. EPA aggregate Level III ecoregion nutrient criteria for rivers and streams were used ([Table 7-6](#); <http://www2.epa.gov/nutrient-policy-data/ecoregional-criteria-documents>). Florida has numeric nutrient criteria for TN for most of the state. The compiled state WQC vary greatly in spatial resolution and N forms addressed. Mississippi applies only one criterion for the entire state. By contrast, California has a patchwork of criteria designated by regional water boards.

U.S. EPA Aggregate Level III Omernik Ecoregion Nutrient Criteria for Rivers and Streams (from U.S. EPA Ecoregional Nutrient Criteria Documents for Rivers and Streams; available at <http://www2.epa.gov/nutrient-policy-data/ecoregional-nutrient-criteria-documents-rivers-and-streams>) were developed for states to provide a more spatially even set of standards for TN and chlorophyll *a* ([Table 7-7](#)). The regionally based criteria are designed to reflect characteristics such as soils, vegetation, climate, geology, and land cover, which are relatively similar within each ecoregion. Pristine or minimally impacted waters from each region are used as a basis for developing ecoregion-specific nutrient criteria. The aggregate ecoregion criteria are mapped in [Figure 7-4](#) and [Figure 7-5](#).

The ambient water quality criteria for NH<sub>3</sub> was recently updated to reflect the sensitivity of freshwater unionoid (order Unionoida) mussels to this nutrient ([U.S. EPA, 2013a](#)). The acute criterion is 17 mg total NH<sub>3</sub><sup>-</sup>-N (TAN)/L, and the chronic criterion is 1.9 TAN/L at pH 7 and temperature 20°C.

**Table 7-6 Numeric nutrient water quality criteria for rivers/streams by state (all values in mg/L).**

State	Subregion	TN	Nitrate (as N)	Nitrite (as N)	Nitrate + Nitrite (as N)	Ammonia (NH <sub>3</sub> )	Chlorophyll <i>a</i>
Alabama	--						
Alaska	-		10	1	10		
Arizona	--	1.1–3.0 <sup>c</sup>	10	1			
Arkansas	--						
California <sup>d</sup>	SWRCB Region 1		10				
California <sup>d</sup>	SWRCB Region 2		10	1	10		
California <sup>d</sup>	SWRCB Region 3		10				
California <sup>d</sup>	SWRCB Region 4		8	1	10		
California <sup>d</sup>	SWRCB Region 5	0.31					0.0018
California <sup>d</sup>	SWRCB Region 6	0.38					0.00178
California <sup>d</sup>	SWRCB Region 7		10		10		
California <sup>d</sup>	SWRCB Region 8	0.38	10				0.00178
Colorado <sup>e</sup>	Remainder of state		10	0.05		0.02	
Colorado <sup>e</sup>	South Platte Basin			0.5			
Connecticut	--						
Delaware	--		10				
Florida <sup>f</sup>	Panhandle West	0.67					0.02
Florida <sup>f</sup>	Panhandle East	1.03					0.02
Florida <sup>f</sup>	North Central	1.87					0.02
Florida <sup>f</sup>	Peninsular	1.54					0.02
Florida <sup>f</sup>	West Central	1.65					0.02
Florida <sup>f</sup>	South Florida						0.02
Georgia <sup>g</sup>	--	4					
Hawaii	--						

**Table 7-6 (Continued): Numeric nutrient water quality criteria for rivers/streams by state (all values in mg/L).**

State	Subregion	TN	Nitrate (as N)	Nitrite (as N)	Nitrate + Nitrite (as N)	Ammonia (NH <sub>3</sub> )	Chlorophyll a
Idaho	-						
Illinois	--		10				
Indiana	--		10	1	10		
Iowa	-		10	1			
Kansas	--		10		10		
Kentucky	--		10	1			
Louisiana <sup>h</sup>	Rest of the state						
Louisiana <sup>h</sup>	Ecoregion 9		0.69				0.00093
Louisiana <sup>h</sup>	Ecoregion 10		0.76				0.0021
Maine	-		10				
Maryland	--						
Massachusetts	--						
Michigan	--		10				
Minnesota <sup>i</sup>	Central River Region						0.018
Minnesota <sup>i</sup>	North River Region						0.007
Minnesota <sup>i</sup>	South River Region						0.035
Minnesota <sup>i</sup>	Remainder of state						
Mississippi	--		10				
Missouri	-						
Montana	--		1		1		
Nebraska	--		10	1			
Nevada	--						
New Hampshire	--						
New Jersey	--						
New Mexico	--						

**Table 7-6 (Continued): Numeric nutrient water quality criteria for rivers/streams by state (all values in mg/L).**

State	Subregion	TN	Nitrate (as N)	Nitrite (as N)	Nitrate + Nitrite (as N)	Ammonia (NH <sub>3</sub> )	Chlorophyll a
New York	--		10		10		
North Carolina	-						
North Dakota					10		
Ohio	--						
Oklahoma <sup>j</sup>	--						0.01
Oregon	--		10				0.015 <sup>k</sup>
Pennsylvania	--			10			
Rhode Island	--						
South Carolina	--						
South Dakota	--						
Tennessee	--		10				
Texas	--						
Utah	--		10				
Vermont <sup>l</sup>	Class A(1) and A(2) waters above 2,500		0.2				
Vermont <sup>l</sup>	Class A(1) and A(2) waters below 2,500		2				
Vermont <sup>l</sup>	Class B waters		5				
Virginia	--		10				
Washington <sup>m</sup>	Ecoregion 1	0.31					0.0018
Washington <sup>m</sup>	Ecoregion 2	0.12					0.00108
Washington <sup>m</sup>	Ecoregion 3	0.38					0.00178
West Virginia	--		10				
Wisconsin	-						

**Table 7-6 (Continued): Numeric nutrient water quality criteria for rivers/streams by state (all values in mg/L).**

State	Subregion	TN	Nitrate (as N)	Nitrite (as N)	Nitrate + Nitrite (as N)	Ammonia (NH <sub>3</sub> )	Chlorophyll a
Wyoming	--		10	1	10		

L = liter; mg = milligram; N = nitrogen; NH<sub>3</sub> = ammonia; SWRCB = State Water Resources Control Board; TN = total nitrogen.

<sup>a</sup>Regulatory status as of November 2017. Subject to change. In addition to codified criteria, select waterbodies may also have unique criteria developed as Clean Water Act Section 303(d) Total Maximum Daily Load (TMDL) impairment restoration planning. See <https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality-criteria>.

<sup>b</sup>10 mg/L for Nitrates and 1 mg/L for Nitrites are nonenforced public health U.S. EPA recommendations for Drinking Water sources.

<sup>c</sup>Arizona R18-11-109F (varies by waterbody) [http://apps.azsos.gov/public\\_services/Title\\_18/18-11.pdf](http://apps.azsos.gov/public_services/Title_18/18-11.pdf).

<sup>d</sup>California State Water Resources Control Board. [https://www.waterboards.ca.gov/water\\_issues/programs/nitrate\\_project/](https://www.waterboards.ca.gov/water_issues/programs/nitrate_project/).

<sup>e</sup>Colorado DPEH. <https://www.colorado.gov/pacific/cdphe/water-quality-control-commission-regulations>.

<sup>f</sup>Florida DEP. <https://floridadep.gov/dear/water-quality-standards/content/numeric-nutrient-criteria-development>.

<sup>g</sup>Georgia 391-3-6-.03 Water use Classifications and Water Quality Standards [https://epd.georgia.gov/sites/epd.georgia.gov/files/related\\_files/site\\_page/EPA\\_Approved\\_WQS\\_May\\_1\\_2015.pdf](https://epd.georgia.gov/sites/epd.georgia.gov/files/related_files/site_page/EPA_Approved_WQS_May_1_2015.pdf).

<sup>h</sup>Louisiana Administrative Code (LAC) Title 33. <https://www.epa.gov/sites/production/files/2014-12/documents/lawqs.pdf>.

<sup>i</sup>Minnesota Specific Water Quality Standards for Class 2 Waters. [Minnesota Administrative Rule 7050.0222, Subpart 2. https://www.revisor.mn.gov/rules/?id=7050&view=chapter#rule.7050.0222](https://www.revisor.mn.gov/rules/?id=7050&view=chapter#rule.7050.0222).

<sup>j</sup>Oklahoma Water Quality Standards 785:45-5-10 (standard for any waterbody designated Sensitive Public and Private Water Supplies [SWS]) [https://www.epa.gov/sites/production/files/2014-12/documents/okwqs\\_chapter45.pdf](https://www.epa.gov/sites/production/files/2014-12/documents/okwqs_chapter45.pdf).

<sup>k</sup>Oregon Water Quality Standards. OAR 340-41-0019 (1)(B) <https://secure.sos.state.or.us/oard/viewSingleRule.action?ruleVrsnRsn=68708>.

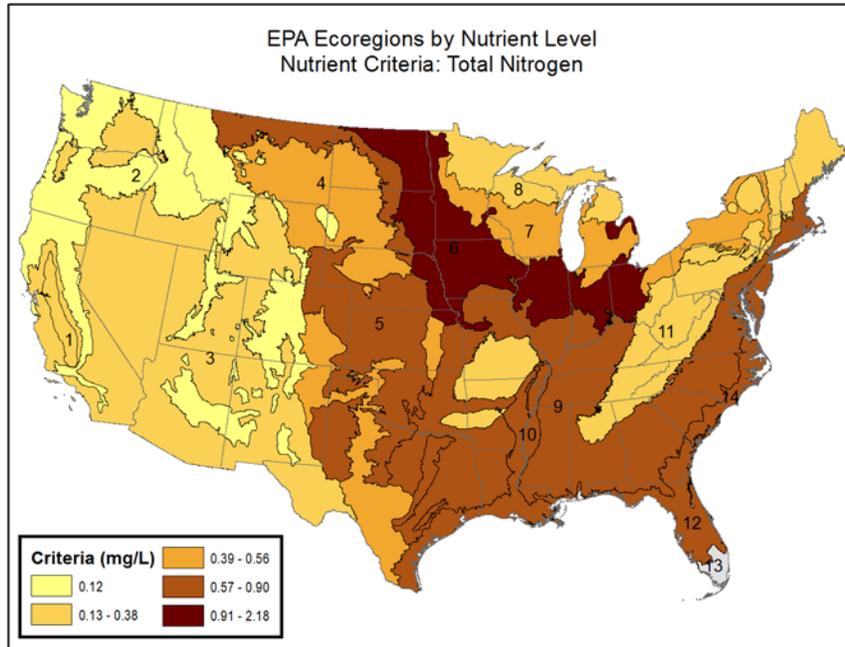
<sup>l</sup>Vermont Water Quality Standards Environmental Protection Rule Chapter 29(a). <https://www.epa.gov/sites/production/files/2014-12/documents/vtwqs.pdf>.

<sup>m</sup>Washington. State cites U.S. EPA Nutrient Aggregate Ecoregion Rivers and Streams criteria [https://www.epa.gov/sites/production/files/2016-06/documents/npwdr\\_complete\\_table.pdf](https://www.epa.gov/sites/production/files/2016-06/documents/npwdr_complete_table.pdf).

**Table 7-7 U.S. EPA aggregate Level III ecoregion nutrient criteria (all values in mg/L; U.S. EPA ecoregional nutrient criteria documents for rivers and streams).**

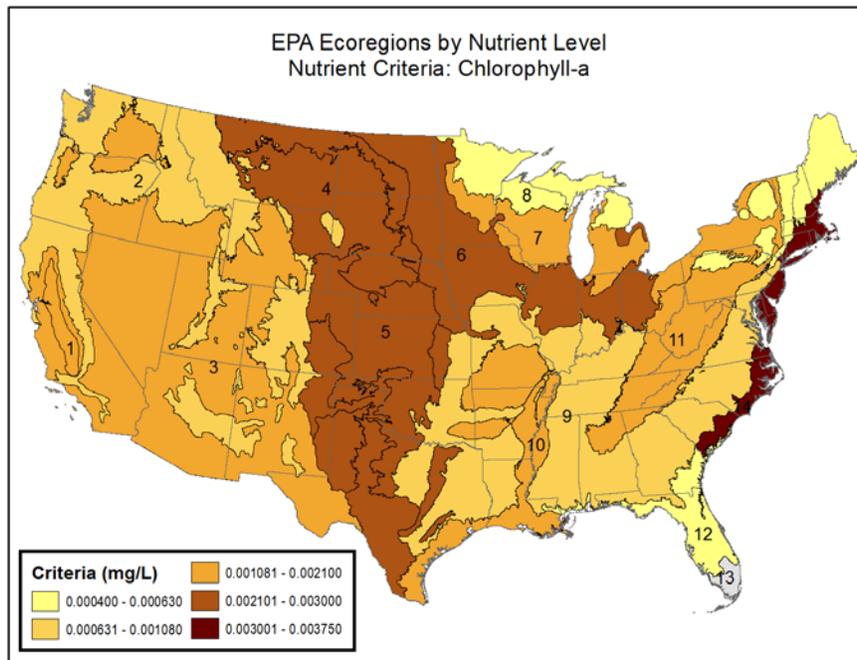
Ecoregion	TN	Chlorophyll <i>a</i>
1	0.31	0.0018
2	0.12	0.00108
3	0.38	0.00179
4	0.56	0.0024
5	0.88	0.003
6	2.18	0.0027
7	0.54	0.0015
8	0.38	0.00063
9	0.69	0.00093
10	0.76	0.0021
11	0.31	0.00161
12	0.9	0.0004

TN = total nitrogen.



L = liter; mg = milligram.

**Figure 7-4** Total nitrogen criterion values by ecoregion.



L = liter; mg = milligram.

**Figure 7-5** Chlorophyll a criterion values by ecoregion.

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### 7.1.7 Freshwater Biogeochemistry Summary

In the 2008 ISA, the body of evidence was sufficient to infer a causal relationship between N and S deposition and the alteration of biogeochemical cycling of N and C in freshwater ecosystems, and between acidifying deposition and changes in biogeochemistry of fresh waters. The strongest evidence for a causal relationship between acidifying deposition and aquatic biogeochemistry comes from studies of changes in surface water chemistry, including concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , inorganic Al, Ca, sum and surplus of base cations, ANC, and surface water pH. Data from long-term monitoring, experimental manipulations, and modeling studies provide consistent and coherent evidence for biogeochemical changes associated with acidifying N and S deposition. As reviewed in the 2008 ISA and newer studies, biogeochemical processes and surface water chemistry are influenced by characteristics of the catchment and the receiving waters. Atmospheric deposition affects the chemistry, and often also the biology, of each type of freshwater environment. These waters may be chronically acidified or subject to occasional episodes of decreased pH, decreased ANC, and increased inorganic Al concentration. Increased N deposition to freshwater systems via runoff or direct atmospheric deposition, especially to N limited and N and phosphorus (P) colimited systems, can stimulate primary production. New information on biogeochemical cycling of N and S, acidifying deposition effects on biogeochemical processes and changes to chemical indicators of surface water chemistry associated with acidification and N nutrient enrichment is consistent with the conclusions of the 2008 ISA, and **the body of evidence is sufficient to infer a causal relationship between N and S deposition and the alteration of freshwater biogeochemistry.**

Indicators of altered N cycling include changes in the concentrations of  $\text{NO}_3^-$  in surface waters. It was well known at the time of the 2008 ISA that key processes such as nitrification and denitrification are quantitatively important portions of the N cycle and that they can be influenced by atmospheric inputs of oxidized and reduced N. More recent research has further substantiated these earlier findings and provided additional quantitative context. Some new research suggests that denitrification may, in some situations, produce more  $\text{N}_2\text{O}$  in relationship to surface water  $\text{NO}_3^-$  concentration than was previously widely recognized. The quantity and timing of  $\text{NO}_3^-$  leaching into surface waters is an indicator of terrestrial N cycling in the associated watershed. The concentration of  $\text{NO}_3^-$  in drainage water provides an index of the balance between removal and addition of N to terrestrial ecosystems. Studies of several types have been conducted in recent years to elucidate these processes, including experimental studies, isotopic analyses, monitoring, and observational studies.

As stated in the 2008 ISA, decreases in base cation concentrations in surface waters in the eastern U.S. over the past two to three decades have been ubiquitous and closely tied to trends in  $\text{SO}_4^{2-}$  concentrations in surface waters. As reported in the 2008 ISA, lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern U.S. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations. As stated in the 2008 ISA, the concentration of dissolved inorganic monomeric Al in surface waters is an especially useful indicator of the adverse impacts of acidifying deposition. Since the 2008 ISA, several monitoring studies have reported decreases in inorganic Al suggestive of chemical recovery of surface waters [[Warby et al. \(2008\)](#); [Strock et al. \(2014\)](#); [Driscoll et al. \(2016\)](#); [Baldigo et al. \(2016\)](#); [Appendix 7.1.5.1](#)].

Monitoring data have proven to constitute a reliable means with which to confirm environmental models and evaluate damage/recovery of ecosystems in response to changes in acidic atmospheric deposition. A number of freshwater monitoring studies have documented ecosystem damage and recovery caused by acidifying deposition of S and/or N. Many of these studies have been conducted in the U.S., especially in the northeast and the Appalachian Mountains. Since 2008, TIME, LTM, and other long-term studies have documented and quantified the responses of surface waters to changes in acidic deposition and other ecosystem drivers. Although many of these monitoring programs were in existence at the time of the 2008 ISA and were considered in that analysis, more recent publications reflect the longer period of monitoring record and strengthen previous conclusions.

With long-term decreases in atmospheric S deposition, the effects of future increases in precipitation that may occur in some areas in response to climate change will likely become increasingly important in regulating the amount of  $\text{SO}_4^{2-}$  mobilized from internal watershed sources. A number of S cycling studies ([Rice et al., 2014](#); [Mitchell et al., 2013](#)) have emphasized the importance of S adsorption and desorption and their interactions with soil pH. In addition, internal watershed sources of S, which were earlier believed to be relatively minor in the northeastern U.S., have and will likely continue to become proportionately more important as S deposition continues to decline.

Reductions in  $\text{SO}_x$  deposition have not consistently resulted in increases of ANC in surface water. The quantitatively most important component of the overall surface water acidification and chemical recovery responses has been change in base cation supply. This was highlighted in the assessment of [Charles and Christie \(1991\)](#) and in the 2008 ISA. Base cations are added to watershed soils by weathering of minerals and atmospheric deposition, and are removed by uptake into growing vegetation or by leaching. Acidic deposition increased leaching of base cations, as  $\text{SO}_4^{2-}$  anions in soil

solution carried along base cations to maintain the charge balance. In watersheds that have received high levels of historical acidic deposition, current exchangeable concentrations of  $\text{Ca}^{2+}$  and other base cations are substantially reduced from likely preindustrial levels, having been depleted by many years of acidic deposition. This base cation depletion constrains ANC and pH recovery of surface waters, as described in the 2008 ISA. Recent results have further corroborated earlier findings and have included experiments, modeling, and gradient studies.

Recent research has described an ecosystem recovery response to decreasing  $\text{SO}_4^{2-}$  deposition that was not a major focus of the 2008 ISA: DOC increases in surface water. Such changes have been attributed to increased atmospheric  $\text{CO}_2$  concentration, climate warming, decreased S deposition with associated changes in water pH and ionic strength, and hydrologic changes associated with drought and precipitation. Although not all increases in DOC are directly caused by decreases in acidifying deposition, any changes in DOC concentration or properties can impact the acid-base chemistry of surface waters and perhaps the composition of aquatic biota. It has been recognized that surface water DOC concentrations had decreased to some extent as a result of acidification, and that DOC would likely increase with recovery. However, the strength of this response and the magnitude of DOC changes have exceeded scientific predictions. Recent research on this topic has been diverse and has included experiments, observation, isotope studies, and synthesis and integration work. Overall, these studies illustrate large increases in DOC with acidification recovery in some aquatic systems. Increases in DOC constrain the extent of ANC and pH recovery, but decrease the toxicity of dissolved Al by converting some of it from inorganic to organic forms ([Lawrence et al., 2013](#)). However, DOC is not an indicator of recovery everywhere; some recovering sites have not shown increasing trends in DOC.

Taken together, results of recent acid-base chemistry studies in the northeastern U.S. confirmed the previously observed pattern of gradual surface water ANC and pH recovery, in some cases more marked decrease in inorganic Al concentrations, and important interactions with DOC. It is important to recognize that recent changes in atmospheric S and N deposition, although substantial in many areas of the U.S., have not occurred in a vacuum. Other important ecosystem drivers have also changed, including various kinds of disturbance, and these changes have varied by region. The potential importance of such factors was known at the time of preparation of the 2008 ISA. More recent work has further confirmed the importance of these linkages, especially those related to climate ([Appendix 13](#)).

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## 7.2 Biogeochemistry of Nitrogen in Estuarine and Near-Coastal Systems

In the 2008 ISA, the evidence was sufficient to infer a causal relationship between N deposition and alterations in the biogeochemical cycling of N and carbon (C) in estuarine and near-coastal marine systems. Since the 2008 ISA, additional studies have quantified atmospheric N deposition to estuaries, especially along the Atlantic coast. New evidence supports that total N loading to watersheds includes atmospherically deposited N with other nonatmospheric sources of N and that total N loading, from dominantly oxidized N inputs to dominantly reduced forms of N, have ramifications for N cycling and biological response in some estuaries. There is additional evidence that N alters biogeochemistry of coastal ecosystems, especially regarding microbial-mediated N transformations, which play large roles in N cycling within estuaries. Research and modeling since the 2008 ISA have shown that many of these N processes such as dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  (DNRA) are more important in the estuarine environment than previously thought, and that rates of N cycling can be highly variable. Key processes affected by N loading include nitrification and denitrification. Eutrophication from N loading may also affect carbonate chemistry in coastal areas, along with atmospheric  $\text{CO}_2$  inputs and other factors, contributing to acidifying conditions in some circumstances such as where there is spatial or temporal decoupling of production and respiration processes. Monitoring of coastal areas shows that excess nutrient inputs continues to be a widespread problem in many parts of the U.S. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemistry in estuarine and near-coastal marine systems**, which is consistent with the findings of the 2008 ISA.

Atmospherically deposited N to watersheds, along with other nonatmospheric sources of N, influence processes that operate along the headwater to ocean continuum. Total N loading to estuaries includes riverine transport of N and direct deposition of N to the estuary itself. This influx of N alters N and C cycling and leads to estuary eutrophication, the process of nutrient over-enrichment. Eutrophic systems are characterized by an increase in the rate of supply of organic matter (primary production and organic C accumulation) in excess of what an ecosystem is normally adapted to processing ([Diaz et al., 2013](#); [Nixon, 1995](#)). Estuary eutrophication is indicated by water quality deterioration, including development of hypoxic zones, species mortality, and formation of harmful algal blooms (HABs). Biological indicators of estuarine condition (e.g., chlorophyll *a*, HABs, macroalgae, submerged aquatic vegetation [SAV]) are described in [Appendix 10](#). [Andersen et al. \(2006\)](#) suggested eutrophication be defined as “the enrichment of water by nutrients, especially N and P and organic matter, causing increased growth of algae and higher forms of plant life to produce an unacceptable deviation in structure function and stability of organisms present in the water and to the

quality of water concerned, compared to reference conditions.” This appendix considers biogeochemical processes affected by N loading, which is a topic not covered in detail in the 2008 ISA. Although this ISA includes both N and S deposition, seawater contains high concentrations of  $\text{SO}_4^{2-}$  so atmospheric inputs of S are unlikely to contribute substantially to biogeochemistry in coastal areas and will not be discussed further in the following sections.

Estuarine biogeochemistry is complicated because it directly controls more than just the N cycle; the response to N loading resulting in eutrophication impacts the chemical cycling of metals and DO ([Appendix 7.2.3](#)), redox conditions, pH ([Appendix 7.2.4](#)), and ultimately energy transfer (e.g., food webs from microbes to humans). The response to N loading is also tightly controlled by water residence time, the availability of organic matter (C) and its lability and reactivity. Excess nutrient inputs are occurring within the context of other stressors such as climate change ([Appendix 7.2.6.12](#)) and rising atmospheric  $\text{CO}_2$ , which further modify coastal biogeochemistry ([Doney, 2010](#)). In the complex environment of the freshwater-to-ocean continuum, there are many chemical and biological indicators of eutrophic condition. One approach is to measure total nutrient loading and concentrations; however, these data need to be interpreted in the context of the physical and hydrological characteristics that determine ecosystem response. Water quality measures such as pH and DO, along with key biological indicators, such as chlorophyll *a*, phytoplankton abundance, harmful algal blooms (HABs), macroalgal abundance, and SAV, can all be used to assess responses to nutrient loading ([Table 7-8](#)). The following sections highlight post-2007 research focusing on N biogeochemistry in estuaries and near-coastal areas.

**Table 7-8 Summary of key indicators of nitrogen enrichment in estuaries.**

Endpoint	Section of ISA That Discusses Endpoint
Chemical indicator	
Dissolved oxygen	<a href="#">7.2.3</a> , <a href="#">10.2.4</a>
Water pH	<a href="#">7.2.4</a>
Biological indicator	
Chlorophyll <i>a</i>	<a href="#">10.2.1</a>
Harmful algal blooms	<a href="#">10.2.2</a>
Macroalgal abundance	<a href="#">10.2.3</a>
Submerged aquatic vegetation	<a href="#">10.2.5</a>

### 7.2.1 Nitrogen Sources

In the 2008 ISA, it was well understood that the importance of atmospheric deposition as a cause of estuarine eutrophication is determined by the relative contribution of the atmospheric versus nonatmospheric sources of N input ([U.S. EPA, 2008a](#)).

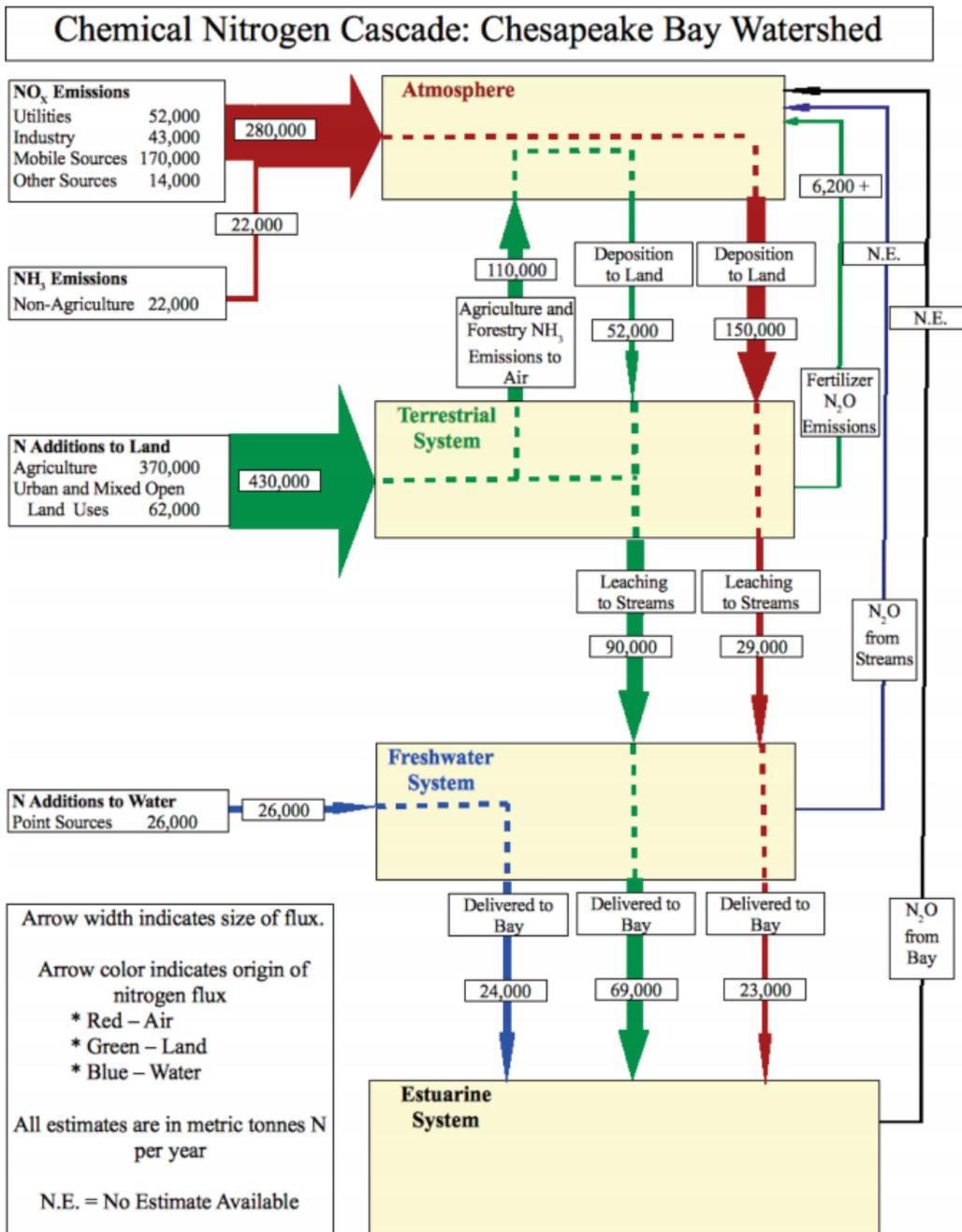
Atmospherically deposited N from combustion of fossil fuels (NO<sub>x</sub>), agricultural sources (NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>) and organic N combine with N from other anthropogenic and natural sources to contribute varying total N inputs in coastal regions. It is the cumulative effects from multiple sources that contributes to ecosystem enrichment ([Paerl et al., 2002](#)).

Atmospheric deposition of reduced N has increased relative to oxidized N in parts of the U.S. including the East and Midwest in the last few decades ([Appendix 2](#)), and this trend is expected to continue in the future under existing emissions controls ([Pinder et al., 2008](#); [U.S. EPA, 2008a](#)). Thus, the form of inorganic N input to coastal areas is changing over time. This has ramifications for N cycling. The increase in highly bioreactive reduced N from deposition and other sources is often a preferred form of N for phytoplankton including unwanted or harmful species ([Appendix 10.3.3](#)). Deposition of oxidized and reduced forms of N are detailed in [Appendix 2](#).

In many places throughout the U.S., nonpoint sources are now the dominant sources of N to water bodies ([Howarth, 2008a, b](#); [Howarth et al., 2002](#)). Releases of N from agricultural, urban, and mixed land uses comprise a significant portion of the nonpoint

sources in many watersheds ([Birch et al., 2011](#); [Alexander et al., 2008](#)). The Chesapeake Bay is an example of a well-studied coastal system where N fluxes have been relatively well characterized (atmospheric inputs represent approximately 25% of total N budget; [Figure 7-6](#)). In management of coastal eutrophication, both point and nonpoint sources have been identified as targets for control of N inputs ([Stephenson et al., 2010](#); [Paerl et al., 2002](#)). Nonpoint sources include diffuse agricultural runoff and wet and dry deposition from the atmosphere. Nitrogen sources also cause production of excess organic matter that feed respiration by microbial decomposers. In estuaries adjacent to areas of coastal upwelling, such as some locations along the Pacific coast of the U.S., oceanic inputs of nutrients can also represent an important source of N to estuarine waters ([Brown and Ozretich, 2009](#)).

Estimates of the contribution of atmospheric deposition to the overall estuary N load exhibit wide variability due in part to the difficulty associated with quantifying multiple agricultural and mobile and stationary fuel combustion emissions sources and N transformations and losses as the N moves from the terrestrial watershed to and within the estuary ([U.S. EPA, 2008a](#); [NRC, 2000](#)). Despite high variability, it appears that atmospheric sources of N loading to estuaries can be quantitatively important, based on studies reviewed in the 2008 ISA and newer studies ([Table 7-9](#)). For example, atmospheric N loads to estuaries in the U.S. were estimated to be as high as 72% for St. Catherine's/Sapelo estuary in Georgia ([Castro et al., 2003](#)). In another study considering atmospheric deposition of N to the East Coast and Gulf of Mexico, direct deposition of N was estimated to contribute from 10 to over 40% of N loading to estuarine, coastal, and open marine waters ([Paerl et al., 2002](#)). In Chesapeake Bay, studies reviewed in the 2008 ISA indicated that atmospheric deposition makes a substantial contribution (up to 50%) to the overall N budget ([Howarth, 2008b](#); [Boyer et al., 2002](#)).



Source: [Birch et al. \(2011\)](#).

**Figure 7-6** Chemical nitrogen cascade in the Chesapeake Bay watershed (metric tons/year).

**Table 7-9 Summary of studies quantifying atmospheric nitrogen contribution to total nitrogen in coastal areas via watersheds and/or direct deposition to estuary surface waters.**

Region	Total N Loading Due to Atmospheric Deposition	Model	Reference
U.S. coastal areas	N deposition to land surfaces that is subsequently exported from watersheds to the coastal zone is responsible for 17 to 21% of the total N input.	NEWS SPARROW	<a href="#">McCrackin et al. (2013)</a>
Gulf of Mexico in the Mississippi/Atchafalaya River basin	Atmospheric deposition contribution, which may include volatilized losses from natural, urban, and agricultural sources, was estimated to be 26% of total N transported to the Gulf of Mexico.	SPARROW using CMAQ total deposition	<a href="#">Robertson and Saad (2013)</a>
Northeast and mid-Atlantic coastal region	Identified wet deposition to the watershed as the dominant source of N to the estuaries of the Connecticut, Kennebec, and Penobscot rivers, but the third largest source (20%) for the region as a whole, after agriculture (37%) and sewage and population-related sources (28%).	SPARROW	<a href="#">Moore et al. (2011)</a>
Narragansett Bay	Combined direct atmospheric deposition to the estuary and atmospheric deposition to the watershed were responsible for 20% of N loading to the bay.		<a href="#">Vadeboncoeur et al. (2010)</a>
Waquoit Bay Estuaries in Cape Cod	Since 1990 wastewater N loads have increased about 80% while loads from atmospheric deposition have decreased by about 41% with no change in total loading on a decadal scale.	NLM	<a href="#">Valiela et al. (2016)</a>
Small-to-medium sized estuaries of southern New England	Direct atmospheric deposition to estuary surface averaged 37%, and indirect atmospheric deposition via the watershed averaged 16% of total N loading, although the percentage varied widely for each individual estuary.	NLM	<a href="#">Latimer and Charpentier (2010)</a>
Tampa Bay	Direct and indirect atmospheric loading were estimated to be 30 and 41%, respectively, of total N loading to the bay.	WDT	<a href="#">Poor et al. (2013b)</a>
	Direct and indirect atmospheric loading were estimated to be 17 and 40%, respectively, of total N loading to the bay.	CMAQ modified with University of California Davis aerosol module	<a href="#">Poor et al. (2013a)</a>
Chesapeake Bay	Atmospheric loading is 24% of total N loading.		<a href="#">Birch et al. (2011)</a>
	Half of the atmospheric source of N to the watershed originates outside of the watershed; indirect loading of atmospheric N via watershed inputs are larger than direct loading to tidal waters.	Chesapeake Airshed Model, combining CMAQ and regression model for wet deposition	<a href="#">Linker et al. (2013)</a>

**Table 7-9 (Continued): Summary of studies quantifying atmospheric nitrogen contribution to total nitrogen in coastal areas via watersheds and/or direct deposition to estuary surface waters.**

Region	Total N Loading Due to Atmospheric Deposition	Model	Reference
Gulf of Mexico in the Mississippi/Atchafalaya River basin	Atmospheric deposition to watersheds in the basin contributed about 16% of the total N load, second to N from corn and soybean production (52%).	SPARROW	<a href="#">Alexander et al. (2008)</a>
Pacific Northwest, Yaquina Bay	Direct deposition represented only 0.03% of N inputs and watershed inputs of N fixing red alder ( <i>Alnus rubra</i> ) was a greater source of N to the watershed than atmospheric deposition (8%).		<a href="#">Brown and Ozretich (2009)</a>
<b>Key pre-2008 literature</b>			
34 Atlantic and Gulf coast estuaries	The contribution of atmospheric deposition (including directly onto the water surface and onto the watershed) was 7–72% of the total N.	WATERS-N	<a href="#">Castro et al. (2001); Castro et al. (2003)</a>
10 estuaries along the U.S. east coast	Total atmospheric inputs (watershed runoff plus direct deposition to the surface of the estuary) accounted for 15 to 42% of total N inputs. In four of the estuaries direct deposition was 35 to 50% of the total atmospheric N inputs.		<a href="#">Castro and Driscoll (2002)</a>
Chesapeake Bay	Atmospheric deposition makes a substantial contribution (about 25%) to the overall N budget.		<a href="#">Howarth (2007)</a>
16 northeastern river basins	Atmospheric deposition averaged 31% of total N inputs; values for watersheds in northern New England were substantially higher and atmospheric deposition dominated. Estimated riverine export of N amounted to 25% of total N inputs.		<a href="#">Boyer et al. (2002)</a>
Based on 34 Atlantic and Gulf coast estuaries	In systems with watershed area to estuarine surface area ratios greater than 15, N deposition is not as important (comprising less than 25% total N input) as in estuaries that are large relative to their watershed.		<a href="#">Castro et al. (2001)</a>

CMAQ = Community Multiscale Air Quality; N = nitrogen; NEWS = Nutrient Export from Watersheds; NLM = Nitrogen Loading model; SPARROW = Spatially Referenced Regressions on Watershed Attributes; WATERS-N = Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen; WDT = Water Deposition Tool.

In a series of studies reviewed in the 2008 ISA, the model Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N) estimated that the contribution of atmospheric deposition (including directly onto the water surface and indirectly onto the watershed) was 7–60% of the total N input to 34 Atlantic and Gulf coast estuaries ([Castro et al., 2003](#); [Castro et al., 2001](#)). Nitrogen deposition contributed 20–86% (average = 48%) of the total N input to 22 watersheds having watershed area to estuarine surface area ratio less than 15. In systems with a ratio greater than 15, N deposition is not as important, comprising less than 25% of total N input across 12 systems ([Castro et al., 2001](#)).

Since the 2008 ISA, additional modeling studies have estimated the amount and proportion of current and future N loading expected to result from atmospheric deposition ([Table 7-1](#)). The Nutrient Export from Watersheds (NEWS) and SPARROW models agreed that 62–81% of N delivered to the coastal zone in the continental U.S. is anthropogenic in source ([McCrackin et al., 2013](#)). Model results showed that atmospheric N deposition that is subsequently transported to estuaries represents 17–21% of the total N exported to the coastal zone ([McCrackin et al., 2013](#); [Moore et al., 2011](#)). Using SPARROW atmospheric N deposition was identified as the dominant source of delivered N to estuaries along the Atlantic Coast and the Gulf of Mexico ([McCrackin et al., 2013](#)). Using SPARROW, the atmospheric deposition contribution (which may include volatilized losses from natural, urban, and agricultural sources) was estimated to be 26% of total N transported to the Gulf of Mexico in the Mississippi/Atchafalaya River basin ([Robertson and Saad, 2013](#)). [Moore et al. \(2011\)](#) found that SPARROW identified atmospheric deposition to watersheds as the dominant source of N to the estuaries of the Connecticut, Kennebec, and Penobscot rivers, but the third largest source (20%) for the Northeast and mid-Atlantic coastal region as a whole, after agriculture (37%) and sewage and population-related sources (28%). In contrast, atmospheric deposition is a less substantial source of N to some estuaries, especially in the Pacific Northwest. In Yaquina Bay estuary, OR, direct deposition represented only 0.03% of N inputs and watershed inputs of N fixing red alder (*Alnus rubra*) trees was a larger (8%) source of N to the watershed than atmospheric deposition ([Brown and Ozretich, 2009](#)). In Yaquina Bay estuary, the ocean is the primary source of N during the dry season and the river is the primary source during the wet season.

A modeling study conducted by [Vadeboncoeur et al. \(2010\)](#) estimated that the third largest source of N loading (via the watershed and directly to the water body) to Narragansett Bay in the year 2000 was atmospheric deposition (20%). Future scenarios suggested that very aggressive reductions in both fertilizer use and atmospheric deposition would be needed for Narragansett Bay to return to early 20th century levels of N loading ([Vadeboncoeur et al., 2010](#)). [Latimer and Charpentier \(2010\)](#) applied the

Watershed N Loading Model (NLM) to small- to medium-sized estuaries of southern New England. Direct atmospheric deposition to the water surface made up an average of 37% of the N input, although the percentage varied widely for individual estuaries ([Latimer and Charpentier, 2010](#)). In the same study, wastewater represented 36% of the total N inputs. Indirect atmospheric deposition within the watershed was estimated to be 16% and the fertilizer component was 12%. The relative magnitudes of these source types varied across estuaries. In another modeling study with NLM using data going back to 1990, atmospheric deposition decreased by about 41% while wastewater inputs have increased 80% with a net result that total loads have not changed on a decadal scale in the Waquoit Bay estuaries in Cape Cod, MA ([Valiela et al., 2016](#)). Using the Watershed Deposition Tool (WDT), [Poor et al. \(2013b\)](#) estimated direct atmospheric loading of 1,080 metric tons of N and 1,490 metric tons of N from indirect atmospheric loading (assuming a watershed-to-bay transfer rate of 18%) for Tampa Bay using data from 2002. Thus, atmospheric sources were an estimated 71% of the total N loading. Key studies from the 2008 ISA on atmospheric N loading to estuaries are summarized in [Table 7-9](#), along with newer estimates.

Near NH<sub>3</sub> emission sources, such as large mammal and poultry livestock operations, N deposition is expected to increase 10–40% by 2020 according to different regulation and reduction scenarios ([Pinder et al., 2008](#)). Many of the agricultural emission sources are located in sensitive watersheds such as the Chesapeake Bay and Pamlico Sound, NC ([Pinder et al., 2008](#)). [Birch et al. \(2011\)](#) estimated that 24% of the reactive N that reached Chesapeake Bay originated as emissions to the atmosphere that were then deposited in the watershed to land and water, 57% came from terrestrial N additions from nonpoint source runoff, and the remaining 19% was estimated to come from direct discharges of N to freshwater ecosystems. The results of a modeling study that integrated the airshed, watershed, and estuary indicated that atmospheric deposition represented one of the largest inputs of N to the Chesapeake Bay watershed, and about half of it originated outside the watershed ([Linker et al., 2013](#)). Atmospheric N loading to tidal waters was included in the Chesapeake Bay 2010 TMDL, the first time that atmospheric deposition has been included in a plan for nutrient load reduction ([U.S. EPA, 2010](#)). The explicit TMDL N allocation was determined to be 7.1 million kg per year of total N atmospheric deposition loads directly to Chesapeake Bay and tidal tributary surface waters. It was based on the 2020 CMAQ N deposition scenario described by [Linker et al. \(2013\)](#). [Appendix 2](#) provides more detailed discussion of N source apportionment.

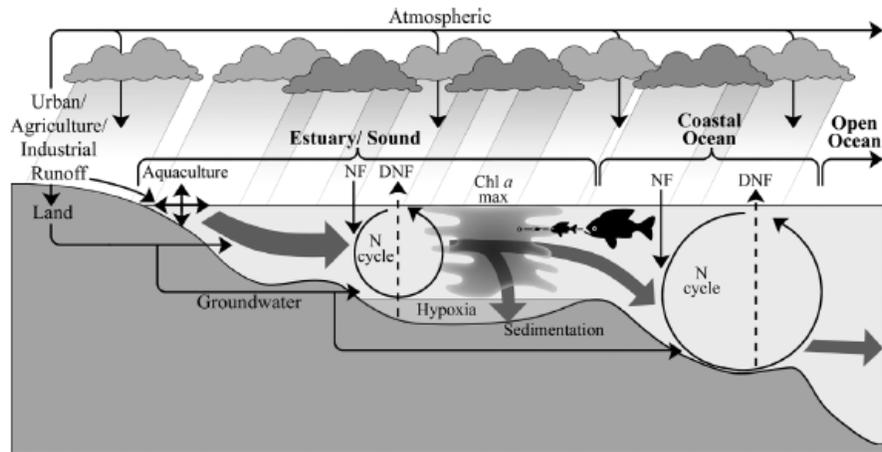
Although the geographic scope of this ISA is limited to estuaries and near-coastal areas of the U.S., some evidence indicates that the open ocean may be affected by atmospheric deposition of N ([Ren et al., 2017](#); [Kim et al., 2011](#)). [Ren et al. \(2017\)](#) provided <sup>15</sup>N stable isotope evidence that N emissions have changed the biogeochemical cycling of N in the

open ocean in nutrient-limited low-latitude regions such as the northwestern Pacific Ocean. Changes in  $\delta^{15}\text{N}$  over time were documented in coral skeletons over a period of 45 years at Dongsha Atoll in the northern South China Sea. The proximity of this water body to anthropogenic N emissions sources in Asia and its depth (1,300 m) both contribute to its sensitivity to N deposition and changes in nutrient cycling.

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## 7.2.2 The Estuary Environment

Atmospherically deposited N, along with other sources of N to coastal systems, influences uptake and conversion processes that operate along the freshwater-to-ocean continuum [[Seitzinger et al. \(2006\)](#); [Paerl and Piehler \(2008\)](#); [Figure 7-7](#)]. Conditions in upstream terrestrial systems, such as nutrient loading or land use, can exert strong influences on coastal habitats and processes [[Ruttenberg and Granek \(2011\)](#); [Appendix 4](#)]. In addition to inputs of N from outside sources, the varying rates of different N cycling processes, as well as C availability and reactivity within estuaries themselves, can also affect the magnitude of eutrophication experienced as a result of external N enrichment ([Newell et al., 2016](#); [Anderson et al., 2014b](#); [Smyth et al., 2013](#); [Crowe et al., 2012](#)). Estuaries are heterogeneous environments characterized by physicochemical gradients of salinity and both naturally and anthropogenically derived nutrients. Water quality in estuaries is highly variable due to physical and chemical aspects of each estuary ([Appendix 10.1.4](#)) and factors such as temperature and precipitation ([Rheuban et al., 2016](#)). At the upstream end of an estuary, the water is primarily fresh much of the time. Nonpoint source runoff of N from the land surface, only a part of which is of atmospheric origin (mainly deposition to land and subsequently leached to the river water), dominates new N inputs. Downstream, freshwater inflows gradually mix with salt water to form mesohaline segments of the estuary. These changes in salinity impact the ionic strength of the water. Further along the salinity gradient, a significant fraction of the terrestrial biologically available N load is assimilated by phytoplankton and benthic flora, removed by microbes in the process of denitrification or advected to the ocean ([Paerl et al., 2002](#)). Direct atmospheric N inputs also impact the lower estuary, although the relative importance of N deposition in this zone is uncertain and variable ([Paerl et al., 2002](#)). In many estuary and sound ecosystems, primary production and phytoplankton biomass are highest at mid-estuary locations, where N loads and decreasing rates of flushing (increasing residence times) overlap.



Chl a = chlorophyll a; DNF = denitrified; N = nitrogen; N<sub>2</sub> = nitrogen; NF = nitrogen (N<sub>2</sub>) fixation.  
 Source: From [Paerl and Piehler \(2008\)](#).

**Figure 7-7** Schematic diagram illustrating sources, transformations, and fate of nitrogen along the estuary-to-ocean continuum. Surface, subsurface, and atmospheric pathways of externally supplied or new nitrogen inputs attributable to anthropogenic activities are shown as internal nitrogen cycling. The combined anthropogenic nitrogen inputs are shown as a thick arrow (upstream), which decreases in thickness downstream as a portion of the nitrogen inputs settles to the bottom sediments and is buried and/or denitrified. Nitrogen (N<sub>2</sub>) fixation is a biologically mediated new nitrogen input. The linkage of anthropogenically enhanced nitrogen inputs to accelerated primary production or eutrophication and its trophic and biogeochemical fate are also shown.

### 7.2.3 Dissolved Oxygen and Hypoxia

Low oxygen (hypoxia) or the absence of oxygen (anoxia) in coastal waters have implications for N cycling. Oxygen depletion mainly occurs in bottom waters under stratified conditions. The extent of hypoxia in U.S. waters and effects of low DO on biota are discussed in [Appendix 10.2.4](#). Biogeochemical processes that occur in the sediment of estuarine and near-coastal ecosystems are important to the cycling of N that is deposited or transported to estuarine ecosystems. Inputs of C and a stratified water column that separates well-oxygenated surface water from bottom water and sediments is generally required for formation of hypoxic zones ([Jewett et al., 2010](#)). Eutrophication-induced hypoxia, which has been documented globally, can be

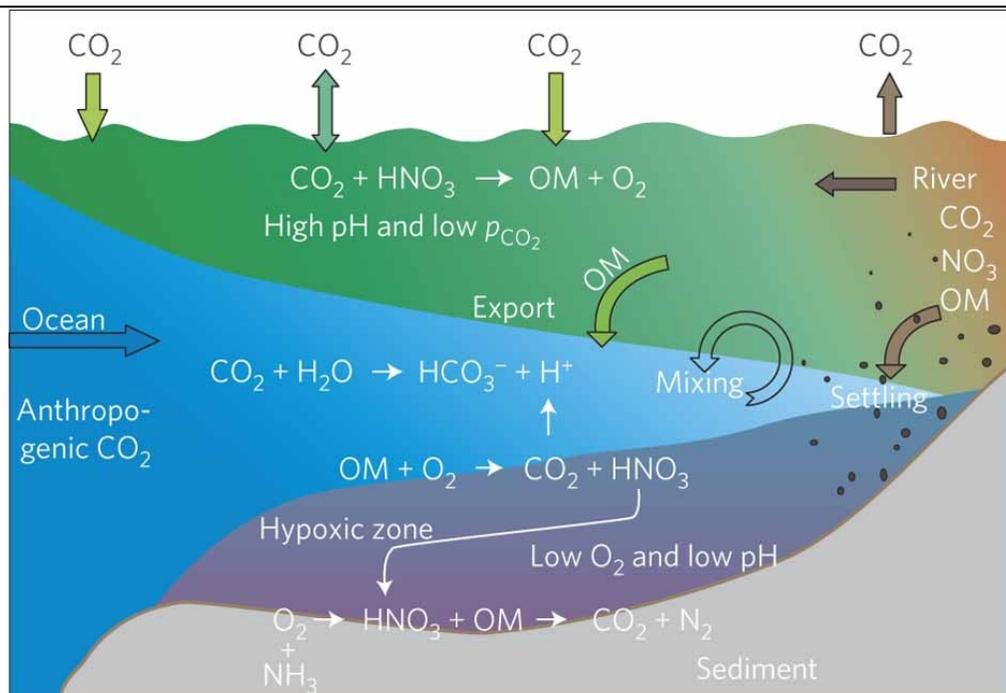
characterized by both the duration of the hypoxic event and the ecosystem response ([Diaz et al., 2013](#); [Diaz and Rosenberg, 2008](#)). Summer hypoxia is most common, followed by systems that experience periodic O<sub>2</sub> depletion that may occur more often than seasonally. Development of seasonal hypoxia is common in shallow coastal regions that receive high inputs of nutrients, including N, from coastal rivers. Development of hypoxia is increasingly becoming a concern throughout the U.S. and internationally ([Jewett et al., 2010](#); [Diaz and Rosenberg, 2008](#)). [Middelburg and Levin \(2009\)](#) provided a review of coastal hypoxia and linkages with biogeochemistry. Changes in bottom water O<sub>2</sub> concentrations influence chemical exchange between sediment and bottom water. [Rabalais et al. \(2010\)](#) provided a synthesis of knowledge regarding hypoxia in coastal waters. Hypoxic water masses (less than approximately 30% saturation) are more likely to occur in marine waters where and when water residence time is long, water exchange is limited, the water column stratifies, and the production and movement of C to bottom waters are relatively high. [Howarth et al. \(2011\)](#) reviewed the complex interactions between biogeochemical cycling, eutrophication, and hypoxia in coastal marine systems. Biochemical feedbacks under eutrophic conditions accelerate further eutrophication and hypoxia. In locations where coastal upwelling can be a large source of nutrient loads such as the Pacific Northwest, advection of upwelled water can introduce hypoxic water into estuaries that is not or poorly related to anthropogenic eutrophication ([Brown and Power, 2011](#); [Brown and Ozretich, 2009](#)).

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#### 7.2.4 Estuarine and Near-Coastal pH

Estuarine carbonate chemistry is complex, responding to a wide variety of natural, anthropogenic, physical (mixing), chemical, and biological drivers ([Cai et al., 2011c](#)). Measured pH is often used as a proxy for the carbonate chemistry system. The pH of estuarine waters can affect N cycling processes and reflect coastal acidification. Since the 2008 ISA, a number of papers have identified links between nutrient enrichment and coastal acidification, and several mechanisms have been identified ([Baumann and Smith, 2018](#); [Cai et al., 2017b](#); [Hu et al., 2015a](#)). One of the initial studies found that CO<sub>2</sub> production during decomposition of organic matter delivered to coastal zones from rivers experiencing eutrophication has enhanced the acidification of coastal subsurface waters ([Figure 7-8](#)) in the Gulf of Mexico and the East China Sea ([Cai et al., 2011c](#)). A key condition for development of hypoxia/anoxia eutrophication responses and acidification responses is the spatial or temporal decoupling of production and respiration. In many systems, the decoupling comes in the form of thermal or salinity driven stratification which limits mixing of surface and bottom water masses. Dissolution of atmospheric anthropogenic CO<sub>2</sub> into the ocean which has led to long-term decreases in pH injects

atmospheric anthropogenic CO<sub>2</sub> into the bottom waters of the system via mixing. Primary production in the surface waters result in localized basification of surface waters and produces particulate organic matter which falls through the pycnocline. In addition, terrestrially derived organic matter is also delivered by rivers and can contribute to respiration further increasing the dissolved inorganic C pool. CO<sub>2</sub> produced from decomposition of this labile and reactive organic matter associated with eutrophication combines with atmospheric anthropogenic CO<sub>2</sub> and reduced buffering capacity to lower pH in a synergistic manner (Cai et al., 2011c). There is also the possibility of increased pH due to N-enhanced rates of photosynthesis. As described in Figure 7-8 vertical decoupling of primary production and respiration can lead to acidification in subsurface waters.



OM = organic matter.  
Source: Cai et al. (2011c).

**Figure 7-8 A conceptual model for a large river plume eutrophication and subsurface water hypoxia and acidification.**

Acidification processes have also been shown to be seasonally variable. Wallace et al. (2014) found that Long Island Sound and Narragansett Bay had partial pressure of CO<sub>2</sub> >1,000 μatm measured in the water during summer months while exposed to extreme eutrophication; temperature changes accounted for <5% of the partial pressure of CO<sub>2</sub>

increase. Consequently, they conclude that the links between eutrophication, hypoxia, and acidification can be a function of nutrient loading rates. This acidification response is driven not only by the remineralization of autochthonous carbon but also inputs of anthropogenic allochthonous carbon as well as the acidic contribution from the discharged sewage itself ([Wallace et al., 2014](#)). In contrast, [Baumann and Smith \(2018\)](#) suggested that the thermal pathway of metabolic coastal acidification driven by increased respiration can be a direct response to warming. Other works also evaluate how reduced buffering capacity caused by changes in riverine delivery of alkalinity in response to climate change also contribute to the development of acidic conditions ([Cai et al., 2017b](#); [Hu et al., 2015a](#)).

Production of CO<sub>2</sub> by living algae and seagrasses during the night can also drive acidification. In a eutrophic seagrass ecosystem in Cape Cod, MA, there was a very pronounced diel pattern of pH, with moderate pH during the day, but by dawn very acidic waters resulted from overnight community respiration ([Howarth et al., 2014](#)). During the daytime, CO<sub>2</sub> was drawn down through primary production, and as a consequence the pH steadily climbed (e.g., basification). In this system, CO<sub>2</sub> remained supersaturated (low pH) and the net effect was to increase acidification, due to slow exchange of CO<sub>2</sub> with the atmosphere. This additional CO<sub>2</sub> further acidifies marine waters as it dissociates into carbonate ions and hydrogen ions ([Sunda and Cai, 2012](#); [Cai et al., 2011c](#); [Howarth et al., 2011](#)). An important additional source of organic matter leading to overall declines in pH is potentially allochthonous organic matter inputs that have been increasing in many coastal watersheds from changing land use ([Wilson et al., 2016](#); [Wetz and Yoskowitz, 2013](#)). Nitrogen-driven eutrophication and anthropogenically enhanced allochthonous organic matter loading operate simultaneously.

Biogeochemical modeling of eutrophically driven ocean acidification coupled to data collected from the Gulf of Mexico, the Baltic Sea, and the East China Sea predicted that eutrophication would cause a 0.24 to 1.1 unit decrease in pH of bottom waters, and also that increasing atmospheric CO<sub>2</sub> will synergistically amplify eutrophically driven acidification ([Sunda and Cai, 2012](#); [Cai et al., 2011c](#)). The increase in atmospheric CO<sub>2</sub> dissolution is also expected to alter the N cycle in the ocean, with implications for the entire ecosystem. Acidification will result in decreased rates of nitrification, which, combined with expected increasing N deposition, will likely cause the NH<sub>4</sub><sup>+</sup> concentration of the water to rise ([Lefebvre et al., 2012](#)). Models show that while the impact of each acidification pathway (N enrichment and atmospheric CO<sub>2</sub> dissolution) may be moderate, the combined effect of the two may be much larger than would be expected by just adding the effects of each pathway together ([Sunda and Cai, 2012](#); [Cai et al., 2011c](#)).

More recent work has identified some similar dynamics in Chesapeake Bay, where anoxia related to eutrophication is driving acidification and carbonate mineral dissolution (Cai et al., 2017b). Ocean acidification has detrimental effects on marine calcifiers and is projected to alter marine habitat and food webs affecting a wide range of marine ecosystem processes (Marshall et al., 2017; Mostofa et al., 2016; Andersson et al., 2015; Sunda and Cai, 2012; Doney et al., 2009). Decreased concentration of carbonate ions (which organisms such as calcareous plankton, oysters, clams, sea urchins, and coral take up to build shells) are observed in acidic conditions [Hettinger et al. (2012); Kroeker et al. (2013); Barton et al. (2015); Chan et al. (2016); Appendix 10.5].

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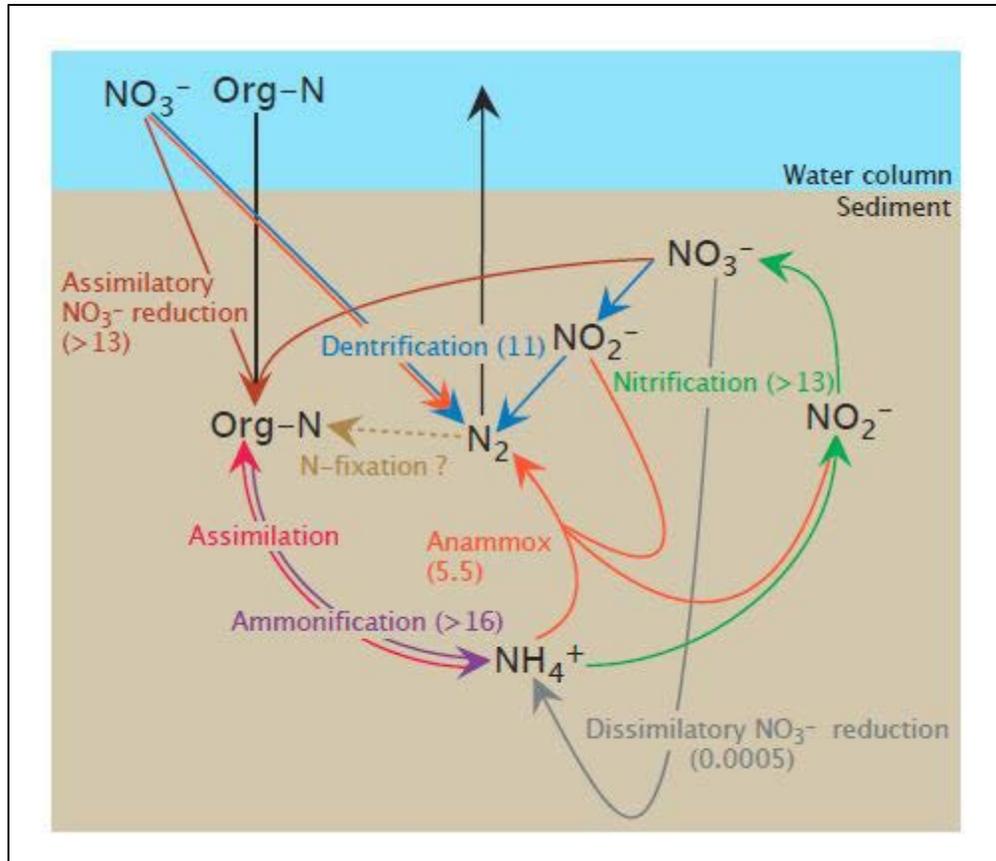
## 7.2.5 Nitrogen in Surface Waters

In most estuaries, N inputs from atmospheric deposition, wastewater and agricultural runoff control eutrophication (Valiela et al., 2016; Howarth et al., 1996a; Vitousek and Howarth, 1991) and can be linked to changes in biological indicators of nutrient enrichment known to be sensitive to shifts in N loading (Appendix 10). In many estuaries, this occurs with a simultaneous increase in P as N, and P runoff loads are often coupled, especially where agricultural or human waste sources dominate. In general, estuaries tend to be N limited (Howarth et al., 2011; Paerl and Piehler, 2008; Elser et al., 2007; Howarth and Marino, 2006; NRC, 2000; Nixon, 1995; Howarth, 1988). However, more recent studies show that some estuaries are P limited, or colimited by N and P, or switch seasonally between N and P limitation (Howarth et al., 2011; Paerl and Piehler, 2008; Howarth and Marino, 2006). To date, several states have developed site-specific or state-wide numeric nutrient criteria to address nutrient pollution problems (Appendix 7.2.9). Adopted criteria include TN,  $\text{NO}_3^-$  as N, DIN as N, or TMDLs. In some estuaries, especially in the Pacific Northwest, nutrients from upwelling and oceanic exchange caused by regional wind patterns likely control primary production rather than anthropogenic nutrient loading (Brown and Ozretich, 2009; Hickey and Banas, 2003). Quantification of N in the estuarine environment can be highly variable both spatially and temporally due to the physiochemical gradients within estuaries (Appendix 10.1.4, the influence of natural and anthropogenic stressors, and factors such as precipitation and warming (Appendix 10.1.4.1). For example, analysis of 22 years of water quality data from Buzzards Bay, MA by Rheuban et al. (2016) indicated that climate related stressors of warming and precipitation appeared to influence ecosystem response to TN over time. Since the 2008 ISA, additional thresholds of response to N have been identified for biological indicators (Appendix 10.6).

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## 7.2.6 Nitrogen Cycling

Some of the key processes involved in N cycling in estuarine and near coastal environments include N sinks such as denitrification and N<sub>2</sub> production via anaerobic ammonium oxidation (anammox), bioavailable N sources such as N fixation and DNRA, and other N cycling processes including nitrification ([Figure 7-9](#)). A major control on these processes is C availability and reactivity ([Plummer et al., 2015](#)). Benthic DO concentrations (hypoxia) and S cycling may also affect the occurrence and rates of many of these N cycling processes. Recent research has shown that many of these N cycling processes are more important in the estuarine environment than previously thought, and that the rates of different N cycling processes can be highly variable, depending on environmental factors such as N availability, organic C source, temperature, seasonality, oxygen levels, microbial community structure, aquatic habitat type, and others ([Newell et al., 2016](#); [Plummer et al., 2015](#)). Some processes were relatively well understood at the time of the 2008 ISA while the role of others such as DNRA has been characterized only recently as an important pathway in which N is conserved in coastal ecosystems.



Notes: Numbers in parentheses are rates of the reactions in  $\mu\text{mol}/\text{m}^2/\text{h}$  as measured by [Crowe et al. \(2012\)](#).

**Figure 7-9** New complexities in nitrogen cycling have been detailed since the 2008 ISA as shown in this illustration of the sedimentary N cycle in the Lower St. Lawrence estuary.

### 7.2.6.1 Nitrogen Fixation

Nitrogen fixation is the microbially mediated conversion of atmospheric nitrogen gas ( $\text{N}_2$ ) to a bioavailable form of N (i.e., ammonia [ $\text{NH}_3$ ]). The community of N fixing microorganisms is more diverse in estuarine and coastal waters than previously thought, and N fixation occurs more widely than previously assumed. Advances in research methods for measuring heterotrophic N fixation have led to the discovery that rates of N fixation in coastal sediments can cause the sediments to be a significant source of N to the ecosystem ([Newell et al., 2016](#)). [Newell et al. \(2016\)](#) reported on several studies of N fixation rates in coastal sediments (measured as sediment  $\text{N}_2$  uptake) with rates ranging from  $-12$  to  $-250 \mu\text{mol N}/\text{m}^2/\text{h}$ . In some cases, these higher rates of N fixation can

potentially exacerbate the eutrophic conditions already experienced in an estuary, as was the case in Narragansett Bay, RI, where up to 30% of the N added to the system came from N fixation in some years ([Newell et al., 2016](#); [Fulweiler and Heiss, 2014](#)).

Research in the past decade has also sought to determine what environmental factors may cause sediments to switch from acting as a sink to acting as a net source of N due to increased N fixation. Organic matter enrichment appears to be one factor. [Fulweiler et al. \(2008\)](#) noted a “threshold” of organic enrichment at 0.3 g C/m<sup>2</sup>/day, below which N fixation took place at high rates but above which the rates of N fixation declined and the sediments became a net sink of N due to denitrification ([Fulweiler et al., 2008](#)).

In Copano Bay, a shallow bay on the Gulf of Mexico in Texas, periods of drought coincided with higher rates of N fixation ([Bruesewitz et al., 2013](#)). Thus, base flow conditions allowed primary production to continue, even when external sources of N via riverine transport and runoff were very low.

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#### **7.2.6.2 Role of Dissolved Organic Nitrogen**

Recent research has shown the importance of measuring DON fluxes, as they can be a more significant internal source of N from the sediments than previously assumed. Terrestrial inputs of DON are poorly characterized, and these fluxes are not routinely included in estuarine nutrient budgets. [Alkhatib et al. \(2013\)](#) found that DON fluxes out of the sediments, at rates of 110 to 430 μmol/m<sup>2</sup>/day, were at times greater than NO<sub>3</sub><sup>-</sup> flux into the sediments in the St. Lawrence estuary and Gulf of St. Lawrence. Many species of algae and bacteria will take up DON; thus, this flux of DON out of the sediments leads to an important sink for N within the system ([Alkhatib et al., 2013](#)). Reactivity of organic matter is another key factor in DON availability.

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#### **7.2.6.3 Dissolved Inorganic Nitrogen**

Dissolved inorganic nitrogen (NH<sub>4</sub><sup>+</sup> plus [NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>]) plays an important role in N cycling and primary productivity. N laden organic matter may be transported to estuaries and coastal waters from river basins. Estuarine benthic communities degrade this allochthonous organic matter, releasing NH<sub>4</sub><sup>+</sup> at the aerobic sediment-water interface, and NH<sub>4</sub><sup>+</sup> further enhances estuarine productivity via oxidation to NO<sub>3</sub><sup>-</sup>. Generally, NH<sub>4</sub><sup>+</sup> is considered the preferred form for some phytoplankton, including harmful species, due to lower energy requirements for uptake [[Glibert et al. \(2016\)](#); [Appendix 10.2.2](#) and [Figure 10-7](#)]. Remineralization of organic matter is sensitive to redox conditions ([Reddy and Patrick, 1984](#)), sediment grain size ([Nowicki and Nixon, 1985](#)), and temperature

([Kemp and Boynton, 1984](#)). If  $\text{NH}_4^+$  has to compete with saltwater cations for adsorption sites, then excess  $\text{NH}_4^+$  becomes free in these saline waters ([Gardner et al., 1991](#)).

The understanding of DIN's role in estuarine and near-coastal nutrient enrichment is an active field of research. [Cornwell et al. \(2014\)](#) measured September 2011 versus March 2012 benthic nutrient fluxes in the San Francisco Bay and delta and ascertained that sediment DIN is an important source of N to the water column and system productivity. [Paudel et al. \(2017\)](#) examined the effect of flow regimes on DIN release at the sediment-water interface. They compared two south Texas estuaries: the Nueces and the Guadalupe. The Guadalupe has eight times the inflow of the Nueces. They observed significantly different  $\text{NH}_4^+$  concentrations between the estuaries; however, the  $\text{NO}_2^- + \text{NO}_3^-$  concentration did not differ significantly. Using the coastal water phytoplankton Redfield ratio (ratio of N:P in phytoplankton) of 16:1, they found the Nueces N:P ratio below the Redfield but the Guadalupe above, suggesting that the Nueces was N limited.  $\text{NH}_4^+$  releases were greater in the Nueces estuary due to its higher organic content in sediment. In the Guadalupe estuary, finer sediment particles may retain N.

[Buzzelli et al. \(2013b\)](#) applied the Land-Ocean Interactions in the Coastal Zone (LOICA) approach to gain understanding about the seasonal budgets for DIN in two south Florida estuaries—Caloosahatchee River estuary (CRE) and the St. Lucie estuary (SLE)—during the years 2002 to 2008. The analysis included the contribution of direct wet atmospheric N deposition to estuarine loading. They compared the production of C, N, and P in the two estuaries and source attribution. These two watersheds are highly disturbed due to urban growth and agriculture and flush at substantially different rates. They sought to understand the optimum metabolism of each estuary from a C, N, and P production and consumption perspective to better inform coastal watershed management planning. Both estuaries have similar agricultural and urban land use; however, study authors observed increased DIN in the CRE during the wet season but not in the SLE. The SLE's "muck-like" sediment reduces light penetration and isolates the water column from the benthic zone ([Buzzelli et al., 2013a](#); [Sime, 2005](#)). External loading influenced the SLE's production of C, N, and P more than the CRE. Even though the CRE is 2.5 times larger (and receives double the freshwater inflow) as compared with the SLE, the CRE's DIP and DIN loadings are only 60–70% of SLE's loadings when spatially normalized.

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#### **7.2.6.4 Nitrification**

Nitrification is the microbially mediated conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$ ; thus, exchanging one bioavailable N form for another. The process includes  $\text{NH}_3$  oxidation to  $\text{NO}_2^-$ ,

followed by  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ . This importance was well known at the time of preparation of the 2008 ISA. More recent research has provided additional quantitative context, including new studies in North America and Europe. Where DIN loading is not dominated by  $\text{NO}_3^-$ , the oxidation of  $\text{NH}_4^+$  to form  $\text{NO}_3^-$  largely controls the relative abundance of oxidized and reduced DIN in estuaries. Nitrification rates are often correlated with suspended particulate matter and  $\text{NH}_4^+$  concentration in water ([Damashek et al., 2016](#)).

There have been new findings about the process of nitrification since the 2008 ISA. It has generally been assumed that the first step of nitrification ( $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ) is the rate-limiting step ([Damashek et al., 2015](#)). However, recent research indicates that physical factors such as salinity, temperature, pH, DO concentration, and light can affect the rates to the extent that the two steps of nitrification may not always be “coupled” as is often assumed ([Heiss and Fulweiler, 2016](#); [Bristow et al., 2015](#)). In some cases, the rate for the second step of the nitrification process may be higher than for the first step. For example, results showed that rates of  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$  were negatively correlated with light and pH, indicating in part that  $\text{NO}_2^-$  oxidation rates are higher when the pH is lower ([Heiss and Fulweiler, 2016](#)). Decoupling of the two nitrification steps was also observed in the Gulf of Mexico hypoxic zone, where the first step occurred at rates of up to 30 times higher than the second step, a result the authors concluded was due to environmental factors such as temperature, substrate availability, and hypoxic conditions ([Bristow et al., 2015](#)). These results add complexity to the understanding of nitrification rate and the degree to which that process is affected by environmental factors and support the need to measure the two steps of nitrification separately to better predict the effects of perturbations to the N cycle in coastal waters.

Nitrification makes denitrification possible to some degree, and the reactions are often assumed to be coupled, as nitrification provides the  $\text{NO}_3^-$  starting point for the N reduction process of denitrification. Since the 2008 ISA, the degree of coupling (and “decoupling”) between nitrification and denitrification reactions has been the subject of much research (see discussion in [Appendix 7.2.6.8](#)).

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#### **7.2.6.5 Dissimilatory Nitrate Reduction to Ammonium**

DNRA has been characterized as an important pathway in which N is conserved in coastal ecosystems ([Giblin et al., 2013](#)). Although DNRA was not discussed in the 2008 ISA, more recent research has established DNRA as a potentially important N reduction pathway, and one that varies in magnitude depending on a range of environmental factors. Ammonium produced via DNRA can enhance productivity and respiration,

which in turn may exacerbate hypoxia ([McCarthy et al., 2015](#)). Rates of DNRA usually vary seasonally and peak in the warmer summer months. [Bernard et al. \(2015\)](#) found that in Little Lagoon, AL, DNRA accounted for up to 30–40% of the annual  $\text{NH}_4^+$  flux, and up to 80% of the seasonal  $\text{NH}_4^+$  flux during summer months. Also in the summer, DNRA rates (study average:  $52.1 \mu\text{mol N/m}^2/\text{h}$ ) outpaced the removal of  $\text{NO}_3^-$  via conversion to  $\text{N}_2$  (denitrification; study average  $7.7 \mu\text{mol N/m}^2/\text{h}$ ), resulting in more bioavailable N retained in the system. This could help promote eutrophic conditions ([Bernard et al., 2015](#)).

Several reasons have been proposed for observed seasonal peaks in DNRA rates. These include warmer temperatures, higher sulfide ( $\text{HS}^-$ ) and oxygen concentrations, and more  $\text{NO}_3^-$  availability. Higher  $\text{HS}^-$  concentrations are shown to favor DNRA rather than denitrification ([Kraft et al., 2014](#); [Howarth et al., 2011](#)). In the Niantic River estuary, CT, one study area with the highest rates of DNRA was also found to have high  $\text{HS}^-$  concentrations and reaction rates of sediment denitrification, anaerobic oxidation of ammonium ([Appendix 7.2.6.7](#)), and DNRA varied considerably within the estuary. Approximately one-third of the total area of the estuary exhibited rates of DNRA that exceeded denitrification by at least 20%, although denitrification accounted for about 90% of  $\text{NO}_3^-$  reduction across the entire estuary ([Plummer et al., 2015](#)). Sulfide was found to predict 44% of the variability in a DNRA ratio metric, while organic carbon abundance and organic carbon source were less strongly correlated with DNRA ([Plummer et al., 2015](#)). [Decleyre et al. \(2015\)](#) observed wide variations in N removal pathway rates over small distances in the Paulina polder mudflat (Westerschelde estuary, Netherlands). Rates of DNRA varied significantly on a small scale of less than 2 m and were significantly related to  $\text{HS}^-$  production.

[Jäntti and Hietanen \(2012\)](#) demonstrated that DNRA controlled the overall  $\text{NO}_3^-$  reduction under conditions of low oxygen. DNRA is thought to provide energy to diatoms in dark and/or hypoxic conditions ([Glibert et al., 2016](#); [Kamp et al., 2011](#)). A study from Australia's Yarra River estuary found that DNRA rates were increased under oxygen saturation and depressed under hypoxic conditions ([Roberts et al., 2014](#)).

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#### 7.2.6.6 Denitrification

Bioavailable N removal from estuarine and near-coastal ecosystems occurs via several different pathways in the N cycle. These pathways include sediment burial, uptake by plants, denitrification ( $\text{NO}_3^-$  reduction to  $\text{N}_2$ ) and anaerobic  $\text{NH}_4^+$  oxidation to  $\text{N}_2$  (termed anammox; [Appendix 7.2.6.7](#)). In some areas, uptake by vegetation such as SAV can represent a significant N sink ([Zarnoch et al., 2017](#); [Boynton et al., 2014](#); [Hayn et al.,](#)

[2014](#)). However, much of the N contributed to estuaries by atmospheric deposition and other nonpoint and point sources of N is removed from the aquatic ecosystem by either denitrification or anammox ([Damashek et al., 2015](#); [Ward, 2013](#); [Boynton and Kemp, 2008](#)). These processes predominate in the anoxic sediments if the water body is well mixed and occur in the water column of stratified hypoxic systems. Since the 2008 ISA, there have been additional insights into factors that affect abundance, biodiversity, and biological activity of denitrifying microbial communities ([Appendix 7.2.6.9](#)).

Denitrification can occur in both the hypoxic water column and hypoxic sediments, although in most estuaries sediment processing probably exceeds water column processing ([Seitzinger et al., 2006](#)). Denitrification is a very important sink for N in most estuaries ([Hayn et al., 2014](#); [Nixon et al., 1996](#)). Because N is such an important limiting factor for primary production in estuaries, the removal of N through denitrification is a valuable ecosystem service in terms of constraining the extent and magnitude of eutrophication ([Smyth et al., 2013](#); [Piehler and Smyth, 2011](#)). In the eutrophic Baltic Sea, denitrification in sediments is important for partially mitigating the adverse effects of eutrophication ([Jäntti and Hietanen, 2012](#)). However, denitrification rates are not always high enough to result in a net sink of N within an estuary or embayment. [Barnes and Upstill-Goddard \(2011\)](#) reported measurements of dissolved nitrous oxide (N<sub>2</sub>O), inorganic N, O<sub>2</sub>, and turbidity in six estuaries in the U.K. and results suggested that the main source of N<sub>2</sub>O was nitrification; denitrification did not appear to be a significant NO<sub>3</sub><sup>-</sup> sink in that ecosystem.

Denitrification was found to be the primary pathway for N reduction in the Niantic River estuary in Connecticut, accounting for an average of 90% of total N reduction, a result that is in line with measurements from other temperate estuaries ([Plummer et al., 2015](#)). Estuaries and coastal embayments with longer water residence times and shallower water depths have also been found to exhibit greater rates of denitrification ([Hayn et al., 2014](#)). Shallow waters enhance denitrification because they lead to a greater level of interaction between N in the water and sediments ([Hayn et al., 2014](#); [Nixon et al., 1996](#)). An analysis of estuary nutrient budgets for North Atlantic estuaries by [Nixon et al. \(1996\)](#) suggested that the fractional transport of nutrients through estuaries to the continental shelf is inversely correlated with water residence time; specifically, the fraction of the total export of N from the estuary is roughly proportional to the log mean residence time of the water in the estuary. [Hayn et al. \(2014\)](#) studied the nutrient dynamics of West Falmouth Harbor on Cape Cod, MA, a shallow estuary that experienced a large increase in N load from human activities without a substantial change in P load. Since the 1990s, this estuary received a threefold increase in N inputs caused by groundwater contamination by a municipal wastewater treatment plant. During summer, the Falmouth Harbor retained most of the N load contribution and also imported some additional N from the

adjacent Buzzards Bay; during spring and fall, N was exported from the harbor to the bay.

Inhibition of denitrification rates by  $\text{HS}^-$  has been widely observed. [Plummer et al. \(2015\)](#) found that denitrification rates were inversely related to pore water  $\text{HS}^-$  (as a measure of  $\text{SO}_4^{2-}$  reduction), consistent with previous studies. Organic carbon abundance and organic carbon source were also shown to be related to denitrification rates in that study ([Plummer et al., 2015](#)).

[Smyth et al. \(2013\)](#) measured the  $\text{N}_2$  fluxes in five major estuarine habitat types in Bogue Sound, southeastern North Carolina: salt marshes, seagrass beds, oyster reefs, and intertidal and subtidal flats. Based on the distribution of habitats across the study estuary, it was estimated that about 76% of the watershed N load was removed by denitrification in the estuary each year. Results suggested that the amount of N removed by denitrification from an estuary depends on the amount and type of habitats located in that estuary. Each habitat had a characteristic impact on N cycling in the sediment ([Smyth et al., 2013](#)). [Piehler and Smyth \(2011\)](#) and [Smyth et al. \(2013\)](#) concluded that more structured habitats such as oyster reefs and seagrass beds provided especially high N removal per unit estuary area. Calculations showed that the SAV habitat produced the highest value of N removal in terms of an ecosystem service valued at \$3,000/ac/year, compared with a \$400/ac/year value provided by a subtidal flat habitat ([Piehler and Smyth, 2011](#)).

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#### 7.2.6.7 Anammox

Anammox removes N from estuaries by producing  $\text{N}_2$  gas. This process can in some cases be a significant pathway for N removal, depending on environmental factors, although it is typically secondary to denitrification in N removal. Anammox and denitrification are usually highly correlated ([Plummer et al., 2015](#); [Lisa et al., 2014](#)). A review of several studies revealed that anammox rates in coastal sediments can potentially range up to  $52 \mu\text{mol N/m}^2/\text{h}$  ([Plummer et al., 2015](#)). [McCarthy et al. \(2015\)](#) found that up to 29% of the N removal (mean =  $11.8 \pm 1.7\%$ ) from the Mississippi River TN load to the Louisiana-Texas continental shelf may be due to anammox under hypoxic conditions. The median denitrification rate measured in that study, which includes anammox, of  $88.1 \mu\text{mol N/m}^2/\text{h}$  was found to be comparable to other studies ([McCarthy et al., 2015](#)). In the Niantic River estuary, CT, anammox rates ranged from 0 to  $3.1 \mu\text{mol N/m}^2/\text{h}$ , accounting for 3.5% of total N reduction, while denitrification accounted for 91% of total N reduction ([Plummer et al., 2015](#)). Anammox was also found to be a significant N sink in the lower St. Lawrence estuary, where it was measured at a

rate of  $5.5 \pm 1.7 \mu\text{mol N/m}^2/\text{h}$  ([Crowe et al., 2012](#)). In the Cape Fear estuary, NC, anammox rates ranged from 0.17 to 4.77 nmol N/g wet sediment/h, with the highest rates measured during the winter ([Lisa et al., 2015](#)). Anammox rates in this study were also found to be inversely related to temperature.

Several studies have linked anammox activity to N loading. In the Chesapeake Bay, higher anammox activity was associated with higher concentrations of  $\text{NO}_3^-$  in the tidal freshwater segment and was not observed in the lower saline part of the estuary ([Rich et al., 2008](#)).

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#### **7.2.6.8 Nitrification/Denitrification Uncoupling**

Sediment N cycling is dynamic, and rates of various processes fluctuate over time. Recent research has highlighted the importance of quantifying each process, the resulting N fluxes, and environmental controls on these reactions. Denitrification has long been assumed to be coupled with nitrification; however, the extent of that coupling is increasingly understood to be dependent on environmental factors. [Hines et al. \(2012\)](#) found that 43% of denitrification was coupled to nitrification in the upper Cape Fear River estuary, NC. [Lisa et al. \(2015\)](#) found that nitrification and denitrification rates were significantly coupled (correlated) in the Cape Fear River estuary, and that this coupling was driven by organic carbon mineralization. The study found that tidal changes and salinity fluctuations did not affect the coupling of nitrification/denitrification on the same scale ([Lisa et al., 2015](#)). Under some conditions, such as warmer summer conditions, DNRA may be the favored N reduction pathway over denitrification, which can also lead to uncoupling of nitrification/denitrification rates. In Little Lagoon, AL, DNRA rates can be much higher in the summer and are correlated with higher concentrations of  $\text{HS}^-$  ([Bernard et al., 2015](#)). Seasonality was also a factor in the San Francisco Bay, where coupling of nitrification/denitrification was more prominent in the late summer; in the spring, high  $\text{NO}_3^-$  concentrations in the water drove denitrification ([Cornwell et al., 2014](#)).

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#### **7.2.6.9 New Insights Regarding the Abundance, Biodiversity, and Biological Activity of Estuarine Microbial Communities**

Since the 2008 ISA, there is new information on the abundance, diversity ([Appendix 10.3.4](#)) and biological activity of microbial communities and their role in N cycling. Quantification of functional genes reflect changes in microbial function and have been linked to forms of N. For example, in seasonally anoxic bottom waters in

Chesapeake Bay, [Eggleston et al. \(2015\)](#) observed that relative expression of genes involved in denitrification and DNRA were coincident with changes in concentrations of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$ . In an analysis of denitrifiers in San Francisco Bay estuary, N was identified as one of the key factors (along with salinity, organic C, and several metals) affecting community structure and function and denitrification rates ([Mosier and Francis, 2010](#)). Seasonal inputs of N loading from the watershed affect microbial community structure and biodiversity, which in turn affect rates of processes involved in N cycling ([Lisa et al., 2015](#); [Lisa et al., 2014](#)).

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### 7.2.6.10 Archaea and Nitrogen Cycling

Prior to the 2000s, it was generally believed that  $\text{NH}_3$  oxidation was accomplished only by Proteobacteria ([Damashek et al., 2015](#); [Kowalchuk and Stephen, 2001](#)). Complexity increased with the discovery that some archaea (also called Thaumarchaeota), a primitive life form separate from bacteria, can also oxidize  $\text{NH}_3$  ([Brochier-Armanet et al., 2008](#); [Könneke et al., 2005](#)). These ammonia-oxidizing archaea (AOA) are dominant in some estuaries ([Moin et al., 2009](#)). Ammonia-oxidizing bacteria (AOB) are important in others ([Abell et al., 2010](#)). These two life forms can vary spatially and seasonally in importance in still other estuaries ([Damashek et al., 2015](#); [Urakawa et al., 2014](#); [Zheng et al., 2014](#)). Benthic  $\text{NH}_3$  oxidizers may be able to oxidize a significant quantity of  $\text{NH}_4^+$  in  $\text{NH}_4^+$  rich systems, such as the Sacramento River ([Damashek et al., 2015](#)). Several studies that have examined changes in AOA and AOB relative abundance and community structure associated with N loading are reviewed in [Appendix 10.3.4](#).

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### 7.2.6.11 Role of Benthic Macrofauna in Nitrogen Cycling

The role of benthic macrofauna (including crustaceans and molluscs) in N and C cycling and their ability to modulate water quality have significant implications for estuarine functioning ([Rose et al., 2015a](#); [Bricker et al., 2014](#); [Petersen et al., 2014](#); [Rose et al., 2014](#); [STAC, 2013](#); [Carmichael et al., 2012](#); [Volkenborn et al., 2012](#); [D'Andrea and DeWitt, 2009](#); [Cerco and Noel, 2007](#)). Activities of burrowing macrofauna can create areas of oxic-anoxic oscillations, which vary on the order of minutes to hours and affect geochemical reactions and microbial activity in sediments ([Volkenborn et al., 2012](#)). Burrowing mudshrimp (*Upogebia pugettensis*) were shown to increase the rate of N cycling processes and DIN fluxes in an intertidal mud flat in the Yaquina River estuary in Oregon ([D'Andrea and DeWitt, 2009](#)). [Stief \(2013\)](#) reviewed the contributions of benthic macrofauna to the turnover of N and to emissions of greenhouse gasses such as nitrous oxide from the estuary to the atmosphere. Sediment burrowing macrofauna stimulated

nitrification and denitrification in the sediment. Together these facilitate removal of N from the estuary system. Benthic macrofauna intensify the coupling among water, benthos, and atmosphere by enhancing turnover and transport of N.

The use of shellfish for remediation of coastal N enrichment has been explored due to the ability of these organisms to modulate nutrient dynamics and water quality ([Reitsma et al., 2017](#); [Ferreira and Bricker, 2016](#); [Petersen et al., 2016](#); [Bricker et al., 2014](#); [STAC, 2013](#); [Cercó and Noel, 2007](#); [Carmichael et al., 2004](#)). These filter feeders store nutrients in shell and tissue that are permanently removed from the estuary with shellfish harvest. Biodeposits (partially digested phytoplankton expelled from suspension feeding bivalves) may remove additional N through acceleration of denitrification processes in underlying sediments ([Pollack et al., 2013](#); [STAC, 2013](#); [Stephenson et al., 2010](#)). For example, in the Mission-Aransas estuary in Texas, oyster reefs were estimated to remove 502.5 kg N/km<sup>2</sup> through denitrification of biodeposits and 251.3 kg N/km<sup>2</sup> in burial of biodeposits to sediments ([Pollack et al., 2013](#)). Oyster harvest in the same estuary was calculated to remove approximately 21,665 kg N/year.

Additional studies have reported N removal by shellfish in U.S. waters. [Carmichael et al. \(2004\)](#) directly measured N removal in the oyster *C. virginica* in transplant studies to five Cape Cod estuaries with different N loadings. Estimated N removal of different sources was ≤15% of land-derived N loads and <1% of phytoplankton. Nitrogen removal by oysters in the Great Wicomico River, which drains into the Chesapeake Bay, was estimated to be 15.2 tons/year [total area 2.8 × 10<sup>5</sup> m<sup>2</sup>; [Cercó \(2015\)](#)]. Based on model estimates for Chesapeake Bay harvesting 7.7 × 10<sup>6</sup> harvest-sized oysters (76 mm) removes 1 ton of N from the bay ([Higgins et al., 2011](#)). In the same study, an offset of approximately 10 to 15% of total N load in some basins (cultivation of 200 × 10<sup>6</sup> oysters/year) was calculated. [Holmer et al. \(2015\)](#) recommended harvest of mussels within 1 year of the production cycle for the most efficient N removal.

Over time, shellfish excretion and subsequent sedimentation may contribute to development of hypoxic conditions. A shellfish farming operation may shift from a net sink to a net source of N. Oyster reef restoration projects in several locations throughout the U.S. have been evaluated for effects on N cycling; however, this process appears to be dependent on local habitat and growing conditions and may vary by orders of magnitude ([Cercó, 2015](#); [Smyth et al., 2015](#); [Kellogg et al., 2014](#); [Plutchak et al., 2010](#)). In Great Bay estuary, NH, eutrophication enhanced oyster feeding rates and enhanced biodeposit quality. Thus, oyster-mediated ecosystem services may be expected to vary with environmental conditions ([Hoellein et al., 2015](#)).

Recent evaluation of oysters in Chesapeake Bay for inclusion in TMDL nutrient reductions reported enhanced denitrification in association with oyster reefs; however,

the effect was highly variable and not reliable unless direct measurements were conducted on individual reefs ([STAC, 2013](#)). The potential for shellfish aquaculture to be included in proposed nutrient trading markets for achieving pollution control under the Clean Water Act is being evaluated in Chesapeake Bay ([Stephenson et al., 2010](#)). Some recent modeling studies showed that mean N removal by shellfish aquaculture compares favorably with reported N removal effectiveness of agricultural best management practices and stormwater control measures ([Rose et al., 2015a](#); [Rose et al., 2014](#)).

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#### **7.2.6.12 Climate Modification of Ecosystem Response to Nitrogen**

Altered biogeochemical processes due to N loading are occurring within the context of climate change. Microbial diversity is affected by environmental gradients within estuaries, a condition that may be exacerbated under climate change. For example, freshwater and nutrient contributions to estuaries are expected to rise due to predicted increases in surface water flow and runoff from watersheds ([Rabalais et al., 2010](#); [Adrian et al., 2009](#); [Whitehead et al., 2009](#)). [Howarth et al. \(2012\)](#) demonstrated larger N fluxes (larger percentage delivery of human N inputs) in wetter climates with more discharge, across 154 different watersheds in the U.S. and Europe. Temperature modification leading to sea level rise and inputs of fresh water will likely influence the delivery of nutrients and organic matter, alter salinity gradients, and increase stratification within estuaries ([Statham, 2012](#)). Eutrophic conditions and the extent and duration of hypoxia are predicted to increase with anticipated changes in temperature and precipitation ([Altieri and Gedan, 2015](#); [Rabalais et al., 2009](#); [Boesch et al., 2007](#)). High organic loads and freshwater inputs associated with extreme weather events may further enhance thermal stratification and contribute to hypoxia ([Wetz and Yoskowitz, 2013](#)). Increased thermal stratification will worsen hypoxia where it already occurs and may facilitate its formation at other locations ([Rabalais et al., 2010](#)).

The “benthic filter” is a term given to the benthic microbe and algal communities that remove N via uptake and denitrification and bury N from shallow estuarine and coastal waters. Nitrogen removal via the benthic filter is an important mediator of nutrient enrichment in shallow estuaries along the Atlantic and Gulf coasts of the U.S. where this feature is common ([Anderson et al., 2014b](#)). The filtering function of this top layer of sediment is affected by nutrient delivery as well as light availability, temperature, and resuspension caused by wind and storms. Thus, the benthic filter and the N removal services it provides are expected to be highly susceptible to climate change impacts ([Anderson et al., 2014b](#)).

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## 7.2.7 Monitoring Data

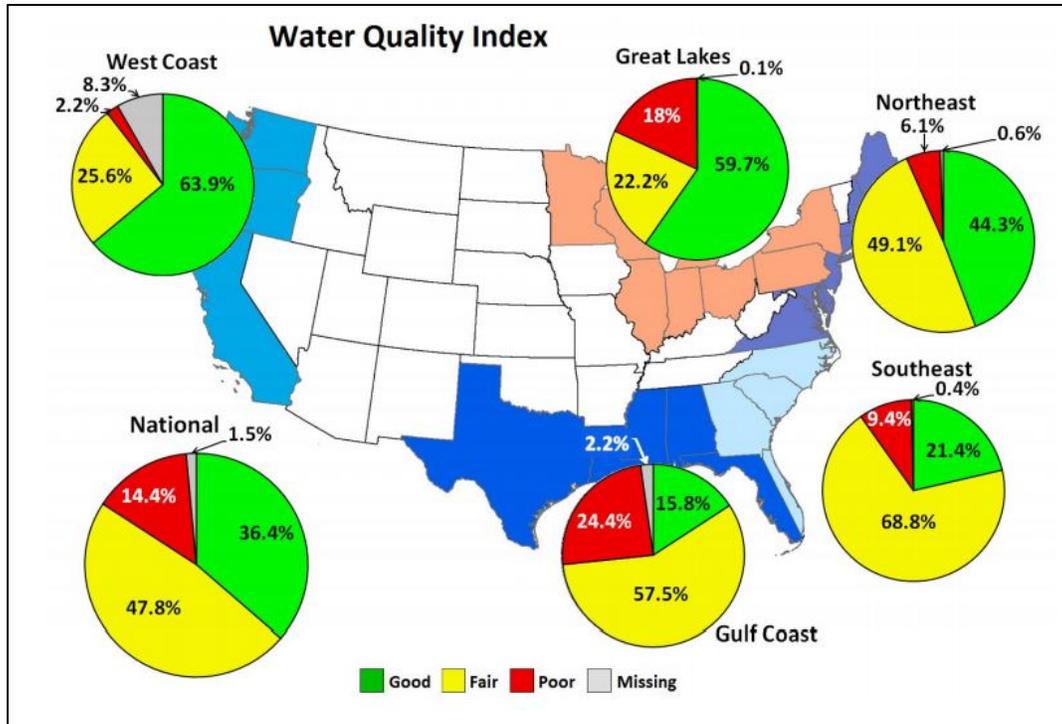
Monitoring data provide temporal trends of biogeochemical processes and indicators associated with eutrophication and coastal acidification in estuaries and coastal ecosystems. These data document and quantify changes that occur in response to environmental stressors, including N deposition. Many monitoring studies for eutrophication have been ongoing for one or two decades, in some cases longer. Monitoring for coastal acidification is more recent. Analysis of historical data suggest that some coastal areas have been experiencing long-term acidification.

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### 7.2.7.1 Eutrophication

Since the 2008 ISA, nearly a decade's worth of additional data have been added to some of the monitoring programs described below. The availability of these additional data facilitates trend detection now, compared to 2008. The U.S. EPA Estuary Data Mapper tool accessed at <https://www.epa.gov/hesc/about-estuary-data-mapper-edm> allows users to retrieve and visualize estuary data from several federal agencies to access water and sediment quality, freshwater discharge, tides, N deposition, and other parameters.

The NARS include a survey of coastal waters called the National Coastal Condition Assessment (NCCA). U.S. EPA, together with the states, tribes, other entities, and individuals, have collaborated on these statistically representative surveys since the early 2000s. The NCCA survey uses standardized field protocols and indicators of coastal condition including N, water clarity, chlorophyll *a*, and DO concentrations. The NCCA 2010 used a consistent set of data from three periods (1999–2001, 2005–2006, and 2010) to evaluate change in coastal conditions over time (U.S. EPA, 2016g). This analysis included only the Northeast, Southeast, Gulf, and West Coast regions. (The change analysis does not include the Great Lakes because they were not part of this survey until 2010.) The change analysis showed that scores on the water quality index remained relatively similar between 2005–2006 and 2010, after a significant decrease in the percentage of area rated good from 1999–2000 to 2005–2006. The Gulf Coast had the greatest proportion of waters (24.4%) rated poor for water quality compared to the other regions surveyed for the NCCA in 2010 (Figure 7-10). The NCCA report noted that these findings support the need for continued attention to coastal stressors at national, regional, state, and watershed scales to identify and mitigate challenges where they exist and protect areas that are still in good condition (U.S. EPA, 2016g).



Source: [U.S. EPA \(2016g\)](#).

**Figure 7-10 Percentage of area in each coastal region scoring good, fair, and poor based on the Water Quality Index for the NCCA 2010.**

Additional long-term monitoring surveys conducted with help from the U.S. EPA include those undertaken by individual National Estuary Programs (NEP) around the U.S. The NEP is a nonregulatory program designed to protect and restore the water quality and ecological integrity of estuaries of national significance, of which there are currently 28. The NEPs develop and implement long-term management plans that contain actions to address water quality priorities, which are defined by local, city, state, federal, private, and nonprofit stakeholders. In many cases these priorities include reducing and mitigating the occurrence of eutrophic conditions in large estuaries, goals often accompanied by long-term monitoring of nutrients and eutrophication indicators. For instance, the Tampa Bay Estuary Program works with the Southwest Florida Water Management District's Surface Water Improvement and Management Program to collect monitoring data on trends in seagrass coverage, which is greatly affected by water clarity [often an indicator of excessive N loads to the bay; [Sherwood \(2017\)](#)]. The most recent analysis of monitoring data showed that Tampa Bay's seagrass area continues to recover, with the addition of 1,360 acres of seagrass coverage reported from 2014 to 2016. Tampa Bay's total seagrass coverage is now estimated to be 41,655 acres as of 2016, which now

exceeds the total estimated seagrass coverage in the 1950s period (40,420 acres) for the first time since monitoring began ([Sherwood, 2017](#)). See the Tampa Bay Case Study ([Appendix 16](#)) for additional information on this coastal system.

The NEP's Long Island Sound Study has conducted two decades of monitoring to identify N sources and track water quality conditions and eutrophic indicators over time. The Long Island Sound Study uses several indicators, including the NCCA's Water Quality Index, to evaluate changes from year to year. Data from 1991–2011 show a gradient in improving water quality from the eastern part of the sound, where population and anthropogenic stressors are lower and water quality was most often rated “good,” to the western side where population and development pressure are both higher and water quality was consistently rated “fair” ([LISS, 2017](#)).

The Chesapeake Bay Monitoring Program established in 1984 is a regional partnership that monitors 19 physical, chemical, and biological characteristics, including nutrients and DO, enabling the study of the bay and long-term trends ([Testa et al., 2017](#)). The original Chesapeake Bay Program agreement of 1983 included Maryland, Virginia, Pennsylvania, Washington, D.C., the U.S. EPA, and regional partners. In 2014, the Chesapeake Watershed Agreement was signed to include representatives from the entire watershed and accelerate restoration of the bay.

The NPS also conducts estuarine water quality monitoring to monitor “Park Vital Signs,” which are elements and processes of park ecosystems that can serve as indicators of the overall health of the park. The Estuarine Nutrient Enrichment Monitoring (ENEM) program monitors nitrogen loading inputs as well as overall water quality and seagrass distribution in park estuaries within the Northeast Coastal and Barrier Network (NCBN) region (covering Massachusetts to Virginia) of the NPS. In this region, the Park Vital Signs are all related to nutrient enrichment, which is considered the stressor with the ability to cause the greatest potential impacts on park health ([USGS US Department of the Interior, 2015](#)). Water quality indicators are defined with the same criteria as U.S. EPA's NCCA methods, and data are available on the program's website for each park in the NCBN region of the NPS at <https://www.nps.gov/im/ncbn/what-we-monitor.htm>.

The National Oceanic and Atmospheric Administration (NOAA) conducts several monitoring programs in estuaries and coastal waters. The National Estuarine Research Reserves System (NERRS) is a federal-state partnership network of 29 coastal sites encompassing 1.3 million acres designated to protect and study estuarine systems. Estuarine water quality monitoring data are collected by the NERRS System-Wide Monitoring Program (SWMP), which identifies and tracks short-term variability and long-term changes in estuarine ecosystems and coastal watersheds. Data are housed in a central online database available at <http://cdmo.baruch.sc.edu/>.

Many NERRS sites work with other groups to analyze and report their overall findings about water quality indicators. In the Great Bay estuary in New Hampshire and Maine, NERR's SWMP collects nitrogen, DO, and temperature data, which is used by the Piscataqua Region Estuaries Partnership (a NEP site) to assess the environmental status and trends in the Bay. The most recent State of the Estuaries report found that total N load to the estuary in 2009–2011 was 1,225 tons per year, which appeared to be strongly influenced by rainfall amounts ([PREP, 2013](#)).

NOAA's Gulf of Mexico Ecosystems and Hypoxia Assessment (NGOMEX) is a large study focusing on a single geographic region in the Gulf of Mexico. NGOMEX has been collecting data and conducting research for more than 30 years to investigate the spatial and temporal dynamics of the hypoxia zone in the Gulf of Mexico, especially with regards to the link between the hypoxia zone size and the amount of nutrient loading, primarily from the Mississippi River watershed ([Appendix 10.2.4](#)). In 2017, work funded by NGOMEX measured the largest Gulf of Mexico hypoxia zone since mapping of the area began in 1985 ([U.S. EPA, 2017f](#)). The size of the 2017 hypoxia zone was accurately forecasted by Mississippi River spring discharge levels and nutrient data, gathered by the USGS and analyzed with NOAA-sponsored models, and clearly indicates that nutrient pollution from the Mississippi River watershed is affecting the health of the coastal Gulf ecosystem.

NOAA also conducts the Monitoring and Event Response for Harmful Algal Blooms (MERHAB) program which helps identify when beaches, shellfisheries, and marine animals are at risk from harmful algae and cyanobacteria. It allows local stakeholders to react as quickly as possible to any human health risk. MERHAB largely funds research projects, but also aims to help routine water quality and shellfish monitoring studies upgrade to better HAB detection methods and technologies. NOAA's Center for Operational Oceanographic Products and Services (CO-OPS) produces HAB forecasts for the Gulf of Mexico to help communities plan for and mitigate the effects of potentially harmful algal blooms. Data for these forecasts come from many sources. The National Aeronautics and Space Administration (NASA) Moderate Resolution Imaging Spectroradiometer (MODIS) satellite collects ocean color data which are processed by NOAA CoastWatch ([NOAA, 2017a](#)). The satellite sensors measure visible light at specific wavelengths to determine the color of the ocean. These color data can be used to estimate chlorophyll concentrations; however, in coastal areas, interpretation can be complicated by the presence of other biota, compounds, and minerals ([NOAA, 2017b](#)). The HAB forecasts prepared by CO-OPS also integrate other data about factors that may affect algal and cyanobacterial bloom formation and intensity such as water temperature, ocean currents, and weather conditions ([NOAA, 2017b](#)). The forecasts also note cell counts of the toxic dinoflagellate *Karenia brevis* (commonly called a "red tide" species)

taken from specific locations along the coast. Another NOAA product called the Harmful Algal Bloom Observing System (HABSOS) integrates these data sources, including cell counts and other environmental information into an interactive mapping application available online at <https://habsos.noaa.gov/> (NOAA, 2017c). HABSOS can map recent satellite data and cell counts to depict areas that may be at risk of HABs in the near future. Trends in HABs and responses to N are discussed further in [Appendix 10.2.2](#) and [Appendix 10.3.3](#).

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### 7.2.7.2 Coastal Acidification

Coastal acidification monitoring programs are developing around the world. In the U.S., ocean acidification has been documented from the New England region, California, Oregon, Washington, and the northern Gulf of Mexico (Laurent et al., 2017; Gledhill et al., 2015; Gruber et al., 2012; Hauri et al., 2009; Feely et al., 2008; Yang, 1998). In a series of sampling cruises and analysis of water sampling data, Wallace et al. (2014) identified concurrent low pH conditions and declining DO in four Northeast estuaries (Long Island Sound, NY; Jamaica Bay, NY; Narragansett Bay, RI; Hempstead Bay, NY). Observed conditions in eutrophic estuaries during late summer were such that marine biota, especially calcifying organisms, may be affected (Appendix 10.5). Analysis of historical (from the late 1960s to 2010) alkalinity and pH data from bays along the northwestern coast of Texas indicated that 16 of 27 systems showed long-term decreases in alkalinity and 22 systems showed decreased pH (Hu et al., 2015a). Cai et al. (2017b) showed that redox reactions and weak buffering capacity are leading to the acidification of Chesapeake Bay. A recent study by Baumann and Smith (2018) of long-term databases of pH and trophic state on numerous EPA-NEP and NOAA-National Estuarine Research Reserve System estuarine sites show no clear relationship between trophic state and acidification including for Chesapeake Bay; however, they did not evaluate within bay spatial patterns.

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### 7.2.8 Modeling Estuaries and Near-Coastal Areas

Since the 2008 ISA, several new applications of existing models have quantified eutrophication processes in estuaries and near-coastal marine ecosystems. These have included studies that focused primarily on N cycling or hypoxia.

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### 7.2.8.1 Models

There are several models that track the sources and movement of N through the landscape and stream network to estuary and near-coastal marine ecosystems. These models vary in scope, level of spatial and temporal resolution, forms of N considered, complexity, and empirical versus deterministic construction ([Alexander et al., 2008](#)). They can be structured as statistical models ([Howarth et al., 2012](#); [Peierls et al., 1991](#)), empirical models ([Caraco and Cole, 1999](#)), export coefficient models ([Johnes, 1996](#)), deterministic models such as SWAT ([Gassman et al., 2007](#); [Nietsch et al., 2002](#)), Generalized Watershed Loading Function [GWLF; [Haith and Shoenaker \(1987\)](#)], and hybrid approaches (SPARROW, NEWS). The principal ecosystem models applied to U.S. waters to assess N enrichment were reviewed in the 2008 ISA and are briefly summarized here ([U.S. EPA, 2008a](#)).

Some of these models have been applied at national or large regional scales to examine N loading to rivers and the coastal zone. SPARROW is a hybrid statistical-mechanistic model that can attribute pollutant sources and contaminant transport to surface waters ([Smith et al., 1997](#)). SWAT is a mechanistic model developed by the U.S. Department of Agriculture, Agricultural Research Service ([Gassman et al., 2007](#); [Nietsch et al., 2002](#)). WATERS-N is a mass balance model that has been used to evaluate N inputs to estuaries ([Castro et al., 2003](#); [Castro et al., 2001](#)).

Since the 2008 ISA, there have been new applications of SPARROW and SWAT, as well as development and application of new models and approaches such as NEWS, Net Anthropogenic Nitrogen Inputs (NANI), and the Dynamic Land Ecosystem Model [DLEM; [Tian et al. \(2012\)](#)]. SPARROW has been used to estimate total N loads within watersheds to estimate sources of N to streams and rivers. It has also been applied at regional and national scales ([Schwarz et al., 2011](#); [Alexander et al., 2008](#)). SPARROW operates on an annual time step, usually integrating several decades of data to develop load relationships and then simulating conditions for 1 year. NEWS is a similar hybrid model. It has been used to estimate the magnitudes and sources of different forms of N (particulate, dissolved inorganic, and organic) to coastal waters ([Glibert et al., 2010a](#)). Recent work with NEWS included a global, seasonal version ([McCrackin et al., 2014](#)). It has been used for scenario comparisons, including predictions about reductions in air deposition resulting from Clean Air Act regulations and other policy actions ([McCrackin et al., 2015](#)). NANI is a simple mass balance model for calculating net anthropogenic nitrogen inputs that takes information about inputs and outputs of nitrogen within a basin and estimates the riverine flux from the landscape to the ocean ([Howarth et al., 2012](#)). It was developed for watersheds across the contiguous U.S. at the county level ([Hong et al., 2013, 2011](#)). Using NANI, [Howarth et al. \(2012\)](#) demonstrated larger N fluxes (larger

percentage delivery of human N inputs) in wetter climates with more discharge, across 154 different watersheds in the U.S. and Europe. The NANI Calculator Toolbox takes into consideration fertilizer N application, agricultural N fixation, net food and feed imports, and atmospheric sources of N. The DLEM is a process-based ecosystem model that couples major biogeochemical cycles, water cycle, and land use and land cover change to make spatially explicit estimates of water, carbon, and N fluxes. and has the advantage of being able to simulate temporal variability of N loads ([Tian et al., 2012](#)).

Deterministic models of N flux are based on mechanistic relationships that simulate N transformations, transport, and removal, often at relatively fine temporal and spatial resolution. SWAT has been recently applied at the regional scale of the Mississippi River basin ([Santhi et al., 2014](#)). It allows examination of the effects of changes in cropland management on delivery of N to coastal waters. Recent SWAT publications do not explicitly include atmospheric deposition as a source of N, but have produced similar overall results as SPARROW and NEWS in terms of load and attribution to agriculture in the Mississippi River basin [ $\approx 54\text{--}61\%$ ; [McCrackin et al. \(2013\)](#); [White et al. \(2014\)](#)].

The watershed models described above route N from the landscape to estuaries and the coastal zone, but generally do not model the contribution of N directly to the estuary surface from the atmosphere. These models also deal with the freshwater components of watersheds and do not predict N fate within estuaries or N effects on estuarine processes or functions. The following sections describe new applications of several models that operate within estuaries.

Additional models and tools that have been applied to assess atmospheric contributions of N to U.S. estuaries since the 2008 ISA included the watershed N Loading Model [NLM; [Latimer and Charpentier \(2010\)](#)] and the Watershed Deposition Tool [WDT; [Poor et al. \(2013b\)](#)]. The latter was developed by the U.S. EPA to map atmospheric deposition estimates to watersheds using wet and dry deposition data from the Community Multiscale Air Quality Model [CMAQ; [Schwede et al. \(2009\)](#)]. This tool links air and water quality modeling data for use in TMDL determinations and analysis of nonpoint-source impacts. The NLM has been used for New England estuaries to estimate total N loading and the relative contributions of the various N sources ([Table 7-9](#)) and develop load response relationships among N inputs and seagrass extent ([Latimer and Rego, 2010](#)).

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### **7.2.8.2 Predicted Response to Nitrogen Loading**

Many of the models that estimate N loads to the coastal zone from the landscape and freshwater inflow have been compared, and there is a good deal of knowledge about their

limitations and uncertainties ([McCrackin et al., 2013](#); [Alexander et al., 2008](#)). In a 2000 National Research Council review, it was determined that these models are hydrodynamically complex and tend to be specific to particular sites. Thus, they are difficult to apply broadly ([NRC, 2000](#)).

The range of coastal ecosystem responses to changing N loads reflect changes in DO, productivity, SAV cover, and impacts on other organisms. Water residence time can influence the response of estuaries to nutrient loading because of the effects of flushing on nutrients, water temperature, plankton, and light penetration. Capturing these dynamics in a model is challenging ([Swaney et al., 2008](#)).

A recent review of hypoxia modeling described trade-offs between details of complex models and the need for simpler, more broadly applicable models ([Peña et al., 2010](#)). [Greene et al. \(2009\)](#) developed a set of multiple regression models to simulate relationships between river loads and concentrations of N and P compared with the extent of hypoxic bottom water. A Bayesian approach was used in combination with a model of hypoxia to project the O<sub>2</sub> demand and extent of hypoxia ([Liu et al., 2010](#)). Estuarine models have been important to policy decision making and formulation of nutrient reduction goals ([Scavia et al., 2006](#); [Scavia et al., 2004](#)). There is an increased interest in developing coupled models that connect physical-chemical-biological nutrient loading and fate models ([Fennel et al., 2011](#)) and that connect chemical eutrophication models to fisheries response models ([Cercio et al., 2010](#)).

The responses of estuaries to N loading is partly determined by environmental characteristics. Nutrient-phytoplankton-zooplankton (NPZ) models examine biological responses including the effects of nutrient limitation and zooplankton predation on phytoplankton dynamics and fish production. The NPZ model described by [Swaney et al. \(2008\)](#) can assess complex responses of estuaries to different climate variables, land use, atmospheric loading, and other stressors ([Appendix 10.3.8](#)).

New studies have focused on increasing understanding of spatial variation in DIN export from the watershed to coastal zones. Seasonal patterns of DIN export influence impacts of coastal eutrophication, including HABs and the development of seasonal hypoxic zones. [McCrackin et al. \(2014\)](#) predicted seasonal DIN export to coastal regions, using the NEWS2 model calibrated to measured DIN yield in 77 rivers distributed globally. The DIN transport efficiency was positively correlated with runoff and negatively correlated with temperature. [McCrackin et al. \(2014\)](#) concluded that because of landscape N attenuation, a better representation of land-to-river N transfers, in particular, might improve models of nutrient cycling.

[Eldridge and Morse \(2008\)](#) developed a combined water-column and sediment model to investigate sediment and water-column metabolism and their impacts on development of hypoxia on the Louisiana shelf. They found that sediment O<sub>2</sub> demand was the primary sink for O<sub>2</sub> at the beginning and end of a hypoxic event. Once hypoxia has developed, however, sediments became isolated from O<sub>2</sub> rich upper waters.

Key drivers of hypoxia in coastal waters include nutrient loading, mainly from anthropogenic sources, C supply, and processes that contribute to thermal stratification. Complex hypoxia models are difficult to validate, however, and this limits the confidence that can be placed on simulation results. [Eldridge and Roelke \(2011\)](#) recommended the use of multiple models and identification of similarities in qualitative model behavior. They provided a brief overview of recent hypoxia models and identified the need for a meta-analysis of simulations produced by these models in search of qualitative similarities. They concluded that more complex models of hypoxia need to be developed that include three-dimensional hydrology. [Sturdivant et al. \(2013\)](#) developed a model of hypoxia impact on macrobenthic production in the lower Rappahannock River, a tributary of the Chesapeake Bay that experiences seasonal hypoxia. Simulation results suggested that macrobenthic biomass was strongly linked with dissolved O<sub>2</sub> concentration. Biomass fluctuations reflected the duration and severity of hypoxia. Results suggested that hypoxia had a negative effect on biomass, with longer duration and greater severity resulting in increased loss of biomass.

[Glibert et al. \(2010a\)](#) reviewed modeling approaches to improve understanding of HABs and their relationship with nutrient inputs. They recommended that predictive capabilities will likely improve if a suite of modeling approaches is used. This might include site-specific loading models of nutrient sources and models that couple nutrient discharge to biological responses.

[Dale et al. \(2011\)](#) investigated biogeochemical processes that affect N cycling in the sediment of Eckernförde Bay in the southwestern portion of the Baltic Sea, where severe bottom water hypoxia (and sometimes anoxia) commonly occurs during late summer. Sediments acted as net sinks for NO<sub>3</sub><sup>-</sup>, of which three-fourths was characterized as derived from reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup>. The other 25% was characterized as derived from denitrification of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup>. The NH<sub>4</sub><sup>+</sup> flux was high (1.74 mmol/m<sup>2</sup>/day), in response to degradation of organic N at the sediment interface and was directed out of the sediment.

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## 7.2.9 National-Scale Sensitivity

Characteristics of coastal systems sensitive to eutrophication are described in [Appendix 10.1.4](#). In the 2008 ISA and the National Estuarine Eutrophication Assessment (NEEA), a comprehensive survey of eutrophic conditions in the Nation's estuaries conducted by the National Oceanic and Atmospheric Administration (NOAA), the most eutrophic estuaries in the U.S. occurred in the mid-Atlantic region, and the estuaries with the lowest degree of eutrophication were in the North Atlantic [[Figure 10-2](#); [Bricker et al. \(2007\)](#)]. Areas of eutrophication-related hypoxia are found on the U.S. East and West coasts and the Gulf of Mexico ([Figure 10-5](#)). During the summer of 2017 the extent of hypoxia in the Gulf of Mexico was the largest ever recorded in the U.S. ([U.S. EPA, 2017f](#)). The most recent NCCA report, based on 2010 data and released by U.S. EPA in 2016, analyzed survey data from 1,104 sites, representing 35,400 square miles of U.S. coastal waters ([U.S. EPA, 2016g](#)). In this most recent NCCA report, water quality was rated good in 36% of coastal and Great Lakes nearshore waters, fair in 48%, and poor in 14%, based on measures of the eutrophication parameters that make up the water quality index (P, N, water clarity, chlorophyll *a*, and DO concentrations; [Figure 7-10](#)).

In the U.S., Chesapeake Bay is perhaps the best-documented case study of the effects of human activities on estuarine eutrophication. Other impacted estuaries identified in the 2008 ISA included Long Island Sound, the Pamlico Estuary in North Carolina, and along the continental shelf adjacent to the Mississippi and the Atchafalaya River discharges to the Gulf of Mexico ([U.S. EPA, 2008a](#)). In many parts of the U.S., especially the Southeast, Midwest, and Mid-Atlantic deposition of reduced N has increased relative to oxidized N in last few decades ([Appendix 2](#) and [Appendix 10.1.2](#)). Since the 2008 ISA, additional evidence has shown that reduced forms of atmospheric N play an increasingly important role in estuarine and coastal eutrophication ([Appendix 10.3.3](#)). The form of N delivered to some coastal areas of the U.S. is shifting from primarily  $\text{NO}_3^-$  to an increase in reduced forms of N.

Coastal acidification was not discussed in the 2008 ISA yet acidification trends reported in some locations has resulted in recent research and monitoring efforts in the U.S. ([Appendix 7.2.7.2](#)). Ocean acidification has been documented from the Gulf of Maine, California, Oregon, Washington, and the northern Gulf of Mexico ([Laurent et al., 2017](#); [Gledhill et al., 2015](#); [Gruber et al., 2012](#); [Hauri et al., 2009](#); [Feely et al., 2008](#); [Salisbury et al., 2008](#); [Yang, 1998](#)) while other long-term monitoring efforts, such as in Chesapeake Bay, have shown no trend of trophic state with pH ([Baumann and Smith, 2018](#)).

Unlike freshwaters where chemical recovery linked to decreased atmospheric deposition of N and S is observed in some systems ([Appendix 7.1.5.1](#)), N inputs from atmospheric and other sources contribute to the continued water quality degradation in U.S. coastal

waters. There are only a few cases of documented recovery of biological indicators in U.S. estuaries such as SAV in Tampa Bay ([Appendix 16](#)) and Chesapeake Bay ([Figure 10-6](#)).

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## 7.2.10 Water Quality Criteria for Estuaries

As discussed for fresh water in [Appendix 7.1.6](#), the U.S. EPA develops WQC using the latest scientific knowledge to determine when water is unsafe for people and wildlife. State and tribal governments may adopt these criteria or use them as guidance in developing their own. Numeric nutrient criteria are critical tools for protecting and restoring a water body's designated uses related to N and P nutrient pollution. These criteria enable effective monitoring of a water body for attaining its designated uses, facilitate formulation of the National Pollutant Discharge Elimination System (NPDES) discharge permits, and simplify development of TMDLs for restoring impaired waters.

Generally, it has been considered more complicated to determine appropriate nutrient criteria for estuaries than for many freshwater systems because estuaries are influenced by so many variable factors such as tidal fluctuations, salinity gradients, and other widely varying physical and chemical conditions which impact water quality. The designation of water bodies within which similar ambient conditions are expected to occur is much more difficult in estuaries, as the ambient values often fluctuate widely under natural conditions within the same estuary. Nevertheless, several states have made progress in the development of numeric nutrient criteria for estuaries. One of the first states to implement its own criteria for estuaries, Florida designated 62 different estuary segments and adopted a TN target value for each segment based on extensive monitoring and modeling studies.

The U.S. EPA is continuing to work with the states to develop numeric nutrient criteria to better define levels of N that affect U.S. marine and estuarine waters. WQC for TN are now available statewide in American Samoa, Florida, Hawaii, and the Northern Marianas Islands ([Figure 7-11](#)). Guam has statewide criteria for  $\text{NO}_3^-$  as N, and Puerto Rico has statewide criteria for DIN. Delaware has criteria for DIN as N in some estuaries. Massachusetts has not developed N criteria for estuaries but there is a TMDL in place that limits N loading to select estuaries on Cape Cod, Martha's Vineyard, Nantucket, and the Buzzards Bay/South Coastal area. California has made progress toward numeric nutrient criteria. Currently, the state has numeric criteria for water clarity in all estuaries statewide, but specific N criteria currently exist only for one location based on a TMDL for nutrient compounds (including N) for the Malibu Creek watershed, which includes the estuarine waters of Malibu Lagoon. By 2020, the following additional states are



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## 7.2.11 Estuary and Near-Coastal Biogeochemistry Summary

In the 2008 ISA, the evidence was sufficient to infer a causal relationship between reactive N deposition and biogeochemical cycling of N and C in estuarine and near-coastal marine systems. Nitrogen pollution is the major cause of harm to the majority of estuaries in the U.S. ([Bricker et al., 2008](#); [NRC, 2000](#)) and can lead to eutrophication, the process of increasing nutrient over-enrichment leading to water quality deterioration. Eutrophic systems are characterized by an increase in the rate of supply of organic matter (primary production and organic carbon accumulation) in excess of what an ecosystem is normally adapted to processing ([Diaz et al., 2013](#); [Nixon, 1995](#)). Evidence reviewed in the 2008 ISA, along with new studies indicate elevated N inputs to coastal areas can alter key processes that influence C and N cycling in near-coastal environments. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemistry in estuarine and near-coastal marine systems** which is consistent with the conclusions of the 2008 ISA.

As N fluxes to coastal areas have increased in recent decades in many parts of the U.S., the varying rates of different N cycling processes within estuaries themselves can also affect the magnitude of eutrophication experienced as a result of external N enrichment. Nitrogen additions not only cause the total pool of N to be larger but may also perturb N cycling in such a way that the system may exacerbate eutrophication to a greater extent than expected based on N additions alone. Research conducted since the 2008 ISA has shown that many of these N cycling processes are more important in the estuarine environment than previously understood. The removal of N through denitrification is a valuable ecosystem service in terms of constraining the extent and magnitude of eutrophication. Additional research has established DNRA as a more important N reduction pathway in some estuaries. Ammonium produced via DNRA can lead to enhanced productivity and respiration, which may exacerbate hypoxia. Recent studies indicate that DNRA rates are higher in warmer months and can also take up a larger percentage of total N reduction activity when temperatures are higher. The roles of sedimentary microbial processes of denitrification and anammox have been further characterized. New research has shown that the community of N fixing microorganisms is more diverse in estuarine and coastal waters than previously thought, and that N fixation occurs more widely than previously assumed. Influence of benthic macrofauna on N cycling has received increased research attention in part due to the potential for these organisms to mitigate external N enrichment.

New studies and evidence reviewed in the 2008 ISA continue to show that at many U.S. coastal areas, atmospheric deposition constitutes an important proportion of N inputs to estuaries; ranging from <10 to approximately 70% of the N inputs ([Table 7-9](#)). As stated

in the 2008 ISA, estuaries tend to be N limited ([Elser et al., 2007](#); [Howarth and Marino, 2006](#); [NRC, 2000](#); [Nixon, 1995](#); [Vitousek and Howarth, 1991](#); [Howarth, 1988](#); [D'Elia et al., 1986](#)), and many currently receive high N loads from human activities (e.g., atmospheric deposition, agricultural runoff, wastewater, and other sources), which can cause eutrophication ([Howarth et al., 1996a](#); [Vitousek and Howarth, 1991](#)). It is well known that the development and continuation of hypoxia in estuary and marine systems can be accelerated by increased nutrient loading. Monitoring efforts across the U.S. ([Appendix 7.2.7](#)) continue to show that N enrichment is a widespread problem. Numeric Nutrient Criteria have been established to varying degrees by coastal states in an effort to manage N inputs ([Appendix 7.2.9](#)). Water quality deterioration from N inputs to estuaries including development of hypoxic zones, can be linked to biological changes. Biological indicators of estuarine condition (e.g., chlorophyll *a*, HABs, macroalgae, SAV) are described in [Appendix 10](#).

Since the 2008 ISA, a number of papers have identified links between nutrient enrichment, effects on carbonate chemistry, and coastal acidification, and several mechanisms have been identified. One of the initial studies found that CO<sub>2</sub> production during decomposition of organic matter delivered to coastal zones from rivers experiencing eutrophication has enhanced the acidification of coastal subsurface waters in the Gulf of Mexico and the East China Sea ([Cai et al., 2011c](#)) and additional studies provide evidence of acidification in estuaries due to this mechanism ([Laurent et al., 2017](#); [Wallace et al., 2014](#); [Cai et al., 2011c](#); [Orr et al., 2005](#)). In addition to microbial degradation of organic matter, respiration of living algae and seagrasses during the night can also drive acidification ([Howarth et al., 2014](#)). The CO<sub>2</sub> produced in eutrophic estuarine waters combines with water molecules, producing carbonic acid, which makes the water more acidic ([Sunda and Cai, 2012](#); [Cai et al., 2011c](#); [Howarth et al., 2011](#)). Acidification of coastal waters tends to occur in locations where there is either thermal or saline stratification with spatial or temporal decoupling of production and respiration processes. Long-term monitoring ([Appendix 7.2.7.2](#)) documents increasing acidification trends in some U.S. coastal areas. Acidification also can be enhanced indirectly through the creation of anoxic waters and oxidation of HS<sup>-</sup> ([Cai et al., 2017b](#)). Modeling of coastal acidification via N enrichment and atmospheric CO<sub>2</sub> dissolution suggests that the combined effects of these two pathways are synergistic.

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## APPENDIX 8 BIOLOGICAL EFFECTS OF FRESHWATER ACIDIFICATION

This appendix characterizes the biological effects of acidifying deposition of nitrogen (N) and sulfur (S) in freshwater systems. Indicators of surface water chemistry are linked to biological endpoints ([Appendix 8.1](#)) in freshwater systems experiencing either chronic or episodic acidification ([Appendix 8.2](#)). Affected biota include plankton, invertebrates, fish, and other organisms ([Appendix 8.3](#)). Next, documentation of biological recovery in previously acidified systems ([Appendix 8.4](#)) is reviewed. [Appendix 8.5](#) includes levels of deposition at which effects are manifested and empirical and modeled critical loads (CLs) for acidifying deposition. A summary section with causal determinations based on a synthesis of new information and previous evidence of biological effects of aquatic acidification is presented in [Appendix 8.6](#). Overall, the updated research synthesized in this ISA reflects incremental improvements in scientific knowledge of aquatic biological effects and indicators of acidification as compared with knowledge summarized in the 2008 ISA. The causal relationships between acidifying deposition and biological effects on aquatic ecosystems are now, and were in 2008, well supported.

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### 8.1 Introduction

In the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria* (2008 ISA), the body of evidence was sufficient to infer a causal relationship between acidifying deposition and changes in freshwater biota. Changes in biogeochemical processes and water chemistry caused by deposition of N and S to surface waters and their watersheds ([Appendix 7](#)) have been well characterized for several decades and have ramifications for biological functioning of freshwater ecosystems. The 2008 ISA and studies since have shown that acidification from acid deposition can result in the loss of acid-sensitive organisms, population declines, and decreased species richness. This evidence is consistent and coherent across multiple species. More species are lost with greater acidification, providing evidence of biological gradients in effects. Both earlier and more recent studies indicate that aquatic biota in sensitive aquatic ecosystems have been affected by acidification at virtually all trophic levels. **New information is consistent with the conclusions of the 2008 ISA that the body of evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biota, including physiological impairment and alteration of species richness, community composition, and biodiversity in freshwater ecosystems.**

As reported in the 2008 ISA, effects of acidifying deposition on biotic integrity of freshwater ecosystems can be linked to changes in several key chemical effects indicators, including pH, dissolved inorganic aluminum (Al) concentration, calcium (Ca), and acid neutralizing capacity (ANC). Biological effects are primarily attributable to low pH and high inorganic Al concentration. The ANC, a measure of the overall buffering capacity against acidification, is commonly used because it integrates overall acid status, it is not affected by dissolved carbon dioxide (CO<sub>2</sub>), and surface water acidification models do a better job projecting ANC than pH and inorganic Al concentrations. However, ANC does not cause harm to biota. The usefulness of ANC lies in the association between it and the surface water constituents that directly cause or ameliorate acidity-related stress, in particular inorganic Al, Ca, and H<sup>+</sup> (measured as pH).

Chemical factors such as pH, Ca, ANC, ionic metals and dissolved organic carbon (DOC) are affected by acid deposition and can profoundly affect the structure and function of biological communities in lakes and streams. Inorganic Al is minimally soluble at soil or surface water pH above about 6.0, but solubility increases markedly as pH values drop below about 5.5. Low concentrations of base cations like Ca enable low pH and high concentrations of inorganic Al to occur ([Baker et al., 1990b](#)). However, DOC can bind to inorganic Al ions and reduce their bioavailability and their toxic impact on aquatic biota. The base cation surplus (BCS) is an alternate index that is similar to ANC and that also adjusts for the organic acid status of surface waters ([Lawrence et al., 2007](#)). BCS is based on a measurement of ANC (calculated from the charge balance of ionic concentrations in water) and also accounts for the influence of natural organic acidity by including the strongly acidic organic acid anions in the calculation.

Acid-sensitive freshwater systems can either be chronically acidified or subject to occasional episodes of decreased pH, decreased ANC, and increased inorganic Al concentration ([Appendix 7](#)). Changes to flow and surface water chemistry, characteristic of these events, reflect the influence of acidic inputs from precipitation, gases, and particles, as well as local geology and soil conditions. As stated in the 2008 ISA, surface water chemistry is a good indicator of the effects of acidification on the biotic integrity of freshwater ecosystems because it integrates the sum of soil and water processes that occur within a watershed. Surface water chemistry reflects and integrates N saturation, forest decline, soil acidification, nutrient cycling, and land use ([U.S. EPA, 2003](#)).

Acidification studies reviewed in the 2008 ISA included laboratory experiments, bioassays, mesocosm exposures, field observations, and whole ecosystem acidification or deacidification studies. [Baker et al. \(1990a\)](#) conducted a rigorous review of the effects of acidification on aquatic biota for the 1990 National Acid Precipitation Assessment Program (NAPAP) State of Science/Technology report series. In the [Baker et al. \(1990a\)](#)

report, hundreds of laboratory studies, in situ bioassays, field surveys, whole-system field experiments, and mesocosm studies on the effects of acidification on aquatic biota were evaluated. The findings in that report, along with literature published after 1990 up to December 2007, were assessed in the 2008 ISA. Measures of health, vigor, reproductive success, and biodiversity of aquatic biota were identified in the 2008 ISA as being affected by acidified waters caused by acidifying deposition. Effects had been most clearly documented for fish, aquatic invertebrates, and algae.

Since publication of the 2008 ISA, the overarching understanding of aquatic acidification has not changed appreciably. More recent research has confirmed and strengthened this understanding and provided more quantitative information, especially across the regional landscape. This appendix highlights post-2007 research findings through the spring of 2017.

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## 8.2 Chronic versus Episodic Acidification

Traditionally acidification involves both chronic and episodic processes. As defined in the 2008 ISA, chronic acidification refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic acidification refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralization of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits lower pH and ANC during episodic than during baseflow conditions. Chronically acidic lakes and streams maintain ANC  $<0$   $\mu\text{eq/L}$ , on average, throughout the year ([Driscoll et al., 2001b](#)). They are no longer prevalent in regions of the U.S. affected by acidic deposition [cf; [Fakhraei et al. \(2016\)](#); [Fakhraei et al. \(2014\)](#)]. The ANC during acidic episodic events may fall below  $0$   $\mu\text{eq/L}$  for only a few hours to weeks in a given year. It is known that the biota in many streams/lakes are impacted when the ANC is consistently below  $50$   $\mu\text{eq/L}$ . For this reason, the U.S. EPA National Lakes Assessment used an ANC threshold of  $>50$   $\mu\text{eq/L}$  as indicative of nonacidified water bodies ([U.S. EPA, 2009b](#)). In addition, dynamic models, such as MAGIC and PnET-BGC, estimate that some lakes and streams in the Adirondack and southern Appalachian Mountains had preindustrial ANC below  $50$   $\mu\text{eq/L}$ , but few or none had preindustrial ANC below  $20$   $\mu\text{eq/L}$ .

A large portion of the available aquatic acidification data reported in the 2008 ISA focused on lakes and streams in the Northeast and the southern-Appalachian Mountains ([U.S. EPA, 2008a](#)) because these systems have been among the most impacted by acidifying deposition in the past and have the best available surface water monitoring

information. Since completion of the literature review for the 2008 ISA, additional research has been conducted on changes in chronic surface water chemistry in the U.S. in response to changing levels of acidic deposition ([Appendix 7](#)). Many of these studies have further documented chemical recovery as S and N deposition continue to decline in most areas in the U.S. Biological recovery has been observed in some systems, but available data generally indicate that it typically lags behind chemical recovery ([Appendix 8.4](#)).

Many streams that exhibit chemical conditions during base flow that are suitable for aquatic life are subject to occasional episodic acidification that may exceed the acid tolerance of many aquatic species. Episodic events vary in timing, duration, and intensity. Episodic acidification is most common in the early spring and late fall, and least common in summer, when high flows tend to be infrequent ([Driscoll et al., 2001b](#)). This seasonality of episodic events reflects to some extent the influence of deposition accumulating in the landscape that is flushed to drainage water during precipitation or snowmelt events. Other natural processes can also be involved, including altered hydrologic flowpaths, biological uptake, and the neutral salt effect, whereby deposition of a neutral salt (e.g., NaCl) can lead to ion exchange of  $H^+$  for  $Na^+$  in soil, followed by drainage water acidification. Episodic processes are mostly natural, but  $SO_4^{2-}$  and  $NO_3^-$  influxes due to atmospheric deposition play important roles in the episodic acidification of some surface waters. Dilution of base cation concentrations in runoff during episodes—a quantitatively important component of the episodic response—may be affected in part by past base cation depletion of watershed soils, due to acidification, which limits the release of Ca and Mg in response to rapid runoff during storms and/or snowmelt ([Wigington et al., 1996a](#); [Wigington et al., 1996b](#)).

As reported in the 2008 ISA, episodes are generally accompanied by changes in two or more of the following chemical parameters: ANC, pH, concentrations of base cations,  $SO_4^{2-}$ ,  $NO_3^-$ , aluminum ions, organic acid anions, and DOC ([Sullivan, 2000](#)). During short-term episodes (hours or days), both flow and water chemistry can change markedly. Biological effects of episodes sometimes include fish mortalities, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems, and regions. The U.S. EPA's Episodic Response Project (ERP) in the 1980s confirmed the chemical and biological effects of episodic pH depressions in lakes and streams in parts of the U.S. ([Wigington et al., 1993](#)). In the ERP report, streams having acidic episodes showed long-term effects on fish populations compared with streams in which ANC remained above 0  $\mu eq/L$ . Results reported in the 2008 ISA from in situ bioassay studies conducted across the eastern U.S. showed that acidic episodes (with associated low pH and elevated inorganic Al concentrations and high stream-water discharge) caused rapid fish mortality under some conditions ([Driscoll et al., 2001b](#); [Bulger et al.,](#)

[1999](#); [Baker et al., 1996](#)). [Baker et al. \(1990a\)](#) concluded that episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. In a later study, acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and inorganic Al concentration exceeded 100 µg/L (3.7 µM), despite the relatively short duration of the episodes studied ([Baker et al., 1996](#)). Research from several regions in the U.S. indicated that acidifying deposition likely has increased the magnitude, frequency, and biological effects of episodic acidification events.

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## 8.3 Aquatic Organisms Impacted by Acidifying Deposition

[Appendix 8.3.1](#) through [Appendix 8.3.8](#) describe effects of acidification on phytoplankton, zooplankton, benthic invertebrates, fish, birds, and other biota. Changes in biota are linked to chemical indicators ([Appendix 7](#)) in surface water. In the 2008 ISA, biological effects were divided into two major categories: (1) effects on health, vigor, and reproductive success of taxonomic groups and (2) effects on biodiversity. The first category included changes at the species level of biological organization such as cumulative sublethal physiological effects (individual condition factor) and recruitment success. Effects on biodiversity include changes in community structure, species composition, and taxonomic richness. Studies reviewed in the 2008 ISA showed that the earlier aquatic lifestages were particularly sensitive to acidification.

In [Appendix 8.3.1](#) through [Appendix 8.3.8](#), findings from the 2008 ISA are summarized for each major taxonomic group, followed by a review of new literature including studies that report physiological alterations, changes in the abundance or presence of taxa, community shifts, and other biological responses associated with acidifying conditions. Effects on organisms at lower trophic levels, such as plankton and invertebrates, are discussed first followed by observations for fish and other vertebrates. Ecological thresholds of chemical indicator(s) associated with the observed responses are included, when available, from the reviewed studies. [Appendix 8.4](#) considers the evidence for biological recovery of different taxa.

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### 8.3.1 Plankton

Plankton, floating or drifting organisms in the water column, play an important role in freshwater ecosystems. Phytoplankton, or suspended algae, are primary producers at the base of the aquatic food web. These photosynthetic organisms, encompassing diatoms, cyanobacteria, dinoflagellates, and other groups of algae, vary in tolerance of acidic

conditions. Zooplankton comprise many groups of freshwater organisms including protozoans, rotifers, cladocerans, and copepods. Zooplankton feed on phytoplankton or other zooplankton. Abundance and community composition of plankton respond to changes in surface water chemistry associated with acidifying deposition to water bodies.

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### 8.3.1.1 Phytoplankton

Studies reviewed in the 2008 ISA reported reduced species richness of phytoplankton with decreases in pH and increases in inorganic Al concentrations associated with acid-affected surface waters ([U.S. EPA, 2008a](#)). There was also a shift in the composition of dominant taxa, but species composition shifts could not be accurately predicted. This kind of effect was most prevalent in the pH 5 to 6 range ([Baker et al., 1990a](#)). It appeared that the phytoplankton community restructured as the water became acidified. However, the response of phytoplankton communities often vary, with some lakes showing increasing biomass, others decreasing, and others having no change in phytoplankton biomass ([Baker et al., 1990a](#)). [Leavitt et al. \(1999\)](#) suggested that the complex interactions between pH, DOC, and light can explain the high variability in phytoplankton-biomass-acidification relationships.

More recent studies of the responses of phytoplankton to changes in surface water acidity have been limited. Effects on primary productivity are uncertain. In regards to phytoplankton species composition, changes were not apparent in the lake diatom communities or the diatom-inferred lake pH of sequential core segments in four alpine/subalpine lakes in the Cascade Mountains of Washington and Oregon that have not experienced substantial water acidification ([Eilers et al., 2016](#)). The study lakes were very low in specific conductance ( $\leq 3.6 \mu\text{S}/\text{cm}$ ) and ANC ( $\leq 11 \mu\text{eq}/\text{L}$ ). Sediment cores were collected from each lake and analyzed for nutrients and diatom microfossils in dated (210-Pb and 14-C) core segments. Water chemistry was simulated using a modified version of the CE-QUAL-W2 model to account for the assumed large influence of in-lake chemical processes. Model projections of future chemistry suggested that the three study lakes in Oregon will not change their acid-base chemistry in the future under N and S deposition increases to 3 times ambient, largely due to long lake water residence times, which allow in-lake processes to neutralize acid inputs. Foehn Lake in Washington was much more acid-sensitive, increasing in acidity in response to projected increases in N and S deposition at levels of 50% above ambient. Shallow depth, large amount of exposed bedrock, and sparse sediment accumulation enhance its acid sensitivity. This lake was formed less than a century ago, probably in response to climate warming and melting of an adjacent snowfield.

[Lacoul et al. \(2011\)](#), reviewed information on the effects of acidification on plankton and other organisms in Atlantic Canada and observed that the greatest changes in phytoplankton species richness occurred over a pH range of 4.7 to 5.6, just beyond the interval (pH 5.5 to 6.5) where bicarbonate becomes rapidly depleted in the water. Under acidifying conditions, phytoplankton communities shifted from dominance by chrysophytes, other flagellates, and diatoms to dominance by larger dinoflagellates. However, biomass and productivity were not much affected. Algal biomass in five Pennsylvania streams decreased with the severity of episodic acidification ([Macdougall et al., 2008](#)). Although no significant trends were observed for taxon richness or diversity, the degree of acidification during episodes appeared to affect the quantity of algae in the streams. [Bloch and Weyhenmeyer \(2012\)](#) evaluated physical and chemical time-series data for 13 nutrient-poor Swedish lakes across a latitudinal gradient. Phytoplankton biomass and species richness showed only weak relations with water chemistry. The only significant association observed across seven of the surveyed lakes was the number of chlorophyte taxa and changes in water temperature and color.

As stated in the 2008 ISA, diatoms, which comprise an important component of the phytoplankton, are excellent biological indicators of environmental change in aquatic ecosystems, being sensitive to changes in acidity, nutrient status, salinity, and climate ([Stoermer and Smol, 1999](#); [Sullivan and Charles, 1994](#)). Since the 2008 ISA, studies have further linked phytoplankton community shifts to acidification using paleolimnological analysis of fossil diatoms or long-term sampling of phytoplankton from the water column. Most of these studies have documented phytoplankton recovery in historically acidified lakes ([Appendix 8.4.1](#)). Stratigraphy of sediment chrysophyte remains in Brooktrout Lake in the Adirondack Mountains, NY revealed shifts in *Mallomonas* spp. and *Synura* spp., with some species declining and others increasing. After the 1950s, *Fragilariforma acidobiontica*, a diatom that is often abundant at pH <5.0, was present in lake sediments. These observations in Brooktrout Lake correspond to historical acidification, which was most severe during the 1970s and 1980s ([Sutherland et al., 2015](#)). Phytoplankton have also been used as indicators of acidification and recovery in Canada and Europe. In a recent analysis of diatom fossils from 10 lakes located about 80–250 km east and northeast of the oil sands development near Fort McMurray and Fort Mackay, northwestern Saskatchewan, [Laird et al. \(2013\)](#) observed increases in scaled chrysophytes and diatom flux rates in post-1980 sediments potentially related to atmospheric deposition in the oil sands region. A slight decrease (0.25 pH unit) in diatom-inferred pH occurred in one study site closest to the oil sands development, but there was no evidence of widespread acidification. Over time, phytoplankton assemblages in Swedish lakes recovering from acidification have become more similar to those in reference lakes ([Johnson and Angeler, 2010](#)).

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### 8.3.1.2 Zooplankton

In studies reviewed in the 2008 ISA, decreases in ANC and pH and increases in inorganic Al concentration were shown to contribute to the loss of zooplankton species or decreased abundance in lakes ([Keller and Gunn, 1995](#); [Schindler et al., 1985](#)). A decrease in pH from 6 to 5 reduced species richness in lake zooplankton communities ([Holt et al., 2003](#); [Holt and Yan, 2003](#); [Locke and Sprules, 1994](#)). [Sullivan et al. \(2006a\)](#) found that zooplankton communities varied with ANC in Adirondack lakes, with lower taxonomic richness (number of species of crustaceans, rotifers, and total zooplankton) in lakes having lower ANC. In general, lake-water ANC explained nearly half of the variation in total zooplankton and crustacean taxonomic richness, but less for rotifer richness. Particularly low zooplankton community richness occurred when ANC levels were below 0 µeq/L (15 species in highly acidic lakes compared to 35 at the highest values of ANC in the study [near 200 µeq/L]). Observations from in situ enclosure acidification studies at Emerald Lake in the Sierra Nevada showed shifts in zooplankton community with decreased pH ([Barmuta et al., 1990](#)). *Daphnia rosea* and *Diaptomus signicauda* were eliminated below pH 5.0 while other species such as *Bosmina longirostris* and *Keratella taurocephala* became more abundant. Possible mechanisms for zooplankton sensitivity to low pH and ANC include ion regulation failure, reduced oxygen uptake, inability to reproduce, and Al toxicity ([U.S. EPA, 2008a](#)).

A number of studies have been conducted since the 2008 ISA to determine the response of zooplankton to lake acidification. Highlighted here are several studies conducted in the U.S. and Canada. Many of these studies indicate that multiple factors could influence zooplankton community changes. *Bosmina* is among the most common North American temperate lake pelagic invertebrate genera. It is a genus of cladoceran filter feeders that can change body size and appendage length over multiple generations in response to changing environmental conditions. This makes it a good candidate ecological indicator. [Labaj et al. \(2016\)](#) evaluated *Bosmina* size responses in lakes near Sudbury, Ontario, Canada, that had been acidified and then chemically recovered in response to changes in nearby metal smelter emissions. Even with the recent return to presmelter lake pH, the *Bosmina* size structure has not yet recovered to preacidification conditions. [Labaj et al. \(2016\)](#) suggested that the observed effects of acidification and deacidification on the size of *Bosmina* may have been mediated by food web dominance of small copepod predators. [Vinebrooke et al. \(2009\)](#) reported variations in zooplankton communities during a whole-lake experimental acidification of Lake 302S in the Experimental Lakes area in Ontario, Canada. There was a negative effect on zooplankton species richness as pH decreased from 6.8 to 4.5. However, no correlation was found between functional properties (productivity or net total biomass) and species richness with this pH change, indicating that other factors such as multiple stressor interactions, species occurrences,

and altered trophic interactions might also influence zooplankton community change. In northwestern boreal shield lakes downwind of N emissions from the Athabasca oil sands extraction in Saskatchewan, Canada, zooplankton community structure was influenced by local environmental factors, including acidity, predation, and lake productivity. The role of regional atmospheric deposition on zooplankton community composition could not be distinguished from natural variability due to a lack of baseline data prior to oil extraction operations ([Anas et al., 2014](#)). Thus, the role of acidic deposition in driving changes in zooplankton community composition in that region was not clear.

Acidification often reduces Ca availability in lake water, which may impact invertebrates that require Ca for growth such as *Daphnia* spp. and crayfish ([Appendix 8.4.3](#)). [Jeziorski et al. \(2012b\)](#) examined the growth and survival of daphnid species across a Ca gradient (from 50 to 150 µeq/L) in central Ontario soft-water lakes. Considerable variability in growth and survival was observed within the *Daphnia pulex* species complex, and the variation across all cladoceran genera was best explained by pH and lake depth. This research adds support to the previous observation that among the cladocerans, daphnids are especially sensitive to decreases in Ca which leads to declines in their growth and survival as lake water acidifies with inputs of acidifying deposition.

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### 8.3.2 Periphyton

Periphyton mats are biofilms of algae, cyanobacteria, fungi, microinvertebrates, organic detritus, inorganic particles, and heterotrophic microbes imbedded within a matrix and attached to submerged substrates in aquatic systems (e.g., stream or lake bottoms or submerged vegetation). Periphyton is an important food source for invertebrates, tadpoles, and some fish. As reported in the 2008 ISA, acidification impacts periphyton species differently, with some excluded from impacted water bodies while others become dominant. Such changes decrease species richness and alter community structure ([U.S. EPA, 2008a](#)). For example, many of the brown algae and cyanobacterial periphyton species cannot tolerate acidic conditions, causing their abundance to decline along with pH, while green algae, particularly the filamentous Zygnemataceae, increase in relative abundance at lower pH ([Baker et al., 1990a](#)). There is evidence that the biomass of attached periphyton increases at lower pH. No new studies of acidifying effects on periphyton were identified for this review.

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### 8.3.3 Benthic Invertebrates

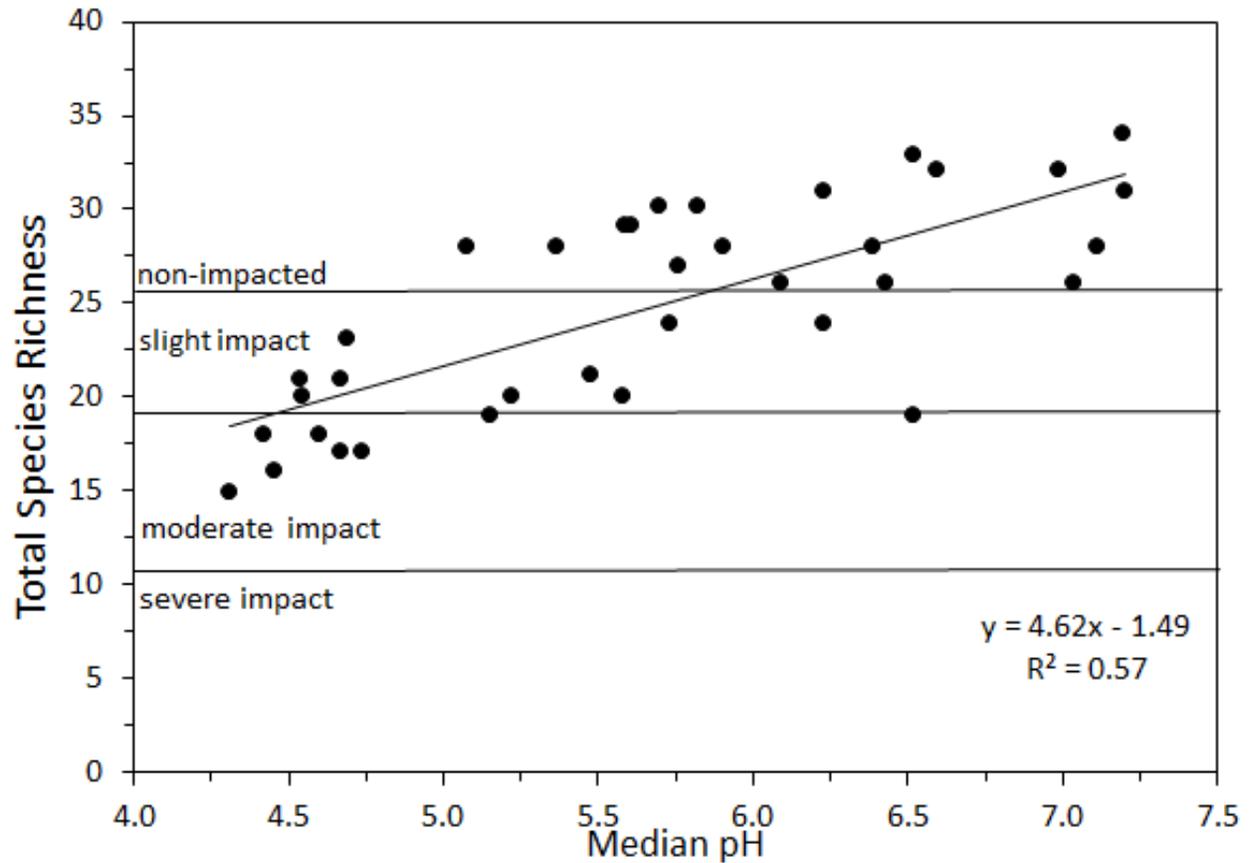
Benthic invertebrates live in freshwater sediments and include groups such as bivalves, worms, gastropods and insect larvae. As reviewed in the 2008 ISA, acidification as measured by decreases in ANC and pH and increases in inorganic Al concentration has been shown to contribute to the loss or decline in abundance of benthic invertebrate species in streams. The Ephemeroptera (mayflies)-Plecoptera (stoneflies)-Tricoptera (caddisflies; EPT) Index is a common measure of stream macroinvertebrate community integrity. The EPT metric is calculated as the total number of families present in those three insect orders. Mayflies tend to be the most sensitive of the three, and stoneflies tend to be the least sensitive ([Peterson and Van Eeckhaute, 1992](#)). The mayfly order alone is often selected for study because it includes a number of genera and species having varying degrees of sensitivity to acidification, including some that are highly sensitive ([Sullivan et al., 2003](#)). Typically, pH values below 5 result in the virtual elimination of all mayflies along with some other aquatic organisms from some streams ([U.S. EPA, 2008a](#); [Baker and Christensen, 1991](#)). These benthic invertebrates are impacted by acidification because  $H^+$  and inorganic Al can be directly toxic, causing disruption of their ion regulation and reproductive success. U.S. EPA first published freshwater criteria for Al in 1988 and is in the process of updating the Aquatic Life Criteria. The current 1988 acute and chronic criteria are 750 and 87  $\mu\text{g/L}$ , respectively, not to be exceeded once every 3 years on average ([U.S. EPA, 1988](#)).

Work since the 2008 ISA by [Baldigo et al. \(2009\)](#) assessed effects of acidification on benthic macroinvertebrate community dynamics in the southwestern Adirondack Mountains. Water chemistry and benthic macroinvertebrates were surveyed in 36 streams with different levels of acidity to characterize community response and identify thresholds for biological effects ([Figure 8-1](#)). In the study streams, macroinvertebrate assemblages were severely impacted at  $\text{pH} < 5.1$ , moderately impacted at  $\text{pH}$  from 5.1 to 5.7, slightly impacted at  $\text{pH}$  from 5.7 to 6.4 and usually unaffected above  $\text{pH}$  6.4. Inorganic Al concentrations reached potentially toxic levels in two-thirds of the study streams. The authors applied the Acid Biological Assessment Profile [acidBAP] index, which is based on percentage mayfly richness and percentage acid-tolerant macroinvertebrate taxa ([Burns et al., 2008b](#)). The acidBAP was strongly correlated with  $\text{pH}$ , ANC, BCS, and the concentration of inorganic Al, indicating the loss of mayflies in the stream as the surface water  $\text{pH}$  declines from  $\text{pH}$  7.0 to 4.2. A loss of about 12 species occurred in streams that had a  $\text{pH}$  between 7 and 4.2. Regression across all 36 streams showed a loss of 4.6 species per unit  $\text{pH}$  decrease ([Figure 8-1](#)). Inorganic Al toxicity was likely the main cause of the loss of macroinvertebrates. The Al concentration is strongly correlated with surface water  $\text{pH}$  (as  $\text{pH}$  decreases solubility of inorganic Al increases) and acid-base balanced as measured by BCS.

Several pH thresholds for aquatic invertebrate response have been published since the 2008 ISA ([Table 8-1](#)). [Lacoul et al. \(2011\)](#) reviewed available information on the effects of water acidification on aquatic organisms in Atlantic Canada. The median pH for sensitive invertebrate species occurrence was between 5.2 and 6.1, below which species tended to be absent. For example, several species of mayfly and most gastropods are intolerant of acidity and only occur at pH  $\geq 5.5$  and  $\geq 6$ , respectively.

The make-up of the stream invertebrate community is governed in part by the condition of riparian vegetation and associated humic acid levels in surface water. [O'Toole et al. \(2017\)](#) investigated riparian vegetation condition under high and low humic acid influence as affected by riparian vegetation. Both perennial and intermittent streams in western Australia were evaluated. Streams having well-developed riparian vegetation showed proportionately more algal grazers and detritivores. Intermittent streams with high humic content had lower numbers of cladocerans and chironomids and higher numbers of grazing gastropods as compared with intermittent streams that had relatively low humic content.

Several European studies published since the 2008 ISA have evaluated the use of benthic invertebrates as biological metrics to classify the ecological status of water bodies. These studies have developed or applied indices to predict dose-response relationships between macroinvertebrate communities and water chemistry. One study by [Schartau et al. \(2008\)](#) applied existing macroinvertebrate metrics developed for river acidification to lakes and also developed and tested new species-based indicators of lake acidification based on 668 samples of littoral macroinvertebrates taken from 427 lakes across Sweden, the U.K., and Norway. Although there was high variation in the data, a response threshold between pH 5.8 and 6.5 was identified for littoral macroinvertebrate communities, suggesting they could be used to assess ecological quality of lakes.



Source: Modified from [Baldigo et al. \(2009\)](#).

**Figure 8-1** Total macroinvertebrate species (community) richness as a function of median pH in 36 streams sampled in the western Adirondack Mountains of New York, 2003–2005; the four standard (New York State) impact categories for species richness are defined.

**Table 8-1 Thresholds of biological response to changes in water acidity for benthic invertebrates published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Life Forms	Region	Potential Thresholds	Reference
Sensitive invertebrates present	Atlantic Canada	pH 5.2 to 6.1	<a href="#">Lacoul et al. (2011)</a>
Littoral macroinvertebrates	Northern Europe	pH 5.8 to 6.5	<a href="#">Schartau et al. (2008)</a>
Stream macroinvertebrates	Southwestern Adirondacks Mountains	pH 5.1 to 5.7	<a href="#">Baldigo et al. (2009)</a>
Stream macroinvertebrates	Sweden	pH 5.7 to 6.0	<a href="#">Andrén and Wiklund (2013)</a>

Using macroinvertebrate monitoring data (1,462 samples) from Northern Europe [Moe et al. \(2010\)](#) tested new and existing acidification metrics with the aim of selecting a common metric to assess pH effects on biota in this region. Most investigated metrics responded to pH, with most of the variance explained by a few variables, including the number of Ephemeroptera families and the proportion of sensitive Ephemeroptera. Most biological metrics were higher (less impacted) in humic than in clear waters, suggesting smaller acidification effects in humic waters. [Murphy et al. \(2013\)](#) described an approach for developing diagnostic indices for assessing acidity in British streams that could be useful in the U.S. Variation in macroinvertebrate assemblages in 76 test sites was quantified with a 197-site calibration set. The Acid Water Indicator Community Index expressed at the species level was related to base-flow pH and to storm-flow pH and ANC, accounting for 38 to 56% of the variation in acid condition.

Interactions among Al, pH, and organic matter, and their collective influence on toxicity to aquatic biota, are discussed in [Appendix 8.3.6](#). In general, decrease in pH brings larger amounts of Al into solution whereas when dissolved organic matter is also present, it binds with Al, converting it into organo-Al complexes, decreasing its toxicity. In six humic (mean total organic carbon [TOC] 10–18 mg/L) streams in central Sweden, [Andrén and Wiklund \(2013\)](#) evaluated acute and sublethal toxicity of macroinvertebrate salmonid prey items exposed to episodes of acidity during spring snowmelt. The threshold for mortality was pH <5.7 and inorganic Al >20 µg/L (0.7 µM) for mayflies (*Baetis rhodani*) and pH <6.0 and inorganic Al >15 µg/L (0.6 µM) for the freshwater amphipod *Gammarus pulex*. [Traister et al. \(2013\)](#) investigated shifts in macroinvertebrate communities and food webs in nine small forested streams in the Czech Republic across a

pH gradient from 4.0 to 7.7. Acidification was related to reduced taxon richness and reduced Ephemeroptera family richness and lower population densities.

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### 8.3.4 Bacteria, Macrophytes, and Bryophytes

At the time of the 2008 ISA, most observations of biological effects of acidification were for phytoplankton ([Appendix 8.3.1.1](#)), benthic invertebrates ([Appendix 8.3.3](#)), and fish ([Appendix 8.3.6](#)), and relatively little information was available regarding the response of other biological taxa to surface water acidification. This has not changed appreciably. A few studies have been conducted on bacteria, macrophytes (aquatic plants), and bryophytes, as described below.

[Percent et al. \(2008\)](#) assessed bacterioplankton community diversity and structure in 18 Adirondack lakes across a range of acid-base chemistry using sequencing and amplified ribosomal DNA restriction analysis of constructed rRNA gene libraries. Based on principal components analysis, pH was positively correlated with bacterioplankton community richness and diversity. The richness of several bacterial classes, including Alphaproteobacteria, was directly correlated with pH. However, other environmental factors, such as lake depth, hydraulic retention time, dissolved inorganic C, and nonlabile (organically bound) monomeric Al, were also important in explaining bacterioplankton community richness and diversity, suggesting that acidity is only one factor that controls community composition.

Macrophyte studies provide additional information on the biological responses to acidic conditions in lakes. For example, a pH threshold for the absence of sensitive macrophytes was determined to be 5.5 in Atlantic Canada lakes by [Lacoul et al. \(2011\)](#). In an analysis of factors affecting the distribution of aquatic macrophytes in lakes in the Pyrenees Mountains of southern Europe, [Pulido et al. \(2015\)](#) constructed statistical models to predict optimum ranges and ecological niches of 11 aquatic macrophyte species. Macrophytes were most suited to lakes with low water concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in vegetated watersheds at low elevation. It was possible to delineate individual species ranges along gradients of specific conductance and water pH.

Bryophytes, most notably mosses and liverworts, are nonvascular plants that often constitute an important component of the biodiversity and productivity of low-order streams. [Tessler et al. \(2014\)](#) assessed bryophyte assemblages in southeastern New York streams and found that some species like *Hygrohypnum egyptium* and *Codriophorus aduncooides* were generalists and able to tolerate pH in the range from approximately 4 to 7, whereas others were more strongly limited by pH. For example, *H. ochraceum* occurred only at circumneutral pH near 6.5, while *Andreaea rothii* was restricted to pH

<5. Stream pH and amount of bedrock substrate were identified in this study as the primary determinates of bryophyte assemblage composition.

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### 8.3.5 Amphibians

Amphibians such as frogs, newts, toads, and salamanders have aquatic lifestyles and may be in contact with acidified waters in areas affected by acidifying deposition. Although some species of amphibian are on the decline, in the 2008 ISA, there was no evidence to suggest that acidic deposition was an important factor that impacts the health and abundance of amphibian communities ([U.S. EPA, 2008a](#)). Nevertheless, there are both relatively acid-sensitive and acid-tolerant amphibians. Examples of acid-sensitive amphibians in [Baker et al. \(1990a\)](#) include the spotted salamander (*Ambystoma maculatum*) and Jefferson salamander (*Ambystoma jeffersonianum*). Jefferson salamanders were absent from ponds with very low pH [ $<4.5$ ; [Freda and Dunson \(1986\)](#)]. Based on transplant studies into ponds or to the laboratory, embryos of this species did not hatch in water with pH less than about 4.5. Acid-tolerant embryos such as the Pine Barrens treefrog (*Hyla andersonii*) may hatch at a pH of 3.7 ([Freda and Dunson, 1986](#)). Toxicity is not solely a matter of pH, but is also influenced by  $\text{Ca}^{2+}$ , inorganic Al, and DOC concentrations, lifestyle, and water temperature ([Baker et al., 1990a](#)). Large-scale amphibian extinctions due to acidifying deposition had not been detected in any geographic region at the time of the 2008 ISA ([Baker et al., 1990a](#)) and have not been documented in more recent years.

Studies published since the 2008 ISA further indicate that amphibian species are relatively tolerant of acidifying conditions. In a review of toxicity data for amphibian species found in Atlantic Canada, [Lacoul et al. \(2011\)](#) concluded that some amphibians can survive at pH as low as 3.5 to 4.0. [Chambers et al. \(2013\)](#) explored the relationship between pH and hormonal response in salamanders. In their field studies with Jefferson salamander larvae from eight natural breeding populations and a mesocosm experiment with varying pH, they observed an increase in baseline corticosterone concentration with lower pH (in the range of 5 to 5.8). Elevation of baseline corticosterone level is a physiological alteration associated with stress response. In contrast, no significant relationship was observed between corticosterone and pH in adult Allegheny Mountain dusky salamanders (*Desmognathus ochrophaeus*) living in nine streams in the Central Appalachian ecoregion with differing pH ([Woodley et al., 2014](#)). Three-week laboratory exposures with the same species showed that low pH (3.5) decreased locomotory activity but had no effect on plasma corticosterone levels. A change of average pH from pH 7 to pH 6 resulted in a shift in the skin microbial community composition on larval American bullfrogs [*Rana catesbeiana*; [Krynak et al. \(2015\)](#)]. Following metamorphosis, shifts in

pH did not alter skin microbial community structure significantly in juvenile frogs. However, antimicrobial peptide production was affected by interactions between pH and degree of shading, suggesting that environmental variability may influence amphibian susceptibility to fungal pathogens.

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### 8.3.6 Fish

Physiological and population-level responses associated with exposure of fish to acidified waters have been well characterized for many decades. As summarized in the NAPAP report by [Baker et al. \(1990a\)](#) and studies reviewed in the 2008 ISA, fish populations in acidified streams and lakes of Europe and North America have declined, and some have been eliminated due to atmospheric deposition of acids and the resulting decrease in pH and ANC and increase in inorganic Al concentrations in surface waters. By 1990, it was well established that freshwater acidification could cause significant adverse biological effects on fish, although the effects were not uniform across species. Summary information from the 2008 ISA for pH, ANC, and Al and effects on fish are presented in [Appendix 8.3.6.1](#) to [Appendix 8.3.6.5](#) along with results of new studies. In general, understanding of the effects of acidification on fish has not changed since the 2008 ISA. Effects of acidification on fish and other organisms must be viewed in the context of other stressors and management actions, in particular climate change and the effects of fish stocking.

Responses among fish species and lifestages within species to changes in pH and Al in surface waters are variable. In general, early lifestages such as larvae and smolts are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults ([Baker et al., 1990a](#); [Johnson et al., 1987](#); [Baker and Schofield, 1985](#)). Some of the most commonly studied species have been brown trout (*Salmo trutta*), brook trout (*Salvelinus fontinalis*), and Atlantic salmon (*Salmo salar*). Among these three species, [Gjedrem and Rosseland \(2012\)](#) recently showed substantial additive genetic variation in tolerance to acidic water, with heritabilities ( $h^2$ ) ranging from 0.09 to 0.27 for dead-eyed eggs (a development period that is highly sensitive to low pH [4.7 to 5.2]).

Several new studies of Atlantic salmon provide additional information documenting the sensitivity of this species to acidification during different lifestages. Evidence suggests that acidification has been an important stressor that has limited the distribution and abundance of Atlantic salmon in the northeastern U.S. Atlantic salmon are anadromous and they are susceptible to physiological effects of acidification as they develop and move to different habitats. The salmon start their life cycle in freshwater then migrate to the ocean, returning to freshwater to spawn. In rivers, eggs hatch into fry, which develop

into parr. Before migrating to the ocean, parr start developing into smolt, which are more sensitive to acidification than the parr lifestage ([Kroglund et al., 2008](#); [Monette and McCormick, 2008](#)). Recent research has shown that exposure to concentrations of inorganic Al that have no apparent effects in freshwater may subsequently affect smolt survival in seawater. Thus, the timing of acidification episodes in relation to fish lifestage and migration from freshwater to seawater may impact fish survival due to the delayed response to inorganic Al exposure ([Kroglund et al., 2008](#); [Kroglund et al., 2007](#)).

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### 8.3.6.1 Physiological Responses to Acidification

The modes of action of biological impacts on fish from surface water acidification were reasonably well known at the time of the 2008 ISA. Physiological disturbances to fish exposed to acidic waters reported in the 2008 ISA included iono- and osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure. These impacts can often be directly attributed to effects on gill function or structure. Al has been shown to accumulate on the gill surface when fish are exposed to water having high inorganic Al concentration. The primary mechanism for the toxic effects of low pH and elevated inorganic Al on fish involves disruption of normal ion regulation at the gill surface, resulting in increased rates of ion loss and inhibition of ion uptake ([Bergman et al., 1988](#); [Wood and McDonald, 1987](#); [Leivestad, 1982](#); [McWilliams and Potts, 1978](#)). The disruption of salt and water balance causes red blood cells to rupture and blood viscosity to increase ([Driscoll et al., 2003b](#)). Additional effects might include disruption of Ca metabolism ([Reader et al., 1988](#); [Gunn and Noakes, 1987](#); [Peterson and Martin-Robichaud, 1986](#)) and loss of Ca from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability ([Exley and Phillips, 1988](#); [Havas, 1986](#); [Mcdonald, 1983](#)).

Newly available literature since the last review supports previous findings of effects of acidification on fish physiology. Several in situ studies on brook trout in the southeastern U.S. and New England provide additional information on sensitivity of different fish lifestages to episodic acidification. Changes in native brook trout physiology were determined during two acid runoff episodes in the Great Smoky Mountains National Park by [Neff et al. \(2008\)](#). Results of an in situ bioassay of whole-body sodium concentrations before and after acidification showed that stream acidification negatively impacted native trout physiology. Loss of whole-body sodium when stream pH dropped below 5.1 indicated that trout lost the ability to ionoregulate. Stream water ANC and pH decreased episodically during the stormflow events studied. An ANC contribution analysis indicated that acidic deposition may have been the major cause of episodic stream acidification; increased concentrations of organic acid anions and base cation dilution

during episodes also appeared to be important. Subsequently, [Neff et al. \(2009\)](#) investigated the effects of hydrologic episodes on loss of blood plasma  $\text{Na}^+$  in native southern brook trout, a response associated with physiological stress from acid exposure. In situ bioassays were conducted at three sites during a 2-year period. Whole-body  $\text{Na}^+$  concentrations decreased by 10 to 20% following acidic episodes during which 24-hour mean pH values of 4.88, 5.09, and 4.87 and total dissolved Al concentration of 210, 202, and 202  $\mu\text{g/L}$  (7.8, 7.5, and 7.5  $\mu\text{M}$ ) were observed.

In a combination lab and field study designed to establish whether the smolt or parr lifestage is more sensitive to short-term acid/Al pulses, [Monette and McCormick \(2008\)](#) observed that compared with control fish, smolts exposed to elevated acid/Al levels showed greater losses of blood plasma  $\text{Cl}^-$  (9–14 mM) after 2 and 6 days and increases in plasma cortisol (4.3-fold) and glucose (2.9-fold) levels after 6 days of exposure, while parr were not affected. Gill  $\text{Na}^+/\text{K}^+$ -ATPase (NKA) activity was not affected in either lifestage. Smolts were shown to be more sensitive than parr to short-term acid/Al exposure although gill accumulation of Al was observed in both lifestages.

[McCormick et al. \(2009\)](#) determined the effects of pH and Al on survival, development of smolts, ion regulation, and stress levels of Atlantic salmon in southern Vermont. Two 6-day field studies during the peak of smolt development (late April and early May) were conducted in five streams having different acid-base chemistry. The researchers found increased mortality, loss of blood plasma chloride ( $\text{Cl}^-$ ), altered NKA activity in the gills, and higher gill Al in fish that were caged in streams that experienced low pH (5.4–5.6) and high inorganic Al concentration (50–80  $\mu\text{g/L}$  [1.9–3  $\mu\text{M}$ ]). Fish confined at sites that were less impacted by acidification showed more moderate decrease in blood plasma  $\text{Cl}^-$  and more moderate increase in plasma cortisol, glucose, and gill Al.

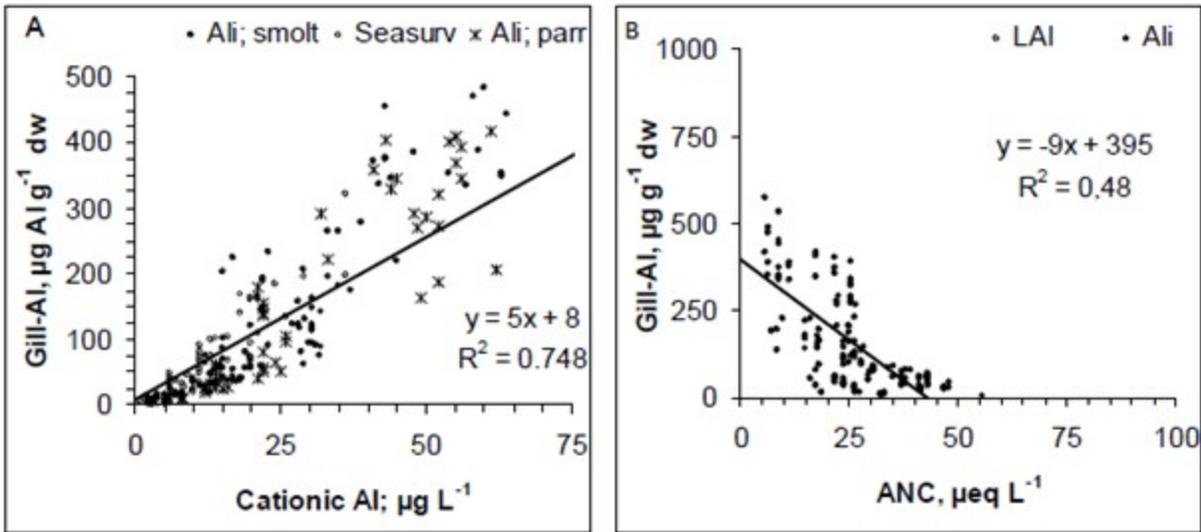
Individual Atlantic salmon physiological responses were strongly inter-correlated, with a single principal component axis (PC1) that comprised cortisol, glucose,  $\text{Cl}^-$ , and NKA accounting for 90% of the total variation in the physiological response variables data set ([McCormick et al., 2009](#)). The authors suggested that physiological impairment was the most appropriate interpretation of PC1. In a stepwise linear regression model using water chemistry variables only, PC1 scores were best explained by low pH ( $r^2 = 0.53$ ). Gill Al also was a strong predictor of physiological impairment.

Recent studies on salmon examined Al toxicity following transfer to seawater to simulate the physiological changes associated with migration to the marine environment. In an exposure to high acidity and inorganic Al followed by 24-hour seawater exposure, blood plasma  $\text{Cl}^-$  levels were higher in exposed fish than in controls, suggesting reduced seawater tolerance ([Monette et al., 2008](#)). Loss of seawater tolerance was accompanied by lower levels of gill NKA activity. Exposure to acidity and inorganic Al also caused

decreased plasma insulin-like growth factor (IGF-I) and levels of 3,3',5'-triiodo-L-thyronine (T-3). Results of this research suggest that smolt development and seawater tolerance can be affected by exposure to high acidity and inorganic Al despite an absence of detectable impacts on blood plasma ion regulation in freshwater. In 2- and 5-day Al/acid exposures of Atlantic salmon followed by a seawater challenge test, [Monette et al. \(2010\)](#) showed that seawater tolerance of smolt is reduced by prior acute exposure to acidic conditions and low levels of Al, and that the mechanisms of blood ion regulation depend on the extent and duration of Al exposure. In both seawater and freshwater, exposure to pH 5.3 and moderate Al levels led to accumulation of gill Al, alterations in gill morphology, reduced gill NKA activity, and impaired ion regulation. In contrast, gill Al accumulation was decreased, with only slight effects on gill morphology in smolts exposed to acidic conditions and the lowest level of Al concentration.

Sockeye salmon (*Oncorhynchus nerka*) fry were raised in freshwater for 126 days under sublethal conditions of low to moderate pH (4.8–6.8) by [Kennedy and Picard \(2012\)](#). Effects on growth, stress, and seawater tolerance were determined after smoltification. At the lower pH treatment (5.0), fish gained significantly less mass (average 46% of control [pH 6.8] values), exhibited lower condition factor, and showed lower liver somatic index values than control fish. The concentrations of liver glycogen (49% of control values) and whole-body lipids (65% of control values) were also significantly lower. Acid exposure caused increased stress, as measured by increased concentrations of blood plasma cortisol. Fish exposed to pH 5.0 in freshwater for 30 days, and then challenged with seawater, exhibited 14% higher mortality, on average, compared to control fish. They also showed osmoregulatory stress (increased blood plasma Na<sup>+</sup> and Cl<sup>-</sup> concentrations) and lower critical swimming speed (22% reductions compared to control fish). Results suggested that sockeye salmon are acid sensitive and do not acclimate to low pH under chronic exposure conditions. This sensitivity could decrease the probability of fish surviving after moving to the marine environment.

In a synthesis of results of bioassay studies on Atlantic salmon in Norway, gill Al concentration was significantly correlated with water inorganic Al and ANC [[Figure 8-2; \(Kroglund et al., 2008\)](#)]. They also analyzed results of seawater challenge tests showing that the fish had impaired hyporegulatory capacity due to inorganic Al exposure in freshwater.



Al = aluminum; Ali = inorganic monomeric aluminum; ANC = acid neutralizing capacity; dw = dry weight; g = gram; L = liter; LAI = labile aluminum; µg = microgram; seasurv = seawater survival.

Notes: Linear relationships are entered into the graphs whenever significant.

Source: [Kroglund et al. \(2008\)](#).

**Figure 8-2 Relationship between (a) inorganic monomeric aluminum and gill aluminum for parr and smolt, and (b) acid neutralizing capacity and gill aluminum.**

To assess the ability of Atlantic salmon smolts to recover from acid/Al exposure, [Nilsen et al. \(2013\)](#) subjected salmon for 2- and 7-day periods to low pH (5.7) and inorganic Al (40 µg/L [1.5 µM]). Fish were subsequently transferred to good quality water (control exposure; pH 6.8; inorganic Al <14 µg/L [0.52 µM]). Accumulations of Al on fish gills measured after 2 and 7 days of acid/Al exposure were  $35.3 \pm 14.1$  and  $26.6 \pm 11.8$  µg/g (dry weight), respectively. High gill Al decreased 2 days after moving exposed fish to control water, but gill Al was still higher than under sustained control conditions (5–10 µg/L [0.18–0.37 µM] inorganic Al) over the following 2-week period. Decreases in blood plasma  $\text{Na}^+$  levels were observed in both test groups and remained significantly lower than in control fish for the 2-week period after transferring fish to control water. Blood plasma  $\text{Cl}^-$  levels in smolts exposed for 7 days were significantly lower than in control smolts and then remained low in both treatments following transfer to control water. Treated smolts maintained high blood plasma glucose levels, indicative of increased stress, after being transferred to control water and for more than a week following exposure.

Responses of Atlantic salmon smolts to episodic pH fluctuations were assessed during in situ experiments in rivers and streams in eastern Maine ([Liebich et al., 2011](#)). Altered plasma chloride and plasma glucose were strongly correlated with pH, consistent with the laboratory findings of [Monette and McCormick \(2008\)](#) and others. High DOC concentrations in streams could reduce the inorganic Al impact by enhancing complexation with organic ligands.

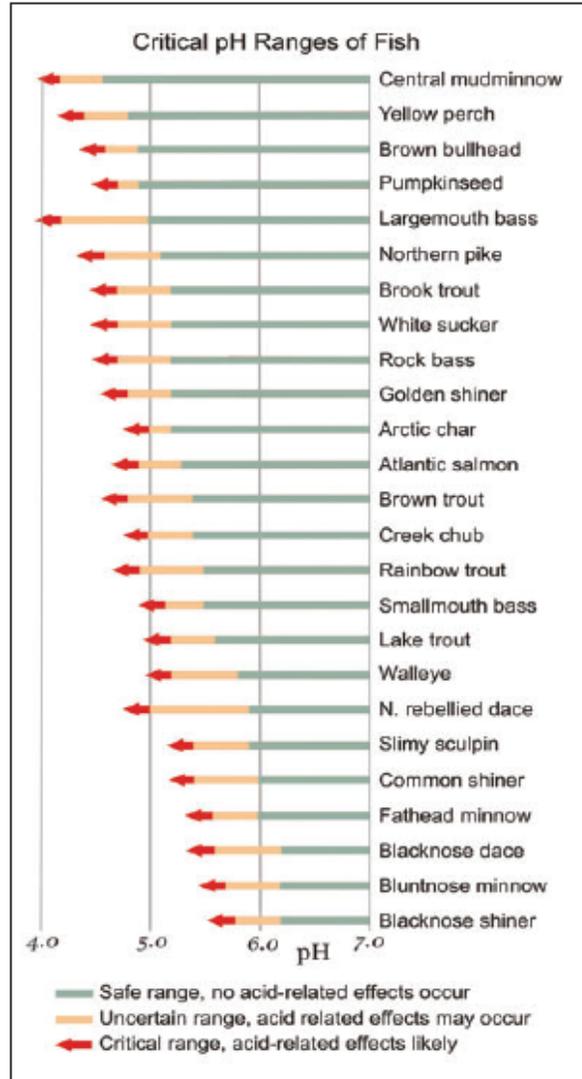
Recently, gill Al and NKA activity were assessed in smolts migrating downstream in New England ([Kelly et al., 2015](#)). Smolt immigrating from the Connecticut River, where most tributaries were well buffered, had low levels of gill Al and high levels of NKA activity. In the Merrimack River watershed, where most tributaries were characterized by low pH and high inorganic Al concentrations, salmon smolt immigrating downstream showed higher gill Al and lower gill NKA activity. Stocked salmon return rates were lower in the Merrimack River watershed, and the authors suggested that episodic acidification could be affecting salmon smolts in poorly buffered streams in New England.

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### **8.3.6.2 Fish and pH Thresholds**

The detrimental effects on fish associated with pH are also closely tied to ANC, which is strongly correlated with water pH and Al [[Appendix 8.3.6.4](#); ([Driscoll et al., 2001b](#))]. In the 2008 ISA, pH effects on fish were well characterized. A pH range of 5.0 to 5.5 was found to cause the absence of several fish species ([Haines and Baker, 1986](#)). Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH higher than 6.5 ([Driscoll et al., 2001b](#); [Baker et al., 1990b](#)). The observations from field studies of pH effects on fish have been corroborated by bioassay data ([Figure 8-3](#)). Some species and lifestages experienced significant mortality in bioassays at relatively high pH [e.g., pH 6.0–6.5 for eggs and fry of striped bass and fathead minnow; [McCormick et al. \(1989\)](#); [Buckler et al. \(1987\)](#)], whereas others were able to persist at quite low pH without adverse effects. Many minnows and dace (Cyprinidae) are highly sensitive to acidity, but some common game species such as brook trout, largemouth bass, and smallmouth bass are less sensitive (threshold effects at pH <5.0 to near 5.5). In many Appalachian Mountain streams that have been acidified by acidic deposition, brook trout is the last fish species to disappear; it is generally lost at pH near 5.0 ([MacAvoy and Bulger, 1995](#)), which usually corresponds in these streams with ANC near 0 µeq/L ([Sullivan et al., 2003](#)). While brook trout and other fish species may be absent at pH <5.0, detrimental effects on

population size and density may occur at higher pH values ([Baker et al., 1990a](#); [Baker and Schofield, 1985](#)).



Notes: [Baker and Christensen \(1991\)](#) generally defined bioassay thresholds as statistically significant increases in mortality or by survival rates less than 50% of survival rates in control waters. For field surveys, values reported represent pH levels consistently associated with population absence or loss.

Source: [Fenn et al. \(2011b\)](#) based on [Baker and Christensen \(1991\)](#).

**Figure 8-3 Critical aquatic pH ranges for fish species.**

Studies in the Adirondack Mountains reviewed in the 2008 ISA demonstrated the effect of acidification on fish species richness. Of the 53 fish species recorded in Adirondack lakes, about half (26 species) were absent from lakes with pH below 6.0. Those 26 species included important recreational species plus ecologically important minnows that serve as forage for sport fish ([Baker et al., 1990b](#)). There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100  $\mu\text{eq/L}$  ([Cosby et al., 2006](#); [Sullivan et al., 2006a](#); [Driscoll et al., 2003b](#); [Bulger et al., 1999](#)).

Since the 2008 review, additional pH thresholds have been published for fish species ([Table 8-2](#)). A pH threshold of  $<5.9$  was identified as potentially harmful to Atlantic salmon smolts in eastern Maine ([Liebich et al., 2011](#)). [Kirby et al. \(2008\)](#) showed that when streams in central Pennsylvania had pH below 5 because of their underlying geology, brook trout were only present in 9 of 28 streams, whereas all streams that had  $\text{pH} \geq 6$  had brook trout. Overall, the available data suggested that the threshold for brook trout mortality is at about  $\text{pH} = 5.0$ .

Despite recent reductions in acidic deposition in northern Europe, mobilized Al remains a threat to brown trout that are native to many European fresh waters and stocked in many U.S. waters. [Andrén and Rydin \(2012\)](#) identified a threshold for healthy brown trout populations by exposing yearling trout to a pH and inorganic Al gradient in humic streams in Scandinavia. Results suggested a threshold of less than 20  $\mu\text{g/L}$  (0.74  $\mu\text{M}$ ) inorganic Al and pH higher than 5.0. Toxic effects beyond these thresholds included Al accumulation on the gills, increased hemoglobin and plasma glucose, decreased plasma chloride, and increased mortality.

Brown trout embryo and first-year juvenile survival in 12 streams in northern Sweden were investigated by [Serrano et al. \(2008\)](#) during snowmelt using in situ bioassays. The study streams had high DOC, which causes a pH decrease, but also protects fish against Al toxicity. High juvenile brown trout mortality was documented during the spring flood, in association with low pH. No significant effect of inorganic Al concentration on juvenile or embryo mortality was observed, likely due to Al complexation by organic acid anions. An empirical model developed to predict juvenile brown trout mortality in high-DOC streams suggested a critical chemical threshold of pH in the range of 4.8–5.4. High embryo and yolk sac fry survival was recorded, even at stream sites with pH as low as 4.0. As expected, the observed pH threshold in DOC-rich water was lower than previously observed thresholds for low-DOC freshwaters. First-year juveniles are likely to be most sensitive to adverse effects of low pH in northern boreal stream ecosystems, especially during snowmelt-driven episodic pH depressions.

**Table 8-2 pH thresholds in fish published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Fish Species and Effects	Region	Potential Thresholds	Reference
Atlantic salmon smolts reduction of plasma ions	Eastern Maine	pH 5.9	<a href="#">Liebich et al. (2011)</a>
Brook trout loss of whole-body Na	Great Smoky Mountains NP	pH 5.1	<a href="#">Neff et al. (2008)</a>
Brook trout loss of whole-body Na of 10 to 20%	Great Smoky Mountains NP	pH 4.9 to 5.1	<a href="#">Neff et al. (2009)</a>
Juvenile brown trout mortality in high DOC streams	Sweden	pH 4.8 to 5.4	<a href="#">Serrano et al. (2008)</a>
Brown trout embryo and yolk sac fry survival during episodes in DOC-rich lakes	Sweden	pH 4.0	<a href="#">Serrano et al. (2008)</a>
Toxicity to brown trout in humic streams	Northern Europe	pH 5.0; inorganic aluminum 20 µg/L	<a href="#">Andrén and Rydin (2012)</a>
Response of Atlantic salmon to alarm cues after episodic exposure <sup>a</sup>	Canada	6.2	<a href="#">Leduc et al. (2009)</a>
Interference of chemical alarm cues to assess predation risk in juvenile Atlantic salmon <sup>a</sup>	Canada	pH <6.6	<a href="#">Elvidge and Brown (2014)</a>

DOC = dissolved organic carbon; Na = sodium; NP = national park.

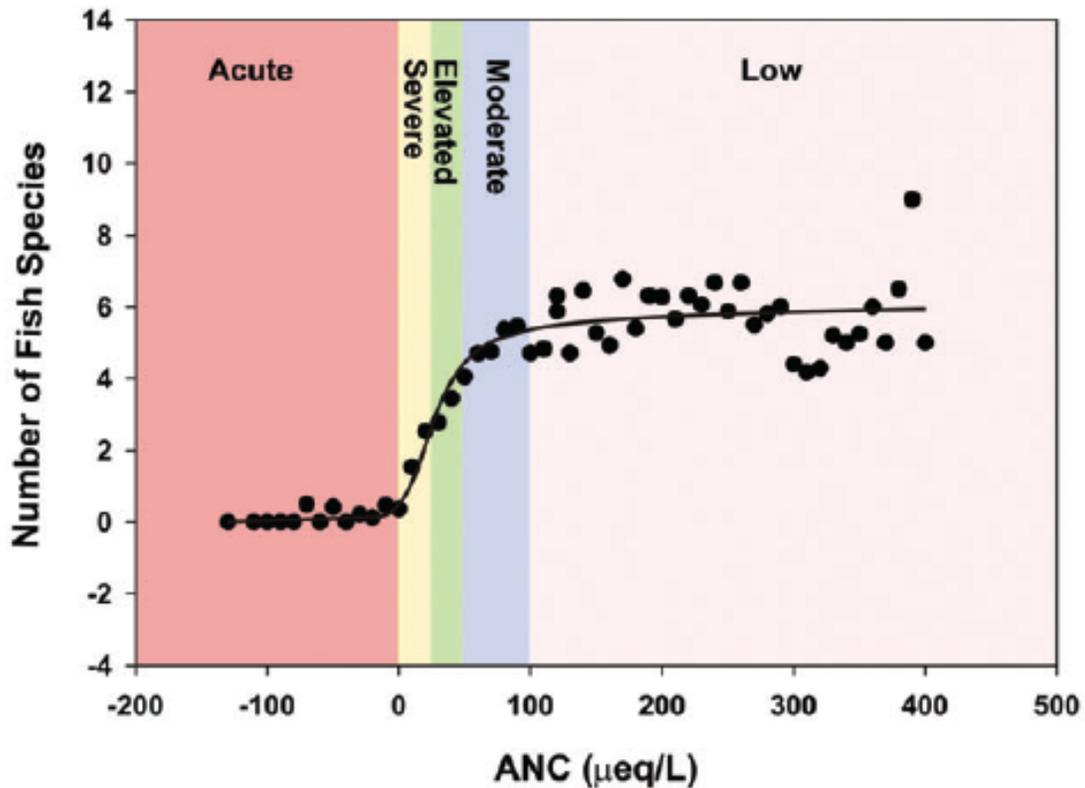
<sup>a</sup>Behavioral responses of fish are discussed in [Appendix 8.3.6.5](#). Table B-23 and Table B-24 in the 2008 ISA summarize pH thresholds from the NAPAP report ([Baker et al., 1990a](#)).

### 8.3.6.3 Fish and Acid Neutralizing Capacity Thresholds

ANC has been found in various studies reviewed in the 2008 ISA to be a good single indicator of the biological response and health of aquatic communities in acid-sensitive systems ([U.S. EPA, 2008a](#); [Sullivan et al., 2006a](#)). For fish and other aquatic biota, ANC is closely tied to pH ([Appendix 8.3.6.2](#)) and the bioavailability of Al [[Appendix 8.3.6.4](#); ([Driscoll et al., 2001b](#))]. There is often a positive relationship between pH or ANC and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 µeq/L ([Cosby et al., 2006](#); [Sullivan et al., 2006a](#); [Bulger et al., 1999](#)). In Shenandoah National Park streams in Virginia, fish species richness was lower by one species, on average, for every 21 µeq/L decrease in ANC ([Sullivan et al., 2003](#); [Bulger et al., 1999](#)). Interpretation of species richness can be difficult, however,

because more species tend to occur in larger lakes and streams as compared with smaller ones, irrespective of acidity (Sullivan et al., 2003). This might be due to increased aquatic habitat complexity and diversity in larger watersheds (Sullivan et al., 2003).

As summarized in the 2008 ISA, lakes and streams having an annual average ANC < 0  $\mu\text{eq/L}$  generally do not support fish (Figure 8-4). The analysis shown in this figure suggests that there could be a loss of fish species with decreases in ANC below a threshold of approximately 50 to 100  $\mu\text{eq/L}$  (Sullivan et al., 2006a).



ANC = acid neutralizing capacity; L = liter;  $\mu\text{eq}$  = microequivalent.

Notes: The data are presented as the mean (filled circles) of species richness within 10  $\mu\text{eq/L}$  ANC categories, based on data collected by the Adirondacks Lakes Survey Corporation.

Source: Modified from Sullivan et al. (2006a).

**Figure 8-4** Number of fish species per lake verses acidity status, expressed as acid neutralizing capacity, for Adirondack lakes.

Various ecological effect criteria, including effects on fish communities, have been used to classify ranges of ANC values (Table 8-3). The use of these criteria lies in the

association between ANC and the surface water constituents that directly affect acidity-related stress. These include, in particular, pH,  $\text{Ca}^{2+}$ , and inorganic Al concentration. [Bulger et al. \(2000\)](#) developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia. Across the eastern U.S., brook trout are often selected as a biological indicator of aquatic acidification because they are native to many eastern surface waters and because residents place substantial recreational and aesthetic value on this species. Note that because brook trout are comparatively acid tolerant, adverse effects on many other fish species would be expected at higher ANC than the threshold values that impact brook trout. Annual average ANC greater than about 50  $\mu\text{eq/L}$  is generally considered suitable for brook trout in southeastern U.S. streams. Such streams have sufficient buffering capacity to prevent acidification from eliminating this species, and there is reduced likelihood of lethal storm-induced acidic episodes. In streams having ANC > 50  $\mu\text{eq/L}$ , reproducing brook trout populations are expected if the habitat is otherwise suitable ([Bulger et al., 2000](#)), but some streams may periodically experience episodic chemistry that affects species more sensitive than brook trout. Streams having annual average ANC from 20 to 50  $\mu\text{eq/L}$  may experience episodic acidification during storms to pH and ANC levels that can be lethal to brook trout, as well as other fish ([Bulger et al., 2000](#)). Streams that are designated as episodically acidic (chronic ANC from 0 to 20  $\mu\text{eq/L}$ ) are considered marginal for brook trout because acidic episodes are likely ([Hyer et al., 1995](#)), although the frequency and magnitude of episodes can vary widely. Streams that are chronically acidic (average ANC less than 0  $\mu\text{eq/L}$ ) are not expected to support healthy brook trout populations ([Bulger et al., 2000](#)).

[Hesthagen et al. \(2008\)](#) used a regional water chemistry database to determine critical values of pH, ANC, and inorganic Al for survival of brown trout in 790 Norwegian lakes. The threshold value ( $\text{ANC}_{\text{limit}}$ ) to avoid fish damage was compared with that found in a similar study conducted in 1986. In 1995, the threshold ANC value to avoid toxic effects to fish and retain unaffected fish populations was 67  $\mu\text{eq/L}$ , compared with 20  $\mu\text{eq/L}$  in 1986. The higher  $\text{ANC}_{\text{limit}}$  found for 1995 was attributed to lower pH and higher inorganic Al concentration at a given ANC value in 1995 than in 1986. This, in turn, was attributed to increases in total organic carbon in these lakes. Thus, the value of ANC as an indicator of biological effects may differ between acidification and recovery periods.

**Table 8-3 Expected ecological effects and concern levels in freshwater ecosystems at various levels of acid neutralizing capacity.**

Category Label	ANC Level µeq/L	Expected Ecological Effects
Low concern (no effect)	>100	Fish species richness may be unaffected. Reproducing brook trout populations are expected where habitat is suitable. Zooplankton communities are unaffected and exhibit expected diversity and distribution.
Moderate concern (minimally impacted)	50 to 100	Fish species richness begins to decline (sensitive species are lost from lakes). Brook trout populations are sensitive and variable, with possible sublethal effects. Diversity and distribution of zooplankton communities begin to decline as species that are sensitive to acid deposition are affected.
Elevated concern (episodically acidic)	0 to 50	Fish species richness is greatly reduced (more than half of expected species are missing). On average, brook trout populations experience sublethal effects, including loss of health and reproduction (fitness). During episodes of high acidity, brook trout may die. Diversity and distribution of zooplankton communities decline.
Acute concern	<0	Near complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acid-tolerant forms. The numbers of individuals of plankton species that are present are greatly reduced.

ANC = acid neutralizing capacity; L = liter; µeq = microequivalent.

Based on data from southern Appalachian streams and from Shenandoah National Park.

Source: based on [U.S. EPA \(2009c\)](#).

### 8.3.6.4 Fish and Aluminum Thresholds

The detrimental effects of Al on fish are closely tied to Al solubility, complexation, and speciation, which are all strongly influenced by pH ([Appendix 8.3.6.2](#)), ANC ([Appendix 8.3.6.3](#)), and concentrations of organic acids ([Driscoll et al., 2001b](#)). Al has no established biological function and dissolved inorganic Al can be highly toxic to fish and other aquatic biota. The current U.S. EPA acute and chronic Aquatic Life Criteria for Al are 750 and 87 µg/L, respectively, and not more than once every 3 years on average ([U.S. EPA, 1988](#)). In the 2008 ISA, elevated concentrations of inorganic Al associated with acidification of surface waters were shown to affect fish populations and communities in parts of the Adirondack Mountains of northern New York ([Simonin et al., 1993](#); [Kretser and Gallagher, 1989](#); [Johnson et al., 1987](#); [Schofield and Driscoll, 1987](#); [Baker and Schofield, 1982](#)), in acid-sensitive streams of the Catskill Mountains of southeastern New York ([Charles and Christie, 1991](#)), and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina ([Bulger et al., 2000](#); [Bulger et al., 1999](#); [SAMAB, 1996](#)). In one study reviewed in the 2008 ISA, 20% mortality of caged young-of-year brook

trout in poorly buffered headwater streams in the Adirondacks was documented during a 30-day period with a median inorganic Al concentration of 54 µg/L [2 µM/L; [Baldigo et al. \(2007\)](#)]. The authors estimated that 90% mortality would occur over 30 days, in response to a median inorganic Al concentration of 108 µg/L (4.0 µM/L). Threshold values for Al from [Baker et al. \(1990a\)](#) for various species and effects were summarized in the 2008 ISA. These values, along with additional Al thresholds for various fish species and endpoints, are listed in [Table 8-4](#). Field studies of the effects of Al on aquatic biota are typically confounded by simultaneous pH effects. Both inorganic Al and H<sup>+</sup> can be toxic, and the solubility of inorganic Al is strongly pH-dependent.

Since the 2008 ISA, additional Al thresholds for salmonids have been published ([Table 8-4](#)). In a synthesis of 347 short term (<14 days) exposures (in tanks fed river water or in tanks where water quality was manipulated) of salmon parr and smolt performed between 1990 and 2003 in Norway, [Kroglund et al. \(2008\)](#) identified dose-response relationships for pH, inorganic Al concentration, ANC, gill Al, and time of first fish mortality over a 10-day exposure period ([Figure 8-5](#)). Results of smolt releases were also evaluated after pre-exposure to moderately acidic waters. All smolt survived at pH >5.8 and inorganic Al <200 µg/L (7.4 µM). For parr, mortality increased at pH <5.6 or inorganic Al >45 µg/L (1.7 µM). In the same study, seawater challenge tests were analyzed where smolts were pre-exposed to sublethal concentrations of Al in freshwater and then moved to saltwater. As freshwater pH decreased and inorganic Al concentration increased, hypo-osmoregulatory capacity decreased, and increased mortalities were observed. Smolt exposed to >5 to <10 µg/L (0.18–0.37 µM) inorganic Al in freshwater and then released into seawater had a 25 to 50% reduction in survival based on data from a sea survival program in the River Imså in Norway ([Kroglund et al., 2008](#); [Kroglund et al., 2007](#)).

Additional studies have characterized the role of DOC in influencing Al bioavailability and subsequent effects on fish. In a field study of Atlantic salmon smolts in streams in eastern Maine, observations suggested that streams with moderate to high DOC concentrations buffered the effects associated with low pH and high total Al concentrations ([Liebich et al., 2011](#)). Smolts exposed to high DOC waters had lower gill Al concentrations compared to smolts in low DOC waters having similar pH and Al concentrations.

**Table 8-4 Threshold values of aluminum for various fish species and associated effects.**

Type of Study	Taxa	pH	Al ( $\mu\text{g/L}$ )	Observed Effect	Form of Al	Country	Reference
Field study	Brook trout ( <i>Salvelinus fontinalis</i> )	4.9	286	No survival of trout stocked into lakes with higher total Al (even after accounting for pH effects)	Total	U.S.	<a href="#">Schofield and Troinar (1980)</a>
Laboratory exposure	White sucker ( <i>Catostomus commersoni</i> )	5.2	200	>50% larval mortality	Total	U.S.	<a href="#">Baker and Schofield (1982)</a>
Laboratory exposure	Brown trout ( <i>Salmo trutta</i> )	4.5–5.4	250	>50% fry mortality	Total	-	<a href="#">Brown (1983)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	4.9–5.0	130	Significant increase in mortality of presmolts	Labile	Norway	<a href="#">Rosseland and Skogheim (1984)</a>
Laboratory exposure	Eel ( <i>Anguilla anguilla</i> )	5.1	230	Significant increase in elver mortality	Total	Norway	<a href="#">Fjellheim et al. (1985)</a>
Field mesocosm experiment	Atlantic salmon ( <i>Salmo salar</i> )	5.1	75	>50% mortality of smolts	Labile	Norway	<a href="#">Skogheim and Rosseland (1986)</a>
Field survey	Brown trout ( <i>Salmo trutta</i> )	-	40	Fish absent or rare in streams in Wales and England	Labile monomeric	Wales and England	<a href="#">Turnpenny et al. (1987)</a>
Laboratory exposure	Blueback herring ( <i>Alosa aestivalis</i> )	5.5–5.6	100	>50% larval mortality	Total	U.S.	<a href="#">Klauda and Palmer (1987)</a>
Whole-stream experiment	Atlantic salmon ( <i>Salmo salar</i> ) and brown trout ( <i>Salmo trutta</i> )	5.0	350	>50% mortality of young-of-the-yr	-	Wales	<a href="#">Ormerod et al. (1987)</a>
Laboratory exposure	Brown trout ( <i>Salmo trutta</i> )	5.2	30	Significant reduction in fish growth	-	England	<a href="#">Sadler and Lynam (1988)</a>

**Table 8-4 (Continued): Threshold values of aluminum for various fish species and associated effects.**

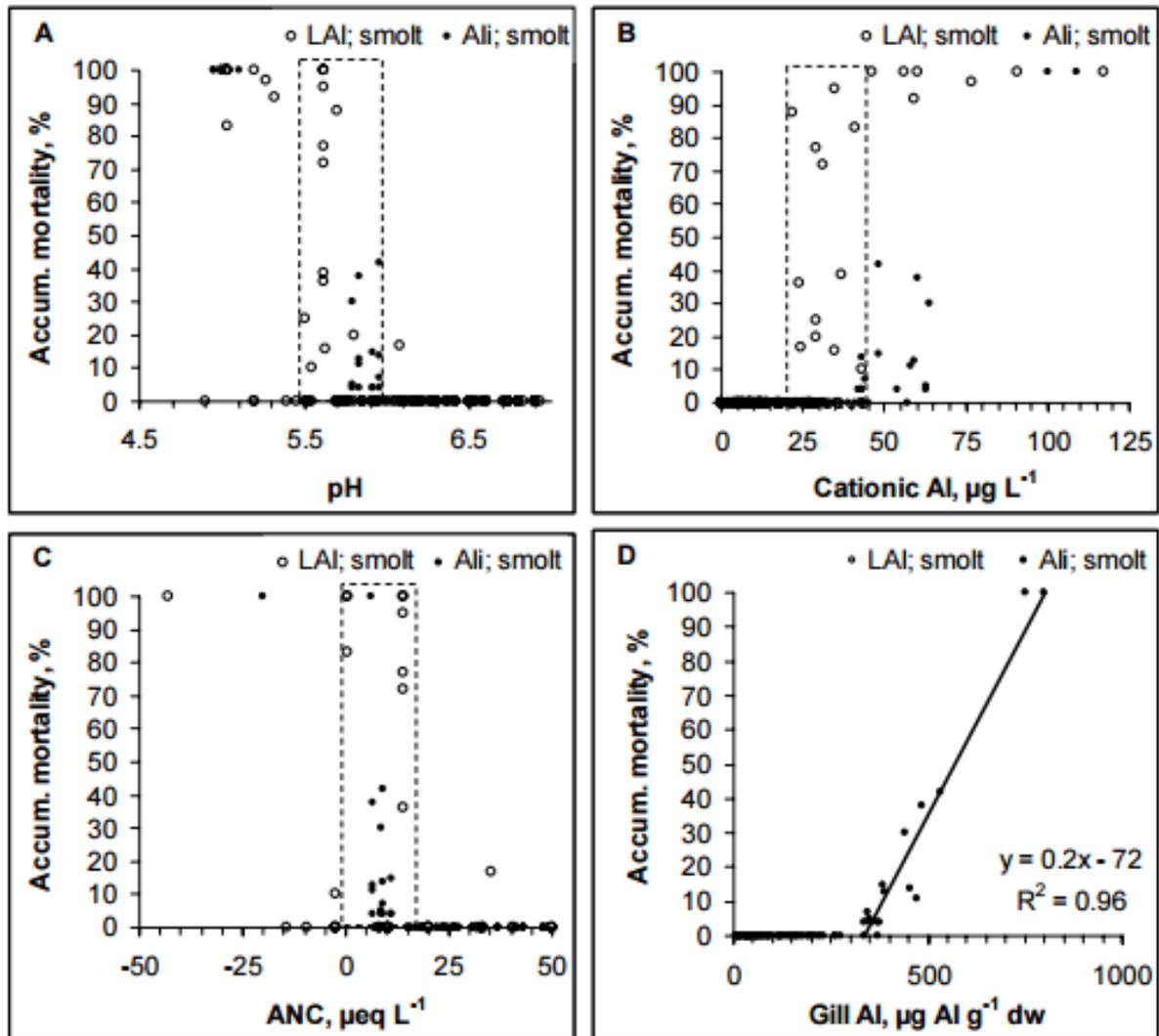
Type of Study	Taxa	pH	Al ( $\mu\text{g/L}$ )	Observed Effect	Form of Al	Country	Reference
Laboratory exposure	Walleye ( <i>Stizostedion vitreum</i> )	4.9	50	>50% mortality of embryos to 4-days post-hatch	Total	Canada	<a href="#">Holtze and Hutchinson (1989)</a>
Laboratory exposure	Brook trout ( <i>Salvelinus fontinalis</i> )	5.2	29	Survival of 1-yr-olds decreased	Inorganic monomeric	U.S.	<a href="#">Ingersoll et al. (1990)</a>
Laboratory exposure	Brook trout ( <i>Salvelinus fontinalis</i> )	4.8	34	Weight of 1-yr-olds decreased after exposure to either pH or Al threshold	Inorganic monomeric	U.S.	<a href="#">Ingersoll et al. (1990)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	5.5	100	Decreased survival of alevins and swim-up larvae	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	5.5	100	Decreased swimming activity in swim-up larvae and alevins	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	5.0	300	Decreased survival of embryos	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	5.0	300	Increased loss of Na ions in embryos	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	6.0	50	Increased loss of Na, K, and Ca ions in alevins (compared to treatment with same pH and without Al)	Total	U.S.	<a href="#">Woodward et al. (1991)</a>

**Table 8-4 (Continued): Threshold values of aluminum for various fish species and associated effects.**

Type of Study	Taxa	pH	Al ( $\mu\text{g/L}$ )	Observed Effect	Form of Al	Country	Reference
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	6.0	50	Decreased feeding strikes in swim-up larvae (compared to treatment with same pH and without Al)	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Laboratory exposure	Greenback cutthroat trout ( <i>Oncorhynchus clarki stomias</i> )	6.0	50	Decreased swimming duration in alevins (compared to treatment with same pH and without Al)	Total	U.S.	<a href="#">Woodward et al. (1991)</a>
Field study	Blacknose dace ( <i>Rhinichthys atratulus</i> )	-	101	Decreased survival of adults when exposed to threshold for more than 6 days	Inorganic monomeric	U.S.	<a href="#">Simonin et al. (1993)</a>
Field study	Brook trout ( <i>Salvelinus fontinalis</i> )	-	225	Juvenile mortality significantly increased (>20%) when exposed to Al threshold for 2 or more days	Inorganic monomeric	U.S.	<a href="#">Baldigo and Murdoch (1997)</a>
Field study	Brook trout ( <i>Salvelinus fontinalis</i> )	-	54/108	Correlations between low (54 $\mu\text{g/L}$ ) and high (108 $\mu\text{g/L}$ ) thresholds and low (20%) and high (50–90%) mortality	Inorganic monomeric	U.S.	<a href="#">Baldigo and Murdoch (1997)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	5.0–5.4	43–68	Ion regulation, stress physiology, gill Al accumulation	Inorganic	U.S.	<a href="#">Monette and McCormick (2008)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	5.4–6.3	28–64	Ion regulation, seawater tolerance, plasma hormone levels, stress physiology	Inorganic	U.S.	<a href="#">Monette et al. (2008)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	5.8	40	Smolt survival	Cationic (inorganic aluminum)	Norway	<a href="#">Kroglund et al. (2008)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	5.6	45	Parr survival	Cationic (inorganic aluminum)	Norway	<a href="#">Kroglund et al. (2008)</a>

**Table 8-4 (Continued): Threshold values of aluminum for various fish species and associated effects.**

Type of Study	Taxa	pH	Al ( $\mu\text{g/L}$ )	Observed Effect	Form of Al	Country	Reference
Field bioassay	Atlantic salmon ( <i>Salmo salar</i> )	5.4–5.6	50–80	Survival, smolt development, ion homeostasis, stress	Inorganic	U.S.	<a href="#">McCormick et al. (2009)</a>
In situ exposure	Brown trout ( <i>Salmon trutta</i> )	5.0	20	Recommended threshold to sustain healthy populations based on gill Al, blood physiology	Inorganic	Sweden	<a href="#">Andrén and Rydin (2012)</a>
Laboratory exposure	Atlantic salmon ( <i>Salmo salar</i> )	5.7	40	Gill Al accumulation	Inorganic	U.S.	<a href="#">Nilsen et al. (2013)</a>



Al = aluminum; Ali = inorganic monomeric aluminum; ANC = acid neutralizing capacity; dw = dry weight; g = gram; L = liter; LAI = labile aluminum;  $\mu\text{eq}$  = microequivalent;  $\mu\text{g}$  = microgram.

Notes: linear relationships are entered into the graph whenever significant. The dashed lines suggest dose levels separating "no effect," "low to high" effect, and/or always "high" effect.

Source: [Kroglund et al. \(2008\)](#).

**Figure 8-5 Relationship between (a) pH, (b) cationic aluminum, (c) acid neutralizing capacity, and (d) gill aluminum as compared with accumulated mortality of Atlantic salmon smolt.**

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### 8.3.6.5 Behavioral Responses to Acidification

New studies in salmonids have shown effects of acidification on behavioral endpoints. Using hatchery-reared juvenile Atlantic salmon, [Elvidge and Brown \(2014\)](#) conducted a tethering experiment in reaches of neutral ( $\text{pH} \geq 6.6$ ) and low pH ( $< 6.6$ ) salmon nursery streams, plus one additional stream that varied between pH classes. The researchers observed that the tethered fish in the low-pH streams were more likely to be preyed upon than fish in the neutral streams although there were fewer predatory fish species, similar availability of physical refugia, and similar threat from terrestrial predators. [Leduc et al. \(2009\)](#) quantified alarm behavior of juvenile Atlantic salmon exposed to chemical alarm cues in a stream before and after rainfall. Before rainfall, fish exhibited an alarm response in the study streams. After rainfall, fish from the higher pH (near 7.5) stream continued to respond, but those from the lower pH (near 6.2) stream did not. The researchers suggested that episodic acidification in small nursery streams may disrupt the information mediated by chemical alarm cues and contribute to higher fish mortality. This may be the first published study documenting the disruption of a chemical messenger by acidification of stream water.

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### 8.3.7 Fish-Eating Birds

The 2008 ISA reviewed the limited studies that documented effects of acidification on birds. Acidification has been shown to disrupt food web dynamics causing alteration to bird diet, breeding distribution, and reproduction. [Lacoul et al. \(2011\)](#) reviewed studies of acidification on aquatic birds and noted that in the Atlantic Canada region, breeding was limited to lakes and streams that had pH higher than 5.5. A substantial amount of research has recently been conducted on air pollution effects on birds, but the focus of that work has been on mercury exposure, and results are not discussed here. Deposition effects of mercury on biota in the Adirondacks are described in [Appendix 12](#).

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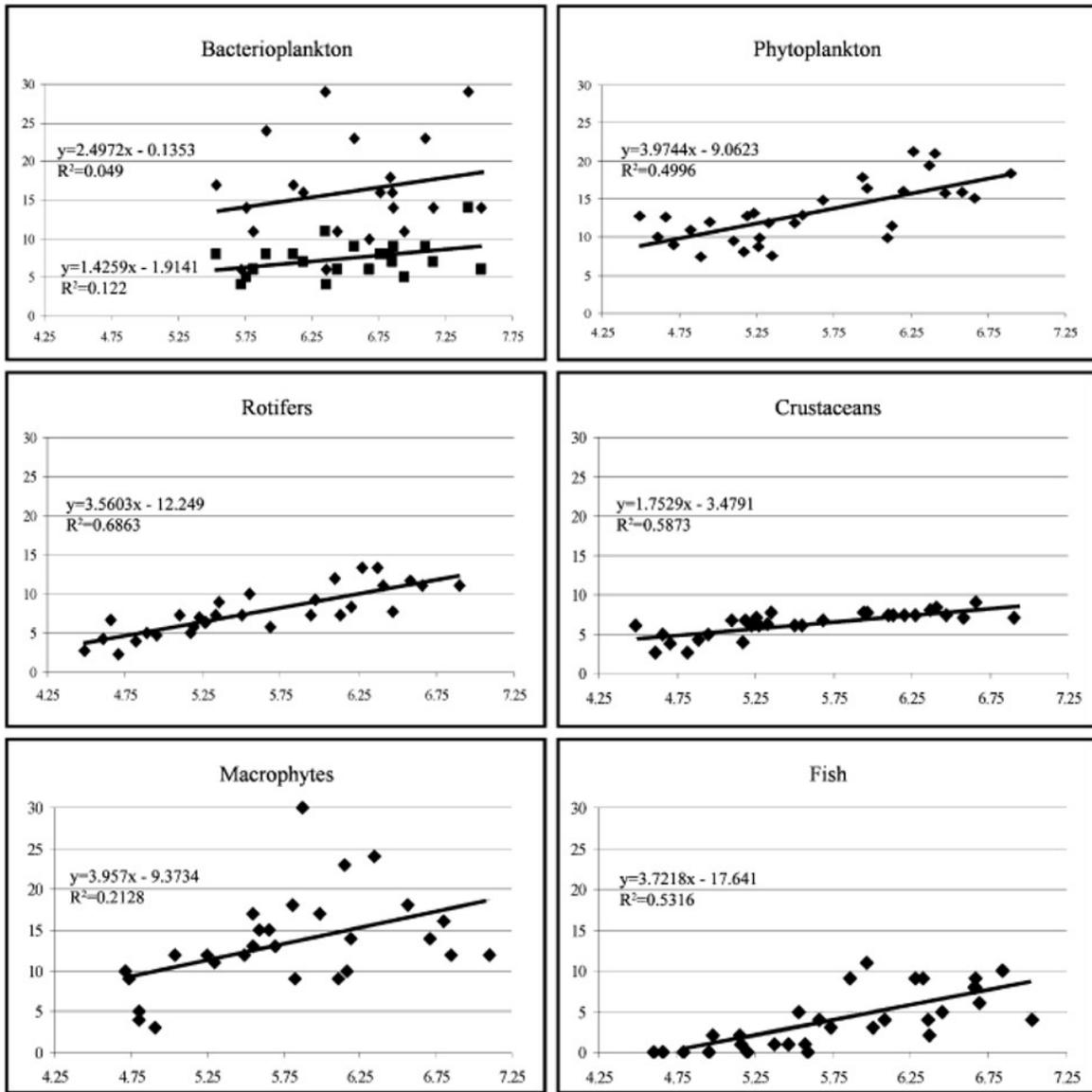
### 8.3.8 Aquatic Assemblages

In the 2008 ISA, decreases in species richness in response to surface water acidification were reported in lakes and streams for all major trophic levels of aquatic organisms ([Baker et al., 1990a](#)), even after adjusting for lake size ([Matuszek and Beggs, 1988](#); [Schofield and Driscoll, 1987](#); [Frenette et al., 1986](#); [Rago and Wiener, 1986](#); [Harvey and Lee, 1982](#)). Acidification was also found to cause decreases in food web complexity (indicated by the number of trophic links or species) in Adirondack lakes ([Havens and Carlson, 1998](#)).

Since the 2008 ISA, several studies have considered effects of species assemblages associated with acid-impacted water bodies. [Nierzwicki-Bauer et al. \(2010\)](#) presented baseline midsummer chemistry and community composition of phytoplankton, bacteria, rotifers, crustaceans, macrophytes, and fish in 30 lakes of the southwestern Adirondacks ([Figure 8-6](#)). Species richness in the lakes was correlated with acid-base chemistry at all trophic levels except bacteria. The decrease in number of taxa per unit pH was similar among groups and ranged from 1.75 (crustaceans) to 3.96 (macrophytes).

Following the 5-year experimental acidification of Little Rock Lake in Wisconsin from pH 6.1 to 4.7, [Hogsden et al. \(2009\)](#) observed greater reductions in species richness at higher trophic levels (fish and zooplankton) compared to algae. The authors suggested that the observed asymmetrical food web response could have implications for biological recovery of lakes. This study was limited, however, by the fact that the experimental acidification only involved the lake and not the watershed. Cladoceran assemblages reconstructed by [Moss crop et al. \(2015\)](#) from lake sediment cores from 30 lakes in Ontario, Canada showed that in shallow lakes, there was no significant difference in the remains of cladoceran taxa deposited in sediments between present-day and preindustrial sediments. In deeper lakes, relative abundance of cladocerans had shifted over time. The researchers hypothesized that cladoceran assemblages in shallower lakes might be influenced more by habitat than by water chemistry and that Ca availability may vary spatially in shallow lake areas or that cladoceran species living in littoral zones may be less sensitive to low Ca.

In an analysis of pH effects on grazing and herbivory in 20 stream food webs across the British Isles, considerable species differences were observed across a pH gradient from 5.0 to 8.4 ([Layer et al., 2013](#)). Three dose-response relationships were characterized for diatom assemblages ([Figure 8-7](#)). Macroinvertebrate taxon richness and benthic density were plotted against stream pH for all primary consumer taxa as well as by trophic group (shredders, herbivore-detritivores, collectors, grazers; [Figure 8-8](#)). At low pH, generalist herbivore-detritivores dominated the primary consumer assemblage. At higher pH, they were partially replaced by specialist grazers. The researchers concluded that the ability of acid-tolerant herbivore-detritivores to exploit food resources and the low nutritional value of basal resources in acidified streams might decrease recolonization by specialist grazers in streams where chemical conditions are becoming less acidic.

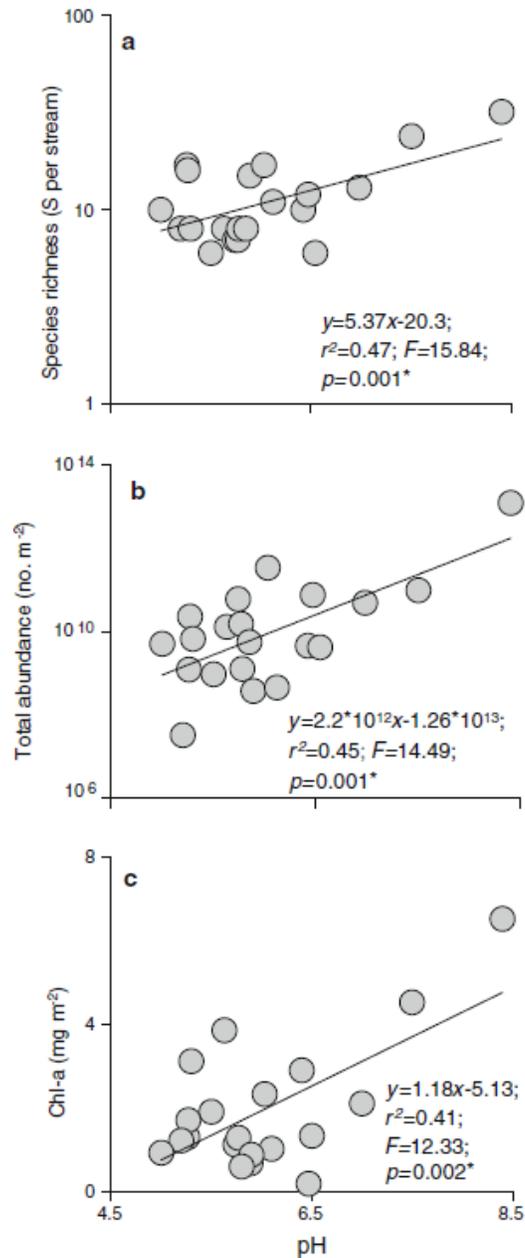


## Lake pH

Notes: The y-axis denotes number of groups (bacteria), taxa (phytoplankton) or species (rotifers, crustaceans, macrophytes, fish). The x-axis denotes the pH range that occurred in the 30 study lakes. Note: in the bacterioplankton graph, two regressions were run on the basis of genera (diamonds) and classes (squares).

Source: [Nierzwicki-Bauer et al. \(2010\)](#).

**Figure 8-6** Species richness of biotic groups in 30 Adirondack study lakes relative to midsummer epilimnetic pH during sample years.

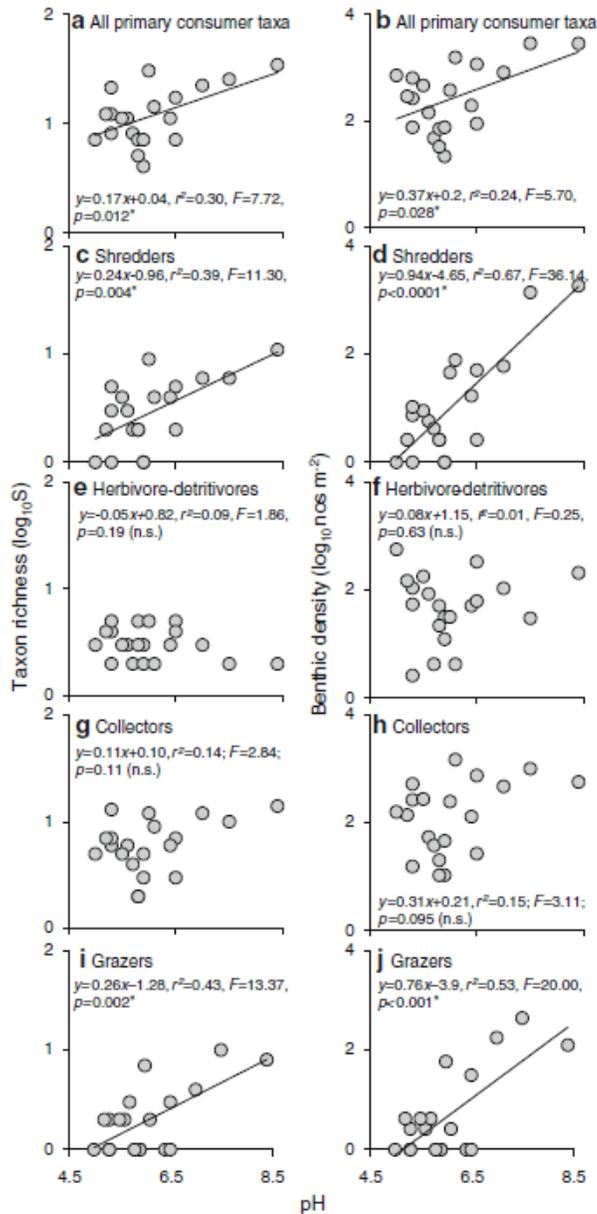


M = meter; mg = milligram; no = number; S = sulfur.

Notes: statistical significance was determined using linear regression analysis. Asterisk denotes a statistically significant result at  $p < 0.05$ .

Source: [Layer et al. \(2013\)](#).

**Figure 8-7** Structure of diatom assemblage in 20 streams across a pH gradient of 4.5–8.5. (a) Species richness ( $\log_{10}$ -transformed numbers of diatom species per stream), (b) total abundance of diatoms ( $\log_{10}$ -transformed numbers of individuals per  $m^2$ ), (c) chlorophyll a concentration (mg chlorophyll a per  $m^2$ ), as a measure of algal biomass.



n.s. = not significant; S = sulfur.

Notes: statistical significance was determined using linear regression analysis. Asterisk denotes a statistically significant result at  $p < 0.05$ .

Source: [Layer et al. \(2013\)](#).

**Figure 8-8** Macroinvertebrate community composition in 20 streams across a pH gradient. Taxon richness (total number of primary consumer taxa; left panel) and benthic density [number of individuals  $\log_{10}(x + 1)$ -transformed; right panel] plotted against stream pH, all primary consumers (a, b), shredders (excluding Leuctridae and Nemouridae) (c, d), herbivore-detritivores (Leuctridae and Nemouridae) (e, f), collectors (g, h) and grazers (i, j).

[Lacoul et al. \(2011\)](#) reviewed available information on the effects of water acidification on aquatic organisms in Atlantic Canada. The pH threshold 5.0 was critical to sensitive macrophytes.

New analytical methods have recently been developed for detecting and quantifying ecological thresholds, such as tipping points for ANC or other acid-base chemical parameters at which adverse impacts on aquatic assemblages occur ([Baker and King, 2010](#)). Previous methods for designating ecological community thresholds have been based on univariate indicators or multivariate dimension-reduction of community structure. They tend to be insensitive to the responses of taxa that have low occurrence frequencies or highly variable abundance. The Threshold Indicator Taxa Analysis (TITAN) statistical tool detects changes in taxa distributions and abundances along an environmental gradient, such as ANC for example. It uses indicator species scores to integrate occurrence, abundance, and directionality of taxa responses by optimizing the value of a continuous variable that partitions sample units while maximizing taxon-specific scores. It emphasizes the relative magnitude of change and increases the contributions of taxa that have low occurrence frequencies and high sensitivity to the gradient. As an example, [Baker and King \(2010\)](#) assessed macroinvertebrate community response to a nutrient (e.g., P) gradient using TITAN. Results supported previous threshold estimates but with lower confidence limits. Several taxa were shown to decline at lower levels of P concentration.

In 28 subwatersheds of the Neversink River Basin in the Catskill Mountains, NY, [Harpold et al. \(2013\)](#) used a simple hydrogeomorphic model as a tool to predict impacts of acidification on biological communities. The model, which considered watershed slope and drainage density to estimate ANC, successfully predicted several measures of macroinvertebrate and fish community richness.

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## 8.4 Documentation of Biological Recovery

The biological impact of acidifying deposition is mediated through changes in water quality that in turn impact biota. Deposition of N and S can lead to a cascade of biogeochemical changes ([Appendix 4](#) and [Appendix 7](#)) that may induce biological effects. It is often difficult to separate nutrient enrichment ([Appendix 9](#)) and acidification stressors, as they act simultaneously in some water bodies. [Posch et al. \(2011\)](#) argued that linking nutrient and acidity chemical criteria to vegetation occurrence on a regional scale is an approach that can be used to identify optimal N and S deposition limits to sustain a prescribed biodiversity goal (see [Appendix 8.5.4](#)).

Trajectories of biological recovery as used in this ISA are defined in [Section IS.11](#). Complete biological recovery would entail a return to similar species make-up, richness, and abundance as existed in the ecosystem in question prior to the advent of human-caused acidic deposition (around the year 1860 in North American ecosystems). Biological recovery from past acidification is a process affected by chemical, climatic, biological, chance, and hydrologic influences over time. It may, under certain conditions, follow chemical recovery of such water quality constituents as pH, ANC, and the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , inorganic Al, and DOC. Both chemical and biological recovery can, and often do, lag behind changes in the levels of S and/or N emissions and deposition because of chemical, hydrological, and biological processes and constraints. In addition, the ANC level that reflects recovery of pH or inorganic Al may differ between the acidification and recovery phases ([Hesthagen et al., 2008](#)). In a practical sense and depending on the level of impact, complete biological recovery may not be attainable at many acidified locations within a reasonable management timeframe because soil reserves of base cations at many locations have been depleted in response to many decades of acidic deposition and because other stressors, in addition to acidic deposition, have also altered ecosystem structure and/or function or will do so in the coming decades. Such stressors include changes in climate, land use, and other perturbations. More commonly, only partial biological recovery may be possible. Ecosystems deemed to be on a recovery trajectory are those found to be moving towards a mix of species presence and abundance that approximates the undisturbed state.

Biological recovery can occur only if chemical recovery ([Appendix 7](#)) is sufficient to allow growth, survival, and reproduction of acid-sensitive plants and animals ([Driscoll et al., 2001b](#)). Also, chemical recovery of ANC or pH may not necessarily follow the reverse of the acidification path due to changes in relationships among ANC, pH, DOC, and Al; depletion of soil base cation pools; hydrology; climate; and/or partially reversible (or irreversible) S adsorption on soils. In the 2008 ISA, studies of biological recovery generally indicated that the time required for biological recovery is uncertain and that biological responses typically lag behind chemical recovery and may take decades from the onset of chemical recovery ([U.S. EPA, 2008a](#)).

Literature reviewed in the 2008 ISA suggested that the time required for recovery of biota varies. In general, macroinvertebrate populations in streams recover more rapidly (within approximately 3 years in response to improved chemical conditions), relative to lake populations of zooplankton, followed by increases in lake fish populations which may occur 5 to 10 years after zooplankton recovery ([Driscoll et al., 2001b](#); [Gunn and Mills, 1998](#)). Biological recovery of previously acidified surface waters can lag behind chemical recovery because of factors such as limits on dispersal and recolonization ([Gray and Arnott, 2011](#)), barriers imposed by water drainage patterns ([Jackson and Harvey, 1995](#)),

the influence of predation ([Layer et al., 2011](#); [Mcnicol et al., 1995](#)), and other environmental stressors ([Yan et al., 1996b](#); [Yan et al., 1996a](#); [Gunn et al., 1995](#); [Havas et al., 1995](#); [Jackson and Harvey, 1995](#); [Mcnicol et al., 1995](#)). Biological recovery is likely to occur in stages due to differences among species in acid sensitivity and the rate of recovery of affected organisms ([Driscoll et al., 2007b](#)). In a study reviewed in the 2008 ISA, recovery of the zooplankton community in an experimentally acidified lake did not retrace the same trajectory as the initial deterioration due to acidification, indicating substantial hysteresis in recovery ([Frost et al., 2006](#)). Biological recovery research from the Sudbury region of Ontario, Canada was highlighted in the 2008 ISA. This region, formerly impacted by smelter operations, has been important for clearly documenting the chemical and biological effects of S and metal deposition as well as subsequent recovery from acidification.

New studies at multiple trophic levels continue to support findings presented in the 2008 ISA that biological recovery has lagged behind chemical recovery in many systems and that the lag response may vary among taxa and water bodies. Several long-term studies of water acidification indicate that biological recovery has been limited despite significant deposition reductions and improvements in water chemistry ([Baldigo et al., 2016](#); [Battarbee et al., 2014](#); [Murphy et al., 2014](#); [Angeler and Johnson, 2012](#)). Other studies, such as Honnedaga Lake and Brooktrout Lake in the Adirondacks, show more evidence for return of biota to levels approaching preacidification levels ([Sutherland et al., 2015](#); [Josephson et al., 2014](#)). In Brooktrout Lake, biological recovery of the food web structure has begun, in part, due to reintroduction and reestablishment of brook trout in the lake. Ongoing biological recovery cannot necessarily be expected to conclude with the return of the biological community to preacidification conditions, however. This is due to factors such as differences in the rate of recovery of aquatic organisms, permanent loss of some acid-sensitive species, and irreversible chemical and physical alterations to aquatic environments during acidification ([NAPAP, 2011](#)). Effects of other stressors can modify the recovery trajectories of aquatic ecosystems that have experienced acidification. Of particular importance in this regard are the introduction of species of fish or other organisms, either purposely as in the case of fish stocking by state agencies or local organizations or inadvertently. In the coming years, warming of surface waters in response to climate change may become increasingly important. For example, ([McDonnell et al., 2015](#)) showed that stream acidity (a top-down stress) together with stream warming (a bottom-up stress) cause a reduction in the extent of stream habitat in the southern Appalachian Mountains that is suitable for cold-water aquatic biota.

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## 8.4.1 Phytoplankton Recovery

In the 2008 ISA, phytoplankton recovery from experimental acidification showed an increase in phytoplankton species richness and diversity with increased lake pH. In Lake 223 in the Experimental Lakes area of Ontario, there was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 ([Findlay and Kasian, 1996](#)). In Lake 302S, profound biological changes began at pH 5.5, with phytoplankton assemblages at pH below 5.5 resembling those in acidified lakes. [Findlay \(2003\)](#) reported that lakes that were previously low in pH (5.0 to 5.5) and are now above pH 6 have shifted towards phytoplankton assemblages more typical of circumneutral environments. Recent studies on responses of phytoplankton to decreased acidity have been limited. [Josephson et al. \(2014\)](#) reported that observed increases in chlorophyll *a* and decreases in water clarity in Honnedaga Lake, NY in recent years reflect an increase in phytoplankton abundance in association with chemical recovery from acidification.

The 2008 ISA reported results of several paleolimnological studies that used fossil remains of diatoms or chrysophytes in lake sediments to infer lake chemistry at discrete time periods in the past. These studies provided valuable information regarding the extent of historical acidification, especially in the Adirondack Mountains, by using well-established relationships between water chemistry and diatom community structure. The studies also provided the foundation for testing the performance of process-based dynamic models, such as Model of Acidification of Groundwater in Catchments (MAGIC), by comparing MAGIC hindcast simulations of water chemistry with diatom inferences of preindustrial pH and ANC ([Sullivan et al., 1990](#)).

Since the 2008 ISA, a number of additional paleolimnological studies have been conducted that have documented historical acidification and subsequent recovery ([Table 8-5](#)); however, most of the studies have been conducted in other countries. In one study from the U.S., diatom shifts were linked to historical changes in pH at Brooktrout Lake in the Adirondacks. *Fragilariforma acidobiontica*, a diatom that is often abundant at pH <5.0, was present in lake sediments deposited since the 1950s and shifts in *Mallomonas* and *Synura* were also observed ([Sutherland et al., 2015](#)). In another study, [Arseneau et al. \(2016\)](#) concluded that Adirondack lakes that were not previously acidified by acidic deposition will likely not recover to predisturbance chrysophyte community structure because of the influence of other stressors, including changes in climate.

**Table 8-5 Paleolimnological responses to changing lake chemistry published since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Lake(s) Sampled/Region	Observation	Reference
Brooktrout Lake, Adirondacks	<i>Fragilariforma acidobiontica</i> , a diatom that is often abundant at pH <5.0, was present in lake sediments deposited since the 1950s.	<a href="#">Sutherland et al. (2015)</a>
Glasgow Lake, Nova Scotia	Diatoms inferred to have responded to acidification in response to a peak S loading of about 14 kg S/ha/yr during the mid-1970s.	<a href="#">Gerber et al. (2008)</a>
Four sampled lakes in Nova Scotia	Decline in <i>Daphnia</i> beginning in the early 20th century.	<a href="#">Korosi and Smol (2012)</a>
36 small headwater lakes in the Boreal Shield of south central Ontario	Large declines documented in relative abundances of Ca rich <i>Daphnia</i> spp. and increases in the Ca poor species <i>Holopedium glacialis</i> .	<a href="#">Jeziorski et al. (2012a)</a>
Lakes downwind of iron sintering plant northeast of Wawa, Ontario	Recent cladoceran sedimentary assemblages remain in an altered state, although lakes have returned to circumneutral pH.	<a href="#">Jeziorski et al. (2013)</a>
Low-Ca lakes (mean 2 mg/L) from the Experimental Lakes area, Ontario	Present-day cladoceran assemblages including <i>Bosmina</i> spp. and <i>H. glacialis</i> differed from preindustrial assemblages.	<a href="#">Jeziorski et al. (2014)</a>
Middle Lake (limed in 1973) in the Experimental Lakes area, Ontario	Cladoceran assemblages have not returned to preacidification levels, and many rare species are not present.	<a href="#">Labaj et al. (2014)</a>
Two boreal lakes in the Killarney lakes region, Ontario recovering from acidification	Cladoceran assemblages varied little from preindustrial times to recovery. <i>Bosmina</i> spp. dominated in the lakes.	<a href="#">Labaj et al. (2015)</a>
54 lakes in the Muskota-Haliburton region of Ontario	Numbers of planktonic diatoms such as <i>Cyclotella stelligera</i> have increased with lake DOC and warming from 1992 to present.	<a href="#">Hadley et al. (2013)</a>
Four boreal lakes recovering from acidification and four minimally disturbed lakes in Sweden	Phytoplankton and littoral assemblages in acidified lakes become more similar to reference lakes over time. Differences were greatest for phytoplankton assemblages.	<a href="#">Johnson and Angeler (2010)</a>

Ca = calcium; DOC = dissolved organic carbon; L = liter; mg = milligrams; S = sulfur.

In a lake study from Sweden, [Johnson and Angeler \(2010\)](#) compared phytoplankton and littoral assemblages in four boreal lakes recovering from acidification and four minimally disturbed reference lakes over a two-decade period. They observed that assemblages in the previously acidified lakes became more similar to assemblages in reference lakes over

time. Differences were greater for phytoplankton assemblages than for invertebrate assemblages. Biological responses were correlated with inter-annual variability in climate, in addition to decreased water acidity. [Hadley et al. \(2013\)](#) conducted a resurvey of 54 lakes in the Muskota-Haliburton region of south-central Ontario. They documented recent changes in chemistry and biology for the lakes using sediment cores and diatom transfer functions. Observed pH increases were accompanied by decreases in acidophilic diatoms. However, diatoms were observed to be moving toward a novel assemblage rather than the preacidification assemblage. Lake DOC concentration has increased from 1992 in the lakes sampled [Hadley et al. \(2013\)](#), as have the numbers of planktonic diatoms such as *Cyclotella stelligera* commonly linked to climate warming. The concentration of Ca has decreased, and land use changes have further impacted the lakes. All of these factors may be influencing diatom assemblage recovery.

Sixteen lakes in Cape Breton Highlands National Park in Nova Scotia were assessed through sedimentary records for historical trends in water chemistry and changes in diatom assemblages. Only one lake (Glasgow Lake) was inferred to have acidified under peak S deposition (about 438 eq S/ha/yr) in the 1970s ([Gerber et al., 2008](#)). Six of the lakes, including Glasgow Lake, were modeled using the MAGIC model. The five other lakes that were modeled showed simulated patterns of acidification and subsequent chemical recovery but no evidence of acidification from the diatom analysis ([Gerber et al., 2008](#)). The authors suggested that the diatom approach was conservative and/or that the MAGIC model slightly overestimated changes in acid-base chemistry.

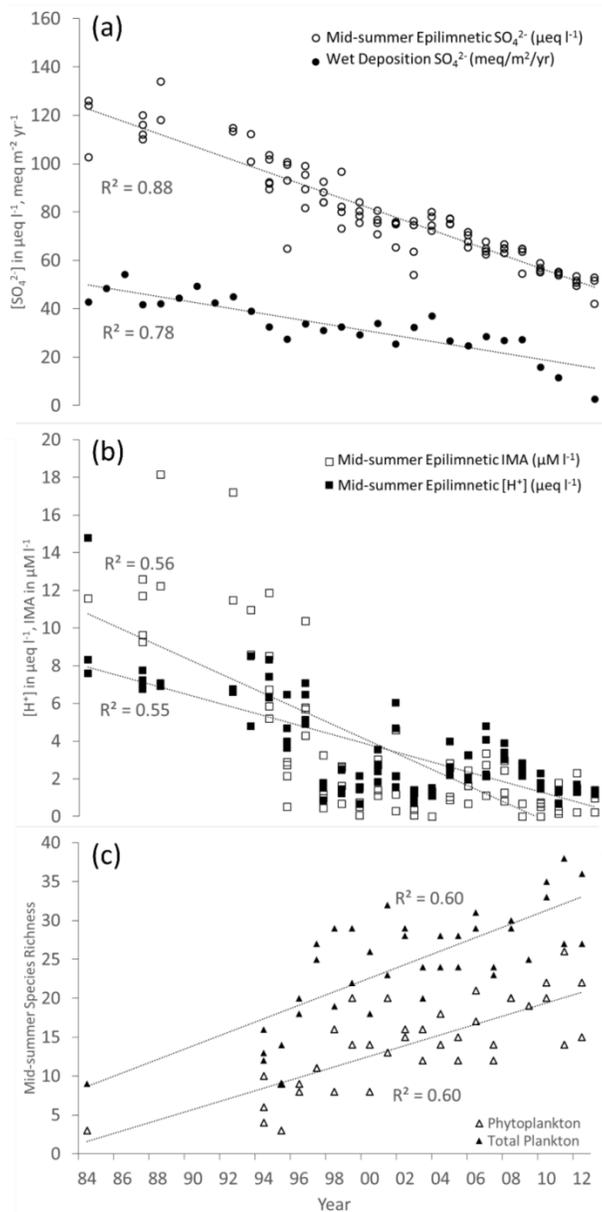
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#### 8.4.2 Zooplankton Recovery

Several studies reviewed in the 2008 ISA reported zooplankton recovery in response to experimental deacidification of lakes. Zooplankton recovery was observed in experimentally acidified Lake 223 in the Experimental Lakes region in Canada as pH increased back to 6.1 ([Malley and Chang, 1994](#)). A lag of 1 to 6 years was observed in recovery of zooplankton in the experimentally acidified Little Rock Lake in Wisconsin ([Frost et al., 2006](#)). [Locke and Sprules \(1994\)](#) reported that acidification below pH 5 in the 1970s overcame the resistance stability of the zooplankton community in Ontario Precambrian Shield lakes. The subset of study lakes that showed pH recovery from acidification 20 years later in 1990 also showed recovery in the stability of the zooplankton community. [Holt and Yan \(2003\)](#) also noted recovery in zooplankton community composition (based on similarity to neutral lakes) in the subset of Killarney Park (Ontario) lakes in which the pH increased to over 6 during the 1971 to 2000 study period. They did not, however, note differences in the increase in species richness between the recovering lakes and nonrecovering lakes.

Studies published since the 2008 ISA provide further evidence for plankton recovery. In Brooktrout Lake in the Adirondacks, phytoplankton and rotifer taxonomic richness showed substantial increases ([Figure 8-9](#)) in association with pronounced decreases in lake  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and inorganic Al concentrations ([Table 8-6](#)). In contrast, species richness of crustaceans changed little. [Sutherland et al. \(2015\)](#) suggested that the absence of crustacean recovery may have been due to the severity of the initial stress and continuing toxic pH conditions during some seasons, and/or to a large population of predatory chaoborus larvae present since the early 1980s when fish were absent from the lake. Paleolimnological evidence of zooplankton responses to changing lake chemistry published since the 2008 ISA is summarized in [Table 8-5](#).

Evidence from newly published studies in lakes near the former smelting complexes at Sudbury, Ontario, Canada indicate some evidence of biological recovery, although the relative recovery due to decreasing acidification versus recovery from decreased metal emissions and deposition is not clear. [Valois et al. \(2011\)](#) surveyed zooplankton community structural changes related to gradients of acidification, metal contamination, trophic status, and lake depth in 87 lakes around the smelter area. At  $\text{pH} > 6.0$ , community composition of copepods and cladocerans did not differ substantially from those in reference lakes. Recovery was evident in lakes that had  $\text{pH} > 5.5$ , with decreased community richness of copepod communities in lakes with lower pH. In the lakes around Sudbury, the survival of some zooplankton species, especially *Daphnia mendotae*, is limited by fish populations, notably yellow perch [*Perca flavescens*; ([Valois et al., 2010](#))]. The relative importance of changing acidity and metal contamination in driving the observed biological responses is not known. Nevertheless, results suggest that the re-establishment of the zooplankton community in lakes recovering from acid and metal stress may require improvements in both habitat quality and the integrity of the food web. [Babin-Fenske et al. \(2012\)](#) reported results of phylogenetic analyses of freshwater amphipod (*Hyalella* spp.) colonization in lakes near Sudbury. Two major groups of *Hyalella* were revealed, based on mitochondrial cytochrome c oxidase I sequences. One group was associated with recolonization of lakes that had historically been most acidified. The second group was associated with the more peripheral, less impacted, lakes.



H = hydrogen; IMA = inorganic monomeric aluminum;  $\mu\text{eq}$  = microequivalent;  $\mu\text{M}$  = micromolar; m = meter;  $\text{SO}_4^{2-}$  = sulfate; yr = year.

Source: [Sutherland et al. \(2015\)](#).

**Figure 8-9** (A) Midsummer sulfate concentration in the epilimnion of Brooktrout Lake ( $\circ$ ) and in annual wet deposition ( $\bullet$ ) at local National Atmospheric Deposition Program/National Trends Network Station NY52 from 1984–2012. (B) Midsummer epilimnetic concentrations of inorganic monomeric aluminum ( $\square$ ) and [hydrogen ion] ( $\blacksquare$ ) in Brooktrout Lake from 1984–2012. (C) Midsummer phytoplankton ( $\triangle$ ) and total plankton (phytoplankton, rotifers, crustaceans) ( $\blacktriangle$ ) species richness in Brooktrout Lake from 1984–2012.

**Table 8-6 Midsummer values and productivity analytes in the epilimnion of Brooktrout Lake in the Adirondack Park from the 1980s through 2010–2012.<sup>a</sup>**

Analyte	(a) 1980s Mean ( $\pm$ SD)	(b) 2010–2012 Mean ( $\pm$ SD)
[H <sup>+</sup> ] ( $\mu$ eq/L)	8.15 (2.54)	1.30 (0.26)
ANC ( $\mu$ eq/L)	-1.90 (10.31)	11.73 (3.77)
SO <sub>4</sub> <sup>2-</sup> ( $\mu$ eq/L)	118.18 (9.16)	52.09 (3.88)
NO <sub>3</sub> <sup>-</sup> ( $\mu$ eq/L)	17.06 (7.36)	7.52 (2.43)
Total P ( $\mu$ g/L)	3.29 (1.80)	4.00 (2.09)
DOC (mg/L)	0.71 (0.49)	2.40 (0.46)
Ca ( $\mu$ eq/L)	68.22 (7.56)	41.65 (12.46)
Secchi (turbidity) (m)	8.89 (1.97)	5.92 (0.66)
Chl a ( $\mu$ g/L)	0.85 (0.68)	1.86 (1.04)
Reactive silica (mg/L)	3.31 (0.21)	2.39 (0.28)
Total Al ( $\mu$ M/L)	19.11 (7.13)	7.52 (3.10)
Labile monomeric Al ( $\mu$ M/L) [IMA]	12.17 (2.93)	1.02 (0.77)

Al = aluminum; ANC = acid neutralizing capacity; Ca = calcium; Chl a = chlorophyll a; DOC = dissolved organic carbon; H<sup>+</sup> = hydrogen ion; IMA = inorganic monomeric aluminum; L = liter;  $\mu$ eq = microequivalent;  $\mu$ g = microgram;  $\mu$ M = micromolar; m = meter; mg = milligrams; NO<sub>3</sub><sup>-</sup> = nitrate; P = phosphorus; SD = standard deviant; SO<sub>4</sub><sup>2-</sup> = sulfate.

<sup>a</sup>Values presented in (a) and (b) are means ( $\pm$  standard deviation). The 1980s samples were collected in 1984 (three dates), 1987 (four dates), and 1988 (two dates). The values presented in (b) represent 10 sampling dates during 2010–2012.

Source: [Sutherland et al. \(2015\)](#).

In a synthesis of 21 regional surveys of zooplankton recovery in lakes affected by acidic deposition in North America and Europe, [Gray and Arnott \(2009\)](#) identified the most commonly used metrics and factors indicating and limiting recovery of acid-impacted lakes. In the studies evaluated, species richness, the presence of indicator species, and relative species abundances were commonly assessed. At pH >6.0, recovery of zooplankton was significant, although often incomplete in both North American and European lakes. The authors identified slow chemical recovery, dispersal limitation, and community resistance as primary factors limiting biological recovery although the relative importance varied across the lakes and regions evaluated.

[Gray et al. \(2012\)](#) assessed the chemical and biological recovery of 45 previously acidified lakes in Killarney Park, Ontario. Zooplankton data were compared for the periods 1972–1973 and 2005. Significant increases in pH over time were documented for the majority of the study lakes. Species richness and diversity of many acid-damaged lakes only increased to a minor extent. They observed differing importance of biotic and abiotic conditions and dispersal processes in determining the relative contribution of copepod and cladoceran zooplankton in the post-recovery community structure, suggesting different expectations for recovery among different taxonomic groups. In a study of zooplankton communities in four of the lakes, dispersal limitation was identified as a factor impeding biological recovery ([Gray and Arnott, 2011](#)). The researchers observed a relatively quick return of acid-sensitive zooplankton species that disperse from streams and the egg bank and a slower return of species that depend on overland dispersal via wind or animal transport.

Several studies have focused on changes in cladoceran assemblages in response to lake chemistry. Cladocerans require relatively large amounts of available Ca for growth and survival. Soil Ca pools and drainage water concentration can be reduced under acidifying conditions. Under conditions of partial chemical recovery of previously acidified surface waters, Ca concentrations have remained chronically low in some waters in some regions, likely impeding biological recovery ([Jeziorski et al., 2012a](#)).

An important approach for studying biological effects of aquatic acidification entails long-term monitoring of biological community composition. This can be done via evaluation of sedimentary remains of aquatic organisms in sequential slices of lake sediment cores. Cladocerans have commonly been the focus of long-term monitoring and paleolimnological studies to document biological responses to changes in water chemistry and trophic structure [e.g., ([Cooper et al., 2016](#); [Nevalainen et al., 2014](#); [Davidson et al., 2010](#); [Kurek et al., 2010](#))].

[Jeziorski et al. \(2008\)](#) documented major reductions in the abundance of Ca-rich *Daphnia* spp. in association with decreases in the concentration of Ca in lake water. They reported that a high proportion of Canadian Shield lakes had Ca concentration near or below the threshold level (1.5 mg/L) for decreased survival and fecundity in laboratory studies. In a study from Nova Scotia, cladoceran remains from three of four sampled lakes showed a decline in *Daphnia* beginning in the early 20th century that suggested limnological changes in response to acidic deposition or increased fish predation ([Korosi and Smol, 2012](#)). Following closure of a S emitting iron sintering plant in 1998 in the region northeast of Wawa, Ontario, pH from three previously acidified lakes returned to circumneutral conditions due to the high buffering capacity of the local geology. However, biological recovery has lagged behind, with no recovery observed in

cladoceran sedimentary assemblages ([Jeziorski et al., 2013](#)). Analysis of sedimentary cladoceran assemblages from low-Ca lakes (mean < 2 mg/L) in the Experimental Lakes area of Ontario, Canada, [Jeziorski et al. \(2014\)](#) indicated differences between present-day and preindustrial cladoceran assemblages. In Middle Lake, a lake in the Experimental Lakes area that was limed in 1973, alterations in cladoceran assemblages were assessed using the sedimentary record ([Labaj et al., 2014](#)). Overall, the results suggested that biological recovery has not occurred in the lake because many rare species have not yet returned to preacidification levels.

Bosminids dominated the sedimentary cladoceran assemblage from two acidified lakes in the Killarney Lake region in Ontario, and minimal shifts were observed in the paleolimnological record from preacidification conditions to recovery ([Labaj et al., 2015](#)). In contrast, cladoceran abundance in acidified lakes near Sudbury, Ontario experienced greater shifts in cladoceran abundance best explained by contamination by copper (Cu) and nickel (Ni). In an earlier study, [Jeziorski et al. \(2012a\)](#) documented large declines in the relative abundances of Ca rich *Daphnia* spp. and increases in the Ca poor species *H. glacialis* in 36 small headwater lakes in the Boreal Shield of south central Ontario having Ca concentration <3 mg/L. [Reid and Watmough \(2016\)](#) estimated that timber harvesting at planned levels in the Muskoka River watershed in Ontario, Canada, will cause approximately a 30% increase in the number of sampled lakes that decline to Ca levels below 1 mg/L, too low to support some key aquatic species, including *D. pulex*, compared with a scenario of no further tree harvesting.

[Vrba et al. \(2016\)](#) evaluated the recovery of planktonic and littoral invertebrate communities over 12 years (1999–2011) in eight Bohemian Forest lakes in Europe. During the decades of the 1990s and 2000s, S and N deposition decreased by 86 and 44%, respectively. Half of the study lakes (those having Al concentrations lower than 200 µg/L [7.4 µM]) showed some degree of biological and chemical recovery. The lakes having Al concentrations higher than 200 µg/L (7.4 µM) did not show pronounced decreases in lake acidity or improved biological condition. Differences between data collected in 1999 and data collected in 2011 showed pronounced differences in biological recovery depending on the Al conditions, with largest recovery responses observed for zooplankton. Such changes were driven by species gains in ciliates and crustaceans and replacements of species of rotifers in the high-Al lakes. Changes in the low-Al lakes were dominated by both species gains and losses. Results of multivariate analyses suggested that the major driver of differences in biological recovery was Al concentration. Species in low-Al lakes responded to improved chemistry by exhibiting gradual patterns of change. Recovery of high-Al lakes was constrained by a toxicity threshold response. Overall, biological recovery in these Bohemian lakes lagged behind recovery of water

acid-base chemistry. Species gains and losses were due to responses of many aquatic species rather than to changes in a relatively few indicators.

Effects of regional landscapes on trait divergence in a freshwater copepod (*Leptodiaptomus minutus*) were investigated by testing differences in acid tolerance in three spatially distinct groups of lakes in northern Canada: (1) exclusively circumneutral lakes (pH >6.0) in Quebec, (2) heterogeneous mix of acidic and circumneutral lakes of Killarney, Ontario, and (3) a mainly acidic group of largely bog-influenced lakes interspersed with some circumneutral lakes at Cape Race in Newfoundland ([Dastis and Derry, 2016](#)). Acid-tolerant *L. minutus* from an acidic source pond survived better subsequent to transfer to both low (3.6) and high (7.0) pH conditions. Nevertheless, copepod survival was dependent on the population source. Copepods from the circumneutral source pond were negatively impacted after 5 days of exposure to water having pH 3.6. For copepods from the acidic source pond, survival was higher, and the negative impact occurred after a much longer period of time, 17 days. The authors interpreted this result as being indicative of a fitness trade-off regarding tolerance of acidity. To assess community responses to multiple stressors, the researchers contend that it will be important to understand contingencies that are landscape-dependent, including pH tolerance.

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### 8.4.3 Benthic Invertebrate Recovery

In the 2008 ISA, few studies reported benthic recovery in previously acidified waters. One study by [Soulsby et al. \(1995\)](#) indicated recovery in some streams in Scotland that experienced ANC increases although recovery was not observed in the most severely acidified streams.

Since the publication of the 2008 ISA, additional studies have been conducted that assess recovery of benthic organisms. Most of that research has been conducted in Canadian and European waters. Indices to evaluate biological effects of aquatic acidification on benthic communities commonly rely on species of Ephemeroptera, Plecoptera, Trichoptera, Gastropoda, and Crustacea. In a study from the Neversink River basin in the Catskill Mountains in New York, [Burns et al. \(2008b\)](#) collected water chemistry data and surveyed macroinvertebrates, fish, and periphytic diatoms from 12 streams. This survey was conducted in 2003 and compared with a 1987 survey conducted at the same locations. Differences between the two surveys were not significant overall. However, a shift toward a less acid-tolerant macroinvertebrate community in the 2003 survey in streams in the upper river basin that were the most acidic in 1987 suggests biological

changes that are consistent with improvement in water chemistry. Further monitoring will be needed to determine the eventual extent of biological recovery.

Crayfish and other benthic invertebrates that require large amounts of Ca for growth may be reduced or absent in acidified water bodies that have experienced Ca depletion, reducing Ca bioavailability, caused by acidification ([U.S. EPA, 2008a](#); [Baker et al., 1990a](#)). [Hadley et al. \(2015\)](#) studied the limnological record of four lakes in Algonquin Park, Ontario where native populations of the crayfish *Cambarus bartonii* have not recovered despite improvements in pH. Cladoceran remains were used as proxies for historical Ca trends. Ca levels in the lakes are currently <2 mg/L, which is below the minimum requirement for crayfish survival (2 to 10 mg/L). Depletion of Ca in the soils and reduced Ca export from soil to lakes appear to contribute to the lack of recovery of crayfish populations in the region.

Two studies examined the response of littoral benthic macroinvertebrate community composition to changing water chemistry in 17 lakes on the Precambrian Shield in eastern Canada that were recovering from acidification. The first study [Lento et al. \(2008\)](#) tracked benthic invertebrate community composition over a 14-year period (1988–2002). There was a strong correlation between changes in chemical variables and shifts in benthic invertebrate communities. The rate of change in invertebrate community composition was greatest between 1993 and 1997, which corresponded most closely with water chemistry changes. The second study ([Lento et al., 2012](#)) evaluated temporal trends in 15 years of data from the same lakes. In analyses of both single and multiple lakes, decreasing proportions of Chironomidae and increasing proportions of Ephemeroptera, Plecoptera, and Trichoptera (quantified collectively as the EPT Index) were observed. Six of the nine lakes that showed significant recovery trends in more than one benthos metric exhibited a significant decrease in Chironomidae and concurrent increase in EPT. The results of these two studies, thus, suggested that the benthic macroinvertebrate communities of these study lakes changed in response to deacidifying changes in lake chemistry by shifting towards more acid-sensitive taxa. The observed response was consistent with benthic invertebrate recovery from acidification.

Some species of the order Odonata (including dragonflies) respond to changes in water acidity. For example, reduced water acidity in response to surface water liming can cause direct or indirect effects on some of the most common dragonfly species. ([Al Jawaheri and Sahlen, 2017](#)) investigated aquatic dragonfly communities in 47 Swedish lakes. Several were currently (n = 13) or previously (n = 8) limed. Seven of the most common dragonfly species were less common in limed lakes as compared with reference lakes that were not limed perhaps due to fish predation. [Al Jawaheri and Sahlen \(2017\)](#) suggested use of this order of stream invertebrate as indicators of water quality.

In a bioassessment in the Athabasca oil sands region of Alberta, Canada, [Parsons et al. \(2010\)](#) sampled 32 lakes to assess potential impacts of pollutant emissions and acid deposition on benthic macroinvertebrate communities. Five of the lakes were selected from an area with modeled high deposition. All of the statistical methods used (one sample *t*-tests, multivariate analysis of variance, and test site analysis) showed that assemblages differed between test lakes and reference lakes. However, results suggested these differences were more due to intrinsic lake physicochemical factors, such as geology and water chemistry, than to atmospheric deposition.

Several studies conducted in Europe have also considered macroinvertebrate recovery following ongoing chemical recovery. [Frame et al. \(2016\)](#) tested whether the growth of *Baetis rhodani* (an acid-sensitive mayfly nymph) is decreased by competition with *Leuctra inermis* (an acid-tolerant stonefly nymph) in a stream in the U.K. recovering from acidification. This experiment tested the biotic resistance hypothesis, which suggests that past acidification of surface waters has changed acidified waters to an extent that prevents reinvasion of acid-sensitive species even if acidity is substantially reduced. Introduction of *Baetis* to water containing different densities of *Leuctra* had no effect on *Baetis* growth. In one of the previously most acidified areas of Europe, [Svobodová et al. \(2012\)](#) compared water chemistry and macrozoobenthos composition of the outflows from two lakes in the Bohemian Forest. The water chemistry was recovering in response to reduced levels of acidic deposition. Evidence of biological recovery was found for Lake Laka (current pH  $\approx 5.2$ ), but not for the more strongly acidified Lake Čertovo (pH  $\approx 4.6$ ). At the Lake Laka outflow, increasing numbers of Ephemeroptera and Tricoptera taxa were observed. Comparable changes were not observed at the outflow for the more strongly acidified lake. In an analysis of a 20-year data set (1988–2008) from the Acid Waters Monitoring Network (AWMN) in the U.K., macroinvertebrate recovery was observed in 5 of the 11 stream sites and at 5 of 12 lakes ([Murphy et al., 2014](#)). An increase in ANC over time was observed at all 10 sites where biological recovery was evident based on trends in the macroinvertebrate community. An additional seven sites showed ANC recovery but no recovery of the macroinvertebrate community. The authors attributed this observation to differences in chemical environments and/or ecological interactions that interfere with recovery such as food-web dynamics and predation. In another 20-year data set, [Angeler and Johnson \(2012\)](#) analyzed littoral invertebrates in acidified and circumneutral lakes in Sweden. The concentration of  $\text{SO}_4^{2-}$  decreased in both acidified and circumneutral lakes but converged in the latter part of the study. Chemical recovery was generally weak in the acidified lakes, with pH increasing by only about 0.1 to 0.2 pH units in the study lakes. These results from Sweden suggest that because invertebrate communities respond to complex processes, including both local and regional factors, partial recovery of water chemistry from acidification is at times not accompanied by observable biological recovery, especially as related to biodiversity.

Data from two national-scale benthic macroinvertebrate surveys, the AWMN in the U.K. and a lakes survey in Norway, were used to compare field sampling results to predictions of maximum species richness as a function of chemical conditions in surface waters recovering from acidification ([Stockdale et al., 2011](#)). In general, there was good agreement between model predictions and observed trends in EPT taxa. Biological recovery rates for actual and predicted species richness were generally consistent with each other, at 1.2 to 2.0 species per decade change. However, actual recovery rates in the AWMN lakes were less than in the rivers (0.6 vs 2.0 species per decade recovery), whereas predicted rates were similar (1.7 vs 2.0 species per decade). At sites where there was poorer agreement between model predictions and observations, differences in water chemistry explained some of the observed reduction in species richness. The authors speculated that factors not included in the model, such as biotic interactions and site conditions, could also affect species richness.

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#### **8.4.4 Fish and Amphibian Recovery**

Some of the most in-depth studies of the effects of acid stress on fish ([Appendix 8.3.6](#)) have been conducted in streams in Shenandoah National Park, VA ([Cosby et al., 2006](#)) and lakes in the Adirondack Mountains, NY ([Sullivan, 2015](#)). Effects on fish have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina ([Baldigo and Lawrence, 2001](#); [Bulger et al., 2000](#); [Bulger et al., 1999](#); [SAMAB, 1996](#); [Charles and Christie, 1991](#)). Since the 2008 ISA, several studies have documented vertebrate recovery that corresponds to decreasing acidic deposition.

Evidence for recovery of fish populations following reduction in acidic deposition or through liming ([Appendix 8.4.6](#)) was reported in several studies reviewed in the 2008 ISA ([Gunn et al., 1988](#); [Kelso and Jeffries, 1988](#); [Beggs and Gunn, 1986](#); [Dillon et al., 1986](#); [Keller and Pitblado, 1986](#); [Raddum et al., 1986](#); [Hultberg and Andersson, 1982](#)). There have been additional studies of fish response to surface water acidification and subsequent recovery since the 2008 ISA. These studies have been conducted in both North America and Europe.

[Sutherland et al. \(2015\)](#) documented the reintroduction and re-establishment of a naturalized native fish species (brook trout) in an Adirondack lake (Brooktrout Lake) from which this species had previously been extirpated. The historical decline in water quality and loss of the fishery were reconstructed from available data dating back more than a century. Lake chemistry has improved substantially in response to decreases in acidifying deposition since the 1980s, with pronounced decreases in midsummer

epilimnetic inorganic Al and H<sup>+</sup> concentrations. In Brooktrout Lake, the mean ANC increased from -2 µeq/L during the 1980s to 12 µeq/L during the period 2010–2012 ([Table 8-6](#)). Substantial changes were also noted for other variables, including SO<sub>4</sub><sup>2-</sup>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, DOC, and inorganic Al. During the period from 2005–2007, brook trout were reintroduced to the lake and have subsequently survived and successfully reproduced. In 2012, young brook trout were observed and photographed, documenting reproduction in, or in tributary streams near, the lake. Other acid-impacted lakes in the Adirondacks such as Honnedaga Lake lost acid-sensitive fish species between 1920 and 1960 while continuing to support brook trout ([Josephson et al., 2014](#)). By the late 1970s, brook trout were also considered extirpated from Honnedaga Lake, but persisted in tributary refugia. By 2000, brook trout had recolonized the lake coincident with reductions in surface-water SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and inorganic Al concentrations.

In addition to these studies of recolonization of lakes by brook trout where acid-base chemical conditions were improving, new reports of shifts in fish communities in response to acidification have been published since the 2008 ISA. [Warren et al. \(2008\)](#) used historical records to document a fish community shift in the upper mainstem of Hubbard Brook in New Hampshire corresponding to chronically acidified conditions in the 1970s. Records indicated that there were at least three fish species in the 1960s: slimy sculpin (*Cottus cognatus*), blacknose dace (*Rhinichthys atratulus*) and brook trout. Only brook trout were present in surveys conducted in 2005, 2006, and 2007. In an evaluation of fish recovery in nearly 5,000 small headwater lakes in Finland where at the end of the 1980s populations were either diminished by acid deposition or extirpated, [Rask et al. \(2014\)](#) noted recovery of perch (*Perca fluviatilis*), a relatively acid-tolerant species, starting in the 1990s. The perch population structure has returned to normal during the monitoring period, which ended in the mid-2000s. Little or no recovery of the acid-sensitive roach (*Rutilus rutilus*) was observed over that time period.

Despite observed reductions in acidic deposition and improvement in water quality of New York lakes, [Baldigo et al. \(2016\)](#) found no evidence of widespread or substantial biological recovery of brook trout populations or broader fish communities in the Adirondack Mountains. The study focused on 43 lakes sampled by the Adirondack Lakes Survey Corporation during three time periods (1984–1987, 1994–2005, and 2008–2012). Metrics reflecting fish species richness, abundance of fish species, and abundance of brook trout did not change significantly over the 28-year period across the group of study lakes despite a significant average ANC increase and a decrease in inorganic Al over time. Fish species richness and catch of all fish species per net-night were positively related to lake chemistry reflecting some limited degree of biological recovery. The authors speculated that additional time may be needed for fish recolonization.

Recovery of fish populations in streams may be affected by habitat considerations as well as water chemistry. [Warren et al. \(2010\)](#) evaluated the relative influence of stream habitat and pH on total fish biomass in 16 streams in the northeastern U.S. Physical and chemical factors evaluated in the study included total pool area, cover, large wood frequency, and water temperature. Both pool area and pH were closely correlated with prediction of fish biomass. Physical habitat is likely more important at pH >5.7 (at low flow) and becomes less important at lower pH when conditions are too acidic to support fish.

Recovery of young brown trout (*Salmo trutta*) in acidified streams in southern Norway was assessed by [Hesthagen et al. \(2016\)](#) over the period 1987–2010. The density of fish, both young-of-the-year and older parr, increased significantly during the study period. Water quality also improved (pH 5.0–5.5 increasing to 5.8–6.0). Nevertheless, the densities of both fish age groups (young-of-the-year and older parr) decreased for a period of time in the early 1990s. This was attributed to seasalt acidification associated with severe weather conditions that caused increased marine salt deposition. This finding emphasizes the fact that recovery from acidification should be evaluated in the context of other changes, including natural or other human-caused disturbance regimes.

Even if the preindustrial acid-base chemistry of a water body is fully restored, there is no guarantee that any aquatic species that had previously been eliminated in response to acidification will in fact return to that water body. There may be physical, chemical, or biological barriers to species reintroduction. Methods have not been well developed and tested for reintroduction of species other than fish.

Potential impacts of aquatic acidification on amphibian species occur in the context of multiple stressors, including fish introductions and the presence of fungal pathogens. A dramatic example of environmental stress in amphibians is the widespread prevalence of the disease chytridiomycosis, which is caused by the fungus *Batrachochytrium dendrobatidis*. Major die-offs of frogs, toads, salamanders, and other amphibians have been documented in the U.S. and elsewhere ([Martel et al., 2014](#); [Rosenblum et al., 2010](#)). These die-offs have not been attributed to acidification.

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#### **8.4.5 Bird Recovery**

Common loon (*Gavia immer*) breeding success was assessed from 1982 to 2007 in 38 lakes historically impacted by deposition from smelter activities in the Sudbury, Ontario region ([Alvo, 2009](#)). No fledglings were observed on any lakes that had pH <4.4. In two of the lakes that were previously too acidic for loon reproduction, chicks were observed as acid conditions improved over the duration of the study. However, it was not clear from the results whether there is a critical pH for loon fledging survival.

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#### 8.4.6 Mitigation

Application of lime or other sources of base cation(s) is well known to increase the bioavailability of nutrient bases to terrestrial and aquatic biota. Neutralization of acidity by addition of limestone or other Ca source to watershed soils or directly to water bodies has been used for several decades in Europe and to a lesser extent in North America to mitigate effects of acidifying deposition. Analyses of long-term data suggest that liming watershed soils increases Ca availability to aquatic and terrestrial biota and limits mobilization of Al from soils to surface water. Watershed liming of soils generally promotes long-lasting effects whereas direct liming to streams and lakes causes short-term chemical fluctuations and less pronounced ecosystem recovery ([Lawrence et al., 2016](#)). Prior to the 2008 ISA, relatively few studies were conducted in the U.S. that focused on mitigation of harm to aquatic organisms caused by acidification. Limited lake liming had occurred in the Adirondacks in an effort to reverse the adverse effects of water acidification ([Schofield and Keleher, 1996](#)).

It has been well documented that the intensity and duration of acidity mitigation achieved by Ca addition depends to a large degree on the method of Ca application. In particular, different results have been achieved depending on the site of Ca addition: directly to the water body and/or more broadly across the watershed that contributes drainage water (and associated base cations) to the water body in question. Application of lime to the terrestrial watershed leads to acidity mitigation that is more gradual and of longer duration than lime application directly to surface waters ([Davis and Goldstein, 1988](#)).

A liming study at the Woods Lake watershed in the Adirondack Mountains applied calcite ( $\text{CaCO}_3$ ) to two paired watersheds, with and without pronounced wetland influence ([Driscoll et al., 1996](#)). Lake water showed gradual improvements in pH, ANC, and the concentration of Ca at the site of watershed liming, in contrast to the more abrupt and short-lived effects of direct surface water lime application. The liming decreased the concentrations of inorganic Al and increased DOC. Water quality improvements affected both the treated stream and the downstream lake ([Burns, 1996](#)). Brook trout spawning was restored to the tributary stream ([Schofield and Keleher, 1996](#)). Only limited additional research has been conducted in the U.S. in more recent years. [Knoepp et al. \(2016\)](#) estimated that about 11.6 to 21.1 Mg/ha of  $\text{CaCO}_3$  would be needed to increase surface soil (upper 30 cm) pH to 5.0 in three high-elevation watersheds in the Appalachian Mountains. Stream acid-base chemistry was related to the concentrations of N and Al in the soil O-horizon and to the total amount of C and Ca in the soil.

[Lawrence et al. \(2016\)](#) re-examined the liming approach as a method for accelerating the recovery of acidified ecosystems where chemical and/or biological recovery have lagged behind reductions in atmospheric S and N deposition. They presented evidence

suggesting that recovery rates are fastest for lakes and slowest for soils, with intermediate stream recovery rates. They also emphasized that lime should not be applied to environments, including wetlands, where indigenous species are adapted to naturally acidic conditions.

An experimental stream and watershed liming study is currently in progress in the Adirondacks. This work is being conducted by a group of researchers under the coordination of the U.S. Geological Survey in Troy, NY. Results are not yet available at the time of this writing.

In an effort to mitigate Atlantic salmon population declines in Norway due to acidification, liming was implemented in 21 acid-impacted rivers. [Hesthagen et al. \(2011\)](#) electrofished 13 rivers 1 year before and annually for 12 years after initiation of liming. Increases in salmon parr densities were slow, and the authors estimated that it will take more than 20 years of liming to restore lost salmon stocks. Rivers that were stocked and those lacking hydropower developments generally had higher fry densities and faster increase in parr densities subsequent to lime application.

[Mant et al. \(2013\)](#) conducted a review and meta-analysis of the impacts of liming streams and rivers on the biological recovery of fish and aquatic invertebrates. The meta-analysis included studies in the U.K., Norway, Sweden, U.S., and Canada. On average, liming increased the abundance and richness of acid-sensitive invertebrates and increased fish abundance. Nevertheless, benefits were variable and did not occur in all rivers.

The large national-scale lake and stream liming program in Sweden offers a unique opportunity to evaluate the expected recovery of fisheries in response to water deacidification at the national level. ([Holmgren et al., 2016](#)) reported results from monitoring since the 1980s of 1,029 limed streams and 750 limed lakes, plus reference (unlimed) sites (195 streams and 101 lakes). Over time, the proportion of limed streams that had no fish decreased. Species richness and the percentage of streams in which brown trout (*Salmo trutta*) was detected both increased over time after initiation of liming. The abundance of several species, including brown trout, perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*), increased more at sites that were limed as compared with sites that were not limed. Species richness increased slightly in limed streams (less than 2 on average before liming to more than 2.6 species 16 years after initiation of liming). Nonlimed streams did not show a change in richness over time. Patterns were less clear for lakes, perhaps due to the influence of lake size and/or productivity, either of which might mask the effects of liming.

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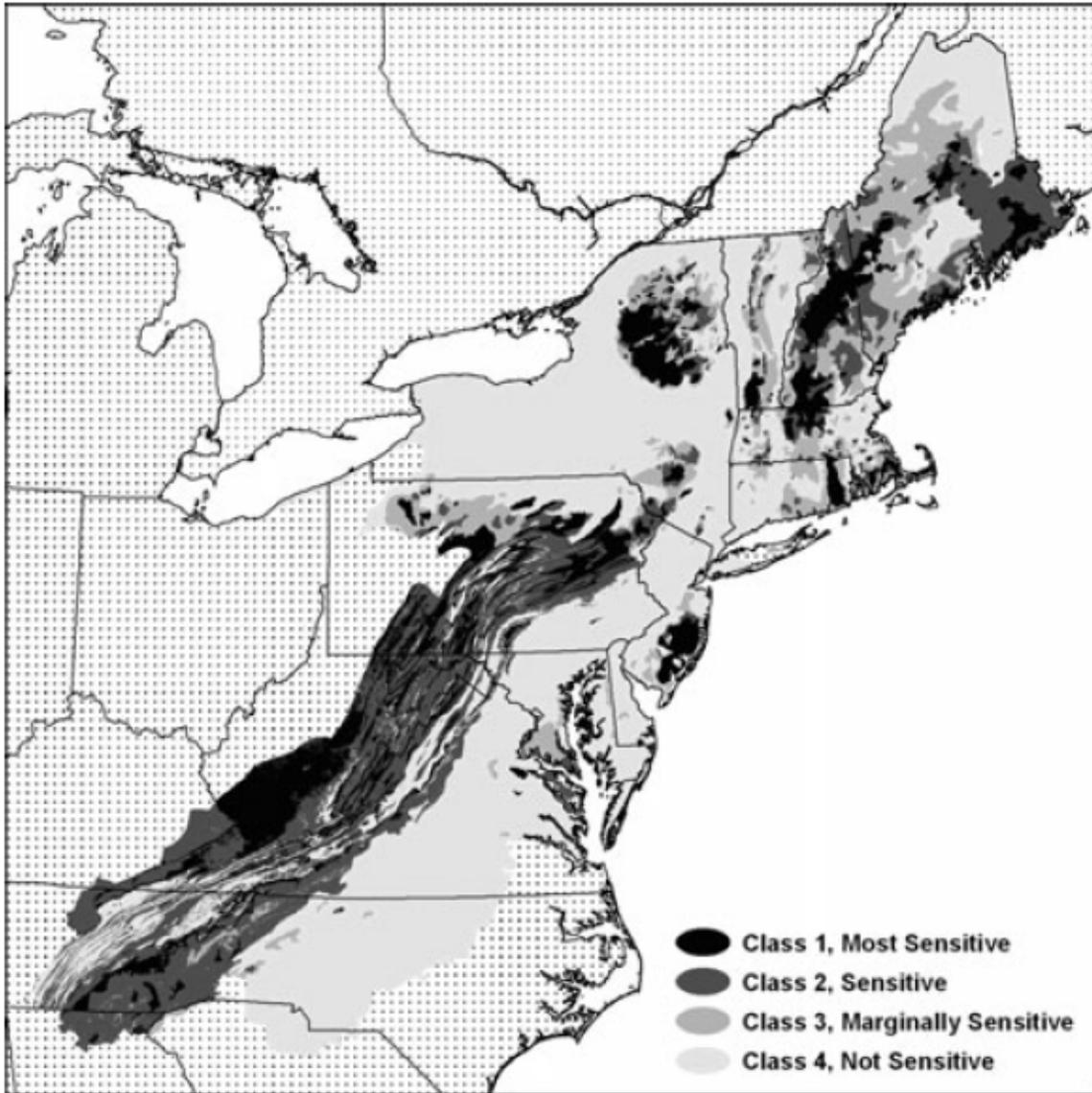
## 8.5 Levels of Deposition at Which Effects Are Manifested

The level of N and S deposition and their impacts vary across the landscape. Not all environments are sensitive to acidifying deposition at the levels seen in the past and present. Effects on biological communities are related to both the characteristics ([Appendix 8.5.1](#)) and extent and distribution ([Appendix 8.5.2](#)) of acid sensitive freshwaters across the U.S. as well as climate factors ([Appendix 8.5.3](#)). [Appendix 8.5.4](#) includes both empirical and modeled thresholds (critical loads) of effects of acidifying deposition.

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### 8.5.1 Most Sensitive and Most Affected Ecosystems and Regions

The characteristics of acid-sensitive ecosystems were well known and summarized in the 2008 ISA. In brief, the effects of acid deposition on aquatic systems depend largely upon the ability of an ecosystem to neutralize additional acid inputs. No one level of deposition can be used to generalize the sensitivity or impacts of acidifying deposition across a region or the country. The principal factor governing the sensitivity of aquatic ecosystems to acidification from acidifying deposition is geology [particularly surficial geology; ([Greaver et al., 2012](#))]. Geologic formations having low base cation supply, due mainly to low soil and bedrock weathering, generally underlie the watersheds of acid-sensitive lakes and streams. Till thickness has been shown to be a key control on the pH and ANC of Adirondack lakes ([Driscoll et al., 2016](#)), whereby lakes in watersheds inferred to be underlain by thin till tend to be highly sensitive to acidification ([Driscoll and Newton, 1985](#)). [Figure 8-10](#) is a map of aquatic ecosystem sensitivity in the eastern U.S. based on underlying geology in unglaciated areas and ANC in the glaciated region. Other factors contribute to the sensitivity of surface waters to acidifying deposition, including topography, soil chemistry and physical properties, land use and history, and hydrologic flowpath.



Source: [Lovett et al. \(2009\)](#).

**Figure 8-10** Map of landscape sensitivity to acidic deposition for the northeastern and mid-Atlantic U.S. Stippled areas were not considered.

The 2008 ISA summarized findings from several national surveys on the effects of acidifying deposition, including the National Lakes Survey and the National Streams Survey conducted in the mid-1980s, the Wadeable Streams Assessment (WSA) in 2004, the U.S. EPA Long-Term Monitoring program that began in 1983, and the Temporally Integrated Monitoring of Ecosystems probability surveys that began in 1991. Results of

these surveys suggested that acidifying deposition had acidified surface waters in the southwestern Adirondacks, New England uplands, eastern portion of the upper Midwest, forested Mid-Atlantic highlands, and Mid-Atlantic coastal plain ([U.S. EPA, 2008a](#)).

At ANC of 100  $\mu\text{eq/L}$  or less, acid-sensitive aquatic species may be adversely affected [[Figure 8-4](#); ([U.S. EPA, 2008a](#); [Sullivan et al., 2006a](#); [Bulger et al., 2000](#); [Bulger et al., 1999](#))]. Sensitive water bodies, therefore, can be defined as those that have ANC of 100  $\mu\text{eq/L}$  or less. Sensitivity increases with further decreases in ANC. In general, streams in the eastern U.S. that are sensitive tend to be headwater streams of first- to third-order. Streams and lakes in the western U.S. tend to be headwater systems in high elevation areas. Recent research has not changed this understanding but rather has served to strengthen it ([Appendix 7](#)).

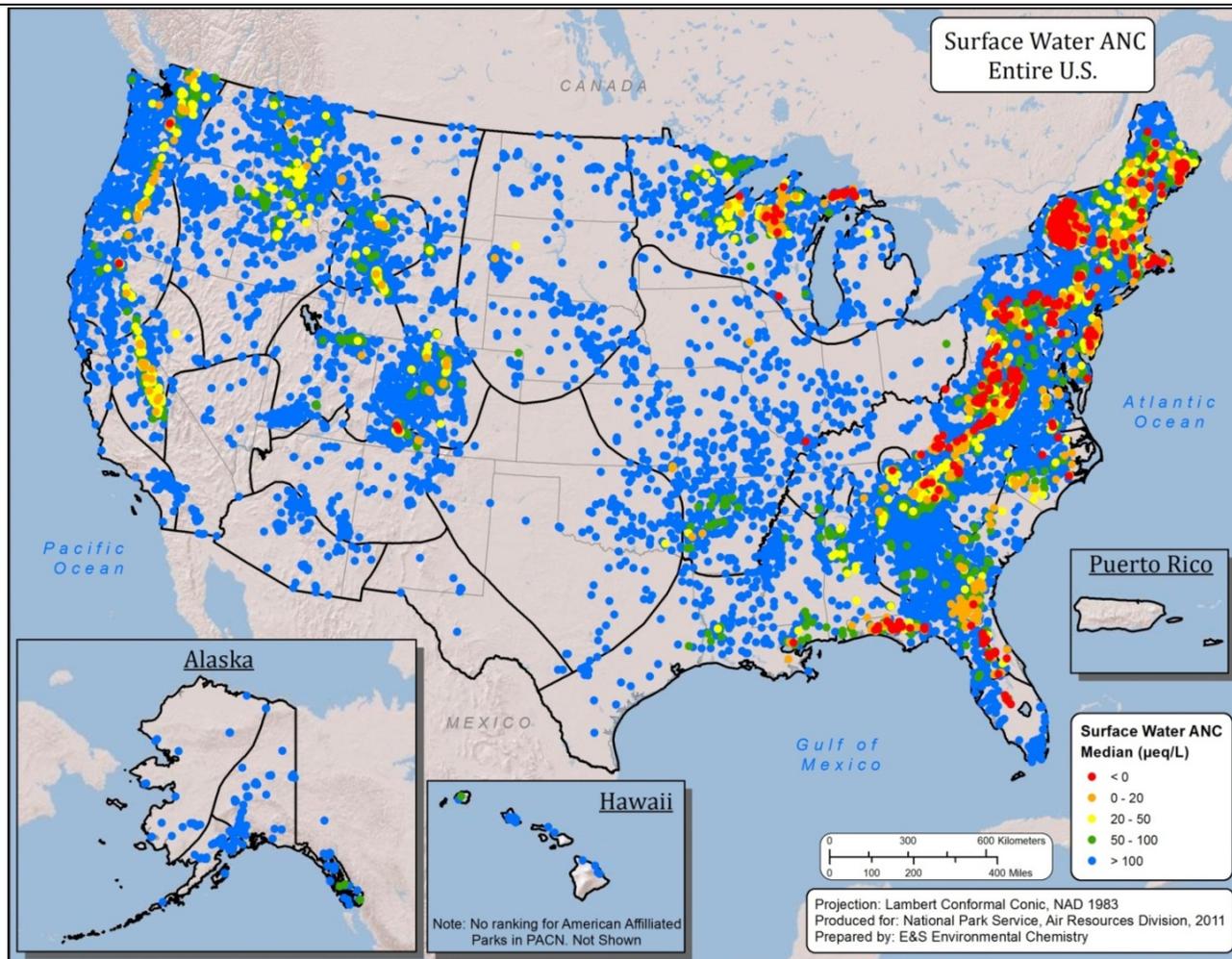
Controls on surface water acidification and recovery are not necessarily spatially homogeneous. For example, the adsorption and desorption of S on soils can exert major controls on acidification, and likely chemical recovery from acidification, in the unglaciated soils of the southeastern U.S. ([Rice et al., 2014](#)). Limitations in the extent of S driven acidification and recovery attributable to S adsorption is less pronounced in the northeastern U.S.

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## 8.5.2 Extent and Distribution of Sensitive Ecosystems/Regions

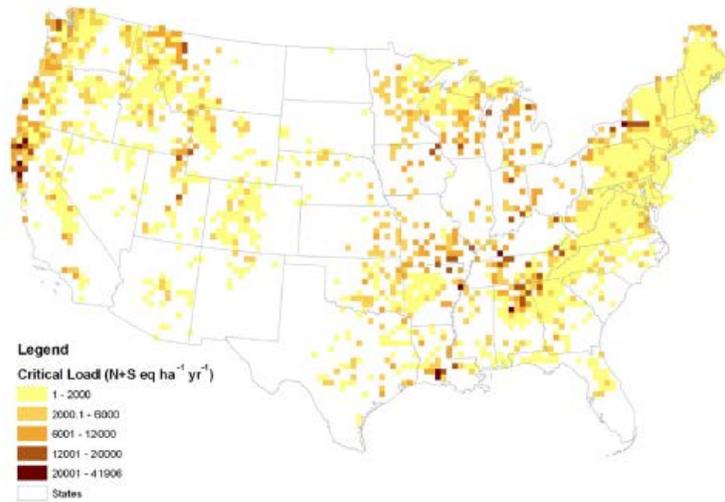
The 2008 ISA summarized the extent and distribution of freshwater ecosystems sensitive to acidifying deposition. Measured data on lake and stream ANC across the U.S. exhibit clear spatial patterns. In the U.S., surface waters that are most sensitive to acidification based on ANC are largely found in the Northeast, southern Appalachian Mountains, Florida, the upper Midwest, and the mountainous West ([Sullivan, 2017](#); [McDonnell et al., 2014b](#); [Greaver et al., 2012](#); [Campbell et al., 2004a](#); [Driscoll et al., 2001b](#); [Baker et al., 1990b](#); [Omernik and Powers, 1983](#)). [Figure 8-11](#) is a national map of surface ANC for the U.S. that includes nearly 200,000 measurements taken at nearly 20,000 spatially unique locations sampled between 1980 and 2011 ([Sullivan, 2017](#)). Samples expected to be strongly influenced by acid mine drainage, sea salt spray, or road salt application were excluded. Thus, the included data represent sites not likely confounded by major disturbances not related to acidic deposition. [Sullivan \(2017\)](#) found 6,065 sites that had ANC < 100  $\mu\text{eq/L}$ . Acidic waters were mostly restricted to northern New York, New England, the Appalachian Mountain chain, upper Midwest, and Florida (see [Figure 8-11](#)). Low, but positive, ANC values were depicted for these same regions plus high-elevation portions of the West and parts of Arkansas and the Gulf states. These geographical patterns are thought to largely reflect base cation supply in soils. Levels of acidifying

deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has been limited ([Sullivan, 2017](#); [Charles and Christie, 1991](#)). Episodic acidification, however, occurs in both the East and West at some acid-sensitive locations. These areas can be identified by CL maps for the U.S. based, for example, on an ANC target of 50  $\mu\text{eq/L}$  [[Figure 8-12](#); ([Blett et al., 2014](#))].

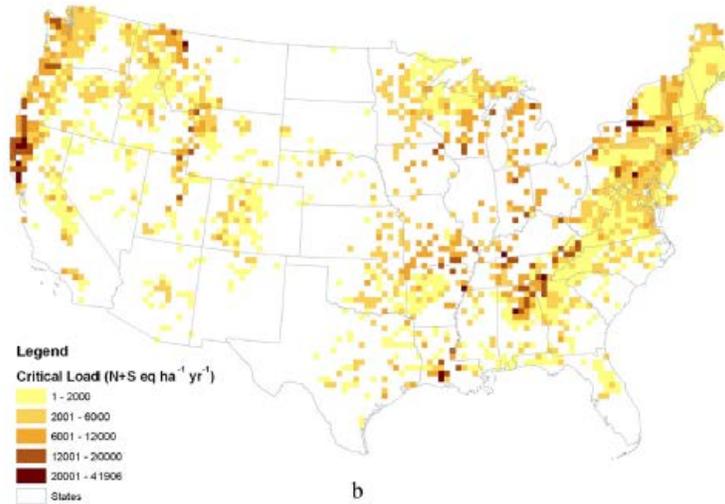


Source: [Sullivan \(2017\)](#).

**Figure 8-11.** Surface water Acid Neutralizing Capacity (ANC) map, based on data compiled by [Sullivan \(2017\)](#)



a



b

ha = hectare; eq = equivalent; km = kilometer; L = liter; N = nitrogen; S = sulfur;  $\mu\text{eq}$  = microequivalent; yr = year.

Source: [Blett et al. \(2014\)](#).

**Figure 8-12** (a) Minimum critical loads of surface water acidity for nitrogen and sulfur. Grids represent the minimum calculated critical load from all data within the 36 × 36-km grid cell (b) Mean critical loads of surface water acidity. Grids represent the average calculated critical load from all data within the 36 × 36-km grid cell. The critical chemical criterion used was an acid neutralizing capacity 50  $\mu\text{eq/L}$ .

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### 8.5.3 Climate Modification of Ecosystem Response to Nitrogen and Sulfur

Acidification and recovery of freshwaters will be affected by the physical, chemical, and biological modifications to acid inputs projected to occur with changes in annual mean temperature and magnitude of precipitation ([Greaver et al., 2016](#)). Projected shifts in runoff and timing and quantity of flushing will alter the frequency and duration of episodic events ([Whitehead et al., 2009](#)). In acid sensitive regions, altered hydrologic regimes are likely to affect weathering rate of base cations, lake water levels and organic matter inputs to catchments ([Adrian et al., 2009](#); [Porcal et al., 2009](#)). Air temperature increases will lead to warmer surface waters altering thermal stratification of water bodies, distribution of aquatic biota in streams and lakes and community composition ([Adrian et al., 2009](#); [Keller, 2007](#)). Climate change may play a role in shifting baselines for ecosystem recovery in previously acidified lakes ([Appendix 8.4](#)). [Warren et al. \(2017\)](#) suggested that the major stressor affecting native coldwater fish species in the eastern U.S. is shifting from acidification to thermal stress and some lakes recovering from acidification may provide a degree of protection against climate affects. As DOC in the water increases with increasing lake pH in recovering lakes, decreased water clarity may create cooler refuge habitat for fish. [Appendix 13](#) includes a more detailed discussion of how climate (e.g., temperature and precipitation) modifies ecosystem response to acidification.

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### 8.5.4 Critical Loads

A critical load (CL) is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge [([Spranger et al., 2004](#); [Nilsson and Grennfelt, 1988](#)) Chapter 1.2.2.3]. The following sections express deposition in eq/ha/yr of S, N, or S + N because one or both pollutants could be contributing to the observed effects.

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#### 8.5.4.1 U.S. Critical Loads

The 2008 ISA documented use of the CL approach to determine sensitivity to acidification. Critical load applications for surface water in the U.S. have been reviewed by [Porter et al. \(2005\)](#), [Burns et al. \(2008a\)](#), [Pardo et al. \(2011a\)](#), [NAPAP \(2011\)](#), [Lovett \(2013\)](#), and [Sullivan and Jenkins \(2014\)](#). Most aquatic CL studies conducted in the U.S. have used surface water ANC as the metric of water quality change in response to acidifying deposition. This should not be taken as an indication that ANC should

necessarily be the only environmental predictor of harm to aquatic species on which to base CLs. Other potentially useful variables include water pH or BCS. Either, or both, can be used instead of, or in addition to, ANC.

The initial step in developing a CL is to define a threshold for a significantly harmful effect. This biological change can be defined for the protection of a single species or an entire biological community, and defining varying levels of protection for either can be achieved through adoption of different indicators of harm. Because CLs depend on what is being protected, any given biological community requires a set of CLs. The closely related target load (TL) estimates the reduction needed to achieve a certain condition at a designated future time period. A target load can be less than, equal to, or greater than the CL. As described in the 2008 ISA, there are different types of CLs: empirical CL, modeled steady-state CL (time invariant), and modeled dynamic CL [change through time with a specific target date, often to the year 2100 as a management TL; ([U.S. EPA, 2008a](#))]. Several CL studies were summarized in the 2008 ISA.

As discussed in the 2008 ISA, a useful aspect of the CL approach is the calculation of exceedance. Knowledge of where and to what extent ambient air pollutant loads exceed levels that are sustainable without causing ecological harm can inform vulnerability assessments ([Sullivan and Jenkins, 2014](#)). Therefore, the exceedance is calculated as the difference between the ambient deposition of S, N, or S + N and the CL or the TL. It can be expressed as an absolute deposition amount or as a percentage.

Since 2006, the primary forum for coordination of research on CL development in the U.S. has been the Critical Loads of Atmospheric Deposition (CLAD) science committee of the National Atmospheric Deposition Program [NADP; ([Blett et al., 2014](#))]. Efforts are underway in association with CLAD to collect needed data and improve methods for CL calculations throughout the U.S.

#### **8.5.4.1.1 Empirical Critical Loads**

An empirical CL is developed from observational spatial or temporal gradient studies or additions of pollutants to determine the deposition load at which chemical or biological changes (e.g., changes to foliage, lichens, soil, aquatic chemistry/biota) occur in the environment. Empirical CLs are generally applied to sites or landscapes that are ecologically comparable to location(s) from which the CLs were determined [cf; [Pardo et al. \(2011a\)](#)]. Empirical CLs for acidification are difficult to apply to sites other than those used in defining them and to generalize across the landscape because sensitivity to acidification is highly spatially variable (see [Appendix 8.5.1](#)). A given CL for

acidification often only applies to a narrow subset of environmental conditions, in some cases only to a single water body.

At the time of the 2008 ISA, very few empirical CLs were available for U.S. freshwater ecosystems. Rocky Mountain National Park has been the site of research addressing the environmental effects of N deposition. [Williams and Tonnessen \(2000\)](#) reported ANC in surface water  $< 0$   $\mu\text{eq/L}$  near the park as a result of acidifying inputs of N deposition, suggesting that current deposition levels are having an observable impact on catchments in the Colorado Front Range. The authors recommended a CL of 286 eq N/ha/yr to prevent episodic freshwater acidification in alpine lakes (ANC  $< 0$   $\mu\text{eq/L}$ ). However, determination of biological change in the field was not a focus of this study.

Other studies conducted in the western U.S. have identified CLs for freshwater systems ([Table 8-7](#)). In Moat Lake in the Sierra Nevada mountains, acidic deposition ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) equal to about 74 eq/ha/yr was correlated with the decline in ANC observed in the lake between 1920 and 1930 ([Heard et al., 2014](#)). This was taken by the authors to be the CL to protect against acidification for Moat Lake, but they did not specify the level of acidification or how the biological community would be protected. Diatom-reconstructed ANC of Moat Lake changed from near 100  $\mu\text{eq/L}$  prior to 1920 to near 60  $\mu\text{eq/L}$  during the 1970s. Reconstructed ANC patterns were not correlated with climate, productivity, or  $\text{NO}_x$  emissions.

Although most CLs are focused on chronic acidification, and by strict definition as a steady-state metric must be, [Baron et al. \(2011b\)](#) estimated CLs to be about 571 eq N/ha/yr in the Northeast and 286 eq N/ha/yr in the Rocky Mountains for  $\text{NO}_3^-$  concentrations as triggers of episodic acidification. CLs for N deposition in California were estimated based in part on changes in  $\text{NO}_3^-$  leaching in stream water, which can cause or contribute to water acidification ([Fenn et al., 2008](#)). The empirical CL and the CL simulated by the DayCent model for  $\text{NO}_3^-$  leaching were both 1,214 eq N/ha/yr. Nitrogen deposition exceeds that level at some locations in California.

#### **8.5.4.1.2 Modeled Critical Loads**

Steady-state and dynamic models are used to quantify relationships between deposition and biogeochemistry for watersheds in order to develop CL estimates (see description of models in [Appendix 7](#)). Modeled CLs for aquatic acidification are summarized in [Table 8-8](#).

**Table 8-7 Recent empirical critical loads to protect against aquatic acidification in U.S. ecosystems.**

Ecosystem	Site	Critical Load for N Deposition	Response	Study
Alpine lakes	Central Rockies/Colorado Front Range	286 eq N/ha/yr	Episodic freshwater acidification	<a href="#">Williams and Tonnessen (2000)</a>
Mediterranean California stream water	California	1,214 eq N/ha/yr	Changes in NO <sub>3</sub> <sup>-</sup> leaching in stream water	<a href="#">Fenn et al. (2008)</a>
Hardwood and coniferous forests drainage water or stream	Northern forests	571 eq N/ha/yr	Increased surface water NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a> <a href="#">Aber et al. (2003)</a>
Eastern hardwood forests drainage water	Eastern temperate forests	571 eq N/ha/yr	Increased surface water NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a> <a href="#">Aber et al. (2003)</a>
Mixed conifer forests drainage water	Mediterranean California	1,214–1,850 eq N/ha/yr	Increased surface water NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a> <a href="#">Fenn et al. (2010)</a> <a href="#">Fenn et al. (2008)</a> <a href="#">Breiner et al. (2007)</a>
Pine forest drainage water	Temperate Sierra Nevada	1,071 eq N/ha/yr	Elevated NO <sub>3</sub> <sup>-</sup> in spring and stream water	<a href="#">Fenn and Geiser (2011)</a> <a href="#">Pardo et al. (2011a)</a>
N rich forests drainage water	Subtropical humid forests	<357–714 eq N/ha/yr	NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a>
Lakes	Western U.S.	143 eq N/ha/yr	NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a> <a href="#">Baron (2006)</a>
Lakes	Eastern U.S.	571 eq N/ha/yr	NO <sub>3</sub> <sup>-</sup> leaching	<a href="#">Pardo et al. (2011a)</a> <a href="#">Aber et al. (2003)</a>
High elevation lakes	West and Northeast	571 eq N/ha/yr (Northeast) 286 eq N/ha/yr (West)	Episodic freshwater acidification	<a href="#">Baron et al. (2011b)</a>
High elevation lakes	Sierra Nevada	74 eq/ha/yr	Lake acidification as measured by change in ANC	<a href="#">Heard et al. (2014)</a>

ANC = acid neutralizing capacity; eq = equivalent; ha = hectare; kg = kilograms N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate; yr = year.

**Table 8-8 Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification.**

Region	Model	Type of Ecosystem	Focus	Critical Loads	Publication
Conterminous U.S.	SSWC and empirical	Lakes and streams	Implementation of a consistent process for calculating and mapping steady-state CLs	A consistent CL process was documented.	<a href="#">Blett et al. (2014)</a>
Adirondack Mountains	MAGIC and regional extrapolation of model	Lakes	TL for lakes in 2050 and 2100	To achieve ANC = 50 µeq/L in 2100, about 30% of lakes had simulated TL of S deposition <500 eq/ha/yr and about 600 lakes were in exceedance.	<a href="#">Sullivan et al. (2012a)</a>
Adirondack Mountains	PnET-BGC	Lakes	TL link to fish and zooplankton richness	The magnitude of simulated historical acidification represented by ANC loss ranged from about 26 to 100 µeq/L. The amount of historical acidification of the lakes was related to the total ambient deposition of SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> , the Ca weathering rate, and the simulated preindustrial ANC in the year 1850. Adirondack lakes have lost fish and total zooplankton species richness beginning with the onset of acidic deposition. Modeling results suggested that complete recovery to preindustrial conditions may not be possible for most acidified lake ecosystems.	<a href="#">Zhou et al. (2015b)</a>

**Table 8-8 (Continued): Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification.**

Region	Model	Type of Ecosystem	Focus	Critical Loads	Publication
Adirondack Mountains	PnET-BGC	Lake	Effects of biophysical factors on the TL	Model simulations suggested that future decreases in $\text{SO}_4^{2-}$ deposition would be more effective in increasing the lake water ANC than equivalent decreases in $\text{NO}_3^-$ deposition. The difference was a factor of 4.6 during the period 2040 to 2050 but decreased to a factor of 2 by the year 2200. Lakes that had longer hydrologic residence exhibited less historical acidification and therefore could achieve a higher ANC in response to chemical recovery compared with lakes that had short hydrologic residence times.	<a href="#">Zhou et al. (2015c)</a>
Adirondack Mountains	PnET-BGC	Lakes	TMDLs for 128 acid-impaired lakes	Model simulations suggested that an S TL equal to 79 eq S/ha/yr (representing a 60% decrease from ambient deposition) would lead to ANC recovery at a rate of 0.18 $\mu\text{eq/L/yr}$ through 2050, with reduced rate of recovery thereafter.	<a href="#">Fakhraei et al. (2014)</a>
Adirondack Mountain lakes and Appalachian Mountain streams	SSWC	Lakes and streams	Combined deposition load of sulfur and nitrogen to which a stream and its watershed could be subjected and still have a surface water concentration ANC of 50 $\mu\text{eq/L}$ on an annual basis	To achieve ANC = 50 $\mu\text{eq/L}$ on average, critical load of sulfur and nitrogen for lakes in the Adirondack Mountains is 1,620 eq/ha/yr, while for central Appalachian streams is 3,700 eq/ha/yr.	<a href="#">NAPAP (2011)</a>
NY	MAGIC and regional extrapolation of model	Streams and lakes	Development and application of tools to document and quantify TL and their exceedances	To achieve ANC values of 50 and 20 $\mu\text{eq/L}$ in the year 2050 and 2100, the TL to protect against acidification of surface waters was exceeded throughout the Adirondack Mountains.	<a href="#">Sullivan (2015)</a>

**Table 8-8 (Continued): Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification.**

Region	Model	Type of Ecosystem	Focus	Critical Loads	Publication
Hubbard Brook Experimental Forest, NH	PnET-BGC	Stream	Importance of incorporating base cation deposition and climate in calculating TLs	Authors developed three-dimensional dynamic TL surfaces as function of $\text{NO}_3^-$ , S, and base cation deposition under varying climate scenarios.	<a href="#">Wu and Driscoll (2010)</a>
Virginia, West Virginia	SSWC	Streams	Estimation of CL and exceedance for stream watersheds exposed to S deposition	To achieve ANC = 50 $\mu\text{eq/L}$ , one-third of the stream length in the Blue Ridge ecoregion had CL $\leq 500$ eq/ha/yr. About half of the stream reach in the study region was in exceedance under assumed N saturation at steady state.	<a href="#">Sullivan et al. (2012b)</a>
Southern Appalachian Mountains	SSWC	Streams	Regional CLs	To achieve ANC = 50 $\mu\text{eq/L}$ , nearly one-third of the stream length in the southern Appalachian Mountain region had a critical load of S deposition <500 eq/ha/yr, which was less than the estimated regional average S deposition (600 eq/ha/yr). Due to the local geology, elevation, and cool and moist forest conditions, the percentage of streams in exceedance was highest for mountain wilderness areas and national parks, and lowest for privately owned valley bottom lands.	<a href="#">McDonnell et al. (2014b)</a>
Great Smoky Mountains National Park	PnET-BGC	Streams	TL values for 12 streams to achieve ANC of 0, 20, and 50 $\mu\text{eq/L}$ by 2050	To achieve ANC values of 0, 20, and 50 $\mu\text{eq/L}$ , the level of $\text{NO}_3^- + \text{SO}_4^{2-}$ deposition necessary to achieve a given ANC target was approximately a linear function of current ANC. Most streams could not achieve ANC = 50 $\mu\text{eq/L}$ ; some could not achieve ANC = 20 $\mu\text{eq/L}$ . Simulated mean projected stream ANC of 71 $\mu\text{eq/L}$ (range 32 to 107 $\mu\text{eq/L}$ ) prior to industrial development (~1850) decreases in response to historical acidic deposition to 33 $\mu\text{eq/L}$ (-13 to 88 $\mu\text{eq/L}$ ) in 2007.	<a href="#">Zhou et al. (2015a)</a>

**Table 8-8 (Continued): Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification.**

Region	Model	Type of Ecosystem	Focus	Critical Loads	Publication
Great Smoky Mountains NP	PnET-BGC	Streams	TL to achieve preindustrial ANC and estimated preindustrial ANC minus 20 µeq/L	The median value of the simulated background (1,850) stream ANC was 50 µeq/L, with estimates for individual watersheds ranging from 28 to 80 µeq/L. Simulated ANC recovery per equivalent decrease in the deposition of NH <sub>4</sub> <sup>+</sup> was more pronounced than that driven by comparable decreases in the deposition of SO <sub>4</sub> <sup>2-</sup> . This finding was attributed to continued S adsorption and low levels of N retention in the modeled watersheds.	<a href="#">Fakhraei et al. (2016)</a>
Great Smoky Mountains NP	PnET-BGC	Streams	TL to achieve a pH of 6.0 by 2150	Critical loads ranged between 240 and 960 eq/ha/yr of SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> + NH <sub>4</sub> <sup>+</sup> deposition to eight of the twelve watersheds. For the remaining four watersheds, no reduction in deposition was sufficient to achieve pH of 6 by 2150.	<a href="#">Fakhraei et al. (2017a)</a>
Shenandoah	MAGIC	Stream	TL values for 14 streams to achieve ANC = 50 µeq/L in 2100	To achieve ANC = 50 µeq/L in the year 2100, median modeled streams located on siliciclastic geology had TL about 214 eq S/ha/yr, substantially lower than ambient deposition.	<a href="#">Sullivan et al. (2008)</a>
NE, Rocky Mountains, Sierra, NV	Empirical	Lakes	CL of N for acidification of lakes	To achieve ANC = 0 µeq/L, critical loads to protect against episodic acidification were 286 eq N/ha/yr in west and 571 eq N/ha/yr in NE.	<a href="#">Baron et al. (2011b)</a>
Sierra, NV	SSWC	Lakes	CL of acidity for 208 lakes	To achieve ANC = 10 µeq/L, median CL was 149 eq/ha/yr and 16–17% of study lakes were in exceedance.	<a href="#">Shaw et al. (2014)</a>

**Table 8-8 (Continued): Recent aquatic critical load and target load modeling studies in the U.S. to protect against aquatic acidification.**

Region	Model	Type of Ecosystem	Focus	Critical Loads	Publication
N/A	Various	Various	Application of CL and ES principles for public land management and natural resources policy decision making	A conceptual framework was proposed that illustrates how CL and ES can be combined, using as an example aquatic acidification.	<a href="#">Sullivan (2012)</a>

ANC = acid neutralizing capacity; Ca = calcium; CL = critical load; eq = equivalent; ES = ecosystem service; ha = hectare; kg = kilogram; L = liter; m = meter;  $\mu\text{eq}$  = microequivalent; MAGIC = Model of Acidification of Groundwater in Catchments; N = nitrogen; NE = northeast;  $\text{NO}_3^-$  = nitrate; PnET-BGC = Photosynthesis and Evapotranspiration-Biogeochemical; S = sulfur;  $\text{SO}_4^{2-}$  = sulfate; SSWC = Steady-State Water Chemistry; TL = target load; yr = year.

#### 8.5.4.1.2.1 Steady-State Critical Load Modeling

Steady-state CLs can be derived from mathematical mass-balance models under assumed or modeled equilibrium conditions based in part on water quality measurements. The models used to derive steady-state CLs vary in complexity with regard to process representation. However, a fundamental aspect of the various modeling approaches is the calculation of elemental mass balances.

[NAPAP \(2011\)](#) calculated steady-state aquatic CLs to protect southern Appalachian Mountain streams and Adirondack Mountain lakes against the combined load of S and N deposition below which the ANC level would be expected to support healthy aquatic ecosystems. Research has shown that surface waters with ANC values greater than  $50 \mu\text{eq/L}$  tend to protect most fish (including native [to eastern U.S.] brook trout) and other aquatic organisms [see [Table 8-3](#), which describes these changes; [Driscoll et al., 2001b](#)]. The CL can be calculated to represent the individual or combined deposition load of S and/or N to which a stream and its watershed could be subjected and still have a surface water ANC of  $50 \mu\text{eq/L}$  on an annual basis.

[Sullivan et al. \(2012b\)](#) and [McDonnell et al. \(2012\)](#) developed an approach for deriving regional estimates of base cation weathering to support steady-state CL estimates for the protection of southern Appalachian Mountain streams against acidification in three ecoregions of Virginia and West Virginia. Weathering estimates at the study watersheds were developed using MAGIC and extrapolated to the full study region using landscape characteristics available as regional coverages. Calculated CL values were low at many locations, suggesting high acidification sensitivity. In the Blue Ridge ecoregion, calculated CL values to maintain stream ANC at  $50 \mu\text{eq/L}$  were less than  $500 \text{ eq/ha/yr}$  at

one-third of the study sites. About half or more of the stream length in the study region was in exceedance of the CL of S for protecting aquatic resources to an ANC level of 50  $\mu\text{eq/L}$  over the long term.

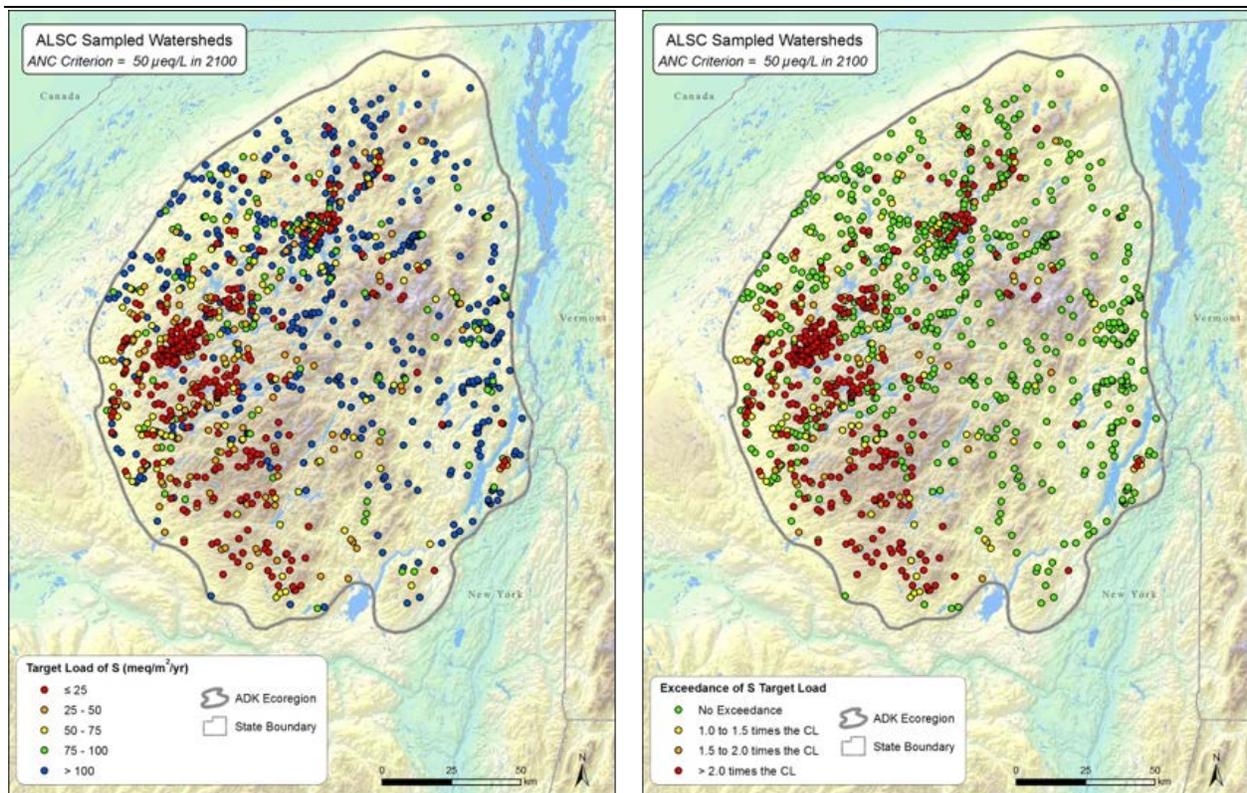
In another model simulation for Appalachian Mountain streams, [McDonnell et al. \(2014b\)](#) calculated critical values, including steady-state aquatic CLs to protect streams against acidification. They considered an ANC threshold of 50–100  $\mu\text{eq/L}$  to be generally protective of ecological health [cf; [U.S. EPA \(2009c\)](#); [Cosby et al. \(2006\)](#)]. The study area included mainly streams in southern Pennsylvania, Maryland, Virginia, West Virginia, North Carolina, Tennessee, and northern Georgia. Weathering values were first determined using the MAGIC model ([Povak et al., 2014](#)) and extrapolated to the full study region using machine learning/linear regression models. These values were then used as inputs to the Steady-State Water Chemistry (SSWC) model to calculate regional CLs. Nearly one-third of the stream length assessed in the study region had a CL of S deposition <500 eq/ha/yr, which was below the estimated regional average S deposition (600 eq/ha/yr). The percentage of streams in exceedance was highest for mountain wilderness areas and national parks and lowest for privately owned valley bottom lands.

[Shaw et al. \(2014\)](#) applied two variants of the SSWC model (one based on the F-factor approach and the other determined empirically) to estimate CLs for 2008 lakes in Class I and II wilderness areas in the Sierra Nevada. It was estimated that slightly more than one-third of the lakes received acidic deposition higher than the estimated CL. Lakes included in the model runs were generally dilute, with mean ANC = 56.8  $\mu\text{eq/L}$ . Critical loads for acid deposition were estimated to protect ANC to benchmark values of 0, 5, 10, and 20  $\mu\text{eq/L}$ , which span the range of minimum ANC values observed in Sierra Nevada lakes. Median CLs were 217, 186, 157, and 101 eq (S + N)/ha/yr to achieve ANC = 0, 5, 10, and 20  $\mu\text{eq/L}$ , respectively. The median CL for granitic watersheds based on a critical ANC limit of 10  $\mu\text{eq/L}$  was 149 eq/ha/yr.

#### **8.5.4.1.2.2 Target and Dynamic Critical Load Modeling**

To simulate the dynamic aspects of damage and recovery, a dynamic model based on hydrogeochemical processes is required. Dynamic models can be used to simulate soil or water chemistry or biological response or to calculate a TL within a specified management timeframe, such as for example the year 2100. Alternatively, a dynamic model can be used to calculate a comparable long-term steady-state CL by applying the model to a point in the distant future. Since the 2008 ISA, dynamic modeling of CLs has been focused on the Adirondacks, Appalachians, and the Rocky Mountains/Sierra Nevada ([Table 8-8](#)).

In the Adirondacks region, the MAGIC model was used by [Sullivan et al. \(2012a\)](#) to estimate the TLs that would protect the acid-base chemistry of lakes at different ANC levels. The 117 TLs were calculated for two time periods (2050 and 2100) and three levels of protection (ANC = 0, 20, and 50  $\mu\text{eq/L}$ ) based on the MAGIC model. Results of the 117 simulated TLs, and associated exceedances, were extrapolated to the regional population of Adirondack lakes. About 30% of the lakes had TL <500 eq/ha/yr to protect lake ANC to 50  $\mu\text{eq/L}$ . About 600 lakes received S deposition in exceedance of the TL required to protect to ANC = 50  $\mu\text{eq/L}$ , in some cases by more than a factor of two. Based on the model simulations, some critical criteria threshold values were not obtainable, even when S deposition was decreased to zero ([Figure 8-13](#)).



ADK = Adirondack; ALSC = Adirondack Lakes Survey Corporation; ANC = acid neutralizing capacity; CL = critical load; L = liter; meq = milliequivalent;  $\mu\text{eq}$  = microequivalent.; S = sulfur.

To convert mapped values to units of eq S/ha/yr, multiply by 10.

Source: [Sullivan et al. \(2012a\)](#).

**Figure 8-13 Target loads for sulfur deposition in the Adirondack Park to protect lake acid neutralizing capacity to 50  $\mu\text{eq/L}$  in the year 2010 (left map) and their exceedance (right map).**

Simulations using the dynamic PnET-BGC model ([Zhou et al., 2015c](#)) for the Constable Pond watershed (a chronically acidified drainage area in the Adirondack Park) suggested that future decreases in  $\text{SO}_4^{2-}$  deposition would be more effective in increasing the lake water ANC than equivalent decreases in  $\text{NO}_3^-$  deposition. Biophysical factors that affected CLs and TLs included hydrologic residence time. Lakes with longer hydrologic residence time exhibited less historical acidification and, therefore, could achieve a higher ANC in response to chemical recovery compared with lakes that had short hydrologic residence times. This difference was attributed to in-lake production of ANC in the lakes having long hydrologic residence time. The model outputs further suggested that forest cutting could enhance acidification by the removal of nutrient base cations along with the removal of forest biomass. However, forest cutting could also enhance retention of atmospherically deposited N in an aggrading forest ecosystem.

In another modeling study using PnET-BCG, [Zhou et al. \(2015b\)](#) evaluated lake water chemistry and the species richness of fish and total zooplankton in 20 Adirondack watersheds in response to historical acidic deposition and under future deposition scenarios. Historical acidification in the lakes was related to the total ambient deposition of  $\text{SO}_4^{2-} + \text{NO}_3^-$ , the Ca weathering rate, and the simulated preindustrial ANC in the year 1850. In the modeled watersheds, changes in the concentration of  $\text{Al}^{3+}$  since the onset of acidic deposition were related to the Ca weathering rate and the hindcast value of ANC in the year 1850. Estimated preindustrial ANC for the study lakes ranged from 18 to 190  $\mu\text{eq/L}$ . Modeling results suggested that lake ANC, fish richness, and total zooplankton species richness would increase under hypothetical decreases in future acidic deposition. However, the simulations suggested that biological and chemical recovery may not be attainable in all of the lakes ([Zhou et al., 2015b](#)).

Total maximum daily load (TMDL) modeling analysis by [Fakhraei et al. \(2014\)](#) for 128 Adirondack lakes designated by New York as acid-impaired under the Clean Water Act suggested that a further decrease in S deposition of 60% from ambient levels would allow about 30% of the impaired lakes to achieve the brook trout protection ANC level of 11  $\mu\text{eq/L}$  by the year 2050, with an additional 30% recovering by the year 2200.

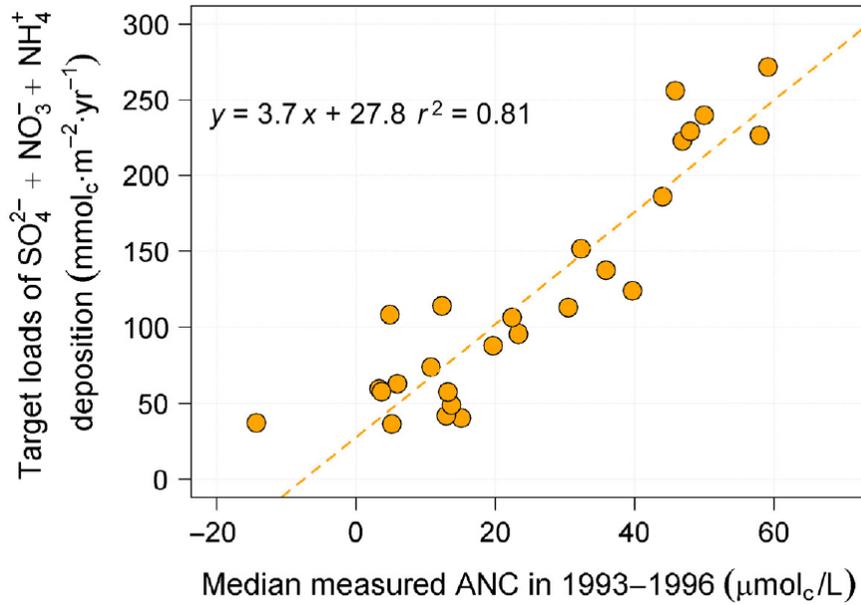
Using the same model (PnET-BGC), [Zhou et al. \(2015a\)](#) simulated past and future effects of N and S acidity on stream chemistry of 12 watersheds in the Great Smoky Mountain National Park. Three target levels of ANC (0, 20, and 50  $\mu\text{eq/L}$ ) were based on a range of protection of aquatic life from “minimal” to “considerable.” Model simulations suggested that the level of  $\text{NO}_3^- + \text{SO}_4^{2-}$  deposition necessary to achieve a given ANC target was approximately a linear function of current ANC. Target loads of  $\text{NO}_3^- + \text{SO}_4^{2-}$  deposition for the 12 study streams ranged from 270 to 3,370  $\text{eq/ha/yr}$  to reach an ANC of 0  $\mu\text{eq/L}$  by 2050, 0–2,340  $\text{eq/ha/yr}$  to reach ANC of 20  $\mu\text{eq/L}$  by 2050, and 0–1,400  $\text{eq/ha/yr}$  to

reach an ANC of 50  $\mu\text{eq/L}$  by 2050. However, the majority of the 12 streams could not achieve the ANC target of 50  $\mu\text{eq/L}$  by 2050. This was also true to a lesser extent for the target of ANC = 20  $\mu\text{eq/L}$ .

[Fakhraei et al. \(2016\)](#) and [Fakhraei et al. \(2017a\)](#) addressed the likelihood that acidified streams in Great Smoky Mountains National Park (GRSM) can recover from the adverse impacts of S and N deposition and restore biotic health, and how long that might take. They defined the point of harmful effects on the aquatic ecosystems based on converting pH criteria to ANC then modeling ANC below defined thresholds, using the PnET-BGC biogeochemical model. The studies updated the previous model application by [Zhou et al. \(2015b\)](#) by including recent large decreases in S and oxidized N deposition and all streams in the park listed by Tennessee as water quality impaired under the Clean Water Act (303(d) listed). Model simulations suggested that TLs varied with measured ANC ([Figure 8-14](#)) and that stream recovery from previous acidification has lagged behind decreases in S and N deposition due to the dynamics of S adsorption on soils. The TLs varied with measured ANC in this simulation because the relationship between pH and ANC is not linear and because stream  $\text{CO}_2$  can have a strong impact on pH. Simulated ANC increases were larger per unit decrease in  $\text{NH}_4^+$  deposition than per unit decrease in  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  deposition. This finding was attributed to high S adsorption and limited N retention in watershed soils. Modeling results were extrapolated to other streams throughout the park. The extrapolation was based on observed linear relationships between median ANC measured during the period 1993–1996 and the TLs to achieve various ANC targets. A fixed ANC target of 20  $\mu\text{eq/L}$  was considered, along with two other targets that were based on model simulation of preindustrial ANC (ANC in 1850 and ANC 20  $\mu\text{eq/L}$  lower than ANC in 1850). The latter target was selected because the model suggested that ANC in 1850 was generally not obtainable in response to further decreases in S and N deposition. [Figure 8-15](#) shows spatial patterns in TL exceedance of ambient S and N deposition for two endpoint years (2050 and 2150) and two ANC recovery targets (20  $\mu\text{eq/L}$  and 20  $\mu\text{eq/L}$  less than modeled preindustrial ANC). For the 303(d)-listed stream watersheds at high elevations within the park critical loads ranged between 240 and 960  $\text{eq/ha/yr}$  of  $\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$  deposition to eight of the twelve watersheds ([Fakhraei et al., 2017a](#)). For streams in the remaining four watersheds, no reduction in deposition was sufficient to achieve pH of 6 by 2150 and recovery in these streams is projected to take centuries.

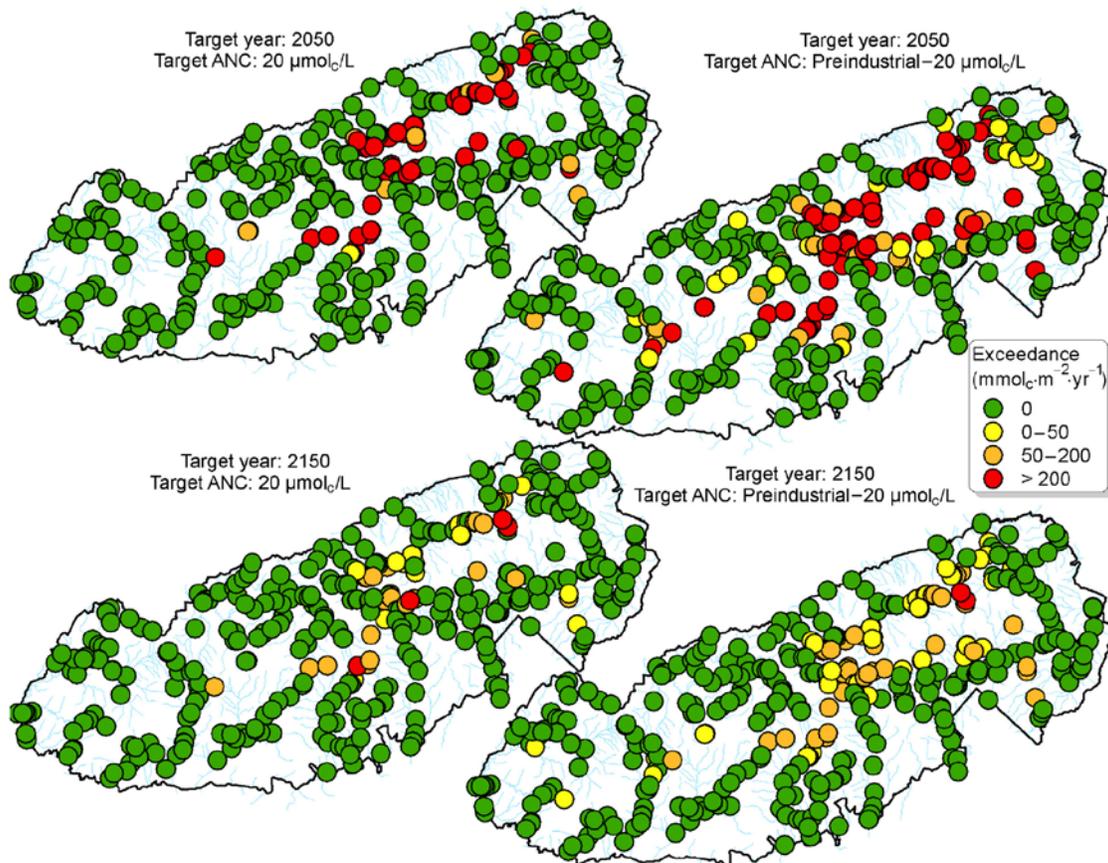
MAGIC modeling based on simulations of past and future acid-base chemistry of 14 streams in Shenandoah National Park identified a TL of about 188  $\text{eq S/ha/yr}$  in the median modeled stream located on sensitive (siliciclastic) bedrock to achieve ANC = 50  $\mu\text{eq/L}$  in 2100. This was 77% lower than the S deposition in 1990 ([Sullivan et](#)

al., 2008). Many streams had ambient ANC < 20  $\mu\text{eq/L}$ . Hindcast simulations suggested that preindustrial ANC was above 50  $\mu\text{eq/L}$  in all of the study streams.



Source: [Fakhraei et al. \(2016\)](#).

**Figure 8-14.** Modeled target loads and median measured Acid Neutralizing Capacity (ANC) in the period 1993 to 1996 from 30 Great Smoky Mountain National Park (GRSM) streams to achieve an ANC of 20  $\mu\text{eq/L}$  by the year 2150.



Source: [Fakhraei et al. \(2016\)](#).

**Figure 8-15.** Exceedance level of current  $\text{NO}_3^- + \text{SO}_4^{2-}$  atmospheric deposition for 387 stream sites in the GRSM. Exceedances were calculated for the years 2050 and 2150 using two targets for modeled stream ANC recovery of  $20 \mu\text{molc/L}$  and  $20 \mu\text{molc/L}$  less than the simulated preindustrial ANC.

#### 8.5.4.2 International Critical Loads

Critical load concepts were initially developed in Europe and only more recently widely applied in the U.S. and Canada. Work on CLs has continued internationally as a basis for setting environmental policy. Some of the recent work conducted outside the U.S. is summarized below. Previous regional CL assessments in Canada have often employed an empirical clay-based soil texture approximation to estimate weathering as input for aquatic and terrestrial steady-state CL modeling [Krzyzanowski and Innes \(2010\)](#)

estimated steady-state CLs, using the SSWC model, and associated exceedances for protecting freshwater ecosystems in First Nations territory in British Columbia against water acidification. Estimates of acidic deposition were not in exceedance of the CL at any of the study lakes.

The 1999 Gothenburg Protocol, under the Long-Range Transboundary Air Pollution (LRTAP) Convention of the United Nations Economic Commission for Europe (UNECE) was aimed at reducing the total area of Europe where acidic deposition exceeded CLs. In 2007, the Coordination Centre for Effects (CCE) of the International Cooperative Programme for Modeling and Mapping (part of the LRTAP Convention) issued a call to European countries for results from dynamic models of soil and water acidification. In response to this call, Norwegian scientists used the MAGIC model to project recovery of surface waters in Norway. [Larssen et al. \(2010\)](#) described the results for water quality and fish population status and considered implications for policy options. The modeling results suggested that surface waters will continue to recover slowly under existing emissions controls, but about 18% of Norway will still have lakes that receive acidic deposition that exceeds the CL to protect against aquatic acidification and in which water quality will continue to be insufficient to support viable populations of fish and other aquatic organisms.

Both measured and modeled data indicate past acidification and suggest some future chemical recovery at acid-sensitive locations throughout northern Europe. Some surface waters have experienced much greater levels of acidification than have acid-sensitive sites in the eastern U.S., For example, the MAGIC model was used by [Skeffington et al. \(2016\)](#) to simulate past and future trajectories in stream chemistry of a seriously acidified small forest watershed in England. Hindcast simulations suggested that ANC decreased from about 150 to 100  $\mu\text{eq/L}$  and pH decreased from 7.1 to 4.2. Hypothesized decreases in future acidic deposition suggested slow and prolonged chemical recovery over a period of 250 years to ANC = 43  $\mu\text{eq/L}$ .

[Bishop et al. \(2008\)](#) applied the SSWC model to lakes in northern Sweden, many of which are rich in organic matter. They argued that the SSWC model is not suitable for judging the acidification of individual lakes in regions such as northern Sweden where the extent of chronic acidification is relatively small and where organic influence on lake chemistry is pronounced. A variant of the SSWC model predicted preindustrial lake chemistry at 58 sites where paleolimnological reconstructions of lake chemistry were available. The authors noted a large discrepancy between SSWC predictions and diatom reconstructions, and this was attributed largely to short-term fluctuations in modern lake chemistry.

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## 8.6 Aquatic Acidification Summary and Causal Determinations

In the 2008 ISA, the body of evidence was sufficient to infer a causal relationship between acidifying deposition and changes in freshwater biota. Overall, the updated research synthesized in this ISA reflects incremental improvements in scientific knowledge of aquatic biological effects and indicators of acidification as compared with knowledge summarized in the 2008 ISA. Studies indicate that aquatic organisms have been affected by acidification at virtually all trophic levels in sensitive ecosystems and that these responses have been well characterized for several decades. Research and observations reported in the 2008 ISA showed consistent and coherent evidence for effects on aquatic biota, especially algae, benthic invertebrates, and fish that are most clearly linked to chemical indicators of acidification (pH, ANC, inorganic Al concentration). Effects on fish species are especially well understood, and many species have been documented to be adversely affected. Both in situ and lifestage experiments in fish support previous thresholds of chemical indicators and biological effects. Physiological perturbations at the organism level of biological organization can lead to effects on reproduction, growth, and survival. More species are lost with greater acidification, providing evidence of a biological gradient in effects. Biological shifts such as loss of acid-sensitive organisms, population declines, and decreased species richness have been reported from acid-sensitive regions of the U.S. and other countries. Despite reductions in acidifying deposition, many aquatic ecosystems across the U.S. are still experiencing effects on ecological structure and functioning at multiple trophic levels. New information is consistent with the conclusions of the 2008 ISA that **the body of evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biota, including physiological impairment and alteration of species richness, community composition, and biodiversity in freshwater ecosystems.** [Baker et al. \(1990a\)](#) conducted a rigorous review of the effects of acidification on aquatic biota for the 1990 National Acid Precipitation Assessment Program (NAPAP) State of Science/Technology reports. In the review, hundreds of laboratory studies, in situ bioassays, field surveys, whole-system field experiments, and mesocosm studies were evaluated to provide a synthesis of the effects of acidification on aquatic biota. The findings in that report, along with literature published after 1990 up to 2007, were included in the 2008 ISA. The summaries below integrate information known at the time of the 2008 ISA with newer studies. For most topics related to aquatic acidification, the fundamental understanding of mechanisms and biological effects has not changed; rather, additional studies lend further support to the findings from the previous ISA.

The effects of acidification on freshwaters in the U.S. and elsewhere were well characterized at the time of the 2008 ISA. The sensitivity of a watershed depends on watershed characteristics such as underlying geology and hydrological flowpaths

([Appendix 7](#)), and the sensitivity of species that make up the local biological community. Changes in biota are linked to chemical indicators in surface water ([Appendix 7](#); [Table 8-9](#)). As stated in the 2008 ISA, biological effects are primarily attributable to low pH and high inorganic Al concentration. ANC is also used as a chemical indicator of acidification because it integrates overall acid-base status and because surface water acidification models do a better job projecting ANC than pH and inorganic Al concentrations. However, ANC does not relate directly to the health of biota. The usefulness of ANC lies mainly in the association between ANC and the surface water constituents or parameters that directly cause or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

Acid-sensitive freshwater systems can either be chronically acidified or subject to periodic episodes of decreased pH and ANC and increased inorganic Al concentration. Chronically acidic lakes and streams were traditionally defined as having ANC <0 µeq/L. The ANC in freshwater systems where episodic acidification occurs may fall below 0 µeq/L for only a few hours to weeks in a given year ([Driscoll et al., 2001b](#)). During these acid episodes, water chemistry may exceed acid tolerance of resident aquatic biota. Biological effects of episodes may include fish mortality, changes in species composition, and declines in aquatic species richness across multiple taxa. Biological effects of chronic and episodic acidification have been most clearly documented for phytoplankton, zooplankton, aquatic invertebrates, and fish and can be linked to changes in the chemical indicators of aquatic acidification ([Table 8-9](#)). An ANC of >50 ueq/L was used as an indicator for acidification to an ANC level that may harm biota in the U.S. EPA National Lake Surveys ([U.S. EPA, 2009b](#)).

**Table 8-9 Ecological indicators for aquatic acidification.**

Key Indicators	Ecological Effect	Key References
Acid neutralizing capacity	Commonly set at ANC values less than 0, 20, 50, and 100 $\mu\text{eq/L}$ to correspond with decreasing levels of concern ( <a href="#">Figure 8-4</a> )	<a href="#">Driscoll et al. (2001b)</a> , <a href="#">MacAvoy and Bulger (1995)</a> , <a href="#">Baker et al. (1990a)</a> , <a href="#">U.S. EPA (2009b)</a>
Base cation surplus	0 $\mu\text{eq/L}$ —risk of inorganic Al leaching to streams	Section 3.2.1.5 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria <a href="#">U.S. EPA (2008a)</a> <a href="#">Lawrence et al. (2007)</a>
pH	<6.0—reduced number of fish species	<a href="#">Driscoll et al. (2001b)</a> , <a href="#">MacAvoy and Bulger (1995)</a> , <a href="#">Baker et al. (1990a)</a>
Inorganic Al	>2 $\mu\text{mol/L}$ (54 $\mu\text{g/L}$ )—toxic to brook trout and likely other aquatic biota	<a href="#">Baldigo et al. (2007)</a> , <a href="#">Driscoll et al. (2001b)</a> , <a href="#">Wigington et al. (1996a)</a> , <a href="#">MacAvoy and Bulger (1995)</a>

Al = aluminum; L = liter;  $\mu\text{eq}$  = microequivalent;  $\mu\text{g}$  = microgram.

Source: modified from [Fenn et al. \(2011b\)](#).

### 8.6.1 Phytoplankton

Phytoplankton, photosynthesizing forms of plankton, play important roles in freshwater systems as primary producers at the base of the aquatic ecosystem food web. These organisms, encompassing diatoms, cyanobacteria, dinoflagellates, and other algae, vary in tolerance of acidic conditions. Studies reviewed in the 2008 ISA reported reduced species richness of phytoplankton with the decreases in pH and increases in inorganic Al concentrations that are associated with acid-affected surface waters ([U.S. EPA, 2008a](#)). Effects were most prevalent in the 5 to 6 pH range ([Baker et al., 1990a](#)). Since the 2008 ISA, several paleolimnological and field studies have further linked phytoplankton community shifts to chemical indicators of acidification. For example, [Lacoul et al. \(2011\)](#) reviewed information on the effects of acidification on plankton in Atlantic Canada and observed that the greatest changes in phytoplankton species richness occurred over a pH range of 4.7 to 5.6, just beyond the interval (pH 5.5 to 6.5) where bicarbonate becomes depleted in the water.

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## 8.6.2 Zooplankton

Zooplankton, the animal forms of plankton, comprise many groups of small freshwater organisms including protozoans, rotifers, cladocerans, and copepods. Decreases in ANC and pH and increases in inorganic Al concentration were shown to contribute to the loss of zooplankton species and/or abundance in lakes in studies reviewed in the 2008 ISA ([Keller and Gunn, 1995](#); [Schindler et al., 1985](#)). Possible mechanisms for zooplankton sensitivity to low pH and ANC include ion regulation failure, reduced oxygen uptake, inability to reproduce, and inorganic Al toxicity ([U.S. EPA, 2008a](#)). Reported pH thresholds for zooplankton community alteration generally ranged from 5 to 6 in studies reviewed in the 2008 ISA. For example, a decrease in pH from 6 to 5 caused decreased species richness in zooplankton communities in lakes ([Holt et al., 2003](#); [Holt and Yan, 2003](#); [Locke and Sprules, 1994](#)). Newer studies support effects in a similar pH range. [Vinebrooke et al. \(2009\)](#) reported variations in phytoplankton and zooplankton communities during a whole-lake experimental acidification of Lake 302S in the Experimental Lakes area in Ontario. There was a negative effect on zooplankton species richness as pH decreased from 6.8 to 4.5. Acidification often reduces Ca availability in lake water and can affect growth and survival of *Daphnia* spp., an important prey item in many freshwater food webs ([Jeziorski et al., 2012b](#)). At ANC <0 µeq/L, zooplankton richness was low in Adirondack lakes [15 species in highly acidic lakes compared to 35 species at the highest values of ANC in the study [near 200 µeq/L; [Sullivan et al. \(2006a\)](#)].

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## 8.6.3 Benthic Invertebrates

Sediment-associated invertebrates such as bivalves, worms, gastropods, and insect larvae can be impacted by acidification because H<sup>+</sup> and Al can be directly toxic, causing disruption of ion regulation and reduced reproductive success. As reviewed in the 2008 ISA, decreases in ANC and pH and increases in inorganic Al concentration have been shown to contribute to the decline in abundance or loss of benthic invertebrate species in streams. Typically, pH below 5 virtually eliminate all mayflies, a common taxa used to assess water quality, along with other aquatic organisms from some streams ([U.S. EPA, 2008a](#); [Baker and Christensen, 1991](#)). Since the 2008 ISA, a survey of benthic macroinvertebrates by [Baldigo et al. \(2009\)](#) in 36 streams in the southwestern Adirondack Mountains indicated that 44 to 56% of macroinvertebrate communities were severely impacted by acidification at pH <5.1, moderately impacted at pH 5.1 to 5.7, and unaffected at pH above 6.4 ([Baldigo et al., 2009](#)). Thresholds of pH 5.2 to 6.1 were identified for sensitive invertebrates from Atlantic Canada; below these pH values,

changes in the abundance or presence of invertebrate taxa were observed ([Lacoul et al., 2011](#)).

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#### 8.6.4 Fish

The primary mechanism that controls the toxic effects of acidification on fish involves disruption of normal ion regulation at the gill surface, resulting in increased rates of ion loss, inhibition of ion uptake, and loss of gill function ([Bergman et al., 1988](#); [Wood and McDonald, 1987](#); [Leivestad, 1982](#); [McWilliams and Potts, 1978](#)). Responses to acidifying conditions include respiratory and circulatory failure. The effects of low pH, low ANC, and high inorganic Al concentrations have been well characterized in fish for many decades. Responses among fish species and lifestages within species to pH and Al in surface waters have been variable. In general, early lifestages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults ([Baker et al., 1990a](#); [Johnson et al., 1987](#); [Baker and Schofield, 1985](#)). Some of the most commonly studied species include brown trout, brook trout, and Atlantic salmon.

Further characterization of physiological responses (ion regulation, stress responses, gill Al accumulation) to acidification in fish, mostly Atlantic salmon, trout, and other salmonids, adds to the existing information on sublethal effects on individual fish species. Many of the newer studies were conducted in situ and reported varying sensitivity of different lifestages. Findings are consistent with physiological alterations in fish reported in the 2008 ISA. Several studies have assessed physiological changes associated with migratory activities. For example, a recent study assessed gill Al and NKA activity in smolts moving downstream in well-buffered and acid-impacted migration corridors in the northeastern U.S. ([Kelly et al., 2015](#)). In the acid-impacted river basin, the fish had elevated gill Al and lower gill NKA activity.

As summarized in [Baker et al. \(1990a\)](#) and studies reviewed in the 2008 ISA, fish populations in acidified streams and lakes of both Europe and North America have declined, and some have been eliminated as a result of atmospheric deposition of acids and resulting changes in pH, ANC, and inorganic Al concentrations in surface waters. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5 ([Cosby et al., 2006](#); [Sullivan et al., 2006a](#); [Driscoll et al., 2003b](#); [Bulger et al., 1999](#)). Additional pH thresholds published since the 2008 ISA generally reinforce these ranges, and several new studies consider the role of DOC in modulating pH and subsequent effects on biota. New studies on fish responses to chemical alarm cues show behavioral effects at pH <6.6. Characterization of ANC and its levels of concern have not changed appreciably with the newly available information.

Few or no fish species are found in lakes and streams that have very low ANC (near zero) and low pH [near 5.0; ([U.S. EPA, 2008a](#); [Sullivan et al., 2006a](#))]. The number of fish species generally increases at higher ANC and pH. The pH largely controls the bioavailability of Al ([Driscoll et al., 2001b](#)). Al is very toxic to fish, and thresholds of response to elevated concentrations of this metal in acidified waters are summarized in [Table 8-4](#).

Some of the most in-depth studies of the effects of acid stress on fish have been conducted in streams in Shenandoah National Park, VA ([Cosby et al., 2006](#)), and lakes in the Adirondack Mountains, NY ([Sullivan, 2015](#)). Effects on fish have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina ([Bulger et al., 2000](#); [Bulger et al., 1999](#); [SAMAB, 1996](#); [Charles and Christie, 1991](#)).

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### **8.6.5 Thresholds of Response**

As reviewed above, new thresholds have been identified in aquatic organisms ([Table 8-10](#)). However, this new information does not appreciably change the understanding of biological effects associated with chemical indicators or the levels at which effects occur. Evidence continues to strengthen findings in the 2008 ISA that high levels of acidification (especially to pH values below 5) eliminate sensitive species from freshwater streams.

**Table 8-10 Results of recent biological effects studies in surface waters indicative of thresholds of biological response to changes in water acidity.**

Life Forms and Effects	Region	Potential Tipping Points	Reference
Sensitive invertebrates present	Atlantic Canada	pH 5.2 to 6.1	<a href="#">Lacoul et al. (2011)</a>
Littoral macroinvertebrates	Northern Europe	pH 5.8 to 6.5	<a href="#">Schartau et al. (2008)</a>
Brook trout loss of whole-body Na	Great Smoky Mountains NP	pH 5.1	<a href="#">Neff et al. (2008)</a>
Brook trout loss of whole-body Na of 10 to 20%	Great Smoky Mountains NP	pH 4.9 to 5.1	<a href="#">Neff et al. (2009)</a>
Fish damage in lakes	Norway	ANC 67 µeq/L	<a href="#">Hesthagen et al. (2008)</a>
Juvenile brown trout mortality in high DOC streams	Sweden	pH 4.8 to 5.4	<a href="#">Serrano et al. (2008)</a>
Embryo and yolk sac fry survival during episodes in DOC-rich lakes	Sweden	pH 4.0	<a href="#">Serrano et al. (2008)</a>
Toxicity to brown trout in humic streams	Northern Europe	pH 5.0; inorganic aluminum 20 µg/L	<a href="#">Andrén and Rydin (2012)</a>
Presence of macrophytes	Atlantic Canada	pH 5.0	<a href="#">Lacoul et al. (2011)</a>
Aquatic bird breeding	Atlantic Canada	pH 5.5	<a href="#">Lacoul et al. (2011)</a>

ANC = acid neutralizing capacity; DOC = dissolved organic carbon; L = liter; µeq = microequivalent; µg = microgram; Na = sodium; NP = National Park.

### 8.6.6 Biological Recovery

Biological recovery ([Section IS.11](#)) can occur only if chemical recovery ([Appendix 7](#)) is sufficient to allow growth, survival, and reproduction of acid-sensitive plants and animals ([Driscoll et al., 2001b](#)). Modeling studies in the northeastern and southeastern U.S. suggest that full chemical recovery may take many decades or not occur at all due to the dynamics of S adsorption and desorption and to long-term Ca depletion of soils. As reported in the 2008 ISA, biological recovery lags behind chemical recovery in many aquatic systems, and the time required for biological recovery after chemical recovery is complete is uncertain ([U.S. EPA, 2008a](#)). Ecosystems deemed to be on a recovery trajectory are those found to be moving towards a mix of species presence and abundance that approximates the undisturbed state.

Since the publication of the 2008 ISA, additional studies have assessed recovery of benthic organisms, although most of this research has been conducted in Canadian and European waters. New studies continue to support these earlier observations. In general, recovery of plankton and benthic invertebrates is observed prior to recovery of fish populations, although most biological communities studied to date have not returned to preacidification conditions, even after recovery of chemical parameters. In a study reviewed in the 2008 ISA, zooplankton recovery in experimentally acidified Little Rock Lake in Wisconsin took one decade, with approximately 40% of the zooplankton species experiencing a lag time of 1 to 6 years ([Frost et al., 2006](#)). In an experimentally acidified lake in Canada, zooplankton species diversity partially rebounded to preacidification levels as pH returned back to 6.1, with rotifers recovering less than crustaceans ([Malley and Chang, 1994](#)). Newer studies from the Sudbury Lakes region of Canada indicate substantial recovery of copepods and cladocerans at pH 5.5 and higher in previously acidified lakes ([Valois et al., 2011](#)).

In the 2008 ISA, recovery of fish populations following liming or reduction of deposition was reported in several studies. Newer studies have documented successful reintroduction of brook trout in previously acidified Adirondack water bodies (Brooktrout Lake) or recolonization (Honedaga Lake) by populations in tributary refuges ([Sutherland et al., 2015](#); [Josephson et al., 2014](#)). Fish community shifts from historical acidification have been observed in the upper mainstem of Hubbard Brook ([Warren et al., 2008](#)) and other locations.

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### 8.6.7 Most Sensitive and Most Affected Regions

The extent and distribution of sensitive ecosystems and regions in the U.S. were well known at the time of the 2008 ISA. In the U.S., surface waters that are most sensitive to acidification based on ANC are largely found in the Northeast, southern Appalachian Mountains, FL, the upper Midwest, and the mountainous West ([McDonnell et al., 2014b](#); [Greaver et al., 2012](#); [Campbell et al., 2004a](#); [Driscoll et al., 2001b](#); [Baker et al., 1990b](#); [Omernik and Powers, 1983](#)). Levels of acidifying deposition in the West are low in most areas, acidic surface waters rare, and the extent of chronic surface water acidification that has occurred to date has been limited ([Charles and Christie, 1991](#)). Episodic acidification does occur in both the East and West at some acid-sensitive locations, and this is part natural and part human-caused. Geographic patterns in acidification sensitivity vary in response to spatial differences in geology, hydrologic flow paths, presence and depth of glacial till, climate, and others. [Sullivan \(2017\)](#) mapped the locations of known lakes and streams that had low ANC across the country ([Figure 8-11](#)).

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## 8.6.8 Critical Loads

Since the 2008 ISA, considerable CL research has been conducted in the U.S. New generalized empirical CL estimates include 571 eq N/ha/yr in the Northeast and 286 eq N/ha/yr in the West for episodic acidification of high elevation lakes under high-flow conditions ([Baron et al., 2011b](#)). [Heard et al. \(2014\)](#) estimated CL = 74 eq/ha/yr to protect against chronic acidification in high-elevation lakes in the Sierra Nevada. Steady-state CLs have been derived at many locations since the 2008 ISA. Steady-state CLs of S and N for lakes in the Adirondack Mountains (1,620 eq/ha/yr) and for the central Appalachian streams (3,700 eq/ha/yr) were calculated for maintaining a surface water ANC of 50  $\mu\text{eq/L}$  on an annual basis ([NAPAP, 2011](#)). [Sullivan et al. \(2012b\)](#) calculated CL values in the Blue Ridge ecoregion for maintaining stream ANC at 50  $\mu\text{eq/L}$ . The calculated CLs were less than 500 eq/ha/yr at one-third of the study sites. Observations showed that about one-half or more of the stream length in the study region was in exceedance of the CL of S deposition for protecting aquatic resources to an ANC = 50  $\mu\text{eq/L}$  over the long term. [McDonnell et al. \(2014b\)](#) calculated steady-state aquatic CLs to protect southern Appalachian Mountain streams against acidification to ANC = 50  $\mu\text{eq/L}$  and other critical benchmark values. Results showed that nearly one-third of the stream length in the study region (mainly streams in Virginia, West Virginia, North Carolina, and Tennessee) had a CL of S deposition <500 eq/ha/yr, which was less than the estimated regional average S deposition (600 eq/ha/yr). Critical loads for acid deposition to lakes in Class I and II wilderness areas of the Sierra Nevada were estimated in 2008 to protect ANC to 0, 5, 10, and 20  $\mu\text{eq/L}$  levels, which span the range of minimum ANC values observed in those lakes. Median CLs were 217 (ANC = 0), 186 (ANC = 5), 157 (ANC = 10), and 101 (ANC = 20) eq/ha/yr. The median CL for granitic watersheds based on a critical ANC limit of 10  $\mu\text{eq/L}$  was 149 eq/ha/yr. It was estimated that slightly more than one-third of the lakes received acidic deposition higher than their CL.

In addition to the steady-state and empirical CLs described above, CL estimates are available from dynamic modeling.  $\text{NO}_3^-$  leaching in stream water in California was both simulated (by the DayCent model) and determined empirically to be approximately 1,214 eq N/ha/yr ([Fenn et al., 2008](#)). [Zhou et al. \(2015a\)](#) simulated past and future effects of N and S on stream chemistry of 12 watersheds in the Great Smoky Mountain National Park. Three target levels of ANC (0, 20, and 50  $\mu\text{eq/L}$ ) were used, based on a range of protection of aquatic life from minimal to considerable. TLs of  $\text{NO}_3^- + \text{SO}_4^{2-}$  deposition for the 12 study streams ranged from 270 to 3,370 eq/ha/yr to reach ANC = 0  $\mu\text{eq/L}$  by 2050, 0 to 2,340 eq/ha/yr to reach ANC = 20  $\mu\text{eq/L}$  by 2050, and 0 to 1,400 eq/ha/yr to reach ANC = 50  $\mu\text{eq/L}$  by 2050. However, the majority of streams could not achieve the ANC target of 50  $\mu\text{eq/L}$ . This was also true to a lesser extent for the target of

ANC = 20  $\mu\text{eq/L}$ . Modeling studies also suggested that complete recovery may not be possible in the Appalachian Mountains ([Sullivan et al., 2011b](#)). For some sites, one or more of the selected critical ANC levels (0, 20, 50, 100  $\mu\text{eq/L}$ ) could not be achieved by 2100, even if S deposition was decreased to zero and maintained at that level throughout the simulation. MAGIC modeling based on simulations of past and future acid-base chemistry of 14 streams in Shenandoah National Park identified a target load of about 188 eq kg S/ha/yr to achieve ANC = 50  $\mu\text{eq/L}$  in 2100 in the median modeled stream located on sensitive (siliciclastic) bedrock, which was 77% lower than the S deposition in 1990 ([Sullivan et al., 2008](#)). Many streams had ambient ANC <20  $\mu\text{eq/L}$ , although hindcast simulations suggested that preindustrial ANC was above 50  $\mu\text{eq/L}$  in all of the study streams.

In the Adirondack Mountains, TLs were calculated for two time periods (2050 and 2100) and three levels of protection (ANC = 0, 20, and 50  $\mu\text{eq/L}$ ). Results of simulated TLs, and associated exceedances, were extrapolated to the regional population of lakes. About 30% of the lakes had TL <500 eq/ha/yr to protect lake ANC to 50  $\mu\text{eq/L}$  ([Sullivan et al., 2012a](#)). Also in the Adirondack Mountains, [Zhou et al. \(2015c\)](#) ran simulations using the PnET-BGC model, which suggested that future decreases in  $\text{SO}_4^{2-}$  deposition would be more effective in that region in increasing the lake water ANC than equivalent decreases in  $\text{NO}_3^-$  deposition. In another modeling study of 20 Adirondack watersheds, lake ANC and fish and total zooplankton species richness were projected to increase under hypothetical decreases in future acidic deposition, but model projections suggested that lake ecosystems may not achieve complete chemical and biological recovery in the future ([Zhou et al., 2015b](#)). Estimates of preindustrial ANC for the study lakes ranged from 18 to 190  $\mu\text{eq/L}$ . The magnitude of simulated historical acidification represented by ANC loss ranged from about 26 to 100  $\mu\text{eq/L}$ .

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## APPENDIX 9    BIOLOGICAL EFFECTS OF FRESHWATER NITROGEN ENRICHMENT

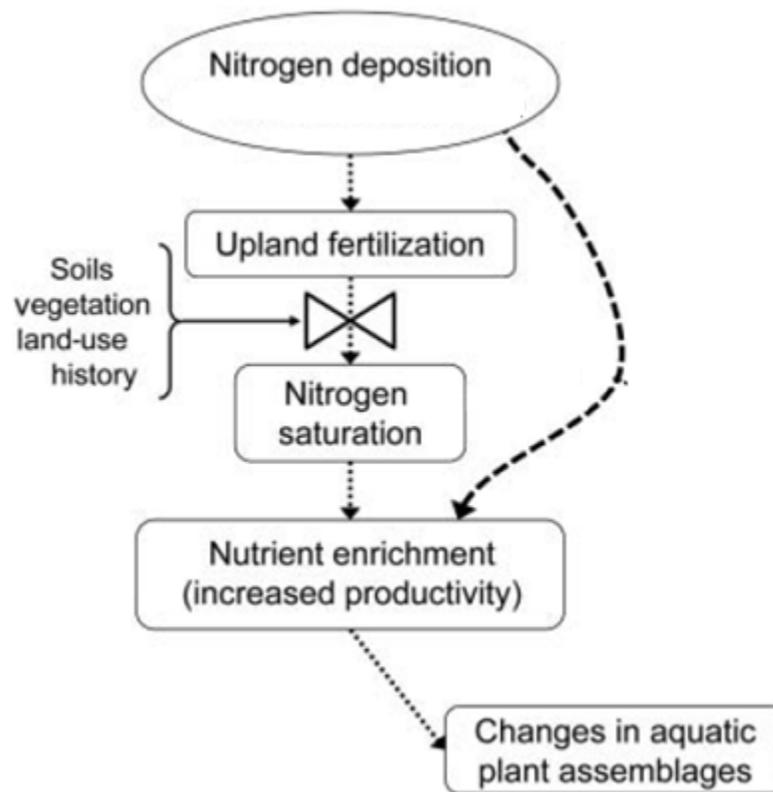
This appendix characterizes the biological effects of nitrogen (N) nutrient enrichment from atmospheric deposition to freshwater systems. Biogeochemical processes and chemical indicators associated with nutrient enrichment of fresh waters are discussed in [Appendix 7](#). Atmospheric deposition constitutes only a portion of total N load in many water bodies; however, it may be the dominant source of N in some remote aquatic ecosystems, such as headwater and lower order streams and alpine lakes, which are more affected by N deposition than other sources of N. [Appendix 9.1](#) presents an overview of freshwater nutrient enrichment in these systems and includes a discussion on the characteristics of water bodies sensitive to N deposition, the effects of N deposition on nutrient limitation, phosphorus (P) interactions, and climate modification of N response. Inputs of P have direct implications for how ecosystems respond to N deposition, and recent trends in increased atmospheric deposition of P are discussed in this context. Indicators of biological responses to nutrient enrichment ([Appendix 9.2](#)) effects of N on species diversity, ecosystem structure, and function ([Appendix 9.3](#)) and emerging research on the links between nutrient enrichment and animal behavior and disease ([Appendix 9.4](#)) provide a basis for identifying thresholds of biological response ([Appendix 9.5](#)) and determining causation based on new information and evidence from prior N assessments ([Appendix 9.6](#)).

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### 9.1    Introduction to Nitrogen Enrichment and Eutrophication in Freshwater Systems

In the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria* (2008 ISA), the body of evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in freshwater ecosystems ([U.S. EPA, 2008a](#)). Increased atmospheric N inputs to freshwater systems via runoff or direct deposition, especially to N limited and N and phosphorus (P) colimited systems, can stimulate primary productivity ([Figure 9-1](#)). Eutrophication is the process of enriching a water body with nutrients resulting in increased growth and change in the composition of primary producers (algae and/or aquatic plants). One of the consequences of eutrophication is low oxygen levels in the water body when these primary producers decompose. Changes in biological indicators of N enrichment, including chlorophyll *a*, phytoplankton

(free-floating algae) biomass, periphyton (algae attached to a substrate) biomass, and diatoms (major algal group with cell walls made of silica), provide evidence for N effects. The transport of atmospheric N inputs downstream can exacerbate eutrophic conditions in higher order streams, rivers, and lakes. Atmospheric deposition to watersheds affects processes along the freshwater-to-ocean continuum, including coastal and estuarine systems ([Appendix 10](#)). New information is consistent with the conclusions of the 2008 ISA that **the body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota, including altered growth and productivity, species richness, community composition, and biodiversity due to N enrichment in freshwater ecosystems.**



Source: Modified from [Baron et al. \(2011b\)](#).

**Figure 9-1** Conceptual model of the influence of atmospheric nitrogen deposition on freshwater nutrient enrichment.

Based on the studies described throughout [Appendix 9](#) and in the 2008 ISA, the freshwater ecosystems in the U.S. most likely to be sensitive to N deposition are headwater streams, lower order streams, and alpine lakes, which have very low nutrients and productivity and are far from local pollution sources ([U.S. EPA, 2008a](#)). Even small inputs of N in these water bodies can increase nutrient availability or alter the balance of N and P, which can stimulate growth of primary producers and lead to changes in species richness, community composition, and diversity. Remote mountain lakes in the western U.S. are naturally oligotrophic and are considered among the aquatic ecosystems most sensitive to N deposition ([Williams et al., 2017b](#)). A portion of these lakes and streams in the western U.S. are in Class I wilderness areas ([Williams et al., 2017b](#); [Clow et al., 2015](#); [Nanus et al., 2012](#)). Survey data and fertilization experiments from studies reviewed in the 2008 ISA have documented increases in algal productivity as well as species changes and reductions in diversity at high-elevation lakes in the western U.S. in response to increased availability of N ([U.S. EPA, 2008a](#)). Some examples include the Snowy Range in Wyoming, the Sierra Nevada, Lake Tahoe, and the Colorado Front Range. In studies reviewed in the 2008 ISA, atmospheric N deposition (approximately 1 to 5 kg N/ha/yr) can cause an increase in phytoplankton and periphyton biomass in some alpine lakes. For example, in both the Beartooth Mountains of Wyoming and the Rocky Mountains of Colorado, N deposition as low as 1.5 kg N/ha/yr affects algal productivity ([Baron, 2006](#); [Saros et al., 2003](#)). The responses of high-elevation lakes can vary considerably depending on catchment characteristics and the amount of deposition ([Appendix 9.1.1](#)).

With increased characterization of nutrient inputs in remote high-elevation lakes and streams, fate and transport processes, N and P dynamics, phytoplankton response, and downstream effects in coastal/estuarine systems, the understanding of the role of N in freshwater eutrophication has evolved in recent decades. As conveyed in the 2008 ISA, the historical emphasis on P as a major cause of freshwater eutrophication was based on a number of highly influential studies in the 1960s and 1970s that focused on the role of wastewater, in particular phosphate detergents, in causing excessive algal blooms in Lake Mendota (WI), Lake Washington (WA), Lake Erie, and many other locations ([Edmondson, 1991](#); [Schindler, 1974](#); [Schindler et al., 1971](#); [Edmondson, 1969](#); [Vollenweider, 1968](#); [Hasler, 1947](#)). These observations guided approaches to freshwater lake and stream ecology for many years. Over time, an increasing recognition that N inputs can stimulate phytoplankton growth under certain conditions, coupled with further understanding of aquatic biogeochemistry ([Appendix 7](#)) and of the connectivity between freshwater and receiving estuaries and coastal waters, has led to recommendations to consider both N and P in nutrient reduction strategies ([Dodds and Smith, 2016](#); [Gobler et al., 2016](#); [Paerl et al., 2016b](#); [Lewis et al., 2011](#); [Scott and McCarthy, 2010](#); [Conley et al., 2009](#); [Paerl, 2009](#); [Lewis and Wurtsbaugh, 2008](#)).

There is increasing understanding of the frequency and shifts in the types of nutrient limitation in various systems. In oligotrophic clear water lakes where atmospheric N inputs are low and light is not limiting, phytoplankton primary production is typically N limited ([Bergstrom et al., 2015](#); [Hessen, 2013](#)). In the 2008 ISA, results from surveys, paleolimnological reconstructions, experiments, and meta-analyses of hundreds of studies have shown N limitation to be common in fresh waters, especially in remote areas, and a nearly universal eutrophication response to N enrichment in lakes and streams that are N limited ([U.S. EPA, 2008a](#); [Elser et al., 2007](#); [Bergström et al., 2005](#); [Elser et al., 1990](#)). Tropical and subtropical lakes, and lakes having small watersheds relative to the lake surface/volume, also tend to be N limited ([Paerl and Scott, 2010](#); [Elser et al., 2007](#)). As reported in the 2008 ISA, some alpine lakes have exhibited shifts from N limitation to between N and P limitation or to P limitation ([U.S. EPA, 2008a](#)). In a meta-analysis reviewed in the 2008 ISA, [Elser et al. \(2007\)](#) found that N limitation occurred as frequently as P limitation in freshwater ecosystems. Newer studies published since the 2008 ISA add to the evidence that reservoirs, rivers, and freshwater lakes can exhibit N limitation and N and P colimitation ([Paerl et al., 2014](#); [Lewis et al., 2011](#); [Conley et al., 2009](#); [Sterner, 2008](#)). N limitation appears to be increasingly common in freshwater systems, probably because their nutrient dynamics are being altered significantly by growing agricultural and urban P inputs ([Paerl et al., 2016b](#); [Grantz et al., 2014](#); [Paerl et al., 2014](#); [Finlay et al., 2013](#)).

A source of P to remote water bodies is deposition of dust. In an analysis of data from the U.S. EPA National Lakes surveys and National Rivers and Streams surveys [Stoddard et al. \(2016\)](#) found continent-wide increases in total phosphorus (TP) between 2000 and 2014, especially at sites that exhibited low disturbance ([Appendix 9.1.1.2](#)). Among the large natural P emission sources are soils, vegetation, and biomass combustion ash. Other notable sources include industry, agriculture, and mining. Although P is not a criteria pollutant, inputs of P may contribute to eutrophication and effect shifts in lake trophic status from P to N limitation or to colimitation. In addition, [Stoddard et al. \(2016\)](#) observed that total N (TN) was strongly correlated with TP in lakes and streams on a national scale. Although the authors determined that TP was increasing at “minimally disturbed sites,” they observed that TN was not increasing at those sites. Responses of aquatic ecosystems to atmospheric N deposition are heavily dependent on surface water P concentrations. Thus, because P inputs can alter N response, the impact of recent trends in increased P deposition is important to consider when evaluating nutrient status in water bodies sensitive to atmospheric inputs ([Appendix 9.1.1.4](#)).

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## 9.1.1 Deposition to Freshwater Systems

Both N and P inputs to fresh waters sensitive to atmospheric deposition can affect nutrient limitation. The composition of N deposition is shifting in the U.S. from oxidized to reduced forms of N, with implications for the receiving systems. Atmospheric deposition of P may affect lake response to N inputs, and recent trends point to widespread increases in P deposition in the U.S. ([Stoddard et al., 2016](#)) and globally [[Brahney et al. \(2015\)](#); [Tipping et al. \(2014\)](#); [Appendix 9.1.1.2](#)].

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### 9.1.1.1 Nitrogen Deposition Sources and Trends

Sources of N and trends in atmospheric deposition are described in [Appendix 2](#). Briefly, N is deposited in various reduced and oxidized forms, including organic N. Deposition can be wet (rain or snow), or dry. Atmospheric deposition of reduced N has increased relative to oxidized N in parts of the U.S. including the East and Midwest in the last few decades, shifting from a  $\text{NO}_3^-$  dominated to a  $\text{NH}_4^+$  dominated condition, and this trend is expected to continue under existing emissions controls ([Li et al., 2016d](#); [Pinder et al., 2008](#); [U.S. EPA, 2008a](#)). In the soil or water, much of the deposited  $\text{NH}_4^+$  is either taken up by biota or nitrified to  $\text{NO}_3^-$  and leaches to water bodies mainly as  $\text{NO}_3^-$  ([Hessen, 2013](#)). Up to 70% of deposited  $\text{NO}_3^-$  in remote alpine lakes in the western U.S. is anthropogenic in origin, with the largest sources being atmospherically delivered fertilizers from agriculture (approx. 60%) and fossil fuel combustion [approx. 10%; [Hundey et al. \(2016\)](#)]. N deposition to snow and glaciers are important sources of N to alpine lakes and streams that are fed by meltwaters. For example, approximately 50% of lakes in Glacier National Park and 10–20% of lakes in the central Rockies receive glacial meltwater ([Saros et al., 2010](#)). At high-elevation sites like those in the Rockies and Sierra Nevada, N deposition estimates are uncertain, especially for dry deposition ([Appendix 9.5](#)).

Moving from lower order streams to higher order streams, atmospheric N from direct deposition, runoff, and leaching from terrestrial ecosystems combines with other diffuse and point sources of N. The contribution from other terrestrial sources of N, such as fertilizer, livestock waste, septic effluent, and wastewater treatment plant outflow, often becomes much more important in downstream than in upland areas. About 75% of N inputs are retained in the watershed or denitrified, and 25% are exported to surface waters regardless of the dominant N input, including deposition ([Howarth et al., 2012](#); [Howarth et al., 1996a](#)). [Table 7-1](#) summarizes studies quantifying N deposition contribution to total N loading in U.S. freshwater systems.

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### 9.1.1.2 Characteristics of Freshwater Systems Sensitive to Atmospheric Deposition of Nitrogen

Various factors affect the sensitivity of remote water bodies to atmospheric deposition. These factors include the spatial and temporal patterns of nutrient limitation and the physical and chemical attributes of the catchment ([Williams et al., 2017b](#); [Hundey et al., 2014](#); [Nanus et al., 2012](#); [U.S. EPA, 2008a](#)). Thus, the same amount of N deposition can lead to different N loading depending on the characteristics of the receiving watershed and water body ([Hessen, 2013](#); [Bergström, 2010](#)).

In high-elevation lakes above the tree line in areas with steep slopes, sparse vegetation, exposed bedrock, and shallow rocky soils, changes in productivity and biodiversity of algal assemblages can occur with little or no lag time ([Baron et al., 2011b](#)). The hydrology of these systems is dominated by spring snowmelt ([Spaulding et al., 2015](#)). Seasonal meltwaters can deliver a nutrient pulse to alpine lakes and streams, with glacial meltwater contributing more  $\text{NO}_3^-$  than snowmelt does ([Slemmons et al., 2015](#); [Slemmons et al., 2013](#); [Saros et al., 2010](#); [Baron et al., 2009](#)). Other freshwater systems, such as some nonalpine freshwater lakes, reservoirs, and rivers that exhibit N limitation and N and P colimitation, are sensitive to additional N inputs ([Paerl et al., 2016b](#); [Paerl et al., 2014](#); [Lewis et al., 2011](#); [Conley et al., 2009](#); [Elser et al., 2009b](#); [Sterner, 2008](#)). N from atmospheric deposition represents a proportion of total N in these systems, although agricultural and wastewater inputs are often predominant.

In the 2008 ISA, lakes and streams with high concentrations of  $\text{NO}_3^-$ , indicative of ecosystems being N saturated ([Appendix 7.1.2.1](#)), were reported at a variety of locations throughout the U.S., including the San Bernardino and San Gabriel mountains within the Los Angeles Air Basin ([Fenn and Poth, 1999](#); [Fenn et al., 1996](#); [Riggan et al., 1985](#)), the Front Range of Colorado ([Williams et al., 1996a](#); [Baron et al., 1994](#)), the Allegheny Mountains of West Virginia ([Gilliam et al., 1996](#)), the Catskill Mountains of New York ([Stoddard, 1994](#); [Murdoch and Stoddard, 1992](#)), the Adirondack Mountains of New York ([Wigington et al., 1996b](#)), and the Great Smoky Mountains in Tennessee ([Cook et al., 1994](#)). All of these regions, except the Colorado Front Range, received more than about 10 kg N/ha/yr atmospheric deposition of N throughout the 1980s and 1990s. The Front Range of Colorado received up to about 5 kg N/ha/yr of total (wet + dry) deposition ([Sullivan et al., 2005](#)), less than half of the total N deposition received at many of these other locations. Since the 2008 ISA, several long-term monitoring studies have shown temporal decreases in surface water  $\text{NO}_3^-$  concentration corresponding to decreases in atmospheric N deposition ([Appendix 7.1.2.1](#)). These regions include the Appalachian Mountains, the Adirondacks, and the Rocky Mountains ([Driscoll et al., 2016](#); [Kline et al., 2016](#); [Strock et al., 2014](#); [Eshleman et al., 2013](#); [Elser et al., 2009b](#); [Bergström and](#)

[Jansson, 2006](#)).  $\text{NO}_3^-$  in extremely high concentrations can have direct adverse effects on fish, as well as invertebrates and amphibians. These effects are observed at concentrations much higher than would commonly be attributable to atmospheric deposition, are not included in this ISA, and were not defined as a primary biological indicator in the 2008 ISA.

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### 9.1.1.3 Nitrogen Deposition Effects on Nutrient Limitation

The 2008 ISA reported on gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition. These studies found strong relationships between N limitation and primary productivity where N deposition was low and between P and N + P limitations where N deposition was high ([Bergström and Jansson, 2006](#); [Bergström et al., 2005](#); [Fenn et al., 2003a](#)). As reviewed in the 2008 ISA, a comprehensive survey of 42 unproductive lakes (oligotrophic lakes with TP less than or equal to 25  $\mu\text{g/L}$ ) along gradients of N deposition in Europe and North America showed increased inorganic N concentration and productivity to be correlated with atmospheric N deposition ([Bergström and Jansson, 2006](#)). Unproductive lakes receiving low atmospheric N deposition were N limited (<2.5 kg N/ha/yr). At about 2.5 to 5 kg N/ha/yr, colimitation of N and P was observed, while at N deposition above 5 kg N/ha/yr, the lakes were P limited. Based on the study findings and paleolimnological evidence, [Bergström and Jansson \(2006\)](#) suggested that most lakes in the northern hemisphere may have originally been N limited and that atmospheric N deposition has changed the balance of N and P in lakes.

Studies published since the 2008 ISA have continued to characterize nutrient relationships and evaluate the potential for N deposition to contribute to the eutrophication of water bodies ([Table 9-1](#)). Consistent with the 2008 ISA findings, research literature after 2007 indicates that N deposition is correlated with a shift from N to P limitation in certain high-elevation water bodies ([Hessen, 2013](#)). [Elser et al. \(2009b\)](#) conducted a nutrient-limitation study across a gradient of lakes in the Rocky Mountains of Colorado that receive low (<2 kg N/ha/yr; N = 20) and high (>6 kg N/ha/yr; N = 16) N deposition. Nutrient enrichment bioassays indicated that P limitation or colimitation was prevalent in the population of high-deposition lakes (9 of 16 lakes), while only one of the lakes showed N limitation. In contrast, only 4 of 20 low-deposition lakes showed P limitation. Based on relative response ratios (RR; chlorophyll concentration in a given treatment normalized to chlorophyll in control), chlorophyll responded more strongly to N relative to P in low-deposition lakes where N limitation was stronger ([Figure 9-2](#)). These data were included in [Elser et al. \(2009a\)](#) who reported that lakes in Norway, Sweden, and Colorado affected by N deposition showed a similar pattern. In lakes with

high N deposition, phytoplankton was predominately P limited, whereas in lakes with low N deposition, N limitation was more common.

Based on an analysis of lake water chemistry data from 106 alpine lakes in Sweden, Slovakia, Poland, and the Rocky Mountains of Colorado and nutrient bioassays from high mountain lakes in Sweden and the Rocky Mountains of Colorado, [Bergström \(2010\)](#) documented how N:P mass ratios (TN:TP and dissolved inorganic N (DIN):TP) vary in oligotrophic lakes located in northern Europe and the Rocky Mountains. Nutrients (N, P, N + P, control) were added to water from 28 unproductive lakes. The majority of the lakes were N limited and the shift from N to P limitation was strongly affected by N deposition. More than half (54%) of the oligotrophic study lakes had a TN:TP mass ratio <25. A DIN:TP ratio of 1.5 was indicative of an N limited lake while a ratio of 3.4 was P limited. The DIN:TP ratio was a better indicator than the TN:TP ratio for nutrient limitation of phytoplankton because TN may include a large fraction of biologically unavailable N.

**Table 9-1 Summary of studies using diatoms as biological indicators of nitrogen enrichment evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur— Ecological Criteria.**

Study Site	Ambient N Deposition	Diatom Response	Species	Reference
Three national parks in Washington State (Mt. Rainier, North Cascades, and Olympic)	0.25 ± 0.15 to 1.10 ± 0.21 kg/ha/yr NH <sub>4</sub> <sup>+</sup> -N; 0.34 ± 0.04 to 1.32 ± 0.19 kg/ha/yr NO <sub>3</sub> <sup>-</sup> -N; 0.59 ± 0.07 to 2.42 ± 0.27 kg/ha/yr inorganic N	Overall, only one lake (Hoh Lake) of 10 study lakes where cores were collected showed clear evidence of impacts from N deposition based on changes in sediment diatom communities.	<i>A. formosa</i> , <i>F. crotonensis</i> , and <i>F. tenera</i>	<a href="#">Sheibley et al. (2014)</a>
Western U.S. (Glacial National Park, Greater Yellowstone Ecosystem, and eastern Sierra Nevada)	Sierra Nevada = 2 kg/ha/yr (current) to 4 kg/ha/yr (early 1990s) total wet inorganic N deposition. GNP = 0.5–1.5 kg/ha/yr (1980–2006). GYE = 0.5–1.1 kg/ha/yr (1980–2006)	A critical load of 1.4 kg N/ha/yr wet deposition changed diatom community structure in both the eastern Sierra Nevada and the Greater Yellowstone Ecosystem, although N deposition rates between the two regions and the timing of diatom community shifts were different. No diatom community changes were observed in Glacier National Park lakes.	<i>A. formosa</i> and <i>F. crotonensis</i>	<a href="#">Saros et al. (2011)</a>
Rocky Mountains	Central Rockies NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup> = 1.4–2.5 kg N/ha/yr. N. Rockies = 2.0–3.4 kg N/ha/yr.	Lakes fed by snowpack meltwater had greater sediment diatom taxonomic richness over the last century (35 to 54 taxa) compared with lakes that were fed by both glacial and snowpack meltwater (12 to 26 taxa) which are higher in NO <sub>3</sub> <sup>-</sup> . (~50% of Glacier National Park lakes and ~0–20% of lakes in central Rockies receive glacial meltwater).	Multiple	<a href="#">Saros et al. (2010)</a>
Rocky Mountains	Wet deposition ranged from 0.8 to 3.2 kg N/ha/yr at study sites.	High abundance of key indicator species of N enrichment ( <i>A. formosa</i> , <i>F. crotonensis</i> ) in lakes with low to moderate NO <sub>3</sub> <sup>-</sup> precluded an attempt to quantify the surface water NO <sub>3</sub> <sup>-</sup> concentrations that elicit diatom community changes in high-elevation lakes using a diatom-based transfer function.	Multiple	<a href="#">Arnett et al. (2012)</a>

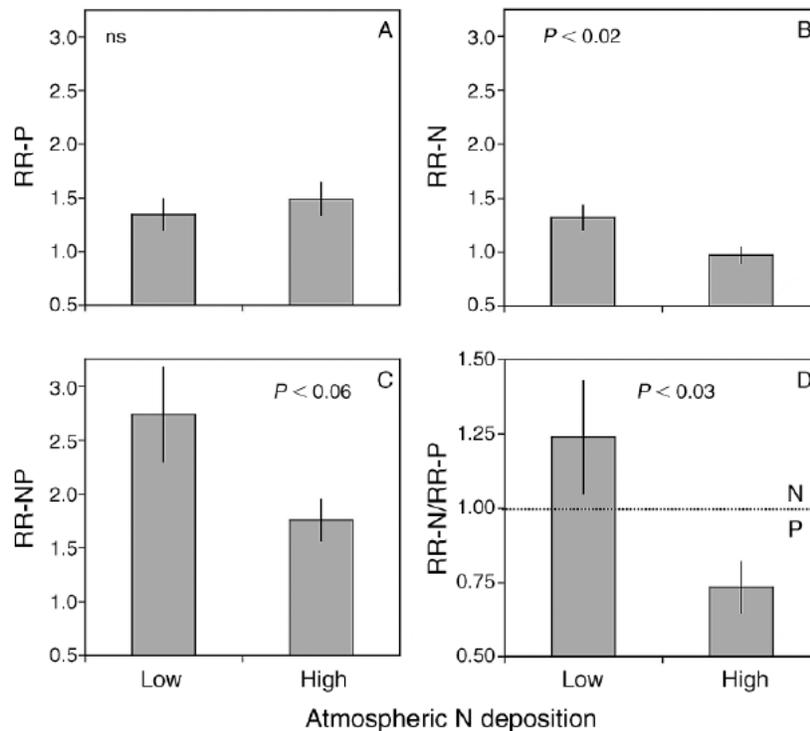
**Table 9-1 (Continued): Summary of studies using diatoms as biological indicators of nitrogen enrichment evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	Diatom Response	Species	Reference
Rocky Mountains	>3 kg N/ha/yr	A maximum growth rate of $0.2 \pm 0.04$ /day at $0.5 \mu\text{M}$ N for the diatom <i>A. formosa</i> was measured following N addition to identify a $\text{NO}_3^-$ threshold for this species in surface water.	<i>A. formosa</i>	<a href="#">Nanus et al. (2012)</a>
Central Rocky Mountains/Beartooth Mountains located along the Montana and Wyoming borders	Not specified	Fossil-diatom assemblages from two lakes near each other (one snowpack-fed and one glacier-fed) indicated greater diatom assemblage turnover in the glacier-fed lake. The glacier-fed lake showed evidence for mild N enrichment starting approximately 1,000 yr ago, and the increase in abundances of <i>A. formosa</i> and <i>F. crotonensis</i> occurred much earlier, suggesting glacial meltwater was a source of N.	<i>A. formosa</i> and <i>F. crotonensis</i>	<a href="#">Slemmons et al. (2015)</a>
Central Rocky Mountains/Beartooth Mountains located along the Montana and Wyoming borders	Not specified	Diatom species richness from the top of sediment cores was $1.8\times$ higher in snowpack-fed lakes compared with glacier- and snowpack-fed lakes, whereas richness did not differ between core bottoms (ca. 1850) of the lakes. Compared with snow-fed lakes, N enriched glacial snowpack-fed lakes were dominated by <i>A. formosa</i> and <i>F. crotonensis</i> .	<i>A. formosa</i> and <i>F. crotonensis</i>	<a href="#">Slemmons and Saros (2012)</a>
Grand Teton National Park	Estimated at 2.5 kg N/ha/yr	Directional change in benthic diatom assemblages after 1960 that is correlated with atmospheric deposition.	Benthic diatoms	<a href="#">Spaulding et al. (2015)</a>
Uinta Mountains, UT	0.02–0.04 kg km <sup>2</sup>	Four of five lakes with recent increase in productivity (between 1940 and 1960) show comparable shifts in diatom community composition linked to atmospheric deposition of N and P. Lake sediment records show an increasing abundance of nitrophilous <i>A. formosa</i> .	<i>A. formosa</i>	<a href="#">Hundey et al. (2014)</a>
Mount Rainier, North Cascades, and Olympic national parks, WA	0.38–3.24 kg N/ha/yr (wet)	20 taxa of phytoplankton responded to N enrichment. <i>F. tenera</i> and <i>F. crotonensis</i> are recommended as indicators of N enrichment in the Pacific NW. The threshold for phytoplankton biomass growth was 13–25 $\mu\text{g}$ DIN/L.	Multiple	<a href="#">Williams et al. (2016a)</a>
Northern Cascade Mountains, WA	1.1 to 3.4 kg N/ha/yr	No significant difference in diatom biovolume or phytoplankton community structure between snow-fed lakes and glacial snowpack-fed lakes.	Multiple	<a href="#">Williams et al. (2016b)</a>

**Table 9-1 (Continued): Summary of studies using diatoms as biological indicators of nitrogen enrichment evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	Diatom Response	Species	Reference
National parks of the western Great Lakes (Superior and Michigan) region	1.5–5 kg N/ha/yr (1980–2010)	In 63% of study lakes, change in diatom community correlates with lake sediment $\delta^{15}\text{N}$ , which in turn relates to measured $\text{N}_r$ inputs (deposition and indirect watershed inputs). In about 36% of the lakes, sediment $\delta^{15}\text{N}$ was statistically correlated to some form of deposited $\text{N}_r$ . A number of such lakes are in watersheds believed to have high N retention associated with shallow subsurface flow during snowmelt. The authors consider this to be the primary path for $\text{NO}_3^-$ transport. Diatom community change is also expected to be related to nutrient inputs indirectly by runoff and climate variability.	Multiple, including <i>F. crotonensis</i> and <i>A. formosa</i>	<a href="#">Hobbs et al. (2016)</a>
U.S.	Not specified	Shifts in diatom community composition away from N intolerant species.	Multiple	<a href="#">Pardo et al. (2011a)</a>
North America and Greenland	0.8 to 2 (<50°N) to <0.5 (>50°N)	A meta-analysis of 52 alpine, Arctic, and boreal montane lakes showed increased beta diversity in the 20th century. Observed diatom assemblage turnover in alpine and Arctic lakes is related to temperature changes, while in mid-latitude alpine lakes changes are linked to N deposition.	Multiple	<a href="#">Hobbs et al. (2010)</a>
Baptiste Lake, Alberta, Canada	Not specified	Lake sediment cores indicate prevalence of diatom assemblages that favor nutrient-rich conditions for at least the last 150 yr. From ~1980 to present, a distinct increase in <i>Stephanodiscus hantzschii</i> was observed.	Multiple	<a href="#">Adams et al. (2014)</a>
George Lake, Killarney Provincial Park, Ontario, Canada	6–7 kg N/ha/yr (2013)	Relative abundance of <i>A. formosa</i> increased over a 20-yr period while lake total N concentration and regional N deposition decreased. Increases in <i>A. formosa</i> were directionally related to increases in air and epilimnetic temperatures.	Multiple, including <i>A. formosa</i>	<a href="#">Sivarajah et al. (2016)</a>
Whitefish Bay, Ontario, Canada, also meta-analysis of 200 lakes in North America and Europe	<5 to <1 kg N/ha/yr	No effects of N deposition were observed on diatom community structure in Whitefish Bay. Observed shifts in Arctic lakes (1850) and temperate lakes (1970) were in response to climate change.	Multiple planktonic and benthic diatoms	<a href="#">Rühland et al. (2008)</a>

Ha = hectare; kg = kilogram; km = kilometer;  $\mu\text{M}$  = micromole; N = nitrogen;  $\text{NH}_4^+ \text{-N}$  = nitrogen as ammonium;  $\text{NO}_3^-$  = nitrate; P = phosphorus; yr = year.



N = nitrogen; P = phosphorus.

The response ratio (RR) has no units. (A) Response to P enrichment alone (RR-P); (B) response to N enrichment alone (RR-N); (C) response to combined N and P enrichment (RR-NP); (D) relative response to N vs. P (RR-N/RR-P, equivalent to final chl N/final chl P). For RR-N/RR-P, a value >1 indicates stronger N limitation while a value <1 indicates stronger P limitation. Error bars indicate  $\pm$  SE. The result of *t* tests comparing low- and high-deposition means for each parameter are given in each panel.

Source: [Elser et al. \(2009b\)](#)

**Figure 9-2** **Phytoplankton responses to nitrogen and/or phosphorus enrichment for Rocky Mountain lakes receiving low or high atmospheric nitrogen deposition, given as the ratio of final chlorophyll concentration in the enriched treatment (+phosphorus, +nitrogen, or +nitrogen + phosphorus) to the chlorophyll concentration in the unenriched control.**

N deposition gradient studies conducted in Sweden support findings of shifts from N to P limitation in lakes. [Liess et al. \(2009\)](#) compared a population of lakes in northern Sweden with lower N deposition (N = 7) to lakes in the south with higher deposition (N = 6). Atmospheric N deposition showed a strong positive correlation with TN. In the sampled lakes, northern lakes received 2 to 6 kg N/ha/yr, while southern lakes received 10 to 12 kg N/ha/yr. Sampling of epilithic communities indicated a weakly positive correlation of atmospheric N deposition to epilithon N:P ratios, suggesting that epilithic communities

were generally more N limited in the northern lakes and more P limited in the southern lakes, which received higher N deposition. [Bergström et al. \(2008\)](#) evaluated phytoplankton responses to N and P enrichment in unproductive Swedish lakes along a gradient of atmospheric N deposition. They found that regional and seasonal patterns in nutrient limitation were related to the level of N deposition. In the south, high N deposition was accompanied by high lake DIN concentrations during early summer, with subsequent P limitation. Later in the summer, DIN concentrations declined, and lakes switched to N and P colimitation, and then to N limitation. [Bergström et al. \(2008\)](#) concluded that N limitation is probably the natural state of these unproductive lakes and that P limitation has been induced by increased N availability caused by atmospheric N deposition.

Other studies in high alpine systems have shown that N deposition does not necessarily have a consistent effect on N or P limitation. In an assessment of 29 alpine lakes and ponds in the Canadian Rocky Mountains (Banff National Park, Alberta and Yoho National Park, British Columbia), certain ponds appeared to be N limited while most water bodies sampled did not show evidence of N limitation ([Murphy et al., 2010](#)). DIN:TP ratio analysis indicated N limitation in only 14% of the sampled water bodies. N limitation was observed more frequently in shallow ponds than lakes, and during the late summer sampling period, the ponds had a significantly lower mean DIN:TP ratio. In another study from the Rocky Mountains, surface sediment samples and surface water  $\text{NO}_3^-$  concentrations were collected from an N deposition gradient (1 to 3.2 kg N/ha/yr in wet deposition) across 46 high-elevation lakes to characterize diatom community changes ([Arnett et al., 2012](#)). The researchers found that even in lakes with  $\text{NO}_3^-$  concentrations below quantification (<1  $\mu\text{g/L}$ ), diatom assemblages were already dominated by key indicator species characteristic of moderate N enrichment, and the authors were unable to identify a threshold. They noted that small inputs of reactive N can shift diatom species composition along the length of the  $\text{NO}_3^-$  gradient and that the lakes switch from N limited oligotrophy to P limitation. In a study of 11 lakes in northern subarctic Sweden situated along an altitudinal/climate gradient with low N deposition (<1 kg N/ha/yr), the lakes did not show a shift from mainly N to mainly P limitation reported from U.S. lakes where N deposition was higher. However, mainly P limitation was observed in high alpine lakes with rocky catchments and high DIN:TP ratios, while mainly N and N + P colimitation was occurring in subalpine and lower mid-alpine lakes ([Bergström et al., 2013](#)). The authors attributed these observations to climate and catchment characteristics and suggested warming would have a greater impact than N deposition on the subset of sparsely vegetated high alpine lakes, in contrast to the majority of subarctic lakes with N or N + P colimitation, where both warming and N inputs will alter phytoplankton response.

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#### 9.1.1.4 Phosphorus Deposition Interactions

P deposition has direct implications for how ecosystems respond to N deposition. Although this appendix is focused on the biological effects of N enrichment, inputs of P may effect shifts in lake trophic status from P to N limitation or to colimitation and increase the total nutrient supply to water bodies affecting how the system responds to N. Since the 2008 ISA, several meta-analyses have reported an increase in P deposition to water bodies ([Stoddard et al., 2016](#); [Brahney et al., 2015](#); [Tipping et al., 2014](#)). This recent evidence suggests that the predominantly dry deposition of fine (<10  $\mu$ ) and coarse (<100  $\mu$ ) particulates (“dust”) containing P play a role in the enrichment effects of N deposition to fresh waters and their catchments. Data from the U.S. EPA National Lakes Assessment and National Rivers and Streams Assessment were analyzed by [Stoddard et al. \(2016\)](#) to determine whether total P (TP) concentrations changed between 2000 and 2014. The authors found continent-wide increases in TP, especially at sites with low disturbance. Median stream TP concentrations increased from 26  $\mu\text{g/L}$  (2000–2004) to 56  $\mu\text{g/L}$  (2013–2014); median lake TP increased from 20  $\mu\text{g/L}$  (2007) to 37  $\mu\text{g/L}$  (2012). From the 2004–2014 surveys, the percentage of stream length where TP was  $\leq 10 \mu\text{g/L}$  decreased from 24.5 to 1.6; the percentage of lakes where TP was  $\leq 10 \mu\text{g/L}$  decreased from 24.9 to 6.7 between 2007 and 2012. Additional research has corroborated the findings of [Stoddard et al. \(2016\)](#) in other locations ([Zhu et al., 2016a](#); [Brahney et al., 2015](#); [Tipping et al., 2014](#)) and has investigated shifts from N to P limitation or colimitation, as well as P deposition’s role in prolonging N limitation ([Appendix 9.2.2](#)).

In a regression analysis of deposition and water quality data in 700 upland lakes across 21 alpine regions globally, [Brahney et al. \(2015\)](#) suggested that P deposition may play a large role in alpine lake trophic status. The authors evaluated the strength in N, P, and N:P relationships in deposition and in lakes. Their 5-year, Community Atmospheric Model (CAM4) simulation modeling indicates that P deposition may have increased globally by 1.4 times the preindustrial deposition rate. TIN:TP of deposition and in lakes showed a strong relationship ( $r^2 = 0.82$ ,  $p < 0.0001$ ) with P deposition and lake water ( $r^2 = 0.64$ ,  $p < 0.0001$ ) and N deposition and lake water ( $r^2 = 0.20$ ,  $p < 0.05$ ). Where the deposition’s molar ratio of N:P was less than 20, intermittent or persistent N limitation was observed to be induced atmospherically. The authors concluded that the chemistry of atmospheric deposition influences nutrient limitation of alpine oligotrophic lakes by changing nutrient ratios as well as increasing the absolute supply of nutrients to these ecosystems. A global-scale analysis by [Tipping et al. \(2014\)](#) supported the observation by [Brahney et al. \(2015\)](#) about oligotrophic lakes and indicated the importance of accounting for sustained P deposition to assess the impact of productivity of anthropogenically emitted N deposition. The authors analyzed data on P deposition measured globally (82% of sites were in Europe and North America) from 1954–2012 at 250 sites. They found

that “oligotrophic lakes, tropical forests, and ombrotrophic peatlands” are the most likely to experience significant effects of atmospheric P deposition increase.

[Zhu et al. \(2016a\)](#) examined P deposition in China’s forest, grassland, desert, lake, marsh, and karst ecosystems and confirmed that China’s wet P deposition in terrestrial ecosystems (0.21 kg P ha/yr) is comparable to [Tipping et al. \(2014\)](#) TP deposition estimates (2013 ambient mean wet deposition =  $13.69 \pm 8.69$  kg N/ha/yr with fluxes ranging from 0.47 to 47.71 kg N/ha/yr). The average N:P ratio for wet deposition in China was reported as 77:1. The mean annual N concentration at 41 monitoring sites correlated linearly with precipitation ( $r^2 = 0.120$ ;  $p = 0.0027$ ), and N deposition also correlated significantly with rainfall ( $r^2 = 0.217$ ,  $p = 0.002$ ). The authors suggested that the high N:P ratios in atmospheric wet deposition could shift systems to P limitation, influencing ecosystem structure and function.

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### 9.1.1.5 Climate Modification of Ecosystem Response to Nitrogen

Nutrient inputs to fresh waters are occurring within the context of physical, chemical, and biological modifications caused by increased annual mean temperature and magnitude of precipitation associated with climate change ([Greaver et al., 2016](#)). Projected shifts in runoff and timing and quantity of flushing will alter local and regional hydrology ([Whitehead et al., 2009](#)). Nutrient loads to surface waters are expected to increase due to predicted increases in surface water flow ([Adrian et al., 2009](#); [Whitehead et al., 2009](#)). Air temperature increases will lead to warmer surface waters, altering the thermal stratification of water bodies and affecting the community composition and distribution of aquatic biota in streams and lakes ([Adrian et al., 2009](#); [Keller, 2007](#)). The increased surface water temperatures will increase the rate of algal growth ([Whitehead et al., 2009](#)). In regions with no evidence of increased atmospheric nutrient inputs, warming trends are observed to enhance competitiveness of planktonic diatoms like *Asterionella formosa*, which are typically associated with elevated N, indicating that climate change has significant direct and indirect effects on algal species composition. Climate change may thus enhance the effects observed in areas with nutrient increases alone ([Rühland et al., 2015](#)). [Appendix 13](#) includes a more detailed discussion of how climate (e.g., temperature and precipitation) modifies ecosystem response to N loading.

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## 9.2 Biological Indicators

Increased  $\text{NO}_3^-$  in surface water is a chemical indicator of freshwater N nutrient enrichment ([Appendix 7.1.2.1](#)). Many of the critical loads discussed in [Appendix 9.5](#) are

based on  $\text{NO}_3^-$  in surface water. A critical load is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge [[Spranger et al. \(2004\)](#); [Nilsson and Grennfelt \(1988\)](#); [Section IS.2.2.3](#)]. Biological indicators of freshwater N enrichment discussed in the 2008 ISA included chlorophyll *a*, phytoplankton and periphyton biomass, and changes in lake nutrient status ([U.S. EPA, 2008a](#)). Paleolimnological records of shifts in diatom community composition were also used to assess the effects of N deposition. Dose-response relationships between N and biological indicators were reported in the 2008 ISA, and the new literature continues to support these findings. Diatom community shifts ([Appendix 9.2.1](#)), and phytoplankton biomass nutrient limitation shifts ([Appendix 9.2.3](#)) have been used as a basis for determining critical loads for nutrient enrichment ([Appendix 9.5](#)). These same biological indicators are discussed further below along with new studies. In the current review, the response of microbial enzymes to N and P and increased incidence of harmful algal blooms (HABs) in freshwater habitats are discussed as possible biological indicators of the effects of elevated N.

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### 9.2.1 Diatoms

Diatoms are commonly used to monitor environmental conditions in water bodies over time. While many diatom studies explain patterns of variation in community composition in relation to environmental ([Smol and Stoermer, 2010](#)), as well as spatial factors ([Soininen et al., 2016](#); [Vilmi et al., 2016](#)), few studies have used experimental methods to address the processes underlying the patterns ([Smol and Stoermer, 2010](#); [Pither and Aarssen, 2006](#)). Changes in diatom species assemblages in paleolimnological studies of mountain lakes disturbed only by atmospheric deposition and climate change were reported in the 2008 ISA. Chlorophytes, such as *A. formosa* and *Fragilaria crotonensis*, generally prefer high concentrations of N and are able to rapidly dominate the flora when N concentrations increase ([U.S. EPA, 2008a](#); [Findlay et al., 1999](#)). These two nitrophilous species of diatom are used as biological indicators of the effect of N in water bodies; however, increased relative abundance of *A. formosa* has also been attributed to lake warming in some regions where N deposition is decreasing ([Sivarajah et al., 2016](#)). [Table 9-1](#) summarizes diatom studies published since the 2008 ISA. The majority of these studies highlight the observed influence of 20th century N deposition on diatoms, causing an increasing abundance of nitrophilous diatoms such as *A. formosa* and *F. crotonensis*. [Appendix 9.3](#) considers the effects of N deposition on diatom diversity. Thresholds of diatom response are reported in [Appendix 9.5](#).

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## 9.2.2 Ratios of Nitrogen and Phosphorus

Trophic status is a way to characterize bodies of water in terms of their productivity. Increasing deposition of N to water bodies shifts element ratios, which in turn affect algal growth, diversity, and community structure ([Appendix 9.3.2](#)). Algal species have different nutrient optima for growth and cellular uptake of N, and P alters the elemental composition of primary producers at the base of the freshwater food web. When N is the limiting nutrient, atmospheric deposition of N will increase benthic algal ([Liess et al., 2009](#)) and phytoplankton ([Hessen, 2013](#); [Elser et al., 2010](#)) N:P ratios. Nutritional responses of aquatic ecosystems to atmospheric N deposition are heavily dependent on surface water P concentrations, which may also be affected by atmospheric P inputs ([Appendix 9.1.1.4](#)). Thus, various chemical ratios of N to P can be useful for evaluating biological responses of water bodies affected by deposition ([Table 9-1](#)).

In the 2008 ISA, several studies reported N:P ratios in which a shift in nutrient limitation was observed. When DIN:TP values are greater than reference values, growth stimulation, N and P colimitation, or P limitation commonly occur ([Sickman et al., 2003](#)). In a Swedish lake survey reviewed in the 2008 ISA, N limitation occurred in lakes where the DIN:TP mass ratio was less than 7 (DIN concentrations <33  $\mu\text{M}$ ). Colimitation of N and P was found in lakes with DIN:TP ratio between about 8 and 10, and P limitation occurred at DIN:TP values greater than 10 ([Bergström et al., 2005](#)). Other thresholds for N limitation were reported in the literature to occur at DIN:TP ratios <4 ([Lohman and Prisco, 1992](#)) and <10 ([Wold and Hershey, 1999](#)). [Bergström et al. \(2005\)](#) reported an index (DIN:[chlorophyll *a*:TP]) to assess the eutrophication of lakes in response to N deposition.

[Hundey et al. \(2014\)](#) assessed trophic status for six remote alpine lakes in the Uinta Mountains, UT based on TP, TN, chlorophyll *a*, Secchi depth, and N:P relationships. One of six lakes was P limited, two were N limited, one varied by month, and the limitation was uncertain in the other two. Trophic status was difficult to determine in some of the lakes because the ratios were values that could indicate either N or P limitation depending on the threshold used, and some lakes were on the boundary between oligotrophic and mesotrophic. In Green Lake in Colorado's Front Range, the ratio of DIN:TP in the epilimnion over the course of the study was consistently above 4 and averaged  $16.3 \pm 2.76$ , suggesting the lake was P limited ([Gardner et al., 2008](#)). Nutrient ratios (TN:TP, DIN:TP, and  $\text{NO}_3^-$ :TP) were compared to nutrient bioassays to evaluate the use of these ratios in predicting the limiting nutrient. There was agreement in 29% of the bioassay results, suggesting that nutrient ratios are not the best predictor of nutrient limitation in this subarctic region.

In an in situ mesocosm bioassay study of two subalpine lakes in the Sierra Nevada, CA, [Heard and Sickman \(2016\)](#) modeled the effective dose of N addition along an N gradient (N as  $\text{KNO}_3$  and  $\text{NaNO}_3$  ranging from 0 to 50  $\mu\text{mol/L}$ ) with P addition as  $\text{KH}_2\text{PO}_4$  held constant at 1.5  $\mu\text{mol/L}$ . DIN:TP ratios in the two lakes were  $<4.0$ . Given that DIN:TP ratios  $<0.6$  indicate N limitation and DIN:TP ratios  $>0.6$  indicate intermediate limitation, both lakes were deemed N limited. The authors observed that the P addition delayed the shift to P limitation (prolonged N limitation) for phytoplankton. Effective doses for N for the two lakes were lower than the other study lakes receiving N addition only. They acknowledged the spatial and temporal variation in lake P concentrations, as well as concern for increased P deposition.

In a comparison of diatom-inferred lake nutrient records and surface water monitoring data (collected since the early 1980s) from Baptiste Lake in the Canadian Rockies, [Adams et al. \(2014\)](#) found total Kjeldahl nitrogen (TKN) was a significant predictor of chlorophyll *a*, where chlorophyll *a* was independent of TP. They observed that the lake experienced eutrophic conditions for  $>150$  years based on diatom sediment core data. Diatom-inferred TKN data tracked current TKN dynamics measured in the water column.

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### 9.2.3 Phytoplankton Biomass Nitrogen (N) to Phosphorus (P) Limitation Shift

As described in [Appendix 9.1.1.3](#), lakes may shift from N limitation to P limitation with elevated N deposition and this can be assessed using a response ratio (RR) considering the RR-N compared to the RR-P [[Figure 9-2](#); [Elser et al., 2009b](#)]. Phytoplankton biomass growth may shift from N to P enrichment, altering lake primary production ([Hessen, 2013](#)). [Williams et al. \(2017a\)](#) used the RR-N/RR-P to define a biological threshold of RR-N/RR-P = 1 above which phytoplankton biomass P limitation is more likely than N limitation and developed critical loads for western U.S. mountain lakes ([Appendix 9.5](#)).

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### 9.2.4 Periphyton/Microbial Biomass

Periphyton mats are biofilms of algae, cyanobacteria, fungi, microinvertebrates, organic detritus, inorganic particles, and heterotrophic microbes imbedded within a matrix and attached to submerged substrates in aquatic systems (e.g., stream or lake bottoms). In the 2008 ISA, no studies reported resource requirements for periphyton, although several papers described stimulated growth with N amendments in ecosystems throughout the U.S. (Annex C of the 2008 ISA), including streams in Alaska, Arizona, Iowa, Texas, Minnesota, and Missouri and lakes in California, Colorado, and Massachusetts ([U.S.](#)

[EPA, 2008a](#)). Additional lake bioassay experiments that enriched the water column down into the sediments found enhancement of periphyton growth on bioassay container walls in experiments in California, Wyoming, and Massachusetts ([Smith and Lee, 2006](#); [Nydic et al., 2004](#); [Axler and Reuter, 1996](#)). Strong N limitation of benthic algae has also been inferred in streams of Arizona ([Grimm and Fisher, 1986](#)), California ([Hill and Knight, 1988](#)), Missouri ([Lohman et al., 1991](#)), and Montana ([Lohman and Priscu, 1992](#)).

Since the 2008 ISA, few studies on N effects on periphyton biomass have been identified. In Ditch Creek, WY, a relatively undisturbed stream with N accumulation primarily from high N<sub>2</sub> fixation, biofilm growth on rocks increased after snowmelt and N<sub>2</sub> fixers dominated the algal assemblage ([Kunza and Hall, 2014](#)). A shift to non-N<sub>2</sub> fixing taxa was observed later in the season. In this stream with little to no anthropogenic influence, N fixation was higher than denitrification. [Burrows et al. \(2015\)](#) assessed microbial respiration and biomass using nutrient-diffusing substrata in 20 boreal streams in Sweden. An increase in N availability led to increased microbial activity. Microbial biomass was primarily N limited, and distinct microbial communities were associated with inorganic N in stream water. In a series of nutrient-diffusing substrata studies across rivers in the U.S. mountainous West, arid West, and the Midwest, [Reisinger et al. \(2016\)](#) assessed nutrient limitation patterns of benthic biofilms. Regarding regional differences, there was little evidence of N limitation in midwestern rivers due to high nutrient concentrations, while nutrient limitation of biofilms was common in the summer in mountainous western rivers. Increasing developed lands decreased the probability of nutrient-limited river biofilms. In a meta-analysis of nutrient-diffusing substrate studies from North America [Beck et al. \(2017\)](#), broad spatial factors such as ecoregion described most of the variation in nutrient limitation. Variables affecting algal biomass response to N included land use, riparian canopy cover, the presence of soluble reactive P, and season.

Microbial communities involved in plant litter decomposition in streams have been shown to be altered by nutrient concentrations. Most studies have examined the effects of N and P in combination. However, [Fernandes et al. \(2014\)](#) conducted a series of N addition studies in microcosms to assess leaf litter decomposition with increasing N concentration and temperature in streams. In general, increased temperature led to an increase in decomposer activity and a decrease in the amount of N needed. Field studies in six low-order streams spanning an N gradient in the Ave River basin, Portugal, suggested that eutrophication modulates leaf litter decomposition processes ([Lima-Fernandes et al., 2015](#)). Leaf litter diversity synergistically affected leaf litter decomposition while biomass fungal and invertebrate decomposers increased with stream eutrophication status but decreased in the most eutrophic of the six streams. [Dunck et al. \(2015\)](#) reported decreased primary production and leaf litter decomposition in highly

eutrophic streams and streams with little human influence compared to streams that were intermediate along the trophic gradient. [Kominoski et al. \(2015\)](#) observed that microbial litter breakdown rates increased across low to moderate nutrient enrichment gradients in experimental stream channels where N:P ratios were varied to allow for examination of N effects. A meta-analysis of plant matter decomposition in streams by [Ferreira et al. \(2015\)](#) suggested that the effects of nutrient inputs might be strongest in oligotrophic streams due to the low background nutrient concentrations and high magnitude of nutrient enrichment in these systems.

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### 9.2.5 Chlorophyll *a*

The concentration of chlorophyll *a*, a pigment present in all photosynthetic organisms, is a common measure of algal productivity and is hence an easily documented biological indicator of change in aquatic ecosystem productivity. Quantification of chlorophyll *a* is one approach for estimating phytoplankton biomass. Chlorophyll *a* is used as the primary indicator of trophic state in the U.S. EPA National Lakes Assessment and as a water quality indicator in many state and federal monitoring programs ([U.S. EPA, 2016h, 2009b](#)). Chlorophyll *a* is being used as an indicator of nutrient enrichment in U.S. EPA's National Nutrient Program [([U.S. EPA, 1998b](#)); [Appendix 7.1.6](#)]. The U.S. EPA is working with the states to develop numeric nutrient criteria to better define levels of N and P that affect U.S. waters. The numeric values include both causative (N and P) and response (chlorophyll *a*, turbidity) variables to assess eutrophic conditions. The U.S. EPA's National Nutrient Program to reduce eutrophication in water bodies developed recommended nutrient criteria for rivers and streams in 14 U.S. ecoregions for the states to use as a starting point to develop their own criteria ([U.S. EPA, 1998b](#)).

Surveys and fertilization experiments reported in the 2008 ISA show increased inorganic N concentration and aquatic ecosystem productivity, as quantified by chlorophyll *a* concentration, to be strongly related ([U.S. EPA, 2008a](#)). At the time of the 2008 ISA, increases in lake phytoplankton biomass (as chlorophyll *a*) with increasing N deposition were reported in several regions, including the Snowy Range in Wyoming ([Lafrancois et al., 2003b](#)) and across Europe ([Bergström and Jansson, 2006](#)). A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America reported in the 2008 ISA found algal growth enhancement from N amendments to be common in slightly less than half of the studies ([Elser et al., 1990](#)). There was a mean increase in phytoplankton biomass of 79% in response to N enrichment ([Elser et al., 1990](#)). This meta-analysis was repeated, incorporating study sites from multiple countries and a much larger data set, with similar results ([Elser et al., 2007](#)). Chlorophyll *a* continues to be a common biological indicator of N nutrient enrichment in the research literature from 2008 to

present. [Dodds and Smith \(2016\)](#) conducted a review of N and P dynamics in stream ecosystems and concluded that both N and P are strongly correlated to chlorophyll and algal biomass. In the western U.S., [Elser et al. \(2009b\)](#) examined chlorophyll *a* response in Rocky Mountain, CO lakes where atmospheric deposition ranged from 2 to 7 kg N/ha/yr. Concentrations of chlorophyll were 2 to 2.5 times greater in high-deposition lakes relative to low-deposition lakes.

Since the 2008 ISA, nutrient threshold values for chlorophyll *a* responses have been identified for a subset of western mountain lakes. [Williams et al. \(2016a\)](#) calculated an average DIN threshold of 13  $\mu\text{g}$  DIN/L for increased chlorophyll *a* concentration across nine western mountain lakes (25  $\mu\text{g}$  DIN/L for increased chl *a* concentration beyond interannual variation). More than 25% of 207 lakes in Mount Rainier and the northern Cascades exceeded the 13  $\mu\text{g}$  DIN/L threshold. [Heard and Sickman \(2016\)](#) determined threshold values for phytoplankton growth for Sierra Nevada lakes. The doses of N that characterize the initial phytoplankton growth response (10% effective dose), rapid phytoplankton growth (50% effective dose), and saturating nutrient level (90% effective dose) in early- and late-season conditions within two high-elevation lakes were established. These doses were then compared with monitoring data from lakes within Yosemite, Sequoia, and Kings Canyon national parks. The range of threshold values for the 10–50% effective doses were in the range of 0.3 to 4  $\mu\text{mol}$  N/L (5–56  $\mu\text{g}$  N/L). The 50% effective doses were exceeded by 18% (late season) to 29% (early season) of monitored lakes, suggesting that N inputs via atmospheric deposition affect phytoplankton in many lakes in this region. The lakes that exceeded effective doses tended to be at high elevation on steep, north-facing slopes with limited vegetative growth.

Chlorophyll *a* can also be used as a bioindicator of lake response over decadal and longer periods. [Hundey et al. \(2014\)](#) took sediment cores from six remote alpine lakes in Utah to assess trends in lake productivity. In five of the six lakes, sedimentary chlorophyll *a* and percentage of organic matter was observed to be relatively constant from the beginning of the record (mid 1800s using  $^{210}\text{Pb}$  dating; 1200 to 1800 estimated by linear regression) until 1940–1960 when lake production progressively increased.

As reported in the 2008 ISA and discussed further in [Appendix 7.1.2.9](#), dissolved organic carbon (DOC) affects acidity and N cycling and is increasing in some U.S. surface waters ([Monteith et al., 2007](#); [Evans et al., 2006](#)). Recent studies indicate different phytoplankton responses to N and dissolved organic matter (DOM) inputs depending on nutrient status of the lakes and background DOC ([Deininger et al., 2017a](#); [Daggett et al., 2015](#)). [Daggett et al. \(2015\)](#) selected a low DOC, N and P colimited water body (Jordan Pond in Acadia National Park, ME) and an N limited lake with higher DOC (Sargent

Lake in Isle Royale National Park, MI) to assess the effects of an N gradient on algal biomass following addition of DOM. Both of these Class I areas have a similar N deposition rates (6–7 kg total inorganic N/ha/yr wet deposition). DOM addition stimulated phytoplankton biomass in both lakes regardless of nutrient limitation or background DOC concentration. Phytoplankton biomass in N limited Sargent Lake increased with both N and DOM inputs, while in N and P colimited Jordan Pond, algae were sensitive primarily to DOM addition. [Appendix 9.3.2.3](#) discusses a whole-lake N fertilization study along a gradient of DOC.

Not all studies have shown a positive relationship between N inputs and increased chlorophyll *a*. In the Canadian Rockies, [Murphy et al. \(2010\)](#) performed nutrient enrichment bioassays on 29 water bodies in Banff and Yoho national parks using 1 mg N/L additions. They found that N amendment did not significantly increase final total phytoplankton chlorophyll concentration across all of the water bodies sampled during either early or late summer 2007. Although phytoplankton collected from ponds showed several responses to nutrient amendment, the effect of N on total chlorophyll did not differ significantly between pond and lake communities. Harvested final total chlorophyll concentrations from the bioassays were significantly higher for ponds than lakes. In water bodies in Wapusk National Park, Manitoba, a significant linear relationship occurred between chlorophyll *a* and TP across all ponds but not between chlorophyll *a* and total N [TN; ([Symons et al., 2012](#))]. In another study in Colorado's Front Range in Green Lake Valley (part of the Niwot Ridge Long-Term Ecological Research Project), Green Lake 4, a well-studied lake in the area, was sampled weekly throughout the ice-free summer period to assess chlorophyll response ([Gardner et al., 2008](#)). Epilimnetic chlorophyll *a* concentrations peaked at 4 µg/L in late July. In the same study, NO<sub>3</sub><sup>-</sup> addition to an in situ mesocosm on the lake (930 µg/L NO<sub>3</sub><sup>-</sup>, for a final exposure of 1,240 µg/L NO<sub>3</sub><sup>-</sup> given background concentrations) did not increase algal biomass significantly in comparison with the control, while phytoplankton chlorophyll *a* increased in P and P + NO<sub>3</sub><sup>-</sup> additions, indicating the lake was P limited during the summer.

Although hypothesized to be driven by industrial point source emissions, an increase in aquatic primary production in some lakes in the Athabasca Oil Sands Region in Alberta, Canada appears to follow regional patterns of annual and seasonal changes in temperature. In a comparison of spectrally inferred chlorophyll profiles of lake sediments in 23 diverse undisturbed lakes, [Summers et al. \(2016\)](#) observed higher chlorophyll *a* concentrations in surface sediments compared with concentrations inferred for the period before oil sands development, irrespective of lake morphology, landscape position, N deposition, or other limnological characteristics. Spatial and temporal patterns in inferred chlorophyll *a* were positively correlated with annual and seasonal changes in temperature

and were consistent across the region, suggesting a regional impact on productivity rather than impacts associated with point source emissions.

Some research has been conducted regarding the biological impacts of changes in N retention. [Heini et al. \(2014\)](#) examined chlorophyll *a* at various depths in a lake in southern Finland and found that algae and cyanobacteria can affect water chemistry instead of just responding to it. Differences in phytoplankton strongly affected observed short-term differences in chemical properties. The chemical conditions in the deeper waters during summer were generally more stable than in the layers near the surface of the lake.

Since the 2008 ISA lake surveys, fertilization experiments and nutrient bioassays continue to show a strong correlation between N inputs and chlorophyll *a*. Determination of additional thresholds for chlorophyll *a* in remote high-elevation lakes have further linked this indicator to atmospheric inputs of N. The relative importance of DOC in modulating lake response to nutrients is better understood than at the time of the 2008 ISA ([Appendix 7.1.2.9](#)). The use of chlorophyll *a* as an indicator in national lake and stream assessments and for state numeric nutrient criteria ([Appendix 7.1.6](#)) is further supported by studies reported in this ISA.

**Table 9-2 Summary of additional evidence for nitrogen limitation on productivity of freshwater ecosystems that has been evaluated since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	N Deposition	N Addition	Biological Effects	Reference
Sierra Nevada, CA	Not specified	Gradient of N (as KNO <sub>3</sub> and NaNO <sub>3</sub> ) ranging from 0 to 50 µmol/L (dose-finding study), then range used to model biological response was only up to about 18 µmol/L	10, 50, and 90% effective doses for excess phytoplankton growth were calculated for two high-elevation lakes. The modeled doses were compared with lake chemistry monitoring data to assess nutrient status. The 50% effective doses were exceeded by 18% (late season) to 29% (early season) of monitored lakes, suggesting that N inputs via atmospheric deposition affect phytoplankton in many lakes in this region. The threshold for stimulation of phytoplankton (10 to 50% ED) was 5–56 µg N/L.	<a href="#">Heard and Sickman (2016)</a>
Rocky Mountains, CO	2–7 kg N/ha	None	Atmospheric N deposition increased the stoichiometric ratio of N and P in lakes. Phytoplankton growth in 16 high N deposition lakes (~7 kg N/ha) was P limited whereas in 20 low N deposition lakes (~2 kg N/ha) growth was primarily N limited.	<a href="#">Elser et al. (2009a)</a>
Rocky Mountains, CO	High >6 kg N/ha/yr; low <2 kg N/ha/yr (NADP)	Enrichment of 7.5 µmol/L N (as NH <sub>4</sub> NO <sub>3</sub> ) for N, there was also a P and N + P treatment	Phytoplankton response to increased inputs of N was inferred from chlorophyll changes in bioassay data from 20 low N deposition lakes and 16 high N deposition lakes. Concentrations of chlorophyll and seston C were 2–2.5 times higher in the high N deposition lakes relative to the low N deposition lakes, while high-deposition lakes also had higher seston C:N and C:P (but not N:P) ratios.	<a href="#">Elser et al. (2009b)</a>
Rocky Mountains, CO	Not specified	Added 930 µg/L NO <sub>3</sub> <sup>-</sup> ; with background, exposure was 1,240 µg NO <sub>3</sub> <sup>-</sup> ; added 93 µg/L TDP	In in situ mesocosm experiments with water from Green Lake 4, chl <i>a</i> did not increase significantly with addition of NO <sub>3</sub> <sup>-</sup> in comparison with the control, while P and N + P treatments resulted in increases.	<a href="#">Gardner et al. (2008)</a>

**Table 9-2 (Continued): Summary of additional evidence for nitrogen limitation on productivity of freshwater ecosystems that has been evaluated since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	N Deposition	N Addition	Biological Effects	Reference
Utah	Not specified	None	Using sediment core data from six remote alpine lakes, chl <i>a</i> and percentage of organic matter are relatively constant from the beginning of the record until 1940–1960 in five of six lakes, when production progressively increased. The authors found the limiting nutrient difficult to identify.	<a href="#">Hundey et al. (2014)</a>
Alberta, Canada	Not specified	None	TKN was a significant predictor of chl <i>a</i> in Baptiste Lake where chl <i>a</i> was independent of TP measured in the water column.	<a href="#">Adams et al. (2014)</a>
Wapusk National Park, Canada	Not specified	N (NH <sub>4</sub> NO <sub>3</sub> ) and P (KH <sub>2</sub> PO <sub>4</sub> ) were added to increase the nutrient concentrations by 10× mean ambient concentrations	Nutrient enrichment bioassays were conducted on water samples from 21 lakes and ponds with chl <i>a</i> concentrations from 1.2 to 10.8 µg/L. In total, 13% of the lakes and ponds were found to be N limited, 26% P limited, 26% colimited, and 38% did not respond to either N or P additions.	<a href="#">Symons et al. (2012)</a>
Sweden	Gradient rates of N deposition ranging from 100 to 1,000 kg N/km <sup>2</sup> /yr in four regions during summers of 2004–2006	N: 1 mg/L and/or the concentrations of P by 100 µg/L (molar N:P ratio, 23:1)	Phytoplankton were N limited in northern lakes (low N deposition), while in the southern lakes higher N deposition was accompanied by increased lake DIN concentrations and a switch from N to P limitation. N limitation was common during the summer. As summer progressed, P limitation in these systems switched to dual and colimitation of N and P, and to N limitation, due to exhaustion of the DIN pool in the lakes.	<a href="#">Bergström et al. (2008)</a>
Sweden	<1 kg N/ha/yr	Nutrients were added to increase [N] as NH <sub>4</sub> NO <sub>3</sub> by 100 µg/L (7.2 µmol/L) and/or [P] as KH <sub>2</sub> PO <sub>4</sub> by 10 µg/L (0.3 µmol/L)	In phytoplankton nutrient addition bioassays using water from high-elevation lakes, phytoplankton was subject to P limitation and became increasingly N and NP colimited at lower elevation. Chlorophyll concentrations in the bioassays were lower with increasing elevation and this pattern held over the whole growing season.	<a href="#">Bergström et al. (2013)</a>

**Table 9-2 (Continued): Summary of additional evidence for nitrogen limitation on productivity of freshwater ecosystems that has been evaluated since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	N Deposition	N Addition	Biological Effects	Reference
Sweden	2 to 12 kg/ha/yr	None	N deposition positively related to total N and total P. The highest proportion of N fixing cyanobacteria (although only consisting of 5% of the algal biovolume) was found where N deposition was lowest. Epilithic periphyton N:P ratios increased with higher N availability from deposition.	<a href="#">Liess et al. (2009)</a>

C = carbon; chl = chlorophyll; ED = effective dose;  $\text{KH}_2\text{PO}_4$  = monopotassium phosphate; N = nitrogen; NADP = National Atmospheric Deposition Program;  $\text{NH}_4\text{NO}_3$  = ammonium nitrate;  $\text{NO}_3^-$  = nitrate; P = phosphorus; TDP = total dissolved phosphorus; TKN = total Kjeldahl nitrogen; TP = total phosphorus.

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## 9.2.6 Potential Biological Indicators

In addition to widely used biological indicators of nutrient enrichment (chlorophyll *a*, periphyton/microbial biomass, diatoms), freshwater harmful algal blooms (HABs) and enzymes are altered by N availability. Formation of HABs are more relevant downstream where multiple sources of N contribute to elevated nutrient levels sufficient for bloom formation. Only a limited number of studies have used enzymes to date.

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### 9.2.6.1 Harmful Algal Blooms

Freshwater HAB formation has become more prevalent in the U.S. in recent decades ([Lopez et al., 2008](#)), coinciding with increased N in surface waters. Although risk of bloom formation remains low for high-elevation oligotrophic water bodies with atmospheric N as the dominant source, atmospheric N may combine with other sources to contribute to total N loading in downstream lacustrine and riverine systems. Freshwater HABs can affect taste and odor of drinking water, lead to hypoxic conditions, impact recreational uses of surface waters, and produce toxins harmful to humans, domestic animals, and wildlife ([Lopez et al., 2008](#)). The major harmful algal group in freshwater environments are the cyanobacteria (blue-green algae). Cyanobacterial toxins are produced by several genera including *Microcystis*, *Anabaena*, *Nodularia*, *Aphanizomenon*, *Cylindrospermopsis*, and *Oscillatoria*. These toxins may target the liver (hepatotoxins such as cylindrospermopsins and microcystins), the nervous system (neurotoxins such as anatoxins and saxitoxins), or the skin (dermatotoxins).

There is evidence of the role for N in freshwater HABs in water bodies across the U.S. In western Lake Erie, cyanobacterial growth was N limited during bloom conditions in late summer, and the N fixing cyanobacterium *Anabaena* became dominant following the observed N limitation ([Chaffin et al., 2013](#)). In a survey of eutrophic midcontinent lakes, microcystins (common cyanobacterial toxins associated with HABs), were detected in all blooms ([Graham et al., 2010](#)). In another U.S. survey, TN was strongly correlated to microcystin concentration in lakes and reservoirs ([Beaver et al., 2014](#)). The highest cyanobacteria abundance was observed in the Midwest where agriculture is a dominant land use, and TN concentrations are higher. Using data from the U.S. EPA National Lakes Assessment ([U.S. EPA, 2009b](#)), [Yuan et al. \(2014\)](#) modeled a threshold for the probability of occurrence of *Microcystis*, a common non-N<sub>2</sub> fixing cyanobacterial genus. In their analysis, the frequency of occurrence of high microcystin concentrations depended most strongly on TN, with weaker associations to chlorophyll *a*. The calculated

threshold is based on the range of possible combinations of TN and chlorophyll *a* and the World Health Organization drinking water provisional guideline for microcystin of 1 µg/L (WHO, 1998). The recommended threshold ranges to protect against frequency of occurrence of high microcystin concentrations ( $0.1 \text{ MC} \leq 1 \text{ µg/L}$ ) were 570 or 1,100 µg/L TN paired with chlorophyll *a* concentrations of 37 and 3 µg/L, respectively (Yuan et al., 2014). Decreasing the frequency of microcystin occurrence to 5% gave TN concentrations of 250 or 400 µg/L paired with chlorophyll *a* concentrations of 14 and 1 µg/L. In the most recent U.S. EPA National Aquatic Resource Surveys, microcystin was detected in 12% of wetlands where water depth was sufficient to allow for microcystin sampling (U.S. EPA, 2016j) and in 39% of lakes (U.S. EPA, 2016h). The U.S. EPA has recently provided human health advisories on allowable limits of 0.3 µg/L microcystins and 0.7 µg/L cylindrospermopsin in drinking water over a 10-day exposure period (U.S. EPA, 2015a, b).

Since the 2008 ISA, additional studies have indicated that the availability and form of N influences algal bloom composition and toxicity, and inputs of inorganic N selectively favor some HAB species. A recent bloom in Lake Okeechobee in Florida was dominated by *Microcystis*, which depends on DIN for growth (Paerl and Scott, 2010). Multiyear monitoring data from western Lake Erie showed that microcystin concentration peaks coincided with inorganic N and that microcystin was significantly lower in years with less inorganic N loading (Gobler et al., 2016). In nutrient amendment experiments with water collected from Lake Agawam in New York, abundances of toxic strains of *Microcystis* were enhanced more than nontoxic strains by inorganic N, while nontoxic strains responded to organic N more frequently than inorganic N (Davis et al., 2010). *Microcystis* populations were stimulated more frequently by N than by P in the assays. Similarly, in a series of nutrient addition experiments using water from Sandusky Bay, Lake Erie, bloom growth and microcystin concentrations responded more frequently to the addition of inorganic and organic forms of N than to P addition, indicating that N inputs may affect bloom size and toxicity (Davis et al., 2015). Donald et al. (2011) reported differential responses of phytoplankton to various forms of N in mesocosm experiments in Wascana Lake, Saskatchewan. In this naturally P rich lake, addition of  $\text{NH}_4^+$  and urea promoted nonheterocystous cyanobacteria and algae, while increased chlorophytes and some cyanobacteria were observed with  $\text{NO}_3^-$  and urea. Microcystin production increased with added N, although the response varied by the form of N and the predominant algal taxon. In the same mesocosms, species-specific analyses indicated 144 individual taxa that exhibited distinct responses to N addition: 45 species showed stimulated growth, 93 species had a limited response, and 6 species had suppressed growth (Donald et al., 2013).

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### 9.2.6.2 Enzymes

A recent study analyzed enzyme activity to characterize nutrient limitation in aquatic systems. Microbial enzyme response to changes in N and P was found to vary in terrestrial and aquatic compartments in Bear Brook watershed in Maine, the site of a whole-watershed N enrichment experiment ([Mineau et al., 2014](#)). Stronger effects were typically observed in aquatic habitats. Although not explicitly the focus of the study, the authors imply that P limitation is caused by N availability. Since 1989, ammonium sulfate ( $[\text{NH}_4]_2\text{SO}_4$ ) has been applied bi-monthly to the watershed by helicopter, (25.2 kg N/ha/yr). The activity of three enzymes (b-1,4-glucosidase [BG], b-1,4-N-acetylglucosaminidase [NAG], acid phosphatase [AP]) in soil, leaf litter in both terrestrial and stream habitats, and in stream biofilms were compared with the activities of these enzymes in a reference watershed. In both terrestrial and aquatic habitats in the Bear Brook watershed, BG and NAG activities were unaffected. Stream biofilms had fivefold higher AP activity, while stream litter had eightfold higher AP activity. Increased AP activity is indicative of enhanced P limitation in the treated watershed. Shorter experimental P enrichments were used to characterize potential P limitation under ambient and elevated N availability. In streams, the effects of acute P additions were strongest with reduced AP activity and increased BG activity.

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## 9.3 Community Composition, Species Richness, and Diversity

Increased N deposition to water bodies, either directly or via N leaching from soils, increases available nutrients to aquatic biota and alters the balance of N and P. As reported in the 2008 ISA, differences in resource requirements allow some species to gain competitive advantage over others when nutrients are added, causing shifts in freshwater community composition and structure as N concentration increases ([Saros et al., 2005](#); [Lafrancois et al., 2004](#); [Wolfe et al., 2003](#)). In eutrophic systems, water quality changes associated with excess N nutrient inputs like lowered DO and algal blooms, which alter habitat by covering up substrate, can also lead to declines in biodiversity ([Hernández et al., 2016](#)). These pathways of N impacts have been identified as a threat for 50 aquatic invertebrate species (mollusks) and 14 fish species that are listed, or candidates for protection, under the U.S. Federal Endangered Species Act ([Hernández et al., 2016](#)). The authors did not consider the sources of N in their analysis of biota affected by N pollution.

Evidence for N effects on biodiversity in phytoplankton, zooplankton, and macroinvertebrates in the 2008 ISA included observations from paleolimnological studies, bioassays, and mesocosm and laboratory experiments. Community shifts and

decreased species richness of phytoplankton have been described in multiple studies while fewer studies have considered zooplankton. The new literature described below continues to report the effects of N enrichment on algal biodiversity and shows limited evidence of effects at higher trophic levels ([Table 9-3](#)).

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### 9.3.1 Archaea and Bacterial Diversity

The recent identification of ammonia-oxidizing archaea (AOA) and the classification of these microbes in a distinct and novel phylum within Archaea (Thaumarchaeota) has led to a large research effort to characterize their prevalence, community dynamics, and ecological distribution ([Schleper and Nicol, 2010](#); [Spang et al., 2010](#)). Spatio-temporal dynamics and community structure of AOA appear to be affected by lake trophic status and form of N ([Mukherjee et al., 2016](#); [Bollmann et al., 2014](#); [Berdjeb et al., 2013](#)). In a survey of nitrifying microbes in Lake Erie and Lake Superior, AOA outcompeted ammonia-oxidizing bacteria (AOB) where ammonium concentrations are lower [i.e., oligotrophic Lake Superior 0.287  $\mu\text{M NH}_4^+$  versus 2.45  $\mu\text{M}$  in mesotrophic Lake Erie; [Mukherjee et al. \(2016\)](#)].

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### 9.3.2 Phytoplankton Diversity

Survey data, paleolimnological studies, and fertilization experiments in the 2008 ISA reported species changes and reductions in plankton diversity in sensitive high-elevation lakes in the western U.S. in response to increased availability of N ([U.S. EPA, 2008a](#)). Available data reviewed in the 2008 ISA suggested that the increases in total N deposition do not have to be large to elicit an ecological effect. [Interlandi and Kilham \(2001\)](#) demonstrated that the highest species diversity was maintained at very low N levels ( $<3 \mu\text{M N}$ ) in lakes in the Yellowstone National Park region. A hindcasting exercise determined that a change in Rocky Mountain National Park lake algae occurred between 1850 and 1964 at only about 1.5 kg N/ha/yr wet N deposition ([Baron, 2006](#)). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha/yr deposition ([Saros et al., 2003](#)). Preindustrial inorganic N deposition is estimated to have been only 0.1 to 0.7 kg N/ha/yr based on measurements from remote parts of the world ([Holland et al., 1999](#); [Galloway et al., 1995](#)). In the western U.S., preindustrial, or background, inorganic N deposition was estimated by [Holland et al. \(1999\)](#) to range from 0.4 to 0.7 kg N/ha/yr.

**Table 9-3 Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	Endpoint	Deposition kg N/ha/yr	N Addition	Observation	Species	Ecosystem Type	Reference
Isle Royale National Park, MI and Acadia National Park, ME	Phytoplankton community structure	6–7 kg total inorganic N/ha/yr wet deposition	0, 5, 10, 20, or 40 µg/L	Chlorophytes had a reduced response to DOM addition when N was added to the N limited lake (Sargent Lake in Isle Royale National Park). Increase in abundance of diatoms ( <i>F. crotonensis</i> and <i>Tabellaria flocculosa</i> ) with DOM addition to the lake.	Multiple	Boreal lakes	<a href="#">Daggett et al. (2015)</a>
Lake Tahoe, CA and NV	Survey	Not specified	None	Endemic benthic invertebrate taxa have declined by 80 to 100% since a survey of Lake Tahoe was conducted in the 1960s. Changes in the density and assemblage structure of benthic invertebrates mirrors increases in nutrient enrichment and non-native species in the lake. Macrophyte occurrence has also declined.	Amphipods <i>Stygobromus laticolus</i> and <i>S. tahoensis</i> declined 99.9% No endemic turbellarians but abundant in 1960s. Endemic stonefly <i>Capnia lacustra</i> decreased 93.5% Endemic ostracods <i>Candona tahoensis</i> density decreased 83.4%	Subalpine, oligotrophic lake in California	<a href="#">Caires et al. (2013)</a>
Ditch and Spread Creeks in Grand Teton National Park, WY and Spring Creek near Wilson, WY	Algal biofilm assemblage	Not specified	0.5 M NaNO <sub>3</sub> ; 0.5 M KH <sub>2</sub> PO <sub>4</sub> ; 0.5 NaNO <sub>3</sub> , and 0.5 KH <sub>2</sub> PO <sub>4</sub>	Nutrient additions altered algal biofilm assemblages in the streams. NO <sub>3</sub> <sup>-</sup> addition inhibited N <sub>2</sub> fixer accumulation.	Phytoplankton	Streams	<a href="#">Kunza and Hall (2013)</a>

**Table 9-3 (Continued): Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	Endpoint	Deposition kg N/ha/yr	N Addition	Observation	Species	Ecosystem Type	Reference
Front Range of the Colorado Rocky Mountains	Phytoplankton community composition	Not specified	Added 930 µg/L NO <sub>3</sub> <sup>-</sup> (with background, exposure was 1,240 µg NO <sub>3</sub> <sup>-</sup> ; added 93 µg/L TDP)	Diatom abundance increased and phytoplankton species composition shifted in nutrient-enriched mesocosms. Principal component analysis suggested that 21% of the variance in phytoplankton community composition was related to added nutrients, while 34% of the variance was due to seasonal changes.	Phytoplankton	Alpine lake	<a href="#">Gardner et al. (2008)</a> .
12 alpine ponds in Banff National Park, Canadian Rockies	Phytoplankton and periphyton biomass/ zooplankton biomass/ community diversity	6.5–2.3 kg N/ha /yr (2000–2010) Highest levels (30–90 kg N/ha/yr) downwind of urban and agricultural sources.	1 mg N/L 30 µg P/L Simulating deposition = 20 kg/ha/yr	Periphyton outcompeted phytoplankton for limiting nutrients, indicating the importance of considering both benthic and pelagic primary producers. High grazing pressure by fairy shrimp affected results predicted from chemical inference and bioassay results regarding effects of added nutrients on algal communities.	Phytoplankton, zooplankton, invertebrate grazers, (fairy shrimp, <i>Anostraca: Branchinecta paludosa</i> )	Fishless, nonglacial ponds located above tree line	<a href="#">Vinebrooke et al. (2014)</a>
Banff National Park, Canadian Rockies	Phytoplankton abundance, effect on zooplankton		1,200 mg/L N added to aquaria with and without sediment	A taxonomic shift from omnivorous, raptorial-feeding copepods to more effective filter-feeding herbivorous daphnids was observed with warming and N addition. Warming and N fertilization increased phytoplankton abundance while herbivory by <i>Daphnia</i> decreased but only in the presence of sediment. Effects of warming and N differ both between trophic levels and aquatic alpine habitats.	Zooplankton: herbivorous <i>Daphnia middendorffiana</i> and omnivorous <i>Hesperodiaptomus arcticus</i>	Alpine lake	<a href="#">Thompson et al. (2008)</a>

**Table 9-3 (Continued): Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	Endpoint	Deposition kg N/ha/yr	N Addition	Observation	Species	Ecosystem Type	Reference
Wapusk National Park, Canada	Phytoplankton abundance, effect on zooplankton	Not specified	N (NH <sub>4</sub> NO <sub>3</sub> ) and P (KH <sub>2</sub> PO <sub>4</sub> ) were added to increase the nutrient concentrations by 10× mean ambient concentrations	N limited lakes had statistically significant different phytoplankton community composition with more chrysophytes and <i>Anabaena</i> spp. compared to all other lakes.	41 phytoplankton taxa including <i>Chlamydomonas</i> spp., <i>Sphaerocystis</i> spp., <i>Diatoma</i> spp. and <i>Crugienella</i> spp.	Subarctic lakes and ponds	<a href="#">Symons et al. (2012)</a>
Northern Sweden	Phytoplankton response to whole lake inorganic N fertilization	<2	Dissolved KNO <sub>3</sub> 14 M N as KNO <sub>3</sub> (in 2012) and 16 M HNO <sub>3</sub> (in 2013)	As DOC increased along a gradient, community composition shifted from nonflagellated toward high DOC-adapted flagellated autotrophs in the three fertilized lakes. In the same set of lakes, although phytoplankton biomass increased, net zooplankton responses were modest and attributed by the authors to incompatible stoichiometry of food (phytoplankton) to consumers (zooplankton)	Taxonomic groups: chrysophytes, cryptophytes, chlorophytes, diatoms, dinoflagellates, euglenophytes, cyanobacteria, picophytes. Functional groups: mixotrophic flagellates, autotrophic flagellates, nonflagellates, heterotrophic flagellates, cyanobacteria, picophytoplankton.	Boreal lakes	<a href="#">Deininger et al. (2017a)</a>
Northern Sweden	Pelagic food web response to whole lake N fertilization	<2	Dissolved potassium nitrate (14 M N as KNO <sub>3</sub> ) in 2012 and concentrated nitric acid (14 M N as HNO <sub>3</sub> ) in 2013	Although phytoplankton biomass increased, net zooplankton responses were modest and attributed to incompatible stoichiometry of food (phytoplankton) to consumers (zooplankton). Therefore, unconsumed phytoplankton could accumulate in unproductive boreal lakes with increased N deposition.	Crustacean zooplankton: calanoid copepods ( <i>Eudiaptomus</i> spp.), cyclopoid copepods ( <i>Cyclops</i> spp.), and cladocerans (mainly <i>Ceriodaphnia</i> spp., <i>Daphnia</i> spp., <i>Bosmina</i> spp., <i>Diaphanosoma brachyurum</i> , <i>Holopedium gibberum</i> , and <i>Sida</i> spp.).	Boreal lakes	<a href="#">Deininger et al. (2017b)</a>

**Table 9-3 (Continued): Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	Endpoint	Deposition kg N/ha/yr	N Addition	Observation	Species	Ecosystem Type	Reference
Denmark	Macroinvertebrate occurrence	Not specified	None	Macroinvertebrate communities did not change significantly with TN based on an analysis of a large number of concurrent samples of macroinvertebrate communities and chemical indicators of eutrophication and organic pollution (TP, TN, NH <sub>4</sub> <sup>+</sup> -N, biological oxygen demand [BOD5]) from 594 Danish stream sites.	Plecopteran <i>Leuctra</i> spp. Isopod <i>Asellus aquaticus</i> Dipteran <i>Chironomus</i> spp.	Streams	<a href="#">Friberg et al. (2010)</a>
French Alps	Phytobenthos species richness, grazing pressure	7	Nutrient-diffusing substrata N treatment: N = 113 µg/N/hr N + P: N = 181 µg/N/hr P = 13 µg/P/hr	A shift in taxonomic composition of phytobenthos toward green algae (less palatable to grazers) from cyanobacteria and diatoms was observed with N enrichment. Benthic grazing by macroinvertebrates was not reduced.	Diatoms Green algae Cyanobacteria	Alpine lakes	<a href="#">Lepori and Robin (2014)</a>

**Table 9-3 (Continued): Summary of studies on nitrogen effects on species composition and biodiversity that have been evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Region	Endpoint	Deposition kg N/ha/yr	N Addition	Observation	Species	Ecosystem Type	Reference
Bavaria, Germany	Phytoplankton community composition and abundance		0, 1, 2, 8, 16, and 32 mL of solution of 30 g/L NO <sub>3</sub> <sup>-</sup> and 10 mg/L NH <sub>4</sub> <sup>+</sup>	Increasing N enrichment gradient affected phytoplankton stoichiometry and community composition and heterotrophic nanoflagellate and ciliate abundances, indicating N load alters basal food web.	Dominant phytoplankton were Bacillariophyceae, dinoflagellates, Chrysophyceae, and Cryptophyceae. Only a few individuals of a few Chlorophyceae and Cyanophyceae (mainly <i>Anabaena</i> spp.) were observed. Bacillariophyceae's most abundant species were <i>Asterionella formosa</i> , <i>Cyclotella</i> spp., and <i>Fragilaria crotonensis</i> . Another abundant Chrysophyceae species <i>Dinobryon divergens</i> and the dinoflagellate <i>Ceratium hirundinella</i> .	Oligotrophic lake	<a href="#">Poxleitner et al. (2016)</a>

DOM = dissolved organic matter; KH<sub>2</sub>PO<sub>4</sub> = monopotassium phosphate; N = nitrogen; NaNO<sub>3</sub> = sodium nitrate; TN = total nitrogen; TDP = total dissolved phosphorus; TP = total phosphorus.

Some freshwater algae are particularly sensitive to the effects of added N and experience shifts in species diversity and community composition with increased N deposition. A general shift from chrysophytes that dominate lakes with low N to cyanophytes and chlorophytes in lakes with higher N has been observed in studies reported in the 2008 ISA ([Lafrancois et al., 2004](#); [Wolfe et al., 2003](#); [Jassby et al., 1994](#)) and newer studies ([Symons et al., 2012](#); [Pardo et al., 2011a](#); [Saros et al., 2010](#)). For example, in phytoplankton sampling from 21 lakes and ponds in Wapusk National Park, Canada, [Symons et al. \(2012\)](#) observed that the N limited lakes had significantly different phytoplankton community composition, with more chrysophytes and *Anabaena* spp. compared to all other lakes.

Using data from the U.S. Geological Survey National Water Quality Assessment, [Passy \(2008\)](#) assessed the responses of 2,426 benthic and 383 planktonic diatom communities from 760 and 127 distinct localities, respectively, to nutrient limitation. As more resources (basic cations, silica, iron,  $\text{NH}_3$ ,  $\text{NO}_3^-$ , and dissolved P) became limiting, benthic diatom richness declined while phytoplankton richness increased.

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### 9.3.2.1 Paleolimnological Studies

In the 2008 ISA, changes in diatom species assemblages, increases in cell numbers, and pigment-inferred increases in whole-lake primary production were reported from paleolimnological studies of mountain lakes that have only been disturbed by atmospheric deposition and climate change. Sediment cores in oligotrophic lakes receiving  $<5$  kg N/ha/yr showed diatom community shifts that in part could be also related to climate change. As reported in the 2008 ISA and [Appendix 9.2.1](#) of this appendix, two opportunistic species of diatom, *A. formosa* and *F. crotonensis*, now dominate the flora of at least several lakes in the Rocky Mountains ([Slemmons et al., 2015](#); [Arnett et al., 2012](#); [Saros et al., 2010](#); [Saros et al., 2005](#); [Saros et al., 2003](#); [Wolfe et al., 2003](#); [Wolfe et al., 2001](#); [Interlandi and Kilham, 1998](#)). In the southern Rocky Mountains, this shift occurred in the 1950s in the south, with more recent shifts (1970s) in the central region ([Baron et al., 2011b](#)). In most, but not all, of these studies, the observed responses in phytoplankton were concordant with effects from increased atmospheric N deposition. Increased abundance of *A. formosa* is also linked to changes in lake temperature under conditions of declining N deposition and decreasing lake total N concentration ([Sivarajah et al., 2016](#)).

Studies available since the 2008 ISA (summarized here and in [Table 9-1](#)) provide additional evidence from historical records of lake sediments in assessing biological changes associated with N enrichment over time. In a survey of 28 lakes in national parks

across the western Great Lake region, 63% of study lakes experienced changes in the diatom community correlated with lake sediment  $\delta^{15}\text{N}$  (Hobbs et al., 2016). About 36% of sediment  $\delta^{15}\text{N}$  was statistically correlated to some form of deposited N. Sediment records from lakes in the Uinta Mountains, UT showed shifts in diatom community composition and increasing abundance of the nitrophilous diatom *A. formosa* linked to atmospheric deposition (Hundey et al., 2014). In sediment core sampling from high-elevation lakes from national parks in Washington, Sheibley et al. (2014) analyzed a total of 56 sediment samples for diatom presence and abundance over time. In the survey, over 250 diatom species were identified; however, only Hoh Lake in Olympic National Park showed clear evidence of impacts from N deposition based on changes in sediment diatom assemblages and the presence of *A. formosa*, *F. crotonensis*, and *Fragilaria tenera*. In high-elevation lakes in the Rocky Mountains with low atmospheric deposition (<2 kg N/ha/yr) and low to moderate surface water  $\text{NO}_3^-$  concentrations (<1  $\mu\text{g/L}$  [below detection] to 30  $\mu\text{g/L}$ ), Arnett et al. (2012) observed that diatom assemblages were already dominated by nitrophilous species like *A. formosa* or *F. crotonensis*. Because of the abundance of species indicative of moderate N enrichment even at  $\text{NO}_3^-$  concentrations below the detection limit, it was not possible to identify a threshold of reactive N response for diatom community change. In Baptiste Lake in Alberta, Canada, a general shift in diatom assemblages away from N intolerant species and proliferation of *Stephanodiscus hantzschii*, a nitrophilous diatom species, was observed (Adams et al., 2014). Paleolimnological analysis suggests that eutrophic conditions were present in the lake for at least 150 years.

N deposition, along with climate change, was identified as a driver of diatom compositional turnover (or beta diversity) in a synthesis of paleolimnological core samples of 52 Arctic, alpine, and boreal montane lakes in North America and western Greenland. Hobbs et al. (2010) stated that in all lakes, beta diversity was significantly greater during the 20th century than the 19th century, with only a small and nonsignificant difference in turnover between the 19th century and the 1550–1800 intervals ( $p = 0.86$ ). Compared with forested montane boreal sites, both alpine and Arctic lakes reveal greater diatom assemblage turnover in the 20th century. In Arctic lakes, temperature appears to be the main factor affecting diatom composition turnover, while in temperate lakes, N deposition appears to play a larger role. A meta-analysis of 200 lakes in Europe and North America showed diatom shifts in Arctic lakes around 1850 and temperate lakes around 1970 (Rühland et al., 2008). Observed changes were primarily attributed to warming trends. The authors examined the diatom record from one lake in detail (Whitefish Lake in Ontario) and reported that observations of diatom shifts in this lake were not explained by N deposition but rather corresponded to temperature changes.

New information on relative  $\text{NO}_3^-$  inputs from glacial versus snowpack meltwaters reported in [Appendix 7](#) indicates water of glacial origin has higher levels of  $\text{NO}_3^-$ , which may influence the interpretation of biological data from high-elevation lakes and streams in some regions of the U.S. ([Slemmons et al., 2015](#); [Slemmons et al., 2013](#); [Saros et al., 2010](#); [Baron et al., 2009](#)). In the central Rockies and Glacier National Park, fossil diatom richness in snowpack-fed lakes was found to be higher (34 to 54 taxa) relative to lakes fed by both glacial and snowpack meltwaters [12 to 26 taxa; [Saros et al. \(2010\)](#)]. In the central Rockies, N deposition was 1.4 to 2.5 kg Nr/ha/yr, with 10 to 20% of the lakes there receiving glacial meltwater. In Glacier National Park in the northern Rockies, approximately 50% of lakes receive glacial meltwater and deposition was 2.0 to 3.4 kg Nr/ha/yr. In another study comparing sedimentary fossil diatom assemblages in two adjacent lakes (one glacier-fed and the other snow-fed) in the central Rocky Mountains, increased abundances of *A. formosa*, and *F. crotonensis* were observed in the glacier-fed lake starting 1,000 years ago along with a decrease in diatom species richness ([Slemmons et al., 2015](#)). Shifts in the planktonic diatom communities occurred after 1970 in snow-fed lakes ([Slemmons et al., 2017](#)). These observations suggest increased N inputs associated with glacial meltwater have altered the fossil algal record and continue to affect algal communities in some glacier-fed lakes. No significant differences in phytoplankton biomass and community structure were observed between snowpack-fed and glacier and snowpack-fed lakes in the northern Cascade Mountains in Washington in a comparison of data collected in 1989 and 2013 ([Williams et al., 2016b](#)).

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### 9.3.2.2 Bioassay, Mesocosm, and Laboratory Studies

Several experimental nutrient additions (mesocosm and bioassay studies) described in [Appendix 9.1.1.3](#) show that N limitation is common in freshwater systems ([Elser et al., 2009b](#); [Elser et al., 2009a](#); [Bergström et al., 2008](#)). Since the 2008 ISA, several N addition studies have explored the effects of increased nutrients on phytoplankton biomass and community structure ([Daggett et al., 2015](#); [Gardner et al., 2008](#)). In the Colorado Front Range, diatom abundance increased, and phytoplankton species composition shifted in nutrient-enriched mesocosms ([Gardner et al., 2008](#)). Principal component analysis suggested that 21% of the variance in phytoplankton community composition was related to added nutrients, while 34% of the variance was due to seasonal changes. In a bioassay comparison of phytoplankton community structure following N and DOM addition to a low DOC and N and P colimited water body (Jordan Pond in Acadia National Park, ME) and an N limited lake (Sargent Lake in Isle Royale National Park, MI), [Daggett et al. \(2015\)](#) observed increased chlorophytes following DOM inputs in both lakes. In the N limited lake, an increase in the abundance of *F.*

*crotonensis* and *Tabellaria flocculosa* was observed. There was a reduced response of chlorophytes to DOM addition when N was added to the N limited lake.

Most N addition studies of phytoplankton communities have focused on N limited systems. [Poxleitner et al. \(2016\)](#) conducted an N addition mesocosm experiment during the spring season in a P limited oligotrophic lake in Upper Bavaria, Germany. An increasing N enrichment gradient affected phytoplankton stoichiometry and community composition. Only small effects of N enrichment were documented using the biovolume of phytoplankton, the amount of particulate organic carbon, and the concentration of chlorophyll *a* as indicators. There was an effect, however, on phytoplankton community composition and heterotrophic nanoflagellate and ciliate abundances. Thus, changes in food web dynamics were suggested for P limited lakes when N levels are increased.

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### 9.3.2.3 Whole Lake Studies

Altered phytoplankton community composition and increased phytoplankton biomass resulted from inorganic N fertilization of Reindeer Lake in northern Sweden ([Jansson et al., 2001](#)). In a whole-lake N fertilization study of three small boreal lakes in northern Sweden, [Deininger et al. \(2017a\)](#) observed that changes in community composition of phytoplankton were related to DOC rather than N addition. As DOC increased along a gradient, community composition shifted from nonflagellated toward high DOC-adapted flagellated autotrophs in the three fertilized lakes. In the same set of lakes, phytoplankton biomass increased but net zooplankton responses were modest, attributed by the authors to incompatible stoichiometry of food (phytoplankton) to consumers [zooplankton; [Deininger et al. \(2017b\)](#)].

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### 9.3.3 Benthic Algal Diversity

Benthic algae are typically less sensitive than planktonic algae to nutrient inputs because the former are associated with nutrient-rich substrates where sunlight reaches the sediment surface ([Spaulding et al., 2015](#)). Periphyton is typically more abundant than phytoplankton in these shallow habitats ([Vinebrooke et al., 2014](#); [Nydick et al., 2004](#)). Several recent studies have considered the effects of N on benthic algae characteristic of shallow lakes and littoral zones where primary production is mainly controlled by the availability of light ([Vadeboncoeur et al., 2008](#)). In a stable isotope tracer study in Bull Trout Lake, a subalpine lake in Idaho, the largest portion of added N was retained within the periphyton ([Epstein et al., 2012](#)). A directional change in benthic diatom species after 1960 that correlates with atmospheric deposition was observed in lake sediment cores

from high-elevation shallow lakes in Grand Teton National Park ([Spaulding et al., 2015](#)). [Liess et al. \(2009\)](#) conducted a survey of periphyton along an N deposition gradient (2 to 12 kg N/ha/yr) in Sweden. Benthic algal composition in lakes in the northern part of the country where N deposition was lower had a higher contribution from N fixing cyanobacteria (5% of algal biovolume) than in the south. Overall, lakes were more N limited in the North and P limited in the South. In another study using nutrient-diffusing substrata in two small Alpine lakes in the Rhone Alps, France, N enriched substrata had a greater phytobenthic biomass, and the taxonomic composition of the phytobenthos was different between the treatment and control ([Lepori and Robin, 2014](#)).

In pond fertilization experiments in 12 fishless, nonglacial ponds in Snow Pass within the Cascade Valley catchment of Banff National Park, Alberta, periphyton outcompeted phytoplankton for limiting nutrients, indicating the importance of considering both benthic and pelagic primary producers ([Vinebrooke et al., 2014](#)). In these N limited ponds, phytoplankton biomass increased significantly only when N was applied in the absence of fairy shrimp. High grazing pressure by fairy shrimp appeared to suppress the effects of added nutrients on algal communities, suggesting that trophic interactions are important to consider to avoid missing the effects of N in alpine water bodies.

The algal assemblage response following 6 weeks of nutrient amendments in Wyoming streams indicated that both N and P altered community structure of epilithic biofilm ([Kunza and Hall, 2013](#)). Depending on which nutrient was added, N<sub>2</sub> fixers reacted differently than non-N<sub>2</sub> fixers; an increase in non-N<sub>2</sub> fixing diatoms in the N and N + P additions was observed compared to N<sub>2</sub> fixer dominance in control and P treatment.

Other studies consider how changes in benthic algal biodiversity affect ecosystem processes such as chemical uptake. NO<sub>3</sub><sup>-</sup>-N uptake differed among benthic algal assemblages on transplanted rocks in a stream in Boise National Forest in central Idaho ([Baker et al., 2009](#)). Uptake of NO<sub>3</sub><sup>-</sup> was highest in the green filamentous algae, (dominated by the chlorophytes *Spirogyra* spp. and *Rhizoclonium* spp.), lowest in the yellow patch type (dominated by the chlorophytes *Spirogyra* spp. and *Bulbochaete* spp.), and intermediate in the brown patch type (dominated by diatoms, including *Synedra* spp., *Cymbella* spp., *Fragilaria* spp., and *Epithemia* spp.). NO<sub>3</sub><sup>-</sup>-N uptake normalized to chlorophyll *a* increased with algal composition and species richness in the three patch types.

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### 9.3.4 Zooplankton Diversity

Changes to aquatic food webs in response to N enrichment have not been as thoroughly explored as changes to algal assemblages, but a few studies in the 2008 ISA showed

declines in zooplankton biomass ([Lafrancois et al., 2004](#); [Paul et al., 1995](#)) in response to N related shifts in phytoplankton biomass toward less palatable taxa with higher C:P ratios ([Elser et al., 2001](#)). New studies provide additional evidence for N deposition effects on zooplankton through altered trophic interactions.

The nutritional status of zooplankton is influenced by the quantity and quality of food items ([Elser et al., 2001](#)). In lakes across an N deposition gradient in Norway, zooplankton feeding on seston (organisms and nonliving matter in the water column) were found to be affected by P limitation in phytoplankton ([Elser et al., 2010](#)). The seston in lakes with high N deposition had significantly higher C:P and N:P ratios due to phytoplankton P limitation. Using an assay to measure alkaline phosphatase activity (APA), which is overexpressed in animals with dietary P deficiency, [Elser et al. \(2010\)](#) observed that the biomass-specific APA value differed considerably among taxa and that N deposition was significantly associated with some species such as seston-feeding zooplankton but not others, leading the authors to conclude that P limitation was transferred up the food chain. In three P deficient lakes in Germany, N enrichment experiments showed declines in mesozooplankton density and biomass, especially cladocerans, with N additions in the range of projected increasing atmospheric deposition ([Trommer et al., 2017](#)). An increase in seston C:P ratios was observed in one of the three P deficient lakes in response to N enrichment.

A taxonomic shift from omnivorous, raptorial-feeding copepods to filter-feeding herbivorous daphnids was observed with warming and N addition in a growth chamber experiment ([Thompson et al., 2008](#)). The study was conducted with water and sediment collected from Pipit Lake in the Canadian Rockies in Banff National Park, Alberta. While warming and N fertilization increased phytoplankton abundance, herbivory by *Daphnia middendorffiana* decreased but only in the presence of sediment (pond conditions). Findings demonstrated that the effects of warming and N differ both among trophic levels and aquatic alpine habitats.

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### 9.3.5 Macroinvertebrate Diversity

Macroinvertebrates such as aquatic insects, crustaceans, worms, and mollusks are commonly sampled to assess water quality in federal and state monitoring programs ([U.S. EPA, 2016j](#)). These organisms feed on algae and organic material and are an important food source for fish and other wildlife. Few studies have considered the effects of atmospheric N enrichment on biodiversity of freshwater macroinvertebrates. Due to the existence of a survey of benthic invertebrates in Lake Tahoe, NV conducted in the 1960s, it was possible to assess how the populations have changed with enrichment and the

introduction of non-native species. In this high alpine lake, atmospheric N contributions are a significant portion (approximately 57%) of the total N loading to the lake ([Sahoo et al., 2013](#)). [Caires et al. \(2013\)](#) resurveyed the lake in 2008–2009 and observed declines of 80 to 100% in endemic benthic invertebrate taxa and changes to the community structure of benthic invertebrate assemblages. Corresponding to these changes in lake biota, a decrease in water clarity over the four decades between studies has been associated with a shift in the bottom of the euphotic zone (1% light penetration) from 80 to 57 m ([Chandra et al., 2005](#)).

A recent study from Denmark suggests that macroinvertebrates may be poor indicators of N enrichment. [Friberg et al. \(2010\)](#) measured stream macroinvertebrate occurrence along gradients in organic pollution and eutrophication in 594 streams. They observed that the occurrence of many taxa showed a stronger relationship to habitat condition than to chemical variables. Overall, macroinvertebrate occurrence appeared to be related primarily to biological oxygen demand,  $\text{NH}_4^+\text{-N}$ , and TP rather than TN. In a principal component analysis using the United States Geological Survey (USGS) National Ambient Water Quality Assessment (NAWQA) data set, [Carlisle et al. \(2007\)](#) identified nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , TP) as a factor affecting macroinvertebrate occurrence, although specific conductance, pH, and  $\text{SO}_4^{2-}$  explained the greatest effects on macroinvertebrate abundance. A 20% loss of macroinvertebrate taxa was identified as a threshold for degraded streams based on benthic macroinvertebrate sampling data from a subset of basins in the eastern and midwestern U.S. ([Carlisle and Meador, 2007](#)).

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### 9.3.6 Macrophyte Diversity

No U.S. studies of N effects on macrophyte (aquatic plant) community biodiversity in atmospherically N enriched lakes and streams have been identified in the recent literature, although declines in total macrophyte occurrence were noted in a resurvey of Lake Tahoe that compared current samples with those from a lake survey conducted in the 1960s ([Caires et al., 2013](#)). Benthic invertebrate declines were most severe in sampling sites where macrophytes were present in the 1960s but now absent, suggesting that macroinvertebrate and macrophyte assemblages are closely associated in the lake. [Barker et al. \(2008\)](#) conducted a mesocosm experiment using water and sediment from a stream in Norfolk, U.K. Experimental tanks were planted with 11 macrophyte species from the local environment. Constant P loadings were given to all tanks (50  $\mu\text{g P/L}$ ). Nitrate loading varied from 1 to 10 mg  $\text{NO}_3^-\text{-N/L}$ . Macrophyte species richness decreased with increasing N during the first year of treatment, and decreased in all treatments above 1 mg  $\text{NO}_3^-\text{-N/L}$  during the second year. [Barker et al. \(2008\)](#) estimated a threshold of 1.5 mg N/L for maintaining a stable species richness.

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### 9.3.7 Amphibian Diversity

No studies on N enrichment effects on amphibian diversity were reviewed in the 2008 ISA or identified in the current literature.

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### 9.3.8 Fish Diversity

No studies of direct effects of N enrichment on freshwater fish diversity were reviewed in the 2008 ISA. Post-2007 literature includes several behavioral endpoints in fish. ([Appendix 9.4.1](#)).

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## 9.4 Animal Behavior and Disease

In addition to changes in biological indicators (i.e., chlorophyll *a*, periphyton/microbial biomass, diatoms, nutrient limitation shifts) and altered biodiversity, there is increasing evidence for a role of N in behavior and disease in biota. These indirect responses may impact the fitness of organisms inhabiting nutrient-enriched waters.

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### 9.4.1 Behavior

Nutrient enrichment of freshwater systems has recently been shown to alter behavioral endpoints in an invertebrate, an amphibian, and a fish species in laboratory exposures. NO<sub>3</sub><sup>-</sup> exposure (21.4, 44.9, 81.8, 156.1 mg NO<sub>3</sub><sup>-</sup>/L) was shown to decrease the velocity of movement in the aquatic snail *Potamopyrgus antipodarum* ([Alonso and Camargo, 2013](#)). Reproductive impairments (decreased number of newborns) were observed at all tested concentrations. The NO<sub>3</sub><sup>-</sup> concentrations used in this study are much higher than typically measured in remote freshwater catchments affected by atmospheric deposition.

In the presence of chemical cues of the predator nymphs of the dragonfly (*Anax imperator*), western spadefoot toad (*Pelobates cultripes*) tadpoles typically decrease swimming activity by 44% ([Polo-Cavia et al., 2016](#)). When predator chemical cues were added to water containing NH<sub>4</sub>NO<sub>3</sub> tadpoles did not alter swimming activity. The concentrations of NH<sub>4</sub>NO<sub>3</sub> used in the study (20 mg/L and 80 mg/L) were not lethal to the tadpoles, and no altered swimming activity was observed with the added N except in the presence of predator chemical cues.

In the three-spined stickleback *Gasterosteus aculeatus*, a fish that inhabits both freshwater and brackish habitats, changes to water quality associated with eutrophication

(i.e., turbidity associated with algal blooms) have impacted social and reproductive behaviors in laboratory studies. These studies are reviewed in [Appendix 10](#).

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#### 9.4.2 Disease

The interactions of N enrichment and disease in biota is a relatively new area of research in N impacted freshwater systems. The interactions characterized to date are complex and involve indirect effects on host-parasite interactions ([Johnson et al., 2010](#); [Johnson et al., 2007](#)). A host-parasite relationship potentially impacted by increased N to aquatic systems is that of the fungal pathogen *Metschnikowia bicuspidata*, which is parasitic to crustacean zooplankton *Daphnia dentifera* ([Dallas and Drake, 2014](#)). In a series of bioassays designed to assess the effects of N on host and pathogen, *D. dentifera* were exposed to six  $\text{NO}_3^-$  concentrations (0.4, 2, 4, 8, 16, and 32 mg  $\text{NO}_3^-/\text{L}$ ) and then inoculated with *M. bicuspidata*.  $\text{NO}_3^-$  decreased *D. dentifera* population size and increased infection prevalence. Next, ambient levels of N (0.4 mg  $\text{NO}_3^-/\text{L}$ ) and a concentration representative of a moderately polluted system (12 mg  $\text{NO}_3^-/\text{L}$ ) were used to test the influence of  $\text{NO}_3^-$  on pathogen dose, infection prevalence, and host fitness (growth and fecundity). No effects were observed on the growth rate of *D. dentifera*; however, greater infection prevalence was associated with increased  $\text{NO}_3^-$ , and in general, both host fecundity and infection intensity decreased with increasing pathogen dose.

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### 9.5 Summary of Thresholds, Levels of Deposition at Which Effects Are Manifested, and Critical Loads

Since the 2008 ISA, additional thresholds of response to N have been identified that are useful for critical load development in water bodies impacted by N nutrient effects. Critical loads for N nutrient enrichment in U.S. freshwater ecosystems are summarized in [Table 9-4](#). Factors contributing to uncertainty in N deposition estimates for assessment of critical loads according to [Pardo et al. \(2011a\)](#) include “(1) the difficulty of quantifying dry deposition of nitrogenous gases and particles to complex surfaces; (2) sparse data, particularly for arid, highly heterogeneous terrain (e.g., mountains); and (3) sites with high snowfall or high cloud water/fog deposition, where N deposition tends to be underestimated.” N deposition estimates at high-elevation sites such as those in the Rocky and Sierra Nevada mountains are associated with considerable uncertainty, especially uncertainty for estimates of dry deposition ([Appendix 2](#)). For sensitive receptors such as phytoplankton shifts in high-elevation lakes, N deposition model bias may be close to, or exceed, predicted critical load values ([Williams et al., 2017a](#)).

Physical, chemical, and ecological variability across lakes affect their response to N deposition and contribute to uncertainty of critical load estimates ([Appendix 9.1.1.2](#)). A review by [Bowman et al. \(2014\)](#) noted that current N critical loads for sensitive alpine systems may not be protective under future climate scenarios of warmer summer temperatures and a shorter duration of snow cover.

Available data from the 2008 ISA suggest that the increases in total N deposition do not have to be large to elicit an ecological effect in remote alpine lakes. A hindcasting exercise determined that the shift in Rocky Mountain National Park lake algae composition that occurred between 1850 and 1964 was associated with wet N deposition that was only about 1.5 kg N/ha/yr ([Baron, 2006](#)). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming occurred at about 1.5 kg TN/ha/yr deposition ([Saros et al., 2003](#)).

**Table 9-4 Summary of critical loads for nitrogen eutrophication for surface water in the U.S. [adapted from [Pardo et al. \(2011c\)](#) with newer studies added].**

Ecosystem	Site	Critical Load for N Deposition kg N/ha/yr	Comments	Reference/ HERO ID
Alpine stream	Southern Rockies/Loch Vale Rocky Mtn. Nat. Park	2	Modeled	<a href="#">Baron et al. (1994)</a>
Alpine lake	Northern Rockies/Beartooth Mtns., WY	1.5	Paleolimnological, shifts in diatom assemblages with <i>Fragilaria crotonensis</i> and <i>Cyclotella bodanica</i> increasing to comprise approximately 30% each of total assemblage	<a href="#">Saros et al. (2003)</a>
Alpine lakes	Rocky Mountains	2.5	Surveys and references therein	<a href="#">Bergström and Jansson (2006)</a>
Alpine lakes	Eastern Sierra Nevada and Greater Yellowstone Ecosystem	1.4	Paleolimnological, increase in the relative abundances of <i>Asterionella formosa</i> and <i>Fragilaria crotonensis</i>	<a href="#">Saros et al. (2011)</a>
High-elevation lakes of western and eastern U.S.	Rocky Mountains, Sierra Nevada, Northeast	1.0 to 3.0 (western lakes) 3.5 to 6.0 (northeastern lakes)	Based on N deposition calculated in three different ways and on lake NO <sub>3</sub> <sup>-</sup> concentrations	<a href="#">Baron et al. (2011b)</a>

**Table 9-4 (Continued): Summary of critical loads for nitrogen eutrophication for surface water in the U.S. [adapted from Pardo et al. (2011c) with newer studies added]**

Ecosystem	Site	Critical Load for N Deposition kg N/ha/yr	Comments	Reference/ HERO ID
Remote lakes		2.0 (western lakes) 8.0 (eastern lakes)	Based on value of N deposition at which significant NO <sub>3</sub> <sup>-</sup> leaching begins to occur	<a href="#">Pardo et al. (2011c)</a>
Alpine lakes	Rocky Mountain National Park	>1.5	Based on NO <sub>3</sub> <sup>-</sup> threshold of 0.5 μM (concentration which elicits a growth effect in the diatom <i>A. formosa</i> )	<a href="#">Nanus et al. (2012)</a>
Alpine lake	Hoh Lake, Olympic National Park, WA	1.0–1.2	Increased relative abundances of <i>Asterionella formosa</i> and <i>Fragilaria tenera</i> Diatom assemblage shift	<a href="#">Sheibley et al. (2014)</a>
Alpine lakes	Greater Yellowstone area	<1.5 to >4.0 <sup>a</sup>	Modeled; based on threshold value of NO <sub>3</sub> <sup>-</sup> (0.5 to 2.0 μeq/L)	<a href="#">Nanus et al. (2017)</a>
Western U.S. lakes	Remote mountain lakes across the western U.S.	4.1 <sup>a</sup>	Based on phytoplankton biomass nutrient limitation shifts	<a href="#">Williams et al. (2017b)</a>
Western U.S. lakes	Remote mountain lakes across the western U.S.	2.0 <sup>a</sup>	Modeled to reduce occurrence of false negatives to near zero	<a href="#">Williams et al. (2017b)</a>

N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate.

<sup>a</sup>total N

Since the release of the 2008 ISA, work has continued on identifying thresholds of response to N deposition that can be used to calculate critical loads in sensitive freshwater systems. Threshold values for phytoplankton biomass growth have been identified for nine western mountain lakes in North Cascades, Mount Rainier, and Olympic national parks [13 to 25 μg DIN/L; [Williams et al. \(2016a\)](#)] and in lakes in the Sierra Nevada [0.3 to 4 μmol N/L (5 to 56 μg N/L); ([Heard and Sickman, 2016](#))]. [Williams et al. \(2017b\)](#) identified nutrient limitation shift thresholds (21 to 53 μg N/L) for remote western U.S. mountain lakes. A nutrient threshold for surface water NO<sub>3</sub><sup>-</sup> for growth of the diatom *A. formosa* was developed for high-elevation lakes in the Rocky Mountains where N deposition is prevalent ([Nanus et al., 2012](#)). The NO<sub>3</sub><sup>-</sup> threshold of 0.5 μmol/L (31 μg/L) was then used to estimate areas in Rocky Mountain National Park that exceed critical load values.

Additional critical loads for nutrient enrichment of freshwaters developed since the 2008 ISA include those in the western and northeastern U.S. [Pardo et al. \(2011c\)](#) estimated a critical load of 2.0 kg N/ha/yr for western lakes and 8.0 kg N/ha/yr for eastern lakes based on the value of N deposition at which significant  $\text{NO}_3^-$  leaching begins to occur. Using data from 125 lakes in the Greater Yellowstone area, including sensitive lakes in both Grand Teton and Yellowstone national parks, [Nanus et al. \(2017\)](#) estimated aquatic critical load values and identified locations with predicted critical load exceedances based on a threshold value of  $\text{NO}_3^-$  concentration in lake water selected as indicative of biological harm (0.5 to 2.0  $\mu\text{eq/L}$  in this study). Critical loads of TN deposition ranged from  $<1.5 \pm 1.0$  kg N/ha/yr to  $>4.0 \pm 1.0$  kg N/ha/yr. Exceedance estimates were as high as 48% of the Greater Yellowstone area study region.

[Baron et al. \(2011b\)](#) found that in the western high-elevation lakes, increased primary productivity and changes to algal diversity can occur with only minimal inputs of N deposition. They estimated that the thresholds, or critical loads, for nutrient enrichment are 1.0 to 3.0 kg N/ha/yr for the western mountains (Sierra Nevada and Rocky mountains; [Table 9-5](#)). For minimally disturbed lakes in the Northeast, a critical load of 3.5 to 6.0 kg N/ha/yr was estimated, but independent biological measures for nutrient enrichment are lacking in this region. In another study from the eastern Sierra Nevada and Greater Yellowstone Ecosystem, [Saros et al. \(2011\)](#) determined a critical load of 1.4 kg N/ha/yr wet N deposition by modeling wet deposition rates from the period in which diatom shifts first occurred. The shifts were identified from sediment cores between 1960 and 1965 in the eastern Sierra Nevada, and starting in 1980, in the Greater Yellowstone Ecosystem. Using core samples, [Sheibley et al. \(2014\)](#) identified diatom changes corresponding to N inputs from 1969–1975 in Hoh Lake in Washington and established a critical load of  $1.0\text{--}1.2 \pm 0.01$  kg N/ha/yr for the lake.

Using phytoplankton biomass N to P limitation shifts as the basis for critical load calculations, [Williams et al. \(2017b\)](#) determined an empirical critical load of 4.1 kg/TN/ha/yr for remote high-elevation lakes across the western U.S. The critical loads were calculated as the total (wet + dry) N deposition rate at which point below the critical load, N limitation is more likely than P limitation and above the critical load, P limitation is more likely than N limitation. Modeled critical loads using DIN:TP and DIN response categories yielded an average critical load of 3.8 kg/TN/ha/yr for the lakes. Modeled critical loads ranged from 2.8 to 5.2 kg/TN/ha/yr and correctly predicted exceedances in 69% of lakes using  $\text{NO}_3^-$ -N. The authors conducted a performance evaluation using the  $\text{NO}_3^-$ -N univariate model and identified a critical load of 2.0 kg/TN/ha/yr to reduce the likelihood of false negatives to near zero.

**Table 9-5 Summary of mean lake nitrate (NO<sub>3</sub><sup>-</sup>) concentrations, inorganic nitrogen deposition amounts, and nutrient enrichment inflection points where lake NO<sub>3</sub><sup>-</sup> concentrations reflect increased nitrogen deposition. [from [Baron et al. \(2011b\)](#)].**

Region	Mean Lake NO <sub>3</sub> <sup>-</sup>	Mean 1997–2006 NADP N Deposition	Nutrient Enrichment Inflection Point (NADP)	Mean 1997–2006 (PRISM + NADP) Deposition	Nutrient Enrichment Inflection Point (PRISM + NADP)	2002 Total N Deposition	Nutrient Enrichment Inflection Point (Total N)
Sierra Nevada (n = 30)	2.7 (1.10)	1.5 (0.22)	1.5	2.5 (0.34)	1.5	3.4 (0.47)	2.0
Rocky Mountains (n = 285)	3.7 (1.90)	1.2 (0.27)	1.0	3.0 (0.28)	2.0	2.0 (0.24)	3.0
Northeast (n = 216)	14.4 (0.76)	4.7 (0.18)	3.5	5.2 (0.18)	3.5	3.5 (0.20)	6.0

N = nitrogen; NADP = National Atmospheric Deposition Program; NO<sub>3</sub><sup>-</sup> = nitrate; PRISM = Parameter-Elevation Regressions on Independent Slopes Model; PRISM + NADP = concentrations from NADP with PRISM precipitation values.

Note: Inorganic N deposition was calculated three ways, as was described in [Baron et al. \(2011b\)](#). Coefficients of variation are in parentheses.

Mean lake NO<sub>3</sub><sup>-</sup> (in micromoles per liter), inorganic nitrogen (N) deposition amounts (in kg N/ha/yr), and nutrient enrichment inflection points where lake NO<sub>3</sub><sup>-</sup> concentrations increase in response to increasing N deposition.

Source: [Aber et al. \(2003\)](#), [Sickman et al. \(2002\)](#), U.S. Forest Service's Air Resource Management online database ([www.fs.fed.us/ARMdata](http://www.fs.fed.us/ARMdata)).

## 9.6 Summary and Causal Determination

In the 2008 ISA, the body of evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, community composition, and biodiversity in freshwater ecosystems. New evidence from 2008 to the present, from paleolimnological surveys, fertilization experiments, gradient studies, phytoplankton community responses, and indices of biodiversity continue to show effects of N loading to sensitive freshwater systems. As reported in the 2008 ISA, freshwater systems in which N has been observed to influence ecological processes either received extremely high inputs [e.g., ([Dumont et al., 2005](#))], or had very low initial N concentrations and responded rapidly to the additional inputs ([Bergström and Jansson, 2006](#); [Baron et al., 2000](#)). As summarized in the 2008 ISA and supported by data in newer studies, nutrient enrichment effects on freshwater ecosystems from atmospheric deposition of N are most likely to occur in lakes and streams that have low primary productivity and low nutrient levels and that are located in the most undisturbed areas with no local pollution sources.

Even small inputs of N in these water bodies can increase nutrient availability or alter the balance of N and P, which can stimulate growth of phytoplankton. As reported in the 2008 ISA and further strengthened with new evidence in this review, there is consistent and coherent evidence for species composition changes and reductions in diversity, especially for primary producers from high-elevation lakes in the western U.S., in response to increased availability of N. New information is consistent with the conclusions of the 2008 ISA that **the body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota, including altered growth and productivity, species richness, community composition, and biodiversity due to N enrichment in freshwater ecosystems.**

New data have not appreciably changed the consistent and coherent evidence at the time of the 2008 ISA that freshwater systems that are likely to be most impacted by nutrient enrichment due to atmospheric deposition of N are remote, oligotrophic, high-elevation water bodies with limited local nutrient sources and with low N retention capacity. N inputs to these ecosystems are linked to changes in biota, especially increased algal growth and shifts in algal communities. Freshwater systems sensitive to N nutrient enrichment include those in the Snowy Range in Wyoming, the Sierra Nevada Mountains, and the Colorado Front Range. A portion of these lakes and streams where effects are observed are in Class I wilderness areas ([Williams et al., 2017b](#); [Clow et al., 2015](#); [Nanus et al., 2012](#)).

Recent research further supports the 2008 ISA findings that N limitation is common in oligotrophic waters in the western U.S. ([Elser et al., 2009b](#); [Elser et al., 2009a](#)). Shifts in nutrient limitation, from N limitation, to between N and P limitation, or to P limitation, were reported in some alpine lake studies reviewed in the 2008 ISA and in this review. Since the 2008 ISA, several meta-analyses have reported an increase in P deposition to water bodies ([Stoddard et al., 2016](#); [Brahney et al., 2015](#); [Tipping et al., 2014](#)) and highlight the need to account for how sustained P deposition can modify the effects of anthropogenically emitted N deposition on productivity. P addition delayed the shift to P limitation (prolonged N limitation) for phytoplankton.

The body of evidence for biological effects of N enrichment and altered N:P ratios in remote freshwater systems (where atmospheric deposition is the predominant source of N) is greatest for phytoplankton, the base of the freshwater food web. Lake surveys, fertilization experiments, and nutrient bioassays reported in the 2008 ISA and in this review show increased pelagic and benthic algal productivity (as indicated by chlorophyll *a* concentration) to be strongly related to increased N concentration. An increase in lake phytoplankton biomass with increasing N deposition was reported in several regions, including the Snowy Range in Wyoming and across Europe. New studies

in the Rocky Mountains of Colorado where atmospheric deposition ranged from 2 to 7 kg N/ha/yr support observations from the 2008 ISA which showed correlations between greater chlorophyll *a* response and higher rates of deposition ([Elser et al., 2009a](#)). Several recent studies have considered the effects of N on benthic algae characteristic of shallow lakes and littoral zones where availability of light is the main factor controlling primary production. A few studies have shown that periphyton outcompeted phytoplankton for limiting nutrients, indicating the importance of considering both benthic and suspended primary producers.

Changes in phytoplankton species diversity and community structure reported in the 2008 ISA ([Lafrancois et al., 2004](#); [Wolfe et al., 2003](#); [Jassby et al., 1994](#)) and newer studies ([Symons et al., 2012](#); [Saros et al., 2010](#)) show a general shift from chrysophytes that dominate lakes with low N to cyanophytes and chlorophytes in lakes with higher N. In the 2008 ISA, diatom assemblage shifts were reported from the literature at total N deposition as low as 1.5 kg N/ha/yr ([Saros et al., 2003](#)). This evidence was further supported by a hindcasting exercise that determined the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha/yr ([Baron, 2006](#)). Two nitrophilous species of diatoms, *A. formosa* and *F. crotonensis*, are dominant in lakes with higher N and serve as biological indicators of N enrichment; however, increased relative abundance of *A. formosa* has also been attributed to lake warming in some regions where N deposition is decreasing ([Sivarajah et al., 2016](#)). Some shifts in algal biodiversity observed in high-elevation waters are attributed to climate change or nutrient effects and climate as costressors ([Appendix 13](#)).

The role of N in freshwater HAB formation has been further researched since the 2008 ISA. Additional evidence continues to show that the availability and form of N influences algal bloom composition and toxicity and that inputs of inorganic N selectively favor some HAB species, including those that produce microcystin. Microcystin is prevalent in U.S. waters as reported in recent regional and national surveys. Although the risk of HAB formation is low in high-elevation oligotrophic water bodies where N deposition is the dominant source of N, transport of atmospheric inputs can exacerbate eutrophic conditions in downstream water bodies. Increased understanding of the role of N as a limiting nutrient in many freshwater systems has led to recommendations to consider both N and P in nutrient reduction strategies ([Dodds and Smith, 2016](#); [Gobler et al., 2016](#); [Paerl et al., 2016b](#); [Lewis et al., 2011](#); [Scott and McCarthy, 2010](#); [Conley et al., 2009](#); [Paerl, 2009](#); [Lewis and Wurtsbaugh, 2008](#)).

Since the 2008 ISA, empirical and modeled critical loads for the U.S. have been estimated based on surface water NO<sub>3</sub><sup>-</sup> concentration, diatom community shifts, and

phytoplankton biomass growth nutrient limitation shifts. A critical load ranging from 3.5 to 6.0 kg N/ha/yr was identified for high-elevation lakes in the eastern U.S. based on the nutrient enrichment inflection point [where  $\text{NO}_3^-$  concentrations increase in response to increasing N deposition; ([Baron et al., 2011b](#))]. Another critical load of 8.0 kg N/ha/yr for eastern lakes based on the value of N deposition at which significant increases in surface water  $\text{NO}_3^-$  concentrations occur was estimated by [Pardo et al. \(2011c\)](#). In both Grand Teton and Yellowstone national parks, critical loads for total N deposition ranged from  $<1.5 \pm 1.0$  kg N/ha/yr to  $>4.0 \pm 1.0$  kg N/ha/yr ([Nanus et al., 2017](#)). Exceedance estimates were as high as 48% of the Greater Yellowstone area study region, depending on the threshold value of  $\text{NO}_3^-$  concentration in lake water selected as indicative of biological harm.

Additional critical loads have been identified since the 2008 ISA for eastern Sierra Nevada lakes, Rocky Mountain lakes, the Greater Yellowstone Ecosystem, and Hoh Lake, Olympic National Park [[Table 9-4](#); ([Nanus et al., 2017](#); [Sheibley et al., 2014](#); [Pardo et al., 2011c](#); [Saros et al., 2011](#))]. The identified values fall near or within the range of 1.0 to 3.0 kg N/ha/yr for western lakes ([Baron et al., 2011b](#)). An empirical critical load of 4.1 kg/TN/ha/yr above which phytoplankton biomass P limitation is more likely than N limitation was identified by [Williams et al. \(2017b\)](#) for the western U.S. Modeled critical loads ranged from 2.8 to 5.2 kg/TN/ha/yr, and a performance analysis indicated that a critical load of 2.0 kg/TN/ha/yr would likely reduce the occurrence of false negatives to near zero.

The evidence for N effects on other freshwater biota is not as extensive as for phytoplankton. Since the 2008 ISA, new research on archaea and bacterial diversity in freshwater systems suggests that these organisms respond to lake trophic state and the form of N present. At higher trophic levels, zooplankton responses to N inputs are attributed to changes in food quality which can potentially alter food web interactions ([Deininger et al., 2017b](#); [Meunier et al., 2016](#); [Elser et al., 2009a](#)). A few studies in the 2008 ISA showed declines in zooplankton biomass ([Lafrancois et al., 2004](#); [Paul et al., 1995](#)) in response to N related shifts in phytoplankton biomass toward less palatable taxa with higher C:P ratios ([Elser et al., 2001](#)). Limited studies since the 2008 ISA suggest that atmospheric N inputs are linked to taxonomic shifts and declines in some invertebrates, although the effects attributed to N are difficult to separate from other stressors such as climate change and invasive species. Water quality changes associated with excess N nutrient inputs, such as lowered DO and algal blooms that alter habitat by covering up substrate, can also lead to declines in biodiversity in macroinvertebrates and fish including species listed under the federal Endangered Species Act ([Hernández et al., 2016](#)). Although little research has been conducted in freshwater systems, some evidence suggests that increased turbidity associated with algal blooms may affect reproductive

and social behaviors in fish ([Appendix 10](#)). Emerging research on disease in biota suggest that N enrichment may modify relationships such as host susceptibility to parasites and pathogens.

Since the 2008 ISA, further studies have shown that both trophic interactions and DOC modify ecosystem response to N loading. In a whole-lake N fertilization study, [Deininger et al. \(2017a\)](#) observed that changes in community composition of phytoplankton were related to DOC rather than N addition to small N limited boreal lakes. As DOC increased along a gradient, community composition shifted from nonflagellated toward high DOC-adapted flagellated autotrophs in the three fertilized lakes. In the same set of lakes, although phytoplankton biomass increased, net zooplankton responses were modest and attributed by the authors to incompatible stoichiometry of food (phytoplankton) to consumers [zooplankton; [Deininger et al. \(2017b\)](#)]. A study in Banff National Park, Canada indicated that grazing pressure on algae may have negated the effects of nutrient inputs on primary producers ([Vinebrooke et al., 2014](#)). Limited evidence suggests a decreased rate of leaf litter decomposition by microbial communities with N loading to streams.

New studies show that the N contribution from glacial meltwater (which has higher  $\text{NO}_3^-$  relative to water from melting snow) affects diatom community composition in high-elevation lakes and streams in some regions of the U.S. ([Slemmons et al., 2015](#); [Slemmons et al., 2013](#); [Saros et al., 2010](#)). N deposition to snow and glaciers are important sources of N to alpine lakes and streams that are fed by meltwaters. In a comparison of biological response in snowpack-fed lakes versus lakes with both glacial and snowpack meltwater in the Rockies, fossil diatom richness was higher in the snowpack-fed lakes (34 to 54 taxa) compared to lakes with both glacial and snow meltwater inputs [12 to 26 taxa; ([Saros et al., 2010](#))]. Characterizing diatom community responses to meltwater sources is important for interpreting the biological effects of N deposition in high-elevation systems with both glacial and snow inputs.

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# APPENDIX 10 BIOLOGICAL EFFECTS OF NITROGEN ENRICHMENT IN ESTUARIES AND NEAR-COASTAL SYSTEMS

This appendix characterizes the biological effects of nitrogen (N) enrichment in estuaries (areas where freshwater from rivers meets the salt water of oceans), coastal lagoons, coral reef ecosystems, and open ocean areas near coastlines. An overview of N inputs to coastal systems, including characteristics and identification of areas of the U.S. sensitive to nutrient over-enrichment ([Appendix 10.1](#)) is followed by discussions of the indicators of nutrient enrichment ([Appendix 10.2](#)), its effects on biodiversity and ecosystem structure and function ([Appendix 10.3](#)), animal behavior, and disease ([Appendix 10.4](#)), and the role of N enrichment and acidification on calcifying organisms ([Appendix 10.5](#)). [Appendix 10.6](#) summarizes the thresholds of biological effects of N in coastal regions, and [Appendix 10.7](#) reviews the causal determination based on a synthesis of new information and previous evidence from prior N assessments.

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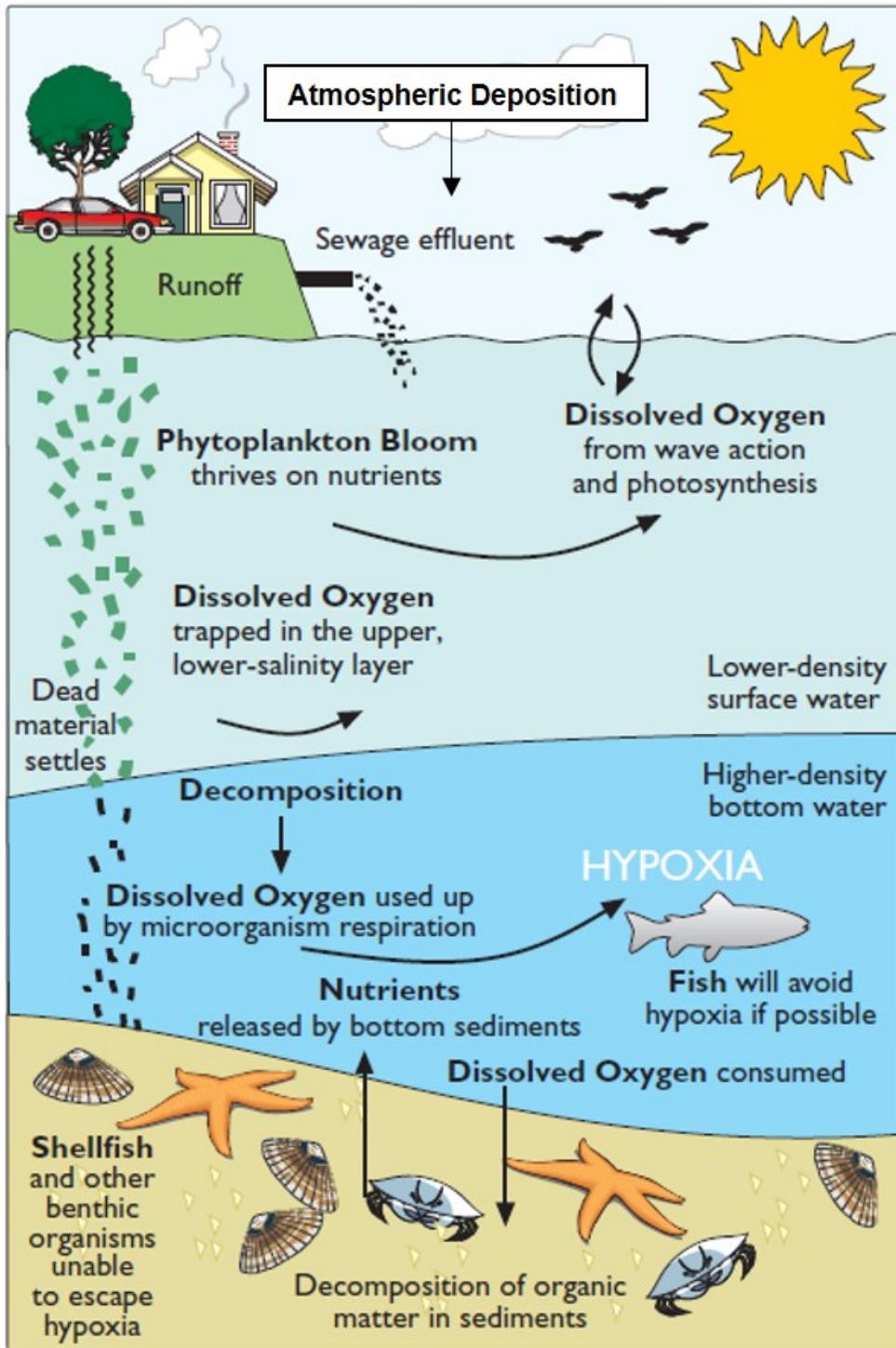
## 10.1 Introduction

In the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria* (2008 ISA), the body of evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in estuarine systems ([U.S. EPA, 2008a](#)). Nitrogen pollution is the major cause of harm to the majority of estuaries in the U.S. ([Bricker et al., 2008](#); [NRC, 2000](#)). In estuaries, N from atmospheric and nonatmospheric sources contributes to increased primary productivity, leading to eutrophication ([Figure 10-1](#)). Estuary eutrophication is a process of increasing nutrient over-enrichment indicated by water quality deterioration, resulting in numerous adverse effects including areas of low dissolved oxygen (DO) concentration (hypoxic zones), species mortality, and harmful algal blooms (HABs). Eutrophic systems are characterized by an increase in the rate of supply of organic matter (primary production and organic carbon accumulation) in excess of what an ecosystem is normally adapted to processing ([Diaz et al., 2013](#); [Nixon, 1995](#)). In the 2008 ISA the strongest evidence for a causal relationship was from changes in biological indicators of nutrient enrichment including chlorophyll *a*, macroalgal “seaweed” abundance, HABs, DO, and submerged aquatic vegetation (SAV). Biological effects of increasing nutrient enrichment also include changes in biodiversity in these systems ([Section IS.2.2.4](#)). For this ISA, new information is consistent with the 2008 ISA and the causal determination

has been updated to reflect more specific categories of effects. **The body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota, including altered growth, total primary production, total algal community biomass, species richness, community composition, and biodiversity due to N enrichment in estuarine environments.**

In the previous ISA, there was a strong scientific consensus that N is the principal cause of coastal eutrophication in the U.S. ([U.S. EPA, 2008a](#); [NRC, 2000](#)). On average, human activity has likely contributed to a sixfold increase in the N flux to the coastal waters of the U.S. over the past several decades, and excessive N represents the most significant coastal pollution problem ([Bricker et al., 2008](#); [Bricker et al., 2007](#); [Howarth and Marino, 2006](#); [Bricker et al., 2003](#); [Howarth et al., 2002](#); [NRC, 2000](#)). Many coastal areas receive high enough levels of N input from human activities to cause eutrophication ([Bricker et al., 2007](#); [Howarth et al., 1996a](#); [Vitousek and Howarth, 1991](#)). As reported in the 2008 ISA, N driven eutrophication of shallow estuaries has increased over the past several decades, and environmental degradation of coastal ecosystems is now a widespread occurrence ([Bricker et al., 2007](#); [Paerl et al., 2000](#)).

Coastal systems are linked to terrestrial N processes along the freshwater to ocean continuum as nutrients deposited to the watershed move downstream. As described in the 2008 ISA, in coastal ecosystems, the nutrients most commonly associated with phytoplankton growth are N, phosphorus (P), and silicon (Si). The relative proportions of these nutrients are important determinants of primary production, food web structure, and energy flow through the ecosystem ([Turner et al., 1998](#); [Justic et al., 1995b](#); [Justic et al., 1995a](#); [Dortch and Whitley, 1992](#)). In general, estuaries tend to be N limited [[D'Elia et al. \(1986\)](#); [Howarth \(1988\)](#); [Nixon \(1995\)](#); [NRC \(2000\)](#); [Howarth and Marino \(2006\)](#); [Elser et al. \(2007\)](#); [Paerl and Piehler \(2008\)](#); [Appendix 10.1.3](#)]; however, some estuaries are P limited, or colimited by N and P, or switch seasonally between N and P ([Howarth et al., 2011](#); [Paerl and Piehler, 2008](#); [Howarth and Marino, 2006](#)).



N = nitrogen.

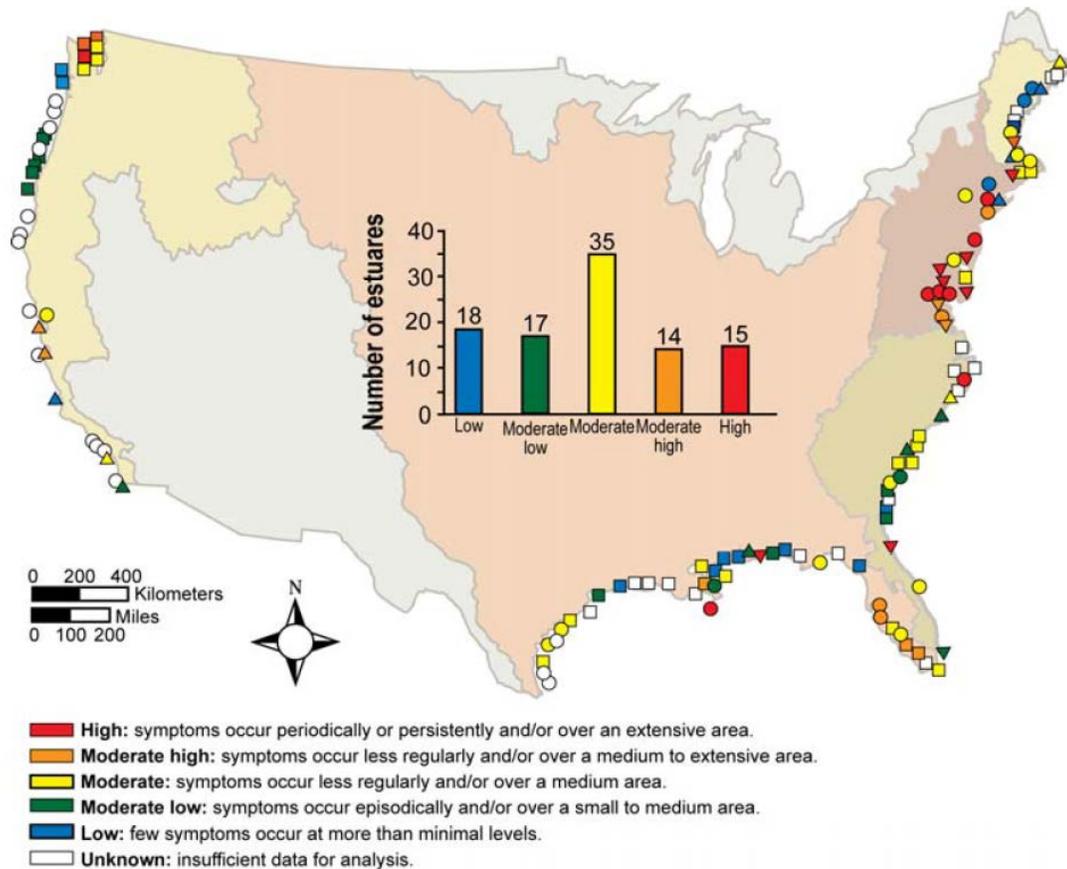
Notes: Atmospheric N deposition is one of the sources of nutrient enrichment to coastal areas.

Source: Modified from [U.S. EPA \(2012b\)](#).

**Figure 10-1 Eutrophication can occur when the availability of nutrients increases above normal levels.**

Altered biogeochemical processes associated with N loading ([Appendix 7](#)) may affect aquatic biota in a diversity of coastal habitats. Habitats associated with coastal areas include shallow open waters, sandy beaches, mud and sand flats, rocky shores, oyster beds, coral reefs, mangrove forests, river deltas, tidal pools, and seagrasses ([U.S. EPA, 2016g](#)). [Appendix 11](#) will cover wetland ecosystems, including those located on coasts in which soils and/or sediments are periodically inundated by tides or flooding. Estuaries in the U.S. are located on both coasts with varying levels of eutrophication occurring [[Bricker et al. \(2007\)](#); [Figure 10-2](#)]. SAV, including the eelgrass *Zostera marina*, are important ecological communities found within some coastal bays and estuaries that are sensitive to elevated nutrient loading ([Appendix 10.2.5](#)). Estuaries provide breeding grounds, nurseries, and shelter for aquatic biota. Near-coastal coral reefs have a more limited distribution in the U.S. occurring off south Florida, Texas, Hawaii, and U.S. territories in the Caribbean and Pacific. Elevated N loading appears to play a role in susceptibility of coral species to disease and bleaching ([Appendix 10.4.2](#)).

In the 2008 ISA and the National Estuarine Eutrophication Assessment (NEEA), a comprehensive survey of eutrophic conditions in the Nation's estuaries conducted by the National Oceanic and Atmospheric Administration (NOAA), the most eutrophic estuaries in the U.S. occurred in the mid-Atlantic region, and the estuaries with the lowest degree of eutrophication were in the North Atlantic [[Bricker et al. \(2007\)](#) and [Figure 10-2](#)]. In the NEEA, 65% of assessed estuaries had moderate to high overall eutrophic conditions ([Bricker et al., 2007](#)). In the U.S., Chesapeake Bay is perhaps the best-documented case study of the effects of human activities on estuarine eutrophication. Human disturbances, such as landscape changes, have exacerbated the negative impacts of N deposition by reducing N removal and retention in the upper watershed region. Anthropogenic N inputs have substantially altered the trophic condition of Chesapeake Bay over the last 50 to 100 years. Signs of eutrophication in the bay include high algal production, low biodiversity, and large hypoxic and anoxic zones. Other estuaries identified in the 2008 ISA where the extent of hypoxia and algal blooms have increased included Long Island Sound, the Pamlico Estuary in North Carolina, and along the continental shelf adjacent to the Mississippi and the Atchafalaya River discharges to the Gulf of Mexico ([U.S. EPA, 2008a](#)). This appendix updates the state of the science on N-nutrient enrichment, focusing on U.S. waters, since the release of the 2008 ISA.



Source: [Bricker et al. \(2007\)](#).

**Figure 10-2 Overall eutrophication condition on a national scale.**

### 10.1.1 Nitrogen Sources to Estuaries and Coasts

Sources of N are described in detail in [Appendix 2](#). Briefly, coastal waters are influenced by N enrichment from upstream sources that may undergo biogeochemical transformations along the freshwater-to-ocean continuum as well as direct inputs from the atmosphere. In estuaries adjacent to areas of coastal upwelling, such as some locations along the Pacific coast of the U.S., oceanic inputs of nutrients may also represent an important source of N ([Brown and Ozretich, 2009](#)). N inputs can be attributed to point sources from a single outfall or discharge point and nonpoint sources, which are diffuse ([U.S. EPA, 2008a](#)). Both point and nonpoint sources have been identified as targets for control of N inputs in coastal systems ([Stephenson et al., 2010](#); [Paerl et al., 2002](#)).

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### 10.1.2 Trends in Atmospheric Deposition of Nitrogen (N)

Trends in atmospheric deposition are discussed in [Appendix 2](#). In summary, in many parts of the U.S., including the Southeast, Mid-Atlantic, and Midwest, deposition of reduced N has increased relative to oxidized N in last few decades, shifting from a nitrate ( $\text{NO}_3^-$ ) dominated to an ammonium ( $\text{NH}_4^+$ ) dominated condition. This trend is expected to continue in the future under existing emission controls and current projections of atmospheric deposition ([Li et al., 2016d](#); [Ellis et al., 2013](#); [Pinder et al., 2008](#); [U.S. EPA, 2008a](#)). Wet deposition is now primarily  $\text{NH}_4^+$  at nearly 70% of U.S. air monitoring locations and reduced N dominates dry deposition in most parts of the country ([Li et al., 2016d](#)). This relative increase in  $\text{NH}_4^+$  is attributed to intensified industrial-scale animal operations, increased application of fertilizer, and successful  $\text{NO}_x$  emission controls ([Li et al., 2016d](#); [Xing et al., 2013](#)). Mobile source emissions, especially emissions from diesel vehicles, which increasingly use urea to control  $\text{NO}_x$  emissions, also contribute to total reduced N loading as well as near-road runoff in regions receiving heavy traffic ([Bettez et al., 2013](#)). The increase in highly bioreactive reduced N from deposition and other sources is often a preferred form of N for phytoplankton, including harmful species ([Appendix 10.3.3](#)). In coastal areas of the U.S., atmospheric inputs are heterogeneous ranging from <10 to approximately 70% of the N inputs ([Table 7-8](#)).

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### 10.1.3 Nitrogen Limitation

As reported for several decades prior to the 2008 ISA, N enrichment of marine and estuarine waters can alter the ratios among nutrients such as P and Si and affect overall nutrient limitation. N is the most common limiting nutrient in estuarine and coastal waters and continued inputs have resulted in N over enrichment and subsequent alterations to the nutrient balance in these systems ([U.S. EPA, 2008a](#); [Elser et al., 2007](#); [Howarth and Marino, 2006](#); [NRC, 2000](#); [Paerl et al., 2000](#); [Nixon, 1995](#); [Howarth, 1988](#); [D'Elia et al., 1986](#)). As described in the 2008 ISA, nutrient limitation may shift along the estuarine to ocean continuum ([U.S. EPA, 2008a](#)). For example, Chesapeake Bay exhibits a shift in nutrient limitation with P most commonly limited at upstream freshwater locations. At the transition between fresh and salt water, N and P may be colimiting, whereas the saltwater environments in the lower bay and sound regions are usually N limited ([Fisher et al., 1998](#); [Rudek et al., 1991](#)). Levels of N limitations are affected by seasonal patterns in estuaries, with N limited conditions likely occurring during the peak of annual productivity in the summer ([U.S. EPA, 2008a](#)).

Since the 2008 ISA, N limitation in estuarine and marine systems has been further evaluated, with recognition of the shifting nature of nutrient limitation based on relative

nutrient inputs and other ecosystem conditions. The rate of nutrient delivery, especially N, to coastal waters is strongly correlated to primary production and phytoplankton biomass (Paerl and Piehler, 2008). Strong input controls causing low riverine P inputs have, in some cases, exacerbated N limitation downstream, with implications for estuarine eutrophication (Paerl, 2009). Likewise, if N inputs are high enough, some estuaries and coastal marine ecosystems can become P or Si limited (Howarth et al., 2011; Paerl and Justić, 2011; Paerl and Piehler, 2008). Under this scenario, if a system becomes P limited, the N input may travel farther away from its sources and contribute to eutrophication at greater downstream distances (Howarth et al., 2011).

The role of N inputs from upstream and the connectivity between freshwater and receiving estuarine and coastal waters have led to recommendations to reduce both N and P in upstream waters (Glibert and Burford, 2017; Paerl et al., 2016b; Woodland et al., 2015; Paerl et al., 2014; Conley et al., 2009; Paerl, 2009). Increased N inputs may be affecting N limitation in the open ocean as well as in near-coastal areas. Kim et al. (2014a) reported a detectable increase in  $\text{NO}_3^-$  concentration in the upper Pacific Ocean. The rate of increased N relative to P was highest near the source of anthropogenic emissions in northeastern Asia with rates decreasing eastward across the upper North Pacific Ocean. The authors suggest that increased N deposition may enhance primary production and potentially lead to a shift from N to P limitation in this region.

Additional studies support observations reported in the 2008 ISA of N and P dynamics in estuaries. P limitation can play an important role, particularly seasonally if the water body has a significant freshwater source (Kemp et al., 2005; Malone et al., 1996). P limited conditions often exist in the low salinity regions while N limitation is more common downstream in higher salinity waters (Paerl and Otten, 2013). Studies in the Chesapeake Bay and in Europe have shown that the phytoplankton community in coastal ecosystems can be P limited over several months in the spring and switch to N limitation for periods of time as short as 1 week later in the season (Trommer et al., 2013; Malone et al., 1996). In the low-nutrient waters of North Carolina's Alligator River estuary, phytoplankton primary productivity and biomass (chlorophyll *a*) increased with N additions, but both indicators showed the greatest increases after treatment with combined N and P, indicating that this system was colimited by N and P (Rossignol et al., 2011). N additions in this region are known to lead to poor water quality and related complications, such as algal blooms, hypoxia/anoxia (water with DO that is too low to support marine biota), fish kills, and to impact ecosystem services, including fisheries and recreation (Paerl and Piehler, 2008).

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#### 10.1.4 Characteristics of Coastal Systems Sensitive to Eutrophication

Each coastal system has site-specific characteristics that influence ecological response to nutrient loading. A variety of factors that govern the sensitivity of estuaries and near-coastal marine waters to eutrophication from atmospheric N deposition are summarized in the 2008 ISA. Of critical importance is the total N input from all sources, including both atmospheric and nonatmospheric sources ([Appendix 10.1.1](#)). Other key elements include the flushing rate and dilution capacity of the watershed which reflects the volume of water available to dilute added N ([NRC, 2000](#); [Bricker et al., 1999](#)). The NEEA defined susceptibility as an estimate of the natural tendency of an estuary to retain or flush nutrients ([Bricker et al., 2007](#)). In estuaries that have longer residence times, nutrients are more likely to be taken up by algae and lead to eutrophic conditions.

As described in the 2008 ISA, the principal watershed features that control the amount of increased N flux to estuaries in the U.S. include human population, agricultural production, and the size of the estuary relative to its drainage basin ([Fisher et al., 2006](#); [Caddy, 1993](#); [Peierls et al., 1991](#)). A study included in the 2008 ISA reported a strong correlation between population density (persons/km<sup>2</sup>) and the total N loading from watershed to estuary ( $r^2 = 0.78$ ) for coastal watersheds in the U.S. ([Turner et al., 2001](#)). This finding is likely due to the prevalence of automobiles in heavily populated areas, along with their associated N emissions and deposition, plus the myriad of nonatmospheric sources of N from human activities, particularly wastewater discharges. The study authors also determined that direct atmospheric deposition becomes increasingly more important as a contributor to the total N loading to an estuary as the water surface area increases relative to total watershed area (terrestrial plus water surfaces). Because of human population growth and the preference for living in coastal areas, there is substantial potential for increased N loading to coastal ecosystems from both atmospheric and nonatmospheric sources.

Freshwater inputs to coastal areas and subsequent response to nutrient inputs depend on residence time of the nutrient-laden freshwater and the degree of tidal exchange within the estuary ([Zaldivar et al., 2008](#)). Residence time is defined by physical and hydrological characteristics of the watershed, such as surface area, volume, depth, and flushing rate ([Paerl et al., 2002](#)). In water bodies with short residence times, there is little opportunity for nutrients to be taken up and for algal blooms to develop ([Bricker et al., 2007](#)). For example, in the heavily N loaded lower Hudson River estuary, phytoplankton are flushed away as fast as they can grow due to high input of freshwater and high rates of flushing ([Howarth and Marino, 2006](#); [Howarth et al., 2000](#)). In the NEEA, systems with longer flushing times were considered more susceptible to eutrophication ([Bricker et al., 2007](#)).

Other factors within the highly variable estuarine environment ([Appendix 7.2.2](#)) that influence the composition of biological communities include salinity, DO, and suspended solids, which vary spatially and temporally along the estuary continuum ([Borja et al., 2012](#)). Mixing depth, temperature, and light penetration depth also affect biological response ([Paerl et al., 2002](#)). A stratified water column that separates well-oxygenated surface water from bottom water and sediments is generally required to form hypoxic zones ([Jewett et al., 2010](#)). In contrast to the seasonal or persistent nature of hypoxic zones, diel-cycling hypoxia typically occurs over hours to days and does not require stratification. Precipitation events like storms and floods or drought can also modulate nutrient effects [[Paerl and Piehler \(2008\)](#); [Appendix 13](#)].

In the 2008 ISA and NEEA, estuaries characterized as eutrophic were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates ([U.S. EPA, 2008a](#); [Bricker et al., 2007](#)). In literature reviewed for this ISA, many studies have re-emphasized the important role that physical mixing and hydrologic factors play in determining which estuaries and coastal ecosystems are the most sensitive to N enrichment ([Hart et al., 2015](#); [Wilkerson et al., 2015](#); [Glibert et al., 2014](#); [Rothenberger et al., 2014](#); [Howarth et al., 2011](#); [Kennison et al., 2011](#)). The hydrodynamics of a system may play an overriding role in controlling phytoplankton growth ([Hart et al., 2015](#); [Yang et al., 2008](#)). These factors, which affect estuarine response to nutrient loading, should be taken into account when establishing N input thresholds so that eutrophication can be controlled for different ecosystem types, hydrologic conditions, and future climate scenarios ([Paerl et al., 2014](#)).

[Bricker et al. \(2014\)](#) evaluated N inputs to the Potomac River Estuary and found that despite some improvements in the upper estuary (i.e., increased DO and decreased chlorophyll *a* in the tidal fresh zone; continued regrowth of sea grasses), eutrophic conditions have worsened in the lower estuary since the early 1990s. Eutrophic conditions in the Potomac were found to be representative of the Chesapeake Bay region and other U.S. estuaries, with moderate to high levels of nutrient-related degradation, particularly compared with similar river-dominated low-flow systems ([Bricker et al., 2014](#)). These river-dominated watersheds with low flow (>10 days residence time), high population density (i.e., >100 people/km<sup>2</sup>), and >40% of land use classified as urban and/or agriculture were predicted to be likely impacted by eutrophication.

[Scavia and Liu \(2009\)](#) evaluated a nutrient-driven phytoplankton model that provides a first-order screening tool for estuarine susceptibility classification. Using data from 75 estuaries, they found that the susceptibility of an estuary to nutrient loading could be estimated based on the ratio of river inflow ( $Q$ ) to estuarine volume ( $V$ ). In this analysis, efficiency appeared to decrease roughly with the inverse square root of  $Q/V$ :

$\varepsilon = 0.908(Q/V)^{-0.47}$  ( $R^2 = 0.53$ ), where  $\varepsilon$  represents mean values arising from the 75 estimated normal distributions. Model results showed that estuaries with a  $Q:V$  value greater than 2.0/year are less susceptible to nutrient loads, and those with  $Q:V$  values between 0.3 and 2.0/year are moderately susceptible. Case studies showed that  $Q:V$ —and thus estuarine sensitivity to nutrient loading—can vary between seasons and with storm events due in part to fluctuations in river inflow.

In some estuaries, especially in the Pacific Northwest, upwelling and oceanic exchange caused by regional wind patterns likely control primary production rather than anthropogenic nutrient loading ([Brown and Ozretich, 2009](#); [Hickey and Banas, 2003](#)). Nutrient inputs from local and regional upwelling in these systems can be difficult to discern from anthropogenic sources. Upwelling-dominated areas are characterized by short water residence time and have a moderately low expression of eutrophication symptoms, although nutrient concentrations are high ([Kaldy et al., 2017](#); [Brown and Ozretich, 2009](#); [Bricker et al., 2008](#); [Bricker et al., 2007](#)). Transfer of hypoxic water from upwelling to estuaries can also occur but is not linked to anthropogenic nutrient additions ([Brown and Power, 2011](#)).

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#### 10.1.4.1 Climate Modification of Ecosystem Response to Nitrogen

Climate-related changes including temperature, precipitation, wind patterns, extreme weather events, stronger estuary stratification, increased metabolism and organic production, and sea level rise are all expected to modify coastal habitats ([Altieri and Gedan, 2015](#); [Statham, 2012](#); [Rabalais et al., 2009](#)). These interacting factors will alter sensitivity to N loading and ecosystem response to nutrient inputs. For example, eutrophic conditions and the extent and duration of hypoxia are predicted to increase with changes in temperature and precipitation ([Altieri and Gedan, 2015](#); [Rabalais et al., 2009](#); [Boesch et al., 2007](#)). Freshwater and nutrient contributions to estuaries are expected to rise due to predicted increases in surface water flow and runoff from watersheds ([Rabalais et al., 2010](#); [Adrian et al., 2009](#); [Whitehead et al., 2009](#)). [Howarth et al. \(2012\)](#) demonstrated larger N fluxes (larger percent delivery of human N inputs) in wetter climates with more discharge, across 154 different watersheds in the U.S. and Europe. High organic loads and freshwater inputs associated with extreme weather events may enhance stratification and contribute to hypoxia ([Wetz and Yoskowitz, 2013](#)). Temperature modification leading to sea level rise and inputs of freshwater will likely alter salinity gradients and increase stratification within estuaries ([Statham, 2012](#); [Najjar et al., 2010](#)).

In estuaries affected by nutrient enrichment and climate-associated alterations described above, conditions favor a shift in phytoplankton toward greater abundance and distribution of toxic cyanobacteria associated with increased prevalence of HABs and declines in SAV ([Paerl et al., 2016a](#); [Najjar et al., 2010](#)). Research indicates that N and climate change will interact to drive losses in biodiversity that will be more than additive compared to each independent force ([Porter et al., 2013](#)). Decreases in pH associated with nutrient-enhanced coastal eutrophication combined with elevated atmospheric CO<sub>2</sub> could increase susceptibility of fauna to ocean acidification [[Cai et al. \(2011c\)](#); [Appendix 10.5](#)]. Coral reef ecosystems are particularly susceptible to combined effects of acidification, rising sea level, warming trends, and eutrophication. [Appendix 13](#) includes a more detailed discussion of how climate (e.g., temperature and precipitation) modifies ecosystem response to N loading.

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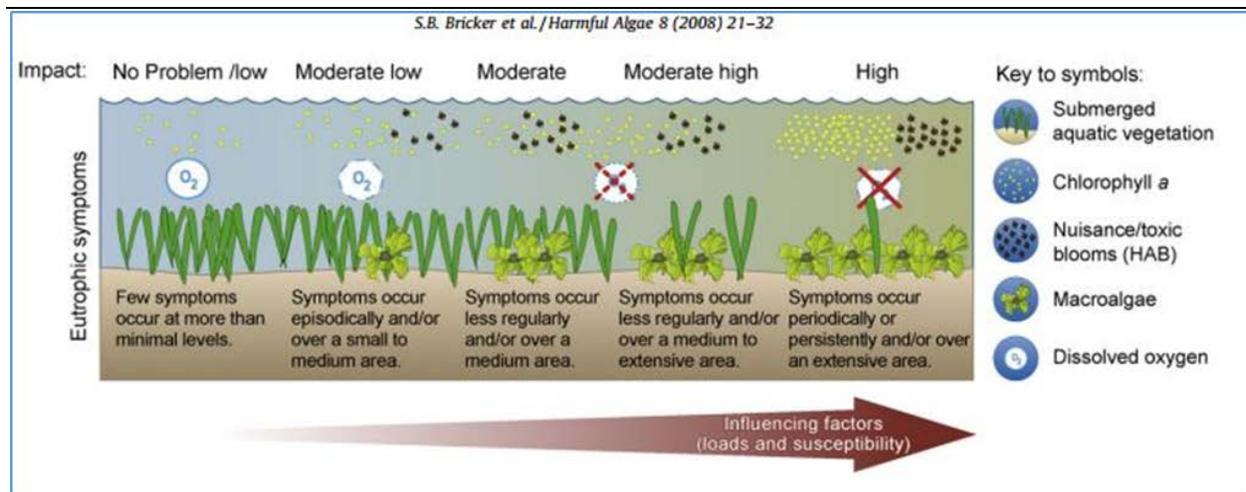
## 10.2 Indicators of Nutrient Enrichment

In the complex environment of the freshwater-to-ocean continuum there are many chemical and biological indicators of eutrophic conditions ([Table 7-8](#)). One approach is to measure total nutrient loading and concentrations; however, these data need to be interpreted in the context of the physical and hydrological characteristics that determine ecosystem response. Water quality measures (water clarity, DO) and quantification of nutrients along with biological indicators such as chlorophyll *a*, phytoplankton abundance, HABs, macroalgal abundance, SAV, and fish kills can all be used to assess responses to nutrient loading. Some biological indicators such as chlorophyll *a* are directly linked to nutrient enrichment and provide evidence of early response to added nutrients, while other indicators such as low DO and decreases in SAV indicate that the degree of eutrophication has progressed ([Borja et al., 2012](#)). A summary of key indicators of estuarine eutrophication is provided in [Table 10-1](#), and these indicators are discussed in the following sections. The 2008 ISA used the five ecological indicators shown in [Figure 10-3](#) (chlorophyll *a*, harmful/nuisance/toxic algal blooms, macroalgae, DO, and SAV) included in the Assessment of Estuarine Trophic Status (ASSETS) categorical Eutrophication Condition Index (ECI) in the NEEA to estimate the likelihood that an estuary is experiencing eutrophication or will experience eutrophication ([Bricker et al., 2007](#)).

**Table 10-1 Indicators of Estuarine Eutrophication.**

Indicator	Description
Chlorophyll <i>a</i>	Excess N input will stimulate primary productivity, and chlorophyll <i>a</i> concentration is an indicator of phytoplankton biomass. Phytoplankton biomass is strongly controlled in coastal waters by the availability and supply rates of nutrients, especially N ( <a href="#">Paerl and Piehler, 2008</a> ).
Harmful/nuisance/toxic algal blooms (HABs)	Excess N input can cause nuisance or toxic algal blooms, which release toxins in the water that can poison aquatic animals and threaten human health ( <a href="#">Baron et al., 2012</a> ). Problem occurrences of HABs increased 13% from 1997 to 2007 in Mid-Atlantic estuaries, the only region for which data were available, along with increasing N loading ( <a href="#">Bricker et al., 2008</a> ).
Macroalgal abundance	Macroalgal blooms can cause the loss of important submerged aquatic vegetation by blocking sunlight, and opportunistic macroalgae can outcompete many seagrass species ( <a href="#">Kennison et al., 2011</a> ). They can also cause hypoxia and smother seagrass, coral, clams/oysters, and other benthic organisms. High biomasses also cause “stinky beach” by rafting onto beaches and decaying.
Dissolved oxygen (DO)	Dissolved O <sub>2</sub> concentration decreases with increasing algal abundance under elevated N because microbes consume O <sub>2</sub> as they decompose dead algae. Oxygen depletion mainly occurs in bottom waters under stratified conditions. Increased atmospheric N deposition combined with N loading from other sources will likely affect the size, frequency, and severity of hypoxia events ( <a href="#">Rabalais et al., 2010</a> ). Hypoxia also contributes to ocean acidification, which is detrimental to the growth and development of calcifying organisms ( <a href="#">Howarth et al., 2011</a> ). The largest documented zone of hypoxic coastal water in the U.S. is located in the northern Gulf of Mexico ( <a href="#">Dale et al., 2010</a> ).
Submerged aquatic vegetation (SAV)	Excess N input stimulates algal growth, and opportunistic macroalgae may block the penetration of sunlight into the water column and outcompete seagrasses, leading to reduced SAV coverage. Increased epiphyte loads on the surface of macrophytes from nutrient enrichment may reduce biomass, shoot density, percentage cover, production and growth of SAV ( <a href="#">G.Nelson, 2017</a> ). Reduced extent of eelgrass was found to correspond to increased loading of N (from wastewater, fertilizer, and atmospheric deposition) to small to medium shallow estuaries in New England ( <a href="#">Latimer and Rego, 2010</a> ), and the distribution of SAV in Chesapeake Bay is used as an indicator of diversity and biological balance in the <i>U.S. EPA Report on the Environment (U.S. EPA, 2016k)</i> .

Chl = chlorophyll; DO = dissolved oxygen; EPA = Environmental Protection Agency; HAB = harmful algal blooms; N = nitrogen; O<sub>2</sub> = oxygen; SAV = submerged aquatic vegetation.



Source: [Bricker et al. \(2008\)](#).

**Figure 10-3 Biological indicator responses to nutrient enrichment.**

### 10.2.1 Chlorophyll *a*

Chlorophyll *a* is part of the light harvesting complex (group of pigments) used by photosynthetic organisms to convert light energy into carbohydrates through a series of biochemical reactions. The concentration of chlorophyll *a* is often used as a proxy for phytoplankton biomass. Algae form the base of the coastal food web and excess algal growth is often directly linked to nutrient enrichment. This indicator can be easily quantified and linked to aircraft and satellite-based remote sensing and autonomous monitoring platforms to assess effects at the regional and ecosystem level ([Appendix 7.2.7](#)). Chlorophyll *a* is widely used to assess eutrophic conditions because of its sensitivity to nutrient inputs and was one of the indicators of overall eutrophic condition of U.S. coastal areas in the 2008 ISA ([U.S. EPA, 2008a](#)). Increased levels of chlorophyll *a* can signal an early stage of water quality degradation related to nutrient loading and measurements of chlorophyll *a* are incorporated into water quality monitoring programs ([Appendix 7.2.7](#) and [Appendix 7.2.10](#)). High concentration of chlorophyll *a* suggests that algal biomass is sufficiently high to contribute to low DO concentration from increased decomposition of dead algae. Due to the strength of hydrologic forces (i.e., freshwater inputs and tidal flushing) in some types of coastal systems, benthic chlorophyll *a* may be a more sensitive indicator of ecosystem response to N enrichment than planktonic chlorophyll *a* in well-flushed systems ([Paerl and Piehler,](#)

[2008](#)). Phytoplankton blooms can also be advected into estuarine systems from the coastal ocean ([Brown and Ozretich, 2009](#)).

Chlorophyll *a* concentrations are commonly included in standardized frameworks of eutrophic condition [[Appendix 10.2.6](#); [Borja et al. \(2012\)](#)]. Many of these indices define spatial extent and temporal sampling periods and statistical measures to determine representative concentrations. Several chlorophyll *a* thresholds have been identified for U.S. water bodies ([Table 10-2](#)). The U.S. EPA National Coastal Condition Assessment (NCCA; formally known as National Coastal Assessment) measures chlorophyll *a* from an annual index period (June to October) and compares the samples to reference conditions to determine a rating [ $>20$   $\mu\text{g/L}$ , poor;  $5\text{--}20$   $\mu\text{g/L}$ , fair;  $<5$   $\mu\text{g/L}$ , good; [U.S. EPA \(2016g\)](#); [U.S. EPA \(2012b\)](#)]. For the NEEA ASSETS, the 90th percentile of annual values for chlorophyll *a* combined with spatial coverage and frequency of occurrence of blooms are reported for distinct salinity zones (tidal fresh  $0\text{--}0.5$  ppt), mixing zone ( $0.5$  to  $25$  ppt), and seawater ( $>25$  ppt);  $0\text{--}5$   $\mu\text{g/L}$  is a water body with low risk of eutrophication,  $5\text{--}20$   $\mu\text{g/L}$  is moderate,  $>20$   $\mu\text{g/L}$  is high ([Bricker et al., 2007](#)).

**Table 10-2 Chlorophyll *a* thresholds used in methods to evaluate the status of phytoplankton in U.S. coastal and estuarine water bodies.**

Method/ Approach	Chlorophyll <i>a</i> Thresholds and Ranges ( $\mu\text{g/L}$ )	Sample Time Frame	Statistical Measure	Other Characteristics	Community Composition	Indicators in Overall Eutrophication Index
U.S. EPA NCCA	Poor $>20$ Fair $5\text{--}20$ Good $0\text{--}5$	Index period (June–Oct.)	Concentration percentage of coastal area in poor, fair, and good condition based on probabilistic sampling design for 90% conf. in areal result		No	Chlorophyll <i>a</i> , water clarity, DO, DIP, DIN
ASSETS (eutrophic condition component only)	Poor $>20$ Fair $5\text{--}20$ Good $0\text{--}5$	Annual	90th percentile chlorophyll <i>a</i> concentration of annual data	Spatial coverage, frequency occurrence	Nuisance and toxic bloom occurrence, frequency, duration	Chlorophyll <i>a</i> , macroalgae, DO, seagrasses, nuisance/toxic algal blooms

ASSETS = Assessment of Estuarine Trophic Status; conf. = confidence; DIN = dissolved inorganic nitrogen; DIP = dissolved inorganic phosphorus; DO = dissolved oxygen; EPA = Environmental Protection Agency; L = liter; NCCA = National Coastal Condition Assessment.

Source: [Borja et al. \(2012\)](#).

In the NEEA, elevated chlorophyll *a* concentration was the most widespread documented symptom of eutrophication ([Bricker et al., 2007](#)). Half of the estuaries for which data were available exhibited high chlorophyll *a* concentration ([Bricker et al., 2007](#)). In the 2008 ISA, San Francisco Bay, CA was an example of an estuary that has experienced considerable increases in chlorophyll *a* concentrations in recent years.

Phytoplankton biomass, as indicated by chlorophyll *a* concentration, is strongly controlled in estuaries by the availability and supply rates of nutrients, especially N ([Paerl and Piehler, 2008](#)). Bioassays conducted in the low-nutrient Alligator River estuary in North Carolina showed that N enrichment is directly related to increasing chlorophyll *a* concentration. Although the highest increase occurred in response to addition of both N and P, dissolved inorganic N (DIN) treatment alone stimulated chlorophyll *a* in some treatments ([Rossignol et al., 2011](#)). A 3-year data set from Raritan Bay, NJ indicates that nutrient loading contributed to high concentrations of chlorophyll *a* from 2010–2012 ([Rothenberger et al., 2014](#)). Winter and spring N loading to Mattawoman Creek estuary and other shallow estuaries in the Chesapeake Bay region was highly correlated to summer chlorophyll *a* concentrations ([Boynton et al., 2014](#)). However, after point source nutrient (N and P) reductions were enacted, a decrease in chlorophyll *a* was observed in Mattawoman Creek. In North Carolina's Neuse River estuary, which is part of the Albemarle-Pamlico estuary, it appears that the elevated loading of total N (TN) contributed to higher annual average chlorophyll *a* values from 2000–2009 ([Lebo et al., 2012](#)).

While recent research indicates that N loading remains a strong predictor of chlorophyll *a* concentrations under most conditions, there has been increasing discussion regarding the role of other factors in altering the strength of this relationship. The impact of nutrient inputs can at times be overtaken by hydrologic features, seasonal variations, climatic changes, and oscillations exerting greater control over phytoplankton dynamics ([Paerl et al., 2010](#)). In Buzzard's Bay, MA, both nutrient loading and shape of the embayment were factors in determining spatial and temporal water quality trends including the observation that chlorophyll *a* is increasing at a faster rate than N enrichment ([Rheuban et al., 2016](#)). It appears that more chlorophyll *a* per unit of TN was produced as the 22-year time series progressed. In Corpus Christi Bay, TX, rainfall events altered nutrient N:P ratios but did not affect chlorophyll *a* ([Turner et al., 2015](#)). Instead, chlorophyll *a* concentration in weekly samples mainly followed seasonal trends by increasing in spring and summer and decreasing in fall and winter. No significant relationships were observed between annual TN, total phosphorus (TP) load, and annual mean chlorophyll *a* concentrations in the Guana Tolomato Matanzas estuary in Florida, rather phytoplankton biomass in this well-flushed system was influenced by temperature, precipitation, water residence times, and tidal exchange ([Hart et al., 2015](#)). [Glibert et al. \(2014\)](#) found

significant increases in chlorophyll *a* over time at only three out of seven study areas in the Maryland/Virginia coastal lagoon, although regionally chlorophyll *a* concentrations increased due to increasing anthropogenic nutrient loads and increased freshwater flow in the early 2000s. In the Neuse River estuary, NC, which has a long residence time allowing for detection of nutrient stimulation, nutrient addition bioassays along the estuary indicated strong N limitation at the chlorophyll *a* maximum and downstream where there was a strong preference of  $\text{NH}_4^+$  over  $\text{NO}_3^-$  as a DIN source ([Paerl and Piehler, 2008](#)).

Using satellite and meteorological data from U.S. Atlantic coastal waters, [Kim et al. \(2014b\)](#) found that precipitation events were associated with increased levels of chlorophyll *a* in low nutrient areas (defined as having  $\text{NO}_3^-$  concentrations of less than 1  $\mu\text{M}$ ), but precipitation was correlated with lower chlorophyll *a* concentrations in high nutrient areas (defined as having  $\text{NO}_3^-$  concentrations greater than 1  $\mu\text{M}$ ). This is likely because in low nutrient areas, new N input from precipitation stimulated phytoplankton growth. In areas already high in nutrients, wind associated with precipitation events may have deepened the mixed layer and the resulting loss of light availability caused chlorophyll *a* concentrations to decline ([Kim et al., 2014b](#)). Two studies modeling historical data from Chesapeake Bay indicate that variation in climatic conditions dominated phytoplankton dynamics in the bay in recent years ([Harding et al., 2016a](#); [Harding et al., 2016b](#)). Much of the bay is producing more chlorophyll *a* per unit TN than in the past, leading Harding and others to suggest that return to the historical relationship between N and chlorophyll *a* is unlikely.

In four coastal estuaries that shifted from eutrophication to oligotrophication (reduction in nutrients), the degree of return of chlorophyll *a* to reference status varied, likely due to concurrent changes in the estuaries from costressors and the time elapsed from eutrophication to nutrient reduction ([Duarte et al., 2009](#)). Due to these shifting baselines the authors suggest that the current paradigm of nutrient reduction to a historical level needs to be replaced by targets that maintain key ecosystem functions in the context of changing conditions in the estuaries over time.

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## 10.2.2 Harmful/Nuisance/Toxic Algal Blooms

Harmful algal blooms (HABs) reflect the proliferation of a toxic or nuisance algal species that negatively affects natural resources or humans. Blooms are increasing in outbreak frequency and extent in the U.S. and other countries, and N is one of the nutrients known to promote HAB formation ([Baron et al., 2012](#); [Heisler et al., 2008](#)). A concurrent increase in atmospheric sources of N to coastal areas and proliferation of harmful algal

bloom formation have been recognized for several decades ([Paerl et al., 2002](#); [Paerl and Whitall, 1999](#); [Paerl, 1997](#)). The form of N delivered to coastal regions of the U.S. from atmospheric and other sources is changing from primarily  $\text{NO}_3^-$  to an increase in reduced forms of N ([Appendix 10.1.2](#)), which are favored by some HAB forming species ([Glibert et al., 2016](#)). HABs caused by N enrichment can release toxins that are harmful to fish and shellfish and that may accumulate in predators and organisms higher in the food web ([Johnson et al., 2010](#)). For example, cyanobacteria blooms (cyanoHAB) have been documented in estuaries along the U.S. Mid-Atlantic and Southeast coasts as well as Gulf coast estuaries ([Preece et al., 2017](#)). Other blooms are not toxic but may cause low DO events due to very high biomass. In addition to effects on biota, HABs cause a range of responses in humans from direct dermatitis, such as swimmers itch, to severe food poisoning, liver and kidney toxicity, and paralysis ([Peel et al., 2013](#); [Johnson et al., 2010](#)).

The frequency and duration of algal blooms is one of five indicators used in the NEEA and was included as an indicator of eutrophic conditions in the 2008 ISA ([U.S. EPA, 2008a](#); [Bricker et al., 2007](#)). Of the 81 estuary systems for which data were available in the NEEA, 26 exhibited a moderate or high symptom expression for nuisance or toxic algae ([Bricker et al., 2007](#)). In the previous 2008 ISA review, the frequency of phytoplankton blooms and the extent and severity of hypoxia were documented to have increased in the Chesapeake Bay ([Officer et al., 1984](#)) and Pamlico Sound estuaries in North Carolina ([Paerl and Piehler, 2008](#)) and along the continental shelf adjacent to the Mississippi and Atchafalaya river discharges to the Gulf of Mexico ([Eadie et al., 1994](#)). New tools and monitoring approaches to further characterize HABs have become available since the 2008 ISA ([Appendix 7.2.7](#)). For example, solid phase adsorption toxin tracking (SPATT), a passive sampling tool which simulates the contamination of filter-feeding bivalves, has been used recently in the field to detect the presence of algal toxins with greater accuracy than grab-sampling methods ([Gibble and Kudela, 2014](#); [Kudela, 2011](#); [Lane et al., 2010](#)). Remote sensing systems are increasingly being used to forecast and monitor HABs in coastal waters ([Klemas, 2012](#)).

Harmful effects of HAB toxins on fish and wildlife are readily transferred through the food web and may persist even when the bloom conditions have passed. Microcystin, a class of toxins produced by many cyanoHABs is found in all trophic levels from shellfish to finfish to top level predators and can persist in the food web for months ([Preece et al., 2017](#)). [Wood et al. \(2014\)](#) found that microcystin persisted in overwintering populations of estuarine finfish, common wedge clam (*Rangia cuneata*), and blue crab (*Callinectes sapidus*) in the James River estuary, VA although the highest tissue concentrations and greatest percentage of individuals affected were observed when toxins in the water column were at maximum levels. The toxin was present in both muscle and viscera of

blue crabs at concentrations that have been shown to have physiological effects on other species of estuarine crab ([Wood et al., 2014](#)). Accumulation of microcystin measured over the course of 2 years in the James River estuary, near Chesapeake Bay, was found to be highest in suspension feeding animals while top predators (piscivores), scavengers, and benthic feeders all had lower levels of microcystin ([Bukaveckas et al., 2017](#)). In Monterey Bay, CA, deaths of 21 sea otters (*Enhydra lutris*), a federally listed threatened species, were attributed to hepatotoxic shellfish poisoning due to trophic transfer of microcystin observed in this study to have originated from nutrient-impaired lakes and rivers discharging to the bay ([Miller et al., 2010](#)). Other HAB toxins, such as domoic acid, are also known to be transferred up the food web ([Trainer et al., 2012](#)). Domoic acid from recent blooms of the diatom *Pseudo-nitzschia* along the U.S. West Coast has impacted razor clam (*Siliqua patula*) and Dungeness crab (*Metacarcinus magister*) fisheries, led to symptoms of domoic acid poisoning in California sea lions (*Zalophus californianus*), and was detected in additional marine mammals from southern California to northern Washington ([McCabe et al., 2016](#)).

Research on HAB-forming species have shown that the form of N supplied affects phytoplankton growth ([Glibert et al., 2016](#)). Generally,  $\text{NH}_4^+$  is considered to be the preferred form of N for some phytoplankton due to lower energy requirements for uptake and assimilation; however, diatoms specialize in use of oxidized N forms ([Glibert et al., 2016](#)). For example, the HAB-forming dinoflagellate species *Heterosigma akashiwo* is able to grow well with a pulsed supply of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and urea under low light conditions and assimilate stores of N nutrients, suggesting that this species could outcompete diatoms in silicate-limited, N enriched coastal areas ([Kok et al., 2015](#)). In *Pseudo-nitzschia* spp., laboratory experiments showed that both of the species studied were able to grow on  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and urea, although urea was the preferred form of N ([Melliti Ben Garali et al., 2016](#)). These findings were supported by a field experiment in which chlorophyll *a* concentration significantly increased and exponential growth occurred in all N-enriched in situ microcosms until the end of the experiment, with specific growth rates highest in the urea and  $\text{NO}_3^-$  additions. The dinoflagellate *Akashiwo sanguinea* showed different growth profiles and N assimilation with form of N and concentration, growing faster in  $\text{NH}_4^+$  and with greater enzyme affinity for urea ([Liu et al., 2015](#)). Differential growth responses of HAB species to reduced N can alter phytoplankton community composition and biodiversity ([Appendix 10.3.3](#)).

There is also evidence, mostly from freshwater systems, that the form of N affects toxin production of some HAB species ([Appendix 9.2.6.1](#)). In nutrient amendment experiments with water collected from the tidally influenced Transquaking River, which flows into Chesapeake Bay, *Microcystis* was stimulated by N more frequently than P, and abundances of toxic and nontoxic strains were enhanced to different degrees by inorganic

and organic N ([Davis et al., 2010](#)). Response of *Alexandrium fundyense* to nutrient addition varied throughout the course of bloom events in Northport-Huntington Bay, NY ([Hattenrath et al., 2010](#)). Addition of  $\text{NH}_4^+$  to bloom water most frequently resulted in statistically significant increases of *A. fundyense* density and toxin concentration compared to other forms of N (glutamine,  $\text{NO}_3^-$ , and/or urea). [Davidson et al. \(2012\)](#) found that, in general, laboratory studies show that toxin production can be influenced by nutrient ratios, but extrapolation of those results to the specific species and conditions in the field is difficult.

Modeling studies have reported on potentially altered future scenarios of phytoplankton community changes and HAB formation, intensity, duration, and toxicity due to changes in N deposition ([Lee and Yoo, 2016](#); [Glibert et al., 2010b](#)). [Pinder et al. \(2008\)](#) reported on modeled scenarios that predict alterations in the frequency, intensity, toxicity, and species composition of algal blooms due to higher rates of N deposition and changes in the reduced N to oxidized N ratio. Future changes in HAB dynamics will be affected by climate change ([Appendix 10.1.4.1](#)) and increased N loading, and integrated ecosystem models that couple the atmosphere, land, and coastal ocean are needed to estimate these HAB responses ([Glibert et al., 2010a](#)). Long-term monitoring (1987–2005) of phytoplankton populations in the Bay of Fundy in southwestern New Brunswick, Canada did not link HABs to nutrients, rather many species abundances are explained by climate and weather patterns ([Martin et al., 2009](#)). For *A. fundyense* there was a negative relationship with cell density and  $\text{NO}_3^-$ .

[Table 10-3](#) summarizes new studies from U.S. waters on levels and forms of N at which effects are manifested in phytoplankton.

**Table 10-3 Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	N Additions	Ecological/Biological Effects	Species	Reference
Northport-Huntington Bay complex, NY		Addition of NH <sub>4</sub> <sup>+</sup> (10 μM–40 μM)	Addition of NH <sub>4</sub> <sup>+</sup> significantly increased <i>A. fundyense</i> densities compared to the control. The addition of NH <sub>4</sub> <sup>+</sup> (40 μM) yielded a significant increase in both <i>A. fundyense</i> densities and toxin concentrations four and 8×, respectively, compared to controls.	Phytoplankton ( <i>Alexandrium fundyense</i> )	<a href="#">Hattenrath et al. (2010)</a>
Raritan Bay, NJ		Ambient levels	Multivariate analyses of a 3-yr data set indicated that the abundance of HAB species <i>Heterosigma akashiwo</i> is positively associated with NO <sub>3</sub> <sup>-</sup> in Raritan Bay. Both climatic conditions and nutrient concentrations affect phytoplankton bloom composition in the bay.	Phytoplankton ( <i>Heterosigma akashiwo</i> and 13 other HABs identified)	<a href="#">Rothenberger et al. (2014)</a>
Raritan Bay, NJ		Nutrients (N and Fe) added alone or in combination to different treatments. N was added as a single pulse sodium nitrate (NaNO <sub>3</sub> ) to increase NO <sub>3</sub> <sup>-</sup> concentrations by approximately 10 μM. The N additions lowered the Si:N ratios from ~3 to <1	Dinoflagellates and HAB-forming taxa increased to a greater extent when NO <sub>3</sub> <sup>-</sup> levels were high (which led to a low Si:N ratio of less than one). Centric and chain-forming diatoms resulted from enriched NO <sub>3</sub> <sup>-</sup> concentrations, differing from the pennate diatoms and green flagellates that accompanied ambient NO <sub>3</sub> <sup>-</sup> concentrations. Dinoflagellates in the genus <i>Dinophysis</i> , which could be HAB-forming, also resulted from enriched NO <sub>3</sub> <sup>-</sup> and lowered Si:N.	Phytoplankton Dinoflagellates, diatoms	<a href="#">Rothenberger and Calomeni (2016)</a>

**Table 10-3 (Continued): Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	N Additions	Ecological/Biological Effects	Species	Reference
Ocean surface from 28°N to 44°N and from the East Coast of the U.S. to 60–70°W	Based on direct measurements of wet deposition along the East Coast of the U.S., the N supply through wet deposition was estimated to be 25–45 mmol N/m <sup>2</sup> /yr		Precipitation events in coastal waters of the eastern U.S. increased the chlorophyll <i>a</i> concentration up to 15% in low-nutrient areas (<1 μM NO <sub>3</sub> <sup>-</sup> ) but decreased the chlorophyll <i>a</i> concentration in nutrient-replete areas (>1 μM NO <sub>3</sub> <sup>-</sup> ). The authors suggested that in nutrient-depleted areas (south of 36°N), the added nutrients were a dominant factor increasing the chlorophyll <i>a</i> concentration, whereas in the nutrient-replete areas (north of 36°N), where phytoplankton growth was light limited, reduced light availability was the dominant factor determining reduced chlorophyll <i>a</i> concentration.	Phytoplankton	<a href="#">Kim et al. (2014b)</a>
Mattawoman Creek, Chesapeake Bay	Used atmospheric deposition data from <a href="#">Boynton et al. (2008)</a> , including N from both wet and dry deposition (0.81 mg N/L as an annual average concentration). Direct atmospheric deposition to surface waters of the creek contributed about 6,000 kg N/yr or about 16 kg N/day to the creek system.		Strong relationships were found between N loading and algal biomass and between algal biomass and water clarity. Winter–spring N loading and summer chlorophyll <i>a</i> were found to be highly correlated, a relationship which appears to be linear.	Phytoplankton and SAV	<a href="#">Boynton et al. (2014)</a>

**Table 10-3 (Continued): Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	N Additions	Ecological/Biological Effects	Species	Reference
Tidally influenced Transquaking River which flows into Chesapeake Bay		20 µM (NO <sub>3</sub> <sup>-</sup> ), 20 µM NH <sub>4</sub> <sup>+</sup> (NH <sub>4</sub> <sup>+</sup> ), 10 µM (= 20 µM N) urea, 10 µM (= 20 µM N), L-glutamine (GA), P (1.25 µM orthophosphate), or a combined treatment of NO <sub>3</sub> <sup>-</sup> and P	<i>Microcystis</i> was simulated by N more frequently than P, and abundances of toxic and nontoxic strains were enhanced to different degrees by inorganic N and organic N. Toxic <i>Microcystis</i> abundance increased more with inorganic N than organic N.	Toxic and nontoxic strains of <i>Microcystis</i>	<a href="#">Davis et al. (2010)</a>
Maryland and Virginia coastal bays	Measurements of atmospheric deposition since 2000, based on the NADP, suggest that NO <sub>3</sub> <sup>-</sup> is decreasing and NH <sub>4</sub> <sup>+</sup> from deposition is stable for the coastal bays.		N in the water column is dominated by reduced N (primarily NH <sub>4</sub> <sup>+</sup> ) with low concentrations of NO <sub>3</sub> <sup>-</sup> also present, resulting in phytoplankton community shifts to those species that can do well under such conditions. Submerged aquatic vegetation has decreased.	Phytoplankton and SAV	<a href="#">Glibert et al. (2014)</a>
Alligator River estuary, NC	Potential for atmospheric deposition of N from nearby farm (wet NH <sub>4</sub> <sup>+</sup> concentrations increased greatly close to farm).	DIN additions: 140 µg N-NH <sub>4</sub> <sup>+</sup> /L, 140 µg N-NO <sub>3</sub> <sup>-</sup> /L, and 70 µg N-NH <sub>4</sub> <sup>+</sup> /L plus 70 µg N-NO <sub>3</sub> <sup>-</sup> /L	Significant increase in phytoplankton biomass (chl <i>a</i> ) and rates of primary productivity due to N enrichment. DIN treatments alone significantly stimulated chl <i>a</i> in two out of five tests for all three DIN addition treatments, although DIN + DIP treatments provided the largest increase in chl <i>a</i> .	Phytoplankton	<a href="#">Rossignol et al. (2011)</a>
Neuse River estuary, NC		Ambient, acute DIN inputs via runoff from hydrologic pulses (hurricanes, tropical storms, heavy rainfall events)	Study noted increase in phytoplankton bloom frequency and magnitude (indicated by increasing chl <i>a</i> variability) over time in response to acute DIN inputs from hydrologic pulses. Control of algal bloom duration, thresholds, taxonomic composition, and spatial extent may be dictated by climatic changes and oscillations instead of nutrient inputs.	Phytoplankton	<a href="#">Paerl et al. (2010)</a>

**Table 10-3 (Continued): Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	N Additions	Ecological/Biological Effects	Species	Reference
New River estuary, NC		N addition to estuary water in the form of DIN, organic N from river water (with dissolved inorganic P) or urea	Varying the form of nutrients promoted growth of different phytoplankton groups based on photopigment analysis. Dinoflagellates, chlorophytes, and cyanobacteria responded to dissolved organic N while cyanobacteria increases were most frequent with inorganic N addition.	Phytoplankton	<a href="#">Altman and Paerl (2012)</a>
Four sites with tidal influence, South Carolina coast		NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , and urea treatments applied separately to bioassays. N forms were added at Redfield ratios (N:P = 16:1)	Along a gradient from highly developed to undeveloped sites, phytoplankton communities at the more developed sites had higher biomass and growth rate with N (particularly urea) additions and potentially HAB forming species were more often found at the more developed sites.	Phytoplankton	<a href="#">Reed et al. (2016)</a>
Ten Mile Creek, Indian River Lagoon, FL		High median concentrations of total N (0.988 mg/L), NO <sub>3</sub> <sup>-</sup> -N (0.104 mg/L), NH <sub>4</sub> <sup>+</sup> -N (0.103 mg/L), and total Kjeldahl N (0.829 mg/L)	Chl a was negatively correlated with N concentrations and the highest chl a concentrations were related to the conditions of static and open water with long residence time. Hydrodynamics of a system may play an overriding role in controlling phytoplankton growth.	Phytoplankton	<a href="#">Yang et al. (2008)</a>
San Francisco Bay/estuary		NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup> measured from two source estuaries	A comparison of N isotopes in cells of the HAB species <i>Microcystis aeruginosa</i> with N in rivers flowing into the bay suggested that NH <sub>4</sub> <sup>+</sup> , not NO <sub>3</sub> <sup>-</sup> was likely the primary source of N that supported the bloom.	Phytoplankton (cyanobacteria <i>Microcystis aeruginosa</i> )	<a href="#">Lehman et al. (2015)</a>

**Table 10-3 (Continued): Levels and forms of nitrogen at which effects on phytoplankton are manifest in U.S. coastal waters evaluated in the literature since the 2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur—Ecological Criteria.**

Study Site	Ambient N Deposition	N Additions	Ecological/Biological Effects	Species	Reference
San Francisco Bay/estuary		Ambient nitrate ranged from 0.19 to 0.36 mg/L. Ambient ammonia ranged 0.02 to 0.06 mg/L.	The greatest chl <i>a</i> concentration and cell density occurred in the San Joaquin River estuary which had a high average nitrate concentration (0.36 mg/L). The second highest chl <i>a</i> concentration and cell density occurred in the Old River estuary which had relatively low N concentration (mean 0.19 mg/L). Differences in chl <i>a</i> were correlated with environmental conditions, particularly streamflow and water temperature and secondarily to nutrient concentrations and ratios.	Phytoplankton (cyanobacteria <i>Microcystis aeruginosa</i> )	<a href="#">Lehman et al. (2008)</a>

Chl = chlorophyll; DIN = dissolved inorganic nitrogen; DON = dissolved organic nitrogen; HAB = harmful algal blooms; N = nitrogen; NADP = National Atmospheric Deposition Program; NH<sub>4</sub><sup>+</sup> = ammonium ion; NO<sub>3</sub><sup>-</sup> = nitrate; P = phosphorus; SAV = submerged aquatic vegetation; W = west.

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### 10.2.3 Macroalgal Abundance

The abundance of macroalgae, which are generally referred to collectively as “seaweed,” was an indicator of eutrophic condition in the 2008 ISA ([U.S. EPA, 2008a](#)). Macroalgae have been combined with other indicators to classify estuarine condition ([Borja et al., 2012](#)). For example, NEEA includes an assessment of macroalgae ([Bricker et al., 2007](#)). Macroalgal blooms can contribute to loss of important SAV by blocking the penetration of sunlight into the water column. Although macroalgal data for estuaries in the U.S. were generally sparse, the NEEA reported high macroalgal expression in 15 of the 64 estuaries evaluated ([Bricker et al., 2007](#)). In some lagoons with limited oceanic exchange, macroalgae may be a more sensitive biological indicator than phytoplankton [e.g., [Nobre et al. \(2005\)](#); [McLaughlin et al. \(2014\)](#)]. For example, in most estuaries of the Southern California Bight, macroalgae is the dominant primary producer and a key indicator of eutrophication ([McLaughlin et al., 2014](#)). Macroalgae may not be a good indicator of eutrophication in some upwelling-influenced estuaries in the Pacific Northwest because an increase in macroalgal biomass in these systems does not appear to be associated with temporal declines in eelgrass ([Hessing-Lewis et al., 2015](#); [Hessing-Lewis and Hacker, 2013](#); [Hessing-Lewis et al., 2011](#)).

Opportunistic, fast-growing macroalgae can exhibit very high rates of N uptake during periods of high N availability and can often outcompete or block out light for other macrophytes when N loads are high and variable ([Abreu et al., 2011](#)). This growth of macroalgae can also smother corals, clams, oysters, and other biota ([Bricker et al., 2007](#)) and contribute to declines in seagrasses ([Olyarnik and Stachowicz, 2012](#)). These macroalgae also tend to preferentially uptake N in the form of  $\text{NH}_4^+$ . In a Danish study, sea lettuce (*Ulva lactuca*), which is a common species of macroalgae in U.S. coastal waters, grew faster and exhibited greater biomass when subjected to  $\text{NH}_4^+$  as the N source compared to  $\text{NO}_3^-$  ([Ale et al., 2011](#)). This difference was thought to be due to reduced N being more easily assimilated and used by algae. Similarly, in experimental manipulations with *Gracilaria tenuistipitata*, an opportunistic macroalgal species from China, when both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were available,  $\text{NH}_4^+$  was assimilated more rapidly and algal biomass was higher than with  $\text{NO}_3^-$  addition alone ([Wang et al., 2014a](#)). Growth of *Caulerpa cylindracea*, an invasive macroalga in the Mediterranean Sea, was not inhibited by high  $\text{NH}_3$ , and was able to outcompete native macroalgae in experimental plots with nutrient addition ([Gennaro et al., 2015](#)).

Southern California estuaries, some of the most nutrient enriched in the world, have not been well studied in the past, but recent work is providing important information about macroalgal growth in response to N loading to these systems. Opportunistic macroalgae

(*Ulva intestinalis* and *Ulva expansa*) were shown to take up  $\text{NO}_3^-$  from the water very efficiently at many concentration levels, giving these species the ability to outcompete other algae in estuaries subject to varying nutrient loads ([Kennison et al., 2011](#)). Algae that were depleted in N took up  $\text{NO}_3^-$  at higher rates than enriched algae, and uptake rates slowed as the algae became saturated with N.

However, macroalgal abundance was not found to be directly related to water or sediment N concentrations in Southern California estuaries ([Kennison and Fong, 2014](#)). Rather, macroalgal blooms occurred throughout the year and appeared to be influenced by the unique physical and hydrological differences between estuaries. For instance, in one estuary with high nutrient levels in both water and sediment, little to no macroalgal biomass was present, possibly due to high water velocities that prevented young algal filaments from attaching ([Kennison and Fong, 2014](#)). In other estuaries, comparatively high algal biomass was found year-round even when nutrient supplies were lower than other sites (although still N enriched), perhaps due to low rates of tidal flushing and longer water residence times. Internal nutrient processing, variable hydrological regimes, and multiple external nutrient sources may all contribute to eutrophic conditions ([Kennison and Fong, 2014](#)).

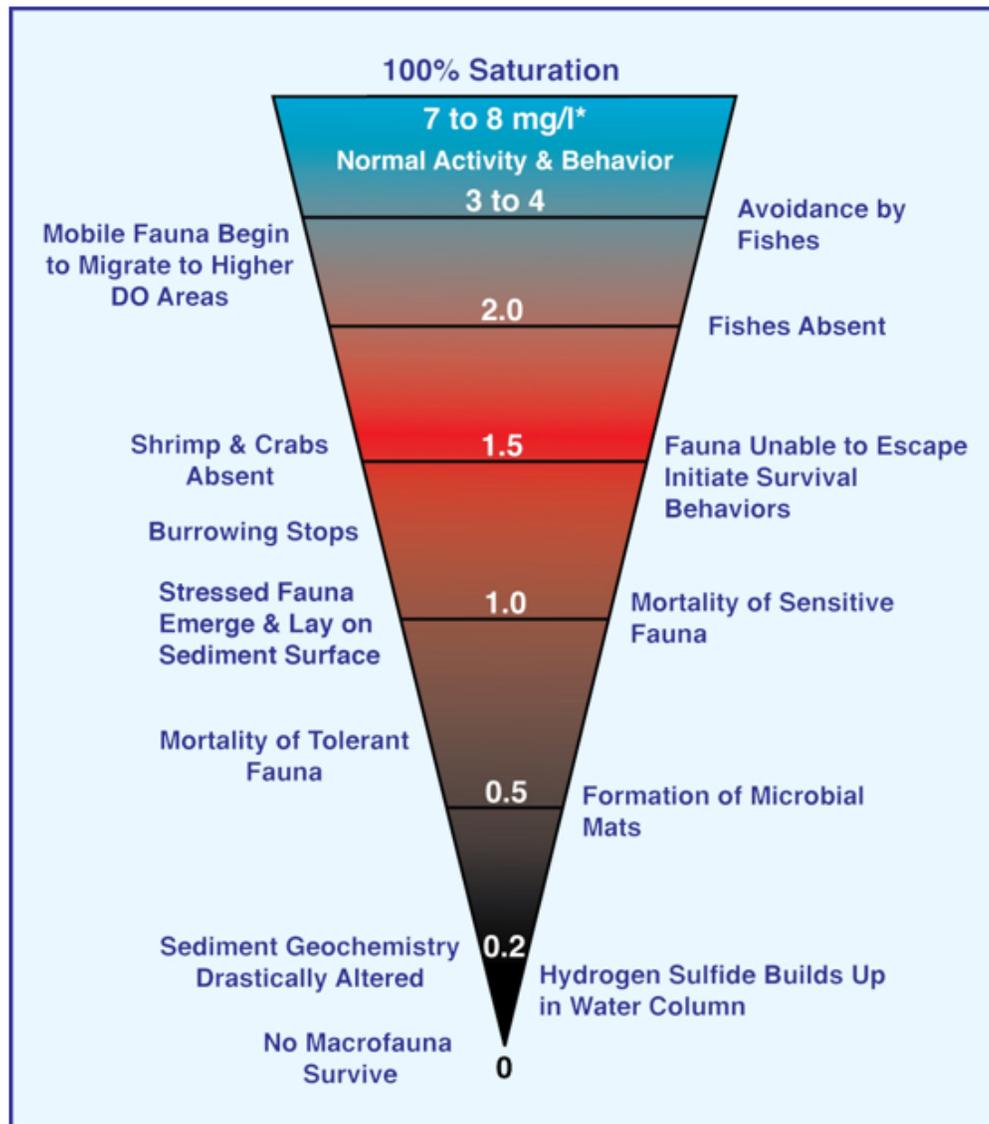
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## 10.2.4 Dissolved Oxygen

DO was included in the 2008 ISA, the NCCA, and the NEEA as an indicator of eutrophic condition ([U.S. EPA, 2008a](#)). Additional information on DO is provided in [Appendix 7.2.3](#). Oxygen depletion largely occurs only in bottom waters under stratified conditions, not throughout the entire water column. The decomposition of organic matter associated with increased algal abundance consumes DO and can reduce DO concentrations in eutrophic waters to levels that cannot support aquatic life ([Jewett et al., 2010](#)). Respiration of microbes, macrophytes, and animal biota can also reduce DO to very low levels such as primary producers in the dark, deeper portions of the well-mixed Hudson River estuary ([Howarth et al., 1996b](#)) and as seen every night in a eutrophic seagrass-dominated system on Cape Cod ([Howarth et al., 2014](#)). In the Cape Cod seagrass system, hypoxia is common at dawn, following hours of darkness, yet oxygen levels are supersaturated at the end of the daylight period.

Generally, some biota are impacted at DO levels from 3 to 4 mg/L, and increasingly adverse effects are observed on biota at lower DO concentrations ([Figure 10-4](#)). Decreased DO can lead to the development of hypoxic or anoxic zones that are inhospitable to fish and other life forms and can impact ecosystem processes ([Diaz et al., 2013](#); [Levin et al., 2009](#); [Diaz and Rosenberg, 2008](#)). For example, in Chesapeake Bay,

[Sturdivant et al. \(2014\)](#) observed that macrobenthic production was 90% lower during hypoxic conditions, resulting in a biomass loss similar to 7,320–13,200 metric tons C over an area of 7,720 km<sup>2</sup>. The authors estimated this change represented a displacement of 20 to 35% of macrobenthic activity during the summer.



DO = dissolved oxygen; l = liter; mg = milligrams.

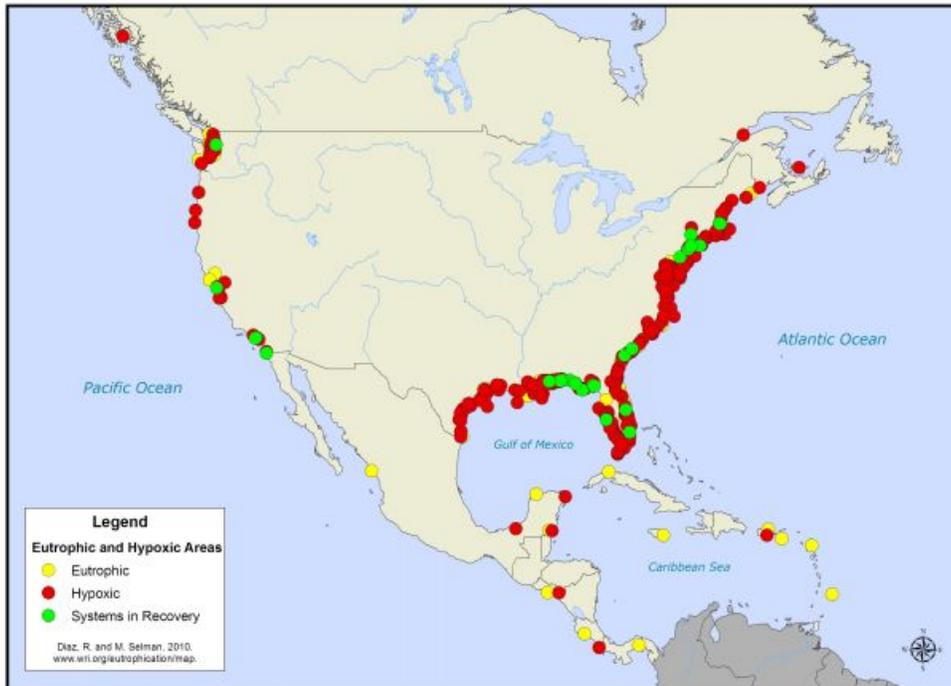
Source: [Diaz et al. \(2013\)](#).

**Figure 10-4** The range of ecological impacts exhibited as dissolved oxygen levels drop from saturation to anoxia.

In the U.S., the incidence of hypoxia has increased almost 30-fold from 1960 to 2008 and is now reported in more than 300 systems ([Jewett et al., 2010](#)). Climate change and increasing N loading to coastal ecosystems are both expected to widen the distribution and increase the size of areas affected by eutrophication-induced hypoxia, while also increasing the frequency and persistence of these events [[Rabalais et al. \(2010\)](#); [Appendix 13](#)]. Areas of eutrophication-related hypoxia are found on the U.S. East and West coasts and the Gulf of Mexico ([Figure 10-5](#)). Eutrophication-induced hypoxia, which has been documented globally, can be characterized by both the duration of the event and the ecosystem response ([Diaz et al., 2013](#); [Diaz and Rosenberg, 2008](#)). Summer hypoxia is most common, followed by periodic oxygen (O<sub>2</sub>) depletion that may occur in some systems more often than seasonally. In these hypoxic and anoxic areas (“dead zones”) only organisms that can live with little or no O<sub>2</sub> are present ([Diaz et al., 2013](#); [Jewett et al., 2010](#)). Once an ecosystem reaches severe seasonal hypoxia, there is a shift to benthic organisms with shorter life spans and smaller body size ([Diaz and Rosenberg, 2008](#)).

[Zhou et al. \(2014b\)](#) estimated the hypoxic volume of Chesapeake Bay over a 25-year period. The date of onset of hypoxia occurs earlier in the summer and the end of hypoxia also shifted to earlier in the fall with no trend in the seasonal-maximum hypoxia itself from 1985 to 2010. Nutrient loading from the Rappahannock, Susquehanna, and Potomac Rivers explains >85% of the seasonally averaged interannual variability in hypoxic volumes. [Testa and Kemp \(2012\)](#) investigated interactions between hypoxia and nutrient cycling in Chesapeake Bay, based on analysis of long-term monitoring data collected during two time periods: 1965 to 1980 and 1985 to 2007. They found that bottom water in the upper bay region, where seasonal hypoxia first develops, was enriched in NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> relative to other regions of the bay. This might help explain the occurrence of extensive and persistent hypoxia during the month of June even during years of lower N loading.

## Eutrophic and Hypoxic Coastal Areas of North America and the Caribbean



Source: <http://www.wri.org/resources/maps/coastal-eutrophic-and-hypoxic-areas-north-america-and-caribbean> modified from [Diaz et al. \(2013\)](#).

**Figure 10-5 Coastal eutrophic and hypoxic areas of North America and the Caribbean.**

Recent research has shown that the duration of a hypoxic event is one of the most important factors affecting macroinvertebrate density and species composition. [Baustian and Rabalais \(2009\)](#) found that hypoxia duration (the number of days during which O<sub>2</sub> concentrations were below 1 mg/L) was highly correlated with both reduced species density and diversity in the northern Gulf of Mexico. Very low O<sub>2</sub> levels can be lethal to fish with no means of escape, and it has been suggested that even sublethal hypoxia may lower the breeding rate and affect fish populations ([Moran et al., 2010](#)). Hypoxia has been shown to act as an endocrine disruptor in Atlantic croaker (*Micropogonias undulatus*) in laboratory studies and biomarkers of reproductive function and endocrine disruption are observed in field-collected individuals ([Murphy et al., 2009](#); [Thomas and Rahman, 2009](#); [Thomas et al., 2007](#)). Hypoxic conditions increase nitric oxide and super oxide radicals in brain tissue in croakers, causing cellular oxidative damage and inhibited protein expression in the hypothalamus and leading to neuroendocrine effects ([Rahman and Thomas, 2015](#)). Low O<sub>2</sub> conditions have also been shown to alter animal behavior ([Appendix 10.4.1](#)). O<sub>2</sub> content influences hatching rate and parental effort among other

reproductive behaviors in three-spined sticklebacks (*Gasterosteus aculeatus*), so eutrophication-induced hypoxia may alter reproductive output in some fish populations (Candolin, 2009). However, hypoxia does not appear to negatively affect fisheries below what would be predicted from N loadings alone, except under circumstances in which raw sewage is released or when critical habitat is lost for very sensitive species (Breitburg et al., 2009). In a review of long-term chronic effects of hypoxia on commercially important fishery species Townhill et al. (2017) noted that effects range from positive to negative, and from physiological to ecosystem-level. Some fish can acclimate to hypoxic conditions and/or take advantage of more susceptible prey, affecting food web dynamics. Other species cannot avoid hypoxia (especially shellfish) and suffer physiological stress, mortality, and/or increased predation. Other species have been shown to move away from the area to avoid stress (Appendix 10.4.1), which also has cascading food web implications.

The effects of low DO are influenced by the presence of multiple stressors. For example, Gobler et al. (2014) examined concurrent effects of low DO and acidification on the early lifestages of bay scallops (*Argopecten irradians*) and hard clams (*Mercenaria mercenaria*). Observations in later lifestages of the clams indicated that growth rates decreased by 40% in combined exposures to hypoxia and acidification. Additional studies with earlier lifestages indicated effects were more severe with costressors than with either hypoxia or acidification alone. Juvenile oysters (*Crassostrea virginica*) grown under varying conditions of low pH and duration of hypoxia seemed to acclimate and were only negatively affected by the most severe pH experiment (Keppel et al., 2016). Growth rates were reduced 30–37% initially by both brief, repeated hypoxia and long moderate hypoxia events; however, at the end of the study most oysters were the same size regardless of treatment. This study also reported that the initial effects on oyster growth were more pronounced by constant moderate hypoxia (1.3 mg/L) than they were by severe but cyclical hypoxia (0.5 mg/L).

At the time of the last review, it was documented that the largest zone of hypoxic coastal water in the U.S., and the second largest in the world, was the northern Gulf of Mexico Hypoxic Zone on the Louisiana-Texas continental shelf (Dale et al., 2010; Jewett et al., 2010; U.S. EPA, 2008a). Since the 2008 ISA, observations continue to indicate a large zone of hypoxia in the northern Gulf of Mexico during the summer months associated with increased N loading from the Mississippi and Atchafalaya River Basins. The size of the midsummer bottom-water hypoxia area (<2 mg/L DO) in the northern Gulf of Mexico has varied considerably since 1985, with a long-term average of 13,751 km<sup>2</sup> [5,240 mi<sup>2</sup>; U.S. EPA (2015c)]. In the summer of 2017, the hypoxic zone in the Gulf was the largest ever measured at 14,123 km<sup>2</sup> [8,776 mi<sup>2</sup>; U.S. EPA (2017f)]. Alexander et al. (2008) used the SPARROW water quality model to show that atmospheric deposition to watersheds in

the Mississippi River Basin is the second largest source of N (16%) to the Gulf, after effluents from corn and soybean production (52%).

The Hypoxia Task Force (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force) is a federal/state partnership (five federal agencies, the National Tribal Water Council and 12 states bordering the Mississippi and Ohio rivers) established in 1997 with the goal of reducing nutrient inputs and the size of the hypoxic zone in the Gulf of Mexico ([U.S. EPA, 2017e](#), [2015c](#)). The task force is working toward the goal of reducing the areal extent of the Gulf of Mexico hypoxic zone to less than 5,000 km<sup>2</sup> by 2035, with an interim target of 20% nutrient load reduction by 2025. This was revised from the 2001 action plan that called for the described reductions by 2015 ([U.S. EPA, 2001](#)). Each state in the task force has a nutrient reduction plan, and progress toward stated goals are reported in the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force Report to Congress ([U.S. EPA, 2015c](#)) as required by the *Harmful Algal Bloom and Hypoxia Research and Control Amendments Act of 2014* ([HABHRC Act, 2014](#)). Other states not included in the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force have nutrient reduction programs in place.

Hypoxic conditions are reported from other U.S. locations ([Figure 10-5](#)). For example, in the shallow estuary of Long Island Sound, atmospheric deposition is considered to comprise a significant fraction of total N loading [19%; [Whitall et al. \(2004\)](#)], and DO levels below 3 mg/L are common, with levels below 2 mg/L known to occur. During some years, portions of the Long Island Sound bottom waters become anoxic [DO <1 mg/L; [Latimer et al. \(2014\)](#)]. The maximum extent and duration of hypoxic events (<2 mg/L DO) in Long Island Sound has varied considerably since the 1980s ([U.S. EPA, 2016k](#)). Between 1987 and 2014, the average annual maximum extent was 98 km<sup>2</sup> (61 mi<sup>2</sup>). In 2014, the hypoxic area was 32 km<sup>2</sup> (20 mi<sup>2</sup>), with the lowest DO levels occurring in the western end of the Sound. The shortest hypoxic event occurred in 2014, lasting 2 days. The longest hypoxic event was 71 days in 1989. Over the full period of record (1987–2014), the average annual maximum duration was 31 days. Other estuaries identified in the 2008 ISA where hypoxic conditions occur included Chesapeake Bay and the Pamlico Estuary in North Carolina ([U.S. EPA, 2008a](#)). [Murphy et al. \(2011\)](#) analyzed a 60-year record of Chesapeake Bay hypoxic zone volumes and found a slight but significant decreasing trend in late summer hypoxia, which aligns with the decrease in N loading due to management controls. This analysis also showed a correlation between N loading and the duration of summer hypoxia events ([Murphy et al., 2011](#)). In a modeling study in Chesapeake Bay using analysis of monitoring data, nutrient loading was identified as the main mechanism driving interannual hypoxia variability ([Li et al., 2016b](#)). In upwelling regions such as along the West Coast, hypoxic events driven by

upwelling can be advected into estuaries from global ocean circulation rather than anthropogenic nutrient additions ([Brown and Power, 2011](#); [Brown and Ozretich, 2009](#)).

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### 10.2.5 Submerged Aquatic Vegetation

SAV, rooted vascular plants that grow to the surface but do not emerge from the water, is important to the quality of coastal ecosystems because it provides habitat for a variety of aquatic organisms, serves as nursery grounds for estuarine invertebrates and fish, absorbs excess nutrients, and traps sediments ([Lefcheck et al.](#); [U.S. EPA, 2008a](#); [Handley et al., 2007](#)). Recently, the presence of seagrass beds was linked to decreased bacterial pathogens of humans, fishes, and invertebrates in the water column and a lower incidence of disease in adjacent coral reefs ([Lamb et al., 2017](#)). The loss of SAV can, therefore, have a cascade of effects on other ecosystem characteristics and ecosystem services. Water clarity is important for photosynthesis of SAV ([Handley et al., 2007](#)). Water quality changes associated with excess N nutrient inputs, such as excessive algal growth and hypoxia can impact SAV extent. For example, declines of Johnson's sea grass (*Halophila johnsonii*) which is currently listed as threatened under the U.S. Endangered Species Act has been linked to eutrophication of coastal waters, specifically low DO and algal blooms that alter habitat by covering up substrate ([Hernández et al., 2016](#)). Elevated levels of N tend to increase epiphytes on the surface of SAV, in the absence of other limiting factors, contributing to declines in seagrass biomass, shoot density, percentage cover, production, and growth ([G.Nelson, 2017](#); [Nelson, 2017](#)).

Seagrass loss is occurring globally with nutrient enrichment as a major driving factor contributing to declines in SAV coverage ([Latimer and Rego, 2010](#); [Waycott et al., 2009](#)). SAV is included as a biological indicator for estuarine condition for U.S. coastal waters in ASSETS-ECI in the NEEA and in U.S. EPA's *Report on the Environment* ([U.S. EPA, 2016k](#); [Bricker et al., 2007](#)). At the time of the 2008 ISA, estimates of historical losses of SAV and declines in habitat were available for some coastal regions of the U.S.; although, there were few data documenting the long-term response of SAV to N loading. In Waquoit Bay, MA, [Valiela et al. \(1992\)](#) reported a strong negative relationship between modeled N loading and measured eelgrass (*Zostera marina*) area based on measurements of eelgrass coverage from 1951 to 1990. In the NEEA report, only a small fraction of the estuary systems evaluated reported high severity of SAV loss from the 1990s to 2004 ([Bricker et al., 2007](#)), in part, because historical losses wiped out seagrasses in many estuaries, and recent changes do not seem of high severity.

Since the 2008 ISA, additional studies are available on the relationship between N loading and SAV abundance, including the development of thresholds of response to N

loading in seagrasses ([Table 10-4](#)). Seagrass dieback in Snug Harbor Cape Cod, MA in 2010 was linked to N loading, which stimulated growth of epiphytes on the seagrasses ([Howarth et al., 2014](#)). [Orth et al. \(2010\)](#) observed a consistent negative correlation between SAV abundance and N loading based on water quality data in Chesapeake Bay from 1984–2006. In the Potomac River, a major tributary to Chesapeake Bay, a reduction in total N from point and nonpoint sources was significantly correlated to increased SAV abundance and diversity using field data from 1990 to 2007 ([Ruhl and Rybicki, 2010](#)). Similarly, the reduction of N and P input from point sources into Mattawoman Creek, a tributary to Chesapeake Bay, led to large increases in SAV coverage and density ([Boynton et al., 2014](#)). [Benson et al. \(2013\)](#) identified a tidal-averaged total N concentration of <0.34 mg/L as a threshold for healthy eelgrass in a survey of 19 Massachusetts estuaries. Eelgrass coverage decreases markedly in shallow estuaries in New England with N loading rates  $\geq 100$  kg N/ha/yr (based on nitrogen loading model [NLM] estimates from wastewater, fertilizer, and atmospheric deposition inputs). Loading rates above 50 kg/ha/yr are likely to impact habitat extent ([Latimer and Rego, 2010](#)). These ranges were found to be comparable to loading thresholds identified in other East Coast estuaries ([Table 10-4](#)). In a modeling study using NLM applied to small- to medium-sized estuaries of southern New England, direct atmospheric deposition to the water surface made up an average of 37% of the N input, while indirect deposition via the watershed averaged 16% of N loading. The percentage, however, varied widely for individual estuaries ([Latimer and Charpentier, 2010](#)).

**Table 10-4 Nitrogen loading thresholds from multiple watershed sources versus eelgrass loss.**

Loading Threshold (kg/ha/yr)		Description			
>20		• Areal cover of eelgrass sharply reduced			
100		• Meadows disappeared [Cape Cod estuaries, n = 10; <a href="#">Bowen et al. (2007)</a> ]			
~30		• Substantial eelgrass loss (80–96% of bed area)			
≥60		• Total disappearance [Cape Cod estuaries, n = 7; <a href="#">Hauxwell et al. (2003)</a> ]			
≥64 <sup>a</sup>		• Threshold based on nonparametric change-point analysis [95% probability of change; Chesapeake Bay estuaries, n = 101; <a href="#">Li et al. (2007)</a> ]			
≥52		• Threshold based on nonparametric change-point analysis [95% probability of change; New England estuaries, n = 57; <a href="#">Latimer and Rego (2010)</a> ]			
Consensus of Literature		Percentage of Eelgrass Area Loss (n = 57)			
		Mean %	Median %	25th Percentile	75th Percentile
≤50		62	73	39	78
51–99		88	89	82	98
≥100		93	100	95	100

<sup>a</sup>This only includes point source inputs.

Source: [Latimer and Rego \(2010\)](#).

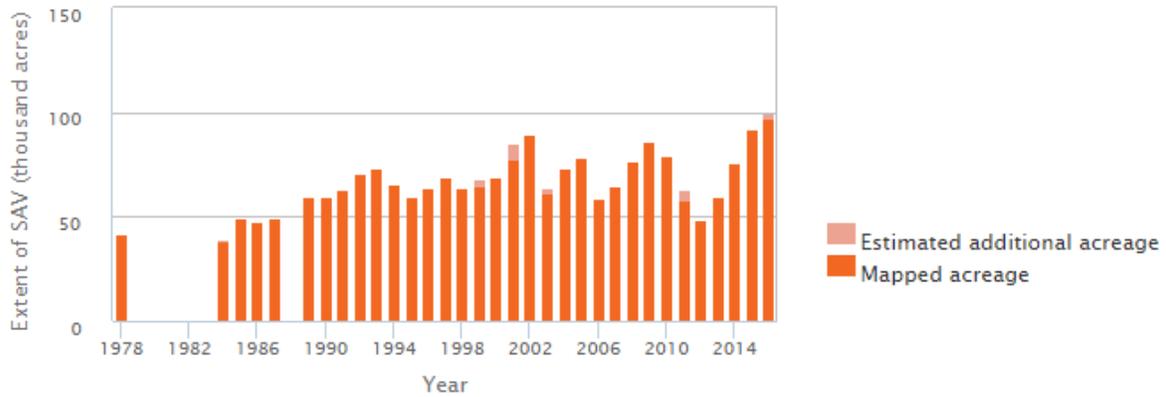
The extent of SAV is stable or increasing in some coastal areas of the U.S. In Chesapeake Bay, SAV coverage has increased from 41,000 acres (16,600 hectares) in 1978 to a peak of 97,000 acres (39,250 hectares) in 2016 based on data collected by the Virginia Institute of Marine Science [[VIMS \(2016\)](#); [Figure 10-6](#)] as reported in U.S. EPA’s *Report on the Environment* ([U.S. EPA, 2016k](#)). SAV acreage has fluctuated in the bay since 2002, covering an estimated 60,000 acres in 2013 then increasing in the most recent surveys conducted in 2015 and 2016. This estimate is based on black-and-white, 1:24,000-scale aerial photographs of the Chesapeake Bay. Aerial monitoring first occurred in 1978 and has occurred annually since 1984 (except during 1988). The SAV survey targets SAV species, which as a group are sensitive to disturbance, particularly from eutrophication and associated reductions in light availability. Pilots follow fixed flight routes to comprehensively photograph all tidal shallow water areas of the bay and its tidal

tributaries. [Orth et al. \(2010\)](#) reported a strong correlation between tributaries where nutrient reductions have occurred and increases in seagrass abundance; however, further reductions are necessary to meet SAV restoration targets. ([Lefcheck et al.](#)) project a catastrophic 95% loss of eelgrass *Z. marina* in Chesapeake Bay (and the associated ecosystem services provided by this habitat type) in the next 30 years given the conservative expectation of 2°C increase in temperature and continued trajectory of 40% decline in water clarity due to the additive effects of these stressors especially on shallow eelgrass beds. They report a 29% decline in eelgrass area in Chesapeake Bay since 1991 using high-resolution aerial imagery and water quality data. The authors note that eelgrass abundance has increased in recent years, but that recovery is limited to shallow, nearshore areas and represents only a fraction of pre-1970s distribution of this species. Despite extensive restoration efforts in the Chesapeake Bay watershed, water quality indicators (chlorophyll *a*, DO, and Secchi depth) and biotic metrics of ecological condition have shown little improvement during a 23-year period ([Williams et al., 2010](#)) The one exception to the pattern of no improvement in water quality was an observed increase in the amount of SAV. Overall, water quality has decreased and chlorophyll *a* levels have increased since 1986.

In Tampa Bay, FL (see [Appendix 16.4](#)), data on seagrass (primarily *Thalassia testudinum*) extent is available as far back as the 1950s. In the 1970s and early 1980s, the bay exhibited signs of increasing eutrophication including loss of seagrasses. Seagrass coverage has recovered to relatively predisturbed conditions (approx. 15,380 ha) following N controls implemented in the mid-1980s ([Greening et al., 2014](#); [Greening et al., 2011](#)). Although the nutrient-load hypothesis of [Brauer et al. \(2012\)](#) suggests that algae can outcompete or block out light for other macrophytes under high or variable nutrient loads, this is not always the case. For example, in Yaquina Bay in Oregon, distribution of eelgrass has remained stable despite high nutrient loads and algal blooms ([Kaldy, 2014](#)), and seagrass populations in Puget Sound, WA have also remained relatively stable for the last 40 years ([Shelton et al., 2017](#)).

In other U.S. coastal areas, SAV coverage has declined. SAV coverage in the coastal lagoon of Maryland and Virginia showed an increase with time until the early 2000s, and then a decrease in the past decade, likely due to increasing anthropogenic nutrient inputs that were accelerated by increased freshwater flow over the same time period ([Glibert et al., 2014](#)). In an analysis of 12 years of data for eelgrass areal coverage along the Massachusetts coastline, there was an overall decrease in seagrass abundance although the amount of change was highly variable between individual embayments ([Costello and Kenworthy, 2011](#)).

### Exhibit 1. Extent of submerged aquatic vegetation (SAV) in the Chesapeake Bay, 1978–2016



There were partial Bay-wide surveys from 1979 to 1983, and no survey in 1988.

Information on the statistical significance of the trend in this exhibit is not currently available. For more information about uncertainty, variability, and statistical analysis, view the technical documentation for this indicator.

**Data source:** Chesapeake Bay Program, 2017

SAV = submerged aquatic vegetation.

Source: [U.S. EPA \(2016k\)](#).

### Figure 10-6 Extent of submerged aquatic vegetation in the Chesapeake Bay 1978–2016.

SAV is often at a competitive disadvantage under N enriched conditions due to the fast growth of opportunistic macroalgae that preferentially take up  $\text{NH}_4^+$  and can block light from seagrass beds ([Abreu et al., 2011](#)). Eelgrass from the Pacific Northwest exhibited increased growth rates with increasing  $\text{NH}_4^+$  concentrations, but growth rate was not related to  $\text{NO}_3^-$  concentration ([Kaldy, 2014](#)). Temperature was found to significantly affect the response of eelgrass to nutrients, but the effects were not synergistic. A significant increase in leaf length and decreases in shoot density and aboveground and belowground biomass in eelgrass was observed concurrent with increased shading by algae in field studies of 12 estuaries in Atlantic Canada ([Schmidt et al., 2012](#)). In the same study, C and N storage (two ecosystem services provided by eelgrass) declined with increasing eutrophication.

A modeling framework to link variable freshwater inputs with seagrass (*Halodule wrightii*, *Thalassia testudinum*) biomass and timing of growth and chlorophyll *a* was

applied to the Caloosahatchee River estuary in southwest Florida ([Buzzelli et al., 2014](#)). The model predicted organic N in the upper estuary, and chlorophyll *a* in time and space reasonably well; however, there was more variation in  $\text{NH}_4^+$  while  $\text{NO}_x^-$  (nitrate-nitrite) was proportional to freshwater inflow. Overall, the model reflected variations in seagrass biomass, although timing and growth did not match the variability of field observations. A spatial model of coastal Australia was used to relate N loading from land to the extent of SAV ([Fernandes et al., 2015](#)). The largest N plume was associated with discharges from an industrialized estuary and a wastewater treatment plants. The location and size of the N plumes changed with seasonal influences. The results of spatial model analysis comparing the plume to seagrass distribution obtained from video surveillance showed that dense seagrass meadows only occurred in areas that were unaffected by N plumes, regardless of the seasonal influences on the plumes.

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## 10.2.6 Indices of Estuarine Condition

Biological and chemical indicators have been used by the states to develop numeric nutrient criteria for estuaries ([Appendix 7.2.10](#)). Indicators may also be combined into an overall condition rating to measure ecosystem function, structure and processes in a standardized approach ([U.S. EPA, 2016g](#); [Borja et al., 2012](#); [U.S. EPA, 2012b](#); [Devlin et al., 2011](#); [Bricker et al., 2007](#)). Several assessment frameworks for eutrophic condition have been developed in the U.S. (e.g., U.S. EPA's NCCA and the NOAA NEEA ASSETS-ECI) and other countries (e.g., Trophic State Index [TRIX], *Institut français de recherche pour l'exploitation de la mer* [IFREMER], transitional water quality index [TWQI]); however, the applicability of a specific framework to areas outside of the region where they were originally developed may be limited ([McLaughlin et al., 2014](#); [Borja et al., 2012](#)). Within the same estuary, results of assessment of eutrophic condition may vary depending on the framework used for evaluation and the associated chemical and biological indicators ([McLaughlin et al., 2014](#); [Garmendia et al., 2012](#); [Devlin et al., 2011](#)). In a comparison of methods to assess nutrient enrichment impacts, [Devlin et al. \(2011\)](#) suggested that indices incorporating annual data, frequency of occurrence, spatial coverage, secondary biological indicators, and a multicategory rating scale are more robust and representative. Two of these methods that have been applied to U.S. waters are ASSETS-NCI ([Bricker et al., 2007](#)) and NCCA ([U.S. EPA, 2016g, 2012b](#)). ASSETS-NCI is only applied to nutrients and focuses on response indicators rather than chemical indicators, while the NCCA can be used for assessing other stressors to coastal areas and integrates both chemical and biological data.

The ASSETS ECI in the NEEA ([Bricker et al., 2007](#)) was used to estimate the likelihood that an estuary is experiencing or will experience eutrophication based on five ecological

indicators: chlorophyll *a*, macroalgae, DO, nuisance/toxic algal blooms, and SAV [Figure 10-3; Bricker et al. (2007)]. ASSETS uses the frequency and spatial extent of algal blooms combined with the 90th percentile of annual values for chlorophyll *a* (Table 10-2). Estuaries are divided into salinity zones, and ratings are combined as an area-weighted sum. Results from the NEEA were included in the 2008 ISA, and the biological indicators are the same in both reports for nutrient effects in estuarine systems.

The NCCA reports represent collaboration between U.S. EPA, NOAA, U.S. Fish and Wildlife Service, and coastal state agencies. The most recent sampling period was 2010 (U.S. EPA, 2016g). NCCAs use chlorophyll *a*, DO, and three additional indicators (DIN, DIP, water clarity) to determine a water quality index (U.S. EPA, 2016g, 2012b). The NCCA include data on water quality, sediment quality, benthic community composition, and fish tissue contaminants to determine the overall condition of the nation's coastal waters. In the most recent NCCA report, water quality was rated good in 36% of coastal and Great Lakes nearshore waters, fair in 48%, and poor in 14%, based on measures of the eutrophication parameters that make up the water quality index (P, N, water clarity, chlorophyll *a*, and DO concentrations).

Additional indices applied to U.S. waters include biological indicators of estuarine condition. Fertig et al. (2014) described a Eutrophication Index applied to Barnegat Bay-Little Egg Harbor Estuary, NJ using weighted indicators of water quality (temperature, DO, TN, TP), light availability (chlorophyll *a*, total suspended solids, Secchi depth, macroalgae percentage cover, percentage surface light, epiphyte biomass), and seagrass (*Zostera* spp.) response (aboveground biomass, belowground biomass, density, percentage cover and length). The biological condition gradient conceptual framework (Davies and Jackson, 2006) was applied to Greenwich Bay, RI to assess estuarine habitat over time (Shumchenia et al., 2015). Biological indicators included seagrass extent, benthic community, primary productivity, and shellfish. In a regional survey of 23 estuaries in southern California, 78% of estuaries were rated “moderate” or “worse” based on macroalgae, 39% based on phytoplankton, and 63% based on DO using the European Union Water Framework Directive (McLaughlin et al., 2014). With the ASSETS framework, 53% of surveyed areas were identified as impaired. The variability in categorizing estuarine condition was influenced by spatial and temporal scales as well as which indicators and thresholds were selected. Additional indices used in other countries for describing estuarine condition are reported in Zaldivar et al. (2008), Borja et al. (2008), Borja et al. (2012), Devlin et al. (2011), Garmendia et al. (2012), and Andersen et al. (2014).

A modeling indicator for ecosystem response to N uptake, which includes a measure of the loss of species richness, was used to create a marine eutrophication Ecosystem

Damage indicator [meED; [Cosme et al. \(2017\)](#)]. The indicator is based on the loss of species richness caused by hypoxia, which is in turn caused by eutrophication. The meED ecosystem damage indicator itself indicates the potential impact of eutrophication in the receiving habitat based on species density estimates. [Cosme et al. \(2017\)](#) supported the meED for inclusion in Life Cycle Impact Assessments (LCIA) when characterizing N emissions. Their paper describes the calculation of the meED indicator for 66 large marine ecosystems and maps risk of ecosystem damage due to eutrophication based on this indicator.

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## 10.3 Effects on Biodiversity

Increased N loading to coastal areas can lead to shifts in community composition, reduced biodiversity, and mortality of biota. Biodiversity is important for ecosystem stability and function, including provision of ecosystem services ([Section IS.2.2.4](#)). Evidence for impacts to biodiversity include paleontological evidence ([Appendix 10.3.1](#)), altered phytoplankton community composition ([Appendix 10.3.2](#)), responses of phytoplankton to reduced versus oxidized N ([Appendix 10.3.3](#)), bacteria/archaea diversity ([Appendix 10.3.4](#)), benthic diversity ([Appendix 10.3.5](#)), and fish diversity ([Appendix 10.3.6](#)). The form of N supplied can significantly affect phytoplankton community composition in estuarine and marine environments ([Glibert et al., 2016](#); [Paerl et al., 2000](#); [Stolte et al., 1994](#)). In hypoxic areas, mortality of benthic biota and avoidance of low-O<sub>2</sub> conditions by mobile organisms lead to changes in biodiversity and loss of biomass ([Diaz and Rosenberg, 2008](#)). Energy transfer through the food web can also be altered by a decrease in predators and an increase in microbes from oxygenated areas to anoxic zones.

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### 10.3.1 Paleontological Diversity

Sediment records from Chesapeake Bay showed alterations in producers and consumers correlated to land use change in the watershed ([Sowers and Brush, 2014](#); [Brush, 2009](#)). In this estuary, diatom community structure has shown a steady decrease in overall diversity since 1760 as estimated by sediment core analysis ([Cooper and Brush, 1993](#)). Diatom populations began to shift from benthic to planktonic in the early 1900s corresponding to the increased N flux and higher sediment inputs [which decreased light penetration; [Brush \(2009\)](#)]. Additional sediment cores from two distinct locations in the estuary show a shift to an estuarine food web that is predominately planktonic ([Sowers and Brush, 2014](#)). An increase in the abundance of the foraminifera *Ammobaculites* spp. and a decrease in the abundance of the polychaete *Nereis* spp. were observed along with the

change in primary producers. Paleontological evidence from England shows significant changes in benthic species composition and ecosystem functioning between periods of extremely low O<sub>2</sub> ([Caswell and Frid, 2013](#)). The evidence suggests that normal benthic functions are maintained during early hypoxia, but these functions collapse once thresholds of severely low O<sub>2</sub> are reached.

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### 10.3.2 Phytoplankton Diversity

As reported in the 2008 ISA, excess N can contribute to changes in phytoplankton species composition ([U.S. EPA, 2008a](#)). High loadings of N and P can also increase the potential for Si limitation, with associated changes in diatoms. Such changes to the phytoplankton community and functional groups (e.g., diatoms, dinoflagellates, cryptomonads, cyanobacteria, chlorophytes) can also affect higher trophic levels because these organisms are the base of the estuarine food web. For example, if the nutrient mix favors species that are not readily grazed (e.g., cyanobacteria, dinoflagellates), trophic transfer will be poor, and relatively large amounts of unconsumed algal biomass will settle to the bottom, which could stimulate decomposition, O<sub>2</sub> consumption, and the potential for hypoxia ([Paerl et al., 2003](#)). Changes in phytoplankton species abundance and diversity have been further documented through in situ bioassay experiments, such as the results reported by [Paerl et al. \(2003\)](#) for the Neuse River estuary, North Carolina. Effects were species specific and varied dramatically depending on whether, and in what form, N was added. The findings illustrate the potential impacts of N additions on phytoplankton.

Several studies published since the 2008 ISA use shifts in diatoms as a measure of N enrichment effects on species diversity. In microcosm studies from Raritan Bay, centric and chain-forming diatoms resulted from enriched NO<sub>3</sub><sup>-</sup> concentrations, differing from the pennate diatoms and green flagellates that accompanied ambient NO<sub>3</sub><sup>-</sup> concentrations ([Rothenberger and Calomeni, 2016](#)). The Si:N ratio was identified as an important factor governing the phytoplankton community dynamics in the bay. Phytoplankton community structure was altered by eutrophication in the Skidaway River estuary, Georgia, as evidenced by a shift away from diatoms and towards nonsilicate nanoplankton ([Verity and Borkman, 2010](#)). There was a strong relationship between diatom taxon distribution and TN concentrations in Charlotte Harbor, FL ([Nodine and Gaiser, 2014](#)). Differences were noted in the phytoplankton community structure during the time periods before, during, and after eutrophication in the Black Sea ([Mikaelyan et al., 2013](#)). Diatoms and dinoflagellates especially were found to be dependent on high N and N:P ratios. While nutrient ratios are known to influence phytoplankton community structure, [Davidson et](#)

[al. \(2012\)](#) pointed out that these nutrient ratios are important only when at least one nutrient is low enough to limit growth.

Shifts in phytoplankton community structure are known to occur in estuaries due to N enrichment, but climatic changes may at times outweigh the impacts of eutrophication [[Paerl et al. \(2010\)](#); [Appendix 10.1.4.1](#)]. Thus, physical changes caused by climate change, such as water temperature, stratification, circulation, and hydrologic variability, must be taken into account when modeling phytoplankton community responses to N enrichment ([Paerl et al., 2014](#)). Likewise, [Glibert et al. \(2014\)](#) noted changes in phytoplankton community composition along with increased anthropogenic N input and a switch to long-term wet conditions in the coastal lagoons area of Maryland and Virginia. A 3-year data set from Raritan Bay indicates that both climatic conditions and nutrient concentrations affected phytoplankton composition from 2010–2012 ([Rothenberger et al., 2014](#)). The abundance of flagellates in the bay over time reflects a shift in dominance away from diatoms that is characteristic of eutrophic systems. Location and surrounding land cover, as well as the type of N input, are important factors in the response of the phytoplankton community to N addition ([Reed et al., 2016](#)). Phytoplankton community composition in four tidally influenced sites along a gradient from highly developed to undeveloped (natural) in coastal SC were influenced by surrounding land cover and the form of N, with cyanobacteria, dinoflagellates, and other potentially HAB-forming species most often found at the more developed sites.

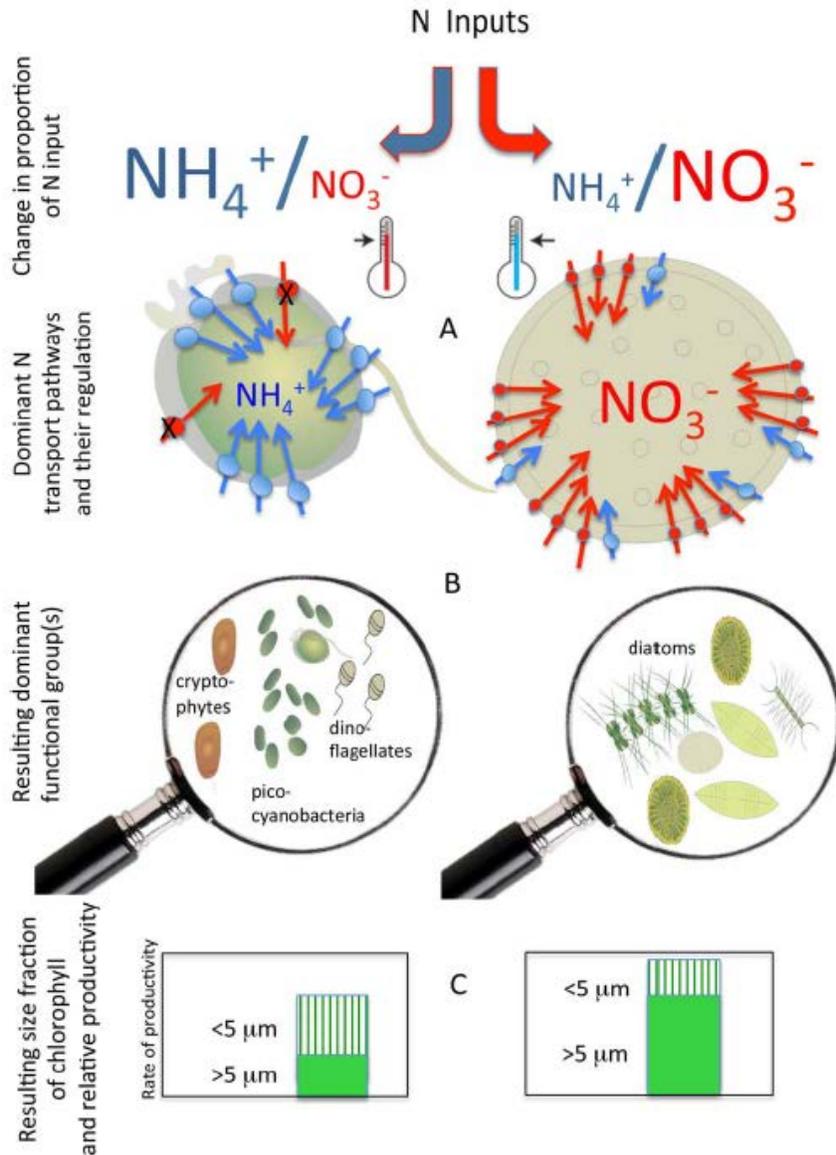
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### 10.3.3 Diversity of Phytoplankton Under Different Forms of Nitrogen (Reduced vs. Oxidized)

Reduced forms of atmospheric N are increasing relative to oxidized N in the U.S. ([Appendix 10.1.2](#)) and play an increasingly important role in eutrophication and HAB dynamics in coastal areas. Specific phytoplankton functional groups have a preference for  $\text{NH}_4^+$  over  $\text{NO}_3^-$  ([Appendix 10.2.2](#)), perhaps leading to selective stimulation of primary production, especially in light-limited estuarine and coastal waters ([Glibert et al., 2016](#); [Paerl et al., 2000](#); [Stolte et al., 1994](#)). Increasing loads of  $\text{NH}_3/\text{NH}_4^+$  have been linked to the expansion of HABs ([Glibert et al., 2016](#); [Esparza et al., 2014](#); [Altman and Paerl, 2012](#); [Blomqvist et al., 1994](#)). For example, in San Francisco Bay, a comparison of N isotopes in cells of the cyanobacterial HAB species *Microcystis aeruginosa* with N in rivers flowing into the bay indicated the primary source of N that supported the bloom formation was likely  $\text{NH}_4^+$  ([Lehman et al., 2015](#)). Phytoplankton response to the form of N supplied ([Appendix 10.2.2](#), and [Table 10-3](#)) could lead to altered phytoplankton growth and community composition and have cascading effects on trophic structure and biogeochemical cycling ([Glibert et al., 2016](#); [Paerl et al., 2000](#)). Cyanobacteria, and many

chlorophytes and dinoflagellates may be better adapted to the use of  $\text{NH}_4^+$ , while diatoms generally thrive in environments with oxidized forms of N such as  $\text{NO}_3^-$ . [Figure 10-7](#) summarizes the dominant functional phytoplankton groups in primarily reduced N and in primarily oxidized N conditions.

Field studies indicate that HAB-forming dinoflagellates are often associated with enrichment of reduced N. In Maryland and Virginia coastal bays, [Glibert et al. \(2014\)](#) observed a regional shift in phytoplankton community composition to species that do well in reduced N conditions. Phytoplankton community dynamics varied with the form of N in nutrient enrichment experiments using water from the New River estuary, NC ([Altman and Paerl, 2012](#)). Photopigment analysis used to identify and quantify taxonomic groups revealed that the addition of riverine dissolved organic nitrogen (DON) promoted dinoflagellates, chlorophytes, and myxoxanthophyll (cyanobacteria) while zeaxanthin (cyanobacteria) was most frequently detected with inorganic N. In the Neuse River estuary, NC where  $\text{NH}_4^+$  concentrations have increased over time, the abundance of raphidophytes (including the potentially toxic dinoflagellate species *H. akashiwo*), haptophytes, chlorophytes, and the bloom-forming dinoflagellate *Heterocapsa rotundata* have also increased ([Rothenberger et al., 2009](#)). Incubation experiments carried out in the Neuse River estuary in spring, early summer, and late summer to test how the growth and community composition of phytoplankton responded to N availability and specific form of N ([Cira et al., 2016](#)). Phytoplankton community composition varied by season, and different taxa were found to be able to uptake both urea and  $\text{NO}_3^-$  when conditions were limiting, although the results varied by taxa. Seasonal experiments suggested that N was not the only factor controlling phytoplankton growth in the spring, as the experiment conducted in March showed that only growth rates of fucoxanthin-containing (brown algae) species were stimulated by N addition. In field studies along a gradient from highly developed to undeveloped (natural) study sites in the southeastern U.S., phytoplankton communities at the more developed sites showed higher biomass and growth rates with N (particularly urea) additions ([Reed et al., 2016](#)). In addition, cyanobacteria, dinoflagellates, and other potentially HAB-forming species were more often found at the more developed sites.



Source: [Glibert et al. \(2016\)](#).

**Figure 10-7** Summary conceptual schematic illustrating the effect of changes in the proportion of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the loads of N provided to a natural system. When  $\text{NH}_4^+$  is the dominant form, and when waters are warmer, flagellates, cyanobacteria, and chlorophytes among other classes may proliferate, leading to overall productivity dominated by the small size class of algae (e.g.,  $<5 \mu\text{m}$ ). In contrast, when  $\text{NO}_3^-$  is the dominant form provided, especially under cooler water conditions, diatoms more likely dominate, and their overall production will be more likely dominated by cells of a larger size class (e.g.,  $>5 \mu\text{m}$ ). Moreover, chlorophyll a yield and total production may be higher than under the  $\text{NH}_4^+$  enrichment condition.

In mesocosm studies in the P-limited Florida Bay ecosystem, chl *a* concentrations (phytoplankton biomass) increased with N + P treatment but did not increase with only N enrichment. However, N only enrichment (especially in the form of  $\text{NH}_4^+$ ) did change the phytoplankton assemblage in the direction of more picocyanobacteria ([Shangguan et al., 2017](#)). A shift of phytoplankton biomass toward diatoms making up a larger portion of the total biomass was observed when N in the form of  $\text{NO}_3^-$  was added, either alone or in combination with P. Using chlorophytes and diatoms from Suisun Bay, CA grown under controlled laboratory conditions [Berg et al. \(2017\)](#) found that the four diatoms species tested grew faster on  $\text{NH}_4^+$  than  $\text{NO}_3^-$  suggesting that diatoms were not under a competitive disadvantage under high  $\text{NH}_4^+$ . Only the chlorophyte *R. planktonicus* grew significantly faster on  $\text{NO}_3^-$ . None of the diatoms tested in controlled lab conditions were sensitive to  $\text{NH}_4^+$  at concentrations that would be found in the local environment. The results show that the responses are highly species specific in tolerance of  $\text{NH}_4^+$ .

Not all studies have found variation in algal response with the form of N. [Richardson et al. \(2001\)](#) examined the effects of different forms of N application ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , urea) on the structure and function of estuarine phytoplankton communities in mesocosm experiments in the Neuse River estuary, NC. Even though  $\text{NH}_4^+$  is more readily taken up by phytoplankton in this estuary than is  $\text{NO}_3^-$  ([Twomey et al., 2005](#)), the results of the [Richardson et al. \(2001\)](#) study suggested that phytoplankton community structure was determined more by the hydrodynamics of the system than by the form of N available for growth. [Twomey et al. \(2005\)](#) measured Neuse River estuary phytoplankton uptake rates of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and urea.  $\text{NH}_4^+$  was the dominant form of N taken up, contributing about half of the total N uptake throughout the estuary. Uptake varied spatially; in particular,  $\text{NO}_3^-$  uptake declined from 33% of the total uptake in the upper estuary to 11 and 16% in the middle and lower estuary, respectively. Urea uptake contributed 45 and 37% of the total N uptake in the middle and lower estuary, showing the importance of regenerated N for fueling phytoplankton productivity in the mesohaline sections of the estuary. Therefore, N budgets based only on inorganic forms may seriously underestimate the total phytoplankton uptake ([Twomey et al., 2005](#)).

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#### 10.3.4 Diversity of Bacteria, Archaea, and Microzooplankton

Since the 2008 ISA, a few studies have explored ammonia-oxidizing bacteria (AOB) and ammonia-oxidizing archaea (AOA) community responses in relation to N in coastal waters. These organisms play a key role in N cycling and the AOA were described relatively recently ([Könneke et al., 2005](#)). [Bouskill et al. \(2012\)](#) examined the distribution and abundance of AOA and AOB across a variety of aquatic environments, including two sites at different salinity levels in Chesapeake Bay. The AOB were dominate in the

freshwater end of the continuum, whereas AOA were more common in open ocean areas. The abundance of both groups was correlated with the concentration of  $\text{NH}_4^+$  in the water, especially relative abundance of AOB. A similar pattern was observed in the Sacramento-San Joaquin Delta where AOB were more abundant in the  $\text{NH}_4^+$ -rich Sacramento River compared to the San Joaquin River and Suisun Bay where AOA were prevalent ([Damashuk et al., 2015](#)). Community structure of benthic ammonia oxidizers differed across the region and appeared to be related to nutrient inputs. In the Puget Sound estuary, WA, AOA were generally more abundant, however, AOB increased relative to AOA during periods of high  $\text{NH}_4^+$  ([Urakawa et al., 2014](#)). Community structure of planktonic ciliates was found to be significantly related to the spatial distribution of  $\text{NO}_3^-$ -N concentrations across a gradient of sites in Jiaozhou Bay, China, suggesting the potential applicability of planktonic ciliate functional groups as a water quality indicator ([Xu et al., 2016a](#)).

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### 10.3.5 Benthic Diversity

Invertebrates associated with bottom substrates of coastal systems are useful indicators of biological change for impacted waters. Several indices based on benthic invertebrates, macroinvertebrates, or macrophytes have been used to assess biological condition in response to the European Water Framework Directive ([Andersen et al., 2014](#); [Zaldivar et al., 2008](#)). A few of these indices have been tested in U.S. waters. [Borja et al. \(2008\)](#) compared the Benthic Index of Biotic Integrity (B-IBI), the AZTI Marine Biotic Index (AMBI), and its multivariate extension the M-AMBI in Chesapeake Bay. There was relative agreement between methodologies, and differences were related to spatial variability and habitat type. Comparable regional benthic indices for the Northeast/Acadian, northeast Virginian, southeast Virginian, southeast Carolinian, and Gulf Louisianan coasts were developed for the U.S. EPA's coastal assessments [[NCCA; U.S. EPA \(2016g\)](#)].

N enrichment has been shown to have significant but complex effects on suspension-feeding macroinvertebrates in estuaries. Shellfish species can respond positively to increased N loading and high phytoplankton biomass levels due to increased quantity and quality of food particles ([Carmichael et al., 2004](#)). A recent study in Long Island's Peconic Estuary suggested that eutrophication affects shellfish through changes in the quality of food and not the quantity ([Wall et al., 2013](#)). Select species (oysters [*C. virginica*] and clams [*Mercenaria mercenaria*]) in eutrophic areas experienced enhanced growth rates that were strongly correlated with high densities of autotrophic nanoflagellates and centric diatoms. Other species (scallops [*Argopecten irradians*] and slipper limpets) suffered negative effects and grew at the slowest rate at the most

eutrophic sites. Bay scallop growth was negatively correlated with densities of dinoflagellates, which were more abundant at the most eutrophic site ( $p < 0.001$ ). In rocky shore environments in Ireland, similar to those of the U.S. northeastern Atlantic coast, N enriched sites near industrial and sewage outfalls have been shown to have reduced total abundance and number of molluscan taxa and altered community composition compared with control sites ([Atalah and Crowe, 2012](#)). Nitrite and  $\text{NH}_3$  levels explained the highest percentages of variation in the molluscan assemblage structure (13 and 12.5%, respectively), owing in large part to the absence of three rare species at contaminated sites. The observed shift in community structure caused by different levels of molluscan tolerance to N enriched conditions has been suggested for use as a biological indicator of eutrophication ([Atalah and Crowe, 2012](#)). The role of benthic invertebrates in coastal N cycling and the use of shellfish for coastal N remediation is discussed in [Appendix 7.2.6.11](#).

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### 10.3.6 Fish Diversity

A few studies have recently reported effects on fish biodiversity in nutrient-impacted estuaries. Comparison of trophic organization of fish in estuarine reaches of nine rivers in Victoria, Australia showed that inorganic N loading was an important factor explaining trophic diversity of fish assemblages. There was greater trophic diversity of fish assemblages with mid to high inorganic N loading suggesting that DIN influences not only estuary primary productivity but is transmitted upward through the food chain ([Warry et al., 2016](#)). In Prince Edward Island estuaries, adult and young-of-the-year abundance of pollution-tolerant mummichogs (*Fundulus heteroclitus*) increased in estuaries with greater intensity of N loading from agricultural land use ([Finley et al., 2013](#)). In this study, eutrophication was associated with changes in habitat variables, which were linked to mummichog abundance. In an estuary in the southern Gulf of St. Lawrence in Canada, loss of eelgrass was linked to declines in fish diversity, but the loss did not change the positions of organisms within the food chain ([Schein et al., 2013](#); [Schein et al., 2012](#)).

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### 10.3.7 Trophic Interactions

Altered trophic transfer following nutrient-associated changes in phytoplankton community composition were reported in the 2008 ISA. Phytoplankton that are not readily grazed, such as cyanobacteria and dinoflagellates, are not transferred to higher trophic levels as efficiently as diatoms [more readily grazed by zooplankton which are then consumed by fish; [Paerl et al. \(2003\)](#)]. Since the 2008 ISA, studies have further

characterized the effects of nutrient enrichment on trophic interactions. In the Skidaway River estuary, GA, increasing nutrient concentrations and changes in nutrient ratios led to increases in eukaryotic organisms (heterotrophic and mixotrophic flagellates, dinoflagellates, ciliates, and metazoan zooplankton) but not diatoms, potentially altering food web predator-prey relationships ([Verity and Borkman, 2010](#)). In an experimental study in Chesapeake Bay, [Reynolds et al. \(2014\)](#) demonstrated that a reduction of crustacean grazers controlling algal growth on seagrasses resulted in 65% reduced seagrass biomass and nearly sixfold increased epiphytic algae. In experimental plots where grazers were removed, aboveground eelgrass biomass was reduced following fertilization. In the presence of grazers, eelgrass biomass increased with fertilization. When predators were excluded, mesograzers were able to limit epiphytic algal growth even when nutrients were added. Based on these findings, the researchers suggested that it is unlikely that reducing nutrient pollution alone would restore seagrass meadows where alterations to food webs have already reduced populations of algae-feeding mesograzers. Similar results were reported in [McSkimming et al. \(2015\)](#) from *Posidonia angustifolia* meadows in Australia where mesograzers responded to nutrient addition by increasing grazing per capita, resulting in greater consumption of epiphytic algae.

A review of nutrient addition studies from the North Atlantic suggests that, overall, the addition of nutrients caused the biomass of opportunistic macroalgae to approximately double. Higher numbers of midlevel predators has the same effect because they lead to a smaller population of grazers eating the macroalgae ([Ostman et al., 2016](#)). Analysis of review data indicated that the effect of midlevel predators on green macroalgae biomass increased with eutrophication. Recovery of sea otter (*Enhydra lutris*) populations in California appear to control algal growth on eelgrass by increased predation of crabs (*Cancer* spp. and *Pugettia producta*) which, in turn, decrease predation of mesograzers such as sea slugs (*Phyllaplysia taylori*) that feed on the algae ([Hughes et al., 2013](#)). Newer literature has provided evidence for complex interactions between eutrophication and other stressors and subsequent effects on trophic interactions. For example, [Burnell et al. \(2013\)](#) used mesocosms to demonstrate the effect of eutrophic conditions on plant-herbivore grazing interactions between the sea urchin *Amblypneustes pallidus* and the seagrass *Amphibolis antarctica* affected by warming and acidification. Nutrient enrichment offset increased grazing associated with acidification and warming; however, it did not fully counter the additive effects of these two stressors.

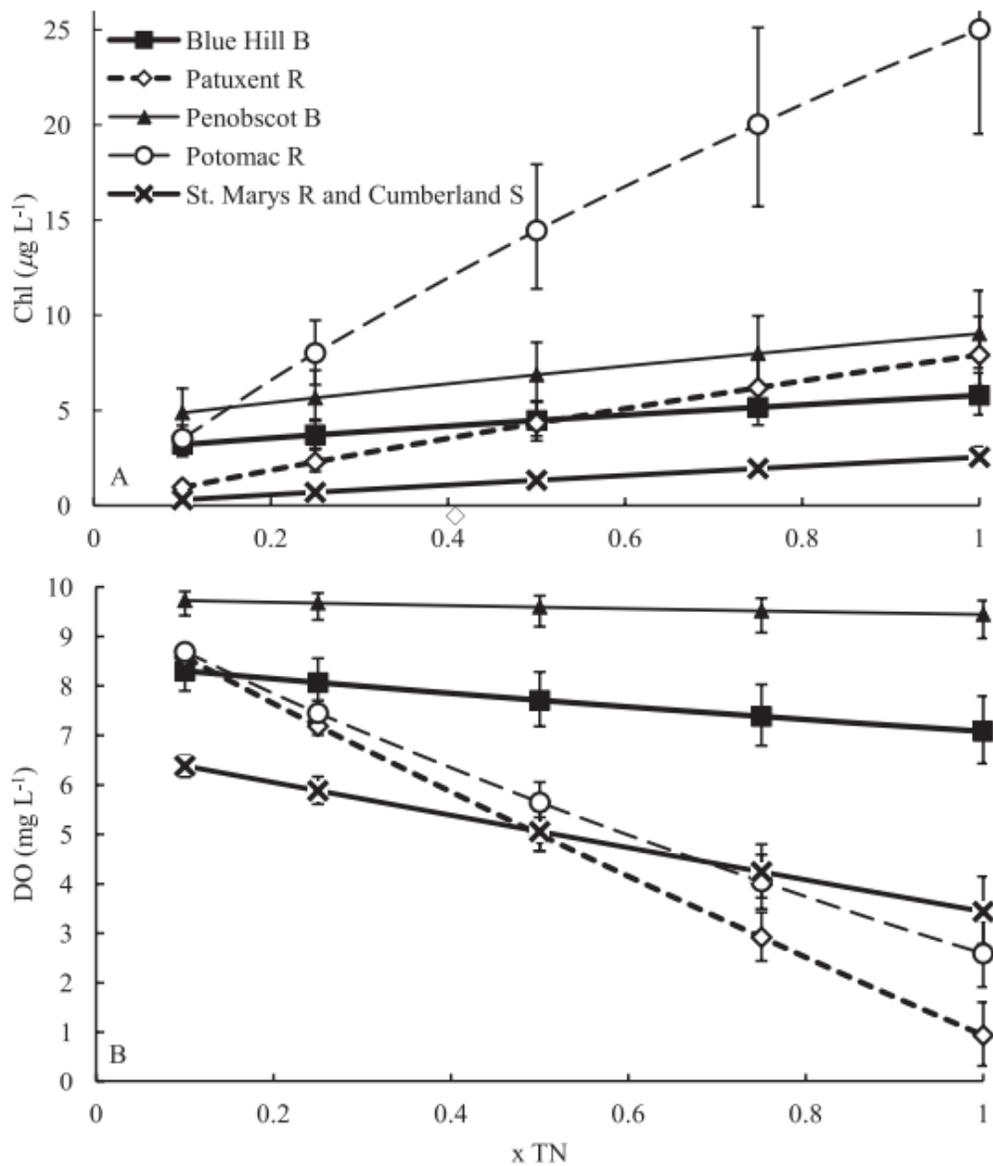
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### 10.3.8 Models Linking Indicators to Nitrogen Enrichment

Process-oriented models such as nutrient-phytoplankton-zooplankton (NPZ) models are used to predict the response of organisms such as HABs to various known and/or

predicted nutrient conditions ([Swaney et al., 2008](#)). A nutrient-driven phytoplankton model developed by [Scavia and Liu \(2009\)](#) was expanded by [Evans and Scavia \(2013\)](#) to test the sensitivity of the response of chlorophyll *a* levels and DO levels to N enrichment. Results indicated that separate processes control chlorophyll *a* and DO sensitivity (estuary flushing time and relative mixing depth, respectively), and that these sensitivities vary among estuaries ([Figure 10-8](#)).

Using the European regional Seas Ecosystem Model for an area of the Japan Sea, [Lee and Yoo \(2016\)](#) showed that the phytoplankton community there will shift to smaller phytoplankton, and the food web structure will likely be altered if atmospheric deposition continues to intensify in the region as predicted. For the study period 2001–2012, the model estimated that the atmospheric N deposition in the Ulleung Basin would increase the annual net primary production by an average of 4.58% (range from 3.77–10.58%).



chl = chlorophyll; DO = dissolved oxygen; TN = total nitrogen.

The x-axis shows river total nitrogen load relative to the 1992 SPARROW total nitrogen load for each estuary. In the figure legend, R = river, B = bay, and S = sound.

Source: [Evans and Scavia \(2013\)](#).

**Figure 10-8 Forecasting curves for effects on total nitrogen loadings on (A) chlorophyll and (B) dissolved oxygen (mean and 95% confidence interval) for selected estuaries demonstrating the full range of sensitivity to relative total nitrogen loading.**

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## 10.4 Animal Behavior and Disease

In addition to changes in biological indicators (i.e., chlorophyll *a*, HABs, macroalgal abundance, SAV) and altered species diversity there is increasing evidence for a role of N in behavior and disease in coastal biota. These indirect responses may affect the fitness of organisms inhabiting nutrient-enriched waters.

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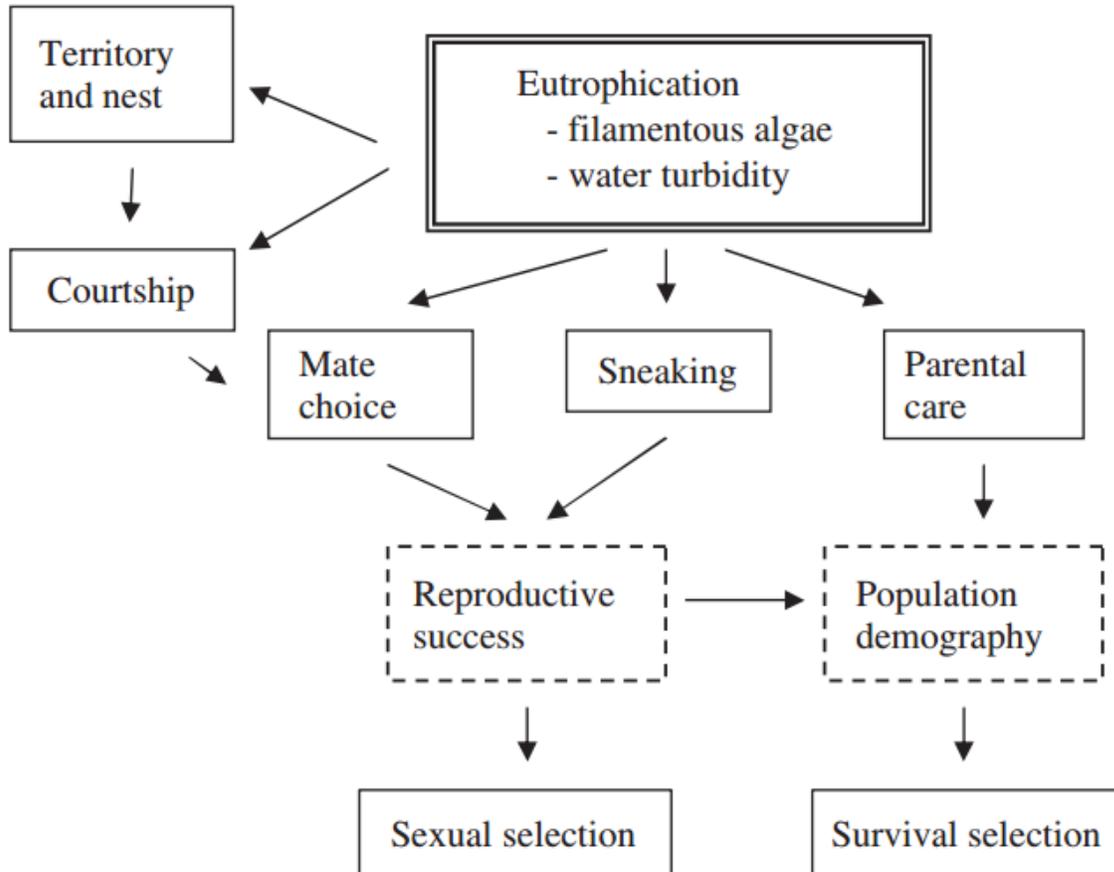
### 10.4.1 Behavior

Coastal biota exhibit behavioral responses to hypoxic conditions, including acclimation or avoidance ([Townhill et al., 2017](#); [Levin et al., 2009](#)). Some fish have the ability for aquatic surface respiration, a behavior in which the fish swims to the surface and is able to take advantage of the relatively higher levels of DO in the water there. [Dixon et al. \(2017\)](#) assessed four common species of shallow estuarine finfish for their reactions to episodic hypoxic conditions and altered pH levels. Severe hypoxia induced surface respiration behavior of three of the four fish species, but all were unaffected by diel variations in pH.

Turbidity caused by excess algae in the water, a secondary effect of eutrophication, has been shown in laboratory studies to potentially alter some fish behaviors, with implications for mate selection and offspring survival rates. It is not known whether some of these behavior changes will be adaptive or if they will have positive or negative effects on the fish populations. For instance, when the strength of sexual selection on several traits is relaxed, the relative importance of survival selection may increase ([Candolin, 2009](#)). The color contrast created by increased turbidity may lead to a heightened feeding response in some fish larvae such as California yellowtail (*Seriola lalandi*), which exhibited elevated growth and survival rates compared to larvae raised in clear (oligotrophic) water ([Stuart and Drawbridge, 2011](#)).

Several studies of the three-spined sticklebacks (*Gasterosteus aculeatus*) indicate that observed alterations of reproductive behaviors are linked to eutrophic conditions ([Figure 10-9](#)). Laboratory manipulations suggest that turbidity caused by eutrophication may affect mate selection and breeding success in this euryhaline fish species ([Heuschele et al., 2012](#); [Heuschele and Candolin, 2010](#)). When given the choice between dense or sparse algae, male sticklebacks preferred to nest in dense algae (which simulated eutrophic conditions). The nests of those males were more likely to be parasitized by other males; however, the males nesting in dense algae also acquired more eggs, and thus, had a higher probability of reproduction ([Heuschele and Candolin, 2010](#)). This may be because reduced visibility leads to reduced mate selectivity searching by females,

although it is unknown whether these behavior changes would have positive or negative impacts on the population ([Heuschele et al., 2012](#)).



Source: [Candolin \(2009\)](#).

**Figure 10-9** The pathway of effects of eutrophication on different reproductive behaviors and selection forces in *Gasterosteus aculeatus*.

Simulated turbidity has also been shown to impair visual mate choice in an eastern Atlantic species of marine pipefish, *Syngnathus typhle* ([Sundin et al., 2010](#)). A follow-up study in the same species allowed other factors to occur, namely mating competition and mate encounter rates which counteracted the effects of lack of visual cues and led to increased sexual selection in turbid waters ([Sundin et al., 2017](#)). In the same species, the latency period between courting and copulation was prolonged in low-O<sub>2</sub> conditions,

although other measures of reproductive behavior (total time spent courting, probability of mating, dancing, male pouch-flap behavior) were unaffected ([Sundin et al., 2015](#)).

Other types of fish mating behaviors are also affected by eutrophication. Male sticklebacks engage in an opportunistic mating behavior called “sneaking” which is less successful under more turbid (eutrophic) conditions ([Vlieger and Candolin, 2009](#)).

Eutrophication has so far been found to have conflicting impacts on nest building behavior in male sticklebacks, with varying implications for the survival rate of stickleback offspring. Male sticklebacks built smaller nests with wider openings during eutrophic (algal bloom) conditions ([Wong et al., 2012](#)). These males also took longer to complete the nest than did males that built during nonbloom conditions. However, under normal water conditions in a laboratory setting, male sticklebacks that had been collected from eutrophic waters built their nests faster than those collected from noneutrophic waters, although the nests did not differ in structure or composition between the two groups ([Tuomainen and Candolin, 2013](#)). In European sand gobies (*Pomatoschistus minutus*), another species that exhibits paternal care of eggs, algal turbidity altered male behaviors ([Järvenpää and Lindström, 2011](#)). Males spent more time away from the nest and exhibited less fanning of the eggs with their pectoral and tail fins. Goby egg survival rates were actually found to be higher under turbid conditions. Although the mechanism for this outcome is unknown, it was proposed that males may have increased other forms of care in the presence of eutrophic conditions, leading to higher egg survival.

Under normal conditions, it is beneficial for sticklebacks to live in larger groups where they gain protection from predators, are able to forage more efficiently, and are able to find a mate more easily than in smaller groups. However, in eutrophic (turbid) water, sticklebacks did not show a preference for joining a larger shoal as they did under normal conditions ([Fischer and Frommen, 2013](#)). This lack of exhibited shoal preference under turbid conditions could eventually reduce individual stickleback fitness. In addition, sticklebacks changed shoals less frequently in turbid water than observed under normal conditions, leading to a decrease in the transfer of important social information, such as the location of foraging routes. Therefore, increased turbidity may reduce social learning opportunities for sticklebacks and may, in turn, impair their foraging efficiency ([Fischer and Frommen, 2013](#)).

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#### 10.4.2 Disease

Diel-cycling hypoxia in estuaries is a natural phenomenon that can be exacerbated by increased biomass and productivity associated with anthropogenic nutrient loadings ([Tyler et al., 2009](#)). [Tyler et al. \(2009\)](#) observed that upper areas of four Delaware

estuaries experienced increased incidence of severe hypoxia ( $DO \leq 2$  mg/L) where nutrient loading was greater. The duration and spatial extent of diel-cycling hypoxia in the estuaries were primarily associated with water temperature, previous day's insolation, hours of morning ebb tide, and daily stream flow. Oysters (*C. virginica*) exposed to periods of diel-cycling hypoxia were demonstrated to have increased incidence and progression of *Perkinsus marinus* infection (Dermo) in field and laboratory experiments ([Breitburg et al., 2015](#)). Field experiments were conducted in Chesapeake Bay. The authors suggest that the likely mechanism is negative effects of hypoxia on host immune response.

Seagrass meadows were recently shown to decrease pathogens harmful to both human health and marine organisms. In field studies adjacent to islands in Indonesia affected by wastewater pollution, bacterial pathogens were reduced by up to 50% in seagrass meadows and coral reefs adjacent to seagrass beds had reduced disease incidence ([Lamb et al., 2017](#)). Several recent studies have suggested that seagrasses may be more susceptible to wasting disease caused by the marine slide mold (genus *Labyrinthula*) under conditions of elevated  $NO_3^-$  loading ([Hughes et al., 2017](#); [Kaldy et al., 2017](#)).

Nutrient enrichment is one of several factors linked to increased disease susceptibility and bleaching in corals ([D'Angelo and Wiedenmann, 2014](#); [Vega Thurber et al., 2014](#); [Wiedenmann et al., 2013](#)). Coral bleaching occurs when the symbiotic relationship between the coral host and microalgae (*Zooxanthellae* spp.) breaks down. Although most research on nutrient loading on corals includes both N and P several studies have isolated effects of N which impacts corals via distinct pathways from P ([Shantz and Burkepile, 2014](#)). [Wiedenmann et al. \(2013\)](#) reported that the coral-algae symbiosis can be interrupted by elevated inorganic N concentration rather than both N and P. In a meta-analysis of nutrient impacts on corals, N reduced coral calcification 11% on average, while increasing photosynthetic rate ([Shantz and Burkepile, 2014](#)). Increased DIN decreases the temperature threshold at which coral bleaching occurs ([Wooldridge, 2009](#)). The threatened status of staghorn coral (*Acropora cervicornis*) and elkhorn coral (*Acropora palmata*) under the U.S. Endangered Species Act has been linked to indirect N pollution effects, specifically low DO and algal blooms that alter habitat, and other non-nutrient stressors ([Hernández et al., 2016](#)).

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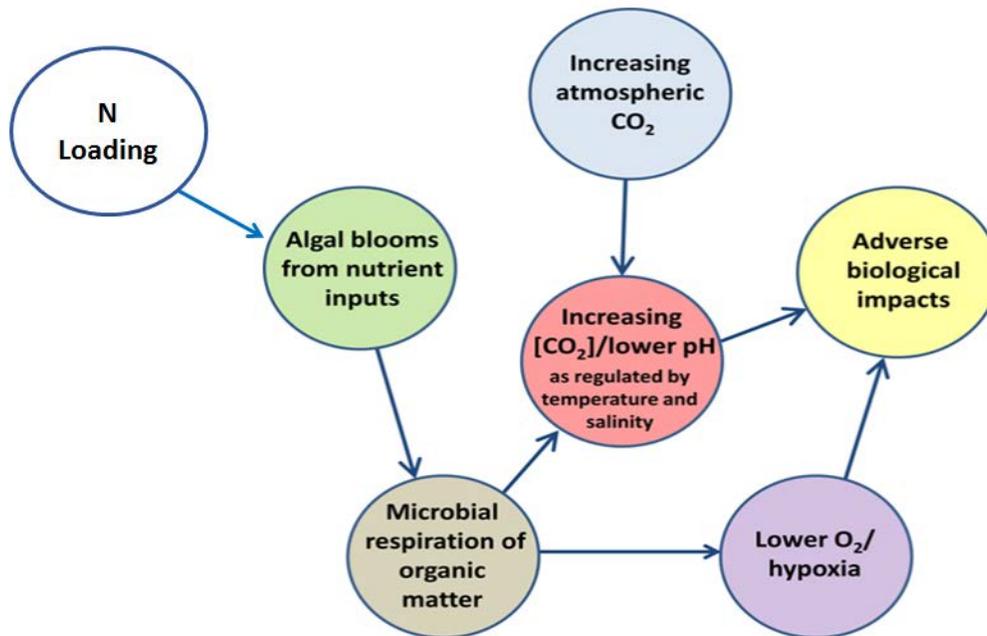
## 10.5 Nitrogen Enrichment and Acidification Effects on Calcifying Organisms

Eutrophication and acidification are complex biogeochemical processes that are driven by the same hydrological (stratification) and biological (production/respiration) processes,

that can result in hypoxia and enhanced organic matter loading ([Wallace et al., 2014](#); [Cai et al., 2011c](#)). Ocean acidification, which can be exacerbated by elevated N input, is projected to alter marine habitat, have a wide range of effects at the population and community level, and affect food web processes ([Mostofa et al., 2016](#); [Andersson et al., 2015](#); [Gaylord et al., 2015](#); [Sunda and Cai, 2012](#); [Doney et al., 2009](#)).

Dissolution of atmospheric anthropogenic carbon dioxide (CO<sub>2</sub>) into the ocean has caused increasing acidification of some coastal waters, resulting in long-term decreases in pH [[Orr et al. \(2005\)](#); [Wallace et al. \(2014\)](#); [Appendix 7.2.7.2](#)]. Decreased alkalinity can impact buffering and influence system response to nutrient inputs ([Cai et al., 2017b](#)). A major finding of The West Coast Ocean Acidification and Hypoxia Science Panel was that, while the dominant cause of ocean acidification in the region is global CO<sub>2</sub> emissions, local discharge of nutrients and organic C is a factor exacerbating ocean acidification and hypoxia ([Chan et al., 2016](#)). Acidification due to direct CO<sub>2</sub> dissolution is more likely observable in open ocean environments but may be masked by enhanced primary production (eutrophication) leading to basification in surface waters. Nutrient-driven eutrophication can trigger algal blooms, which upon decomposition in bottom waters, further reduce oxygen levels in the water column and thus also lower the pH. Consequently, nutrient enhanced acidification is a result of the synergistic input of CO<sub>2</sub> from the atmosphere plus the decomposition of organic matter stimulated by anthropogenic nutrients (e.g., eutrophication). It can be further exacerbated by warming ([Baumann and Smith, 2018](#)) as well as changes in buffering capacity (alkalinity) of freshwater inputs.

Increased respiration of particulate organic matter stimulated by N enrichment exacerbates coastal ocean acidification, which coupled with reduced buffering capacity, leads to an alteration of the carbonate biogeochemistry ([Appendix 7.2.4](#)). Specifically, N enrichment is expected to worsen this acidification because degradation of excess organic matter from blooms generates CO<sub>2</sub> in the water column, which in turn increases acidity [[Figure 7-8](#), [Figure 10-10](#); [Cai et al. \(2011c\)](#); [Howarth et al. \(2011\)](#); [Sunda and Cai \(2012\)](#); [Wallace et al. \(2014\)](#)]. Allochthonous organic matter inputs, which have been increasing in many coastal watersheds from changing land use ([Wilson et al., 2016](#); [Wetz and Yoskowitz, 2013](#)), are an important additional source of organic matter leading to overall increases in acidity. N-driven eutrophication and anthropogenically enhanced allochthonous organic matter loading, as well as reduced buffering capacity operate simultaneously to alter carbonate biogeochemical cycling.



CO<sub>2</sub> = carbon dioxide; N = nitrogen; O<sub>2</sub> = oxygen.

Modified from: [Sunda and Cai \(2012\)](#).

**Figure 10-10 Pathway from nitrogen loading to biological effects of nutrient-enhanced coastal acidification. Both microbial respiration of organic matter and increasing atmospheric carbon dioxide lower pH of coastal waters.**

Acidification of coastal waters may cause varying degrees of harm to marine organisms that produce calcium carbonate shells or skeletons, including oysters, clams, sea urchins, shallow water corals, and calcareous plankton ([Mostofa et al., 2016](#); [Gledhill et al., 2015](#); [Pfister et al., 2014](#); [Kroeker et al., 2013](#); [Sunda and Cai, 2012](#)). The acidifying process decreases the saturation state of the two minerals (aragonite and calcite) that most bivalves use to form their shells ([Barton et al., 2015](#); [Barton et al., 2012](#)). Lower pH of seawater can also potentially impair physiological energetics and spawning capacity of shellfish ([Xu et al., 2016b](#)). Commercially important species from the New England coastal region have shown biological responses to changes in the carbonate system associated with ocean and coastal acidification ([Gledhill et al., 2015](#)). Already, there are declines in oyster production on the U.S. West Coast due to the inability of oysters to create shells due to acidification ([Chan et al., 2016](#); [Barton et al., 2015](#); [Hettinger et al., 2012](#)). However, other factors can confound the response of these sensitive organisms.

More research is needed to accurately determine the interactions and combined impact of ocean acidification and N enrichment and other stressors on U.S. ecosystems like coral reefs and estuaries with sensitive shellfish populations ([Kroeker et al., 2013](#)).

In a recent modeling study of risk of food web and fisheries to ocean acidification in the California current nearshore, invertebrates and associated fishery revenues are expected to be impacted to a greater extent than pelagic species ([Marshall et al., 2017](#)). Although this modeling study did not take N inputs or other measures into account, invertebrates that live in or on the benthic layer (crabs, shrimps, bivalves) will experience the strongest effects of ocean acidification, followed by those species that consume benthic invertebrates such as demersal fish and Dungeness crabs (*Metacarcinus magister*). However, the model also showed that different species of groundfish reacted differently to the changing pH, so some species and associated fishery dynamics may be impacted to a greater degree than others.

Research on costressors associated with conditions of coastal acidification and eutrophication suggest that interactions between elevated CO<sub>2</sub>, increasing acidity, decreasing alkalinity, and nutrient inputs are complex. In macroalga *Ulva pertusa* grown under conditions of low pH and high NH<sub>4</sub><sup>+</sup>, both growth rate and NH<sub>4</sub><sup>+</sup> uptake were significantly higher than in treatments with higher pH and lower nutrient enrichment ([Kang and Chung, 2017](#)). [Young and Gobler \(2016\)](#) tested the effects of elevated concentrations of CO<sub>2</sub> alone, and in combination with elevated nutrient (N + P) levels, on the growth rates of two common species of opportunistic macroalgae, the rhodophyte *Gracilaria* and the chlorophyte *Ulva*. Results showed that higher levels of pCO<sub>2</sub> significantly enhanced the growth rates of both types of macroalgae, and the combination of enriched N + P and pCO<sub>2</sub> did appear capable of synergistically promoting the growth of *Ulva*. Given that eutrophication can yield elevated levels of pCO<sub>2</sub>, this study suggests that the overgrowth of macroalgae in eutrophic estuaries can be further promoted by acidification.

Eelgrass productivity and growth are predicted to increase under conditions of elevated CO<sub>2</sub> because photosynthesis in these plants is thought to be currently limited by CO<sub>2</sub> ([Koch et al., 2013](#); [Alexandre et al., 2012](#); [Palacios and Zimmerman, 2007](#)). However, seagrass productivity responses to combined stressors of pCO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> were found to be variable between different species ([Ow et al., 2016](#)). In mesocosm experiments with the seagrass *Zostera noltii*, photosynthesis increased under enriched CO<sub>2</sub>, but NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> uptake and growth rate were not significantly affected, indicating that seagrass production may be limited by N availability under increased CO<sub>2</sub> ([Alexandre et al., 2012](#)).

Combined effects of  $\text{NO}_3^-$  enrichment, acidification, and temperature resulted in the highest reproductive success for the green tide-forming algae *Ulva rigida*, pointing to potentially more severe green tides under future scenarios than under present conditions, especially in areas where eutrophication is a concern (Gao et al., 2017). A decline in calcification of the coral *Marginopora rossi* was observed at a pH of 7.6 alone or in combination with nutrients (Reymond et al., 2013). In  $\text{NO}_3^-$  enriched seawater, the number of zooxanthellae cells in the host coral increased but with no observable benefits on coral growth. A threshold for ocean acidification at pH 7.6 alone or in combination with eutrophication will lead to a decline in *M. rossi* calcification.

Models show that while the impact of each acidification pathway (N enrichment and atmospheric  $\text{CO}_2$  dissolution) may be moderate, the combined effect of the two may be much larger than would be expected by just adding the effects of each pathway together (Sunda and Cai, 2012; Cai et al., 2011c). These models, which incorporate the expected future higher atmospheric  $\text{CO}_2$  levels and current levels of eutrophication, show dramatic increases in acidification of coastal waters below the pycnocline. Model predictions agreed well with pH data from hypoxic zones in the northern Gulf of Mexico and both the modeled and the measured decreases in pH are well within the range shown to impact marine fauna (Sunda and Cai, 2012). Data from the northern Gulf of Mexico revealed a significant positive correlation between subsurface water pH and  $\text{O}_2$  concentration, linking acidification to low  $\text{O}_2$  levels from organic matter decomposition (Cai et al., 2011c). Results from a coupled physical-biogeochemical model in the Gulf of Mexico point to eutrophication driven by river nutrient input as an important factor in acidification and hypoxia generation (Laurent et al., 2017). Findings from the model showed that acidified waters are predicted in a thin layer close to the bottom of the Gulf, similar to the vertical distribution of the seasonal hypoxia zone.

The increase in atmospheric  $\text{CO}_2$  dissolution is also expected to alter the N cycle in the ocean, with implications for the entire ecosystem. Acidification will result in decreased rates of nitrification, which combined with expected increasing N deposition, is expected to cause the  $\text{NH}_4^+$  concentration of the water to rise (Lefebvre et al., 2012). A study of the coccolithophore *Emiliana huxleyi*, which plays a major role in the global carbon cycle by regulating the exchange of  $\text{CO}_2$  across the ocean-atmosphere interface, found that higher levels of  $\text{NH}_4^+$  can affect the morphology and calcification of the coccolithophore. The combined effect of higher  $\text{NH}_4^+$  levels and greater acidification could reduce calcification rates, suggesting a greater alteration to the ocean's carbon cycle due to the combined effect of increased  $\text{NH}_4^+/\text{NO}_3^-$  and acidification (Lefebvre et al., 2012).

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## 10.6 Summary of Thresholds and Levels of Deposition at Which Effects Are Manifested

Studies linking changes in estuary nutrient status to atmospheric deposition have been limited, although some states are addressing atmospheric inputs as part of their development of total maximum daily loads [TMDLs; [Linker et al. \(2013\)](#)]. Since the 2008 ISA, additional thresholds of response to N have been identified for biological indicators. In general, the identification and application of indicators and thresholds to assess eutrophication in coastal areas is more highly developed in Europe than in the U.S. due to the implementation of the EU's Water Framework Directive ([Zaldivar et al., 2008](#)). Here we limit discussion to indicators and thresholds that have been applied to U.S. water bodies.

For chlorophyll *a*, both NEEA ASSETS and U.S. EPA NCCA have a similar range for categorizing eutrophic conditions; however, ASSETS uses the 90th percentile chlorophyll concentration of annual data and U.S. EPA NCCA uses growing season (June–October) values [[Borja et al. \(2012\)](#); [Table 10-2](#)]. For ASSETS, chlorophyll concentrations of 0–5 µg/L is a water body with low risk of eutrophication, 5–20 µg/L is moderate, >20 µg/L is high with >60 µg/L indicating hypereutrophic conditions. NCCA identified chlorophyll concentration of >20 µg/L as an indicator of an estuary in poor condition. Chlorophyll concentrations between 5–20 µg/L are classified as fair and chlorophyll concentration 0–5 µg/L was good for sites located in the Northeast, Southeast, Gulf, West Coast, and Alaska ([U.S. EPA, 2012b](#)). Values were lower for sites in Hawaii, Puerto Rico, U.S. Virgin Islands, American Samoa, and Florida Bay (0.5 µg/L good, 0.5–1 µg/L fair, >1 µg/L, poor).

For DO, ASSETS uses the 10th percentile of annual data. DO concentrations of 0 mg/L are anoxic, 0–2 mg/L are indicative of hypoxic conditions, and 2–5 mg/L are biologically stressful conditions ([Devlin et al., 2011](#); [Bricker et al., 2007](#)). Spatial coverage (range of 0–10% [low] to >50% [high]) and frequency of occurrence (persistent, periodic, episodic) are also included in determining reference thresholds for DO with ASSETS. For U.S. EPA NCCA, the cutpoint used for poor DO condition is <2 mg/L in bottom waters ([U.S. EPA, 2016g, 2012b](#)). Because many states use higher concentrations, the NCCA considers concentrations between 2 and 5 mg/L as fair, and >5 mg/L as good.

Under the U.S. Clean Water Act, states are in the process of developing numeric nutrient criteria to better define levels of N and P that affect estuaries and coastal marine waters ([Appendix 7.2.10](#)). The numeric values include both causative (N and P) and response (chlorophyll *a*, biocriteria) variables to assess eutrophic conditions. For progress toward state development of numeric criteria for N see <http://cfpub.epa.gov/wqsits/nnc->

[development/](#). Atmospheric deposition as a source of N may represent a potential target for remediation such as TMDL, nutrient budgets, and allocations.

The Chesapeake Bay 2010 TMDL load reductions include atmospheric deposition. This is the first time atmospheric N loads to tidal waters have been included in a TMDL for reduction ([U.S. EPA, 2010](#)). For Chesapeake Bay, a numerical chlorophyll criteria ranging from 1.4 to 15 mg/m<sup>3</sup> (µg/L) based on seasonal mean across salinity zones was proposed as a restoration goal with 90th percentile compliance limits ranging from 4.3 to 45 mg/m<sup>3</sup> [µg/L; [Harding et al. \(2014\)](#)]. These values were based on relationships of chlorophyll *a* concentrations to DO, water clarity, and presence of toxic algae. Chlorophyll *a* concentration ranges of 7.2 to 11 mg/m<sup>3</sup> (µg/L; May–August mean) in the bay and 9 to 14 mg/m<sup>3</sup> (µg/L; annual mean) in the tributaries would be protective of low DO conditions. For SAV growth, a mean chlorophyll *a* concentration of 7.9–12 mg/m<sup>3</sup> (µg/L) with a threshold of 19–28 mg/m<sup>3</sup> (µg/L) during the growing season would allow for sufficient light conditions. For decreased risk for toxic cyanobacteria, a mean summer chlorophyll *a* concentration of 15 mg/m<sup>3</sup> and a threshold of 25 mg/m<sup>3</sup> (µg/L) was recommended.

For seagrasses in New England estuaries, a threshold of N loading (N export of wastewater, fertilizer, and atmospheric deposition from the watershed combined with direct atmospheric deposition to waters)  $\geq 100$  kg N/ha/yr was identified. Eelgrass is essentially absent in areas with these levels of N loading, and levels above 50 kg N/ha/yr are likely to impact habitat extent [[Table 10-4; Latimer and Rego \(2010\)](#)]. These values were based on literature threshold values from [Bowen and Valiela \(2001a\)](#), [Hauxwell et al. \(2003\)](#), [Li et al. \(2007\)](#), and [Latimer and Rego \(2010\)](#). [Greaver et al. \(2011\)](#) identified the range of 50–100 kg N/ha/yr total N loading as the empirical critical load for loss of eelgrass based on [Latimer and Rego \(2010\)](#). These threshold levels for seagrasses were developed in shallow, poorly flushed systems that may not be universally representative of all estuaries.

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## 10.7 Summary and Causality Determination

In the 2008 ISA, the body of evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in estuarine systems ([U.S. EPA, 2008a](#)). The strongest evidence for a causal relationship was from changes in biological indicators of nutrient enrichment (chlorophyll *a*, macroalgal abundance, HABs, DO, SAV) and N was recognized as the major cause of harm to the majority of estuaries in the U.S. ([Bricker et al., 2008](#); [NRC, 2000](#)). Phytoplankton are the base of the coastal food web, and increases in primary

producer biomass and altered community composition associated with increased N can lead to a cascade of direct and indirect effects on higher trophic levels. For this ISA, new information is consistent with the 2008 ISA, and the causal determination has been updated to reflective more specific categories of effects. **The body of evidence is sufficient to infer a causal relationship between N deposition and changes in biota, including total primary production, altered growth, total algal community biomass, species richness, community composition, and biodiversity due to N enrichment in estuarine environments.**

Since the 2008 ISA, additional evidence has shown that reduced forms of atmospheric N play an increasingly important role in estuarine and coastal eutrophication and HAB dynamics. In many parts of the U.S., especially the Southeast, Midwest, and Mid-Atlantic, deposition of reduced N has increased relative to oxidized N in last few decades. The form of N delivered to some coastal areas of the U.S. is shifting from primarily  $\text{NO}_3^-$  to an increase in reduced forms of N. The increase in highly bioreactive reduced N from deposition and other sources is often a preferred form of N for specific phytoplankton functional groups (e.g., cyanobacteria, dinoflagellates) including harmful species ([Glibert et al., 2016](#); [Paerl et al., 2000](#)). Atmospheric inputs to estuaries are heterogeneous across the U.S., ranging from <10 to approximately 70% of the N inputs ([Table 7-9](#)), so deposition may play a significant role in altering nutrient dynamics in some coastal systems (i.e., Mid-Atlantic, Southeast) that support an increasing human population and spatial expansion of industrial scale animal operations ([Li et al., 2016d](#)).

Chlorophyll *a* is a broadly applied indicator of phytoplankton biomass and used as a proxy for assessing effects of estuarine nutrient enrichment. It can signal an early stage of water quality degradation related to nutrient loading and is incorporated into water quality monitoring programs and national-scale assessments, including U.S. EPA's NCCA and the NEEA. In general, 0–5  $\mu\text{g/L}$  chlorophyll concentration is considered to be good, chlorophyll concentrations between 5–20  $\mu\text{g/L}$  are classified as fair, and >20  $\mu\text{g/L}$  indicates an estuary in poor condition. Phytoplankton sampling and sediment core analysis have shown changes in phytoplankton community structure in estuaries with elevated N inputs. These shifts at the base of the food web to species that are not as readily grazed (e.g., cyanobacteria, dinoflagellates) have a cascade of effects that include poor trophic transfer and an increase in unconsumed algal biomass, which could stimulate decomposition,  $\text{O}_2$  consumption, and the potential for hypoxia ([Paerl et al., 2003](#)). Although availability of N is an important factor for productivity in estuaries, many newer studies have emphasized the role of physical and hydrologic factors in increase of chlorophyll *a* and other indicators of N enrichment ([Hart et al., 2015](#); [Turner et al., 2015](#); [Wilkerson et al., 2015](#); [Glibert et al., 2014](#); [Kennison and Fong, 2014](#); [Rothenberger et al., 2014](#); [Paerl et al., 2010](#); [Yang et al., 2008](#)).

Incidence of HAB outbreaks continues to increase in both freshwater and coastal areas, a problem that has been recognized for several decades ([U.S. EPA, 2008a](#); [Bricker et al., 2007](#); [Paerl et al., 2002](#); [Paerl and Whittall, 1999](#); [Paerl, 1997](#)). Of the 81 estuary systems for which data were available in the NEEA reported in the 2008 ISA, 26 exhibited a moderate or high symptom expression for nuisance or toxic algae ([Bricker et al., 2007](#)). HAB bloom conditions and effects of HAB toxins on coastal biota have been further characterized since the 2008 ISA ([Wood et al., 2014](#); [Miller et al., 2010](#)). The form of N affects phytoplankton growth and toxin production of some HAB species. CyanoHAB presence has been documented in estuaries along the U.S. Mid-Atlantic and Southeast coasts as well as Gulf coast estuaries ([Preece et al., 2017](#)).

In addition to phytoplankton, macroalgae growth is also stimulated by increased N inputs. Macroalgal blooms can smother benthic organisms and corals and contribute to the loss of important SAV by blocking the penetration of sunlight into the water column. Studies published since the 2008 ISA provide further evidence that macroalgae respond to the form of N, with some species showing greater assimilation and growth rates with  $\text{NH}_4^+$  than with  $\text{NO}_3^-$  ([Wang et al., 2014a](#); [Ale et al., 2011](#)).

Since the 2008 ISA, seagrass coverage is improving or stable in some estuaries like Tampa Bay and Chesapeake Bay, while many areas continue to see declines in seagrass extent. Loss of SAV habitat can lead to a cascade of ecological effects because many organisms are dependent upon seagrasses for cover, breeding, and as nursery grounds. SAV is often at a competitive disadvantage under N enriched conditions due to the fast growth of opportunistic microalgal epiphytes and macroalgae competitors that preferentially take up  $\text{NH}_4^+$  and can block light from seagrass beds. Since the 2008 ISA, additional studies are available on the relationship between N loading and SAV abundance ([Boynton et al., 2014](#); [Orth et al., 2010](#); [Ruhl and Rybicki, 2010](#)), and several studies have identified specific regional thresholds [[Latimer and Rego \(2010\)](#); [Benson et al. \(2013\)](#); [Table 10-4](#)]. [Greaver et al. \(2011\)](#) identified the range of 50–100 kg/N/ha/yr total N loading as the empirical critical load for loss of eelgrass based on [Latimer and Rego \(2010\)](#).

Increased algal biomass associated with nutrient over-enrichment leads to increased decomposition of organic matter, which decreases DO. Oxygen depletion largely occurs only in bottom waters under stratified conditions, not throughout the entire water column. A variety of ecological impacts are associated with low DO ([Figure 10-4](#)), and this indicator has been used in national assessments of coastal condition including U.S. EPA's NCCA and the NEEA. DO concentrations of 0 mg/L are anoxic, 0–2 mg/L are indicative of hypoxic conditions, and 2–5 mg/L are biologically stressful conditions ([Devlin et al., 2011](#); [Bricker et al., 2007](#)). For example, many fishes are absent at DO levels below

2 mg/L, and mortality of tolerant organisms can occur at approximately 0.5 mg/L. Hypoxia has recently been shown to affect reproductive parameters in fish which may lead to effects at the population level. In laboratory conditions, increased turbidity associated with eutrophic conditions has been shown to alter fish reproductive behaviors ([Candolin, 2009](#)). Macroinvertebrate community structure is also affected by the duration and severity of hypoxia. A shift to benthic organisms with shorter life spans and smaller body size has been observed in coastal areas that experience severe seasonal hypoxia ([Diaz and Rosenberg, 2008](#)). Reduced species density and diversity in the northern Gulf of Mexico are linked to the duration of hypoxic events ([Baustian and Rabalais, 2009](#)).

Post-2007 literature includes additional information on the extent and severity of eutrophication and hypoxia in sensitive regions. [Diaz et al. \(2013\)](#) assessed global patterns in hypoxia from the 1960s to 2011. Areas of eutrophication-related hypoxia are found on the U.S. East and West Coasts and the Gulf of Mexico ([Figure 10-5](#)). Overall, the extent of hypoxia is increasing globally with some areas showing signs of improvement. In the 2008 ISA, the largest zone of hypoxic coastal water in the U.S. was the northern Gulf of Mexico on the Louisiana-Texas continental shelf ([U.S. EPA, 2008a](#)). This area, which forms annually between May and September, continues to be the largest in the U.S. and the second largest in the world, averaging about 16,500 km<sup>2</sup> (10,250 mi<sup>2</sup>) in size ([Dale et al., 2010](#); [Jewett et al., 2010](#)). In the summer of 2017, the hypoxic zone in the Gulf was the largest ever measured at 14,123 km<sup>2</sup> [8,776 mi<sup>2</sup>; [U.S. EPA \(2017f\)](#)]. Atmospheric deposition from watersheds in the Mississippi/Atchafalaya River basins contributes approximately 16 to 26% of the total N load in the Gulf of Mexico ([Robertson and Saad, 2013](#); [Alexander et al., 2008](#)). Long Island Sound also experiences periods of anoxia in some years. In other U.S. coastal systems, the incidence of hypoxia is increasing; however, the severity of DO impacts are relatively limited temporally and spatially ([Jewett et al., 2010](#); [U.S. EPA, 2008a](#); [Bricker et al., 2007](#)). In the Pacific Northwest, coastal upwelling can be a large source of nutrient loads, and advection of upwelled water can introduce into estuaries hypoxic water that is not related to anthropogenic sources.

The indicators described above (chlorophyll *a*, HABs, macroalgal abundance, DO, SAV, and benthic diversity) have been incorporated into indices that describe eutrophic conditions in coastal areas. In the 2008 ISA, the ASSETS ECI developed for the NEEA was used as an assessment framework for eutrophic conditions in coastal U.S. estuaries ([Bricker et al., 2007](#)). The NCCA incorporates indicators that include chlorophyll *a* and DO to assess U.S. waters ([U.S. EPA, 2016g, 2012b](#)). Additional indices of overall condition of estuarine functioning that incorporate biological indicators of eutrophication have since been developed both in the U.S. and other countries ([Borja et al., 2012](#); [Devlin et al., 2011](#); [Borja et al., 2008](#)). Comparisons of these frameworks have led to the

identification of more robust and representative methods to measure estuarine response, including incorporation of annual data, frequency of occurrence, spatial coverage, secondary biological indicators, and a multicategory rating scale ([Devlin et al., 2011](#)).

In addition to having effects on biota in estuarine environments, N enrichment is one of several factors linked to increased disease susceptibility, bleaching, and reduced calcification rate in corals ([Appendix 10.4.2](#)). Near-coastal coral reefs in the U.S. occur off southern Florida, Texas, Hawaii, and U.S. territories in the Caribbean and Pacific. The threatened status of staghorn coral (*Acropora cervicornis*) and elkhorn coral (*Acropora palmata*) under the U.S. Endangered Species Act has been linked to indirect N pollution effects, specifically low DO and algal blooms that alter habitat, and to other non-nutrient stressors ([Hernández et al., 2016](#)).

Increased N enrichment is a contributing factor to coastal acidification under certain conditions such as in systems with strong thermal stratification or with spatial or temporal decoupling of production and respiration processes ([Appendix 7.2.4](#)). Acidification is projected to alter marine habitat, have a wide range of effects at the population and community level, and impact food web processes ([Marshall et al., 2017](#); [Mostofa et al., 2016](#); [Andersson et al., 2015](#); [Gaylord et al., 2015](#); [Sunda and Cai, 2012](#); [Doney et al., 2009](#)). Organisms that produce calcium carbonate shells such as calcareous plankton, oysters, clams, sea urchins, and coral may be affected by long-term decreases in pH [[Pfister et al. \(2014\)](#); [Sunda and Cai \(2012\)](#); [Kroeker et al. \(2013\)](#); [Mostofa et al. \(2016\)](#); [Appendix 10.5](#)]. Although the interactions between elevated CO<sub>2</sub>, increasing acidity, and nutrient inputs are complex, changes in the carbonate system, including decreased pH, have been shown to elicit biological responses in commercially important species from the New England coast and there are documented declines in oyster production on the U.S. West Coast linked to ocean acidification.

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# APPENDIX 11 NITROGEN ENRICHMENT EFFECTS IN WETLANDS

This appendix describes the effects of N deposition on wetland ecosystems. The introduction contains an overview of the relationship between N deposition and wetland endpoints, as well as the wetland classification system used in this appendix ([Appendix 11.1](#)). Regional sensitivity in wetlands is related to position within the watershed ([Appendix 11.2](#)). N deposition causes changes to biogeochemical pools and processes in wetlands, specifically to N ([Appendix 11.3.1](#)) and C cycling ([Appendix 11.3.2](#)). Nitrogen eutrophication affects wetland primary producers via alteration of aboveground plant biomass ([Appendix 11.4](#)), plant stoichiometry and physiology ([Appendix 11.5](#)), plant architecture ([Appendix 11.6](#)), and plant demography ([Appendix 11.7](#)). Nitrogen eutrophication also alters wetland biodiversity via changes to plant community composition ([Appendix 11.8.1](#)) and to consumer communities ([Appendix 11.8.2](#)). There are a number of critical loads published for wetland ecosystems ([Appendix 11.9](#)).

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## 11.1 Introduction

The 1993 Oxides of Nitrogen Air Quality Criteria document (hereafter referred to as the 1993 AQCD) and the 2008 ISA for Oxides of Nitrogen and Sulfur—Ecological Criteria (hereafter referred to as the 2008 ISA) evaluated the effects of nitrogen deposition on wetland ecosystems. The 1993 AQCD found that the three main ecological effects of N deposition on wetland ecosystems were reduced biodiversity, modified microbial processes, and increased primary production. The 2008 ISA supported and extended the conclusions in the 1993 AQCD, especially with regard to the effects of N deposition on species diversity, and also found evidence for alterations of ecosystem nitrogen and carbon cycling. The 2008 ISA found that the evidence was sufficient to infer a causal relationship between N deposition to wetland ecosystems and the alteration of biogeochemical cycling, as well as the alteration of species richness, species composition, and biodiversity. New evidence published between 2008–2015 from observational studies, experimental N additions in the field and in mesocosms, and reanalysis of large data sets supports and extends the conclusions of the 2008 ISA. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling in wetlands.** In addition to new information on species biodiversity, there is recently published evidence of N deposition effects on endpoints not covered in the 2008 ISA, including alterations to plant physiology and plant architecture.

**The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands.**

Wetland vegetative communities are adapted to high levels of natural organic acidity, so S and N deposition are unlikely to cause any acidification-related effects at levels of acidic deposition commonly found in the U.S. ([U.S. EPA, 2008a, in Annex B, in Annex B, in Annex B, in Annex B](#)). Sensitivity of wetlands to N deposition as a nutrient are well documented in the 2008 ISA ([Appendix 11.2](#)). Hydrologic pathways are often the same pathways of N input; therefore, they are useful for discussing the N sources and sensitivity to atmospheric N deposition. In general, wetland types ([Table 11-1](#)) that receive most of their total N input from the atmosphere are most sensitive to atmospheric deposition. Nearly all new N comes from atmospheric deposition in ombrotrophic bogs because these wetlands only receive water inputs via precipitation. They develop where precipitation exceeds evapotranspiration and where there is some impediment to drainage of the surplus water ([Mitsch and Gosselink, 1986](#)). Freshwater fens, marshes, and swamps are characterized by ground and surface water inputs that are often on the same order of magnitude as precipitation ([Koerselman, 1989](#)). Lastly, estuarine and coastal wetlands receive water from precipitation, ground/surface water, and marine/estuarine sources. Therefore, bogs (and presumably vernal pools) are among the most vulnerable wetlands to the nutrient-enrichment effects of N deposition ([Krupa, 2003](#)).

**Table 11-1 Wetland classification used in the Integrated Science Assessment.**

Wetland Term	Definition [adapted from <a href="#">Wakeley (2002)</a> ; <a href="#">Mitsch and Gosselink (2000)</a> ; <a href="#">Cowardin et al. (1979)</a> ]
<b>Soil-based classification</b>	
Peat	Substrate consisting of partially decomposed plant litter. In bryophyte-dominated wetlands (bogs and fens), this layer is composed of dormant or dead moss. In marshes and swamps, peat consists of dead litter, including plant leaves, stems, and roots, as well as undifferentiated soil organic matter and sediments.
Peatland	Any wetland that accumulates or has historically accumulated organic C stores in the substrate. Net primary productivity and accumulation of fixed C exceed decomposition rates. In Europe, the synonymous term "mire" is used.
<b>Hydrology-based classification</b>	
Permanent wetland	Wetland where a zone of the soil profile or peat profile remains saturated with water. The deeper soil profile is typically saturated, anoxic, and often has a high percentage of organic matter.
Intermittent wetland	Wetland where soils are saturated with water for short periods of time, annually or every few years; soils tend to have higher mineral contents than do permanent wetland soils.

**Table 11-1 (Continued): Wetland classification used in the Integrated Science Assessment.**

<b>Wetland Term</b>	<b>Definition [adapted from <a href="#">Wakeley (2002)</a>; <a href="#">Mitsch and Gosselink (2000)</a>; <a href="#">Cowardin et al. (1979)</a>]</b>
Intertidal wetland	Wetlands where soils or sediments are inundated with water at high tide and are exposed to air at low tide. This includes salt marshes, mangroves, and unvegetated mudflats.
<b>Soil-, hydrology-, and vegetation-based classification</b>	
<b>Bog or peat bog</b>	Defined by vegetation. A wetland with high moss cover and a depth profile with high organic content (peat), sometimes comprised of compressed senesced mosses. Ericaceous shrubs and certain graminoids are also particularly adapted for bog conditions.
Ombrotrophic or oligotrophic bog	A peatland dominated by acidophilic mosses, particularly <i>Sphagnum</i> mosses. Water is derived entirely from precipitation, with high [DOC], low pH, and low nutrient concentrations.
Mesotrophic, poor, or intermediate fen	A peatland that supports herbaceous and woody plant species with a wetland surface composed of moss species. Water sources include precipitation, surface water, and groundwater. Water pH (acidic to circumneutral) and nutrient concentrations are intermediate between ombrotrophic bog and minerotrophic fen.
Minerotrophic, rich, eutrophic, or calcareous fen	A peatland dominated by herbaceous graminoid species typical of marshes, with a mat composed of moss species. Water sources include precipitation, surface water, and groundwater. Water has higher pH (circumneutral to alkaline), as well as higher concentrations of calcium ions and other nutrients, than other bog types.
<b>Swamp</b>	Defined by vegetation. A wetland dominated by woody plants, particularly tree and shrub species with physiological adaptations to occasional or constant soil inundation.
Mangrove	An intertidal swamp. A subtropical or tropical swamp dominated by halophytic trees and shrubs. Tidal inundation by ocean or estuarine waters is frequent. In the U.S., dominant species are trees in the <i>Avicennia</i> and <i>Rhizophora</i> genera. Mangroves are important nursery habitats for marine animal species.
<b>Marsh</b>	Defined by vegetation. A wetland dominated by herbaceous plants with physiological adaptations to occasional or constant soil inundation.
Freshwater marsh	Marsh dominated by herbaceous plant community composed of species with physiological adaptations to soil inundation. Includes marshes in lakes, rivers, and nonsaline regions of estuaries. Salt- and sulfide-intolerant marsh plant species are common. Soils may be peat or mineral sediments.
Pothole	A type of freshwater marsh. A shallow pond with herbaceous and submerged aquatic vegetation, common in the prairie ecosystems of the Dakotas and central Canadian plains. A pothole is often not connected by surface water flow to its watershed; water sources include precipitation and groundwater.
Tidal marsh	An estuarine marsh. Used in this document to describe estuarine marshes in which water level fluctuates in response to ocean tides but marsh water has low or no salinity (i.e., water sources are freshwater). Depending on physical location in the estuary, occasional saltwater intrusion may alter biogeochemistry and plant community. A mix of saline-tolerant and saline-intolerant plant species is common.
Salt or coastal marsh	Halophytic herbaceous species are dominant. Tidal inundation by ocean water structures the plant community, which typically forms zones of single species monocultures or low-diversity communities of plants with similar tolerances for salt and water stress. Plant roots trap alluvial sediments to build and maintain the elevation of the marsh surface, or platform. Salt marshes are important nursery habitats for marine animal species.

**Table 11-1 (Continued): Wetland classification used in the Integrated Science Assessment.**

<b>Wetland Term</b>	<b>Definition [adapted from <a href="#">Wakeley (2002)</a>; <a href="#">Mitsch and Gosselink (2000)</a>; <a href="#">Cowardin et al. (1979)</a>]</b>
<b>Intermittent</b>	Defined by hydrology and vegetation. Wetland where soils are saturated, with soil processes typical of aquatic sediments, for short periods annually or every few years; inundation occurs with sufficient frequency to prevent persistence of flooding-intolerant plant species.
Vernal pool	An area with mineral soils which is flooded by rainwater or rising water tables and then isolated from surface water flow as it slowly dries up. These seasonally inundated areas are important nursery habitat for a number of invertebrate and vertebrate species.
Riparian wetland	An area with mineral soils, and a high water table due to close proximity to a river, stream, or lake. Periodic inundation occurs when water levels rise. Vegetation is a mix of terrestrial plants and plants with physiological adaptations to occasional soil inundation.

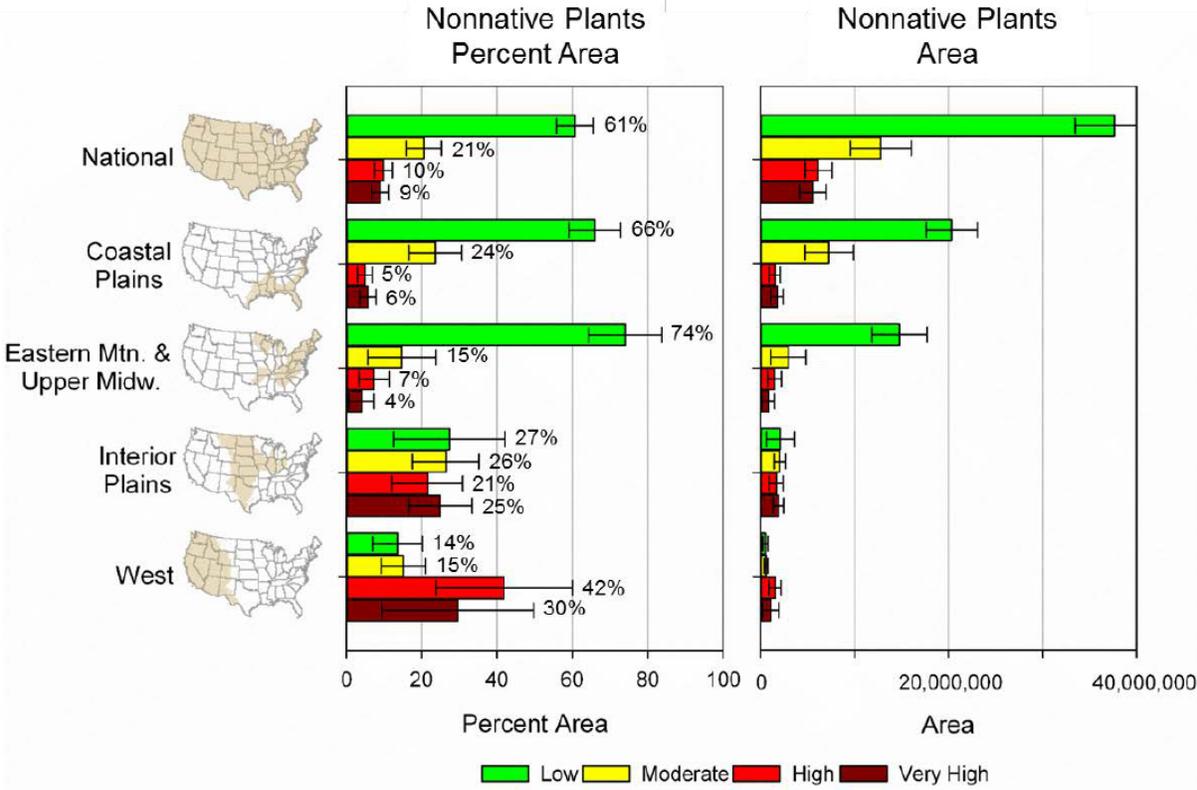
C = carbon; DOC = dissolved organic carbon.

## 11.2 Regional Sensitivity

There is no new information on regional sensitivity of wetlands to N deposition, and models of sources of N to wetland ecosystems are not yet available. In the 2008 ISA, wetlands were described in order of sensitivity to N deposition. Bogs and fens are among the most sensitive wetland ecosystems to N deposition. In the U.S., peat-forming bogs and fens are most common in glaciated areas, especially in portions of the Northeast and Upper Midwest ([U.S. EPA, 1993](#)). N deposition was projected to drastically change species composition based on experimental results in European fens ([Pauli et al., 2002](#); [Aerts and de Caluwe, 1999](#)). N input and output rates of freshwater or riparian marshes and swamps are intermediate between bogs and coastal marshes. N deposition increased primary productivity 30% and increased methane emissions in freshwater marshes. Atmospheric N inputs contribute to eutrophication problems in coastal marshes at many locations through direct deposition to the marsh, indirect deposition to the watershed, or direct deposition to estuaries or coastal waters followed by tidal delivery of aqueous N loads to wetlands (see [Table 7-9](#) for estimates of N deposition to estuaries). However, marine inputs of N are typically higher than direct atmospheric input to coastal wetlands.

The National Wetlands Condition Assessment (NWCA) was conducted by U.S. EPA in 2011 to characterize the condition of North American wetlands under multiple anthropogenic stressors and to provide a baseline for future assessments. The final report did not provide soil N or surface water ammonia, nitrate-nitrite, or total N, although these data were collected as part of the survey and are available ([U.S. EPA, 2016j](#)). Ecological endpoints that the NWCA identified as correlated with total N loading are the Nonnative Plant Stressor Indicator (NPSI; see [Appendix 11.8.1.3](#) for an explanation of the link

between N loading and non-native plants) and microcystin concentrations (see [Appendix 9](#)), although the dataset includes a number of other metrics that may respond to N deposition. Nationally, 39% of wetland area was estimated to experience moderate to very high stress based on the NPSI, with stresses particularly high in wetlands of the Interior Plains and West (see [Figure 11-1](#)). Microcystin, a toxin produced by cyanobacteria in response to available N, was detected in low concentrations in surface water at 12% of national wetland sites, with particularly high detection rates (34%) in the Interior Plains ([U.S. EPA, 2016j](#)).



Source: [U.S. EPA \(2016j\)](#).

**Figure 11-1** Estimated extent of wetlands stressed by nonnative plants as determined by Nonnative Plant Stressor Indicator, at a national or regional level.

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## 11.2.1 Climate Modification of Ecosystem Response to Nitrogen

Changes in mean annual temperature and frequency and magnitude of precipitation will affect the responses of all wetlands to N loading; changes in sea level will affect the response of salt marsh, mangroves, and freshwater tidal wetlands. Temperature effects on wetlands have been demonstrated in European bog ecosystems, where increased temperatures increased cover of woody species and decreased *Sphagnum* moss cover just as N deposition does ([Hedwall et al., 2017](#)). In metaregressions of *Sphagnum* moss response to N addition and temperature, the two factors synergistically depressed *Sphagnum* production, with an 1°C increase in summer temperature having an impact on *Sphagnum* equivalent to an additional 40 kg N/ha/yr ([Limpens et al., 2011](#)). Increasing temperatures may strengthen N effects upon wetland ecosystems.

Hydrologic regimes are important controls on wetland cycling and productivity, so changes in the magnitude and frequency of precipitation can have strong effects on ecosystem N retention and C storage. The same metaregression of *Sphagnum* mosses referenced above found that increased precipitation also increased *Sphagnum* sensitivity to N addition-induced decreases in production ([Limpens et al., 2011](#)). Experimental mesocosms modelling changes in precipitation to salt marshes found that precipitation delivered in infrequent, heavy storm events decreased N retention and plant productivity, even though storm events delivered a higher N deposition load to the marsh ([Hanson et al., 2016](#); [Oczkowski et al., 2016](#)). Shifts in precipitation towards less frequent, more intense rain events may strengthen N deposition-induced decreases in salt marsh N retention while weakening N deposition-induced increases in plant productivity.

Sea level rise will affect tidal wetlands through salt water intrusion into tidal freshwater wetlands ([Barendregt and Swarth, 2013](#)) and through increasing inundation of salt marshes, both of which have the potential to change community composition and decrease wetland extent. Experimental sea level rise of 10 cm increased N stimulation of belowground and aboveground plant biomass in Kirkpatrick Marsh (see ([Langley et al., 2013](#)) in [Appendix 11.3.2.1.2](#) and [Appendix 11.4.1](#)), but the response was species-specific, with only one species responding to the N deposition. Sea level rise effects on marsh response to N deposition are not well understood and may vary by species.

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## 11.3 Soil Biogeochemistry

The 2008 ISA described the relationship between N deposition and the alteration of biogeochemical cycling in wetlands. N deposition alters N cycling by altering microbial

communities, the rates at which they transform N between pools, ecosystem retention or release of transformed N, and the emissions of the greenhouse gas nitrous oxide ([Appendix 11.3.1](#)). N deposition alters C cycling by altering soil processes such as decomposition and respiration (resulting in emissions of the greenhouse gases carbon dioxide and methane), as well as by altering soil pools such as belowground biomass and soil organic matter ([Appendix 11.3.2](#)). There is new evidence since 2008 of N deposition effects upon biogeochemical cycling across wetlands, as well as in salt marshes, mangroves, bogs, and riparian wetlands. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling in wetlands.**

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### 11.3.1 Nitrogen Pools and Processes

Water table depth tends to fluctuate more in wetlands than terrestrial ecosystems. The variable depth creates dynamic anoxic-oxic boundaries and many varied niches for different microbial communities. As a result, wetlands are important disproportionately to their spatial area on the landscape (i.e., hotspots) for the microbial transformation of nitrogen between oxidized and reduced forms. These nitrogen transformations can improve water quality of downstream streams, lakes, and estuaries by removing N in the soil or water of an ecosystem into the atmosphere. However, these transformations can result in emissions of the potent greenhouse gas nitrous oxide. Alteration to N cycling or N cycling microbial endpoints indicate changes to the important wetland function of improving water quality.

N deposition contributes to total N load in wetlands. The chemical indicators that are typically measured include  $\text{NO}_3^-$  and  $\text{NH}_4^+$  leaching, DON leaching, N mineralization, and denitrification rates, including  $\text{N}_2\text{O}$  emissions produced by incomplete denitrification. N dynamics in wetland ecosystems are variable in time and among types of wetlands and environmental factors, especially water availability ([Howarth et al., 1996a](#)). A wetland can act as a source, sink, or transformer of atmospherically deposited N ([Devito et al., 1989](#)), and these functions can vary with season and hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands ([Mitchell et al., 1996](#); [Arheimer and Wittgren, 1994](#); [Koerselman et al., 1993](#); [Devito et al., 1989](#)).

N mineralization (microbial transformation of organic N to inorganic forms of N) has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water ([Groffman, 1994](#)). In general, ecosystem leaching losses of  $\text{NO}_3^-$  from wetlands to downstream aquatic systems are small, although recent

research suggests that N addition to peatlands increases export of N in both inorganic and organic forms ([Edokpa et al., 2015](#)). Bogs and fens in the Marcell Experimental Forest that receive 2.8–4.7 kg N/ha/yr as atmospheric deposition export 0.26 (bogs) and 1.34 kg N/ha/yr (fens), respectively ([Hill et al., 2016](#)). Wetlands tend to have low N export to surface water because anoxic zones within wetlands are favorable for microbial denitrification of N from  $\text{NO}_3^-$  to gaseous N forms. Elevated N inputs to wetlands will often increase the rate of denitrification ([Duffy and Kahara, 2011](#); [Cooper, 1990](#); [Broderick et al., 1988](#); [Dierberg and Brezonik, 1983](#)), because N additions to aquatic environments with high organic C increase denitrifier abundance, activity, and denitrification rates ([Kim et al., 2015b](#)). This mitigates environmental effects associated with increased N supply to soils and drainage waters; however, increased denitrification may also increase the emissions of greenhouse gases (e.g.,  $\text{N}_2\text{O}$ ) to the atmosphere. Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens ([Morris, 1991](#)). Incomplete denitrification and emission of  $\text{N}_2\text{O}$  tend to be higher in freshwater tidal wetlands than in saline wetlands like mangroves or salt marshes ([Welti et al., 2017](#)). In salt marshes, dissimilatory nitrate reduction to ammonium (DNRA) is an important process that cycles N while retaining N within marsh sediments (see also [Appendix 7.2.6.5](#)). N addition decreases DNRA while increasing nitrification and denitrification rates ([Peng et al., 2016](#)), decreasing N retention in salt marshes, and increasing  $\text{N}_2\text{O}$  emissions ([Chmura et al., 2016](#); [Moseman-Valtierra et al., 2011](#)).

New studies summarized below in salt marsh, mangrove, peat bog, and riparian wetlands have evaluated the effects of N loading/N addition on endpoints related to N cycling. In addition, there is a new study on wetland N removal, synthesizing information across wetland types.

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### 11.3.1.1 Across Wetlands

N removal, defined as the sum of denitrification, plant uptake, and burial in sediments, was evaluated by analyzing data from 109 wetlands distributed globally, including agricultural wetlands, freshwater marshes, freshwater swamps, and coastal marshes ([Jordan et al., 2011](#)). Total N loads to these wetlands ranged from 0.2–90,480 kg N/ha/yr; however, the sources of reactive N were not identified by the authors. Across this global data set, wetland N removal as measured in outflow is proportional to wetland N load. N removal efficiency was 26% higher in nontidal wetlands than in tidal wetlands.

The 2008 ISA found evidence that N deposition alters the emission of nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ), which contribute to global warming. A meta-analysis of

19 N addition observations, ranging from 15.4 to 300 kg N/ha/yr, found that N enrichment increased wetland N<sub>2</sub>O emissions by 207% ([Liu and Greaver, 2009](#)).

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### 11.3.1.2 Salt Marsh

New studies have evaluated the effects of N loading/N addition on tidal export, N mineralization, nitrification, and microbial community structure in salt marshes. Tidal export of N from salt marshes was studied in a long-term (>30 years) fertilization experiment in Massachusetts ([Brin et al., 2010](#)) in which tidal export of N increased with increasing N load. Tidal export of ammonia increased linearly with increasing annual N load, and tidal export of nitrate increased exponentially with increasing annual load (see [Table 11-2](#) for equations). Likewise, a linear relationship was documented between increasing N and decreasing potential N mineralization after 7 months of N addition to three salt marshes in California [see [Table 11-2](#) for equation; ([Vivanco et al., 2015](#))]. In this same study, there was no relationship between N addition and net nitrification rates; however, the nitrification rates differed among the marsh sites.

In Kirkpatrick Marsh, MD, N addition decreased N retention in marshes dominated by native plants and by the invasive lineage of *Phragmites australis*. N addition of 250 kg N/ha/yr decreased ecosystem N retention by 55%, driven largely by a 57% decrease in N retention belowground, in roots, rhizomes, and soil ([Pastore et al., 2016](#)). N addition also altered the relative allocation of N to pools in marsh plants. N addition increased the total pool of N stored in aboveground biomass through stimulatory effects on biomass production (see [Appendix 11.4.1](#)), but decreased the total pool of N stored in belowground biomass by 6%. N addition decreased the pool of N in belowground biomass but also shifted the distribution of root N higher in the soil profile than in control plots (to 15–25 cm depth from 40–50 cm depth), making it more vulnerable to leaching and to microbial transformation: N addition increased pore water NH<sub>4</sub><sup>+</sup> concentrations 120% and N<sub>2</sub>O flux out of soils by 220% ([Pastore et al., 2016](#)). The invasive species *P. australis* established roots at depths below the native plant community (see [Appendix 11.3.2.1.2](#)), which increased mineralization deep in the peat profile to increase pore water [NH<sub>4</sub><sup>+</sup>] 9–72% at 40–70 cm ([Mozdzer et al., 2016](#)). Like many terrestrial invasive species, *P. australis* may respond to N loading by creating a positive feedback loop of increasing soil N availability and expanding invasion. Increasing reactive N may change the diversity and composition of microbial communities responsible for denitrification and nitrification. Change in the microbial communities could change the rate of the chemical reactions that microbes perform in the wetland. Increasing N loads alter the abundance of denitrifying bacteria.

In the long-term marsh fertilization experiment in a salt marsh in Massachusetts, *nirS* DNA sequences were amplified to assess denitrifying bacteria ([Bowen et al., 2013](#)). The plots sampled were fertilized with sewage sludge, which contained other nutrients, metals, and organic material in addition to N, and N addition rates were 221, 655, or 1,966 kg N/ha/yr. With the addition of N, denitrifying bacteria communities became more dissimilar, as widely distributed bacteria declined, and abundance and richness of unique denitrifiers increased ([Bowen et al., 2013](#)). [Lage et al. \(2010\)](#) sampled sediments associated with *Spartina patens* in a New England salt marsh. This study used the *amoA* DNA sequence in sediments to sample the ammonia-oxidizing bacteria, which produce nitrites from ammonia in the first step of nitrification. The majority of species affected by N addition were within a clade of *Nitrosospira*-like sequences found in other salt marshes. N addition decreased evenness of distribution and altered composition, specifically the relative abundance of taxa within the marine and estuarine *Nitrosospira*-like clade, suggesting that there are fine-scale genetic differences to the bacteria's ability to use nitrogen.

An incubation experiment of soils collected from different zones of salt marsh in Yancheng Nature Reserve added ammonium or nitrate in equal amounts of N to assess what effects N chemical species had on microbial cycling of N. N addition increased net N mineralization in all marsh zones, with oxidized N increasing net N mineralization 16–29%, and reduced N increasing net mineralization 58–69% ([Zhang et al., 2016c](#)). N forms had similar rates upon net nitrification rates, as  $\text{NO}_3^-$  addition increased nitrification rates 34–54%, and  $\text{NH}_4^+$  addition increased nitrification rates 65–94%. N addition also increased the temperature sensitivity of N mineralization ( $Q_{10}$ ) in low marshes ([Zhang et al., 2016c](#)), suggesting a synergistic stimulation between increased N loading and temperature upon N release from salt marshes to the marine environment.

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### 11.3.1.3 Mangrove

In mangrove ecosystems, N addition suppressed N fixation and increased denitrification ([Whigham et al., 2009](#)). Laboratory incubations showed that the denitrification rate was 15 times higher in soils that had received 100 kg N/ha/yr than in control soils (N load on N deposition in control soils not reported). However, field measurements of  $\text{N}_2\text{O}$  emissions were 5.6 times higher in fertilized than in control soils, indicating incomplete denitrification in fertilized soils. Nitrogen fixation rates were suppressed by 88% in fertilized plots ([Whigham et al., 2009](#)).

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#### 11.3.1.4 Freshwater Tidal Marsh

The Madisonville Nutrient Plots on the Tchefuncte River, LA, have received N addition of 0, 50, 200, or 1,200 kg N/ha/yr for 11 years. There was no measurable effect of N addition upon total N, microbial N, soluble N, denitrification rates, or C cycling in the top 10 cm of soil ([Steinmuller et al., 2016](#)), although there were effects upon aboveground productivity, plant stoichiometry, and plant community (see [Appendix 11.4.2](#), [Appendix 11.5.3](#), and [Appendix 11.8.1.2](#)).

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#### 11.3.1.5 Riparian or Intermittent Wetlands

New studies on riparian wetlands include N addition relationships to denitrification rates and bacterial community composition. In a riparian wetland in Durham, NC, wetland species' potential denitrification activity increased linearly with increasing soil total inorganic N [see [Table 11-2](#) for equation; ([McGill et al., 2010](#))]. In freshwater riparian wetlands along the James River, VA, soils were collected and incubated with added nitrogen. Nitrogen addition increased the abundance of denitrifying bacteria—quantified as copies of the *nirS* sequence—by 541% when labile organic matter was also added ([Morrissey et al., 2013](#)). When N addition occurred simultaneously with the addition of recalcitrant organic matter, denitrifying bacterial abundance decreased 96% with increased N. Community composition of denitrifying bacteria shifted in response to N addition, as did the composition of bacteria capable of dissimilatory nitrate reduction to ammonia [quantified as copies of *nrfA* sequence; ([Morrissey et al., 2013](#))].

In riparian forests, increased N loads altered the symbiotic association between *Alnus incana* ssp. *tenuifolia* (grey alder) and *Frankia* (actinorhizal, N-fixing bacteria). N addition of 100 kg N/ha/yr decreased the density of *Frankia*-hosting root nodules by 62% compared with nodules from unamended control plots. Nodule respiration rates were 28% lower under N fertilization, indicating lower rates of *Frankia* metabolism, and N fixation in nodules was 31% lower than in controls ([Ruess et al., 2013](#)).

A recent study of an alpine meadow and intermittent wetland on the Tibetan Plateau found that adding 30 kg N/ha/yr changed the wetland from a net sink to a net source of N<sub>2</sub>O emissions to the atmosphere, suggesting N addition stimulated microbial denitrification ([Wang et al., 2017c](#)).

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### 11.3.1.6 Bog and Fen

In peat bog ecosystems, N addition decreases ecosystem retention of N and increases N exports in surface water from hydrologically connected bogs. In Mer Bleue Bog, Ontario, N addition decreased the N retention efficiency of the ecosystem, as measured by the recovery of an  $^{15}\text{N}$  tracer. When N was added at the rate of 16 kg N/ha/yr from 2000–2007, a pulse of added  $^{15}\text{N}$  was recovered at lower rates from fertilized plots than from unamended control plots (N deposition was 8 kg N/ha/yr), indicating a 71% reduction in average retention efficiency across biomass pools (Xing et al., 2011). A recent study (samples taken in 2014) in this bog found increases in nitrate and ammonium concentrations in response to N addition in peat, with N addition increasing  $[\text{NO}_3^-]$  71–169% and  $[\text{NH}_4^+]$  90–269%, suggesting that the living *Sphagnum* moss is no longer retaining N but leaching it into the peat below (Pinsonneault et al., 2016).

A European study of N pools in bogs found that N deposition changes the retention of N within vascular plants and peat soil. Under N treatment equivalent to deposition of 2 kg N/ha/yr,  $^{15}\text{N}$  recovery was 66% for mosses, 3.8% for shrubs, and 1.8% for graminoids. Deposition of 47 kg/ha/yr changed  $^{15}\text{N}$  recovery to 12% for shrubs as well as increasing the total N stored in shrubs by 360% compared to mesocosms receiving 2 kg N/ha/yr.  $^{15}\text{N}$  recovery also declined in peat under N deposition, with  $^{15}\text{N}$  recovery of 60% under 2 kg N and  $^{15}\text{N}$  recovery of 36% under 47 kg N (Zajac and Blodau, 2016). Increases in plant N uptake along with decreasing efficiency of plant N retention (see Appendix 11.5.5) can lead to increases in dissolved organic N exports from bogs. A study in a NPK-fertilized and limed (addition of  $\text{CaCO}_3$ ) peatland catchment in the U.K. found high levels of N export (14 kg N/ha watershed/yr) from the wetland to the Kinder River, with over half of the exported N in the form of dissolved organic nitrogen (Edokpa et al., 2015).

The Whim bog experiment in Scotland added N as either ammonium or nitrate to simulate wet deposition, which with ambient N deposition of 8 kg N/ha/yr resulted in treatment N loads of 16, 32, and 64 kg N/ha/yr. Increasing  $\text{NO}_3^-$  loading increased concentrations of dissolved organic nitrogen (DON) in pore water, while increasing  $\text{NH}_4^+$  loading increased cation leaching from moss into pore water, and increased DIN in pore water at the highest N addition level (Chiwa et al., 2016). N addition impaired the ability of the *Sphagnum* moss mat to absorb and retain N, beginning at 32 kg N/ha/yr for oxidized N and 64 kg N/ha/yr for reduced N addition. This study illustrates the different effects of reduced and oxidized N upon bog ecosystems (see also, Appendix 11.5.5). However, a recent analysis by (Wieder et al., 2016) suggested that North American and European *Sphagnum* species have different tolerances for and responses to N loading, so critical loads for North American bogs should be inferred with caution from European bogs.

Recent studies have documented high rates of nitrogen fixation by microbial diazotrophs living on and in dead *Sphagnum* cells (Vile 2014 and Larmola 2014 in [van Den Elzen et al., 2017](#)). Microbial N fixation rates were observed at N deposition of 25 kg N/ha/yr, and added another 6 kg N/ha/yr to moss and peat ([van Den Elzen et al., 2017](#)).

### 11.3.1.7 Summary Table

**Table 11-2 New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Agricultural wetlands; intertidal marshes; freshwater bogs and marshes; freshwater swamps; other wetlands	0.02–90,480 kg N/ha/yr as N load, mean load for each wetland class: agricultural: 426, intertidal: 211, freshwater bogs and marshes: 890, freshwater swamps: 69, other: 280 kg N/ha/yr Deposition = not reported	Removal: wetland N removal ( $N_{\text{removal}}$ ) is proportional to N load ( $N_{\text{load}}$ ): $\log(N_{\text{removal}}) = 0.943 \times \log(N_{\text{load}}) - 0.033$ . N removal efficiency is 26% higher in nontidal than tidal wetlands.	Global	Reanalysis of data from 109 global wetlands	<a href="#">Jordan et al. (2011)</a>
Wetlands (natural and agricultural)	N addition experiments, N addition of 15.4 to 300 kg N/ha/yr Deposition = not reported	N addition increases $N_2O$ emissions 207% across wetlands ( $n = 19$ ).	Global	Meta-analysis of data collected from North America, South America, Europe, and Asia	<a href="#">Liu and Greaver (2009)</a>
Salt marsh	Addition = 180 kg N/ha/yr (as Milorganite, NPK 10-6-4), 520 kg N/ha/yr (as urea or as Milorganite), 1,560 kg N/ha/yr (as Milorganite)	Tidal export of N increases with increasing N addition ( $N_{\text{add}}$ as kg N/ha/yr). For $NH_4^+$ export ( $NH_{\text{export}}$ , in kg N/season): $NH_{\text{export}} = 0.00083 \times N_{\text{add}} + 0.432$ . For $NO_3^-$ export ( $NO_{\text{export}}$ , in kg N/season): $NO_{\text{export}} = 0.122 \times e^{-0.0018N_{\text{add}}}$	Great Sippewissett Marsh, MA	<i>Spartina alterniflora</i> , <i>Spartina patens</i> , and <i>Distichlis spicata</i>	<a href="#">Brin et al. (2010)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	Addition = 0, 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr as urea N deposition = 3–5 kg N/ha/yr as reported in <a href="#">Tonnesen et al. (2007)</a>	Mineralization: potential net N mineralization ( $N_{min}$ ) decreases in a linear response to added N ( $N_{add}$ , in g N/m <sup>2</sup> /yr): $N_{min} = -0.0015 \times N_{add} + 0.022$ . Nitrification: no significant relationship.	Morro Bay National Estuary, Carpinteria Salt Marsh Reserve, Tijuana River Reserve Estuary, CA	<i>Salicornia depressa</i> ( <i>Salicornia virginica</i> ) stands	<a href="#">Vivanco et al. (2015)</a>
Salt marsh	Addition: 50 mg N/kg soil, as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> or NaNO <sub>3</sub> Ambient deposition = not specified	N addition increased net N mineralization in all three marsh zones. NO <sub>3</sub> <sup>-</sup> addition increased net N mineralization 16–29%, and NH <sub>4</sub> <sup>+</sup> addition increased net N mineralization by 58–69%. The most predictive soil parameter for net N mineralization was labile C:labile N ( $r = -0.85$ ) N addition increased net nitrification in all three marsh zones. NO <sub>3</sub> <sup>-</sup> addition increased net nitrification 34–54%, and NH <sub>4</sub> <sup>+</sup> addition increased net nitrification by 65–94%. The most predictive soil parameter for net nitrification was labile C:labile N ( $r = -0.81$ ). N addition increased Q <sub>10</sub> values (stimulatory effect of temperature upon net N mineralization) in <i>P. australis</i> and <i>S. alterniflora</i> marsh zones.	Aerobic soil incubations constructed from core samples from Yancheng National Nature Reserve, China	Monospecific stands across marsh elevation gradient: <i>Suaeda salsa</i> (native) in high marsh, <i>Phragmites australis</i> (native) in low marsh, <i>Spartina alterniflora</i> (invasive, native to North America) in previously unvegetated mud flats	<a href="#">Zhang et al. (2016c)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Intertidal marsh	Addition = 250 kg N/ha/yr (as NH <sub>4</sub> Cl) since 2006 Ambient deposition = not reported Average N loads to Chesapeake Bay are 140 kg N/ha/yr <sup>15</sup> N tracer applied 2006, measure AG 2005–2013, measured BG 2014	Total marsh retention (AG biomass, BG biomass, soil) of <sup>15</sup> N label was 55% lower in N treatment, because belowground (BG biomass + soil) N retention was 57% lower in N treatment. Across elevated CO <sub>2</sub> treatments, belowground N retention was 51% lower in N treatment. N addition increased N mass in AG biomass for C4 grasses. N addition increased N mass in total plant biomass for the first 6 yr, but not for the last 2 yr of measurement. N addition decreased N mass of fine roots. N addition decreased total N BG by 6% by shifting N mass across the soil profile: N addition increased BG N mass at depths of 15–25 cm, but decreased BG N mass at depths of 40–50 cm. N addition increased N <sub>2</sub> O flux from plots by 220% and pore water NH <sub>4</sub> <sup>+</sup> concentrations increased 120%.	Kirkpatrick Marsh, Rhode River, Edgewater, MD	C3 <i>Schoenoplectus americanus</i> ; C4 <i>Spartina patens</i> and <i>Distichlis spicata</i>	<a href="#">Pastore et al. (2016)</a>
Intertidal marsh	Addition = 250 kg N/ha/yr (as NH <sub>4</sub> Cl) Ambient deposition = not reported	N addition increased pore water concentrations of NH <sub>4</sub> <sup>+</sup> by 9 and 72% at depths of 40 and 80 cm, respectively. <i>P. australis</i> increased SOM decomposition in recalcitrant peat 1.8–1.9 times over rates in unvegetated peat.	Mesocosms of invasive (from seeds) or native (from rhizome fragments) plants in Kirkpatrick Marsh, Rhode River, Edgewater, MD	Invasive <i>Phragmites australis</i> ; native community of <i>Spartina patens</i> , <i>Schoenoplectus americanus</i>	<a href="#">Mozdzer et al. (2016)</a>
Salt marsh	Addition = 1,630 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> Deposition = not reported	Bacterial community: N addition decreases evenness of ammonia-oxidizing bacterial community and changes community composition ( $p = 0.017$ ).	Scarborough Marsh, ME	β-proteobacteria containing <i>amoA</i> gene in sediments associated with <i>Spartina patens</i>	<a href="#">Lage et al. (2010)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	Addition = sewage sludge. Low fert = 221 kg N/ha/yr, high fert = 655 kg N/ha/yr, very high fert = 1,966 kg N/ha/yr Deposition = not reported	Bacterial community: ubiquitous <i>nirS</i> sequences declined with increasing N addition (higher abundance and richness of unique denitrifying species in higher N treatments).	Great Sippewissett Marsh, Falmouth, MA	Denitrifying bacteria in sediment (community)	<a href="#">Bowen et al. (2013)</a>
Mangrove	Addition = 100 kg N/ha/yr Deposition = not reported	Denitrification: denitrification rate (lab incubation) was 15x faster in N addition sediments.	Indian River Lagoon, FL (Impoundment SLC-24)	<i>Avicennia germinans</i> and associated sediments	<a href="#">Whigham et al. (2009)</a>
Tidal marsh	Addition = 0, 50, 200, and 1,200 kg N/ha/yr (as slow-release methylene urea, which releases NH <sub>4</sub> <sup>+</sup> ), in combination with 0 or 131 kg P/ha/yr, to mimic Mississippi River diversion N and P loading rates Ambient deposition = not specified	11 yr of N addition had no significant effect on total P, total N, microbial N, potentially mineralizable N, or potential denitrification rates in the top 10 cm of marsh soil.	Madisonville nutrient plots (microtidal pulses of 10 cm), Tchefuncte River, Lake Pontchartrain Estuary, LA	<i>Sagittaria lancifolia</i> , <i>Polygonum punctatum</i> , <i>Eleocharis fallax</i>	<a href="#">Steinmuller et al. (2016)</a>
Riparian wetland	Addition = n/a Deposition = not reported	Denitrification: potential denitrification activity in spring increases with total inorganic N in soil ( $y = 6.96x + 20.52$ ).	Durham, NC	1, 4, or 8 species from <i>Carex crinita</i> , <i>Carex lurida</i> , <i>Scirpus cyperinus</i> , <i>Juncus effusus</i> , <i>Panicum virgatum</i> , <i>Chasmanthium latifolium</i> , <i>Eupatorium fistulosum</i> , <i>Veronia noveboracensis</i> , <i>Asclepias incarnata</i> , and <i>Lobelia cardinalis</i> .	<a href="#">McGill et al. (2010)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Riparian floodplain successional forest	Addition = 100 kg N/ha/yr Deposition = not reported	<i>Frankia</i> nodule densities decreased 62%. Nodule N fixation declined 31% and nodule respiration declined 28%.	Bonanza Forest LTER, AK	<i>Alnus incana</i> ssp. <i>tenuifolia</i> and associated <i>Frankia</i> strains	<a href="#">Ruess et al. (2013)</a>
Riparian wetland	Addition = soil incubations with 0.5, 2, 4 mg N/g wet sediment as KNO <sub>3</sub> Deposition = not reported	Nitrate addition increased DNF (copies <i>nirS</i> ) abundance 541% when labile OM was present and decreased DNF abundance 96% when recalcitrant OM was present. Community composition of DNF and DNRA shifted in response to nitrate addition.	James River, Charles City County, VA	Soil microbial communities involved in denitrification (DNF, gene <i>nirS</i> ) or dissimilatory nitrate reduction to NH <sub>4</sub> <sup>+</sup> (DNRA, gene <i>nrfA</i> )	<a href="#">Morrissey et al. (2013)</a>
Seasonal wetland, alpine meadow	Addition: 30 kg N/ha/yr Ambient deposition = 8.7 to 13.8 kg N/ha/yr	N addition significantly increased N <sub>2</sub> O emissions, changing plots from net sinks to net sources of N <sub>2</sub> O to the atmosphere. N addition reduced the global warming potential (sum of CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O fluxes) of the plots from a net source to a net sink.	Mesocosms at Luanhaizi wetlands, Tibetan Plateau	<i>Carex pamirensis</i> , <i>Carex atrofusca</i> , <i>Hippuris vulgaris</i> , <i>Triglochin palustris</i> , and <i>Heleocharis</i> spp.	<a href="#">Wang et al. (2017c)</a>
Ombrotrophic peat bog	Addition = 16 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> N deposition = 8 kg N/ha/yr as quantified by <a href="#">Turunen et al. (2004)</a>	Retention efficiency: N addition decreased the retention efficiency of ecosystem N pools ( <sup>15</sup> N tracer) by 71%.	Mer Bleue Bog, Ontario, Canada (measured 2007)	Bog plant community: dwarf shrub species and mosses: <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Xing et al. (2011)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Addition = 16 kg N/ha/yr (5N, or 5x background deposition), 32 kg N/ha/yr (10N), or 64 kg N/ha/yr (20N), all as NH <sub>4</sub> NO <sub>3</sub> Also, 64 kg N/ha/yr as NH <sub>4</sub> <sup>+</sup> only (20N-NH <sub>4</sub> ), and 64 kg N/ha/yr as NO <sub>3</sub> <sup>-</sup> only (20N-NO <sub>3</sub> ) Ambient deposition = 3 to 5 kg N/ha/yr, ~50% as NO <sub>3</sub> <sup>-</sup>	Extractable N in peat increases with N addition: [NO <sub>3</sub> <sup>-</sup> ] increases 71% (5N), 125% (10N), and 169% (20N); and [NH <sub>4</sub> <sup>+</sup> ] increases 90% (5N), 197% (10N), and 268% (20N).	Mer Bleue bog, Ottawa, Canada	Nonliving peat in top 10 cm of bog	<a href="#">Pinsonneault et al. (2016)</a>
Ombrotrophic peatland	Ambient deposition = 2 kg N/ha/yr at DS; 12 kg N/ha/yr at WM; 47 kg N/ha/yr at FS Mesocosms were established with NH <sub>4</sub> NO <sub>3</sub> solutions that mimicked relative N deposition levels <sup>15</sup> N tracer was added in 48 applications over 6 mo at a rate of 23 kg N/ha/yr	At DS, <sup>15</sup> N recovery was 60% in peat (depth 5–40 cm), 66% in living <i>Sphagnum</i> , 3.8% in shrubs, 1.8% in graminoids, and 0.01% for DIN (NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup> ). At 47 kg N/ha/yr, <sup>15</sup> N recovery was 36% in peat, 12% in shrubs, and 0.4% for DIN, but otherwise similar to recovery for pools at DS. Data from LV and CF mesocosms are not considered because mesocosm N addition levels (CF: 300% increase over DS N solution, LV: 700% increase over DS) did not reflect ambient N deposition differences (CF: 750% increase over DS deposition, LV: 300% increase over DS).	Mesocosms constructed using peat bog cores from sites in northern and western Europe—Degero Stormyr, Sweden (DS); Fenn's, Whixall, and Bettisfield Mosses NNR, UK (WM); Frolichshaier Sattelmoor, Germany (FS) (Peat cores also collected at Little Vildmose, Denmark [LV]; and Cors Fochno, Wales, UK [CF])	<i>Sphagnum capillifolium</i> , <i>S. fallax</i> , <i>S. magellanicum</i> , <i>S. papillosum</i> , <i>S. pulchrum</i> , <i>S. rubellum</i> , <i>Andromeda polifolia</i> , <i>Calluna vulgaris</i> , <i>Erica tetralix</i> , <i>Rubus chamaemorus</i> , <i>Vaccinium oxycoccos</i> , <i>Eriophorum vaginatum</i> , <i>Eriophorum angustifolium</i>	<a href="#">Zajac and Blodau (2016)</a>

**Table 11-2 (Continued): New studies on nitrogen addition effects on nitrogen cycling in wetlands.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Peatland catchment	9.6% of the catchment area fertilized with NPK at 19.5 kg N/ha in summer 35% of the catchment area is limed, 1,000 kg CaCO <sub>3</sub> /ha in summer 28 kg N/ha/yr (Helliwell et al., 2007)	Positive correlation ( $r = 0.44$ ) between annual fluxes of DIN and DON in stormflow. Negative correlations between fall DON and DIN during baseflow ( $r = -0.73$ ) and stormflow ( $r = -0.92$ ). Annual total dissolved nitrogen flux in river was 14 kg N/ha/yr, of which 54% is DON.	Kinder River catchment, south Pennines, U.K.	Water samples from the Kinder River outlet	<a href="#">Edokpa et al. (2015)</a>
Ombrotrophic peatland	Addition = 8, 24, and 56 kg N/ha/yr as either NH <sub>4</sub> <sup>+</sup> or NO <sub>3</sub> <sup>-</sup> since 2002 Ambient deposition total N = 8 kg N/ha/yr, 3 kg N/ha/yr as wet NO <sub>x</sub> , 3 kg N/ha/yr as wet NH <sub>x</sub> , and 2 kg N/ha/yr as dry NH <sub>x</sub>	In the oxidized N addition plots, increasing uptake of N by <i>Sphagnum</i> increased pore water DON and pore water anion deficit. In the reduced N plots, increasing uptake of N by <i>Sphagnum</i> increased pore water cation (K <sup>+</sup> + Mg <sup>2+</sup> + Ca <sup>2+</sup> + H <sup>+</sup> ). Pore water DIN increased only in the highest addition of NH <sub>4</sub> <sup>+</sup> (56 kg N/ha/yr).	Whim bog, Edinburgh, Scotland	Sphagnum moss ( <i>Sphagnum capillifolium</i> , a hummock-forming species) Heathland community: <i>Calluna vulgaris</i> , <i>Eriophorum vaginatum</i> , <i>Hypnum jutlandicum</i> , <i>Pleurozium schreberi</i> , and <i>Cladonia portentosa</i>	<a href="#">Chiwa et al. (2016)</a>

DNF = denitrification; DNRA = dissimilatory nitrate reduction to ammonium; fert = fertilizer; ha = hectare; kg = kilogram; KNO<sub>3</sub> = potassium nitrate; LTER = Long-Term Ecological Research; N = nitrogen; NH<sub>4</sub><sup>+</sup> = ammonium; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; NPK = nitrogen, phosphorus, potassium; S = sulfur; yr = year.

### 11.3.2 Soil Carbon Cycling

Wetlands can be hotspots for emissions of carbon dioxide and methane. High water levels in wetland soils prevent the rapid decomposition of dead roots and fallen stems by aerobic bacteria or fungi. Over long time periods (decades, centuries, or millennia), these conditions result in large stores of carbon belowground in wetland systems. Methanogens are able to decompose some of these anaerobic, saturated carbon stores to produce methane, and in severe droughts, a larger microbial community can produce large pulses of carbon dioxide by decomposing freshly aerated older organic carbon. Endpoints of

methane and carbon dioxide emissions have important implications for the wetland function of long-term carbon storage and regulation of atmospheric composition.

A meta-analysis that included wetlands with other nonforest ecosystems indicated no effect of N deposition on overall net ecosystem exchange of carbon (see [Appendix 11.3.2.2.1](#)). In other words, any gain in carbon capture by photosynthesis was offset by ecosystem respiration and C leaching. There were not enough studies to evaluate wetlands as a separate category.

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### **11.3.2.1 Belowground Decomposition, Respiration, and Biomass**

Respiration includes the release of carbon dioxide that can be measured in the air. Soil respiration may be the result of root or microbial activity. The process of decomposition often releases carbon dioxide from organic matter. Decomposers feed on dead organic matter, breaking it down into smaller compounds such as carbon dioxide or methane, water, and nutrients. Nitrogen may change the rate of respiration and decomposition.

Low decomposition in wetlands results in the buildup of dead plant material in the soil. In relatively closed systems, such as rain-fed bogs, a nutrient-poor, high-organic-acid ecosystem is produced. In open systems where flowing surface water supplies additional nutrients and sediments, the growth of new root systems on top of undecomposed roots can trap sediment and increase the height of the soil surface. This accretion of new wetland soil depends on both plant growth and maintenance of old carbon stored in soil organic matter. Wetland existence depends on the sum of these processes: if the sum of new plant growth does not exceed the decomposition of the soil organic matter, the wetland may subside until water levels rise above the soil surface. In this case, the drowned wetland area converts to an aquatic system. Wetland accretion is particularly important in estuarine and marine systems, where wave action and tides regularly wash sediment and dead plant material out of the wetland into aquatic systems, where the material nourishes aquatic food webs. Belowground endpoints, such as bulk density, soil organic matter, and root and rhizome production, are all indicators of wetland health and continued existence ([Table 11-3](#)).

#### **11.3.2.1.1 Across Wetlands**

A new study of 90 wetlands around the Gulf Coast from Florida to Texas found that higher N in the soil correlated with lower soil bulk density [see [Table 11-3](#) for equation; ([Nestlerode et al., 2014](#))]. Wetlands included both tidal and nontidal marshes and swamps. Reactive N or atmospheric N deposition loads were not quantified. This result

suggests that higher N in wetlands correlates with a reduction in wetland soil stability, making wetlands more susceptible to erosion.

#### 11.3.2.1.2 Salt Marsh

A new study confirms N loading increases carbon dioxide production from salt marsh soils. The new study uses an older model developed by [Wigand et al. \(2003\)](#), the Nitrogen Loading Model (NLM) for wetlands and estuaries of Narragansett Bay, RI, to determine annual N loads for different watersheds (sum of  $N_r$  from runoff, deposition, and municipal waste, 10.3–6,727 kg N/ha/yr) within the bay. Sampling of cordgrass marshes [*Spartina alterniflora* and *Spartina patens*; ([Wigand et al., 2009](#))] within these watersheds showed that soil respiration of CO<sub>2</sub> increased linearly and at similar rates with increasing annual N load in stands of *S. alterniflora* and *S. patens*. Decreases in sediment soil %C and %N and in belowground biomass were also observed as soil respiration increased ([Wigand et al., 2009](#)). Two additional experiments evaluated how N addition affects soil respiration ([Anisfeld and Hill, 2012](#)) and general CO<sub>2</sub> [see [Wigand et al. \(2015\)](#)]. In both cases, N addition increased these rates; however, the amount of N was over 1,000 kg/ha/yr, too high a level to evaluate the effects of N deposition.

In the Great Sippewissett Marsh fertilization experiment, fertilization with 520 kg N decreased long-term carbon storage in substrates by 31% ([Turner et al., 2009](#)). The stability of the marsh substrate (measured as the physical resistance to force) decreased 60% in urea-only fertilized plots. In contrast, N addition to *S. alterniflora* marshes located in Cocodrie, LA did not affect the physical resistance of the surface marsh substrate, and no changes at any profile were detected with the addition of 1,200 kg N/ha/yr ([Turner, 2011](#)). This study found negative effects upon marsh physical resistance at high rates of N addition (2,300–18,600 kg N/ha/yr) not relevant to evaluating the effects of N deposition.

The stability of marsh peat soils depends in part upon coarse roots and rhizomes, which marsh plants produce for physical support and as perennial storage organs. A long-term study at Goat Island, SC found stimulatory effects of N addition upon *Spartina alterniflora* coarse roots and rhizomes, and organic matter in peat ([Wigand et al., 2015](#); [Davey et al., 2011](#)), but the experimentally added N load was 4,200 kg N/ha/yr, too high to infer N deposition effects. Each year, marsh plants produce a new set of fine roots to acquire nutrients from the sediment and pore water. In Kirkpatrick Marsh, vegetation consisted of *Schoenoplectus americanus*, *Spartina patens*, and *Distichlis spicata*. N addition (250 kg N/ha/yr) decreased fine root production by 42 and 84% compared to control plots in the 3rd and 4th years of the experiment ([Langley and Megonigal, 2012, 2010](#)). When *S. americanus* and *S. patens* were planted in mesocosms for a sea level by

nitrogen fertilization factorial experiment, results were different. There was no belowground response in mesocosms at current sea levels to nitrogen addition ([Langley et al., 2013](#)). However, in a mesocosm mimicking a 10 cm rise in sea level, N addition increased belowground biomass by 130%. In a mesocosm mimicking a productive marsh elevated 15 cm above current sea level, N addition increased fine roots in mesocosms by 20–40% ([Langley et al., 2013](#)). The long-term study at Goat Island found inhibitory effects of N addition upon fine root mass ([Davey et al., 2011](#)), but the experimentally added N load was too high to infer N deposition effects.

North American salt marshes are currently being invaded by the European lineage of *Phragmites australis*, which is identified as a noxious weed or banned from sale or transport by six states ([USDA, 2015b](#)). A Kirkpatrick Marsh study compared establishing *P. australis* mesocosms to mesocosms of the native plant community described by [Langley et al. \(2013\)](#), and found that 250 kg N/ha/yr increased belowground biomass of the invasive species ([Mozdzer et al., 2016](#)). The invasive species had a greater rooting depth than the native community, and N addition increased root biomass 23–69% at depths of 10 to 40 cm, giving *P. australis* a competitive advantage over the native species. *P. australis* roots primed microbial activity and increased decomposition of buried peat by 1.8–1.9 times rates in uncolonized peat ([Mozdzer et al., 2016](#)), creating a positive feedback loop between increasing N and invasive species expansion. A large scale eutrophication experiment conducted at Plum Island Estuary, MA added nitrogen and phosphorus to tidal inflows to raise tidal nitrate concentrations to 15 times the background N load ([Deegan et al., 2012](#)). Although the annual nitrogen load cannot be calculated, the results of this experiment illustrate the mechanisms by which N addition destabilizes salt marshes. Belowground biomass decreased 33% compared to control marshes, and this in turn altered drainage, resulting in 4% higher water content in creek banks in enriched marshes. Creek bank with decreased stabilizing root mats and increased water content were less stable, with increasing numbers and lengths of creek bed fractures over time (see [Table 11-3](#) in [Appendix 11.3.2.1.6](#) for equation). Creek banks were so destabilized by N addition that the number of slumps, or creek edges sliding into creek beds, was 113% higher in enriched than control marsh, which increased the creek channel width:depth ratio by 28%. The unvegetated area of exposed mud was 200% higher in the enriched marsh as a consequence of the marsh destabilization ([Deegan et al., 2012](#)).

#### **11.3.2.1.3 Freshwater Tidal Marsh**

In marshes, coarse roots and rhizomes are produced by plants to serve as physical supports and as storage organs for nutrients and carbohydrates. In a freshwater tidal

marsh dominated by *Zizaniopsis miliacea* in the Altamaha River Estuary, GA, addition of 500 kg N/ha/yr decreased the biomass of live rhizomes by 71%, and the mass of macro-organic matter (living + dead roots) decreased 33% ([Ket et al., 2011](#)). An N-loading experiment added 50, 200, or 1,200 kg N/ha/yr to a freshwater tidal marsh on the Tchefuncte River, LA ([Graham and Mendelssohn, 2016](#)). Researchers used two different sampling methods to assess belowground biomass. Addition of 200 or 1,200 kg N/ha/yr reduced biomass of established roots by 51%. Addition of 1,200 kg N/ha/yr also increased growth of new roots into empty soil 106% over control ([Graham and Mendelssohn, 2016](#)). This suggests that high and very high levels of N loading to tidal freshwater marshes may destabilize existing marshes, while very high N loading may accelerate establishment or expansion of new marshes. However, N addition in this experiment had no measurable effect upon organic matter content, bulk density, total C, total P, or N cycling in the top 10 cm of soil [see [Appendix 11.3.1.4](#); [Steinmuller et al. \(2016\)](#)].

#### **11.3.2.1.4 Intermittent Wetland**

An N addition study was established on the Tibetan Plateau in an alpine meadow that is also an intermittent wetland. N addition of 30 kg N/ha/yr increased belowground biomass 26%. N addition also stimulated CO<sub>2</sub> uptake 25% ([Wang et al., 2017c](#)), which offset the concurrent stimulation of N<sub>2</sub>O emissions (see [Appendix 11.3.1.5](#)).

#### **11.3.2.1.5 Bog and Fen**

In the 2008 ISA, soil respiration in bogs had been studied in European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg N/ha/yr. Studies found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher carbon dioxide emissions. There are three new studies on an Ontario bog and two new studies from European systems.

The Mer Bleue Bog in Ontario is the site of two concurrent fertilization experiments. In one experiment, treatments were initiated in 2000 with nitrogen addition of 16 kg N/ha/yr. The second experiment was initiated in 2005 in separate plots, where nitrogen-only treatments of 32 kg N/ha/yr and 64 kg N/ha/yr were applied. Each experiment had separate control plots. N addition at the rate of 16 kg N/ha/yr decreased the concentrations of CO<sub>2</sub> in peat substrate in the 8th year of N addition (2007), decreasing CO<sub>2</sub> by 19% at a 5-cm depth and 14% at a 25-cm depth ([Wendel et al., 2011](#)). N addition at the rate of 64 kg N/ha/yr did not significantly alter ecosystem respiration when assessed 7 years after fertilization started (2011), but due to changes in

photosynthesis and declines in cover (see [Appendix 11.5.5](#) and [Appendix 11.8.1.5](#)), net ecosystem exchange in the growing season was 46% lower than in unamended bog plots ([Larmola et al., 2013](#)).

In the Mer Bleue ombrotrophic peat bog, 16 kg N/ha/yr added from 2000 to 2007 increased peat biomass 17% in the top 10 cm of the substrate. In addition, median temperature at a 5-cm depth in the peat was 19% lower in plots that received 16 kg N/ha/yr than in control plots ([Wendel et al., 2011](#)), which the authors posited was due to increased shading by increasingly productive shrub species. In contrast, soil temperatures were elevated deeper in the peat substrate; at 20-cm depth, average daily temperature was 0.6°C higher in plots with 16 kg N/ha/yr added than in control plots ([Wendel et al., 2011](#)). More recently, peat samples from Mer Bleue suggest that N addition of 16 kg N/ha/yr, along with the resultant increase in shrub production, has increased soluble phenolics 17% in peat, with peat C:K ratio increasing 45% ([Pinsonneault et al., 2016](#)), indicating a shift towards more recalcitrant C in the peat as well as K limitation of the bog (see [Appendix 11.5.5](#)). In terms of the microbial community responsible for decomposition and respiration in the peat, N addition in all amounts increased P and K limitation, as indicated by increasing soluble C:P and C:K ratios and increasing activity of P and K acquiring enzymes. However, N addition also increased microbial breakdown of carbon, as indicated by 62–97% increases in the activity of  $\beta$ -D-glucosaminidase ([Pinsonneault et al., 2016](#)). A recently initiated addition experiment in the same bog added 64 kg N/ha/yr as either  $\text{NH}_4^+$  or  $\text{NO}_3^-$  and found that reduced N resulted in 15% higher soluble phenolics and suppressed enzyme activities compared to oxidized N ([Pinsonneault et al., 2016](#)). This result suggests that oxidized N is more likely to enhance microbial decomposition of peat than an equivalent amount of reduced N.

A recent study of mesocosms collected from European bogs under a natural gradient of N deposition from 2 to 24 kg N/ha/yr showed that increasing N deposition correlated with increased respiration (and increased gross primary productivity, and increased net C uptake; see [Appendix 11.4.5](#)) up to 15 kg N/ha/yr, but that all C fluxes decreased by 40% between 15 and 24 kg N/ha/yr ([Estop-Aragones et al., 2016](#)). Importantly, N stimulation of respiration continued under drought conditions, although there was no relationship during drought between N deposition and GPP or net carbon uptake. Inference from this study is limited by sample size; there was only one mesocosm per bog ([Estop-Aragones et al., 2016](#)). In a study of decomposition rates conducted in Eastern Europe, N deposition altered decomposition rates in bogs. When a standard cellulose substrate was placed in all bogs, decomposition mass loss was higher at the high N deposition (20–25 kg N/ha/yr) Jizera Mountains site, 170% higher when placed in areas dominated by *Sphagnum rubrum*, and 510% higher mass loss in areas dominated by *S. magellanicum*, than in the

low N deposition (12.5 kg N/ha/yr) Jeseníky Mountains site ([Jirousek et al., 2015](#)). When *S. rubrum* samples were collected from both sites and decomposed in a common site, moss collected from the high N site decomposed more slowly, with 30% less mass lost than from moss collected at the low N site, indicating that N deposition increased the recalcitrance of moss to decomposition ([Jirousek et al., 2015](#)). In contrast, at the Whim Bog N addition experiment, there was no effect of added N as either ammonium or nitrate (treatment N loads of 16, 32, and 64 kg N/ha/yr) upon decomposition of senesced *Sphagnum* moss ([Manninen et al., 2016](#)), although there were effects upon living moss and water quality (see [Appendix 11.5.5](#) and [Appendix 11.3.1.5](#)).

### 11.3.2.1.6 Summary Table

**Table 11-3 Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Estuarine marsh, estuarine shrub swamp, palustrine marsh, palustrine swamp	N dep = not reported S dep = not reported	Soil total N ( $N_{soil}$ , as %N) increased as soil bulk density (SBD, as g/cc) decreased, $\ln(N_{soil}) = -1.9233 \times SBD + 0.4165$ .	90 Gulf Coast wetlands, Texas to Florida	Marsh community, soil and pore water chemistry	<a href="#">Nestlerode et al. (2014)</a>
Salt marsh	Watershed total N load (10.3, 11.5, 27.4, 37.4, 2,729.9, 3,661, and 6,727 kg N/ha/yr) using nitrogen loading model in <a href="#">Wigand et al. (2003)</a> N dep = not reported S dep = not reported	In <i>S. alterniflora</i> stands, soil respiration ( $y$ ) increased linearly with N loading ( $x$ ) ( $y = 0.0006x + 2.04$ ). Soil %C and %N decreased as soil respiration increased.	Narragansett Bay, RI	Bare sediments in <i>Spartina patens</i> and <i>Spartina alterniflora</i> stands, additional <i>S. patens</i> marshes from <a href="#">Wigand (2008)</a> ; <a href="#">Wigand et al. (2003)</a>	<a href="#">Wigand et al. (2009)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	Addition: 1,050 kg N/ha/yr (low) as NaNO <sub>3</sub> , 2,100 kg N/ha/yr (medium) as NH <sub>4</sub> NO <sub>3</sub> or NaNO <sub>3</sub> , 4,200 kg N/ha/yr (high) as NH <sub>4</sub> NO <sub>3</sub> in same plots in over several years N dep = not reported S dep = not reported	Medium N increased annual sediment respiration (g C/m <sup>2</sup> /yr) by 53%.	Hoadley Creek Marsh, Guilford, CT	<i>Spartina alterniflora</i>	<a href="#">Anisfeld and Hill (2012)</a>
Salt marsh	520 kg N/ha/yr in U (N as urea treatment), UP (urea + 208 kg P/ha/yr as phosphate), and HF (milorganite, 10-6-4 NPK) plots, as reported by <a href="#">Brin et al. (2010)</a> N dep = not reported S dep = not reported	Fertilization decreased the organic:inorganic ratio by 31% in older, deeper (pre-1963) marsh substrate, and decreased the physical resistance of the marsh substrate (shear vane strength) by 60% in U plots, 36% in UP plots, and 35% in HF plots.	Great Sippewissett Marsh, MA	<i>Spartina alterniflora</i> , <i>Spartina patens</i> , and <i>Distichlis spicata</i>	<a href="#">Turner et al. (2009)</a>
Coastal salt marsh	Addition: 4,200 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> or (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> N dep = not reported S dep = not reported	N addition increased coarse root volume 63% in the top 10 cm, or 61% in the top 20 cm of sediment. Organic matter increased 20% in the top 21 cm of sediment. CO <sub>2</sub> emission increased 41%.	Goat Island, SC (measured 2008)	<i>Spartina alterniflora</i> and associated sediments	<a href="#">Wigand et al. (2015)</a>
Salt marsh	4,200 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> N dep = not reported S dep = not reported	N addition increased peat mass fraction by 28% and root/rhizome mass fraction by 58% in wet shallow (<10 cm) sediments. Fine root mass decreased 39% in shallow sediments.	Goat Island, SC (measured 2008)	<i>Spartina alterniflora</i>	<a href="#">Davey et al. (2011)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Estuarine salt marsh	250 kg N/ha/yr N dep = not reported S dep = not reported	Total fine root production decreased by 42 and 84% in the 3rd and 4th yr.	Kirkpatrick Marsh, MD (measured in 3rd and 4th yr, 2008–2009)	<i>Schoenoplectus americanus</i> (C3), <i>Spartina patens</i> (C4), and <i>Distichlis spicata</i> (C4)	<a href="#">Langley and Megonigal (2012, 2010)</a>
Estuarine salt marsh	NH <sub>4</sub> Cl solution injected into mesocosm peat at root-level, 250 kgN/ha, increases N by 40% above annual average background concentration Deposition not reported	At increased marsh elevation (15 cm above current sea level), N addition increased total fine root mass by 20–40%. At 10 cm sea level rise, N addition increases BG biomass by 130% under ambient [CO <sub>2</sub> ].	Kirkpatrick Marsh, MD	Factorial mesocosm experiment with varying sea levels: 35 or 15 cm rise in marsh elevation; current sea level; 10, 20, or 30 cm rise in sea level.  Mesocosms planted with 2 rhizomes <i>Schoenoplectus americanus</i> and 10 stems <i>Spartina patens</i> ; harvested each year	<a href="#">Langley et al. (2013)</a>
Salt marsh	Addition = 250 kg N/ha/yr (as NH <sub>4</sub> Cl) Ambient deposition = not reported	N addition did not significantly affect the rooting depth of <i>Phragmites australis</i> , which was significantly deeper than rooting depth of native community. N addition increased belowground biomass of <i>P. australis</i> 37–69% between 10 and 40 cm depth, with peak increases at 10 cm depth. N addition increased pore water concentrations of NH <sub>4</sub> by 9 and 72% at depths of 40 and 80 cm, respectively. <i>P. australis</i> increased SOM decomposition in recalcitrant peat 1.8–1.9x over rates in unvegetated peat.	Mesocosms of invasive (from seeds) or native (from rhizome fragments) plants in Kirkpatrick Marsh, Rhode River, Edgewater, MD	Invasive <i>Phragmites australis</i> ; native community of <i>Spartina patens</i> , <i>Schoenoplectus americanus</i>	<a href="#">Mozdzer et al. (2016)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	<p>Nitrate and phosphate dissolved in tidal inflows to raise aqueous NO<sub>3</sub><sup>-</sup> concentrations to 70–100 μM and raise PO<sub>4</sub><sup>3-</sup> to 5–7 μM.</p> <p>Background load in tides: 5 μM NO<sub>3</sub><sup>-</sup>, 1 μM PO<sub>4</sub><sup>3-</sup>.</p> <p>N dep = not reported</p> <p>S dep = not reported</p>	<p>Marsh stability (F, as creek bank fractures) decreases with cumulative N enrichment (y, in years of N enrichment): F = 0.42y + 0.79. Creek fractures were 4.4x as long in enriched as in control marsh.</p> <p>Water content in creek bank increases 4%.</p> <p>Number of bank slumps into creek bed is 2.1x higher in enriched marsh. Channel width:depth increased 28%.</p> <p>Belowground biomass decreases 33%.</p> <p>Area of unvegetated exposed mud increased 200%.</p>	Plum Island Estuary, MA	Primary tidal creeks with <i>Spartina alterniflora</i> in low marsh along creeks, and <i>Spartina patens</i> in high marsh platforms	<a href="#">Deegan et al. (2012)</a>
Freshwater marsh	<p>500 kg N/ha/yr as NH<sub>4</sub>Cl or urea</p> <p>N dep = not reported</p> <p>S dep = not reported</p>	<p>Addition of 500 kg N/ha/yr decreased the biomass of live rhizomes by 71%, and the mass of macro-organic matter (living + dead roots) decreased 33%.</p>	Altamaha Estuary, GA (2007, 2008)	<i>Zizaniopsis miliacea</i> , <i>Pontederia cordata</i> , and <i>Sagittaria lancifolia</i>	<a href="#">Ket et al. (2011)</a>
Tidal marsh	<p>Addition = 0, 50, 200, 1,200 kg N/ha/yr as urea</p> <p>Ambient deposition = not reported</p>	<p>Addition of 1,200 kg N/ha/yr increased root colonization of soil 106% over control (0 kg added N) as evaluated by living root biomass within ingrowth cores (p-value = 0.03).</p> <p>Addition of 200 or 1,200 kg N/ha/yr reduced biomass of established roots by 51% as evaluated by sampling standing root biomass (p-value = 0.02).</p>	Tchefuncte River, Lake Pontchartrain, LA	<i>Sagittaria lancifolia</i>	<a href="#">Graham and Mendelssohn (2016)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Tidal marsh	Addition = 0, 50, 200, and 1,200 kg N/ha/yr (as slow-release methylene urea, which releases NH <sub>4</sub> <sup>+</sup> ), in combination with 0 or 131 kg P/ha/yr, to mimic Mississippi River diversion N and P loading rates  Ambient deposition = not specified	11 yr of N addition had no significant effect on organic matter content, bulk density, total C, total P in the top 10 cm of marsh soil.	Madisonville nutrient plots (microtidal pulses of 10 cm), Tchefuncte River, Lake Pontchartrain Estuary, LA	<i>Sagittaria lancifolia</i> , <i>Polygonum punctatum</i> , <i>Eleocharis fallas</i>	<a href="#">Steinmuller et al. (2016)</a>
Seasonal wetland, alpine meadow	Addition: 30 kg N/ha/yr  Ambient deposition = 8.7 to 13.8 kg N/ha/yr	N addition increased belowground biomass by 26%.  N addition increased CO <sub>2</sub> uptake by 25%. N addition reduced the global warming potential (sum of CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O fluxes) of the plots from a net source to a net sink.	Mesocosms at Luanhaizi wetlands, Tibetan Plateau	<i>Carex pamirensis</i> , <i>Carex atrofusca</i> , <i>Hippuris vulgaris</i> , <i>Triglochin palustris</i> , and <i>Heleocharis</i> spp.	<a href="#">Wang et al. (2017c)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KHPO <sub>4</sub> )  S dep = not reported  N dep = 8 kg N/ha/yr	Medium and high NPK increased ecosystem respiration in 8th yr by 24 and 32% respectively, and decreased surface temperature by 11 and 13%, respectively. In high NPK, the water table was 42% closer to peat surface.	Mer Bleue Bog, Ontario, Canada	Bog plant community: dwarf shrub species and mosses <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Juutinen et al. (2010)</a>
Ombrotrophic peat bog	Addition: 16 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub>  N dep = 8 kg N/ha/yr as quantified by <a href="#">Turunen et al. (2004)</a>	N addition lowered substrate temperature at 5-cm depth, decreasing median temperature by 19% and increased substrate temperature at 20-cm depth, by an average of 0.6°C.  N addition decreased CO <sub>2</sub> concentrations in substrate by 19% at 5-cm depth and by 14% at 25-cm depth.  N addition increased peat biomass 17%.	Mer Bleue Bog, Ontario, Canada (measured 2007)	Bog plant community: dwarf shrub species and mosses <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Wendel et al. (2011)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KH <sub>2</sub> PO <sub>4</sub> )	Under high N, growing season net ecosystem exchange declined by 46%.	Mer Bleue Bog, Ontario, Canada	Shrub species ( <i>Vaccinium myrtilloides</i> , <i>Ledum groenlandicum</i> , <i>Chamaedaphne calyculata</i> ) and mosses ( <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , <i>Polytrichum strictum</i> )	<a href="#">Larmola et al. (2013)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	<p>Addition = 16 kg N/ha/yr (5N, or 5× background deposition), 32 kg N/ha/yr (10N), or 64 kg N/ha/yr (20N), all as NH<sub>4</sub>NO<sub>3</sub></p> <p>Also, 64 kg N/ha/yr as NH<sub>4</sub><sup>+</sup> only (20N-NH<sub>4</sub>), and 64 kg N/ha/yr as NO<sub>3</sub><sup>-</sup> only (20N-NO<sub>3</sub>)</p> <p>Ambient deposition = 3 to 5 kg N/ha/yr, ~50% as NO<sub>3</sub><sup>-</sup></p>	<p>16 kg N/ha/yr (5N): N addition in this amount increased the peat C:K ratio 45% and increased peat-soluble phenolics 17%. In terms of microbial activity, N addition decreased soluble C:N 17%, and decreased NAG activity by 56%. N addition increased soluble C:P 33% and phosphatase activity 7%. N addition increased soluble C:K 45%. N addition increased BDG activity 62% and phenol oxidase activity 12%.</p> <p>32 kg N/ha/yr (10N) and 64 kg N/ha/yr (20N): N addition in these amounts altered nutrient ratios of peat: 15–23% decrease in C:N, 15% increase in C:P (64 kg N only), and 72–109% increase in C:K compared to control plots. In terms of microbial activity, N addition decreased soluble C:N 30–42%, and decreased NAG activity 72–77%. N addition increased soluble C:P 36–39% and phosphatase activity 41–49%. N addition increased soluble C:K 32–51%. N addition increased BDG activity 80–97% but decreased phenol oxidase activity 31–63%.</p> <p>In comparing the form of N in addition (20N-NH<sub>4</sub><sup>+</sup> vs. 20N-NO<sub>3</sub><sup>-</sup>), peat soluble phenolics were 15% higher under NH<sub>4</sub><sup>+</sup> than under NO<sub>3</sub><sup>-</sup>. Activity of all enzymes was lower under NH<sub>4</sub><sup>+</sup> compared to NO<sub>3</sub><sup>-</sup> addition: BDG decreased 11%, NAG decreased 32%, phosphatase decreased 7%, and phenol oxidase decreased 56%.</p>	Mer Bleue bog, Ottawa, Canada	Nonliving peat in top 10 cm of bog	<a href="#">Pinsonneault et al. (2016)</a>

**Table 11-3 (Continued): Loading effects upon belowground carbon cycling.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Ambient deposition of NO <sub>x</sub> , NH <sub>y</sub> , and SO <sub>x</sub> : 1.95–24.07 kg N/ha/yr and 3.18–36.90 kg S/ha/yr Deposition estimates from EMEP (European Monitoring and Evaluation Programme)-based IDEM (Integrated Deposition Model) from <a href="#">Pieterse et al. (2007)</a>	N and S deposition rates are correlated across these sites ( $r = 0.87$ ). Respiration ( $C_{resp}$ , as g C/m <sup>2</sup> /day) was positively correlated with N deposition ( $N_{dep}$ , as kg N/ha/yr) up to 15 kg N/ha/yr: $C_{resp} = 0.448 + 0.067 \times N_{dep}$ ; $R^2 = 0.61$ . The relationship between N and respiration was weaker during drought ( $R^2 = 0.38$ ) and post-drought ( $R^2 = 0.50$ ) periods. Respiration, GPP, and net carbon uptake were all 40% lower in the mesocosm from the 24 kg N/ha/yr than from the 15 kg N/ha/yr site.	Lab incubations of 14 <i>Sphagnum</i> mesocosms collected in saturated hollows in European bogs: U.K. and Ireland (n = 9), Poland (n = 4) and Slovakia (n = 1) Mesocosms were maintained at a high water table (0–5 cm in depth) for 40 days, then were subject to drought for 100 days, then were rewetted to high water table (0–5 cm in depth) for 200 days.	<i>Sphagnum fallax</i>	<a href="#">Estop-Aragones et al. (2016)</a>
Ombrotrophic bog	Wet + dry deposition, estimated by <a href="#">Jirousek et al. (2011)</a> Jireza: 20–25 kg N/ha/yr (high N) Jeseníky: 12.5 kg N/ha/yr (low N)	Decomposition of a standard substrate (cellulose) is higher at high N site, 170% higher mass loss in <i>S. rubellum</i> zone and 510% higher mass loss in <i>S. magellanicum</i> zone. In comparing decomposition of <i>S. rubellum</i> grown at high N or low N sites, <i>S. rubellum</i> from high N mass loss was 30% lower (i.e., less decomposition).	Two sites: Jizerka in Jireza Mountains (warm suboceanic climate) and Vozka in Jeseníky Mountains (2°C colder)	<i>Sphagnum fallax</i> , <i>Sphagnum magellanicum</i> , and <i>Sphagnum rubellum/russowii</i>	<a href="#">Jirousek et al. (2015)</a>
Ombrotrophic peatland	Addition = 8, 24, and 56 kg N/ha/yr as either NH <sub>4</sub> <sup>+</sup> or NO <sub>3</sub> <sup>-</sup> Ambient deposition = 8 kg N/ha/yr	Decomposition rates of <i>Sphagnum</i> were not affected by elevated N levels. Only the highest level of N addition altered pore water chemistry.	Whim bog, Edinburgh, Scotland	<i>Sphagnum</i> moss ( <i>Sphagnum capillifolium</i> )	<a href="#">Manninen et al. (2016)</a>

ANPP = aboveground net primary productivity; C = carbon; cm = centimeter; CO<sub>2</sub> = carbon dioxide; dep = deposition; g = gram; ha = hectare; kg = kilogram; m = meter; N = nitrogen; NaNO<sub>3</sub> = sodium nitrate; NH<sub>4</sub>Cl = ammonium chloride; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NPK = nitrogen, phosphorus, potassium; S = sulfur; yr = year.

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### 11.3.2.2 Methane Emissions

Methane (CH<sub>4</sub>) is an important greenhouse gas that is over 20 times more effective at trapping heat than carbon dioxide. The primary biological source of methane is microbial (methanogens in the domain Archaea), as is the primary biological sink (methanotrophs among the Bacteria and Archaea). N addition can stimulate methane flux from wetlands by increasing methanogen activity when dissolved labile organic C is abundant ([Kim et al., 2015b](#)), or by decreasing methane oxidation by methanotrophs, as was recently observed in a boreal peatland ([Lozanovska et al., 2016](#)). Therefore, understanding the controls on these microorganisms is important for predicting methane flux from ecosystems. In terms of carbon emissions, the 2008 ISA reported that N deposition alters CH<sub>4</sub> flux in wetland and forested ecosystems. A meta-analysis of 25 N addition observations (N addition 30 to 240 kg N/ha/yr) found that N addition increased CH<sub>4</sub> emissions by 95% from wetlands and grasslands [see [Table 11-4](#) for other nonsignificant results; ([Liu and Greaver, 2009](#))].

There is new evidence that N loading increases methane production in soils. In the N addition experiments replicated in three California marshes ([Vivanco et al., 2015](#); [Irvine et al., 2012](#)), field-measured methane flux from soils increased linearly with increasing N load (0, 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr), such that CH<sub>4</sub> flux from soils increased by 1.23 µg CH<sub>4</sub>/m<sup>2</sup>/day for each 10 kg N/ha/yr added  $R^2 = 0.23$  and  $P = 0.025$  ([Vivanco et al., 2015](#); [Irvine et al., 2012](#)). Methane flux increased from low or nearly negative to net positive values above ~100 kg N/ha/yr, showing that the effect of added N on methanogenesis, the final step in anaerobic decomposition, offset any increase in methanotrophy. Differential effects of N on both methanogenesis and methanotrophy have been documented in other ecosystems ([Irvine et al., 2012](#); [Liu and Greaver, 2009](#)). The linearity of the trend became less robust when the exposure time increased to 14 months.

Soils were collected from the Tijuana River Reserve near the sites used in [Vivanco et al. \(2015\)](#) and incubated in a laboratory microcosm experiment with factorial C and N additions ([Irvine et al., 2012](#)). Adding C and N together increased methane production by 44% above controls ([Irvine et al., 2012](#)), suggesting that N loading will increase microbial methane production disproportionately when accompanied by pulses of labile C. The authors concluded that temperate salt marshes generally emit low levels of methane, but these values are also highly spatially and seasonally variable ([Cheng et al., 2010](#); [Magenheimer et al., 1996](#); [Bartlett et al., 1985](#); [King and Wiebe, 1978](#)). Despite the high variability observed, however, the field experiments suggest that increased N availability

stimulated methanogenesis and increased methane emissions in southern California salt marshes, as in other ecosystems ([Liu and Greaver, 2009](#)).

A study of a salt marsh in the Yellow River Delta, China, added N loads in different chemical forms to the marsh to determine the effects of N form upon microbial communities involved in C cycling. N was added as 50 kg N/ha/yr as  $\text{NH}_4^+$ , 50 kg N/ha/yr as  $\text{NO}_3^-$ , or 100 kg N/ha/yr as  $\text{NH}_4\text{NO}_3$ . All three forms of N increased the abundance of archaeal methanogens as well as the abundance of bacteria that form syntrophies that stimulate methanogen metabolism ([Xiao et al., 2017](#)). Ordination of bacterial community composition suggested that all forms of N shifted the microbial community in the same direction, but that reduced N had much stronger effects on community composition than did oxidized N. N form also affected methane production and fluxes: all N forms increased methane in pore water, but only  $\text{NH}_4^+$  and  $\text{NH}_4\text{NO}_3$  additions increased methane emissions from the plots ([Xiao et al., 2017](#)). Reduced forms of N have stronger effects on microbial C cycling than do equivalent amounts of oxidized N.

#### 11.3.2.2.1 Summary Table

**Table 11-4 Nitrogen loading effects upon methane emissions.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Wetlands (natural and agricultural)	N addition experiments, N addition of 10 to 562 kg N/ha/yr Deposition = not reported	No effect across wetlands (n = 6) of N addition on net ecosystem exchange. N addition increased $\text{CH}_4$ emissions by 95% across grass + wetland + anaerobic agricultural systems (n = 25). No effect across drained wetlands of N addition (n = 6) upon biological $\text{CH}_4$ uptake.	Global	Meta-analysis of data collected from North America, South America, Europe, and Asia	<a href="#">Liu and Greaver (2009)</a>
Salt marsh	100, 200, 400, 800, 1,600, and 3,200 kg N/ha/yr as granular urea	Methane flux (y, as $\text{mg CH}_4/\text{m}^2/\text{day}$ ) increased linearly with N addition ( $N_{\text{add}}$ , as $\text{g N}/\text{m}^2/\text{yr}$ ): $y = 0.00123 \times N_{\text{add}} - 0.0122$ .	Morro Bay, Carpinteria Salt Marsh, Tijuana River Reserve, CA	Marsh dominated by <i>Salicornia depressa</i> (formerly <i>Salicornia virginica</i> )	<a href="#">Irvine et al. (2012)</a>

**Table 11-4 (Continued) Nitrogen loading effects upon methane emissions.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	0, 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr as urea  N dep = 3–5 kg N/ha/yr as reported in <a href="#">Tonnesen et al. (2007)</a>	CH <sub>4</sub> flux from soils increased by 1.23 µg CH <sub>4</sub> /m <sup>2</sup> /day for each 10 kg N/ha/yr added	Morro Bay National Estuary, Carpinteria Salt Marsh Reserve, Tijuana River Reserve Estuary, CA	Stands of <i>Salicornia depressa</i> (formerly <i>Salicornia virginica</i> )	<a href="#">Vivanco et al. (2015)</a>
Salt marsh	Addition of 50 kg reduced N/ha/yr as NH <sub>4</sub> Cl, 50 kg oxidized N as KNO <sub>3</sub> , or 100 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub>  Ambient deposition = not specified	Addition of any form of N increased bacterial abundance of <i>Geobacillus</i> and <i>Clostridium</i> , and increased archaeal abundance of <i>Methanocellaceae</i> .  Reduced-N and NH <sub>4</sub> NO <sub>3</sub> additions decreased bacterial abundance of <i>Flavobacterium</i> , <i>Bacillus</i> , <i>Gillisia</i> , <i>Marinobacter</i> , and <i>Desulfosarcina</i> .  Redundancy analysis found positive correlations between ammonium-N measured in sediment, methane flux, pore water methane concentrations, <i>Geobacillus</i> abundance, <i>Clostridium</i> abundance, and <i>Methanocellaceae</i> abundance.  In dry season, only 50 kg reduced N addition plots are methane sources; all other plots are methane sinks.  In wet season, 50 kg oxidized N increased pore water CH <sub>4</sub> . 50 kg reduced N and 100 kg N increased pore water CH <sub>4</sub> as well as CH <sub>4</sub> emissions from plots.	Marsh of <i>Phragmites australis</i> and <i>Suaeda heteroptera</i> in the Yellow River Delta, China	Bacterial and archaeal communities assessed by bacterial primers <i>Ba338f</i> and <i>Ba806r</i> , and archaeal primers <i>Ar515f</i> and <i>Ar907r</i>	<a href="#">Xiao et al. (2017)</a>

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## 11.4 Production and Aboveground Biomass

Aboveground biomass is a measure of how much carbon is fixed by wetland plants. Changes in this endpoint can affect food webs within the wetland, including dependent migratory species. Changes in aboveground biomass will also be important for food webs in rivers, lakes, or estuaries connected by surface water flow, because plant litter from wetlands is an important base for food webs downstream. In the 2008 ISA, evidence from Canadian and European peatlands showed that N deposition had negative or mixed effects on *Sphagnum* productivity, depending on history of deposition. In Canadian ombrotrophic peatlands experiencing deposition of 2.7–8.1 kg N/ha/yr, peat accumulation increased with N deposition, but accumulation rates had slowed by 2004, indicating a degree of N saturation. Coastal wetlands responded to N enrichment with increased primary production, shifting microbial and plant communities and altering pore water chemistry, although many of the studies in coastal wetlands used N enrichment levels more similar to those of wastewater than atmospheric deposition. The new studies published from 2008–2015 include work on tidal marsh, mangroves, and ombrotrophic bogs.

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### 11.4.1 Salt Marsh

In the 2008 ISA, primary production of plant species in coastal wetlands typically increased with N addition; however, most studies applied fertilizer treatments that were several orders of magnitude larger than atmospheric deposition ([Darby and Turner, 2008](#); [Tyler et al., 2007](#); [Wigand et al., 2003](#); [Mendelsohn, 1979](#)). N fertilization experiments in salt marsh ecosystems show biomass stimulation from 6 to 413% with application rates ranging from 7 to 3,120 kg N/ha/yr ([U.S. EPA, 1993](#)).

A number of new studies have evaluated N effects on production and biomass in coastal wetlands. In Elkhorn Slough, the largest coastal marsh in California, addition of 150 kg N/ha/yr increased *S. pacifica* biomass in two of the six experimental sites ([Goldman Martone and Wasson, 2008](#)); a 36% increase over unamended plots occurred in a site with unrestricted tidal flow, and a 53% increase occurred in a marsh where impoundments restricted regular tidal exchange. [Darby and Turner \(2008\)](#) reported on a nitrogen addition experiment at Cocodrie, LA, in which five loads of nitrogen were applied to *S. alterniflora* marshes. Aboveground biomass increased linearly with increases in N load, although the regressions were not reported. Additions of 230 and 465 kg N/ha/yr did not significantly raise aboveground (AG) biomass above unamended marsh biomass, but 930 kg N/ha/yr increased AG biomass 122%, 1,860 kg N/ha/yr

increased AG biomass 124%, and 3,720 kg N/ha/yr increased AG biomass 141%. A nitrogen addition experiment with seven different N loads (0, 100, 200, 400, 800, 1,600, and 3,200 kg N/ha/yr) was replicated at three different California estuarine reserves [Morro Bay, Carpinteria Salt Marsh, and Tijuana River Marsh Reserve; ([Vivanco et al., 2015](#))]. Aboveground biomass of existing *S. depressa* increased linearly in response to N addition across all three marshes and N addition levels starting at 100 kg N/ha/yr (see [Table 11-5](#) for equation,  $R^2 = 0.58$ ). When harvested plots were resampled, the regrowth of aboveground biomass increased in a saturating response to increasing N load, with no significant increases in biomass in response to N above 1,600 kg N/ha/yr ([Table 11-5](#) for equation). Similar saturation of plant response occurred in N tissue (see [Appendix 11.5](#)).

In the eutrophication experiment at Plum Island, MA, tidal nitrate enriched to 15 times background concentrations, along with P additions, increased aboveground shoot biomass and specific mass of the vascular plant community by 16 and 9%, respectively ([Deegan et al., 2012](#)). When the tidal N enrichment was repeated in later years without P additions, added loads of 620 kg N/ha/yr or 1,200 kg N/ha/yr increased low marsh *Spartina alterniflora* shoot specific mass 3 and 12%, respectively ([Johnson et al., 2016a](#)). In the high marsh at this site, added N loads were smaller: at 140 kg N/ha/yr, *S. alterniflora* and *Distichlis spicata* increased shoot-specific mass 14 and 8% ([Johnson et al., 2016a](#)). There were also changes in plant architecture in the same plots (see [Appendix 11.6.1](#)), but no effects on plant community. The Kirkpatrick Marsh in Maryland is the site of a nitrogen fertilization experiment in a tidal marsh community consisting of *Schoenoplectus americanus*, *Spartina patens*, and *Distichlis spicata*. Over the 4 years of the experiment, nitrogen addition of 250 kg N/ha/yr increased total aboveground biomass by 47–79% ([Langley and Megonigal, 2010](#); [Langley et al., 2009](#)). When the biomass response was partitioned by carbon fixation mechanism (C3 or C4 plants), biomass of C3 plants declined with N addition to 81% in the 3rd year and 55% in the 4th year of initial fertilized *S. americanus* biomass. Biomass of C4 plants *S. patens* and *D. spicata* increased 2–51 times the control over the 4 years of the experiment (see [Appendix 11.8.1](#)), or increased 129% in the 4th year over initial fertilized C4 biomass.

In a related experiment at Kirkpatrick Marsh, mesocosms were constructed to mimic marshes at different sea levels, planted with *Schoenoplectus americanus* and *Spartina patens*, and subjected to the same nitrogen treatment ([Langley et al., 2013](#)). In this experiment, sea level had the strongest impact on biomass. In mesocosms set at the current sea level, N addition increased total AG biomass by 25–75%. The effects of N addition were stronger at other sea levels, but responses at those marsh surface elevations were species-specific. In a scenario of a 10-cm sea level rise, N addition increased total AG biomass 85–570% above biomass of similarly inundated unfertilized mesocosms. This strong response was driven almost entirely by the response of *S. americanus*, which

at a 10-cm sea level rise increased its biomass 150–533% in response to N addition. In mesocosms that mimicked a 15- or 35-cm increase in marsh elevation above sea level (as can occur in a highly productive marsh where productivity + accretion > decomposition + export), total AG biomass increased only 15–95%. This community response was driven by the response of *S. patens*, which at a 15- to 35-cm marsh elevation increase responded to nitrogen addition with 55–145% increases in AG biomass ([Langley et al., 2013](#)). These responses reflect the tolerance of these plants for inundation by tides and suggest that N addition may increase the productivity only of plants growing squarely within the range of their physiological tolerance.

Several other studies have evaluated N addition levels over 1,000 kg N/ha/yr; in all cases, N addition increased biomass, but the high levels of experimental N addition exponentially exceed N loading from deposition, limiting the scope of inference from this literature ([Anisfeld and Hill, 2012](#); [Nelson and Zavaleta, 2012](#); [Ryan and Boyer, 2012](#)).

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#### 11.4.2 Mangrove

Mangrove ecosystems are ecologically and economically important because they provide habitat not just to a diversity of resident species but also serve as nurseries to the juvenile lifestages of many marine fish species. As slow-growing tree species, mangroves are rarely destructively sampled in order to estimate productivity and aboveground biomass. The mangroves at Indian River Lagoon, FL are the site of several nitrogen addition experiments. [Whigham et al. \(2009\)](#) added 100 kg N/ha/yr to plots of dwarf *Avicennia germinans*, black mangrove, which increased productivity by increasing the number of new branches 150% above control plots.

In a long-term (since 1997) N addition experiment that added approximately 11,200 kg N/yr to each tree, growth rate of *Rhizophora mangle*, quantified by measuring shoot elongation rates increased 290% in the shoreline fringe zone and increased 1,340% in the interior scrub zone ([Feller et al., 2009](#)). At Merritt Island National Wildlife Refuge, N addition of 1,400 kg N/ha/yr in the ecotone where mangroves and cordgrasses grow in competition increased *A. germinans* seedlings' production of new leaves by 42%, which increased total leaf biomass by 72% over unamended trees ([Simpson et al., 2013](#)) and altered above- and below-ground stoichiometry (see [Appendix 11.5.2](#)).

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#### 11.4.3 Freshwater Tidal Marsh

In a freshwater tidal marsh on the Tchefuncte River, LA, [Graham and Mendelssohn \(2010\)](#) conducted an N loading experiment that added 50, 200, or 1,200 kg N/ha/yr to a

plant community dominated by *Sagittaria lancifolia*, *Eleocharis fallax*, and *Persicaria punctata* (formerly *Polygonum punctatum*). The aboveground net primary productivity of the community increased with increasing N in a negative quadratic function, with Aboveground Net Primary Productivity (ANPP) not increasing above 200 kg N/ha/yr ([Graham and Mendelsohn, 2010](#)).

At the Altamaha River Estuary, GA, N addition experiments were conducted in tidal freshwater marshes dominated by giant cutgrass *Zizaniopsis miliacea*. Addition of 500 kg N/ha/yr increased aboveground biomass 1.4–3.8 times control biomass in the 2nd through 5th years of fertilization ([Ket et al., 2011](#); [Frost et al., 2009](#)). A nitrogen experiment conducted in estuarine marshes and swamps on the Nanticoke River in the Chesapeake Bay found that while an added load of 670 kg N/ha/yr did not significantly change total herbaceous plant community aboveground biomass, it did increase biomass of the invasive *Typha* spp. by 47% ([Baldwin, 2013](#)). There are several other new studies on the effects of N loading on aboveground biomass of freshwater tidal ecosystems; however, the addition rates are greater than 500 kg N/ha/yr.

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#### 11.4.4 Intermittent Wetland

An N addition study was established in an alpine meadow, which is also an intermittent wetland on the Tibetan Plateau. N addition of 30 kg N/ha/yr increased ANPP of the graminoid and herbaceous plant community by 11.5% ([Wang et al., 2017c](#)), which also affected C and N fluxes of the system (see [Appendix 11.3](#)).

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#### 11.4.5 Bog and Fen

In Sphagnum-dominated ombrotrophic bogs, higher N deposition resulted in higher tissue N concentrations and greater NPP ([Aldous, 2002a](#)), but lower bulk density. A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increasing linearly with N deposition; however, in later years of the study, the rate had begun to slow, indicating limited capacity for N to stimulate accumulation ([Turunen et al., 2004](#)). A study of European bogs under a deposition gradient of 2 to 24 kg N/ha/yr found that gross primary productivity and net carbon uptake of *Sphagnum fallax* mesocosms were positively correlated with increasing N deposition up to 15 kg N/ha/yr, but that the mesocosm collected from a bog receiving 24 kg N/ha/yr had 40% lower GPP and net C uptake than the mesocosm receiving 15 kg N/ha/yr ([Estop-Aragones et al., 2016](#)). However, there was N stimulation of GPP and net C uptake at deposition levels below 15 kg N/ha/yr when mesocosms were subject to

drought conditions. Inference from this study is limited by sample size; there was only one mesocosm per bog ([Estop-Aragones et al., 2016](#)).

In the Mer Bleue ombrotrophic peat bog, 8 years of N addition at the rate of 16 kg N/ha/yr increased biomass of mosses (*Sphagnum magellanicum*, *Sphagnum capillifolium*, and *Polytrichum strictum*) by 30% of moss biomass in control plots ([Xing et al., 2011](#)).

In oligotrophic bogs in Gogebic County, MI, N addition of 60 kg N/ha/yr increased total plant community productivity by 82% over unamended plot productivity, resulting in 2.6 times as much biomass in fertilized plots as biomass in unamended plots ([Iversen et al., 2010](#)). The plant community trends reflected the responses of the dominant vascular shrub *Chamaedaphne calyculata*, which increased its productivity by 87%, thus increasing its biomass in N addition plots 105% over its biomass in control plots ([Iversen et al., 2010](#)).

In general, vascular plants are able to respond more rapidly to N deposition than are moss species. A stable isotope N addition study in Bourtanger Moor, Germany, showed that grass *Lolium multiflorum* and sedge *Eriophorum vaginatum* responded to increasing N addition of approximately 30–55 kg N/ha/yr with linear increases in aboveground biomass ([Hurkuck et al., 2015](#)). Plant interception of N deposition also varied between species and with size for *L. multiflorum* (see [Appendix 5](#)).

Relative changes in biomass can lead to plant community changes. Model results from [Logofet and Alexandrov \(1984\)](#) suggest 7 kg N/ha/yr is the threshold for an oligotrophic bog to become a mesotrophic fen dominated by trees, as found in the 1993 Oxides of Nitrogen AQCD. In freshwater-rich fens in Gogebic County, MI, N addition of 60 kg N/ha/yr increased productivity of dominant grass *Calamagrostis canadensis*, which increased the species' biomass to 600% over its biomass in unamended fen plots ([Iversen et al., 2010](#)).

In many bogs and fens, N addition increases biomass and then abundance of vascular plants and N-tolerant moss species, while N-sensitive species decline. A study of purple pitcher plant, *Sarracenia purpurea*, growing in bogs across a deposition gradient of 3.4–5.0 kg N/ha/yr in the Adirondack Mountains, NY, identified a threshold for plant response to N ([Crumley et al., 2016](#)), with plant growth depressed 8–21% at deposition levels above 4.1 kg N/ha/yr, and with other negative effects on plant physiology (see [Appendix 11.5.5](#)). In a European mesocosm study of four moss species, elevated N concentrations typical of rainwater in the fen depress growth rates 18% compared to mosses growing in N concentrations typical of the fen groundwater ([Andersen et al., 2016](#)). Additional experimental N loading further decreases growth rate of all four

species. Two rare moss species, with declining abundance over the last 100 years, show high sensitivity to N, with more growth rate variation explained by N addition (18–23%) than for the growth rate in the more common moss species [5–7%; [Andersen et al. \(2016\)](#)].

Recent research has addressed differential responses of bogs and fens to reduced or oxidized forms of N addition. In an Irish fen dominated by peat moss *Sphagnum contortum* and brown moss *Scorpidium revolvens*, 50 kg N/ha/yr was applied as NO<sub>3</sub><sup>-</sup> in one treatment and as NH<sub>4</sub><sup>+</sup> in another treatment ([Paulissen et al., 2016](#)). Reduced N decreased *S. revolvens* biomass 67% compared to control plots, while oxidized N had no measurable effect on *S. revolvens* biomass. *S. contortum* biomass was not affected by reduced or oxidized N additions, although the plant's physiology did change in response to both treatments (see [Appendix 11.5.5](#)).

## 11.4.6 Summary Table

**Table 11-5 Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal high marsh	Addition: 150 kg N/ha/yr as urea S dep = not reported N dep = not reported	At two sites with unrestricted and restricted tidal flow, fertilization increased <i>S. pacifica</i> biomass by 36 and 53%, respectively.	Six sites at Elkhorn Slough, Watsonville, CA	Marsh community dominated by <i>Sarcocornia pacifica</i> , also contained <i>Jaumea carnosa</i> , <i>Frankenia salina</i> , <i>Spergularia salina</i> , <i>Distichlis spicata</i> , and <i>Atriplex californica/triangularis</i>	<a href="#">Goldman Martone and Wasson (2008)</a>
Estuarine salt marsh	Addition: 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr as urea N dep = 3–5 kg N/ha/yr as reported in <a href="#">Tonnesen et al. (2007)</a>	Aboveground biomass (AGB) increases in a linear response to N addition (N <sub>add</sub> , as g N/m <sup>2</sup> /yr), AGB = 0.001 × N <sub>add</sub> + 1.117 (R <sup>2</sup> = 0.58), while biomass regrowth (AGR) increases in a saturating response to N, AGR = -1.16 × e <sup>(-0.01N<sub>add</sub>)</sup> + 1.89.	Morro Bay National Estuary, Carpinteria Salt Marsh Reserve, Tijuana River Reserve Estuary, CA	<i>Salicornia depressa</i> ( <i>Salicornia virginica</i> ) stands	<a href="#">Vivanco et al. (2015)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	Nitrate and phosphate dissolved in tidal inflows to raise aqueous NO <sub>3</sub> <sup>-</sup> concentrations to 70–100 μM and raise PO <sub>4</sub> <sup>3-</sup> to 5–7 μM. Background load in tides: 5 μM NO <sub>3</sub> <sup>-</sup> , 1 μM PO <sub>4</sub> <sup>3-</sup> . N dep = not reported S dep = not reported	Vascular plant shoot biomass increased 16%, shoot specific mass increased 9%.	Plum Island Estuary, MA	Primary tidal creeks with <i>Spartina alterniflora</i> in low marsh along creeks, and <i>Spartina patens</i> in high marsh platforms	<a href="#">Deegan et al. (2012)</a>
Salt marsh	Addition of nitrate dissolved in incoming tide 2011–2012, addition of N at 70–100 μM NaNO <sub>3</sub> <sup>-</sup> in tide for added load of 620–1,200 kg N/ha/yr in low marsh and 70–140 kg N/ha/yr in high marsh Ambient deposition = not specified	Low marsh <i>S. alterniflora</i> in enriched creeks received an additional N load of 1,200 kg N/ha/yr in 2011. That year, N addition increased shoot-specific mass 12% above <i>S. alterniflora</i> in reference creek plots. Low marsh <i>S. alterniflora</i> in enriched creeks received an additional N load of 620 kg N/ha/yr in 2012. That year, N addition increased shoot-specific mass 3%. High marsh <i>S. alterniflora</i> and <i>D. spicata</i> in enriched creeks received an additional N load of 140 kg N/ha/yr in 2011. N addition increased <i>S. alterniflora</i> shoot-specific mass 14%. In <i>D. spicata</i> , N addition increased shoot-specific mass 8%.	Plum Island Sound Estuary, MA	<i>Spartina alterniflora</i> , <i>Distichlis spicata</i> , and <i>Spartina patens</i> (high marsh); <i>Spartina alterniflora</i> (low marsh)	<a href="#">Johnson et al. (2016a)</a>
Estuarine marsh	Addition: 1,337 kg N/ha/yr as urea. S dep = not reported N dep = not reported	In <i>S. pacifica</i> , biomass increased 54–185% across habitats.	China Camp State Park, CA	<i>Sarcocornia pacifica</i> dominant (C3 succulent shrub), <i>Distichlis spicata</i> (C4 grass), and <i>Jaumea carnosa</i> (C3 semisucculent forb)	<a href="#">Ryan and Boyer (2012)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	Addition: 3,000 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> S dep = not reported N dep = not reported	AG biomass increased 28 and 216% in successive summers, and increased shoot-to-root ratio 249%.	Elkhorn Slough, Monterey Bay, CA	<i>Sarcocornia pacifica</i> dominant, <i>Distichlis spicata</i> , <i>Frankenia salina</i> , and <i>Jaumea carnosa</i>	<a href="#">Nelson and Zavaleta (2012)</a>
Coastal salt marsh	230, 465, 930, 1,860, or 3,720 kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> S dep = not reported N dep = not reported	AG biomass increased linearly with N load (regression not given). Aboveground live biomass increased 122, 124, and 141% in response to 930, 1,860, and 3,720 kg N.	LUMCON, Cocodrie, LA	<i>Spartina alterniflora</i>	<a href="#">Darby and Turner (2008)</a>
Coastal salt marsh	1,050 kg N/ha/yr (low) as NaNO <sub>3</sub> , 2,100 kg N/ha/yr (medium) as NH <sub>4</sub> NO <sub>3</sub> or NaNO <sub>3</sub> , 4,200 kg N/ha/yr (high) as NH <sub>4</sub> NO <sub>3</sub> in same plots in over several years S dep = not reported N dep = not reported	ANPP increased by 132% in low, 130% in medium, and 120% in high N treatments.	Hoadley Creek Marsh, Guilford, CT	<i>Spartina alterniflora</i>	<a href="#">Anisfeld and Hill (2012)</a>
Estuarine salt marsh	Addition: 250 kg N/ha/yr S dep = not reported N dep = not reported	<i>S. americanus</i> aboveground biomass decreased by 19 and 45% in the 3rd and 4th yr, respectively. Biomass of <i>S. patens</i> and <i>D. spicata</i> increased 129% in the 4th yr over initial fertilized C4 biomass.	Kirkpatrick Marsh, MD (measured in 3rd and 4th yr, 2008–2009)	<i>Schoenoplectus americanus</i> (C3), <i>Spartina patens</i> (C4), and <i>Distichlis spicata</i> (C4)	<a href="#">Langley and Magonigal (2012, 2010)</a>
Estuarine salt marsh	Addition: 250 kg N/ha/yr S dep = not reported N dep = not reported	In the first two growing seasons, fertilization increased aboveground biomass in the second season by 57%.	Kirkpatrick Marsh, MD (measured in 1st and 2nd years, 2006–2007)	<i>Schoenoplectus americanus</i> , <i>Spartina patens</i> , and <i>Distichlis spicata</i>	<a href="#">Langley et al. (2009)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Estuarine marsh	NH <sub>4</sub> Cl solution injected into mesocosm peat at root level, 250 kgN/ha, increases N by 40% above annual average background concentration Deposition not reported	At current sea level, N addition increased total AG biomass by 25–75% in 1st yr. With sea level rise 10 cm, <i>S. americanus</i> AG biomass increases 150–230% in 1st yr, 110–533% in 2nd yr. Total AG biomass at 10 cm increased 85–95% in 1st yr, 100–570% in 2nd yr. At increased marsh elevation (15 and 35 cm above sea level 1st yr, 15 cm 2nd yr), <i>S. patens</i> AG biomass increases 55–145% in 1st yr, 60–90% in 2nd yr. Total AG biomass at these elevations increased 15–95% in 1st yr, 30–35% in 2nd yr.	Kirkpatrick Marsh, MD	Factorial mesocosm experiment with varying sea levels: 35- or 15-cm rise in marsh elevation; current sea level; 10-, 20-, or 30-cm rise in sea level. Mesocosms planted with 2 rhizomes <i>Schoenoplectus americanus</i> and 10 stems <i>Spartina patens</i> ; harvested each year.	<a href="#">Langley et al. (2013)</a>
Mangrove/marsh ecotone	Addition: 1,400 kg N/ha/yr S dep = not reported N dep = not reported	Mangrove leaf production increased by 42% and leaf biomass increased by 72%.	Merritt Island National Wildlife Refuge, FL (Impoundment T9)	<i>Avicennia germinans</i>	<a href="#">Simpson et al. (2013)</a>
Mangrove	Addition: 1,400 kg N/ha/yr S dep = not reported N dep = not reported	Fertilization increases growth rate (shoot elongation) by 290% in the fringe zone and by 1,340% in the scrub zone.	Indian River Lagoon, FL (impoundment MI23)	<i>Rhizophora mangle</i>	<a href="#">Feller et al. (2009)</a>
Mangrove	100 kg N/ha/yr	N addition increased the number of new branches 150% in <i>Avicennia</i> .	Indian River Lagoon, FL (impoundment SLC-24)	<i>Avicennia germinans</i> and associated sediments	<a href="#">Whigham et al. (2009)</a>
Estuarine tidal marsh	Addition: 670 kg N/ha/yr S dep = not reported N dep = not reported	<i>Typha</i> spp. biomass increased by 95%.	Nanticoke River, MD and DE	Plant community	<a href="#">Baldwin (2013)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Freshwater estuarine marsh	50, 200, or 1,200 kg N/ha/yr as Nutralene methylene urea S dep = not reported N dep = not reported	Community ANPP increased with medium N load ( $N_{add}$ as kg N/ha/yr), $ANPP = -0.00165 \times N_{add}^2 + 2.5091 \times N_{add} + 1270.3$ .	Tchefuncte River, Madisonville, LA	Oligohaline plant community dominated by <i>Sagittaria lancifolia</i> , <i>Eleocharis fallax</i> , and <i>Polygonum punctatum</i>	<a href="#">Graham and Mendelssohn (2010)</a>
Freshwater tidal marsh	500 kg N/ha/yr as $NH_4Cl$ or urea	N addition increased aboveground biomass by 140% and plant height by 32% in <i>Z. miliacea</i> . N addition decreased leaf [N] by 99% and leaf [P] by 25%.	Altamaha River, GA	<i>Zizaniopsis miliacea</i>	<a href="#">Frost et al. (2009)</a>
Freshwater marsh	500 kg N/ha/yr as $NH_4Cl$ or urea N dep = not reported S dep = not reported	In <i>Z. miliacea</i> , aboveground biomass increased by 2.9–3.8x the control, as leaf number increased 52% and plant height increased 25–40%.	Altamaha Estuary, GA	<i>Zizaniopsis miliacea</i> , <i>Pontederia cordata</i> , and <i>Sagittaria lancifolia</i>	<a href="#">Ket et al. (2011)</a>
Seasonal wetland, alpine meadow	Addition: 30 kg N/ha/yr Ambient deposition = 8.7 to 13.8 kg N/ha/yr	N addition increased ANPP 11.5% across average (3 cm above soil surface) and lowered (20 cm below soil surface) water table levels.	Mesocosms at Luanhaizi wetlands, Tibetan Plateau	<i>Carex pamirensis</i> , <i>Carex atrofusca</i> , <i>Hippuris vulgaris</i> , <i>Triglochin palustris</i> , and <i>Heleocharis</i> spp.	<a href="#">Wang et al. (2017c)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Ambient deposition of NO <sub>x</sub> , NH <sub>y</sub> , and SO <sub>x</sub> : 1.95–24.07 kg N/ha/yr and 3.18–36.90 kg S/ha/yr Deposition estimates from EMEP (European Monitoring and Evaluation Programme)-based IDEM (Integrated Deposition Model) from <a href="#">Pieterse et al. (2007)</a>	N and S deposition rates are correlated across these sites ( $r = 0.87$ ). Gross primary productivity (GPP, as g C/m <sup>2</sup> /day) increased with N deposition (N <sub>dep</sub> , as kg N/ha/yr) up to 15 kg N/ha/yr: $GPP = 1.262 + 0.219N_{dep}$ ; $R^2 = 0.65$ . There was no relationship between N deposition and GPP during drought and post-drought periods. Net carbon uptake by <i>Sphagnum</i> (C <sub>uptake</sub> , as g C/m <sup>2</sup> /day) was positively correlated with N deposition (N <sub>dep</sub> , as kg N/ha/yr) up to levels of 15 kg/ha/yr: $C_{uptake} = 0.76 + 0.155 \times N_{dep}$ ; $R^2 = 0.52$ . There was no relationship between N deposition and GPP during drought and post-drought periods. Respiration, GPP, and net carbon uptake were all 40% lower in the mesocosm from the 24 kg N/ha/yr than from the 15 kg N/ha/yr site.	Lab incubations of 14 <i>Sphagnum</i> mesocosm collected in saturated hollows in European bogs: U.K. and Ireland (n = 9), Poland (n = 4), and Slovakia (n = 1). Mesocosms were maintained at a high water table (0–5 cm depth) for 40 days, then were subject to drought for 100 days, then were rewetted to high water table (0–5 cm depth) for 200 days.	<i>Sphagnum fallax</i>	<a href="#">Estop-Aragones et al. (2016)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KHPO <sub>4</sub> )	In high NPK, shrub biomass increased, with 40% higher leaf biomass, and 86% higher woody biomass.	Mer Bleue Bog, Ontario, Canada	Bog plant community: dwarf shrub species and mosses <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Juutinen et al. (2010)</a>
Ombrotrophic peat bog	Addition: 16 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> N dep = 8 kg N/ha/yr as quantified by <a href="#">Turunen et al. (2004)</a>	N addition decreased aboveground moss biomass by 30%.	Mer Bleue Bog, Ontario, Canada (measured 2007)	Bog plant community: dwarf shrub species and mosses <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Xing et al. (2011)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Rich fen and ombrotrophic bog	60 kg N/ha/yr as urea S dep = not reported N dep = not reported	In <i>Chamaedaphne calyculata</i> , fertilization increased productivity by 87% and biomass by 105%. In <i>Calamagrostis canadensis</i> , biomass increased 600% over unamended fen plots. The entire plant community responded to N addition with increases in productivity (82%) and biomass (160%).	Gogebic County, MI	Plant community consisting of <i>Sphagnum</i> spp., ericaceous shrubs, dominant vascular plants <i>Carex oligosperma</i> and <i>Chamaedaphne calyculata</i>	<a href="#">Iversen et al. (2010)</a>
Rich fen	Addition: two aqueous treatments: groundwater (0.18 mg N/L, 0.02 mg P/L, 90 mg Ca <sup>2+</sup> /L, pH = 8.0–8.6) and rainwater (0.58–0.98 mg N/L, 0.03 mg P/L, pH 6.5–7.0) Three N addition levels dissolved in each aqueous treatment: no additional N (low), 1 mg N/L added (medium), 3 mg N/L added (high) Ambient deposition = not specified, but rainwater N is 220–440% higher than groundwater N	The daily relative growth rate (RGR) of all four species decreases 18% under rainwater rather than under groundwater. The switch to rainwater accounted for 10% of RGR variation in <i>C. cuspidata</i> , 7% of RGR variation in <i>H. vernicosus</i> , and 32% of RGR variation in <i>P. squarrosa</i> . RGR of all four species decreased by 12% under medium N addition and decreased 24% under high N addition. N addition accounted for 4.6% of RGR variation in <i>B. pseudotriquetrum</i> , 6.7% of RGR variation in <i>C. cuspidata</i> , 18% of RGR variation in <i>H. vernicosus</i> , and 23% of RGR variation in <i>P. squarrosa</i> .	Mesocosms constructed from sand, peat, and chalk, with all four species added to each mesocosm, fully factorial design: two aqueous treatments × 3N addition levels × 3P addition levels	Two bryophyte species common in rich fens in Denmark: <i>Calliergonella cuspidata</i> and <i>Bryum pseudotriquetrum</i> , and two bryophyte species that have been declining in abundance over the past 100 yr: <i>Hamatocaulis vernicosus</i> and <i>Paludella squarrosa</i>	<a href="#">Andersen et al. (2016)</a>

**Table 11-5 (Continued): Nitrogen loading effects upon production and biomass.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic bog	Ambient deposition = 3.4–5.0 kg N/ha/yr across the region, divided for this study into the following ranges: 3.4–3.6, 3.8–4.1, 4.4–4.9, 4.9–5.0 kg N/ha/yr	Pitcher plant growth increased with increasing N deposition between 3.4 and 4.1 kg N/ha/yr. Plant growth measured as plant diameter, which correlates with pitcher opening width, pitcher length, keel width, and total pitcher width. All traits positively correlated with increasing N deposition between 3.4 and 4.1 kg N/ha/yr. Deposition above 4.1 kg N/ha/yr decreased pitcher plant growth by 8–21% as measured by plant diameter (compared to plant diameter measured between 3.8 and 4.1 kg N/ha/yr). Pitcher plant growth was lower at higher deposition levels of 4.4–5.0.	Adirondack Mountains, NY, (11 sites)	<i>Sarracenia purpurea</i>	<a href="#">Crumley et al. (2016)</a>
Calcareous, rich fen	Addition = 50 kg N/m <sup>2</sup> /yr as NO <sub>3</sub> <sup>-</sup> or 50 kg N/m <sup>2</sup> /yr as NH <sub>4</sub> <sup>+</sup> .  Ambient deposition = 7–10 kg N/m <sup>2</sup> /yr, based on <a href="#">Aherne and Farrell (2002)</a>	NH <sub>x</sub> decreased <i>Scorpidium</i> living biomass 67%.	Scragh Bog, central Ireland	<i>Scorpidium revolvens</i> and <i>Sphagnum contortum</i>	<a href="#">Paulissen et al. (2016)</a>

AG = aboveground; ANPP = aboveground net primary productivity; CO<sub>2</sub> = carbon dioxide; dep = deposition; ha = hectare; kg = kilogram; N = nitrogen; NaNO<sub>3</sub> = sodium nitrate; NH<sub>4</sub>Cl = ammonium chloride; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; S = sulfur; yr = year.

## 11.5 Plant Stoichiometry and Physiology

N addition alters the stoichiometry of plant tissue. When inorganic N stores increase in the soil matrix due to N deposition, one of the first plant responses may be to increase N uptake and storage. As a result, the concentration of N in plant tissue (often reported as [N] or %N) is one of the earliest indicators of changing bioavailability of N within an ecosystem. Plants may store the additional N in proteins, use it for further growth if other nutrients and abiotic conditions are not limiting, or curtail growth of belowground,

nutrient-acquiring roots. Plant tissue [N] also has important implications for consumers, as many insect and vertebrate consumers preferentially graze on high N tissues, and plant [N] can also affect decomposition rates. In systems in which N availability increases while other nutrient cycles are unaltered, such as in nutrient-poor bogs, nutrient imbalances develop and plant [K] and [P] decline. This section will consider the effects of N deposition upon plant tissue [N] as a sensitive indicator of plant response, as well as the effects of N deposition upon other elements in plant tissue, which would indicate more detrimental effects of increased N availability upon plant growth.

Plant stoichiometry theory considers the balance of multiple chemical elements in living tissues. The stoichiometry of plant tissue is often connected to its physiological function. Most new studies on physiology and stoichiometry are for bogs and freshwater marshes. There are a few studies on saltwater marshes and fens. The new literature is summarized in the following sections.

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### 11.5.1 Salt Marsh

There are several studies on the effects of N addition on salt marsh plant stoichiometry. In three California salt marshes, N addition at seven different levels (0, 100, 200, 400, 800, 1,600, and 3,200 kg N/ha/yr) showed that the succulent forb *Salicornia depressa* increased leaf %N in a saturating response, with no statistically significant increases in response above 800 kg N/ha/yr ([Vivanco et al., 2015](#)). There are several N addition studies at addition levels greater than 500 kg N/ha/yr [([Baldwin, 2013](#); [Nelson and Zavaleta, 2012](#); [Ryan and Boyer, 2012](#)); see [Table 11-6](#)].

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### 11.5.2 Mangrove

The N addition levels in all new studies on mangroves are generally higher (greater than 500 kg N/ha/yr) than would be relevant to the effects of N deposition. As perennial plants, mangroves respond to increasing N loads by altering tissue storage of N as well as by increasing productivity ([Appendix 11.4.3](#)). In salt-marsh mangrove ecotone, *Avicennia germinans* seedlings responded to addition of 1,400 kg N/ha with 62% higher leaf tissue %N, as well as increased N in belowground biomass ([Simpson et al., 2013](#)). In more mature mangrove ecosystems receiving higher N loads (11,200 kg N/yr per tree), N addition decreased the efficiency with which *Rhizophora mangle* resorbed N from senescing leaves by 7%, which resulted in 39% higher %N in senesced leaves than in unfertilized trees ([Feller et al., 2009](#)).

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### 11.5.3 Freshwater Marsh

N addition is documented to alter plant stoichiometry and physiology in freshwater marshes. This topic was not addressed in the 2008 ISA. Five new studies have been published since 2008.

In freshwater marsh mesocosms planted with wetland obligate graminoid *Bolboschoenus maritimus* [cosmopolitan bulrush, multiple synonyms including *Schoenoplectus maritimus*, listed as Special Concern by Connecticut and Rhode Island, and as endangered by Illinois, New Jersey, and New York; ([USDA, 2015b](#))] N addition increased N stored in plant tissues. Aboveground tissue %N increased 31–114% of %N in control plants with increasing N loads (32, 65, 108 kg N/ha/yr) added in fall 2009, and increased 33–67% with increasing N loads (59, 119, 198 kg N/ha/yr) added in the summer and fall of 2010 ([Duguma and Walton, 2014](#)). N addition also increased tissue N in belowground tissues. In fall 2009, addition of 32 kg N/ha/yr did not affect BG %N, but the addition of 65 kg N/ha/yr increased BG %N by 26%, and the addition of 108 kg N/ha/yr increased BG %N by 126 to 1.29% tissue N. In summer and fall 2010, the addition of 119 and 198 kg N/ha/yr increased BG %N 47 and 37%, with a tissue N value of 1.34 and 1.25% N, respectively ([Duguma and Walton, 2014](#)).

In tidal freshwater marshes of the Tchefuncte River, LA, experimentally added N loads of 50, 200, 1,200 kg N/ha/yr did not alter the relative dominance of *Sagittaria lancifolia* but did alter N storage in plant tissues. Plant tissue N (mg N/g leaf) increased 0.02 mg for every 10 kg N/ha/yr of N load. The change in plant N shifted the N:P ratio of plant tissue, 0.04 N:1 P increase for every additional 10 kg N/ha/yr ([Graham and Mendelssohn, 2010](#)). N addition also decreased the efficiency with which plants resorbed nutrients from senescing leaves for use in future growth. N addition decreased N resorption efficiency (%) by 0.1% for every additional 10 kg N/ha/yr, and decreased P resorption efficiency (%) by 0.09% for every additional 10 kg N/ha/yr ([Graham and Mendelssohn, 2010](#)).

In freshwater marsh mesocosms at the Smithsonian Environmental Research Center (SERC), native and introduced haplotypes of graminoid *Phragmites australis* were grown in a nitrogen addition experiment. The species *P. australis* includes haplotypes (genetic lineages) native to North America, as well as invasive haplotypes capable of forming monocultures that exclude native plant species. Nitrogen fertilization of 250 kg N/ha/yr increased the construction cost (grams of glucose invested in synthesizing a gram of biomass) of leaves for the native F haplotype of *P. australis* by 5% ([Caplan et al., 2014](#)). Nitrogen addition did not significantly alter construction costs of the invasive M haplotype [listed as a noxious weed, banned invasive, or plant pest by Alabama, Connecticut, Massachusetts, South Carolina, Vermont, and Washington; ([USDA, 2015b](#); [Caplan et al., 2014](#))]. These results suggest that N enrichment favors the invasive

haplotype over the native haplotype and may facilitate invasion; this is of concern because *P. australis* tolerates brackish conditions and invades North American wetlands all along the freshwater-freshwater tidal-salt marsh continuum.

In tidal freshwater marshes in the Altamaha River Estuary, GA, N addition of 500 kg N/ha/yr in the 2nd year stimulated productivity ([Appendix 11.4.2](#)) to the extent of diluting N and phosphorus (P) in plant tissues, decreasing leaf N (%) by 22%, and decreasing leaf P ( $\mu\text{g/g}$ ) by 25% ([Frost et al., 2009](#)). In the later years of the experiment, N addition increased leaf N (%) above control plot leaf N by 25–43% ([Ket et al., 2011](#)), and this increase altered leaf nutrient ratios, decreasing leaf C:N 18–28% and increasing leaf N:P 25–61% over leaves from control plots. The increases in productivity combined with alterations in leaf tissue nutrients altered total nutrient pools stored in aboveground biomass, increasing total aboveground N by 236% and total aboveground P by 169% ([Ket et al., 2011](#)).

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#### 11.5.4 Riparian Wetland

In developing riparian forests at Bonanza Forest LTER, Alaska, N addition of 100 kg N/ha/yr increased leaf N 10% in tree species *Alnus incana* ssp. *tenuifolia* growing in late successional riparian forest, but not in recently colonized or midsuccessional sand bars ([Ruess et al., 2013](#)). N addition also altered *A. incana* ssp. *tenuifolia*'s internal P cycling efficiency, decreasing resorption of P from senescing leaves by 21% in midsuccessional forest ([Ruess et al., 2013](#)).

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#### 11.5.5 Bog and Fen

Carnivorous plants grow optimally under low-N conditions, and many are limited in their distribution to bogs and fens. Recent research suggests that N deposition can disrupt their N-acquisition strategy of digesting the invertebrates they trap. Purple pitcher plants (*Sarracenia purpurea*) were measured and sampled across a narrow N deposition gradient (3.4–5.0 kg N/ha/yr) across bogs in the Adirondack Mountains ([Crumley et al., 2016](#)). Plant architecture, plant tissue N, and stable isotope N data suggested a growth and carnivory optima for plants in bogs receiving 3.8–4.1 kg N/ha/yr. At higher deposition rates of 4.4–4.9 kg N/ha/yr, there was no change in plant tissue N, but there were negative effects upon growth (see [Appendix 11.4.4](#)) and a 40% decrease in carnivory ([Crumley et al., 2016](#)). The wetland obligate pitcher plants have previously been shown to experience detrimental impacts of N deposition at physiological and population levels [([Gotelli and Ellison, 2002](#)) in 2008 ISA]. [Bott et al. \(2008\)](#) reciprocally

transplanted *Sarracenia purpurea* ssp. *purpurea* [listed as exploitably vulnerable in New York, threatened in New York, and endangered in Georgia and Illinois; ([USDA, 2015b](#))] between ombrotrophic Sapa bog and the rich Cedarburg fen, both in Wisconsin. Leaf %N was positively and linearly correlated with surface water  $\text{NO}_3^-$  concentration at the site where the plants were transplanted (leaf %N =  $0.9581 + 0.1667 \times \mu\text{M NO}_3^-$ ), confirming Gotelli's designation of pitcher plants as sensitive indicators of N deposition ([Bott et al., 2008](#)).

A deposition-induced shift away from insectivory can lead to deficiency in other nutrients for carnivorous plants. Across a natural deposition gradient in Sweden, the carnivorous plant *Drosera rotundifolia* experienced significant declines of insectivory-derived N at 3.81 and 11.30 kg N/ha/yr ([Millett et al., 2012](#)). Across a broader deposition gradient of European bogs (0.5–27.0 kg N/ha/yr), *D. rotundifolia* insectivory declined in a linear relationship with increasing N deposition, and plants experienced increasing P limitation as evidenced by increasing N:P tissue concentrations ([Millett et al., 2015](#)). These studies support previous research showing negative effects of N deposition upon *D. rotundifolia* populations (see [Appendix 11.7](#)).

Research conducted in European fens and reviewed in the 2008 ISA has shown that N addition favors the growth of grass and sedge species over peat-forming moss species ([U.S. EPA, 2008a](#)). New research suggests that North American sedge and grass species experience positive effects of N loading, and that their responses can alter N dynamics of North American bogs and fens. In a bog in Gogebic County, MI, where sedge *Carex oligosperma* [listed as Special Concern in Connecticut, threatened in Ohio and Pennsylvania, and endangered in Illinois, Massachusetts, and North Carolina; ([USDA, 2015b](#))] was dominant in the plant community, the obligate wetland species responded to 60 kg N/ha/yr addition by decreasing N use efficiency by 89% and N response efficiency by 84% ([Iversen et al., 2010](#)). The response of the sedge altered ecosystem responses in the bog, increasing plant community N uptake by 125% over uptake in unamended plots ([Iversen et al., 2010](#)). These changes increased N stored in biomass pools 171% above biomass N in control plots and increased the concentration of N in vascular plant tissues by 19% ([Iversen et al., 2010](#)). Similarly, the grass *Calamagrostis canadensis* [classified as wetland facultative or obligate in different U.S. regions by ([USDA, 2015b](#))], which was dominant in a closely adjacent rich fen, responded to N addition of 60 kg N/ha/yr by increasing N uptake. Along with increased productivity ([Appendix 11.4.5](#)), this response expanded the total pool of N stored in biomass by 300% ([Iversen et al., 2010](#)). A similar mesocosm study of bogs in western Europe across a deposition gradient of 2 to 47 kg N/ha/yr found that at the highest deposition level, plant tissue N of grasses and sedges was 120% higher than grasses and sedges at the lowest deposition level ([Zajac and Blodau, 2016](#)).

In the same set of experiments in Gogebic County, MI, woody plants increased their productivity in response to N loading, but their efficiency in using N declined, suggesting a mechanism by which N loading lowers N retention of bogs and fens ([Appendix 11.3.1.5](#)). The wetland obligate shrub *Chamaedaphne calyculata* (threatened in Illinois and Maryland) responded to 60 kg N/ha/yr addition by increasing plant N uptake by 75%, which increased productivity ([Appendix 11.4](#)) and increased the pool of N stored in aboveground biomass by 100%. However, nitrogen addition decreased the efficiency of photosynthesis and metabolism in *C. calyculata*, as N use efficiency was 81% lower and N response efficiency was 91% lower in fertilized plots ([Iversen et al., 2010](#)). In an intermediate fen, tree species *Alnus incana* ssp. *rugosa*, speckled alder [hereafter referred to as *A. rugosa*, endangered in Illinois; ([USDA, 2015b](#))], responded to an added 60 kg N/ha/yr with a 45% decline in N response efficiency [net primary productivity relative to available soil N; ([Iversen et al., 2010](#))]. A European study of mesocosms collected across a deposition gradient of bogs found that 12 kg N/ha/yr decreased N retention of shrub species, and 47 kg N/ha/yr increased ecosystem total N stored in shrub biomass ([Zajac and Blodau, 2016](#)).

A long-term fertilization experiment at the Mer Bleue Bog in Ontario, Canada, has documented the effect of more than a decade of elevated N inputs on the same species in an ombrotrophic peat bog. *Chamaedaphne calyculata* responded to 32 g N/ha/yr by increasing P resorption by 42%, and responded to 64 kg N/ha/yr by increasing P resorption by 33% ([Wang et al., 2014b](#)). N Plots that had received 64 kg N/ha/yr for 6 years decreased leaf calcium 22% ([Wang et al., 2014b](#)), and leaf Ca was 34% lower in *C. calyculata* from plots that received 9 years of 16 kg N/ha/yr than in leaves from control plots ([Bubier et al., 2011](#)). An observational study across a deposition gradient in the Adirondack Mountains found effects on *C. calyculata* stoichiometry at much lower deposition levels. There was a 27% increase in plant tissue N in *C. calyculata* when deposition increased from a range of 3.4–3.6 kg N/ha/yr to 4.9–5.0 kg N/ha/yr ([Crumley et al., 2016](#)).

After 9 years of N addition at Mer Bleue, leaf C:N ratios were 15% lower in *C. calyculata* leaves that received 16 kg N/ha/yr than in leaves from control plots, with dependent increases in leaf alanine and  $\gamma$ -aminobutyric acid (GABA; see [Table 11-6](#) for equations), amino acid pools that indicate N saturation in the plant ([Bubier et al., 2011](#)). Leaf aluminum concentrations were 44% lower in these leaves than in leaves from control plots ([Bubier et al., 2011](#)). In plots that received 64 kg N/ha/yr, there was no change in leaf C:N, but there were increases in proteins indicative of increased plant N uptake. *C. calyculata* leaf total chlorophyll was 84% higher than in control leaves, and there were 115% increases in leaf alanine and 94% increases in leaf GABA, indicating N saturation. Leaf manganese was 45% lower in these leaves than in control plot *C.*

*calyculata*, indicating that shrub productivity may be limited by micronutrients in a N-fertilized bog ([Bubier et al., 2011](#)).

At Mer Bleue, the wetland obligate shrub *Rhododendron groenlandicum* (synonym: *Ledum groenlandicum*, rare in Pennsylvania, threatened in Connecticut, and endangered in Ohio) responded to 4 years of 64 kg N/ha/yr with a 16% increase in leaf N and a dependent increase in leaf glutamic acid ([Bubier et al., 2011](#)). Leaf P declined by 54% of control leaf P after 4 years of 64 kg N/ha/yr ([Bubier et al., 2011](#)). After 7 years of 64 kg N/ha/yr, *R. groenlandicum* responded with a 23% decrease in leaf magnesium (Mg) and a 186% decrease in Mg resorption from senescing leaves ([Wang et al., 2014b](#)), indicating increasing limitation by magnesium, which could negatively affect photosynthesis and enzyme activity within the plant. After 7 years of 32 and 64 kg N/ha/yr addition, *R. groenlandicum* increased P and K resorption from senescing leaves; P resorption increased 12–12.2 times the rate of resorption in leaves from unamended plots, and increased K resorption by 92–123% ([Wang et al., 2014b](#)).

In the same experiment, after 7 years, N addition shifted the seasonality of gross photosynthesis, with addition of 64 kg N/ha/yr reducing C uptake 29–45% of control rates in early summer (May–July), and increasing C uptake 25% above rates in control plots in September ([Larmola et al., 2013](#)). After 9 years of 16 kg N/ha/yr addition, *R. groenlandicum* exhibited altered leaf physiology, doubling maximum carboxylation capacity ( $V_{\text{cmax}}$ ) on a per-leaf-mass basis ([Bubier et al., 2011](#)). There was no significant effect of 4 years of 64 kg N/ha/yr upon  $V_{\text{cmax}}$  measured during the same growing season (2008). The study authors posited that plants responded to this level of N availability with a stress response, allocating N to storage in glutamic acid ( $\text{nmol glutamic acid/g leaf} = 37.914 + 252.2 \times \text{leaf \%N}$ ) instead of using it in photosynthetic enzymes ([Bubier et al., 2011](#)).

At Mer Bleue, the wetland facultative shrub *Vaccinium myrtilloides* (designated sensitive in Washington, special concern in Connecticut, threatened in Ohio and Iowa, and endangered in Indiana) responded to nitrogen addition with declines in other leaf nutrients. Leaf calcium declined 23% in response to 9 years of 16 kg N/ha/yr and declined 56% in response to 4 years of 64 kg N/ha/yr ([Bubier et al., 2011](#)), indicating that increasing N will increasingly limit leaf Ca and by extension decrease signaling and structural integrity of plant tissues. Leaf P decreased by 55% after 9 years of 16 kg N/ha/yr and by 68% after 4 years of 64 kg N/ha/yr. Leaf manganese (Mn) decreased 57% under 64 kg N/ha/yr ([Bubier et al., 2011](#)), which could affect photosynthesis or N assimilation because Mn is a component of enzymes involved in these processes. *V. myrtilloides* leaf potassium also declined: 47% in response to 9 years of 16 kg N/ha/yr and 34% in response to 4 years of 64 kg N/ha/yr ([Bubier et al., 2011](#)). Leaf potassium

regulates stomatal movement, activates enzymes, and balances electrical charges associated with ATP production, so K deficiency can decrease photosynthesis and slow growth. Leaf aluminum decreased 45% of control leaf aluminum concentrations in plots receiving 64 kg N/ha/yr for 4 years ([Bubier et al., 2011](#)).

N addition can alter tissue nutrients in nonvascular plants as well. In the Mer Bleue bog, N addition of 32 kg N/ha/yr decreased moss [Ca] by 34%; N addition of 64 kg N/ha/yr increased moss [P] by 39%, and decreased moss [Ca] by 42% ([Wang et al., 2016a](#)). These results are consistent with N addition effects of Ca deficiencies in vascular plants (see above) and ecosystem P limitation (see [Appendix 11.3.2.1.3](#)) within this bog experiment. Surveys of two European bogs located in different mountain ranges found that N deposition altered the stoichiometry of *Sphagnum* moss species. *Sphagnum* tissue K concentrations were lower in samples collected from the high N deposition (20–25 kg N/ha/yr) Jizera Mountains, 64% lower in *S. rubrum* and 62% lower in *S. magellanicum*, than in samples from the lower deposition (12.5 kg N/ha/yr) Jeseníky mountain range. *S. magellanicum* [Mg] was also 45% lower at the high N deposition site than at the lower N deposition site ([Jirousek et al., 2015](#)). [Fritz et al. \(2014\)](#) performed a peat mesocosm study to test how a history of atmospheric N deposition alters the N uptake rates of *Sphagnum magellanicum*, a widely distributed peat-forming species. The researchers collected blocks of living *S. magellanicum* from a pristine bog in Argentina, which received an annual load of 1–2 kg N/ha/yr, and also from a polluted bog in the Netherlands, which received an annual load of 20–30 kg N/ha/yr. Under controlled conditions, nitrogen solutions of 1, 10, or 100  $\mu\text{mol N/L}$  were added to the block. Rates of N uptake were significantly different among bog samples (Argentine or Dutch) for the 10 or 100  $\mu\text{mol}$  solutions, with the pristine (Argentine) *Sphagnum* absorbing nitrogen at 1.4–2.6 times the rate of the uptake rate of the Dutch bog, which receives a higher annual N load ([Fritz et al., 2014](#)). A mesocosm study of four European moss species found that applying rainwater (elevated N and P) rather than groundwater increases moss tissue [N] and [P], while applying additional N in controlled treatments decreases moss tissue [P] ([Andersen et al., 2016](#)). A different European mesocosm study found that *Sphagnum* spp. plant tissue N increased across a N deposition gradient of 2 to 47 kg N/ha/yr, such that C:N ratio declined as a linear function of the natural log of increasing N deposition ([Zajac and Blodau, 2016](#)).

Recent research has addressed differential responses of bogs and fens to reduced or oxidized forms of N addition. In an Irish fen dominated by *Sphagnum contortum* and brown moss *Scorpidium revolvens*, 50 kg N/ha/yr was applied as  $\text{NO}_3^-$  in one treatment and  $\text{NH}_4^+$  in another treatment ([Paulissen et al., 2016](#)). Reduced N forms elicited stronger responses in tissue chemistry for each moss species. In *S. contortum*, oxidized N increased tissue N 29%, tissue P 28%, and concentrations of alanine (a free amino acid

hypothesized to be a mechanism of N storage) 31%; an equivalent addition of reduced N decreased tissue N 13%, tissue K 49%, and dramatically increased (by half to 66 times the control) the concentrations of five free amino acids storing excess N in plant tissue. In the more sensitive species *S. revolvens*, reduced N increased tissue N 76% but decreased tissue K 53%, and increased concentrations of arginine (a free amino acid) 7.3 times concentrations in control plots; these same metrics were unaffected by the equivalent oxidized N treatment (Paulissen et al., 2016). The stronger effects of reduced N on plant chemistry in *S. contortum* than *S. revolvens* may represent species-level differences in N tolerance, as *S. contortum* biomass did not change in response to N addition (see Appendix 11.4.4).

The Whim Bog experiment in Scotland added N as either ammonium or nitrate to simulate wet deposition, which with ambient N deposition of 8 kg N/ha/yr resulted in treatment N loads of 16, 32, and 64 kg N/ha/yr. As in other wetlands, the bog had divergent responses to oxidized and reduced N addition. *Sphagnum capillifolium* plant tissue N and N:P increased in response to increasing oxidized N in a saturating function, but responded to increasing reduced N in a linear function (Chiwa et al., 2016). Reduced N addition also resulted in increasing cation concentrations in pore water, suggesting cation leaching by the moss species as a result of N uptake. These results indicate a stronger effect of reduced N upon *Sphagnum* growth or P limitation, and these physiological changes also affected N cycling and water quality within the bog (see Appendix 11.3.1.5).

## 11.5.6 Summary Table

**Table 11-6 Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	Addition: 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr as urea N dep = 3–5 kg N/ha/yr as reported in <a href="#">Tonnesen et al. (2007)</a>	<i>Salicornia</i> leaf %N increases in a saturating response to added N ( $N_{add}$ , as g N/m <sup>2</sup> /yr), leaf $N = -0.73 \times e^{-0.024 N_{add}} + 2.99$ .	Morro Bay National Estuary, Carpinteria Salt Marsh Reserve, Tijuana River Reserve Estuary, CA	<i>Salicornia depressa</i> ( <i>Salicornia virginica</i> ) stands	<a href="#">Vivanco et al. (2015)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	3,000 kg N/ha/yr as NH <sub>3</sub> NO <sub>3</sub> N dep = not reported S dep = not reported	Plant [N] increased by 224 and 33%, and N pools in AG vegetation increased by 60 and 84% in successive summers.	Elkhorn Slough, Monterey Bay, CA	<i>Sarcocornia pacifica</i> dominant, <i>Distichlis spicata</i> , <i>Frankenia salina</i> , and <i>Jaumea carnosa</i>	<a href="#">Nelson and Zavaleta (2012)</a>
Estuarine salt marsh	1,337 kg N/ha/yr as urea N dep = not reported S dep = not reported	In <i>S. pacifica</i> , tissue N increased 28–46%. <i>D. spicata</i> tissue N increased 19%. <i>J. carnosa</i> tissue N increased by 54%.	China Camp State Park, CA	<i>Sarcocornia pacifica</i> dominant, <i>Distichlis spicata</i> , and <i>Jaumea carnosa</i>	<a href="#">Ryan and Boyer (2012)</a>
Mangrove/salt marsh ecotone	1,400 kg N/ha/yr N dep = not reported S dep = not reported	Mangrove leaf production increased by 42%. Leaf tissue %N increased 62%. Root %N increased 9% and root C:N decreased 25%.	Merritt Island National Wildlife Refuge, FL	<i>Avicennia germinans</i>	<a href="#">Simpson et al. (2013)</a>
Mangroves	No areal rate reported; 11,200 kg N/yr per tree N dep = not reported S dep = not reported	Fertilization increases growth rate (shoot elongation) by 290% in the fringe zone and by 1,340% in the scrub zone. In the fringe zone, fertilization decreases resorption efficiency of N from dying leaves by 7%, resulting in senesced leaves containing 39% more N than control senesced leaves.	Indian River Lagoon, FL	<i>Rhizophora mangle</i>	<a href="#">Feller et al. (2009)</a>
Freshwater marsh	Fall 2009: 32 (low), 65 (medium), 108 (high) kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; summer 2010: 59 (low), 119 (medium), or 198 (high) kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> N dep = not reported S dep = not reported	N addition increased <i>S. maritimus</i> %N of aboveground tissue 31–114% in 2009 and 33–67% in 2010. N addition (medium, high) increased <i>S. maritimus</i> %N of belowground tissue 26–126% in 2009 and 37–47% in 2010.	Mesocosms at UC Riverside research station, CA	<i>Schoenoplectus maritimus</i> , <i>Culex tarsalis</i> , and <i>Anopheles hermsi</i>	<a href="#">Duguma and Walton (2014)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Freshwater tidal marsh (growth chamber)	250 g N/ha/yr as NH <sub>4</sub> Cl solution N dep = not reported S dep = not reported	Nitrogen increases construction cost of leaves by 5% in native <i>Phragmites</i> . Nitrogen under elevated [CO <sub>2</sub> ] increases construction costs by 6% in invasive <i>Phragmites</i> .	Mesocosms at Smithsonian Environmental Research Center, MD	<i>Phragmites australis</i> (native F haplotype and invasive M haplotype)	<a href="#">Caplan et al. (2014)</a>
Freshwater tidal marsh	500 kg N/ha/yr as NH <sub>4</sub> Cl or urea	N addition decreased leaf [N] by 99% and leaf [P] by 25%.	Altamaha River, GA	<i>Zizaniopsis miliacea</i>	<a href="#">Frost et al. (2009)</a>
Freshwater marsh	500 kg N/ha/yr as NH <sub>4</sub> Cl or urea N dep = not reported S dep = not reported	In <i>Z. miliacea</i> , leaf %N increased 25–43% so that leaf C:N decreased 18–28% and leaf N:P increased 25–61%. Total N and total P in aboveground pools increased 236 and 169%, respectively.	Altamaha Estuary, GA	<i>Zizaniopsis miliacea</i> , <i>Pontederia cordata</i> , and <i>Sagittaria lancifolia</i>	<a href="#">Ket et al. (2011)</a>
Freshwater tidal marsh	50, 200, or 1,200 kg N/ha/yr as Nutralene methylene urea N dep = not reported S dep = not reported	In <i>S. lancifolia</i> , N addition (N <sub>add</sub> as kg N/ha/yr) increased plant tissue [N], [N] = 0.00226 × N <sub>add</sub> + 23.271; and N:P ratio, N:P = 0.00404 × N <sub>add</sub> + 16.853.  In <i>S. lancifolia</i> , resorption efficiencies (RE) declined with increasing N addition, for nitrogen: NRE = -0.01048 × N <sub>add</sub> + 31.796, for phosphorus: PRE = -0.00915 × N <sub>add</sub> + 62.778.	Tchefuncte River, Madisonville, LA	Oligohaline plant community dominated by <i>Sagittaria lancifolia</i> , <i>Eleocharis fallax</i> , and <i>Polygonum punctatum</i>	<a href="#">Graham and Mendelssohn (2010)</a>
Freshwater tidal marsh	Addition: 670 kg N/ha/yr S dep = not reported N dep = not reported	Foliar N increased in <i>A. calamus</i> (by 23%) and <i>Typha</i> spp. (by 47%).	Nanticoke River, MD and DE	Plant community	<a href="#">Baldwin (2013)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Riparian floodplain successional forest	100 kg N/ha/yr N dep = not reported S dep = not reported	Specific leaf mass decreased by 12 and 11% in early and late successional forest. Leaf N increased 10% in late successional forest. Leaf P resorption decreased 21%.	Bonanza Forest LTER, AK	<i>Alnus incana</i> ssp. <i>tenuifolia</i> and associated <i>Frankia</i> strains	<a href="#">Ruess et al. (2013)</a>
Ombrotrophic bog	Ambient deposition = 3.4–5.0 kg N/ha/yr across the region, divided for this study into the following ranges: 3.4–3.6, 3.8–4.1, 4.4–4.9, 4.9–5.0 kg N/ha/yr	Pitcher plant foliar N content increased 78% between low N deposition (3.4–3.6 kg N) and medium N deposition (3.8–4.1 kg N). There was no difference in foliar N between medium and higher deposition rates.  Stable isotope ( $\delta^{15}\text{N}$ ) and mass balance suggest that 68% of pitcher plant N was derived from carnivory under low N (3.4–3.6 kg N), 92% under medium N (3.8–4.1 kg N), and 55% under higher N (4.4–4.9 kg N). Increase from medium to higher N deposition decreased pitcher plant carnivory by 40%.  <i>Chamaedaphne calyculata</i> foliar N increased 27% from the lowest (3.4–3.6 kg N) to the highest deposition (4.9–5.0 kg N) sites.	Adirondack Mountains, NY (11 sites)	<i>Sarracenia purpurea</i>	<a href="#">Crumley et al. (2016)</a>
Bog	N deposition gradient: 1.94, 3.81, and 11.30 kg N/ha/yr	N from insectivory decreases with deposition: 55% from insects under 1.94 kg N/ha/yr, 20–30% under 3.81 and 11.30 kg N/ha/yr.	Three bogs in Sweden	<i>Drosera rotundifolia</i>	<a href="#">Millett et al. (2012)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic bog	N deposition gradient: 0.5–27.0 kg N/ha/yr	N derived from insectivory decreases with increasing N deposition ( $N_{dep}$ as g N/m <sup>2</sup> /yr) in a linear relationship: $\delta^{15}N = -2.090 \times N_{dep} - 0.199$ , $R^2 = 0.43$ .  Plant tissue N:P increases with increasing N deposition in a logarithmic relationship: tissue N:P = $1.29 \times \ln(N_{dep}) + 10.00$ , $R^2 = 0.62$ .	13 bogs across Europe	<i>Drosera rotundifolia</i>	<a href="#">Millett et al. (2015)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KH <sub>2</sub> PO <sub>4</sub> ) N dep = 8 kg N/ha/yr S dep = not reported	In <i>R. groenlandicum</i> , leaf %N increased by 25% (low N) and 16% (high N), and leaf C:N ratios decreased by 19% (low N) and 15% (high N). Leaf P declined by 54% (high N). In low N addition, <i>R. groenlandicum</i> V <sub>cm</sub> max increased by 76% on a per-area basis or doubled on a per-mass basis. In <i>C. calyculata</i> , leaf C:N ratios decreased by 15% (low N) and 33% (high N), and total chlorophyll increased by 84% (high N), just as concentrations of leaf alanine increased 115% (high N) and GABA increased 94% (high N). Leaf Ca declined 34% (low N) and 17% (high N), leaf Mn declined 45% (high N), and leaf Al declined 44% (low N). In <i>V. myrtilloides</i> , leaf Ca declined 23% (low N) and 56% (high N), leaf P declined by 55% (low N) and 68% (high N), leaf Mn declined 57%, leaf K declined 47% (low N) and 34% (high N), and leaf Al declined 45% (high N). Amino acid leaf concentrations (y, as nmol/g) increased with leaf N (x, as %N): in <i>R. groenlandicum</i> , glutamic acid increased $y = 252.2x + 37.914$ ; in <i>C. calyculata</i> , alanine increased $y = 221.07x - 52.931$ , and GABA increased $y = 276.82x - 98.682$ .	Mer Bleue Bog, Ontario, Canada	Three ericaceous shrubs: <i>Vaccinium myrtilloides</i> , <i>Rhododendron groenlandicum</i> (formerly <i>Ledum groenlandicum</i> ), and <i>Chamaedaphne calyculata</i>	<a href="#">Bubier et al. (2011)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KH <sub>2</sub> PO <sub>4</sub> )	Under high N, gross PSN declined 29–45% in May–July but increased 25% in September.	Mer Bleue Bog, Ontario, Canada	Shrub species ( <i>Vaccinium myrtilloides</i> , <i>Rhododendron groenlandicum</i> , <i>Chamaedaphne calyculata</i> ), and mosses ( <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , <i>Polytrichum strictum</i> )	<a href="#">Larmola et al. (2013)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KH <sub>2</sub> PO <sub>4</sub> ) N dep = 5–6 kg N/ha/yr S dep = not reported	High N decreased leaf Ca (mg/cm <sup>2</sup> ) by 22% in <i>C. calyculata</i> and decreased leaf Mg (mg/cm <sup>2</sup> ) by 23% in <i>R. groenlandicum</i> . In <i>C. calyculata</i> , medium N increased P resorption by 42% as high N increased it by 33%. In <i>R. groenlandicum</i> , N addition (medium N, high N) increased P resorption by 12–12.2x, and increased K resorption by 92–123%. High N decreased Mg resorption 186% in <i>R. groenlandicum</i> .	Mer Bleue Bog, Ontario, Canada	<i>Chamaedaphne calyculata</i> and <i>Rhododendron groenlandicum</i> (formerly <i>Ledum groenlandicum</i> )	<a href="#">Wang et al. (2014b)</a>
Rich fen and ombrotrophic bog	No addition N dep = not reported S dep = not reported	Leaf N ( <i>y</i> , as %N) was positively correlated with surface water NO <sub>3</sub> <sup>-</sup> concentration ( <i>x</i> ): $y = 0.1667x + 0.9581$	Cedarburg fen and Sapa bog, WI	<i>Sarracenia purpurea</i> ssp. <i>purpurea</i>	<a href="#">Bott et al. (2008)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic bog	60 kg N/ha/yr as urea S dep = not reported N dep = not reported	In <i>Chamaedaphne calyculata</i> , fertilization increases plant N uptake by 75%, N stored in biomass by 100%, productivity by 87%. Fertilization decreases <i>C. calyculata</i> N use efficiency by 81% and N response efficiency by 91%. In <i>Carex oligosperma</i> , fertilization decreases N use efficiency by 89% and N response efficiency by 84%. The entire plant community responded to N addition with increases in N uptake (125%), N stored in biomass (171%), productivity (82%), and [N] in new tissue (19%).	Gogebic County, MI	Plant community consisting of <i>Sphagnum</i> spp., ericaceous shrubs, dominant vascular plants <i>Carex oligosperma</i> and <i>Chamaedaphne calyculata</i>	<a href="#">Iversen et al. (2010)</a>
Fen	60 g N/ha/yr as urea N dep = not reported S dep = not reported	In <i>A. rugosa</i> , fertilization decreases N response efficiency by 45%.	Gogebic County, MI	Dominant vascular plants <i>Calamagrostis canadensis</i> and <i>Alnus rugosa</i>	<a href="#">Iversen et al. (2010)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Ambient deposition = 2 kg N/ha/yr at DS; 12 kg N/ha/yr at WM; 47 kg N/ha/yr at FS Mesocosms were established with NH <sub>4</sub> NO <sub>3</sub> solutions that mimicked relative N deposition levels <sup>15</sup> N tracer was added in 48 applications over 6 mo at a rate of 23 kg N/ha/yr	At 12 kg N/ha/yr, <sup>15</sup> N retention efficiency in shrubs decreased 65% compared to DS. At 47 kg N/ha/yr, plant tissue N of graminoids increased 120% compared to DS. Total N stored in shrubs increased 360% compared to DS. Across five sites and all mesocosms, <i>Sphagnum</i> C:N was a function of N deposition (N <sub>dep</sub> , as g N/m <sup>2</sup> /yr): C:N = -22.9 × ln(N <sub>dep</sub> ) + 68.6. Data from LV and CF mesocosms are not considered because mesocosm N addition levels (CF: 300% increase over DS N solution, LV: 700% increase over DS) did not reflect ambient N deposition differences (CF: 750% increase over DS deposition, LV: 300% increase over DS). Across five sites and all mesocosms, <i>Sphagnum</i> C:N was a function of N deposition: C:N = -22.9 × ln(N <sub>dep</sub> ) + 68.6.	Mesocosms constructed using peat bog cores from sites in northern and western Europe—Degero Stormyr, Sweden (DS); Fenn's, Whixall, and Bettisfield Mosses NNR, U.K. (WM); and Frolichshaier Sattelmoor, Germany (FS)  (Peat cores also collected at Little Vildmose, Denmark [LV] and Cors Fochno, Wales, U.K. [CF])	<i>Sphagnum capillifolium</i> , <i>S. fallax</i> , <i>S. magellanicum</i> , <i>S. papillosum</i> , <i>S. pulchrum</i> , <i>S. rubellum</i> , <i>Andromeda polifolia</i> , <i>Calluna vulgaris</i> , <i>Erica tetralix</i> , <i>Rubus chamaemorus</i> , <i>Vaccinium oxycoccos</i> , <i>Eriophorum vaginatum</i> , <i>Eriophorum angustifolium</i>	<a href="#">Zajac and Blodau (2016)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Addition = 16 kg N/ha/yr (5N, or 5x background deposition), 32 kg N/ha/yr (10N), or 64 kg N/ha/yr (20N), all as NH <sub>4</sub> NO <sub>3</sub>  Ambient (wet) deposition = 8 kg N/ha/yr and up to 0.26 kg P/ha/yr	N addition of 32 kg N/ha/yr decreased moss [Ca] by 34%. N addition of 64 kg N/ha/yr increased moss [P] by 39%, and decreased moss [Ca] by 42%.	Mer Bleue bog, Ottawa, Canada	Evergreen shrubs: <i>Chamaedaphne calyculata</i> and <i>Rhododendron groenlandicum</i> dominant; sparse <i>Kalmia angustifolia</i>  Deciduous shrubs: <i>Vaccinium myrtilloides</i>  Mosses: <i>Sphagnum capillifolium</i> , <i>S. magellanicum</i> , and <i>Polystichum strictum</i>	<a href="#">Wang et al. (2016a)</a>
Ombrotrophic bog	Wet + dry deposition, estimated by <a href="#">Jirousek et al. (2011)</a>  Jireza: 20–25 kg N/ha/yr (high N)  Jeseniky: 12.5 kg N/ha/yr (low N)	<i>S. rubellum</i> [K] was 64% lower at high N site. <i>S. magellanicum</i> [K] was 62% lower and [Mg] was 45% lower at high N site.	Two sites: Jizerka in Jireza Mountains (warm suboceanic climate) and Vozka in Jeseníky Mountains (2°C colder)	<i>Sphagnum fallax</i> , <i>Sphagnum magellanicum</i> , and <i>Sphagnum rubellum/russowii</i>	<a href="#">Jirousek et al. (2015)</a>
Bog	Laboratory incubation. Moss from Argentina (54.75°S, 68.33°W) and Netherlands (52.82°N, 2.42°E)  Pristine site (Argentina): 1–2 kg N/ha/yr, N polluted site (Netherlands): 20–30 kg N/ha/yr	N uptake of 10 and 100 μmol N/L solutions was 40–160% more rapid by <i>Sphagnum</i> from the pristine (Argentinian) bog than the Dutch bog.	Laboratory incubation of moss from pristine site in Argentina and N polluted site in Netherlands	<i>Sphagnum magellanicum</i>	<a href="#">Fritz et al. (2014)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Rich fen	<p>Addition: two aqueous treatments: groundwater (0.18 mg N/L, 0.02 mg P/L, 90 mg Ca<sup>2+</sup>/L, pH = 8.0–8.6) and rainwater (0.58–0.98 mg N/L, 0.03 mg P/L, pH 6.5–7.0)</p> <p>Three N addition levels dissolved in each aqueous treatment: no additional N (low), 1 mg N/L added (medium), 3 mg N/L added (high)</p> <p>Ambient deposition = not specified, but rainwater N is 220–440% higher than groundwater N</p>	<p>Groundwater vs. rainwater: tissue [N] and tissue [P] were higher in rainwater than in groundwater treatment.</p> <p>N addition treatment: tissue [P] was lower in medium and high N addition mesocosms.</p>	<p>Mesocosms constructed from sand, peat, and chalk, with all four species added to each mesocosm, fully factorial design: two aqueous treatments × 3 N addition levels × 3 P addition levels</p>	<p>Two bryophyte species common in rich fens in Denmark: <i>Calliergonella cuspidata</i> and <i>Bryum pseudotriquetrum</i></p> <p>Two bryophyte species that have been declining in abundance over the past 100 years: <i>Hamatocaulis vernicosus</i> and <i>Paludella squarrosa</i></p>	<p><a href="#">Andersen et al. (2016)</a></p>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Calcareous, rich fen	Addition = 50 kg N/m <sup>2</sup> /yr as NO <sub>3</sub> <sup>-</sup> or 50 kg N/m <sup>2</sup> /yr as NH <sub>4</sub> <sup>+</sup> Ambient deposition = 7–10 kg N/m <sup>2</sup> /yr, based <a href="#">Aherne and Farrell (2002)</a>	<p>In <i>Scorpidium</i>, NH<sub>x</sub> increased tissue N 76% and decreased tissue K 53%. NH<sub>x</sub> increased <i>Scorpidium</i> free arginine concentration 7.3x control.</p> <p>In <i>Scorpidium</i>, NO<sub>x</sub> increased phosphomonoesterase (PMEase) 60%, indicating increased P limitation.</p> <p>In <i>Sphagnum</i>, NH<sub>x</sub> increased PMEase 70%, indicating increased P limitation. NH<sub>x</sub> decreased <i>Sphagnum</i> tissue N 13% and tissue K 49%. NH<sub>x</sub> increased the concentrations of free amino acids in <i>Sphagnum</i>: alanine by 55%, arginine 66x control concentrations, asparagine 39x control, glutamine 65x control, and serine 3.8x control.</p> <p>In <i>Sphagnum</i>, NO<sub>x</sub> increased tissue N 29% and tissue P 28%. NO<sub>x</sub> increased <i>Sphagnum</i> free alanine concentration 31%.</p>	Scragh Bog, Central Ireland	<i>Scorpidium revolvens</i> and <i>Sphagnum contortum</i>	<a href="#">Paulissen et al. (2016)</a>

**Table 11-6 (Continued): Nitrogen loading effects upon plant stoichiometry and physiology.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Addition = 8, 24, and 56 kg N/ha/yr as either NH <sub>4</sub> <sup>+</sup> or NO <sub>3</sub> <sup>-</sup> since 2002 Ambient deposition total N = 8 kg N/ha/yr, 3 kg N/ha/yr as wet NO <sub>x</sub> , 3 kg N/ha/yr as wet NH <sub>x</sub> , and 2 kg N/ha/yr as dry NH <sub>x</sub>	Tissue N in <i>Sphagnum capitulum</i> , and tissue N and N:P in <i>Sphagnum</i> stems, increased in a saturating (i.e., logarithmic) relationship with increasing NO <sub>x</sub> deposition. Tissue N and N:P in <i>Sphagnum capitulum</i> , and tissue N in <i>Sphagnum</i> stems, increased in a linear relationship with increasing NH <sub>x</sub> deposition.	Whim bog, Edinburgh, Scotland	<i>Sphagnum</i> moss ( <i>Sphagnum capillifolium</i> , a hummock-forming species) Heathland community: <i>Calluna vulgaris</i> , <i>Eriophorum vaginatum</i> , <i>Hypnum jutlandicum</i> , <i>Pleurozium schreberi</i> , and <i>Cladonia portentosa</i>	<a href="#">Chiwa et al. (2016)</a>

AG = aboveground; Al = aluminum; ANPP = aboveground net primary productivity; C = carbon; Ca = calcium; cm = centimeter; CO<sub>2</sub> = carbon dioxide; dep = deposition; GABA = gamma-Aminobutyric acid; ha = hectare; K = potassium; kg = kilogram; KH<sub>2</sub>PO<sub>4</sub> = potassium phosphate; L = liter; LTER = Long Term Ecological Research; μmol = micromole; mg = milligram; Mn = manganese; N = nitrogen; NH<sub>4</sub>Cl = ammonium chloride; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; NPK = nitrogen, phosphorus, potassium; NRE = nitrogen resorption efficiency; P = phosphorus; PRE = phosphorus resorption efficiency; S = sulfur; yr = year.

## 11.6 Plant Architecture

Plant architecture (plant height, branching) in wetlands is an important endpoint because the architecture of the dominant plants determines the availability of nesting habitats or refugia from flooding and predators. Plant architecture is defined as the three-dimensional organization of the plant body. For the parts of the plant that are aboveground, this includes the branching pattern, as well as the size, shape, and position of leaves and flower organs ([Table 11-7](#)). The 2008 ISA did not have sufficient data on N addition effects on wetland plant architecture to consider plant architecture as a specific endpoint.

### 11.6.1 Salt Marsh

There are several new studies on salt marsh plant architecture. [Darby and Turner \(2008\)](#) reported that for *Spartina alterniflora*, stem height increased linearly with N load starting at 230 kg N/ha/yr, although regression equations were not included. Stem density was

significantly higher than in unamended plots only for the highest N load, 3,720 kg N/ha/yr, which increased stem density by 43%. There are two other addition studies with N addition rates above 500 kg N/ha/yr that evaluated effects in U.S. salt marshes ([Ryan and Boyer, 2012](#); [Davey et al., 2011](#)).

The Plum Island tidal eutrophication experiment added nitrate and phosphate to salt marsh tidal creeks to achieve nitrate concentrations 15 times the concentrations of unamended creeks. In the last 2 years of this experiment, there was N but no P enrichment, and 620 kg N/ha/yr increased *Spartina alterniflora* plant height 4% in low marsh ([Johnson et al., 2016a](#)). In the high marsh, 140 kg N/ha/yr decreased *Distichlis spicata* height 4% ([Johnson et al., 2016a](#)). Across the course of the N and P addition, alterations in plant carbon allocation decreased vascular plant root:shoot biomass ratio by 31% ([Deegan et al., 2012](#)). With the decrease in belowground support and the decreases in shoot lignin (which provides structural support in plant shoots, see Stoichiometry section), a 5% increase in shoot height made plants top-heavy. As a result, lodging (plant stems collapsing to marsh substrate where they are inundated by tides), which was not observed in control marshes, affected 41% of the marsh area in enriched marsh ([Deegan et al., 2012](#)).

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## 11.6.2 Mangrove

In Florida mangroves, [Whigham et al. \(2009\)](#) added 100 kg N/ha/yr to plots of dwarf *Avicennia germinans*, black mangrove, which increased the number of new branches produced 150% above control plots.

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## 11.6.3 Freshwater Tidal Marsh

There are several new studies on freshwater tidal wetlands. In freshwater tidal marshes of Altamaha River Estuary, GA, N addition (500 kg N/ha/yr) increased the number of leaves per m<sup>2</sup> 52% and increasing plant height by 25–40% over the course of the 5-year experiment ([Ket et al., 2011](#)). [Duguma and Walton \(2014\)](#) constructed freshwater wetland mesocosms at UC Riverside, planting *Bolboschoenus maritimus* (formerly *Schoenoplectus maritimus*) and alkali bulrush, and monitoring plant responses as well as the use of mesocosms by mosquito species ([Appendix 11.8.2](#)). N addition of 32 kg N/ha/yr increased plant height 23% with no effect upon plant height when 65 or 108 kg N/ha/yr were added in 2009. However, in 2010 when the experiment was initiated earlier in the year (5 August start date in 2009, 22 March start date in 2010), all N addition

levels (59, 119, 198 kg N/ha/yr) increased plant height 28–44% above control plants ([Duguma and Walton, 2014](#)).

#### 11.6.4 Riparian Wetland

In developing riparian forests at Bonanza Forest LTER, AK, N addition of 100 kg N/ha/yr altered leaf structure of the tree species *Alnus incana* ssp. *tenuifolia* ([Ruess et al., 2013](#)). In the mostly recently colonized sand bars, N addition decreased specific leaf mass (SLM) of *A. incana* ssp. *tenuifolia* 12%, and in midsuccessional riparian forest SLM decreased 11% with N addition.

#### 11.6.5 Summary Table

**Table 11-7 Nitrogen loading effects upon architecture.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	4,200 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub> S dep = not reported N dep = not reported	N addition increased rhizome diameter by 1% in shallow and 5% in deep (10–20 cm) sediments.	Goat Island, SC	<i>Spartina alterniflora</i>	<a href="#">Davey et al. (2011)</a>
Coastal salt marsh	230, 465, 930, 1,860, or 3,720 kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> S dep = not reported N dep = not reported	Stem density and stem height increased linearly with N load (regressions not given). Stem densities increased 43% in response to 3,720 kg N.	LUMCON, Cocodrie, LA	<i>Spartina alterniflora</i>	<a href="#">Darby and Turner (2008)</a>
Estuarine marsh	Addition: 1,337 kg N/ha/yr as urea. S dep = not reported N dep = not reported	In <i>S. pacifica</i> , height increased 207%, number of branches increased 135–283%. <i>J. carnososa</i> height increased 504%.	China Camp State Park, CA	<i>Sarcocornia pacifica</i> dominant (C3 succulent shrub), <i>Distichlis spicata</i> (C4 grass), and <i>Jaumea carnosa</i> (C3 semisucculent forb)	<a href="#">Ryan and Boyer (2012)</a>

**Table 11-7 (Continued): Nitrogen loading effects upon architecture.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Salt marsh	Nitrate and phosphate dissolved in tidal inflows to raise aqueous NO <sub>3</sub> <sup>-</sup> concentrations to 70–100 μM and raise PO <sub>4</sub> <sup>3-</sup> to 5–7 μM. Background load in tides: 5 μM NO <sub>3</sub> <sup>-</sup> , 1 μM PO <sub>4</sub> <sup>3-</sup> . N dep = not reported S dep = not reported	Root:shoot ratio decreases 31%. Shoot height increases 5%. Lodging affects 41% of area in enriched marshes, is not observed in control marsh.	Plum Island Estuary, MA	Primary tidal creeks with <i>Spartina alterniflora</i> in low marsh along creeks, and <i>Spartina patens</i> in high marsh platforms	<a href="#">Deegan et al. (2012)</a>
Salt marsh	Addition of nitrate dissolved in incoming tide 2011–2012, addition of N at 70–100 μM NaNO <sub>3</sub> <sup>-</sup> in tide for added load of 620–1,200 kg N/ha/yr in low marsh and 70–140 kg N/ha/yr in high marsh Ambient deposition = not specified	Low marsh in enriched creeks received an additional N load of 620 kg N/ha/yr in 2012. That year, N addition increased shoot height 4% above <i>S. alterniflora</i> in low marsh at reference creeks. High marsh in enriched creeks received an additional N load of 140 kg N/ha/yr in 2011. In <i>D. spicata</i> , N addition decreased shoot height 4%.	Plum Island Sound Estuary, MA	<i>Spartina alterniflora</i> , <i>Distichlis spicata</i> , and <i>Spartina patens</i> (high marsh); <i>Spartina alterniflora</i> (low marsh)	<a href="#">Johnson et al. (2016a)</a>
Mangrove	100 kg N/ha/yr	N addition increased the number of new branches 150% in <i>Avicennia</i> .	Indian River Lagoon, FL (impoundment SLC-24)	<i>Avicennia germinans</i> and associated sediments	<a href="#">Whigham et al. (2009)</a>
Freshwater marsh	Fall 2009: 32 (low), 65 (medium), 108 (high) kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ; Summer 2010: 59 (low), 119 (medium), or 198 (high) kg N/ha/yr as (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> N dep = not reported S dep = not reported	N addition increased <i>S. maritimus</i> height 23% in 2009 (low N), and 28–44% in 2010.	Mesocosms at UC Riverside research station, CA	<i>Schoenoplectus maritimus</i> , <i>Culex tarsalis</i> , and <i>Anopheles hermsi</i>	<a href="#">Duguma and Walton (2014)</a>

**Table 11-7 (Continued): Nitrogen loading effects upon architecture.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Tidal freshwater marsh	500 kg N/ha/yr as NH <sub>4</sub> Cl or urea	In <i>Z. miliacea</i> , leaf number increased 52% and plant height increased 25–40%.	Altamaha Estuary, GA	<i>Zizaniopsis miliacea</i> , <i>Pontederia cordata</i> , and <i>Sagittaria lancifolia</i>	<a href="#">Ket et al. (2011)</a>
Riparian floodplain successional forest	100 kg N/ha/yr N dep = not reported S dep = not reported	Specific leaf mass decreased by 12 and 11% in early and late successional forest.	Bonanza Forest LTER, AK	<i>Alnus incana</i> ssp. <i>tenuifolia</i> and associated <i>Frankia</i> strains	<a href="#">Ruess et al. (2013)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N (NH <sub>4</sub> NO <sub>3</sub> ) or NPK (NH <sub>4</sub> NO <sub>3</sub> and KH <sub>2</sub> PO <sub>4</sub> ) S dep = not reported N dep = 8 kg N/ha/yr	In medium and high NPK treatments, shrub canopies grew 72 and 82% taller than controls. There were no significant effects of medium or high N on shrub canopies.	Mer Bleue Bog, Ontario, Canada	Bog plant community: dwarf shrub species and mosses <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Juutinen et al. (2010)</a>

AG = aboveground; ha = hectare; kg = kilogram; KH<sub>2</sub>PO<sub>4</sub> = potassium phosphate; LTER = Long Term Ecological Research; LUMCON = Louisiana Universities Marine Consortium; N = nitrogen; NH<sub>4</sub>Cl = ammonium chloride; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; P = phosphorus; S = sulfur; yr = year.

## 11.7 Demography

Plant demography is the change in plant population size and structure through time. Changes to plant demography will determine the long-term stability of wetlands. Information on the effect of N loading on wetland plant demography, including establishment, survival, and reproduction is sparse. Evidence from salt marsh ecosystems shows mixed responses to N loading: two pre-2008 studies found negative effects of N addition upon reproduction in invasive *Spartina foliosa* and *Spartina* hybrids ([Tyler et al., 2007](#)), and a positive effect upon reproduction of native *Salicornia bigelovii* ([Boyer and Zedler, 1999](#)). Work reviewed in the 2008 ISA on *Sarracenia purpurea*, or northern pitcher plant, found that increases in N deposition increased population extinction risk ([Gotelli and Ellison, 2006, 2002](#)), which serves as the scientific basis for the wetland critical load values ([Appendix 11.9](#)). Additionally, an older study of *Drosera rotundifolia* in a Swedish bog found that N addition levels of 20 and 40 kg N/ha/yr significantly

decreased survivorship in comparison to control plots or N addition of 5 or 10 kg N/ha/yr ([Redbo-Torstensson, 1994](#)). The sections below describe two new studies that find negative impacts of high N upon the demography of wetland plants.

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### 11.7.1 Mangrove

[Lovelock et al. \(2009\)](#) considered a global data set of mangrove responses to N fertilization experiments conducted for 3–12 years. N addition (900–2,700 kg N/tree/yr) decreased survival probability by 10%, with trees growing on the land side in hypersaline conditions particularly vulnerable when rainfall was low.

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### 11.7.2 Riparian Wetland

The Great Salt Lake is an inland salt lake ecosystem that provides an important food source for migrating bird species as well as an economically important fishing industry by providing habitat for *Artemia franciscana*, brine shrimp. [Carling et al. \(2013\)](#) studied impounded and floodplain wetlands along the rivers that feed into the GSL, and found that increasing nitrate and nitrite concentrations in water flowing through the wetlands decreased reproduction of the submerged aquatic plants *Ruppia cirrhosa* and *Stuckenia* spp. (equations in [Table 11-8](#)).

### 11.7.3 Summary Table

**Table 11-8 Nitrogen loading effects upon demography.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Mangrove	No areal rate given; 900 kg/yr to 2,700 kg N/yr per tree as urea	Mangrove survival probability decreased 10% with N addition.	12 global sites, including Indian River Lagoon, FL	Mangrove species	<a href="#">Lovelock et al. (2009)</a>
Riparian wetlands and floodplain wetlands	Not reported	Reproduction (Repro, g/m <sup>2</sup> drupelets) declines with increasing surface water nitrate (NO <sub>3</sub> in mg/L): Repro = -4.15 × ln(NO <sub>3</sub> ) + 4.03, R <sup>2</sup> = 0.51; as well as with increasing surface water NO <sub>2</sub> <sup>-</sup> (NO <sub>2</sub> <sup>-</sup> in mg/L): Repro = -13.43 × ln(NO <sub>2</sub> <sup>-</sup> ) -25.27, R <sup>2</sup> = 0.54).	Great Salt Lake, UT	Submerged aquatic vegetation: <i>Ruppia cirrhosa</i> and <i>Stuckenia</i> spp.	<a href="#">Carling et al. (2013)</a>

g = gram; ha = hectare; kg = kilogram; L = liter; m = meter; mg = milligram; N = nitrogen; NO<sub>2</sub><sup>-</sup> = nitrite; NO<sub>3</sub><sup>-</sup> = nitrate; yr = year.

## 11.8 Biodiversity/Community

High biodiversity is a characteristic of wetlands. Fluctuating water levels in open systems such as riparian strips and tidal marshes create zones with distinct abiotic characteristics and multiple niches for microbes, plants, and animals with different biotic and abiotic requirements. More closed systems, such as bogs and fens, are nutrient-poor, high-organic-acid ecosystems that contain rare species including carnivorous plants, ericaceous plants, and bryophytes characterized by low growth rates. Most wetlands contain species with a range of N tolerance and N-acquisition strategies, and one result of eutrophication is to shift the composition and relative abundance of species so that nitrogen-tolerant species become more common as species that are adapted to low nitrogen availability become less common or disappear from the system. Thus, plant cover (percentage of the total wetland area occupied by a particular species) is an important metric of biodiversity. Similarly, communities of aquatic producers contain both nitrogen-tolerant and low-nitrogen-adapted species, and changes in phytoplankton species composition represents a change in biodiversity important for dependent food

webs (see [Appendix 9.3.2](#), [Appendix 10.3.2](#), and [Appendix 10.3.3](#)). Changes in the abundance of herbivorous, omnivorous, or predatory invertebrates are indicative of alterations to trophic interactions and effects, which could cascade up the food web towards economically or culturally important fish, bird, and mammal species.

The 2008 ISA found that the evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in wetland ecosystems. The 2008 ISA noted there are 4,200 native plant species in U.S. wetlands, 121 of which are federally endangered. Wetlands provide habitat to a disproportionately high number of rare plants given their relative area; for example, fens occupy 0.01% of the land area of northeast Iowa, yet contain 17% of the endangered, threatened, or listed species of concern in the area. Wetland species have evolved under N limited conditions, including endangered species in the *Isoetes* (three endangered species) and *Sphagnum* (15 endangered species) genera, as well as the endangered insectivorous plants *Sarracenia oreophila* and *Drosera rotundifolia*.

The 2008 ISA provided evidence from American bogs and fens that showed that *Sarracenia purpurea* (purple pitcher plant) responded to N deposition with changes in morphology and projected population extinction under N deposition levels of 4.5–6.8 kg N/ha/yr. Coastal wetlands responded to N enrichment with increased primary production, shifting microbial and plant communities, and altering pore water chemistry, although many of the studies in coastal wetlands used N enrichment levels more similar to that of wastewater than of atmospheric deposition.

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## 11.8.1 Plants

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### 11.8.1.1 Salt Marsh

Nitrogen was an important factor driving plant diversity in a study on the Patuxent River, where marsh soil  $\text{NO}_3^-$ -N and pore water salinity best explained the variation in plant species richness out of all factors considered, with  $\text{NO}_3^-$ -N accounting for 26% of the variation in the richness of all species. Presence-absence data for all species were used to determine the geographic range for each species, and the 50% of species per river with the smallest range was designated as a “restricted-range” subset. On the Patuxent River, the best model of variation in species richness of restricted range species contained only soil  $\text{NO}_3^-$ -N as an explanatory variable, with a positive relationship between  $\text{NO}_3^-$ -N and species richness [see [Table 11-9](#); ([Sharpe and Baldwin, 2013](#))].

Several new field addition studies further confirm N addition alters plant community composition in salt marshes. In Kirkpatrick Marsh, MD, a limited plant community and resampling of fixed plots allowed researchers to measure the biomass of plots as a proxy for plant cover. C4 plants *Spartina patens* and *Distichlis spicata* plot cover increased over the course of the 4-year fertilization experiment so that C4 biomass was 129% higher in the 4th year than in the 1st year of receiving 250 kg N/ha/yr, while C4 biomass in the control plots remained unchanged over 4 years. The C3 plant species *Schoenoplectus americanus* declined in biomass in the control plots by 8–22% of that produced in the 1st year, but decreased to a greater extent in N addition plots, declining after 4 years by 52% compared to the 1st year plot biomass ([Langley and Megonigal, 2010](#)). In the long-term nutrient addition experiment at Great Sippewissett Marsh, MA, 30 years of addition of sewage sludge altered community composition. Nitrogen addition at 170, 520, and 1,560 kg N/ha/yr altered the relative composition of *Spartina alterniflora* and *Distichlis spicata*, with percentage cover of *S. alterniflora* decreasing 3% with every additional 100 kg N/ha/yr, and percentage cover of *D. spicata* increasing 3% with every additional 100 kg N/ha/yr of total N load ([Fox et al., 2012](#)).

In Elkhorn Slough, CA, marsh community was assessed at six sites. At one site, where impoundment restricted tidal exchange, N addition of 150 kg N/ha/yr altered community composition, decreasing cover of native marsh plants by 52% and increasing cover of non-native upland plants by 80% ([Goldman Martone and Wasson, 2008](#)). There were two studies with N addition above 500 kg N/ha/yr ([Baldwin, 2013](#); [Ryan and Boyer, 2012](#)), but this N addition level was not useful in inferring effects of N deposition upon ecosystems.

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### 11.8.1.2 Freshwater Tidal Marsh

In a freshwater tidal marsh on the Tchefuncte River, LA, N addition shifted the relative dominance of the perennial wetland-obligate monocots dominant at the site ([Graham and Mendelssohn, 2010](#)). Increasing N loads increased the relative dominance of *Persicaria punctata* (formerly *Polygonum punctatum*) with a 0.13% increase (percentage of total biomass consisting of *P. punctata*) for every 10 kg N/ha/yr added. Increasing N loads decreased the relative dominance of *Eleocharis fallax*, with a 0.08% decrease (percentage of total biomass consisting of *E. fallax*) for every 10 kg N/ha/yr added ([Graham and Mendelssohn, 2010](#)). N loading did not affect the relative dominance of *Sagittaria lancifolia*, but did alter its storage of N in plant tissues ([Appendix 11.5](#)).

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### 11.8.1.3 Freshwater Wetland

There are two new studies of N loading in freshwater systems; they do not quantify N deposition or N loading in terms of an areal rate, but rather find correlations between surface water or soil N and changes in plant community diversity across a gradient of N loads. Nitrogen loading is often correlated with invasions of non-native plants and associated reductions in native species abundance and richness ([Green and Galatowitsch, 2002](#)). An observational study of 48 wetlands along the coasts of the Great Lakes found 7 floristically distinct plant communities: 1 *Sphagnum*-dominated wetland, 3 marsh types dominated by native plants, and 3 marsh types dominated by invasive species. A classification and regression tree that successfully classified 79% of the sites to the correct plant community used surface water total N, conductivity, and pH as explanatory variables: one of the invasive plant communities (dominated by the invasive *Typha* spp.) was associated with high total N ([Johnston and Brown, 2013](#)).

In a similar observational study of 28 restored wetlands in Illinois, soil nitrogen significantly correlated with plant invasion and a decline in native plant species richness ([Matthews et al., 2009](#)). There were linear, positive correlations of soil nitrate with relative percentage cover of non-native plants, and with relative percentage cover of invasive *Phalaris arundinacea* (see [Table 11-9](#) for full equations). For each 0.1 ppm increase in soil nitrate, non-native plant cover increased 4%, and *P. arundinacea* cover increased 5%. The surveyed wetlands were diverse communities: there were 483 vascular plant species across all 20 wetlands, and each wetland contained 40–100 native species. For every 0.1 ppm increase in soil ammonium across the wetlands, seven native species disappeared; and for every 0.1 ppm increase in soil nitrate, three native species disappeared ([Matthews et al., 2009](#)).

In addition to these studies, the National Wetlands Condition Assessment (NWCA), conducted by U.S. EPA in 2011, collected soil and water chemistry data as well as plant biodiversity data. In California wetlands sampled for this project, higher surface water nitrate + nitrite concentrations correlated with lower wetland condition scores as measured by the California Rapid Assessment Method [CRAM; [U.S. EPA \(2016j\)](#)].

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### 11.8.1.4 Intermittent Wetland

Vernal pools are intermittent wetlands, which typically flood in the late winter and spring, and serve as important habitat for amphibians and endemic invertebrates. California vernal pools host a number of endangered and threatened animal species during their wet phase, as well as a high diversity of plant species during their dry phase.

There are no studies published that directly test the effect of N deposition or N addition to vernal pools, but there is a mesocosm study, which may allow some inference of N effects on vernal pools. This study added combined N and P solutions to mesocosms and found increased algal biomass, which decreased vascular plant cover and richness in vernal pool mesocosms ([Kneitel and Lessin, 2010](#)). N and P additions were not quantified in areal rates.

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#### 11.8.1.5 Bog and Fen

In Mer Bleue Bog, Ontario, N addition decreased the dominance of *Sphagnum* mosses in the northern ombrotrophic peat bog. After 4 years of N fertilization at the rate of 64 kg N/ha/yr, cover of *Sphagnum* species (of *Sphagnum magellanicum* and *Sphagnum capillifolium*) in fertilized plots was 43% of *Sphagnum* cover in control plots ([Juutinen et al., 2010](#)). At year 12, cover of *Sphagnum* species in 16 kg N/ha/yr fertilized plots was 64% of cover in control plots ([Larmola et al., 2013](#)). Plots measured in the same growing season (2011) that had received 7 years of elevated N at higher N addition rates also experienced declines in *Sphagnum* cover: 26% decline in cover at 32 kg N/ha/yr and 54% decline in cover at 64 kg N/ha/yr ([Larmola et al., 2013](#)). The following year, moss species (*Sphagnum* spp. and *Polystrichum strictum*) cover was 63% lower in 64 kg N/ha/yr plots than in control plots, while the percentage of cover of the vascular plant *Chamaedaphne calyculata* was 202% higher in 32 kg N/ha/yr plots than in control plots ([Wang et al., 2016a](#)). These declines in peat-forming species corresponded to changes in ecosystem C fluxes ([Appendix 11.3.2](#)).

N deposition or addition effects upon plant community composition have been studied in European systems. In an Irish fen, which was also the site of a N addition experiment (see [Appendix 11.4.4](#) and [Appendix 11.5.5](#)), researchers observed plant community composition shifts in control plots over 4 years ([Paulissen et al., 2016](#)). Under ambient deposition of 7–10 kg N/ha/yr, cover of the N-sensitive brown moss *Scorpidium revolvens* decreased 25%, while cover of peat moss *Sphagnum contortum* increased 20% and cover of vascular plants increased qualitatively ([Paulissen et al., 2016](#)). N addition increases vascular plant cover in multiple systems. In an Italian fen, N addition altered plant cover of 4 of the 17 species documented in the marsh ([Gerdol and Brancaloni, 2015](#)). Vascular species cover did not shift in response to 10 kg N/ha/yr; but in response to 30 kg N/ha/yr addition, cover of shrub *Calluna vulgaris* increased 96% and cover of grass *Molinia caerulea* increased 5.6 times that of control plots. Like the vascular plants, moss species *Sphagnum fuscum* (native in the U.S., listed as endangered by North Carolina) did not respond to 10 kg N addition, but its cover decreased 45% in response to 30 kg N addition. The moss species *Polytrichum strictum* (native in the U.S., listed as

endangered in Kentucky) increased in response to both 10 or 30 kg N addition, with cover 190–240% higher after 8 years of N addition. Researchers continued to monitor the plots for 3 years after ceasing N addition treatments to assess wetland recovery: vascular plants and *P. strictum* remained dominant, while *S. fuscum* cover continued to decline, and a different moss species, *Sphagnum magellanicum*, increased its coverage in plots recovering from elevated N addition ([Gerdol and Brancaleoni, 2015](#)).

### 11.8.1.6 Summary Table

**Table 11-9 Nitrogen loading effects upon plant biodiversity and communities.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal high marsh	Addition: 150 kg N/ha/yr as urea S dep = not reported N dep = not reported	At a site where tidal inflow was restricted, fertilization increased cover of non-native upland plants by 80% and decreased cover of native marsh plants by 52%.	Six sites at Elkhorn Slough, Watsonville, CA	Marsh community dominated by <i>Sarcocornia pacifica</i> , also contains <i>Jaumea carnosa</i> , <i>Frankenia salina</i> , <i>Spergularia salina</i> , <i>Distichlis spicata</i> , and <i>Atriplex californica/triangularis</i>	<a href="#">Goldman Martone and Wasson (2008)</a>
Estuarine salt marsh	Addition: 1,337 kg N/ha/yr as urea S dep = not reported N dep = not reported	<i>S. pacifica</i> cover increased at 6.2x the rate of increase in control. <i>J. carnosa</i> cover declined 5.4x as fast as in control.	China Camp State Park, CA	<i>Sarcocornia pacifica</i> dominant (C3 succulent shrub), <i>Distichlis spicata</i> (C4 grass), and <i>Jaumea carnosa</i> (C3 semisucculent forb)	<a href="#">Ryan and Boyer (2012)</a>
Estuarine salt marsh	Addition: 250 kg N/ha/yr S dep = not reported N dep = not reported	<i>S. americanus</i> aboveground biomass decreased by 19 and 45% in the 3rd and 4th yr, respectively.	Kirkpatrick Marsh, MD (measured in 3rd and 4th yr, 2008–2009)	<i>Schoenoplectus americanus</i> (C3), <i>Spartina patens</i> (C4), and <i>Distichlis spicata</i> (C4)	<a href="#">Langley and Megonigal (2012, 2010)</a>

**Table 11-9 (Continued): Nitrogen loading effects upon plant biodiversity and communities.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	Addition: 170 kg N/ha/yr, 520 kg N/ha/yr, 1,560 kg N/ha/yr, all added as sewage sludge (10% N, 6% P <sub>2</sub> O <sub>5</sub> , 4% K <sub>2</sub> O) S dep = not reported N dep = not reported Background total N load = 2 kg/ha/yr (as reported in <a href="#">Bowen and Valiela (2001b)</a> ).	<i>S. alterniflora</i> cover ( $y$ , as % cover) declines in plots with increasing N load ( $N_{add}$ , as kg N/ha/yr), $y = -0.0292 \times N_{add} + 64.6$ . <i>D. spicata</i> cover ( $z$ , as % cover) increases in plots with increasing N load, $z = 0.0327 \times N_{add} + 3.04$ .	Great Sippewissett Salt Marsh, MA	Salt marsh community, dominated by <i>Spartina alterniflora</i> , <i>Spartina patens</i> , <i>Distichlis spicata</i> , and <i>Iva frutescens</i> .	<a href="#">Fox et al. (2012)</a>
Estuarine tidal marsh	Addition: none S dep = not reported N dep = not reported	On the Patuxent River, pore water NO <sub>3</sub> <sup>-</sup> -N and salinity best explained plant species richness (model $R^2 = 0.67$ ), with NO <sub>3</sub> <sup>-</sup> -N accounting for 26% of variation in the full data set and for 5% of variation in widely distributed species. In species with more restricted geographic ranges, NO <sub>3</sub> <sup>-</sup> -N alone best predicted plant species richness (positive relationship, model $R^2 = 0.71$ ).	Nanticoke River and Patuxent River, Chesapeake Bay, MD and DE	Plant community	<a href="#">Sharpe and Baldwin (2013)</a>
Estuarine tidal marsh	Addition: 670 kg N/ha/yr S dep = not reported N dep = not reported	<i>Typha</i> spp. cover increased by 120%.	Nanticoke River, MD and DE	Plant community	<a href="#">Baldwin (2013)</a>
Freshwater estuarine marsh	50, 200, or 1,200 kg N/ha/yr as Nutralene methylene urea S dep = not reported N dep = not reported	N addition ( $N_{add}$ as kg N/ha/yr) decreased the dominance of <i>E. fallax</i> ( <i>Efa</i> , as % biomass) $Efa = -0.00812 \times N_{add} + 15.410$ . Addition increased the dominance of <i>P. punctatum</i> ( <i>Ppu</i> , as % of biomass) $Ppu = 0.03144 \times N_{add} + 9.353$	Tchefuncte River, Madisonville, LA	Oligohaline plant community dominated by <i>Sagittaria lancifolia</i> , <i>Eleocharis fallax</i> , and <i>Polygonum punctatum</i>	<a href="#">Graham and Mendelssohn (2010)</a>

**Table 11-9 (Continued): Nitrogen loading effects upon plant biodiversity and communities.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Restored freshwater wetlands	Ambient deposition; rates not reported	Soil available N (ppm ammonium, abbreviated as $N_{NH4}$ , or ppm nitrate, as $N_{NO3}$ ) correlated with decreasing native species richness (number of species, $y$ ): $y = -73.8N_{NH4} + 122$ , $r^2 = 0.41$ $y = -30.9N_{NO3} + 97.4$ , $r^2 = 0.18$ Soil available N (as ppm nitrate, or $N_{NO3}$ ), correlated with increasing cover by all nonnative plants (relative % cover all non-natives, $z$ ): $z = 41.7N_{NO3} - 3.5$ , $r^2 = 0.31$ Soil available N (as ppm nitrate, or $N_{NO3}$ ), correlated with increasing cover by invasive <i>Phalaris arundinacea</i> (relative % cover, abbreviated PHAR): $PHAR = 52.7N_{NO3} - 29.6$ , $r^2 = 0.58$	28 wetlands restored or created in 1992–2002, Illinois All wetlands surveyed summer 2006	Vascular plant community: 483 species across all wetlands, including 109 non-native species	<a href="#">Matthews et al. (2009)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N ( $NH_4NO_3$ ) or NPK ( $NH_4NO_3$ and $KH_2PO_4$ ) S dep = not reported N dep = 8 kg N/ha/yr	In high N treatment, <i>Sphagnum</i> cover declined by 57%. In all NPK treatments, <i>Sphagnum</i> cover declined over 8 yr to 1–25% of control, as <i>Polytrichum</i> cover increased by 5–10x control and then declined.	Mer Bleue Bog, Ontario, Canada	Bog plant community: dwarf shrub species and mosses: <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , and <i>Polytrichum strictum</i>	<a href="#">Juutinen et al. (2010)</a>
Ombrotrophic peat bog	16 (low), 32 (medium), or 64 (high) kg N/ha/yr as N ( $NH_4NO_3$ ) or NPK ( $NH_4NO_3$ and $KH_2PO_4$ )	After 12 yr of low N, <i>Sphagnum</i> cover decreased 36%. After 5 yr of medium and high N, <i>Sphagnum</i> cover decreased 26 and 54%, respectively.	Mer Bleue Bog, Ontario, Canada	Shrub species ( <i>Vaccinium myrtilloides</i> , <i>Ledum groenlandicum</i> , <i>Chamaedaphne calyculata</i> ) and mosses ( <i>Sphagnum magellanicum</i> , <i>Sphagnum capillifolium</i> , <i>Polytrichum strictum</i> )	<a href="#">Larmola et al. (2013)</a>

**Table 11-9 (Continued): Nitrogen loading effects upon plant biodiversity and communities.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Ombrotrophic peatland	Addition = 16 kg N/ha/yr (5N, or 5x background deposition), 32 kg N/ha/yr (10N), or 64 kg N/ha/yr (20N), all as NH <sub>4</sub> NO <sub>3</sub> Ambient (wet) deposition = 8 kg N/ha/yr and up to 0.26 kg P/ha/yr	N addition increased cover of <i>Chamaedaphne calyculata</i> by 202%(10N), and decreased cover of moss species by 63% (20N).	Mer Bleue bog, Ottawa, Canada	Evergreen shrubs: <i>Chamaedaphne calyculata</i> and <i>Rhododendron groenlandicum</i> dominant; sparse <i>Kalmia angustifolia</i> Deciduous shrubs: <i>Vaccinium myrtilloides</i> Mosses: <i>Sphagnum capillifolium</i> , <i>S. magellanicum</i> , and <i>Polytrichum strictum</i>	<a href="#">Wang et al. (2016a)</a>
Calcareous, rich fen	Addition = 50 kg N/m <sup>2</sup> /yr as NO <sub>3</sub> <sup>-</sup> or 50 kg N/m <sup>2</sup> /yr as NH <sub>4</sub> <sup>+</sup> Ambient deposition = 7–10 kg N/m <sup>2</sup> /yr, based on <a href="#">Aherne and Farrell (2002)</a>	<i>Sphagnum</i> cover increased, <i>Scorpidium</i> cover decreased, and vascular plant cover increased in all plots (including control plots) over the course of the study (2000–2004).	Scragh Bog, Central Ireland	<i>Scorpidium revolvens</i> and <i>Sphagnum contortum</i>	<a href="#">Paulissen et al. (2016)</a>

**Table 11-9 (Continued): Nitrogen loading effects upon plant biodiversity and communities.**

Type of Ecosystem	Additions or Load (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Fen (transitional mire)	Treatment, 2002–2009, solution of NH <sub>4</sub> NO <sub>3</sub> added at 10 kg N/ha/yr (Low N) or 30 kg N/ha/yr (High N) Deposition = not reported	<p><i>C. vulgaris</i> cover does not change in response to low N addition, but 8 yr of high N increased cover (# intercepts) 96%, and cover did not change 3 yr after cessation of N treatment (recovery period).</p> <p><i>S. fuscum</i> cover does not change in response to low N, but 8 yr of high N decreased cover (%) 45%, and cover continued to decline during recovery, when cover was 60% less than in control plots.</p> <p><i>P. strictum</i> cover responded to 8 yr of low and high N with 190–240% cover increase, and although this response declined in recovery period, when cover was 120–140% higher than in control plots.</p> <p><i>M. caerulea</i> cover did not change in response to low N but increased to 5.6x control cover with high N, and was 6.7x control cover during recovery period.</p> <p><i>S. magellanicum</i> cover did not respond to low or high N during 8 yr experiment, but in recovery, cover in plots that had previously received high N increased to 4.3x control plot cover.</p>	Torbiera di Passo San Pellegrino, Italy	Hummocks and lawns: 13 species, <i>Calluna vulgaris</i> , <i>Carex nigra</i> , <i>Carex pauciflora</i> , <i>Carex rostrata</i> , <i>Eriophorum vaginatum</i> , <i>Molinia caerulea</i> , <i>Polytrichum strictum</i> , <i>Sphagnum angustifolium</i> , <i>Sphagnum fuscum</i> , <i>Sphagnum magellanicum</i> , <i>Sphagnum russowii</i> , <i>Vaccinium uliginosum</i> , <i>Vaccinium vitis-idaea</i>  Lawns had an additional four species: <i>Nardus stricta</i> , <i>Potentilla erecta</i> , <i>Trichophorum cespitosum</i> , <i>Vaccinium myrtillus</i>	<a href="#">Gerdol and Brancaleoni (2015)</a>

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## 11.8.2 Consumers

Increased reactive N can alter dynamics among consumers in wetlands. Studies show that increasing N load increases parasitism, decreases overall health condition, and increases the abundance of mosquitos (vectors for zoonotic diseases). There is also a new meta-analysis evaluating consumer behavior in coastal wetlands. [He and Silliman \(2015\)](#) conducted a meta-analysis of herbivory in globally distributed coastal wetlands (marshes and mangroves) and found that N and N + P additions generally increased herbivore abundance and herbivory across salt marsh studies, but not across mangrove studies.

In a survey of the native mud snail *Ilyanassa obsoleta* collected from 15 New England salt marshes, increased N correlated with increasing parasitism of *I. obsoleta*. Sediment N correlated positively with parasitic trematode prevalence ( $R^2 = 0.41$ ) and with infection by the parasitic flatworm *Stephanostomum* spp. ( $R^2 = 0.42$ ).

[Wigand et al. \(2010\)](#) developed a metric for marsh condition using the Nitrogen Loading Model ([Wigand et al., 2003](#)) and data collected on abundance and richness of plants, invertebrates, and soil conditions of 10 coastal marshes in Narragansett Bay, RI. Marsh condition declined as annual N load to the marsh increased.

[Ialeggio and Nyman \(2014\)](#) collected plants dominant in freshwater (*Panicum hemitomon*), freshwater-brackish (*Sagittaria lancifolia*), and brackish (*Spartina patens*) marshes, fertilized the plants with 619 kg N/ha/yr in mesocosms, and then offered the plants along with unfertilized controls in feeding trials to the introduced aquatic rodent *Myocastor coypus* (nutria). Fertilization increased plant tissue N by 140%, from 0.9% N to 2.2% N by mass, and nutria preferentially fed on fertilized plants. N loading increased plant mass loss due to nutria herbivory by 750% ([Ialeggio and Nyman, 2014](#)).

N addition increases the abundance of mosquito species *Culex tarsalis* and *Anopheles hermsi*, which act as vectors for zoonotic diseases. [Duguma and Walton \(2014\)](#) constructed freshwater wetland mesocosms at UC Riverside, planting *Schoenoplectus maritimus* in all mesocosms and monitoring plant growth as well as colonization of mesocosms by mosquito species. N loads were 0, 32, 65, and 108 kg N/ha in 2009, and 0, 59, 119, and 198 kg N/ha in 2010. Sampling retrieved elevated numbers of *Culex tarsalis* (western encephalitis mosquito) larvae and pupae in elevated nitrogen treatments in both 2009 and 2010, and of *Anopheles hermsi* in 2010. In 2009, immature mosquito counts were 56–100% higher in fertilized treatments than in control treatments, but there were no differences among different N loads in mosquito counts. In 2010, total mosquito counts were similar in unenriched mesocosms and in mesocosms receiving 59 kg

N/ha/yr, but increased by 64% with 119 kg N/ha/yr, and by 129% with 198 kg N/ha/yr ([Duguma and Walton, 2014](#)).

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## 11.9 Critical Loads

In the 2008 ISA, no critical loads studies had been published. Since then, critical loads have been published for wetlands in the U.S. ([Greaver et al., 2011](#)).

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### 11.9.1 Freshwater Wetland

There are two published critical loads for North American freshwater wetlands. [Greaver et al. \(2011\)](#) determined that the critical load for altered peat accumulation and NPP is between 2.7 and 13 kg N/ha/yr, based on observations from [Aldous \(2002a\)](#), [Moore et al. \(2004b\)](#), [Rocheffort et al. \(1990\)](#), and [Vitt et al. \(2003\)](#). The upper end of this critical load range is based on measurements of wet deposition only [10 to 13 kg N/ha/yr; ([Aldous, 2002a, b](#))] and, therefore, does not reflect total N loading from all sources. There is evidence showing that N deposition alters both the morphology and population dynamics of the purple pitcher plant. The empirical evidence suggests a critical load to protect the population of purple pitchers of 10–14 kg N/ha/yr ([Gotelli and Ellison, 2006](#)), while matrix modeling to forecast long-term population sustainability based on observations of population demographics suggests a lower value of 6.8 kg N/ha/yr ([Gotelli and Ellison, 2002](#)).

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### 11.9.2 Coastal Wetlands

Coastal wetlands have open hydrologic and nutrient cycles that receive N loads from sources other than atmospheric deposition, so a critical load for atmospheric N deposition has been difficult to establish ([Greaver et al., 2011](#)). Typically, the amount of N added in experimental treatments in these systems simulates total N input and, therefore, far exceeds the atmospheric deposition received by U.S. coastal wetlands. Only two studies have considered N loads below 100 kg N/ha/yr. Based on the results of [Wigand et al. \(2003\)](#), a critical load to protect the community structure of salt marshes is likely to be 63 to 400 kg N/ha/yr. [Caffrey et al. \(2007\)](#) provided additional evidence that 80 N/ha/yr alters microbial activity and biogeochemistry. [Greaver et al. \(2011\)](#) also established a critical load for eelgrass growing in estuarine and marine waters associated with coastal wetlands (see [Appendix 10.6](#)). The critical load for coastal wetlands is based on total N loading to salt marshes. Total loading includes N deposition directly to the marsh surface,

N deposited to the watershed and transported via surface or groundwater, and runoff from agriculture, urban areas, or other sources. Additional experimental evidence on ecosystem response to N loads more similar to N loading from atmospheric deposition is needed to improve the critical load calculation for coastal wetlands in the U.S.

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### 11.9.3 Comparison to Critical Loads from Europe

An assessment of N critical loads in Europe was published in 2003 and designated critical loads for multiple types of wetlands, including raised and blanket bogs, poor fens, rich fens, mountain rich fens, and intertidal wetlands ([Bobbink et al., 2003](#)). There are numerous publications on N effects to wetlands in Europe compared to the U.S. In general, documented responses include effects on growth and species composition, competition among species, peat and peat water chemistry, decomposition, and nutrient cycling. A brief summary of the European critical loads for wetlands is presented here.

[Bobbink et al. \(2003\)](#) assigned a critical load of 5 to 10 kg N/ha/yr for bog ecosystems, based on plant community and species responses to N deposition, and indicated that precipitation and P limitation should be used to assign critical loads to individual sites. The observed changes in the plant communities of ombrotrophic bogs included the replacement of *Sphagnum*-forming species with nitrophilous moss species [20 to 40 kg N/ha/yr in Dutch bogs; ([Greven, 1992](#))] and the absence of characteristic *Sphagnum* species in British bogs [30 kg N/ha/yr; ([Lee and Studholme, 1992](#))]. A recent study along a deposition gradient in Alberta, Canada, compared *Sphagnum* bog and fen responses in that region to previously published European bog and fen responses to N and S deposition. Similar N deposition gradients elicited significant *Sphagnum* and water chemistry responses in European peatlands but no responses in Albertan peatlands ([Wieder et al., 2016](#)). This suggests that critical loads for European *Sphagnum* species, which have experienced a longer history of higher N deposition than North American wetlands, may not be applicable in North American bogs and fens. [Bobbink et al. \(2003\)](#) also suggested a critical load for the carnivorous bog plant roundleaf sundew [10 kg N/ha/yr in Swedish bogs; ([Bobbink et al., 2003](#); [Redbo-Torstensson, 1994](#))] that may be relevant to American bogs where this species also grows. The European critical load for this carnivorous plant is similar to the range of critical loads suggested for freshwater wetlands in the U.S.

There are European critical loads for fens, but they are based on moss decline, and the amount of N causing ecological effects may not be directly relevant to U.S. ecosystems for the reasons outlined by [Wieder et al. \(2016\)](#). European poor fens have a critical load of 10 to 20 kg N/ha/yr based on increased sedge and vascular plants and negative effects

on mosses. The critical load for rich fens in Europe is 15 to 35 kg N/ha/yr based on increased tall graminoids and decreased diversity. The critical load for montane rich fens in Europe was 15 to 25 kg N/ha/yr based on increased vascular plants and decreased bryophytes. These community changes are similar to the increasing vascular plant and declining moss cover observed in American N addition experiments (see [Appendix 11.10](#)), although there has been no critical load established for American bogs and fens based on these community composition changes. In Europe, changes in the vegetation composition and structure likely affect fauna species assemblages, such as ground-breeding birds, spiders, and beetles, living in the originally open bog vegetation. Increased nutrient availability results in an increase of the nutrient content of plant material ([Limpens et al., 2003a](#); [Tomassen et al., 2003](#)) and algal growth ([Limpens et al., 2003b](#); [Gulati and Demott, 1997](#)), which affects herbivorous, detritivorous, and carnivorous invertebrates ([van Duinen et al., 2004](#)).

The European critical load for salt marshes, based on expert judgment, is 30 to 40 kg N/ha/yr ([Bobbink et al., 2003](#)), but studies of European salt marshes are limited. There are no European wetland systems composed of native plants directly equivalent to North American low salt marshes; in European systems, these zones consist of unvegetated mud flats, or of monocultures of invasive plants. High levels of N input (65 to 70 kg N/ha/yr) significantly increased biomass production in the Netherlands ([van Wijnen and Bakker, 1999](#)); however, no changes in species composition and in diversity have been observed at deposition of 15 to 25 kg N/ha/yr at sites in the Netherlands and Germany ([Bobbink et al., 2003](#)). The critical load for N deposition in North American coastal wetlands may be close to these values when considered as part of the total N load that these systems receive.

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## 11.10 Summary

There are chemical and biological effects of N deposition in wetlands. Wetland vegetative communities are adapted to high levels of natural organic acidity, so it is unlikely that S or N deposition would cause any acidification-related effects at levels of acidic deposition commonly found in the U.S. [([U.S. EPA, 2008a](#)), in Annex B]. Wetlands can be sensitive to eutrophication caused by N deposition. These effects were documented in the 2008 ISA. In this appendix, new information published since 2008 is integrated with the information published in the 2008 ISA. Synthesis is made across wetland types for causality statements. Information is also synthesized for freshwater and coastal wetlands because saltwater and estuarine wetlands are typically adapted to much higher N loading.

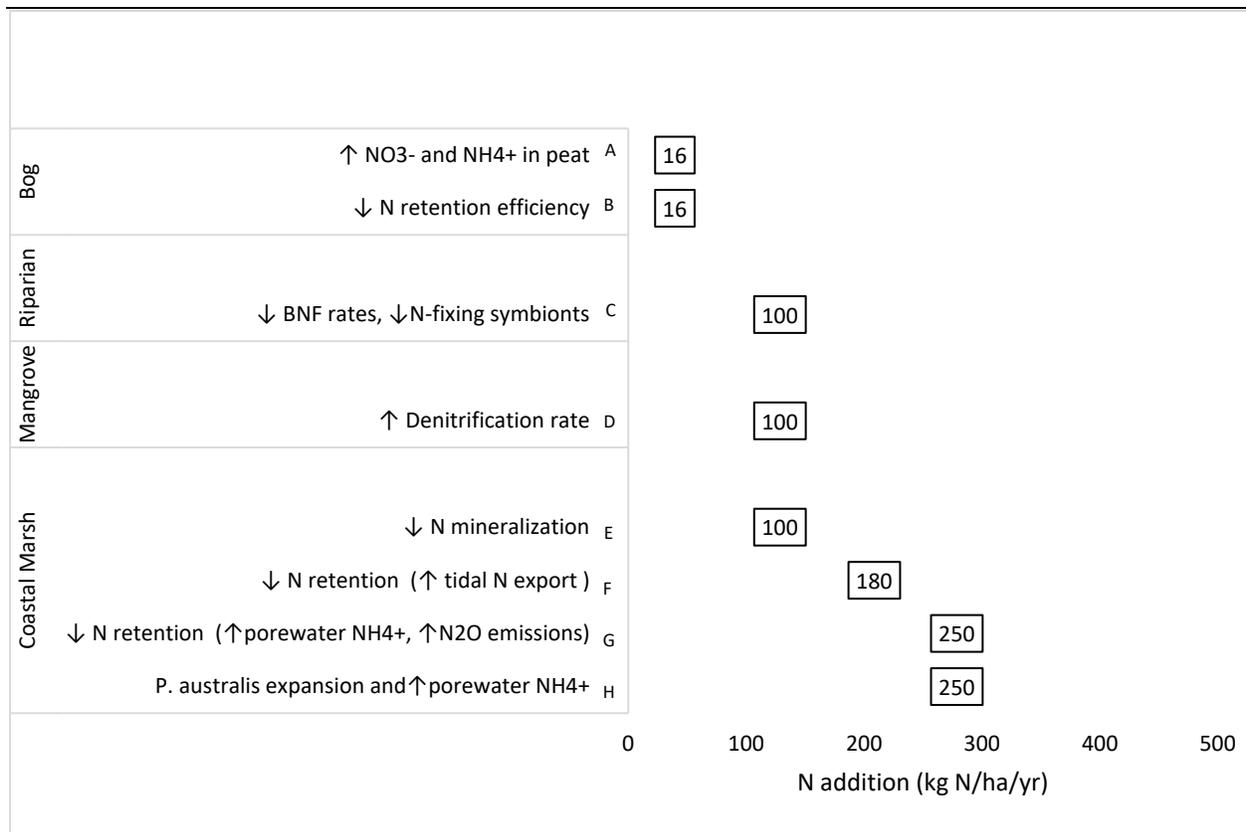
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### 11.10.1 Causality across Wetland Types

New studies published between 2008–2015 support and extend the findings of the 2008 ISA. As in the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling in wetlands.** N deposition changes N and C cycling in wetlands. There is new evidence of N deposition changes to plant physiology, which was not included in the 2008 ISA as an endpoint due to lack of evidence. This evidence expands our understanding of the causal relationship between N deposition and species diversity. **The body of evidence is sufficient to infer a causal relationship between N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands.**

N deposition contributes to total N loading in wetlands, with the relative contribution of deposition to total loading variable among wetland types. Chemical indicators of N deposition in wetlands include  $\text{NO}_3^-$  and  $\text{NH}_4^+$  leaching, DON leaching, N mineralization, denitrification rates, and  $\text{N}_2\text{O}$  emissions. A wetland can serve as a source, sink, or transformer of atmospherically deposited N ([Devito et al., 1989](#)). Source/sink N dynamics in wetlands vary with season, hydrological conditions, vegetation type, climate, and surface geology ([Mitchell et al., 1996](#); [Arheimer and Wittgren, 1994](#); [Koerselman et al., 1993](#); [Devito et al., 1989](#)).

Several new studies provide evidence of N deposition alterations to biogeochemical cycling of N within a wetland ecosystem ([Appendix 11.3](#)). A synthesis study of multiple wetland types across the globe shows wetland N removal is proportional to N load ( $\log[\text{N removal}] = 0.943 \times \log[\text{N load}] - 0.033 \text{ N}$ ) and removal efficiency is 26% higher in nontidal than tidal wetlands ([Jordan et al., 2011](#)). Meta-analysis of 19 N addition observations (N addition 15.4 to 300 kg N/ha/yr) found that N enrichment increased wetland  $\text{N}_2\text{O}$  emissions by 207% ([Liu and Greaver, 2009](#)). The emission factor for the amount of N added to a wetland that is converted to  $\text{N}_2\text{O}$  ranges between 0.007–0.07 ([Liu and Greaver, 2009](#)). There are also new studies that evaluate the effects of N loading/N addition on other endpoints related to N cycling in peat bog, riparian, mangrove, and salt marsh wetlands. The endpoints evaluated include ecosystem N retention, wetland export of N to surface waters, N fixation, N mineralization, denitrification, emission of  $\text{N}_2\text{O}$ ; and bacterial abundance, activity, and composition in wetland soils. The results of North American studies are summarized in [Figure 11-2](#). Across studies, N loading decreases the ability of wetlands to retain and store nitrogen, which may diminish the wetland ecosystem service of improving water quality.



BNF =biological nitrogen fixation; ha = hectare; kg = kilogram; N = nitrogen.

<sup>a</sup>[Pinsonneault et al. \(2016\)](#).

<sup>b</sup>[Xing et al. \(2011\)](#).

<sup>c</sup>[Ruess et al. \(2013\)](#).

<sup>d</sup>[Whigham et al. \(2009\)](#).

<sup>e</sup>[Vivanco et al. \(2015\)](#).

<sup>f</sup>[Brin et al. \(2010\)](#).

<sup>g</sup>[Pastore et al. \(2016\)](#).

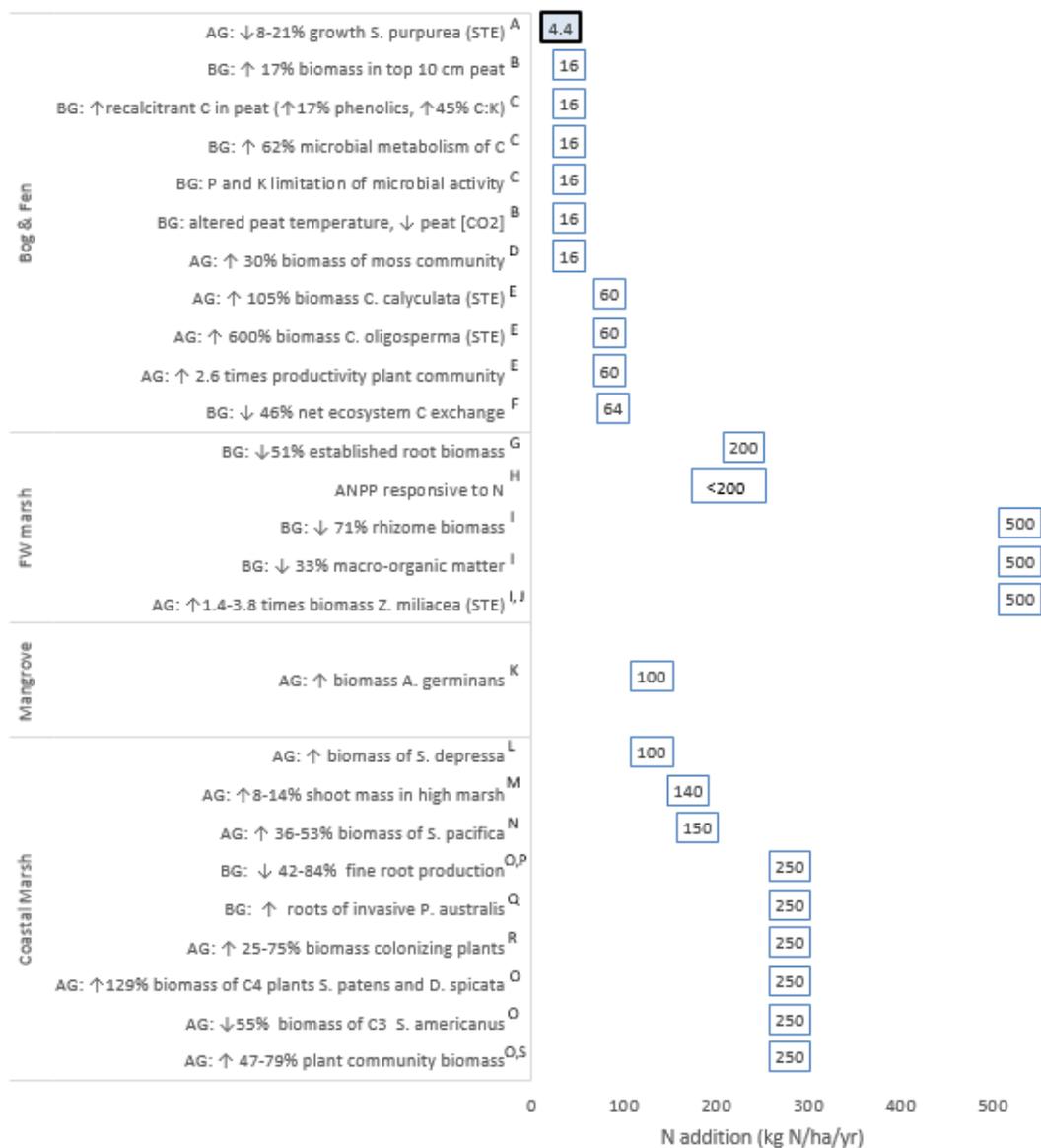
<sup>h</sup>[Mozdzer et al. \(2016\)](#).

**Figure 11-2 Summary of the levels of nitrogen addition where a change to nitrogen cycling is observed.**

There is new information on how N deposition alters biogeochemical cycling of C in wetlands. In the 2008 ISA, evidence from Canadian and European peatlands showed that N deposition had negative effects on *Sphagnum* bulk density and mixed effects on *Sphagnum* productivity depending on the history of deposition. In Canadian ombrotrophic peatlands experiencing deposition of 2.7–8.1 kg N/ha/yr, peat accumulation increased with N deposition, but accumulation rates had slowed by 2004, indicating a degree of N saturation ([Moore et al., 2004b](#)). N addition alters belowground and aboveground pools of carbon and also increases wetland methane emissions, as

summarized by meta-analysis in the 2008 ISA and published in [Liu and Greaver \(2009\)](#). In a study of 90 wetlands around the Gulf Coast from Florida to Texas, [Nestlerode et al. \(2014\)](#) found that higher N in the soil correlated with lower bulk density ( $\ln[\text{soil \%N}] = -1.9233 \times [\text{g/cc}] + 0.4165$ ) which indicates that the marsh is less resilient to physical stresses from tidal or storm flooding, and the marsh platform is more likely to shear off or wash away. New evidence shows that N loading increases methane production from wetland soils. In N addition experiments replicated in three California marshes ([Vivanco et al., 2015](#); [Irvine et al., 2012](#)), field-measured methane flux from soils increased linearly with increasing N load (0, 100, 200, 400, 800, 1,600, 3,200 kg N/ha/yr), such that CH<sub>4</sub> flux from soils increased by 1.23 μg CH<sub>4</sub>/m<sup>2</sup>/day for each 10 kg N/ha/yr added, ([Vivanco et al., 2015](#); [Irvine et al., 2012](#)). Methane flux increased from low or nearly negative to net positive values above ~100 kg N/ha/yr, indicating a shift from net methanotrophy to methanogenesis in the microbial community in response to N loading consistent with other studies ([Liu and Greaver, 2009](#)).

Additional literature evaluates the effects of N deposition, N loading, or experimental N addition on C cycling in salt marshes, mangroves, freshwater tidal marshes, riparian or intermittent marshes, bogs, and fens. Significant effects of N loading upon biogeochemical cycling of C in North American wetlands (in which the N addition was 500 kg N/ha/yr or lower) are summarized in [Figure 11-3](#). Ecological endpoints evaluated to assess N loading effects on C cycling include (1) measures of C pools—plant aboveground biomass and productivity, plant belowground biomass of roots and rhizomes, soil organic matter, and total soil C or peat C; (2) measures of C fluxes—microbial mineralization, decomposition rates, CO<sub>2</sub> emissions, and CH<sub>4</sub> emissions; and (3) measures of physical marsh stability as a proxy for long-term C storage—peat chemical composition, temperature, bulk density, physical resistance, and soil water content. In general across wetlands, nitrogen loading increases aboveground C pools, decreases or does not change belowground C pools, and does not change or increases C fluxes. This shift from belowground to aboveground C storage may diminish the wetland ecosystem services of long-term carbon storage and flood protection, as well as reduce the stability and persistence of wetlands on the landscape. N loading effects upon C cycling are uneven across species, which may affect wetland biodiversity and the wetland ecosystem service of provisioning.



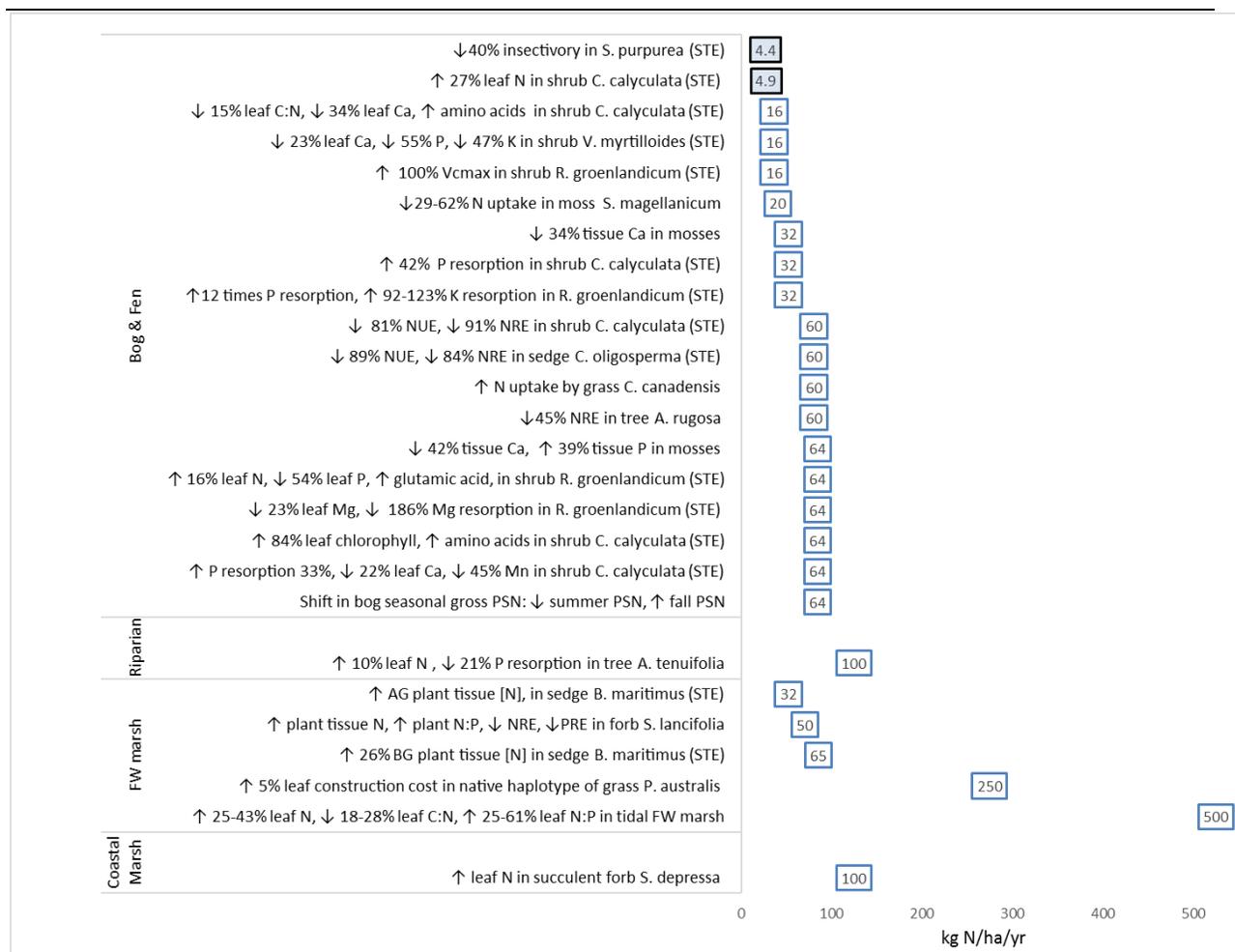
AG = aboveground; ANPP = aboveground net primary productivity; BG = belowground; CO<sub>2</sub> = carbon dioxide; FW = freshwater; ha = hectare; kg = kilogram; N = nitrogen; NPP = net primary productivity; STE = state-listed threatened or endangered species; yr = year.

<sup>A</sup>Crumley et al. (2016); <sup>B</sup>Wendel et al. (2011); <sup>C</sup>Pinsonneault et al. (2016); <sup>D</sup>Xing et al. (2011); <sup>E</sup>Iversen et al. (2010); <sup>F</sup>Larmola et al. (2013); <sup>G</sup>Graham and Mendelssohn (2016); <sup>H</sup>Graham and Mendelssohn (2010); <sup>I</sup>Ket et al. (2011); <sup>J</sup>Frost et al. (2009); <sup>K</sup>Whigham et al. (2009); <sup>L</sup>Vivanco et al. (2015); <sup>M</sup>(Johnson et al., 2016a); <sup>N</sup>Goldman Martone and Wasson (2008); <sup>O</sup>Langley and Megonigal (2010); <sup>P</sup>Langley and Megonigal (2012); <sup>Q</sup>Mozdzer et al. (2016) <sup>R</sup>Langley et al. (2013); <sup>S</sup>Langley et al. (2009).

Grey boxes with black borders represent ambient deposition studies, and white boxes with blue borders represent field nitrogen addition experiments.

**Figure 11-3 Summary of new literature of nitrogen load effects on belowground and aboveground carbon cycling.**

N addition effects on plant stoichiometry and plant architecture were not addressed in the 2008 ISA. Plant stoichiometry theory considers the balance of multiple chemical elements in living tissues, and plant architecture is defined as the three-dimensional organization of the plant body. The stoichiometry of plant tissue is often connected to the tissue's physiological function. Most new studies on physiology and stoichiometry have been conducted in bogs and fens, where N addition typically caused an increase in plant N content, a decrease in N use efficiency and resorption, and an increase in plant production, particularly of vascular plants. At high N loads or cumulative exposure to years of lower N loads plants may experience leaf N saturation and micronutrient limitation (e.g., P, K, and Ca, indicated by altered leaf tissue concentrations or altered reabsorption efficiencies; see [Figure 11-4](#)), which in turn cause leaf damage ([Bubier et al., 2011](#); [Xing et al., 2011](#)) or decreasing plant abundance of sensitive species (see biodiversity section). N loading can disrupt nutrient acquisition of carnivorous plants via their adaptation of capturing and digesting insects; for example, along a narrow N deposition gradient (3.4–5.0 kg N/ha/yr) across bogs in the Adirondack Mountains, purple pitcher plant (*S. purpurea*) experienced negative effects upon growth and insectivory at deposition of 4.4–4.9 kg N/ha/yr ([Crumley et al., 2016](#)). A new European study also found negative effects of N deposition upon insectivory of the wetland plant *Drosera rotundifolia* at 3.81–11.30 kg N/ha/yr ([Millett et al., 2012](#)). Historically low N loads to bogs and fens have made these wetlands and their endemic plant species particularly sensitive to N deposition. New studies of physiology and plant architecture in North American riparian wetlands, freshwater tidal marshes, mangroves, and salt marshes showed that N addition in these systems increased plant tissue N with a cascading effect that increased plant primary production and changed plant architecture. N loading increased plant height in salt and freshwater marshes, which [Deegan et al. \(2012\)](#) showed made salt marshes top-heavy and resulted in a loss of marsh platform stability, with and shredding and loss of marsh surface. In general effects of N loading upon physiology and architecture vary by species across North American wetlands. Even species tolerant of N loading may experience negative effects if N loading causes physiological limitation by other nutrients, including Ca, P, and K. Plant physiology and architecture altered by N loading may affect wetland biodiversity and resiliency to other disturbances.



AG = aboveground; BG = belowground; C = carbon; Ca = calcium; FW = freshwater; K = potassium; Mg = magnesium; Mn = manganese; N = nitrogen; NRE = nitrogen resorption efficiency; NUE = nutrient use efficiency; P = phosphorus; PP = primary productivity; PRE = phosphorus resorption efficiency; PSN = photosynthesis; STE = state-listed threatened or endangered species;  $V_{cmax}$  = maximum velocity of carboxylation.

Grey boxes with black borders represent ambient deposition studies, and white boxes with blue borders represent field nitrogen addition experiments.

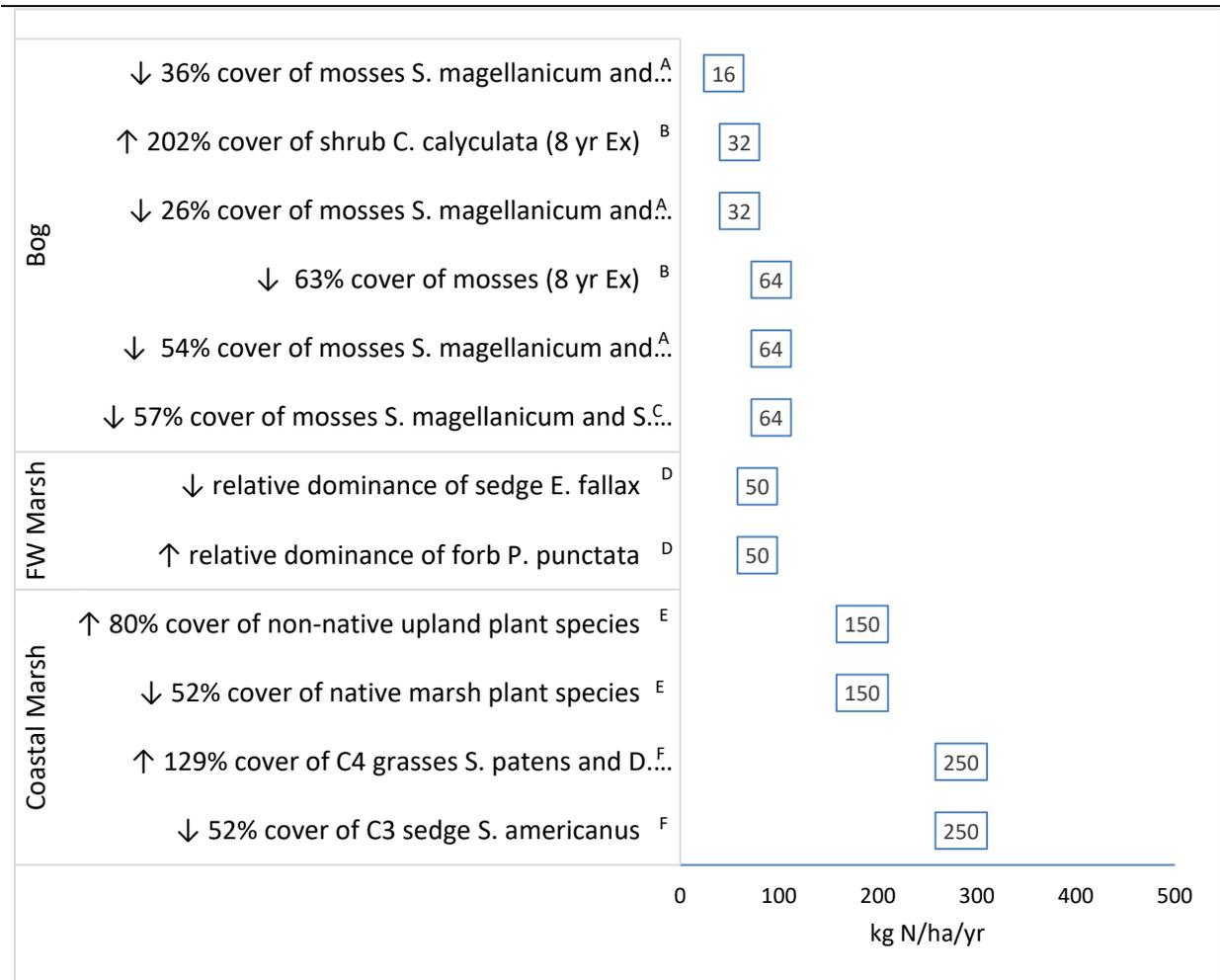
**Figure 11-4 Summary of the level of nitrogen load that caused a change in the response variables of plant stoichiometry and physiology in wetlands.**

The 2008 ISA found that the evidence was sufficient to infer a causal relationship between N deposition and the alteration of species richness, species composition, and biodiversity in wetland ecosystems. Wetlands provide habitat to a disproportionately high number of rare plants given their relative area; for example, fens occupy 0.01% of the land area of northeast Iowa yet contain 17% of the endangered, threatened, or listed species of concern in the area. The 2008 ISA noted that there were 4,200 native plant

species in U.S. wetlands, 121 of which are federally endangered. Wetland species have evolved under N limited conditions, including endangered species in the *Isoetes* (3 endangered species) and *Sphagnum* (15 endangered species) genera, as well as the endangered insectivorous plants *Sarracenia oreophila* and *Drosera rotundifolia*. Plant demography was not specifically addressed in the 2008 ISA, although demography is an important aspect in maintaining species richness and biodiversity. Plant demography is the change in plant population size and structure through time. In bogs and fens, N addition experiments suggest positive population growth rates for *Sarracenia purpurea* at 0 or 1.4 kg N/ha/yr, but population losses at 14 kg N/ha/yr (Gotelli and Ellison, 2006). Demographic modelling of *S. purpurea* found that populations remained stable for 100 years at deposition rates of 4.5–6.8 kg N/ha/yr, but extinction risk for populations increased above 6.8 kg N/ha/yr (Gotelli and Ellison, 2002). Field N addition studies suggest that N addition to bogs and fens will also affect community composition (Figure 11-5). In Mer Bleue Bog, Ontario, N addition decreased the dominance of *Sphagnum* mosses in the northern ombrotrophic peat bog, while increasing dominance of woody shrub species (Larmola et al., 2013; Juutinen et al., 2010). This result is consistent with the earlier European literature summarized in the 2008 ISA, which showed that N deposition decreased moss dominance and increased the dominance of vascular plants in European bogs and fens.

Across freshwater wetlands, N load is correlated with an increase in the abundance of invasive plant species and a decrease in the number of native plant species (see Figure 11-1 and Appendix 11.8.1), as well as an increase in larvae of mosquito species that are vectors for zoonotic diseases (Appendix 11.8.2). In a freshwater tidal marsh on the Tchefuncte River, LA, N addition shifted the relative dominance of the perennial wetland-obligate monocots dominant at the site (Graham and Mendelssohn, 2010). In salt marshes, N addition caused negative reproductive effects in invasive *Spartina foliosa* and *Spartina* hybrids (Tyler et al., 2007), and a positive effect on reproduction in *Salicornia bigelovii* (Boyer and Zedler, 1999). N loading in salt marshes is correlated with species richness. A study on the Patuxent River found marsh soil  $\text{NO}_3^-$ -N and pore water salinity best explained variation in plant species richness out of all factors considered ( $R^2 = 0.67$ ), with  $\text{NO}_3^-$ -N accounting for 26% of the variation in total species richness. In the same system, the best model for rare species richness contained only soil  $\text{NO}_3^-$ -N as an explanatory variable, with a positive relationship between  $\text{NO}_3^-$ -N and species richness [ $R^2 = 0.71$  (Sharpe and Baldwin, 2013)]. In salt marshes in Maryland and California, N addition was shown to alter the relative abundance of plant species [Langley and Megonigal (2010); Goldman Martone and Wasson (2008); Figure 11-5]. N deposition effects can cascade beyond plants up trophic levels to consumers. Meta-analysis showed that N loading increased invertebrate abundance and herbivory, and a field experiment found increased herbivory by the invasive mammal nutria in freshwater tidal and salt

marshes ([Appendix 11.8.2](#)). In New England, N loading decreased salt marsh condition, evaluated by a multidimensional metric that included abundance and richness of plants and invertebrates as well as soil conditions ([Appendix 11.8.2](#)). In general, N loading across North American wetlands decreases richness or abundance of sensitive species while promoting invasive species, with negative effects on biodiversity.



Ex = experimental exposure length; FW = freshwater; h = hectare; kg = kilogram; N = nitrogen; yr = year.

<sup>A</sup>[Larmola et al. \(2013\)](#).

<sup>B</sup>[Wang et al. \(2016a\)](#).

<sup>C</sup>[Juutinen et al. \(2010\)](#).

<sup>D</sup>[Graham and Mendelsohn \(2010\)](#).

<sup>E</sup>[Goldman Martone and Wasson \(2008\)](#).

<sup>F</sup>[Langley and Megonigal \(2010\)](#).

Numbers indicate the lowest addition level in which change is observed.

**Figure 11-5 Summary of nitrogen addition studies on wetland biodiversity.**

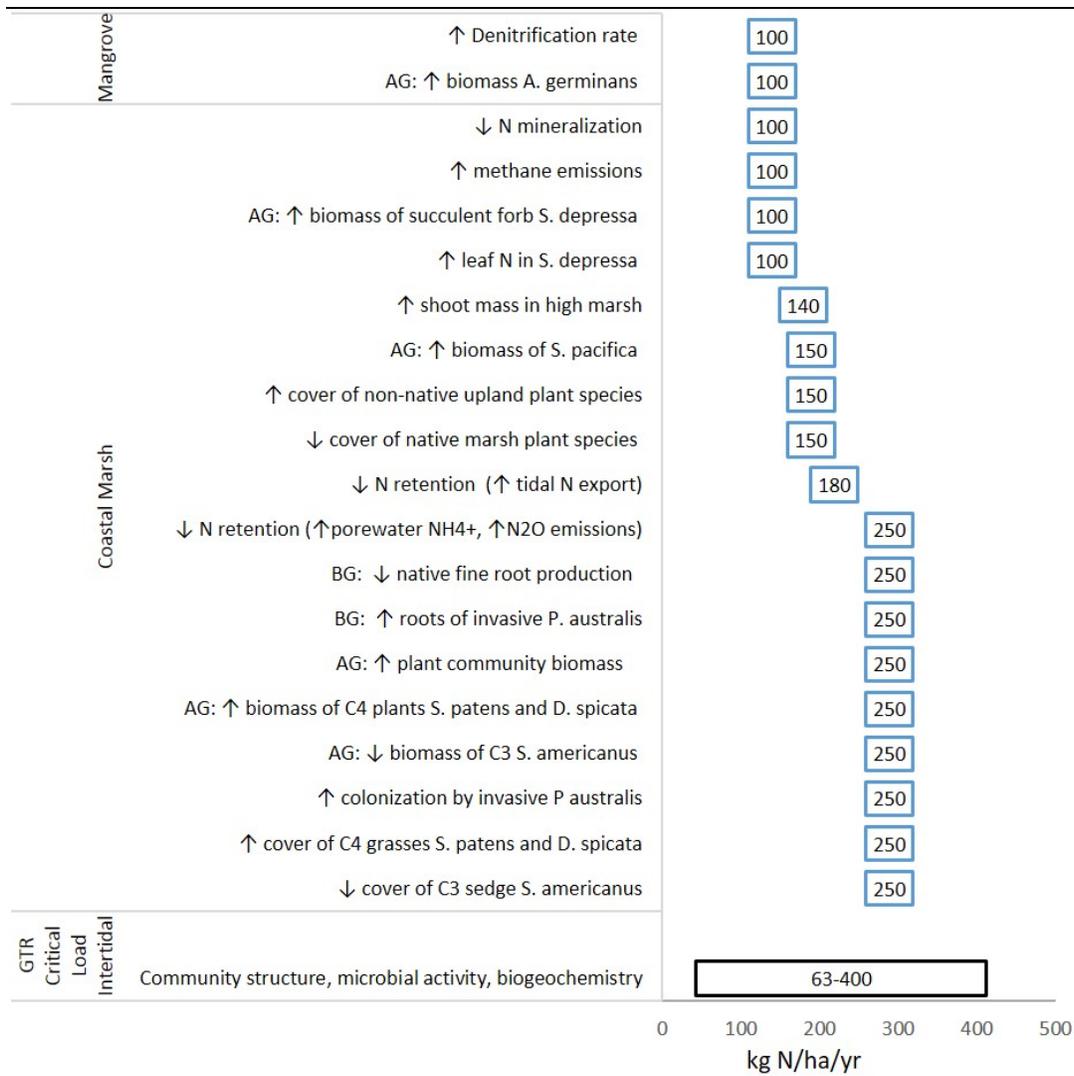
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## 11.10.2 Coastal versus Freshwater Wetlands

Coastal and freshwater wetlands tend to have different sensitivity to N deposition/loading. The effect of N deposition on wetland ecosystems depends on the fraction of rainfall in the total water budget, and the sensitivity to N deposition has been suggested as: bogs (70–100% rainfall) > fens (55–83% rainfall) > coastal wetlands [10–20% rainfall ([Morris, 1991](#))].

[Greaver et al. \(2011\)](#) suggested a critical load to protect biodiversity and biogeochemistry of coastal wetlands based on salt marsh community composition, microbial activity, and biogeochemistry (63–400 kg N/ha/yr as total N load). A comparison of those critical loads with data on N addition levels (15–500 kg N/ha/yr) and associated effects, published since the last ISA, is given in [Figure 11-6](#).

In freshwater systems, [Greaver et al. \(2011\)](#) determined a critical load for wetland C cycling as quantified by altered peat accumulation and NPP, between 2.7 and 13 kg N/ha/yr. [Greaver et al. \(2011\)](#) also set a critical load to protect biodiversity based on morphology and population dynamics of the purple pitcher plant (*Sarracenia purpurea*) between 6.8–14 kg N/ha/yr. A more recent study across an N deposition gradient suggests that purple pitcher plant populations experience negative effects of N deposition at 4.4 kg N/ha/yr ([Crumley et al., 2016](#)). A comparison of freshwater wetland CLs to data from N addition levels (16–500 kg N/ha/yr) and associated effects, published since the CLs for wetlands were set, is given in [Figure 11-7](#). There is information on the relationship between N addition and numerous endpoints. At the lowest experimental addition level (16 kg N/ha/yr), there are observations of altered C and N cycling and altered biodiversity. The endpoints affected include decreases in moss cover, increased peat biomass, decreased N retention efficiency, and altered/damaged leaf stoichiometry in vascular plants.



AG = aboveground; BG = belowground; CH<sub>4</sub> = methane; GTR = general technical report; N = nitrogen.

**Figure 11-6 Summary of field nitrogen addition studies for coastal wetlands (blue borders) versus critical load (black border).**



AG = aboveground; ANPP = aboveground net primary productivity; BG = belowground; BNF = biological nitrogen fixation; C = carbon; Ca = calcium; CO<sub>2</sub> = carbon dioxide; Ex = experimental exposure length; FW = freshwater; GTR = general technical report; K = potassium; Mg = magnesium; Mn = manganese; N = nitrogen; NPP = net primary productivity; NRE = nitrogen resorption efficiency; NUE = nutrient use efficiency; P = phosphorus; PRE = phosphorus resorption efficiency; PSN = photosynthesis; SLM = specific leaf mass; STE = state-listed threatened or endangered species; V<sub>max</sub> = maximum carboxylation velocity; yr = year. Values indicate biotic or chemical changes observed in response to experimental nitrogen addition (boxes with blue borders) or an ambient gradient of N deposition (boxes with black borders).

**Figure 11-7 Summary of nitrogen load studies for freshwater wetlands as well as current critical loads.**

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## APPENDIX 12 NONACIDIFYING SULFUR ENRICHMENT EFFECTS

[Appendix 12](#) summarizes research on the nonacidifying impacts of S deposition on ecosystems, synthesizing literature published since the *2008 ISA for Oxides of Nitrogen and Sulfur-Ecological Criteria* (hereafter referred to as the 2008 ISA) with earlier key studies. The causal statements are presented in the Introduction ([Appendix 12.1](#)).

[Appendix 12.2](#) discusses the effects of sulfur (S) deposition on S storage and cycling in ecosystems, sulfide phytotoxicity in wetlands, internal eutrophication in freshwater aquatic systems, methane emissions from wetlands and lakes, and the microbial communities responsible for methanogenesis.

Increasing bioavailability of mercury (Hg) due to S addition is a major focus, and Hg sources, pools, and fluxes in terrestrial and aquatic ecosystems are briefly described in [Appendix 12.3.1](#) and [Appendix 12.8](#). [Appendix 12.3.2](#) includes a discussion of the current understanding about the distribution of Hg methylation potential across the prokaryotic domains and the key role of sulfur-reducing prokaryotes (SRPs). Mercury methylation occurs in lakes in shallow sediments or below the oxycline; in peat wetlands, at the interface with upland areas and generally near the water surface in peat; in periphyton; in saturated decomposing litter or algal biomass; in saturated forest soils; and in estuarine and marine sediments. In freshwater systems, methylation is strongly seasonal, with methylmercury (MeHg) concentrations peaking in summer or fall. Methylation rates and MeHg concentrations are determined by the biological niche and environmental requirements of microbial methylators; the current state of our understanding of those environmental requirements is briefly summarized in [Appendix 12.3.3](#).

In [Appendix 12.3.4](#), multiple lines of evidence are presented establishing the relationship between SO<sub>x</sub> deposition and increases in bioavailable Hg in the environment, including experimental S addition experiments and case studies from well-studied wetlands where S inputs are primarily agricultural. [Appendix 12.3.5](#) considers observational evidence of the correlations between SO<sub>x</sub> deposition and Hg burdens in fish. [Appendix 12.3.5](#) also presents the results of observational studies in prairie pothole wetlands, peat bogs, freshwater marshes, streams, and rivers that show correlations between ambient sulfate and MeHg concentrations in water and sediment samples. [Appendix 12.4](#) summarizes studies that find higher Hg burdens in mosquitos and fish from ecosystems with increased experimental or anthropogenic S loading. Ecosystems especially sensitive to the effects of S deposition are described in [Appendix 12.5](#).

[Appendix 12.6](#) describes critical loads for Hg from European systems; at this time, there are no established critical loads for nonacid S effects in North American ecosystems. [Appendix 12.7](#) is a summary including causal determinations based on the synthesis of new information and previous evidence.

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## 12.1 Introduction

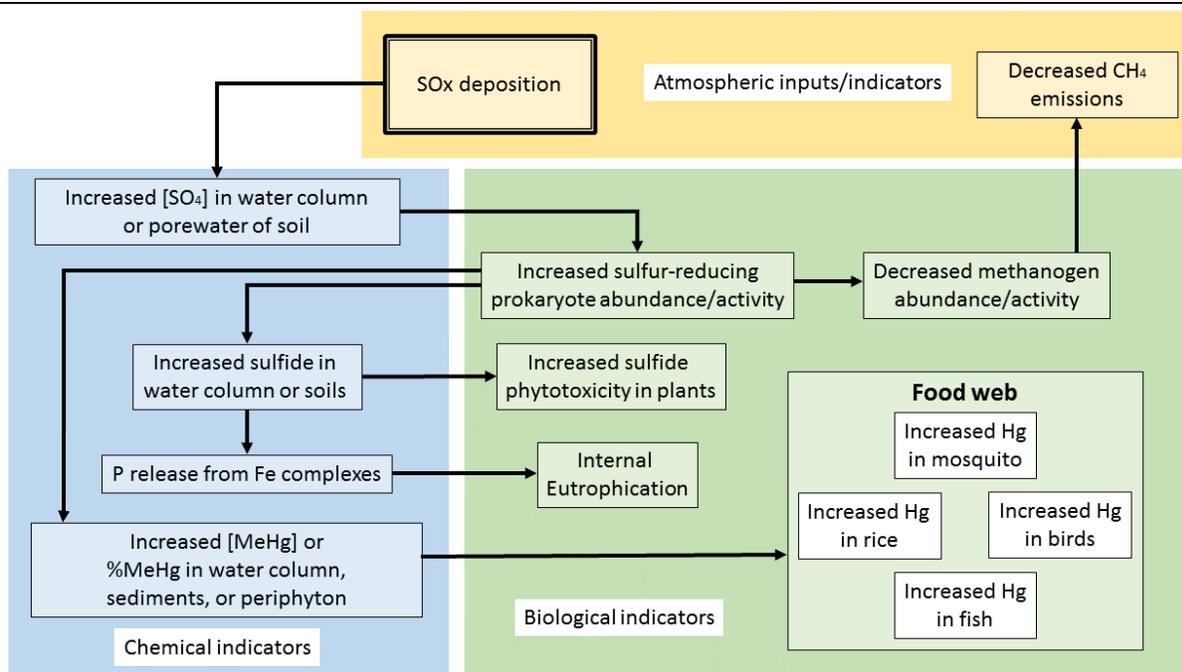
In the 2008 ISA, the evidence was sufficient to infer a causal relationship between S deposition and increased methylation of Hg in aquatic environments where the value of other factors was within adequate range for methylation. Direct atmospheric deposition of S to wetland and aquatic systems, as well as sulfate leaching from terrestrial systems with current or historical S deposition, alters biology and chemistry of these systems. Nonacidifying effects of S deposition in these nonterrestrial systems include toxicity to wetland plants, increased phosphorus (P) availability leading to internal eutrophication, altered methane emissions, and increased Hg methylation and Hg concentration in biota. Consistent with the causal statement in the 2008 ISA, **the body of evidence is sufficient to infer a causal relationship between S deposition and the alteration of Hg methylation in surface water, sediment, and soils in wetland and freshwater ecosystems.** The 2008 ISA described sulfide phytotoxicity in European systems, but there is more recent research demonstrating sulfide phytotoxicity under current conditions in North American wetlands. **The body of evidence is sufficient to infer a causal relationship between S deposition and changes in biota due to sulfide phytotoxicity including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems.**

S deposition contributes to Hg accumulation by stimulating the activity of anoxic-sediment-dwelling sulfur-reducing bacteria (SRB), which convert inorganic Hg to MeHg in the course of metabolism. The 2008 ISA described the activity of SRB, but more recent research indicates that S reducing archaea are also active in wetland sediments, which is why this document will use the broader term sulfur-reducing prokaryotes (SRPs) to denote both bacteria and archaea involved in S reduction. Laboratory and mesocosm-scale experiments reviewed in the 2008 ISA established that only trace amounts of MeHg could be produced in the absence of sulfate. These results were confirmed with larger scale observational studies. MeHg enters the food chain and bioaccumulates in higher trophic levels, and research summarized in the 2008 ISA suggested that numerous wild populations of fish, birds, and mammals experienced MeHg exposures high enough to cause substantial reproductive, behavioral, or health impairment.

At the time of the 2008 ISA, dose-response relationships between S deposition and Hg-methylation rates had not been established, in part because oxygen content, temperature, pH, and labile carbon supply also control the rates of the activity of SRB in aquatic environments. Evidence of commensurate increases in methylation with increased S continued to accumulate, but because of wide variability in those interacting factors, the exact dose-response relationships that have been derived from studies may not be directly applicable to bodies of water under uncontrolled deposition.

Watersheds with conditions known to be conducive to Hg methylation were identified in the northeastern U.S. and southeastern Canada, although significant biotic Hg accumulation had been observed in other regions that had not been studied as extensively. The U.S. EPA set the fish tissue criterion in 2001 for MeHg at 300 ng/g fish tissue (reported as 0.3 mg/kg) for the protection of human health, which resulted in 2,436 fish consumption advisories for Hg in 2004, 2,682 in 2005, and 3,080 in 2006. Forty-eight states, one territory, and two tribes had issued Hg fish-consumption advisories at the time of the 2008 ISA.

[Appendix 12](#) summarizes research on the nonacidifying impacts of S deposition on ecosystems, synthesizing literature published since the 2008 ISA with earlier, key studies ([Figure 12-1](#)).



CH<sub>4</sub> = methane; Fe = iron; Hg = mercury; MeHg = methylmercury; P = phosphorus; SO<sub>4</sub><sup>2-</sup> = sulfate; SO<sub>x</sub> = sulfur oxides.

**Figure 12-1** Effects of sulfur oxide deposition on chemical (blue boxes), biological (green boxes), and atmospheric (yellow boxes) indicators of ecosystem change, as documented by the previous Integrated Science Assessment and more recent research.

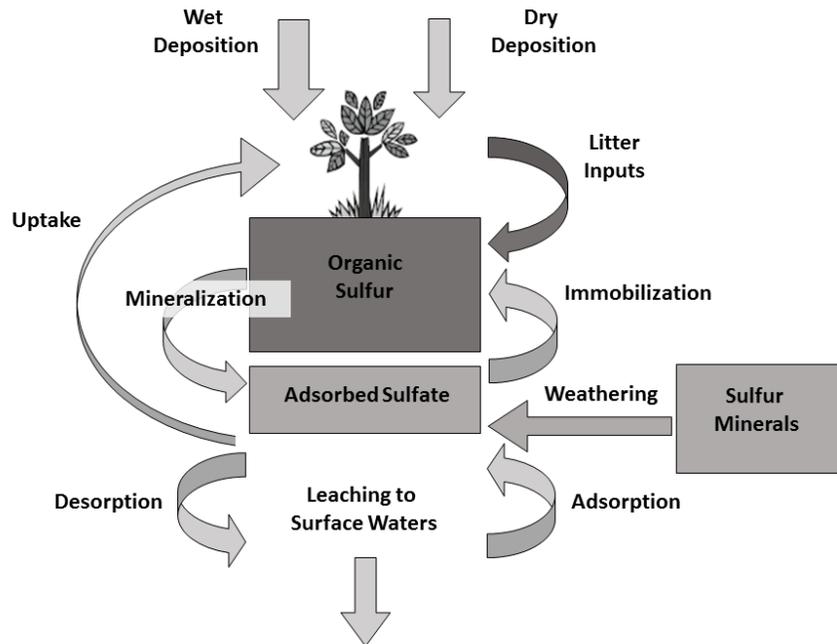
## 12.2 Ecosystem Effects of Altered Sulfur Cycling

This section provides background on the sulfur cycle in terrestrial and aquatic ecosystems ([Appendix 12.2.1](#)). It describes effects of S enrichment (SO<sub>x</sub> deposition or experimental S amendments) upon aquatic S cycling ([Appendix 12.2.2](#)), sulfide toxicity on wetland plants ([Appendix 12.2.3](#)), S enrichment on phosphate cycling in aquatic ecosystems and on uptake of toxic elements by aquatic plants ([Appendix 12.2.4](#)), and S enrichment in altering microbial competition and methanogenesis ([Appendix 12.2.5](#)).

### 12.2.1 The Sulfur Cycle

S cycling in terrestrial ecosystems is relatively well characterized compared to S cycling in aquatic systems. Sulfate is the dominant S source in supplying plant nutrient S

demand. Sulfate in the soil solution, whether its source is weathering of sulfur-containing minerals, mineralization of internal ecosystem S, or atmospheric deposition of  $\text{SO}_x$ , has several possible routes through the S cycle (Figure 12-2).



Source: Adapted from [Mitchell et al. \(2011\)](#).

**Figure 12-2 Sulfur cycle in terrestrial, forested ecosystems.**

Sulfate can be immobilized by incorporation into living cells (microbes, fungi, plants), which ultimately end up in the organic soil S pool. In most North American terrestrial ecosystems, total S pools in soil greatly exceed S stored in living biota (Figure 12-2), with soil S in organic or inorganic molecules. The largest pool of S in soil is organic, typically comprising more than 95% of total soil S in temperate ecosystem soils (Wang et al., 2006; Solomon et al., 2001), although in drained wetland soils of the Florida Everglades Agricultural Area (EAA), the organic fraction was quantified as 87% of total S (Ye et al., 2010). Organic S pools in grassland soils are negatively correlated with mean annual temperature in the North American Great Plains, indicating that climate is a strong control on S cycling (Wang et al., 2006). Organic soil S is found in ester-bound forms (produced via microbial activity) or bound directly to carbon (C) in organic compounds of varying sizes [whose ultimate sources were found to be plant roots or

litter, ([Edwards, 1998](#))]. Organic soil S cannot be taken up by plants directly, but organic S compounds are mineralized back to sulfate by soil microbes under favorable moisture, temperature, and oxic conditions ([Wang et al., 2006](#)). Organic S pools can be indirectly enhanced by SO<sub>x</sub> deposition via microbial and plant incorporation, as indicated by measures of soil [S] and S isotopes. Sulfate in the soil solution can remain in the soil S pool in its inorganic form as it adsorbs to hydrated soil particles. Soil adsorption of sulfate generally results in a smaller S pool than soil organic matter, but this pool can be directly enhanced by SO<sub>x</sub> deposition and associated acidification. Acidification may increase the storage capacity of soils for sulfate. In the case of nonspecific adsorption, increasing acidity and more H<sup>+</sup> held in colloidal suspension create more sulfate binding capacity in soil, while ecosystem recovery towards a more neutral pH may cause desorption of sulfate and higher sulfate concentrations in the soil solution. In the case of specific adsorption, sulfate binds with metal atoms in mineral particles; sulfate specific adsorption to soil also increases with lower pH. However, the rate at which sulfate bound to soil particles is released from adsorption in the soil solution as the ecosystem recovers (see [Appendix 4](#)) towards a more neutral pH will heavily depend upon soil factors such as clay mineralogy, soil age and weathering, calcium availability, content of amorphous iron and aluminum oxides, and glaciation history. Inorganic S storage within terrestrial soils can be directly affected by SO<sub>x</sub> deposition, as indicated by measures of sulfate concentrations in soil fractions and soil solution.

Sulfate in the soil solution may be transported out of the terrestrial ecosystem if it leaches to surface water and into downstream wetland and aquatic ecosystems. Sulfate concentrations in surface water are often measured as an indicator of S fluxes from small terrestrial watersheds. In watersheds that have received historically high S deposition, dissolved organic sulfur (DOS) may also comprise a substantial portion of the S-leaching from terrestrial to aquatic watersheds. In Archer Creek in the Adirondacks, NY, DOS averaged 21% of total dissolved sulfur in the creek ([Kang et al., 2014](#)). Freshwater aquatic S cycling is not as well described in the scientific literature as is terrestrial soil S cycling. The preponderance of evidence is concerned with the locations of redox S reactions within these aquatic systems. Sulfate leached from terrestrial ecosystems, as well as sulfate from direct deposition to surface water, is transformed in aquatic systems under particular conditions. High oxygen levels in the water column or inundated sediments of a wetland, lake, or stream favor S in oxidized form as sulfate. Sulfate in anoxic (very low O<sub>2</sub>) waters or sediments is transformed into more reduced forms such as sulfide or elemental S, which are less soluble and may precipitate into sediments. Sulfur-reducing prokaryotes (SRPs) couple their metabolism to the transformation of sulfate into these reduced forms. SRPs are obligate anaerobes but require sulfate for metabolism, and as a result, they are often present and active at oxic-anoxic boundaries in aquatic environments. In shallow lakes, this boundary (and the majority of sulfate

reduction) occurs at the water-sediment interface, in the top 1–2 cm of sediment ([Rudd et al., 1986](#); [Kelly and Rudd, 1984](#)). In deeper lakes that experience seasonal stratification, the water column may account for up to 15% of sulfate reduction ([Ingvorsen and Brock, 1982](#)), and the anoxic boundary may occur in the flocculant layer (suspended sediment); for example, the boundary occurs 10 cm above the top of the sediment in Little Rock Lake, WI ([Sherman et al., 1994](#)). In wetlands, particularly in peat bogs that depend entirely upon precipitation as their water supply, the anoxic-oxic boundary often coincides with the water table and can be much more dynamic. Finally, recent research suggests that periphyton occupying high-oxygen waters can create anoxic microenvironments that promote the growth and activity of SRPs (see [Appendix 12.3.3](#)). The location and activity of SRPs are important environmentally because some SRPs couple sulfate reduction with Hg methylation (see [Appendix 12.3.2](#)). The transformation of S between reduced and oxidized forms in aquatic and wetland ecosystems occurs in particular locations within these ecosystems but can have broader impacts on chemistry and biota.

Pools of S in freshwater systems (lakes, rivers, streams, and wetlands) and residence times of S in ecosystem pools are addressed in only a few ecological studies. S cycling in lakes removes sulfate from the water column and stores reduced S in sediments. Sulfate in the water column diffuses into sediments where it binds to particulate matter or is incorporated by microbes. Water column sulfate is reduced (by chemical or biological processes) and released into the sediments as sulfide, which can bind to iron and precipitate, or as elemental S, which can precipitate directly. An early study by [Rudd et al. \(1986\)](#) developed a budget for reduction-oxidation cycling of S based on Adirondack lakes, and estimated that 47% of water column sulfate was reduced and stored in sediments. A broader study that included lakes in the Adirondacks, Ontario, the Experimental Lakes Area, Northern Wisconsin, and Southern Norway estimated that 39–80% of annual sulfur load was retained in sediments based on mass balance, or 11–65% based on measured sulfate reduction rates, across all lakes ([Kelly et al., 1987](#)). On average across lakes, one-third to one-half of annual lake sulfate load was transferred to sediments, and variation around this mean correlated with water residence times of lakes. Longer hydraulic residence times correlated with more sulfate removal. The release of reduced S into the water column is responsible for some of the other nonacidifying effects of S deposition, including internal eutrophication and protective effects against certain heavy metals (see [Appendix 12.2.4](#)). The rest of the S originally taken up by microbes as sulfate is incorporated into organic compounds. The growth and activity of SRPs are responsible for Hg methylation in many sediments (see [Appendix 12.3](#)). About one-third of the reduced inorganic S and 57% of the organic S are buried in lake sediments annually, or about 47% of the total sulfate input. The remaining reduced sulfur, 53% of the original sulfate input, is oxidized by chemical reaction with

water molecules ([Bates et al., 2002](#)) and returns to the S cycle ([Rudd et al., 1986](#)). These studies suggest that changes in S inputs to lakes—for example, reductions in SO<sub>x</sub> deposition—could rapidly reduce sulfate concentrations in the water column, assuming other environmental factors remain steady (see below for climatic influences on S cycling).

Wetland S budgets resemble lake budgets in S reduction and burial of reduced S in sediments, but also may include plant uptake and S export if hydrology allows. In a study of depressional freshwater wetlands in two lakes in Germany, the sulfate reduction rate was 2.5 to 7.9 times higher annually in the high sulfate lake (22.7 mg sulfate/L) than in the low sulfate lake [9.0 mg/L; [Kleeberg et al. \(2016\)](#)]. Sulfur budgets have also been determined for the peat soils and freshwater marshes of the Florida Everglades. The EAA has large impacts on S cycling in freshwater marshes in the surrounding designated Water Conservation Areas (WCA), which serve as a water quality buffer around Everglades National Park, a Class I area. In the EAA, the addition of elemental S as an agricultural soil amendment increased sulfate in the soil from 13 to 19% of total soil S, although at the end of the growing season sulfate was 1% of total S due to uptake by growing sugarcane ([Ye et al., 2010](#)) and runoff into surrounding canals and wetlands ([Bates et al., 2002](#)). In an early study quantifying S budgets in the Everglades WCA, ([Bates et al., 2002](#)) determined that most of the sulfate in the system has its source in S agricultural amendments applied in the EAA. In these wetland systems, the pool of S in organic matter is high, and additional sulfate could be rapidly incorporated into organic matter or exported in surface water, in addition to the reduction or burial, which occurs in other aquatic systems.

Weather and climatic factors can disrupt S storage in more stable pools within aquatic and wetland systems. In smaller stratified lakes, sulfate transfer from the epilimnion into lower layers occurs slowly by diffusion between the stable water layers, while in larger lakes, the layers are more prone to perturbation by wind and allow larger transfers of sulfate to zones where SRPs are active ([Ingvorsen and Brock, 1982](#)). Sulfur cycling, like most microbially driven processes, is seasonal; sulfate fluxes to the sediment are 10 times higher in the summer than in winter ([Sherman et al., 1994](#)), and the growing season coincides with peak sulfate reduction in many freshwater systems (see [Appendix 12.3.3.3](#)). In the Experimental Lakes Area (ELA) in Ontario, 10–39% of reduced S ended the summer as sulfide dissolved in the hypolimnion, and this S was reoxidized to sulfate when circulation occurred in the fall ([Kelly et al., 1982](#)). In winter, O<sub>2</sub> can penetrate deeper into sediments or peat, reoxidizing the sulfide ([Sherman et al., 1994](#)). This reoxidation can also occur in water bodies where water levels are controlled by humans, for example in reservoirs ([Eckley et al., 2015](#)). Extreme events like droughts

can also result in reoxidation of reduced S ([Wasik et al., 2015](#)) and can contribute to Hg methylation hotspots upon rewetting and restoration of anaerobic aquatic conditions.

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## 12.2.2 Deposition and Sulfur Stores

In terrestrial ecosystems, atmospheric deposition of S at levels below amounts that trigger acidification may still induce biochemical effects. These effects were described in the 2008 ISA and include nutrient enrichment of plants, increased S storage in soils, and elevated sulfate concentrations in water leaching from soils. New information regarding the effects of S deposition on terrestrial biogeochemical cycling is sparse, but can be found in [Appendix 4](#). Terrestrial plant productivity is commonly limited by N, so SO<sub>x</sub> deposition at levels low enough to provide S enrichment without associated acidification effects is unlikely to have significant effects upon terrestrial plant productivity. Instead, the nonacidifying effects of SO<sub>x</sub> deposition are strongest in freshwater systems such as wetlands and lakes, where hydrology controls storage and release of S.

Changes in water availability and water levels in aquatic systems alter the S cycle and may release additional S to the aquatic environment from storage in sediment. During a drought at Little Rock Lake in Wisconsin, lake sulfate concentrations increased 0.18 mg/L/yr, from 1.5 mg/L in 1998 to 2.9 mg/L in 2006 ([Watras and Morrison, 2008](#)). During this time period, lake water volume decreased only 30%, which would not account for the 93% increase in water sulfate concentration, suggesting that drought released additional S stored in lake sediment or biomass into the water column. [Watras and Morrison \(2008\)](#) calculated that an additional load of 5 kg S/ha/yr from internal ecosystem sources of S would account for the increase of S in Little Rock Lake. In the S addition experiment at the S6 bog in Marcell Experimental Forest, MN (see [Appendix 12.3.4.1](#)), rewetting of the bog after a drought released a pulse of sulfate into surface water in both control and experimental S addition plots. In plots to which 32 kg S/ha/yr had been added, concentrations of sulfate in peat pore water after the drought were 438% higher than in control plots ([Wasik et al., 2012](#)), indicating that S addition decreases the retention of S in drought-stressed wetlands ([Table 12-1](#)). This is particularly important because intensification of drought frequency and severity is one of the possible effects of climate change and suggests that climate change and SO<sub>x</sub> deposition may synergistically contribute to increased sulfate concentrations in surface water and associated water quality impairment.

**Table 12-1 New study on sulfur (S) deposition effects on sulfur (S) cycling.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Bog	Ambient S deposition: 5.5 kg/ha/yr (mid 2000s) as quantified at NADP site MN16 S addition: 32 kg S/ha/yr dissolved in pond water and delivered by sprinklers (mimics 4x the 1990s deposition rate)	Following 2007 drought, pore water SO <sub>4</sub> <sup>2-</sup> concentrations were 438% higher in experimental treatment.	S6 peatland, bog section, Marcell Experimental Forest, MN	Pore water, peat, and <i>Culex</i> spp.(mosquito) larvae	<a href="#">Wasik et al. (2012)</a>

ha = hectare; kg = kilogram; NADP = National Atmospheric Deposition Program; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

### 12.2.3 Sulfide Toxicity

Wetland ecosystems are characterized by occasional or total soil inundation and typically include water and sediment zones with low oxygen levels. Under low-oxygen conditions, sulfate can be used as an electron acceptor by a number of microorganisms and is quickly converted to sulfide during decomposition of organic C. Sulfide inhibits plant root nutrient uptake at high levels [ $>34.1$  mg/L or  $>1$  mM; ([Koch et al., 1990](#))], and sulfide toxicity due to increased sulfate loads was documented by the 2008 ISA and references therein for wetland plants, including *Carex* spp., *Juncus acutiflorus* (not native to or documented in North America), *Galium palustre* (endangered in Ohio, special concern in Tennessee), other species within *Gramineae* (the grass family), as well as the aquatic macrophytes *Stratiotes aloides* (listed as an Class C noxious weed in Alabama, Class 1 prohibited aquatic plant in Florida) and *Elodea nuttallii* (threatened in Kentucky, special concern in Tennessee). As reviewed in the 2008 ISA, [Smolders et al. \(2003\)](#) set a threshold value of  $<48$  mg SO<sub>4</sub><sup>2-</sup>/L in surface water to protect the sensitive aquatic species *Stratiotes aloides* and *Potamogeton acutifolius* (not native to CONUS), as well as to protect *Potamogeton zosteriformis* and *Utricularia vulgaris*, which are both native and widely distributed in CONUS. This threshold would protect against sulfide phytotoxicity and internal eutrophication and was based on correlations between surface water concentrations and plant presence/absence in Dutch fens ([Smolders et al., 2003](#)). A recent survey of water quality and plant presence/absence data from four water management districts in the Netherlands confirmed that the probability of encountering the S-sensitive plants *S. aloides* and six S-sensitive *Potamogeton* (pondweed) species declined significantly at sulfate concentrations greater than 50 mg/L ([Vermaat et al., 2016](#)).

More recent research confirms sulfide toxicity in wetland habitats and suggests that sulfide toxicity can determine plant community composition in freshwater wetlands. A review of the sulfide toxicity literature by [Lamers et al. \(2013\)](#) found sulfide toxicity occurred between 0.3–29.5 mg S<sup>2-</sup>/L (originally reported as 10–920 μmol L<sup>-1</sup>) in freshwater wetland emergent plants and aquatic submerged macrophytes native to North America (see [Table 12-2](#) for species-specific phytotoxicity levels). A recent study sampled pore water chemistry and plant community composition in Junius Pond Fen, Seneca County, NY, and found that sulfide concentrations (range: not detectable to 5.73 mg/L or 168 μM H<sub>2</sub>S) had negative effects on the plant community. Sulfide concentration was negatively correlated with total plant cover and had strong effects on the cover of the dominant plants in the fen ([Simkin et al., 2013](#)). In models, high sulfide concentrations decreased cover of the moss species *Campyllum stellatum*, decreased cover of the monocot and USDA-classified ([USDA, 2015b](#)) wetland obligate *Eleocharis rostellata* (endangered in Florida and Pennsylvania; threatened in Illinois, Minnesota, and Wisconsin; sensitive or special concern in Rhode Island and Washington), and decreased cover of obligate monocot *Cladium mariscoides* (endangered in Pennsylvania). Sulfide concentrations also correlated negatively with dicot diversity ([Simkin et al., 2013](#)). This study shows that sulfide toxicity effects on sensitive plant species can cascade to affect plant community composition in fens. There are also sensitive species in other freshwater wetlands. A greenhouse experiment with *Taxodium distichum* (baldcypress) seedlings collected from a North Carolina riparian field showed negative effects of sulfate addition (sulfate concentrations: 48 mg/L in drought treatment, 129 mg/L in flooded treatment) on seedling height, which the researchers attributed to sulfide toxicity ([Powell et al., 2016](#)). Baldcypress is a foundation species in southeastern freshwater swamps, which if located in estuaries, may also experience elevated sulfate, sulfide, and salinity as a result of saltwater intrusion. SO<sub>x</sub> deposition may exacerbate sulfide toxicity in baldcypress swamps already stressed by sea level rise.

**Table 12-2 Quantitative effects of sulfide on wetland and aquatic plant species.**

Species	Effects of Sulfide	Sulfide (mg S <sup>2-</sup> /L)	Listing	Reference
<i>Calla palustris</i>	Decreased aboveground productivity	4.8	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Caltha palustris</i>	Decreased aboveground productivity	5.5	NRCS wetland obligate	Van der Welle et al., 2007b in <a href="#">Lamers et al. (2013)</a>

**Table 12-2 (Continued): Quantitative effects of sulfide on wetland and aquatic plant species.**

Species	Effects of Sulfide	Sulfide (mg S <sup>2-</sup> /L)	Listing	Reference
<i>Carex nigra</i>	Decreased aboveground productivity	0.3–0.6	NRCS wetland facultative	Lamers et al., 1998 in <a href="#">Lamers et al. (2013)</a>
<i>Ceratophyllum demersum</i>	Decreased aboveground productivity	16	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Cladium jamaicense</i>	Decreased leaf elongation rate	7.0	NRCS wetland obligate	Li et al, 2009 in <a href="#">Lamers et al. (2013)</a>
	Decreased net photosynthetic rate	22.1		
	Aboveground die-off and root (and rhizome) die-off	29.5		
<i>Elodea nuttallii</i>	Decreased aboveground productivity	3.2	NRCS wetland obligate	Van der Welle et al., 2007a in <a href="#">Lamers et al. (2013)</a>
<i>Elodea nuttallii</i>	Decreased aboveground productivity	4.8–16	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Equisetum fluviatile</i>	Decreased aboveground productivity	1.6–16	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Juncus alpinoarticulatus</i> seedlings	Decreased aboveground productivity	1.0–1.6	NRCS wetland obligate	Grootjans et al., 1997 in <a href="#">Lamers et al. (2013)</a>
<i>Juncus effusus</i>	Decreased aboveground productivity	16	NRCS wetland obligate or facultative	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Menyanthes trifoliata</i>	Decreased aboveground productivity (unfertilized/fertilized)	4.8/>4.8	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Menyanthes trifoliata</i>	Decreased aboveground productivity	>7.5	NRCS wetland obligate	Armstrong and Boatman, 1967 in <a href="#">Lamers et al. (2013)</a>
<i>Nitella flexilis</i>	Decreased aboveground productivity	1.6		Van der Welle et al., 2006 in ( <a href="#">Lamers et al., 2013</a> )
<i>Panicum hemitomon</i>	Decreased aboveground productivity, root (and rhizome) die-off	20.2	NRCS wetland obligate	Koch and Mendelssohn, 1989 in <a href="#">Lamers et al. (2013)</a>
<i>Panicum hemitomon</i>	Decreased aboveground productivity, decreased root ADH activity, decreased nutrient uptake	32.1	NRCS wetland obligate	Koch et al., 1990 in <a href="#">Lamers et al. (2013)</a>
<i>Potamogeton compressus</i>	Decreased aboveground productivity	4.8–16	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>

**Table 12-2 (Continued): Quantitative effects of sulfide on wetland and aquatic plant species.**

Species	Effects of Sulfide	Sulfide (mg S <sup>2-</sup> /L)	Listing	Reference
<i>Sphagnum cuspidatum</i>	Aboveground die-off	1.9		Lamers et al., 1999 in <a href="#">Lamers et al. (2013)</a>
<i>Thelypteris palustris</i>	Decreased aboveground productivity	4.8	NRCS wetland obligate	Geurts et al., 2009 in <a href="#">Lamers et al. (2013)</a>
<i>Typha domingensis</i>	Decreased leaf elongation rate, decreased net photosynthetic rate, aboveground die-off, root (and rhizome) die-off	29.5	NRCS wetland obligate	Li et al., 2009 in <a href="#">Lamers et al. (2013)</a>

Source: all columns except "Listing" are from [Lamers et al. \(2013\)](#).

Sulfide toxicity has been proposed as an important causal factor in the expansion of *Typha domingensis* (southern cattail) in the Florida Everglades. Southern cattail is displacing the historically dominant sawgrass, *Cladium jamaicense*, which is the keystone species in the Everglades sawgrass prairies and which has minor agricultural importance as a food source for small mammals and water birds [reported in [Everitt et al. \(1999\)](#)]. In a hydroponic greenhouse study of both species, cattails had a higher tolerance for sulfide in all plant metrics measured. Sulfide concentrations in growth media were 0, 7.5, 15.7, 23.5, 31.4 mg/L sulfide (reported as 0, 0.22, 0.46, 0.69, or 0.92 mM). At 7.5 mg/L sulfide, sawgrass leaf elongation rates decreased 49%; at 15.7 mg/L sulfide, net photosynthetic rate decreased 34%; and at 23.5 mg/L, sawgrass biomass in different compartments decreased 29–41% ([Li et al., 2009](#)). Cattails experienced sulfide toxicity effects on leaf elongation rates at 23.5 mg/L sulfide (38% decrease) and on photosynthesis at 31.4 mg/L sulfide (22% decrease), with no effects of sulfide upon biomass at any concentration ([Li et al., 2009](#)). Together, these results suggest that sulfide toxicity is shifting the competitive balance between these species away from the dominant species in the Everglades. However, studies that assessed cattail and sawgrass growth in mesocosms placed across the naturally occurring sulfate-sulfide gradient in the Everglades ([DeBusk et al., 2015](#)) or in mesocosms with added sulfate ([Li et al., 2009](#)) have not found effects of sulfide toxicity upon sawgrass. Under controlled conditions, sulfide toxicity favors cattails over keystone Everglades species sawgrass, but evidence from field studies in the Everglades ecosystem suggests that geological or ecological factors not reproduced in the greenhouse may mitigate sulfide toxicity.

Recent work by the Minnesota Pollution Control Agency (MNPCA) proposes to incorporate geological and biological factors into water quality regulation in order to prevent sulfide toxicity to an economically important species. Wild rice (*Zizania*

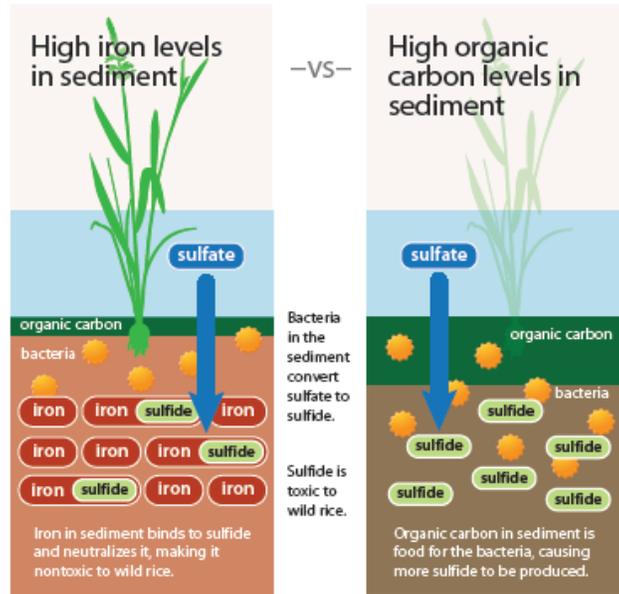
*palustris*) has been protected by the state of Minnesota as ecologically important food for waterfowl and an economically important foraged crop (MPCA, 2015a), and the Ojibwe, Menominee, and Dakota peoples value the plant as a cultural and economic resource (Pastor et al., 2017). The state first set a standard to protect wild rice in 1973, when the water quality standard was set at 10 mg sulfate/L. In 2011, the state began collecting field samples, conducting experiments in hydroponics and mesocosms, and modeling environmental and experimental data in order to revise the standard. The previous standard of 10 mg sulfate/L would only protect 58% of current wild rice sites from sulfide toxicity (MPCA, 2015a). In March 2015, the Minnesota Pollution Control Agency (MPCA) released its recommendations (MPCA, 2015a). Based on the new analyses, the MPCA set a sulfide concentration threshold of 0.165 mg sulfide/L in sediment pore water to protect wild rice, based on 2011–2013 monitoring of 112 Minnesota water bodies in which this level of sulfide corresponded to a 10% decrease in the probability of the species being present (MPCA, 2015b). Sulfide is the end product of microbial sulfate reduction, which is heavily dependent upon other environmental factors, particularly DOC, and sulfide phytotoxicity depends upon its residence time as a free ion in water, which depends upon iron concentrations (see Figure 12-3). As a result, the MPCA did not set a single value of sulfate as a standard to protect wild rice.

Instead, MPCA established a formula that would allow protective sulfate thresholds to be calculated for all wild rice-producing water bodies based on sediment organic carbon and sediment iron concentrations in each water body [Source: (MPCA, 2015b)]:

$$\text{Sulfate} = 0.0000136 \times \text{Organic Carbon} - 1.410 \times \text{Iron} + 1.956$$

**Equation 12-1**

The range in sulfate values that protect wild rice from sulfide toxicity in Minnesota water bodies is from 0.4 to >200 mg SO<sub>4</sub><sup>2-</sup>/L. This proposed standard will require large-scale sediment sampling to determine sediment pore water DOC and Fe concentrations in Minnesota water bodies and is still under review. These regulatory efforts determine protective surface water sulfate concentrations on the basis of a sulfide phytotoxicity threshold protective of wild rice. In hydroponic experiments with *Z. palustris*, sulfate and sulfide exposures did not affect seed germination, but sulfide concentrations of 0.32 mg/L or higher reduced growth rates 88% compared with controls (Pastor et al., 2017). The same research group also conducted growth trials in outdoor tank mesocosms in which surface water sulfate concentrations, and thus sediment sulfide concentrations, could be manipulated. In the mesocosms, 50 mg SO<sub>4</sub><sup>2-</sup>/L did not affect seedlings, but elevated sulfate and sulfide at 100 mg SO<sub>4</sub><sup>2-</sup>/L or higher decreased seed mass, seed viability, seedling emergence rates, and seedling survival rates (Pastor et al., 2017).



Source: [MPCA \(2015b\)](#).

**Figure 12-3 Schematic from Minnesota Pollution Control Agency that illustrates the mitigating effect of iron on the toxicity of sulfide and the stimulatory effect that organic carbon has on sulfide production.**

Sulfide phytotoxicity as a result of  $\text{SO}_x$  deposition alters freshwater wetlands and lakes, but it is unlikely to affect coastal wetlands. Seawater contains high concentrations of sulfate [1 ppt seawater contains 750  $\mu\text{M}$  or 72 mg/L sulfate according to ([Hackney and Avery, 2015](#))], and as a recent study in the Cape Fear Estuary, North Carolina, demonstrates, seawater intrusion and sulfate-reducing conditions structure the distribution of tidal marsh and tidal swamp zones in the estuary. Specifically, tidal marsh plants are salt and sulfide tolerant, and occur in the estuary in areas where sulfate reduction dominates microbial mineralization ([Hackney and Avery, 2015](#)). Tidal swamp plants (such as baldcypress, see above) have been shown to be sensitive to and negatively affected by saltwater intrusion over the decade-long course of the study. This study suggests a biologically plausible link between sulfide increases caused by  $\text{SO}_x$  deposition and tidal marsh intrusion upon tidal swamp zones. However, the authors did not consider sulfate as originating from any source other than seawater, so the effect of salinity could not be separated from the effect of sulfate reduction and resultant sulfide phytotoxicity. There is no evidence of  $\text{SO}_x$  deposition contributing to sulfide phytotoxicity in wetland and aquatic ecosystems with significant seawater contributions.

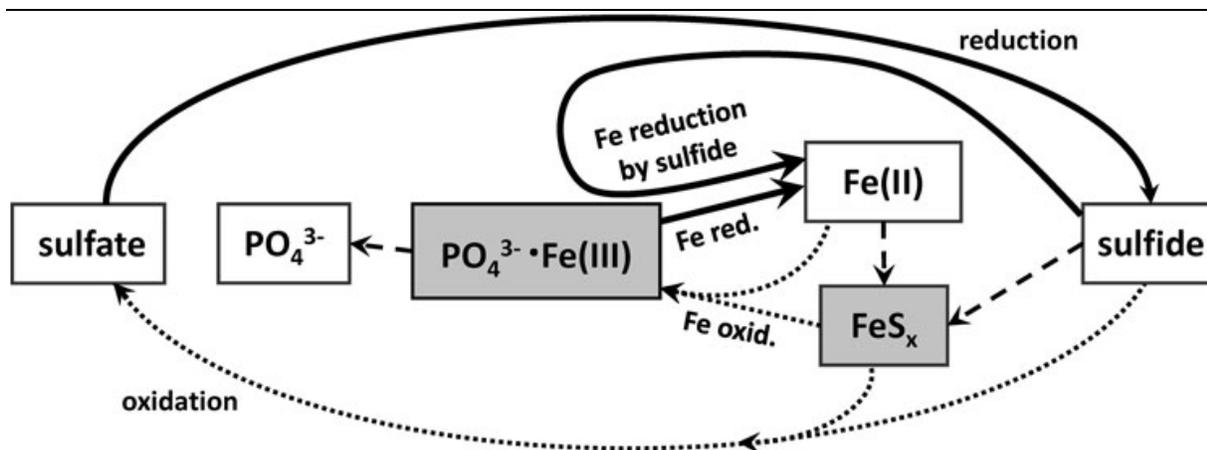
Sulfide toxicity has not been documented for freshwater animal species, since the reducing conditions that produce sulfide also cause hypoxia. However, animal species do vary in their tolerance of sulfate concentrations in water. [Carlisle et al. \(2007\)](#) and [Meador and Carlisle \(2007\)](#) used data from the U.S. Geological Survey's 1993–2003 National Water-Quality Assessment (NAWQA) to generate indicator values for widely distributed North American macroinvertebrates and fish. Each indicator value is the average value for a water quality parameter at which a taxon is detected in NAWQA samples. A follow-up analysis of macroinvertebrates and stream quality in the eastern and midwestern U.S. designated streams with more than 20% loss of expected taxa for the region as degraded habitat ([Carlisle and Meador, 2007](#)). This dataset has identified animals sensitive and tolerant to sulfate and other water quality parameters and allows the evaluation of sulfate impacts on animal species at concentrations lower than those that cause acidification.

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#### 12.2.4 Internal Eutrophication

Internal eutrophication occurs in saturated soils in freshwater wetlands and lakes when sulfate addition results in the release of bioavailable phosphate from soil forms that are not bioavailable. Additional sulfate in surface waters can increase P mobility and cause internal eutrophication of the recipient ecosystem; farmers growing sugarcane in the oxidized peatland soils of the Florida EAA use S as a soil amendment for this reason ([Ye et al., 2010](#)).

Wetland and aquatic systems often retain phosphate as  $\text{FePO}_4$ . When sulfate is reduced, the resultant sulfide binds with iron to create  $\text{FeS}$ , which precipitates out of solution, releasing P into surface waters ([Figure 12-4](#)). This internal eutrophication can alter plant community composition ([U.S. EPA, 2008a](#)), or can speed the accretion of organic matter and infilling of the wetland, reducing wetland habitat ([Kleeberg et al., 2016](#)). In mesocosms resembling shallow lakes planted with wild rice, experimentally elevated surface water sulfate concentrations raised phosphate concentrations in the water column ([Pastor et al., 2017](#)). Water and sediment mesocosms of samples collected from Lake Moshui in China showed that sodium sulfate addition to raise sulfate concentrations to 500 mg/L also raised peak [P] by 180% in the water column, and by 210% in the sediment pore water, above unamended control mesocosms, and the peak [P] with sulfate addition occurred a week later than in control mesocosms ([Yu et al., 2015](#)). Limitation of microbial sulfate reduction achieved through experimental  $\text{NO}_3^-$  enrichment of the hypolimnion in Onondaga Lake, NY, decreased soluble reactive phosphorus in the hypolimnion by 95% ([Matthews et al., 2013](#)). Sulfate addition can alter P dynamics and cause eutrophication in freshwater systems.



Fe(II) = iron (II); Fe(III) = iron (III);  $\text{FeS}_x$  = iron-sulfide complexes;  $\text{PO}_4^{3-}$  = phosphate.

Open boxes indicate pore water components, and shaded boxes indicate solid-phase chemistry. Reduction reactions are indicated by solid arrows, oxidation reactions are indicated by dotted lines, and phase changes (precipitation or dissolution) are indicated by dashed lines.

Source: [Simkin et al. \(2013\)](#).

**Figure 12-4 Mechanisms of linked sulfur, iron, and phosphorus cycling in wetland waters and soils.**

Surface water sulfate may decrease heavy metal bioaccumulation in plants, but the implications of this process for impacts of  $\text{SO}_x$  deposition may be limited. Sulfate addition can decrease the accumulation of toxic elements in aquatic plants. In soil, S addition decreased dissolved arsenic (As) concentrations in soil solution, but increased As(III):As(V), although the researchers suggested that the formation of As-Fe-sulfide minerals prevented plant As uptake ([Jia et al., 2015](#)). In microbially spiked soil mesocosms, the addition of SRB had a stronger stimulatory effect on As(III):As(V) than did S addition. In rice mesocosms, S addition decreased As concentrations in rice roots and in the iron plaques on roots ([Jia et al., 2015](#)). In laboratory mesocosms, accumulation of selenium (Se) in aquatic plants was a function of both sulfate and Se concentrations in water, but increasing sulfate concentrations decreased Se concentrations in both *Lemna minor* (aquatic macrophyte) and *Pseudokrichneriella subcapitata* [unicellular green alga ([Lo et al., 2015](#))]. Sulfate in surface waters may slow bioaccumulation of heavy metals in biota by forming relatively insoluble S-metal complexes and preventing metal uptake by aquatic plants. However, these findings may have limited applicability to  $\text{SO}_x$  deposition. If there is a common source of both  $\text{SO}_x$  and heavy metal deposition to an aquatic environment, it is unlikely that deposition will correlate with decreasing metal bioavailability. Also, mercury is a focus of research into heavy metal environmental transformations and bioavailability, and  $\text{SO}_x$  deposition is linked instead to increased

bioaccumulation of Hg (see [Appendix 12.3](#) to [Appendix 12.6](#)). There is no research on how SO<sub>x</sub> deposition affects Se or As accumulation in plants growing under field conditions.

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### 12.2.5 Sulfur Effects on Methane Emissions

The 2008 ISA documented the suppression of methane emissions from aquatic and wetland ecosystems in response to increases in sulfate concentrations. When sulfate is added to freshwater systems, SRPs outcompete methanogens, and methane emissions are suppressed. The activity and environmental preferences of SRPs are key to understanding the effects of SO<sub>x</sub> deposition upon methane and MeHg production. Under anaerobic conditions, SRPs and methanogens compete for organic C as a metabolic substrate, and the reactions of sulfate reduction coupled with organic C oxidation are thermodynamically favored over the reactions of methanogenesis ([Paulo et al., 2015](#)). In many anaerobic environments, sulfate is in short supply, and methanogens are more active than SRPs in mineralizing organic C. Sulfate addition may swing the competitive balance back towards SRPs, decreasing methane production in saturated soils and surface waters. However, studies summarized in other parts of this appendix show that SRPs and methanogens can form syntrophies (see [Appendix 12.3.2](#)) or coexist and rapidly shift dominance within a single wetland (see [Appendix 12.3.2](#) and [Appendix 12.3.3.1](#)).

The relative primacy of methanogens versus SRB in oxidizing carbon is one of the factors which distinguishes freshwater from coastal wetlands and water bodies. Older literature suggests that when SO<sub>x</sub> deposition is not a factor, methanogens dominate anaerobic decomposition in freshwater systems (including wetlands), with methanogenesis responsible for 72–82% of organic C mineralization at the ELA, Ontario ([Kelly and Rudd, 1984](#)), and methanogenesis responsible for 4 times the electron flow and organic C mineralization of sulfate reduction in Lake Mendota, WI ([Ingvorsen and Brock, 1982](#)). In estuarine and marine ecosystems, on the other hand, SRPs are the dominant anaerobic decomposers. In the saltwater marshes at Kirkpatrick Marsh, MD, methanogenesis is <10% of C mineralization, and sulfate reduction is responsible for 45–85% of total C mineralization in the summer, and 5–25% of C mineralization in the fall ([Mitchell and Gilmour, 2008](#)). Older research suggests that in pristine ecosystems, methanogens dominate anaerobic C mineralization in freshwater systems.

New research on microbial communities in saturated sediments contributes to the biological plausibility of the reduction in methanogenesis caused by SO<sub>x</sub> deposition established by the 2008 ISA. Adding sulfate to freshwater systems can depress methanogenesis because anaerobic C mineralization by SRPs is energetically favored

when sulfate and acetate are available at the sediment surface ([Urban et al., 1994](#)). Newer work also supports this finding (see [Table 12-3](#)). Twitchell Island is a restored wetland in the San Joaquin delta, CA, where researchers sampled sediments and water along a gradient of decreasing riverine S load (14–8 mg sulfate/L in February) from the wetland inlet to a transitional site, and to an interior marsh site. In summer, sulfate was 60% lower and methane emissions were 110% higher at the interior site than at the inlet, and 16S rRNA sequencing confirmed that relative SRP abundance was negatively correlated with methanogen abundance ([He et al., 2015](#)). In the Everglades WCA, FL, similar gradients of S loading occur from agricultural runoff in the freshwater marsh. Sampling at sites F4 (7.1 mg/L or 74  $\mu$ M sulfate in pore water), U3 (3.7 mg/L or 39  $\mu$ M sulfate), and W3 ( $\leq 0.4$  mg/L or  $\leq 4$   $\mu$ M sulfate) found effects of sulfate upon SRB (sulfur-reducing archaea were not sampled) and methanogens ([Bae et al., 2015](#)). SRB abundance increased with increasing sulfate pore water concentrations across the three sites and was 6.9 times higher at U3 and 16.8 times higher at F4 than at W3. Sulfate also affected the competitive interaction between SRB and methanogens, which had equal abundances at the most pristine W3 site. At the sites with higher S loads, SRB were 60–80% more abundant than methanogens. The relative abundance of methanogens was determined by copy number of the *mcrA* gene in environmental samples, which correlated positively with methane production rates and mRNA ([Bae et al., 2015](#)), so sulfate loading alterations to the microbial community in the Everglades WCA may also be lowering methane emissions. Sampling from natural microbial communities confirms that sulfate favors SRB over methanogens.

A laboratory study with controlled redox conditions and microbial communities suggests that even when SRB and methanogens are not in direct competition for anaerobic C, methanogen activity will increase when sulfate concentrations decrease. In an incubation of water and sediment collected from oligotrophic Lake Stechlin, Germany, researchers were able to create fluctuating redox conditions while continuously sampling the water column. When the system was reduced, expression of the *dsrB* gene (present in SRB) increased, and sulfide concentrations increased, indicating that SRB abundance and activity increased in response to anoxic conditions in the water column ([Frindte et al., 2015](#)). Methane also increased in the water column, indicating no competition between SRB and methanogens in this system. Over time, *dsrB* diversity decreased, and expression of *pmoA* (present in methanogens) increased ([Frindte et al., 2015](#)), indicating that although there was no competition between SRB and methanogens, methanogens were able to persist after SRB had exhausted the available sulfate and diminished in abundance. Active methanogenesis occurs when SRB activity is constrained by low sulfate availability. Reductions in SO<sub>x</sub> deposition could increase methanogen activity typical of wetland and aquatic sediments.

**Table 12-3 New studies on nonacidifying sulfur effects on methane emissions.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Restored peatland island in river	River water is the source of the S load, more interior sites have lower S load, as reflected by February sediment surface measurements: Inlet [SO <sub>4</sub> <sup>2-</sup> ] 14 mg/L; Transitional [SO <sub>4</sub> <sup>2-</sup> ] 11.5 mg/L; Interior [SO <sub>4</sub> <sup>2-</sup> ] 8 mg/L	SRP abundance decreases with increasing methanogen abundance ( $r = -0.67$ ). Denitrifier abundance decreases with increasing methanogen abundance ( $r = -0.64$ ). In August, sulfate decreases 60% from inlet to interior, and methane emissions increases 110%. SRP relative abundance increases with sulfate concentration ( $r = 0.96$ ).	Twitchell Island, San Joaquin delta, CA	Island covered with <i>Typhus</i> spp. and <i>Schoenoplectus acutus</i> , sampled at inlet, transitional, and interior marsh sites. Microbial community quantified by 16S rRNA sequencing of peat sample.	<a href="#">He et al. (2015)</a>
Freshwater marsh	W3 pore water [SO <sub>4</sub> <sup>2-</sup> ] ≤4 μM U3 pore water [SO <sub>4</sub> <sup>2-</sup> ] is 39 μM F4 pore water [SO <sub>4</sub> <sup>2-</sup> ] is 74 μM Deposition = not measured	SRB abundance is 6.9x higher in U3 than W3 and 16.8x higher in F4. In W3, abundance of SRB and methanogens are not significantly different. In U3, SRB abundance is 80% higher than methanogen abundance. In F4, SRB abundance is 60% higher than methanogens. <i>mcrA</i> copy number correlates positively with mRNA and methane production rates. Acetotrophic methanogens are dominant at W3, while at high S U3 and F4 sites, hydrogenotrophic methanogens are dominant.	F4, U3, and W3 sites in Water Conservation Area, Everglades, FL	Methanogens as quantified by <i>mcrA</i> copies. Sulfur-reducing bacteria as quantified by <i>dsrB</i> copies.	<a href="#">Bae et al. (2015)</a>

**Table 12-3 (Continued): New studies on nonacidifying sulfur effects on methane emissions.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Coastal salt marsh	Total load = not measured Deposition = not measured	No significant correlation between potential methane emissions and pore water $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , and $\text{Fe}^{3+}$ . Methanogen abundance is 84% lower in <i>S. alterniflora</i> than in <i>P. australis</i> marsh. SRP abundance is 73% lower in <i>S. alterniflora</i> than in <i>P. australis</i> marsh. Methanogen abundance ( <i>M</i> , as 1,000 gene copies/g soil) increases with pore water $\text{NO}_3^-$ concentrations ( $N_{\text{load}}$ , as $\mu\text{M NO}_3^-$ ): $M = 0.3468 + 0.8149 \times N_{\text{load}}$	Shanyutan, Min River Estuary, China	Zones of Chinese native <i>Phragmites australis</i> , Chinese invasive (American native) <i>Spartina alterniflora</i> , and <i>Cyperus malaccensis</i> (subtropical species not present in U.S.) Methanogenic archaea quantified using 16S rRNA SRPs are quantified using <i>dsrA</i> gene	<a href="#">Tong et al. (2015)</a>

16S rRNA = 16S ribosomal ribonucleic acid;  $\text{Fe}^{3+}$  = iron; g = gram; ha = hectare; kg = kilogram; L = liter;  $\mu\text{M}$  = micromolar; mg = milligram;  $\text{NO}_3^-$  = nitrate; S = sulfur;  $\text{SO}_4^{2-}$  = sulfate; SRPs = sulfur-reducing prokaryotes; yr = year.

As with sulfide phytotoxicity, impacts of  $\text{SO}_x$  deposition upon methanogenesis may be present in freshwater but not marine ecosystems, as the high endogenous concentration of sulfate in seawater is likely to overwhelm the impact of anthropogenic S. In marine sediments, sulfate reduction accounts for 50–100% of anaerobic carbon mineralization ([Urban et al., 1994](#)); methanogenesis often persists at depths in organic sediments below the depth to which sulfate can diffuse. In estuarine wetlands in the Cape Fear River system in North Carolina, [Hackney and Avery \(2015\)](#) stated that in vertical soil profiles, a concentration of 28 mg/L (300  $\mu\text{M}$ ) sulfate was the threshold where S reduction switched to methanogenesis as the dominant form of C mineralization. This study also determined that in estuaries, the transition from methanogenic to S-reducing conditions occurs when more than 25% of tidal flooding carries more than 1 ppt of seawater ([Hackney and Avery, 2015](#)). In a study of the Min River Estuary in China, there was no relationship between methane emissions and pore water sulfate, but dominant plant species did affect microbial communities, with lower relative abundance of both methanogens (84% decrease) and SRPs (73% decrease) in *Spartina alterniflora* sediments than in *Phragmites australis*-associated sediments ([Tong et al., 2015](#)). Both of these species are dominant plants in North American eastern coastal marshes, and this result suggests plant community may be more important than sulfate deposition in determining methane emissions in coastal marshes.  $\text{SO}_x$  deposition is unlikely to affect methane emissions from coastal marshes and water bodies. Sulfate addition may also

result in lower methane emissions by stimulating microbial methane oxidation. In marine sediments, this occurs in syntrophic associations (associations among heterotrophs dependent on the metabolic byproducts of other microbes) between anaerobic methanotrophic archaea and SRB, which pair anaerobic oxidation of methane with sulfate reduction, or in a clade (monophyletic group) of anaerobic methanotrophs capable of both sulfate reduction and methanotrophy (Joye, 2012). However, these processes have been observed only in marine deep-sea sediments, and it is not yet clear how widely distributed or important they are in other systems. In peat bog mesocosms, by contrast, S addition of 96 mg/L decreased microbial biomass 23–57% and decreased methane oxidation to almost zero (Lozanovska et al., 2016).

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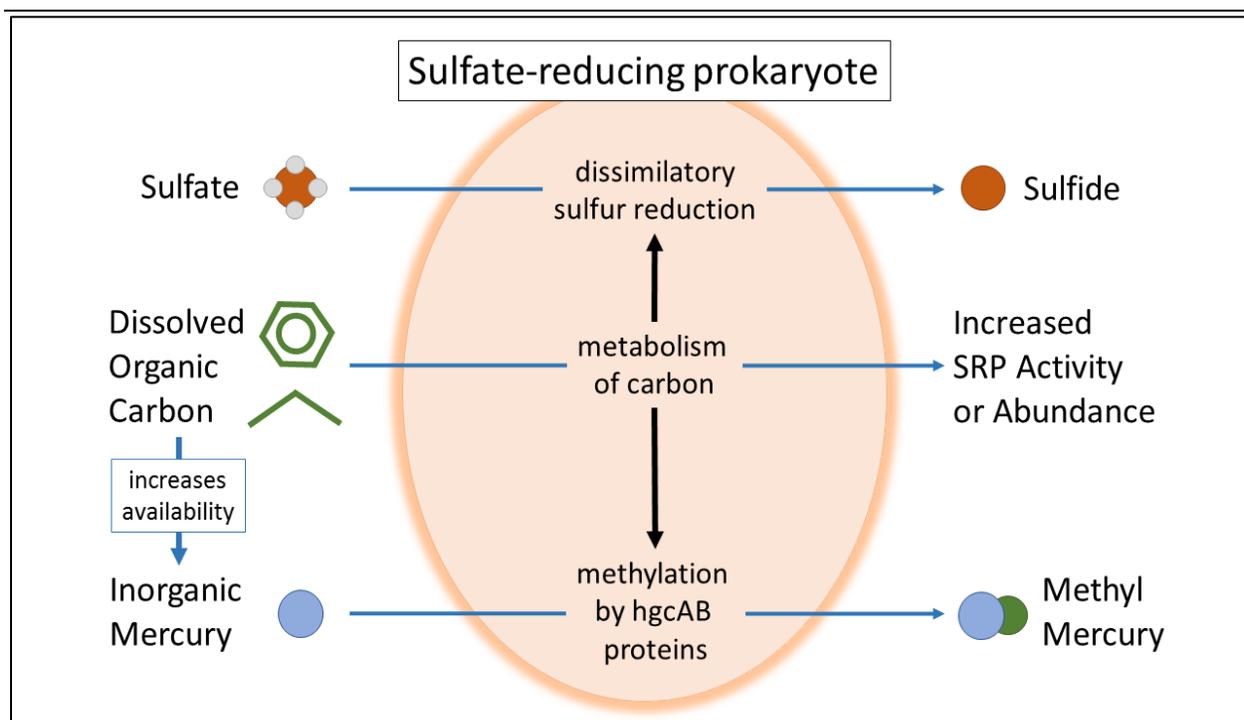
## 12.3 Interactions between Sulfur Deposition and Mercury

The 2008 ISA found the evidence was sufficient to infer a causal relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors was within adequate range for methylation. Recent research, as well as key early papers on the microbial methylation of mercury, is summarized in this section. New evidence is consistent with the 2008 ISA in identifying sulfur-reducing bacteria as a biotic link between increased SO<sub>x</sub> deposition and increased MeHg concentrations in the environment and in biota. New developments since 2008 include identification of both the microbial genes linked to mercury methylation and the methylation capability in certain archaeal strains (Appendix 12.3.1 and Appendix 12.3.2).

Ecosystem areas with high MeHg fractions (as a fraction of total Hg) are considered to indicate active microbial methylation, as well as places where primary producers and animals are at an elevated risk of MeHg accumulation. An active area of research is in identifying areas or zones of ecosystems where %MeHg is elevated. Background information on deposition and biogeochemical cycling of Hg, with particular emphasis on identifying hotspots of mercury methylation, is presented in Appendix 12.8.

Mercury methylation is a microbial process carried out by a subset of prokaryotes that are active under reducing environmental conditions (anoxic water or sediments) while requiring oxidized sulfur and organic C as substrates (see Figure 12-5). As a result, Hg methylation rates are heterogeneous across time and the landscape. Transformation by bacteria and archaea of inorganic Hg to organic MeHg occurs in wetland soils, in Sphagnum mats of wetlands, and at the oxic-anoxic boundary in lakes, estuaries, and the Arctic water column. Hg methylation by SRB embedded in periphyton is a new topic that was not covered in the 2008 ISA (Appendix 12.3.2). Evidence of MeHg production in periphyton has important implications for aquatic MeHg concentrations, because

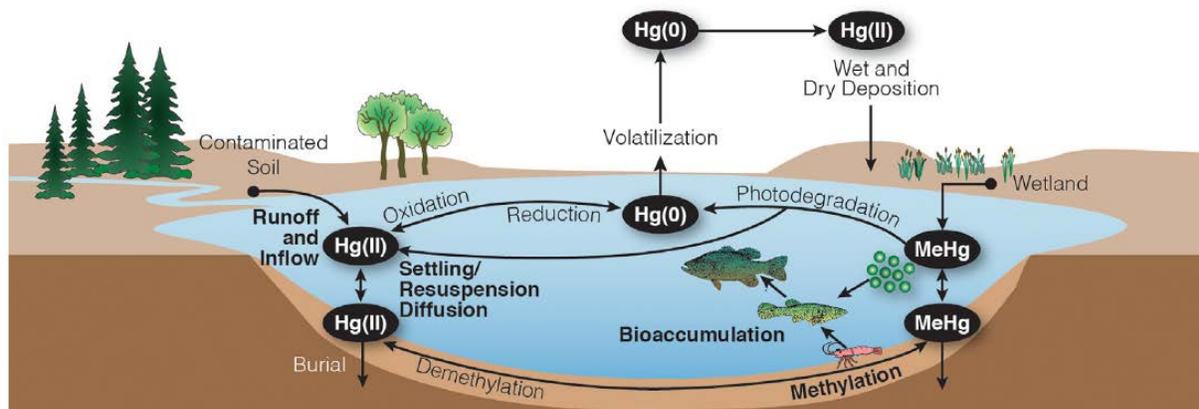
periphyton may extend throughout water columns and are more connected to aquatic and terrestrial food chains than are Hg methylation hotspots in sediment or peat. Regardless of their location within the ecosystem, microbial Hg methylators have specific environmental requirements which affect their rates of Hg methylation ([Appendix 12.3.3](#)). There is new evidence from sulfur addition studies ([Appendix 12.3.4](#)) and from studies of ambient conditions in North American ecosystems ([Appendix 12.3.5](#)) to show that S deposition and ambient sulfate concentrations increase mercury methylation under certain conditions. New evidence is consistent and coherent with the conclusions of the 2008 ISA and **the body of evidence is sufficient to infer a causal relationship between S deposition and the alteration of Hg methylation in surface water, sediment, and soils in wetland and freshwater ecosystems.**



**Figure 12-5. Sulfate, dissolved organic carbon, and inorganic mercury are all important determinants of the rate and amount of methyl mercury produced by sulfate-reducing prokaryotes.**

### 12.3.1 Mercury Cycle and the Importance of Methylation

Mercury is present in ecosystems as elemental  $\text{Hg}^0$ , as  $\text{Hg}^{2+}$  complexed to metals or organic compounds, or as MeHg. Since the Industrial Revolution, Hg emissions have increased Hg concentrations in water and soils above preindustrial levels. Although in recent decades U.S. emissions have declined [79% decrease in Hg emission between 1990 and 2011 as reported by the NEI ([U.S. EPA, 2016a](#))], Hg concentrations remain elevated in air, water, soil, and biota above inferred preindustrial values. Environmental mercury sources and transformations are illustrated in [Figure 12-6](#); important mercury sources to ecosystems that this appendix will consider include geological formations, wet and dry deposition of Hg, and legacy Hg stored in soils from historical deposition or historical (i.e., no longer active) industrial use. Hg released from active industrial sources, active mines, or historical mine sites to soil or water are not considered.



Source: [Bigham et al. \(2017\)](#).

**Figure 12-6** Cycling of mercury (Hg) and methylmercury (MeHg) in ecosystems.

Hg deposition is generally more bioavailable and readily methylated than is Hg already stored in sediments or organic matter within the ecosystem, and sulfate stimulation of methylation favors Hg newly added to the system over Hg already in the ecosystem ([Bigham et al., 2017](#)).

In terrestrial soils, Hg forms complexes with organic matter ([Poulin et al., 2016](#)). New research suggests that disturbances that accelerate carbon fluxes in terrestrial systems also accelerate Hg release from soils and sometimes stimulate methylation. In a study of

*Picea abies* (Norway spruce) stands in Sweden, clear-cutting raised the soil water table and created conditions favorable for Hg methylation. Clear-cutting did not alter Hg concentrations in the organic soil (O) layer, but it did significantly increase MeHg concentrations and %MeHg in the O layer 5–7 times over control conditions ([Kronberg et al., 2016](#)). In a similar study of clear-cutting plantations planted on drained peat soils in Finland, harvesting increased DOC and Hg in drainage waters ([Ukonmaanaho et al., 2016](#)). Peat SRB abundance correlated with MeHg concentrations and varied by geology, with higher MeHg concentrations in watersheds with underlying schist formations (high Hg content). In Oak Ridge, TN, riparian forest soils along East Fork Poplar Creek are contaminated by historical industrial mercury releases and contain 2–3 times the Hg in uncontaminated soils. Soil microcosms showed that flooding of these soils moved mercury bound to soil organic matter into the soil solution, as aqueous Hg<sup>0</sup> or as HgS precipitates, the latter produced by microbial sulfate reduction within the soils ([Poulin et al., 2016](#)). Both Hg<sup>0</sup> and nanoparticulate HgS are bioavailable to microbial methylators, and flooding resulted in a pulse of both aromatic DOC and MeHg in the riparian soil pore waters ([Poulin et al., 2016](#)).

Recent studies using stable isotopes of mercury reviewed by [Paranjape and Hall \(2017\)](#) reported a range of 0.1–15% MeHg in North American and Swedish wetlands, and 0.4–4.6% MeHg in lake sediments. There is new evidence that MeHg concentration in Adirondack surface waters is positively correlated with Hg<sup>0</sup> deposition rate ([Gerson and Driscoll, 2016](#)). Specifically, Hg in terrestrial leaf litter from Arbutus Lake watershed was measured 6 times over 2004–2014 and declined 40% in concert with a 25% decline in Hg<sup>0</sup> atmospheric concentrations. Over the same time period, MeHg concentrations in Arbutus Lake declined ( $p < 0.03$ ), although there was no quantification of the trend reported. [Gerson and Driscoll \(2016\)](#) suggested that these results show that decreases in Hg<sup>0</sup> concentrations will limit the supply of bioavailable Hg to mercury methylators and decrease MeHg in aquatic ecosystems.

Wetlands tend to have higher MeHg fractions than other water bodies at similar locations and order within watersheds. In the Adirondack Mountains, NY, sampling of soils and substrates (upland, riparian, open water, peat bog) at different points in the Sunday Lake watershed found that the highest MeHg fraction was in *Sphagnum* mats ([Yu et al., 2010](#)). In the Archer Creek watershed, also in the Adirondacks, MeHg concentrations in wetland-draining streams were elevated compared to MeHg in upland streams ([Selvendiran et al., 2008a](#)). At a larger scale survey of 44 Adirondack lakes sampled 2003–2004, land cover did not correlate with MeHg in lake water or biota, possibly because variation in wetland cover was low across watersheds ([Yu et al., 2011](#)). In a survey that included 21 freshwater, brackish, and marine wetlands and lakes in the Mississippi River delta near Lake Pontchartrain, LA, MeHg levels in wetlands were

higher than in nearby rivers or lakes with similar salinity levels. In brackish and freshwater wetlands, total MeHg concentrations (ng/L) and MeHg fraction (MeHg/total Hg) were 2 or 3 times as much as in brackish or freshwater rivers ([Hall et al., 2008](#)).

The relationship between Hg and MeHg concentrations may depend heavily on the type and salinity of water body. A recent report on Hg concentrations in streams across the U.S. found no relationship between Hg and MeHg across sites ([Wentz et al., 2014](#)). This is in contrast to an earlier review of Hg methylation and demethylation dynamics found that across studies, there is a positive correlation between Hg and MeHg in estuaries ( $R^2 = 0.78$ ), and weaker positive correlations in rivers ( $R^2 = 0.68$ ) and lakes ( $R^2 = 0.64$ ), but no correlation in wetlands ([Benoit et al., 2003](#)). In a recent study of eight highly Hg-contaminated (up to 226,000 ng Hg/g sediment, reported as 226  $\mu\text{g}$  Hg/g sediment) lakes and water bodies in Sweden, more than 55% of the variation in sediment MeHg was explained by total sediment Hg in three estuary sites, but there was no correlation in the remaining freshwater sites ([Drott et al., 2008](#)). In the freshwater sites, MeHg was instead strongly correlated with potential methylation rates [ $r^2 \geq 0.85$  ([Drott et al., 2008](#))].

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### 12.3.2 Biology of Sulfate-Reducing Prokaryotes

The 2008 ISA attributed Hg methylation to sulfur-reducing bacteria, and there is new evidence of the link between microbial sulfate reduction and Hg methylation. New (and key older) studies include experimental inhibition of different microbial groups in order to demonstrate microbial mechanisms, molecular sequencing techniques to identify potential microbial Hg methylating strains, and sequencing of environmental or experimental samples to determine microbial dynamics of Hg methylation. These studies were conducted with samples from rivers, lakes, wetlands, and laboratory mesocosms ([Table 12-4](#)). Current knowledge suggests mercury is methylated in the environment by certain strains of sulfur-reducing and iron-reducing bacteria in Deltaproteobacteria (*Desulfovibrio*, *Desulfotomaculum*, *Desulfobulbus*, and *Geobacter* genera) as well as methanogens in Archaea, while the genetic potential for methylation has been identified in the bacterial Firmicutes ([Paranjape and Hall, 2017](#)).

Increasing  $\text{SO}_x$  in the microbial environment increases the metabolic activity and growth of sulfate reducers, and one of the metabolic activities that can be stimulated is the methylation of Hg. Peat samples from the Bog Lake fen in the Macell Experimental Forest showed that experimental increases of wet S deposition to historical levels (32 kg S/ha/yr) changed entire bacterial community composition. Experimental S addition also significantly changed the composition of deltaproteobacterial communities, which contain the SRB and IRB, and this community change correlated with bog %MeHg

([Strickman et al., 2016](#)). In recovery sections of the same wetland (S treatment of 32 kg S/ha/yr had ceased 3 years before sampling), entire bacterial community and deltaproteobacterial community compositions were not significantly different from control wetland communities ([Strickman et al., 2016](#)), suggesting a rapid response time of microbial communities to changes in SO<sub>x</sub> deposition.

**Table 12-4 New studies on the biology of sulfate-reducing prokaryotes.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Peatland	Treatment: 32 kg SO <sub>4</sub> <sup>2-</sup> /ha/yr addition, control/ambient: 4.6 SO <sub>4</sub> <sup>2-</sup> kg/ha/yr	Bacterial communities in areas with increased sulfur deposition had significantly different compositions compared to control and recovery areas. Bacterial species diversity was significantly higher in the control than sulfate treated or recovery groups.  Deltaprotobacteria were significantly related to %MeHg in bogs and close to significant in lagg areas ( $p = 0.057$ ).	Marcell Experimental Forest, MN	Pore water, bacterial communities	<a href="#">Strickman et al. (2016)</a>
River	Deposition not reported	Sulfate reduction rates were positively correlated with potential Hg methylation rates ( $r^2 = 0.98$ ).  Methane production in sediment slurries correlated positively with demethylation rates ( $r^2 = 0.61$ ).  Direct inhibition of methanogens decreased demethylation by 83%.	Mesocosms of sediments from St. Lawrence River		<a href="#">Avramescu et al. (2011)</a>
Floating bog	2.0 mM (190 mg/L) sulfate added to slurried samples	Addition of MoO <sub>4</sub> <sup>2-</sup> decreased MeHg production by 44%.  Potential Hg methylation rates (%MeHg/day) were 2.1× higher with SO <sub>4</sub> amendment.	Sunday Lake, Adirondack Mountains, NY	Sphagnum spp.	<a href="#">Yu et al. (2010)</a>

**Table 12-4 (Continued): New studies on the biology of sulfate-reducing prokaryotes.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Lakes	Deposition not reported	Addition of $\text{MoO}_4^{2-}$ decreased methylation by 60–90% in settling particles, and by 80% in sediments.	Lake Geneva, Switzerland	Samples of particles from water column and from lake bottom sediments	<a href="#">Gascón Díez et al. (2016)</a>
Lakes	Deposition not reported	Addition of $\text{MoO}_4^{2-}$ decreased MeHg production by 30% for <i>E. crassipes</i> and by 60% for <i>P. glabra</i> .  qPCR of bacterial genes indicated that 3.34% of the total bacterial community in the periphyton belonged to the SRB families <i>desulfovibrionaceae</i> and <i>desulfobacteraceae</i> .  MeHg fraction was positively correlated with relative abundance of <i>desulfobacteraceae</i> in <i>P. glabra</i> periphyton.	Amazon Oxbow Lakes, Bolivia	<i>Eichhornia crassipes</i> and <i>polygonum densiflorum</i> (currently named <i>persicaria glabra</i> )	<a href="#">Achá et al. (2011)</a>
Freshwater marsh	W3 pore water $[\text{SO}_4^{2-}] \leq 4 \mu\text{M}$ U3 pore water $[\text{SO}_4^-]$ is 39 $\mu\text{M}$ F4 pore water $[\text{SO}_4^{2-}]$ is 74 $\mu\text{M}$ Deposition = not measured	SRB abundance is 6.9x higher in U3 than W3 and 16.8x higher in F4. In W3, abundance of SRB and methanogens are not significantly different. In U3, SRB abundance is 80% higher than methanogen abundance. In F4, SRB abundance is 60% higher than methanogens.  <i>mcrA</i> copy number correlates positively with mRNA and methane production rates.  Acetotrophic methanogens are dominant at W3, while at high S U3 and F4 sites, hydrogenotrophic methanogens are dominant.	F4, U3, and W3 sites in Water Conservation Area, Everglades, FL	Methanogens as quantified by <i>mcrA</i> copies  Sulfur-reducing bacteria as quantified by <i>dsrB</i> copies	<a href="#">Bae et al. (2015)</a>

**Table 12-4 (Continued): New studies on the biology of sulfate-reducing prokaryotes.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Marine	Laboratory cultures with different C sources (pyruvate, fumarate, lactate, ethanol, or malate), control and additional sulfate (30 mM)	Methylation increases with increasing bacterial biomass ( $r = 0.83$ ). During exponential growth phase, S addition increases net MeHg production by 50%. hgcAB expression levels do not correlate with methylation capacities.	Laboratory cultures Sediments from Berre Lagoon, France	<i>Desulfovibrio dechloracetivorans</i> , strain BerOC1 from sediments	<a href="#">Goñi-Urriza et al. (2015)</a>

C = carbon; ha = hectare; kg = kilogram; MeHg = methylmercury; mM = millimolar;  $\mu\text{M}$  = micromolar; S = sulfur;  $\text{SO}_4^{2-}$  = sulfate; SRB = sulfur-reducing bacteria; yr = year.

Sulfate-reducing bacteria (SRB) and iron-reducing bacteria (IRB) are primarily responsible for Hg methylation in natural ecosystems. On a broad scale, these bacteria metabolize organic C by pairing its oxidation with the reduction of sulfate and/or  $\text{Fe}^{3+}$ . The sulfide produced by the reduction of  $\text{SO}_x$  can act as a negative feedback on SRP activity and Hg methylation. Methanogens, SRB, and IRB are facultative anaerobes, ([Paranjape and Hall, 2017](#)), and their presence and activity within wetland and freshwater ecosystems is limited to zones with low oxygen availability. Experimental inoculations suggest that microbial methylators are capable of forming syntrophies, in which microbes link their metabolisms by the exchange of metabolic substrates and products. This suggests that sulfate stimulation of methylation may involve more types of organisms than just the sulfate-reducing bacteria and has led to the classification of the group of interest as sulfate reducing-prokaryotes.

Specific inhibition of SRPs using molybdate ( $\text{MoO}_4^{2-}$ ) is a common tool in studies that determine the contribution of SRPs to Hg methylation. An older study of acidic Dickie Lake in Ontario used different microbial inhibitors to determine whether SRPs or methanogens within the sediments were responsible for Hg methylation. Molybdate inhibited sulfate reduction and decreased %MeHg by 75% of production in controls, while 2-bromo-ethanesulfonate (BESA), an inhibitor of methanogens, did not significantly decrease MeHg production ([Kerry et al., 1991](#)). Researchers inferred that SRPs, not methanogens, were responsible for methylation in the lake, and sulfate reduction rates increased 0.35 mg sulfate reduced/L/day with a 1 mg/L increase in sulfate addition. However, additions of sulfate to concentrations of 5–25 mg sulfate/L in sediment slurries did not affect %MeHg, which was 0.20–0.25% MeHg/g sediment ([Kerry et al., 1991](#)). A similar relationship between MeHg and sulfate reduction was

demonstrated using molybdate inhibition in coastal Georgia marsh soils, where Mo addition decreased sulfate reduction by 90% and decreased MeHg production by 85% ([King et al., 1999](#)), indicating that SRPs were involved in both processes.

An early laboratory study cultivated strains of a SRB, a methanogen, or an acetogen with an Hg spike. The SRBs were the only microbes that methylated added Hg, and they did so at a rate that resembled the rate in aquatic sediments, while molybdate inhibited MeHg production and demethylation of added MeHg ([Pak and Bartha, 1998](#)). In a more recent study, incubations of St. Lawrence River sediments with different inhibitors showed that molybdate inhibited sulfate reduction completely, but did not affect methane production ([Avramescu et al., 2011](#)), indicating that methanogens did not play an important role in reducing S. Moreover, sulfate reduction rates were strongly positively correlated with potential Hg methylation rates ( $r^2 = 0.98$ ). However, when methanogens were inhibited, methylation of Hg increased 16% ([Avramescu et al., 2011](#)), indicating that methanogens compete with SRPs and can depress Hg methylation. In Everglades, FL sediment incubations, molybdate decreased MeHg production by 90% ([Gilmour et al., 1998](#)). In incubations of *Sphagnum* sampled from Sunday Lake, NY, molybdate decreased MeHg production by 44% ([Yu et al., 2010](#)). In core incubations from lakes in Wisconsin, including both basins of Little Rock Lake, molybdate reduced MeHg production by 50% ([Gilmour et al., 1998](#)).

In wetlands within the Allequash Creek watershed, WI, sediment incubations with added  $^{14}\text{C}$ -labelled substrate and sodium molybdate suggested a diverse variable microbial methylation community ([Creswell et al., 2017](#)). In some incubations, addition of molybdate increased  $^{14}\text{CO}_2$  produced from the substrate, suggesting that iron-reducing methylators were dominant; in some incubations molybdate decreased  $^{14}\text{CO}_2$ , suggesting that sulfate-reducing methylators were dominant. Incubations from the lower part of the wetland produced  $^{14}\text{CH}_4$  as their dominant product, suggesting that methanogens dominated the microbial methylation at this location ([Creswell et al., 2017](#)). Dominant microbial methylators varied seasonally and spatially, including by sediment depth.

In Lake Geneva, Switzerland, mercury methylation rates were an order of magnitude higher in settling particles than in sediments, and molybdate inhibition suggested that sulfate-reducing methylators were responsible for 60–90% of methylation in settling particles, and 80% of methylation in sediments ([Gascón Díez et al., 2016](#)). [Gascón Díez et al. \(2016\)](#) suggest that this study may be relevant to the Great Lakes, which like Lake Geneva, are large, deep, and experience algal blooms due to nutrient inputs.

New research suggests that SRPs are important methylators of mercury in disturbed terrestrial soils as well. In a Swedish study of the effects of forest harvesting on mercury dynamics, clear-cutting induced changes in mercury methylators as inferred from soil

incubations ([Kronberg et al., 2016](#)). Additions of sulfate and iron enhanced potential methylation rates in clear-cut but not reference forest soils, indicating that SRPs and iron-reducing bacteria were both active methylators in disturbed soils with high water tables (see [Appendix 12.3.2](#)). The role of SRPs was confirmed by inhibition of methylation by molybdate in soils from clear-cut stands, and a role of methanogens in methylating mercury was shown by BES inhibition of methylation ([Kronberg et al., 2016](#)).

The 2008 ISA did not address the role that periphyton play in hosting SRPs and boosting Hg methylation rates within the oxic water column of aquatic and wetland ecosystems. This section summarizes new (and key older) papers that demonstrate that SRB in periphyton methylate Hg in South American lakes as well as North American lakes and wetlands. Periphyton are ecologically important as they form the base of the aquatic food chain for many invertebrates and vertebrates. Periphyton mats are biofilms of algae, bacteria, fungi, microinvertebrates, organic detritus, and inorganic particles, embedded in a polysaccharide matrix, typically attached to a substrate of sediments or submerged macrophytes. The microbial communities embedded within the periphyton can be quite complex and diverse, including autotrophs and heterotrophs, SRB and S oxidizing bacteria, and methanogens; periphyton microbial composition and microbial activity depend on site conditions ([Correia et al., 2012](#)). The polysaccharide matrix slows exchange with the water column while intense aerobic metabolism at the matrix surface quickly consumes oxygen diffusing into the periphyton, creating anoxic, reducing microenvironments in the interior of periphyton where anaerobes including SRPs thrive. In the case of periphyton attached to macrophytes, plant exudates are an important source of carbon for periphyton microbes, boosting activity above rates of activity of similar microbes residing in sediments.

SRPs embedded in periphyton are more efficient in methylating Hg than are SRPs in sediments. Much of the research demonstrating Hg methylation by periphyton has occurred in South America, in tropical lakes where the genus *Eichhornia* (water hyacinth) is native, and where ambient temperatures can support high levels of bacterially mediated Hg methylation ([Guimarães et al., 2006](#)). *Eichhornia crassipes* is a wetland plant present in 24 states and listed as a noxious or invasive weed by 7 states ([USDA, 2015b](#)). Closely related *Eichhornia azurea* is currently present only in Florida; it is listed by the Animal and Plant Health Inspection Service of the U.S. Department of Agriculture (USDA-APHIS) as a noxious weed ([USDA, 2015b](#)). In incubations of chopped *Eichhornia crassipes* roots spiked with  $^{203}\text{HgCl}_2$ , net MeHg production was high, 1.6–30.2% of total Hg ([Guimarães et al., 2006](#)). Other studies have shown a similarly wide range of methylation by periphyton, with high rates exceeding sediment methylation rates. Intact *E. crassipes* periphyton incubations had potential methylation of 12.1–25.2%

of added Hg, and periphyton isolated from *Polygonum densiflorum* [hereafter called by its current accepted scientific name *Persicaria glabra*; a wetland obligate plant also native to the U.S., classified as endangered in Maryland and New Jersey, ([USDA, 2015b](#))] had potential methylation rates of 0.2–36.1%; by comparison, sediment from the same tropical lakes produced 6.4–12.5% MeHg in incubations ([Correia et al., 2012](#)).

Mo inhibition of sulfate reduction also inhibits MeHg production in periphyton, confirming that SRPs are responsible for a significant portion of Hg methylation within these complex microbial communities. Recently, [Achá et al. \(2011\)](#) and [Correia et al. \(2012\)](#) collected macrophyte samples from oxbow lakes in the Bolivian Amazon for inhibition experiments. Incubations with an array of guild-specific inhibitors show the relative contribution of different microbes to Hg methylation. One set of incubations of periphyton associated with the roots of *E. crassipes* or *P. glabra* suggested that SRB were the most important component of the periphyton in producing MeHg. Molybdate, an inhibitor of sulfate reduction, decreased MeHg production by 30% for *E. crassipes* and by 60% for *P. glabra* ([Achá et al., 2011](#)), indicating that in intact periphyton, SRB alone are responsible for 30–60% of Hg methylation. Quantitative PCR of bacterial genes indicated that 3.34% of the total bacterial community in the periphyton belonged to the SRB families Desulfovibrionaceae and Desulfobacteraceae, and MeHg fraction was positively correlated with relative abundance of Desulfobacteraceae in *P. glabra* periphyton ([Achá et al., 2011](#)). A second set of incubations of six tropical macrophyte species-associated periphyton confirmed that inhibition of sulfate reduction and SRB using molybdate decreased MeHg production, but showed that inhibiting both SRB and methanogens resulted in a 90% reduction of MeHg production across sediments and periphyton ([Correia et al., 2012](#)). Algaecide or fungicide additions significantly inhibited MeHg formation in some but not all incubations, indicating that the microbial composition or activity varied across periphyton samples, even when they were collected from the same site or from the same host plant species grown at different sites ([Correia et al., 2012](#)). Together, these studies show that SRB are important in producing MeHg within periphyton, but that other microbes residing in the periphyton contribute through poorly understood mechanisms to total MeHg production.

Mercury methylation by periphyton has also been documented within North American ecosystems. In an older study in Dickie Lake in Ontario, measured Hg concentrations in periphyton were 56.5 ng/g, 22 times higher than Hg concentrations in sediments ([Kerry et al., 1991](#)). A more recent study of periphyton growing in the epilimnion of boreal Lake Croche in Quebec demonstrated that Hg methylation rates are faster in periphyton, reaching steady-state in 12 hours, than the 4–8 days to steady state of MeHg production in sediments ([Desrosiers et al., 2006](#)). MeHg production by periphyton in the boreal lake was dependent on SRB as well as on photosynthesizers, as demonstrated by inhibition

experiments. Despite the lower temperatures of incubations to reflect the lower temperatures of the boreal lake, potential MeHg production was 16.6–18.5% ([Desrosiers et al., 2006](#)), similar to MeHg production in tropical periphyton.

In the Florida Everglades, periphyton are the base of the aquatic food chain. In an older study, incubation of periphyton collected from different sites along the eutrophic gradient between the EAA to the north and Everglades National Park to the south found MeHg production in periphyton from all sites, although rates varied widely ([Cleckner et al., 1999](#)). MeHg potential production rates were highest in periphyton collected at the northern, eutrophic site, and MeHg production correlated positively with both S reduction and S oxidation by photosynthesizing purple S bacteria ([Cleckner et al., 1999](#)). Periphyton may be an important direct source of MeHg to the food chain in the Florida Everglades.

The gene pair conferring the ability to methylate Hg has been identified only recently, after the 2008 ISA. No ecological or evolutionary advantage of the ability to methylate Hg has been established ([Kerin et al., 2006](#); [Benoit et al., 2003](#)), and it appears to be an inadvertent transformation by a corrinoid-dependent protein produced by prokaryotes for a different metabolic pathway ([Gilmour et al., 2013](#)). Recent phylogenetics work indicates that the gene pair *hgcAB* confers the ability to methylate Hg, and that the gene pair and Hg methylation are present in some but not all species within the SRB, iron-reducing bacteria, syntrophic sulfur reducers in the Syntrophobacterales, methanogens in the Archaea, and bacteria in the Clostridia ([Gilmour et al., 2013](#)). The confirmed and predicted Hg methylators from this study occur across alkaline, neutral, or acidic environments, and are mostly heterotrophs that use sulfate, iron, and CO<sub>2</sub> as terminal electron acceptors.

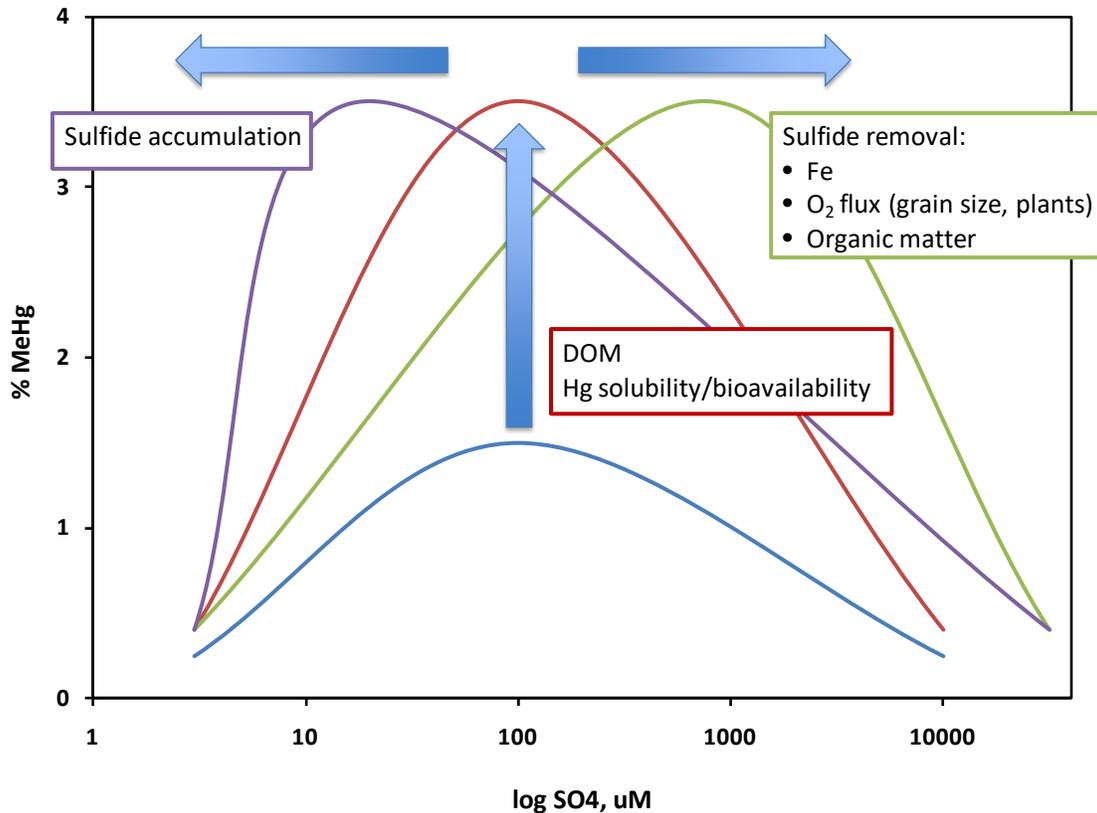
MeHg production rates vary among species, and even among strains within species ([Shao et al., 2012](#)). A recent study of *hgcAB* in the freshwater marshes of the Florida Everglades showed that syntrophs dominated the microbial methylators (49–65% of sequences) and also were the dominant sulfate reducers, as shown by *dsrB* mRNA quantification (75–89%) of sediments sampled within the water conservation areas ([Bae et al., 2014](#)). In a recent study of methylation using a strain of *Desulfovibrio dechloracetivorans*, expression of the *hgcAB* gene did not correlate with methylation capacities of pure cultures, which supports the supposition that Hg methylation is not the main purpose of the proteins encoded by *hgcAB*. However, during the exponential growth phase of the cultures, addition of 2,900 mg/L (30 mM) sulfate increased net MeHg production by 50% ([Goñi-Urriza et al., 2015](#)).

Demethylation is also an important microbial Hg transformation to consider in natural ecosystems. The capacity to transform MeHg to inorganic Hg (elemental Hg or Hg<sup>2+</sup>) is

widely distributed and occurs by different mechanisms in different microbial groups. Microbial demethylation by aerobic and facultative Hg-resistant microbes possessing the *mer* operon break MeHg into methane and Hg<sup>0</sup> via reductive degradation, whereas methanogens, SRPs, and other prokaryotes break MeHg into carbon dioxide, methane, and Hg<sup>2+</sup> via oxidative demethylation. A recent study of St. Lawrence River, Ontario, Canada sediments showed that methane production in sediment slurries correlated positively with demethylation rates ( $r^2 = 0.61$ ), and direct inhibition of methanogens decreased demethylation by 83% ([Avramescu et al., 2011](#)). An earlier study tested a pure culture of the archaeon *Methanococcus maripaludis* and found that it demethylated added MeHg despite no observed methylation potential ([Pak and Bartha, 1998](#)).

Microbial demethylation also occurs in the same prokaryotes that methylate Hg; a laboratory incubation of pure cultures demonstrated that *Desulfovibrio desulfuricans* (an SRB that methylates Hg) demethylated added MeHg at rates similar to those of incubated aquatic sediments ([Pak and Bartha, 1998](#)). In the same study of sediments of the St. Lawrence River, Ontario, inhibition of both SRPs and methanogens decreased demethylation of Hg by 96% ([Avramescu et al., 2011](#)), indicating that while methanogens are responsible for the bulk of demethylation in these sediments, SRPs are involved in demethylation.

New evidence of the genetic basis of Hg methylation and the activity of microbial methylators in the environment and in the laboratory is consistent with the 2008 ISA's link between sulfate reduction and Hg methylation. Mercury methylation by SRP is determined by the same suite of environmental factors that enhance SRP activity or abundance: sulfate, organic matter, and anoxic-oxic conditions ([Figure 12-7](#)). Mercury methylation occurs in wetlands, lakes, reservoirs, streams, and rivers. Algal blooms, periphyton, stratification of the water column, and fluctuating water levels all create favorable conditions for sulfate stimulation of mercury methylation.



Source: [Glimour \(2011\)](#).

**Figure 12-7** The effect of different environmental factors on the relationship between sulfate and mercury methylation. Methylmercury (MeHg) accumulation is minimal at low and high sulfate concentrations, with an optimum near 100  $\mu\text{M}$  sulfate (blue line). High dissolved organic matter (DOM) will increase the magnitude of MeHg production across the range of sulfate concentrations (red line). Sulfide produced by methylators will inhibit further methylation if it accumulates in the aqueous environment where methylation occurs, shifting the MeHg optimum left (purple line). However if ecosystem chemistry (iron [Fe], reoxidation of sulfide, organic matter [OM]) allows for rapid sequestration of sulfide to large particles and sediments, the relaxation of the negative feedback of sulfide to sulfur-reducing prokaryotes (SRPs) will shift the MeHg optimum right (green line).

### 12.3.3 Environmental Drivers of Mercury Methylation Potential

The 2008 causality statement linked S to increased Hg methylation when other conditions are favorable, with a particular emphasis on dissolved organic carbon (DOC) as a control on Hg methylation ([U.S. EPA, 2008a](#)). This section is an overview of factors that control Hg methylation. In a review, [Bigham et al. \(2017\)](#) summarized drivers of mercury methylation in terms of their effect on mercury availability to methylators and on microbial activity associated with Hg methylation ([Table 12-5](#)).

**Table 12-5 Environmental factors that affect mercury (Hg) methylation.**

Geochemical or Physical Parameter Affects	Bioavailability of Hg to Methylators	Microbial Methylator Activity	Notes
Sulfur	Increase or decrease	Increase	Bioavailability of inorganic Hg will increase or decrease depending on Hg-S bonds and chemical species formed.  Increased sulfate can stimulate activity of sulfate-reducing prokaryotes, some which may be capable of Hg methylation.
Organic carbon	Increase or decrease	Increase	Availability of inorganic Hg can decrease if Hg binds to organic carbon molecules of a size or structure that makes the molecules resistant to microbial degradation.  Availability of inorganic Hg can increase if Hg binds to organic molecules that are mobile in water and accessible to microbial degradation.  Increased organic carbon can stimulate microbial activity by increasing electron donors to metabolism.
Iron	Decrease	Increase or decrease	Bioavailability of inorganic Hg can decrease as Fe reduces and binds to Hg.  Fe can increase microbial methylation by binding to sulfide and preventing the negative feedback of this product of sulfate reduction upon its production, which coincides with Hg methylation in some SRP. Also, Fe can stimulate the action of iron-reducing microbial methylators.  Fe can decrease microbial methylation by shifting microbial communities towards nonmethylating organisms.
pH	Increase or decrease	Increase or decrease	Bioavailability of inorganic Hg is reduced at high pH. pH between 4.5 and 9 is optimal for microbial activity.

**Table 12-5 (Continued): Environmental factors that affect mercury (Hg) methylation.**

Geochemical or Physical Parameter Affects	Bioavailability of Hg to Methylators	Microbial Methylator Activity	Notes
Temperature	Increase or decrease	Increase or decrease	Bioavailability of inorganic Hg can increase if weathering of Hg-containing rocks or sediments, or decomposition of older organic matter, increases with higher temperatures. Bioavailability of Hg can decrease if Hg volatilization to the atmosphere increases. Microbial methylators have optimal temperatures for growth.
Oxygen availability	Increase	Decrease	Bioavailability of Hg in reduced chemical species is low. Microbial methylators are anaerobes, methylating Hg under reducing conditions.
Drying and wetting cycles (drought, seasonal variation in water levels, etc.)	Increase	Increase	Fluctuating water levels can increase the release of Hg from particles in sediment. Fluctuating water levels can increase the reoxidation and release of S from sediments as sulfate.

Adapted from [Bigham et al. \(2017\)](#).

Seasonal patterns of Hg methylation and transport of Hg in many systems can affect MeHg accumulation. Also, a number of chemical constituents can stimulate or inhibit Hg methylation. Given our understanding of the microbial mechanisms of Hg transport and methylation, and the complexity and diversity of aquatic environments, chemical controls on MeHg processes are not fully established. This section is meant to lend context to the description of how S deposition affects methylation, but it is not a complete review of the chemical controls on biological Hg methylation in natural environments.

### 12.3.3.1 Sulfur and Methylation Potential

Sulfate in soil pore water, surface water, or in sediment pore waters can stimulate mercury methylation. Sulfate is utilized as a terminal electron acceptor in heterotrophic metabolism by some classes of bacteria, and in the course of this dissimilatory sulfur reduction, these bacteria transform sulfate to sulfide and expel the reduced sulfur into the environment as a waste product. Sulfate-reducing bacteria can also form syntrophies, symbiotic exchanges of metabolic substrates and products, with methanogens and other archaea, so that sulfate stimulates metabolism even in organisms that do not utilize it directly as an electron acceptor. The current scientific understanding is that MeHg is produced as an accidental byproduct in both sulfate-reducing bacteria and syntrophic archaea. Conditions optimal for these organisms and which favor their activity over

competing anaerobic heterotrophs probably occur in short time frames and in shifting locations in many ecosystems. Sulfate stimulation of mercury methylation will probably occur at an annual time scale at very low or undetectable background levels, with occasional peaks of microbial methylation (hotspots) when other controls (temperature, organic matter, anoxic microsites, or hypoxic zones) on microbial metabolism reach their optima. At temporal and spatial hotspots of mercury methylation, sulfate concentrations may drop as sulfate is converted to sulfide, particularly in shallow water bodies with longer water residence times. As a result, concentrations of sulfate in surface water may not correlate with sulfate inputs to the ecosystem or with MeHg produced by sulfate reduction, particularly in aquatic or wetland ecosystems where there are active SRPs.

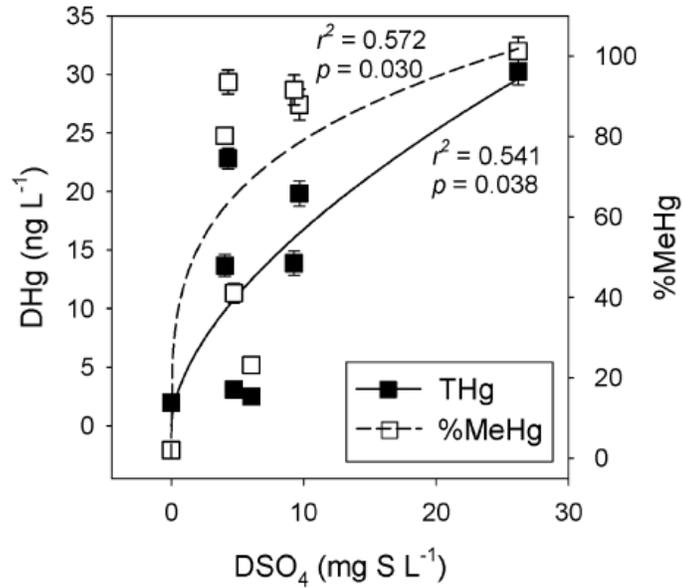
The byproduct of microbial sulfate reduction, sulfide, is also an important regulator of mercury methylation. Sulfide dissolved in surface water or pore water inhibits microbial methylation, and interferes with plant nutrient uptake (see [Appendix 12.2.3](#)). Sulfide can also produce a negative feedback on mercury methylation by binding with inorganic mercury in the water column and precipitating into cinnabar in the sediment, lowering the bioavailability of Hg to microbial methylators. However, in water bodies with a high fraction of mineral sediments or dissolved minerals, particularly iron, iron will bind to sulfide and precipitate out of solution, preventing the formation of a negative feedback to sulfur reduction and mercury methylation. In water bodies with longer residence times, sulfide concentrations in sediments may correlate with microbial sulfate reduction, and if SRPs are the primary methylators in the system, with MeHg concentrations.

Laboratory studies support field research in demonstrating that under controlled conditions, sulfate additions increased Hg methylation in environmental samples. The 2008 ISA reported evidence of Hg methylation in lake water and sediment samples in response to experimental sulfate addition. In slurries of sediment collected from Quabbin Reservoir, MA, adding 4.8 mg/L (reported as 50  $\mu\text{M}$ ) sulfate to the slurry (ambient lake water sulfate = 5.8–7.7 mg/L or 60–80  $\mu\text{M}$ ) increased potential MeHg production 150%, adding 9.6 mg/L sulfate (100  $\mu\text{M}$ ) increased MeHg production 160%, and adding 19.2 mg/L sulfate (200  $\mu\text{M}$ ) sulfate increased MeHg 410% above ambient lake water MeHg ([Gilmour et al., 1992](#)). Slurries can overestimate the potential rates of MeHg production, so this study also incubated intact sediment cores with sulfate concentrations from 0.3–110 mg/L (reported as 3–1,140  $\mu\text{M}$ ). Peak potential MeHg production was at 11 mg/L sulfate (110  $\mu\text{M}$ ), where MeHg was 8.6 ng MeHg/g, a 200% increase from MeHg production at 0.3 mg/L sulfate [3  $\mu\text{M}$  ([Gilmour et al., 1992](#))]. In longer incubations of sediment cores from two lakes in Wisconsin, including Little Rock Lake, adding 5.8–23 mg/L sulfate (60–240  $\mu\text{M}$ ) changed sediments from net demethylating (–100 ng MeHg/m<sup>2</sup>/day or –0.1  $\mu\text{g}$  MeHg/m<sup>2</sup>/day) to net methylating

(5,500 ng MeHg/m<sup>2</sup>/day or 5.5 µg MeHg/m<sup>2</sup>/day) environments ([Gilmour and Riedel, 1995](#)).

Since the 2008 ISA, several new studies have provided experimental evidence of sulfate stimulation of Hg methylation in a broader range of aquatic freshwater environments ([Table 12-6](#)). Laboratory experiments using samples from wetlands at Sunday Lake in the Adirondack Mountains of New York were conducted to determine potential Hg methylation rates. When slurried peat-and-water samples from a floating fen (bog mat composed of *Sphagnum* spp. and ericaceous shrubs) received an addition of sulfate to raise the concentration of sulfate by 190 mg/L (initial sulfate concentration not given), Hg methylation rates (%MeHg/day) were 2.1 times higher than unamended samples ([Yu et al., 2010](#)). This result is consistent with evidence from observational ([Appendix 12.3.5](#)) and S addition studies ([Appendix 12.3.4](#)) in peat bogs that sulfate stimulates Hg methylation in these wetland systems.

There are three new studies that demonstrate sulfate stimulation of water and sediment Hg methylation in samples taken from rivers. Slurried sediments collected in 2010 from the South River, VA, were spiked with sulfate to raise sulfate levels from average ambient levels of 19.2 mg/L to 38.2 or 96.1 mg sulfate/L. Sulfate addition significantly increased the potential methylation rate of Hg (%/day), with methylation rates 1.6–2.6 times higher in sulfate-spiked sediments than in sediments with ambient sulfate concentrations ([Yu et al., 2012](#)). There was a significant difference in methylation rates between the low and high S addition treatments in only one of three sampled river sediments; this sample showed methylation was higher in the sediment when sulfate levels were 96.1 mg/L ([Yu et al., 2012](#)). In microcosm slurries composed of water and sediment samples from the Wupper River in Germany, higher MeHg in water correlated weakly ( $R^2 = 0.28$ , both variables natural log-transformed) with higher sulfate concentrations, with mean pore water sulfate of 32.2 mg/L and range of 2–223 mg/L ([Frohne et al., 2012](#)). Higher total Hg concentrations in water correlated weakly ( $R^2 = 0.20$ ) with higher sulfate, although DOC was a stronger predictor of total Hg [ $R^2 = 0.53$  ([Frohne et al., 2012](#))]. [Tsui et al. \(2008\)](#) constructed mesocosms to mimic leaf decomposition in the hyporheic zone of Minnesota streams and rivers, where conditions are hypothesized to be favorable for the SRB that methylate inorganic Hg. Water samples were collected from seven streams or rivers in Minnesota, with sulfate levels at collection of 4.0–26.2 mg sulfate-S/L (with an ultrapure water sample as a control, 0.0 mg S/L), and incubated with *Acer* sp. (maple) leaves. After 66 days of decomposition, the total Hg released from the decomposing litter into solution as dissolved Hg increased with initial sulfate concentration ( $R^2 = 0.541$ ,  $p = 0.038$ ), and the fraction of total Hg that had been transformed to MeHg increased in a power law dependence upon initial sulfate concentration [ $R^2 = 0.572$ ,  $p = 0.030$ , see [Figure 12-8, \(Tsui et al., 2008\)](#)].



%MeHg = methylmercury fraction; DHg = mercury dissolved in mesocosm water; DSO<sub>4</sub><sup>2-</sup> = sulfate dissolved in mesocosm water; L = liter; mg = milligram; ng = nanogram; S = sulfur; THg = total mercury.  
 Source: adapted from [Tsui et al. \(2008\)](#).

**Figure 12-8 The relationship between surface water sulfate and total mercury or methylmercury fraction in river/leaf litter mesocosms.**

This evidence of sulfate stimulation of Hg methylation in river ecosystems is consistent with observational studies of positive correlations between sulfate and Hg methylation in rivers and streams.

**Table 12-6 New mesocosm or incubation studies on sulfur addition effects on methylmercury.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
River	S deposition not reported Soil: 2.0–2.6 mg S/g soil [SO <sub>4</sub> <sup>2-</sup> ] pore water in microcosm: 2.2–223 mg/L, mean 32.0 mg/L	Total Hg and MeHg were positively correlated with sulfate concentrations: ln(THg) = 2.956 + 0.697 × ln(SO <sub>4</sub> <sup>2-</sup> ), ln(MeHg) = 4.962 + 0.473 × ln(SO <sub>4</sub> <sup>2-</sup> ).	Wupper River, Germany	Sediment pore water	<a href="#">Frohne et al. (2012)</a>
Floating bog	2.0 mM (190 mg/L) sulfate added to slurried samples	Potential Hg methylation rates (%MeHg/day) were 2.1× higher with SO <sub>4</sub> <sup>2-</sup> amendment.	Sunday Lake, Adirondack Mountains, NY	<i>Sphagnum</i> spp.	<a href="#">Yu et al. (2010)</a>
River	Ambient concentration in water is 200 μM (19.2 mg/L) sulfate  Addition of 400 μM (38.4 mg/L) or 1,000 μM (96.1 mg/L) sulfate in anoxic sediment slurries	Sediment MeHg (ng/g) increased linearly with pore water sulfate (μM) concentrations in the river, MeHg = 0.61 × [SO <sub>4</sub> <sup>2-</sup> ] – 0.08.  SO <sub>4</sub> <sup>2-</sup> addition in slurries increased potential methylation rates by 1.6–2.6×.	South River, VA	In-channel surface sediments	<a href="#">Yu et al. (2012)</a>
Fluvial zones (streams and rivers)	S deposition not reported Initial water SO <sub>4</sub> <sup>2-</sup> concentrations (mg/L): range 4.0–26.2, mean 9.2, median 6.1	Following aquatic anoxic decomposition of leaf litter, total dissolved Hg increases in decreasing proportion to initial SO <sub>4</sub> <sup>2-</sup> concentration. Dissolved %MeHg increases in decreasing proportion to initial SO <sub>4</sub> <sup>2-</sup> concentration.	Mesocosms constructed with samples from Cedar Creek LTER (leaf litter) and seven streams or rivers (water), MN	<i>Acer</i> sp. and stream microbial communities	<a href="#">Tsui et al. (2008)</a>

g = gram; ha = hectare; Hg = mercury; kg = kilogram; L = liter; MeHg = methylmercury; mg = milligram; mM = millimolar; μM = micromolar; ng = nanogram; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; THg = total mercury; yr = year.

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### 12.3.3.2 Total Mercury Concentration and Methylation Potential

The 2008 ISA did not present information on how total Hg concentration affects rates of MeHg production, in part because there is no consensus across studies as to whether there is a linear relationship between total Hg and MeHg in water or soil. In part this is because most reported MeHg rates are potential rates determined by experimental incubations with added Hg, and methylation rates have been shown to be dependent on initial concentrations of Hg ([King et al., 1999](#); [Gilmour et al., 1992](#)). Additionally, different chemical forms of inorganic Hg vary in bioavailability and affect methylation rates ([Kucharzyk et al., 2015](#); [Graham et al., 2012](#)).

Two studies that sampled MeHg fractions at different locations within the U.S. provide information at the landscape level about factors that increase probability of detrimental effects upon wildlife due to Hg availability. There is a large variability across systems in MeHg fraction. In a study of five forested watersheds distributed across the U.S. (in Vermont, Wisconsin, Colorado, Georgia, and Puerto Rico), total Hg flux out of the watershed in the streams was highest at Rio Icacos, Puerto Rico (54,400 ng Hg/m<sup>2</sup>/yr, reported as 54.4 µg Hg/m<sup>2</sup>/yr) and lowest at Allequash Creek, WI [250 ng Hg/m<sup>2</sup>/yr or 0.25 µg Hg/m<sup>2</sup>/yr ([Shanley et al., 2008](#))]. MeHg fraction was highest at Allequash Creek (14.8% of total Hg) and lowest at Rio Icacos (0.7%), indicating that watershed flux of total Hg does not directly indicate risk to organisms ([Shanley et al., 2008](#)). In a study of eight streams in Oregon, Wisconsin, and Florida, MeHg fractions and concentrations (range: <0.01–17.8 ng/g sediment) in streambed sediments were higher in nonurban than in urban streams ([Marvin-Dipasquale et al., 2009](#)).

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### 12.3.3.3 Temperature and Methylation Potential

The 2008 ISA did not describe temperature or seasonal effects on Hg methylation. This section presents information from key older papers and recent research on temperature effects in lakes, wetlands, and watersheds. Seasonal patterns of microbial methylation are directly controlled by temperature effects on microbial metabolism, as well as by indirect temperature effects, such as oxygen depletion and stratification and mixing of water bodies.

As a microbial process, Hg methylation is temperature dependent. In Lake Clara, WI, incubation at in situ temperatures of seasonally sampled sediment cores from a lake depth of 10.5 m showed that Hg methylation increased slowly from near 0% in April to peaks of 1% methylation in August and September, with temperature accounting for 30% of methylation rate variation ([Korthals and Winfrey, 1987](#)). Demethylation was also

measured in incubations and displayed slightly different seasonal variation; it increased sharply from 1% in May to 4% in early July, then fell sharply to 1% in late July, staying low for the rest of the sampling year. As a result, the methylation:demethylation ratio (a predictor of MeHg concentrations in water) rose above 1 in late July through August, and then again in late September ([Korthals and Winfrey, 1987](#)). Timing of methylation and demethylation peaks were similar in sediments sampled from a lake depth of 1.0 m, although gross methylation and demethylation rates were slightly higher ([Korthals and Winfrey, 1987](#)). Sampling across the ELA in Ontario suggests that seasonal patterns of methylation in lakes are due to seasonal shifts in oxygen availability, as locations and depths within the lake where methylation was documented in the summer had no methylation potential when resampled in the fall following turnover ([Eckley and Hintelmann, 2006](#)).

Fall mixing of stratified lakes can have significant effects on total MeHg in lake food chains. In all years of sampling at Onondaga Lake, NY, there was a significant peak in MeHg concentrations and in MeHg:total Hg ratios in the epilimnion in the fall following turnover ([Todorova et al., 2014](#)). In Little Rock Lake, WI, researchers inferred that considerable demethylation occurred in the fall following mixing because high MeHg in the summer water column did not accumulate in sediments and was not reflected in low spring MeHg water column concentrations ([Watras et al., 2006](#)). Short weather events can also affect Hg exchange. During the fall of 2006, regular weekly sampling in Onondaga Lake, NY, captured the effects of strong winds and heavy rains mixing the stratified layers of the lake upon MeHg dynamics. Dissolved oxygen values dropped in the sampled surface waters, and MeHg concentrations rose 23% to 0.236 ng/L in surface waters, even as MeHg concentrations dropped in the hypolimnion ([Todorova et al., 2014](#)).

There are seasonal patterns of Hg methylation in wetlands as well. In peatlands of Allequash Creek Watershed, WI, MeHg concentrations and MeHg fraction (percentage of total Hg) peak in early fall ([Creswell et al., 2008](#)). In the Adirondack Mountains, NY, sampling at the inlet stream of Arbutus Lake showed a pulse of MeHg entering the lake in summer months from the upstream wetlands ([Gerson and Driscoll, 2016](#)). Sampling of the streams in the lake watershed showed no seasonal patterns of MeHg in streams draining forest; but in streams draining wetlands, MeHg increased 300% during the growing season compared to winter MeHg concentrations ([Selvendiran et al., 2008a](#)). In freshwater marshes in the Yolo Bypass, CA, seasonal wetland export of MeHg occurs during the winter as well as the summer. In the summer, newly methylated MeHg is drawn into the root zone of the sediment by plant transpiration, and in winter, diffusion releases MeHg from the sediment into the water column ([Bachand et al., 2014](#)). Seasonal changes have also been documented in the salt and freshwater marshes at Kirkpatrick

Marsh on the Chesapeake Bay, MD, with higher MeHg concentrations and higher methylation rates in summer than in fall ([Mitchell and Gilmour, 2008](#)), and temperature effects have been experimentally demonstrated in Georgia coastal marshes, where the methylation rate was 2 times higher at 25°C than at 4°C, and was 30 times higher at 35°C than at 4°C ([King et al., 1999](#)). Seasonal patterns are even observed in the Florida Everglades, where December potential methylation rates were lower than March or July rates, although water temperatures at midday in December were 18°C ([Gilmour et al., 1998](#)).

In addition to affecting Hg methylation rates, seasonal changes in hydrology can alter fluxes of Hg in watersheds. In the Marcell Experimental Forest, MN, water flow during snowmelt over 2 weeks in spring is 30 or 41% of total annual discharge from two wetland catchments ([Mitchell et al., 2008c](#)), and 26 or 39% of total annual Hg export from the catchment occurred during that time. The majority of MeHg within the catchments (79 or 95% of total catchment MeHg) was in the wetlands and exported in high amounts during snowmelt, about 22–23% of annual MeHg export from the catchments ([Mitchell et al., 2008c](#)). In the Adirondacks, there were increases in stream MeHg concentrations and %MeHg in summer months, when stream discharge was low and water residence time was long in the wetlands where methylators were active ([Gerson and Driscoll, 2016](#); [Selvendiran et al., 2008a](#)). High flow events can be important for transporting MeHg through ecosystems but do not necessarily cause methylation of mercury in aquatic ecosystems.

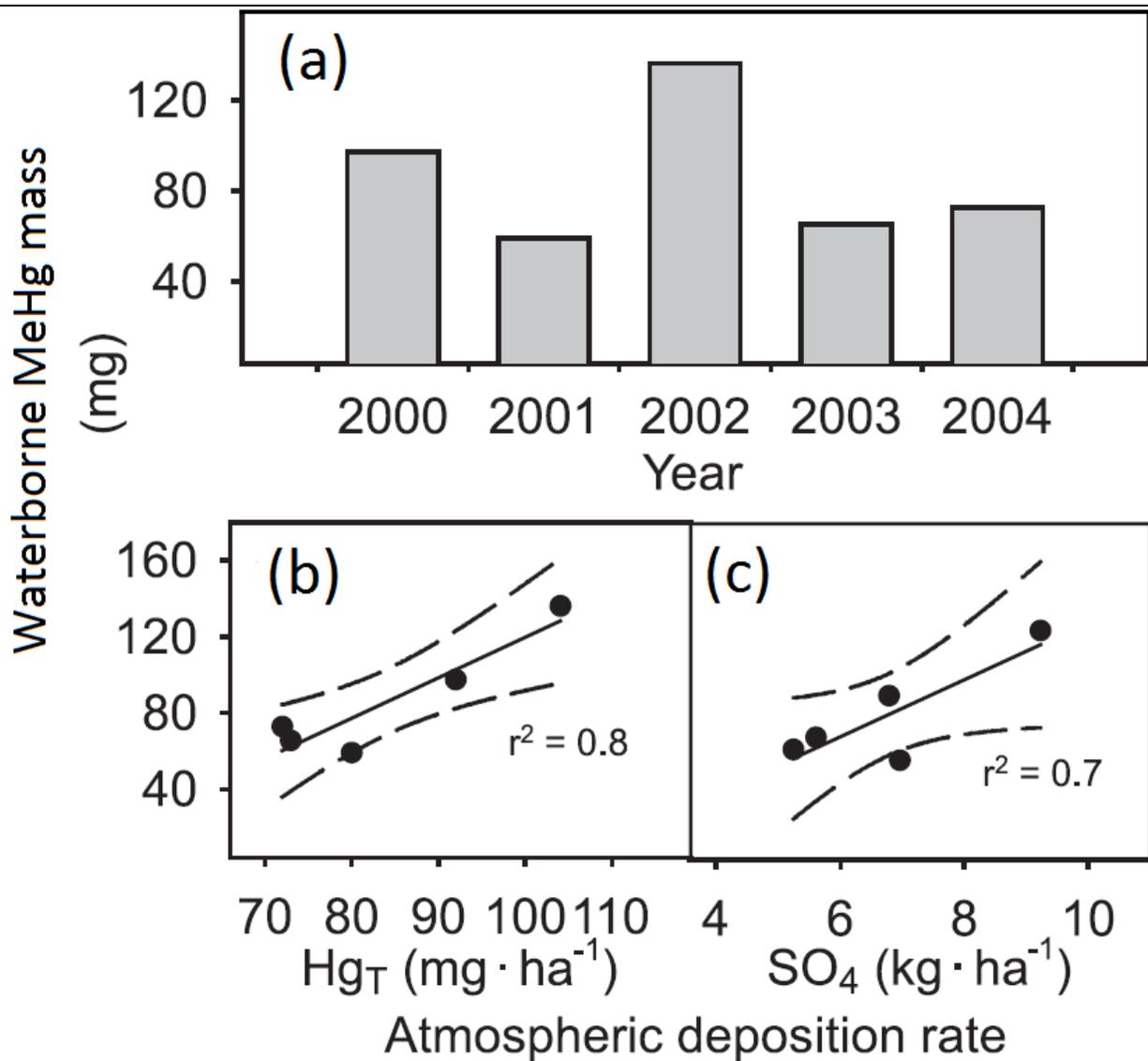
#### **12.3.3.3.1 Climate Modification of S Effects on Ecosystems**

Climate factors that will modify ecosystem response to S include changes in temperature and intensification of hydrologic cycling ([Paranjape and Hall, 2017](#)). Recent evidence from experiments in lakes and bogs allows evaluation of how climate change will affect the relationship between SO<sub>x</sub> deposition and MeHg production. Climate change will affect aquatic and wetland ecosystems via warming temperatures and increasing fluctuations in water tables due to changes in the timing and magnitude of precipitation ([IPCC, 2013](#)). Generally, microbial activity increases with temperature. It is biologically plausible that warming could increase MeHg via stimulation of both the decomposer guilds of microbes producing DOC and of SRPs actively methylating Hg; however, it is also plausible that warming will increase the activity of microbes that demethylate MeHg. [IPCC \(2013\)](#) projected that heavy precipitation events will increase in number and strength due to climate change, which can lead to rapid changes in water table level in wetlands and lakes. These changes in water level can move pulses of labile carbon and sulfate into the anoxic zones of the water, sediment, and periphyton where SRPs are

active, and flooding or rewetting of previously dry zones can create new environments favorable for SRPs. The following studies suggest that drought and warming increase S cycling and Hg cycling. Drought, but not warming, increases MeHg production in lakes and wetlands.

As reviewed in the 2008 ISA, recovery in Little Rock Lake, WI, has been monitored because the lake was experimentally acidified for 5 years (1984–1989). Drought affected sulfate and MeHg concentrations in the lake, which is rain-fed. During the drought years of 1998–2006, MeHg increased 0.004 ng/L/yr, although high variation among samples made this trend marginally significant [ $p = 0.06$  ([Watras and Morrison, 2008](#))]. MeHg increased from 0.04 ng/L in 1997 to 0.07 ng/L in 2006, a 75% increase, which is more than can be attributed to evapoconcentration from the lake's 30% decrease in volume ([Watras and Morrison, 2008](#)). During this time period, there were no significant changes in total Hg deposition; although between 1988 and 2006, the total Hg concentration in Little Rock Lake has declined 0.04 ng/L/yr ([Watras and Morrison, 2008](#)). During the drought, between 2000 and 2004, total MeHg mass in the north basin of the lake was positively correlated with higher Hg and S deposition in precipitation ([Figure 12-9](#)).

Wetlands are characterized by fluctuating water tables, and microbial communities in wetlands are adapted to respond rapidly to changes in substrate and oxygen availability. This is particularly true for SRPs, which methylate Hg in geographic and temporal pulses, resulting in hotspots of high MeHg concentrations within wetlands where Hg is actively methylated ([Appendix 12.8](#)). Fluctuations in water tables caused by periods of drought and periods of flooding can create pulses of SRP activity and hotspots of Hg methylation, raising MeHg concentrations in the environment. The following studies present evidence that climate change (through drought and warming) will interact with S addition to change MeHg and Hg dynamics in wetlands.



ha = hectare;  $Hg_T$  = total mercury deposition  $kg =$  kilogram; MeHg = methylmercury; mg = milligram;  $SO_4^{2-}$  = sulfate.  
 Source: adapted from [Watras and Morrison \(2008\)](#).

**Figure 12-9** Total methylmercury mass in water at Little Rock Lake, WI, annually (a), and in relationship to annual mercury (b) or sulfur (c) deposition.

Drought and rewetting increased MeHg in Bog Lake Fen, and S addition treatments enhanced this effect. A 9-month drought from the summer of 2006 to the spring of 2007 resulted in a pulse of reduced S when the water levels rose again, and the sulfate concentrations were 147% higher in the S addition treatment, and 78% higher in the recovery treatment, than in the control wetland ([Wasik et al., 2015](#)). Sulfate pulses

resulted in proportional increases in Hg methylation, with peak MeHg fraction 150% higher in the S addition and 60% higher in the recovery treatment ([Wasik et al., 2015](#)). The peat experienced drought conditions in summer 2007 as well, and pulses of sulfate in the experimental treatments that fall (165% higher in S addition, 14% higher in recovery wetland than in control wetlands) resulted in higher peak MeHg fractions in fall and the following spring in both the S addition and recovery treatments. Experimental manipulation of water levels in the different wetland treatments showed that higher water levels raised sulfate, total Hg, and MeHg in S addition wetlands, but did not affect these parameters in control and recovery wetlands ([Wasik et al., 2015](#)). In the recovery treatment, S and MeHg pulses were higher than in control plots, indicating persistent effects of S addition several years after addition ceased. However, because experimentally raising water levels did not alter S or Hg chemistry in control or recovery wetlands, the recovery wetland was returning to S and Hg processes more similar to the control plots.

Warming may ameliorate the effect of S upon MeHg production in wetlands, but experimental evidence suggests that it will also increase sulfate and MeHg export from peatlands into downstream aquatic ecosystems. Degerö Stormyr in Sweden is the site of a wetland experiment that addresses the effects of S and N deposition as well as warming due to climate change. Warming altered the S and Hg dynamics under S deposition at Degerö Stormyr. Total Hg (per mass of peat) was 19% lower in 20 kg S/ha/yr + warming plots than in S only plots, indicating increased mobilization or volatilization of Hg from the peat. The Hg methylation constant in S + warming was similar to the rate in unamended control plots, much lower than the rate in S only plots ([Akerblom et al., 2013](#)). MeHg concentrations in the S and warming treatment were lower than in any other treatment, 73% lower in the 20 kg S/ha/yr + warming treatment than in the 20 kg S/ha/yr treatment, and 54% lower than in the control treatment ([Akerblom et al., 2013](#)). This last result suggests that the combination of warming and S addition increases MeHg mobility beyond current ambient rates. Given the decreases in both total Hg and MeHg, it appears that all forms of Hg were mobilized and either exported or volatilized by the warming + S addition treatment, despite decreases in Hg methylation rate.

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#### **12.3.3.4 pH and Methylation Potential**

The 2008 ISA described the state of knowledge current at the time that lower pH waters had higher MeHg production. This relationship was assumed to be causal. However, the laboratory body of evidence suggests that if all other factors are held equal, methylation is highest at near neutral pH and drops with increasing acidity. The apparent discrepancy

is due to the fact that SO<sub>x</sub> deposition causes both elevated sulfate concentrations and acidification in aquatic ecosystems.

Studies from the early 1980s assumed that acidification, not sulfate concentration, was the causal factor in observed increases of MeHg in water and increased Hg burdens in fish in response to SO<sub>x</sub> deposition. For example, samples from circumneutral lakes at the ELA in Ontario that were experimentally acidified with H<sub>2</sub>SO<sub>4</sub> had increased methylation and decreased demethylation, so that methylation:demethylation rates were 2.9 to 4 times higher at pH 5.1 than at pH 7.1 ([Xun et al., 1987](#); [Ramial et al., 1985](#)).

Recent research on the role of S reducing bacteria in methylating Hg ([Appendix 12.3.2](#)) suggests reinterpretation of an acid pH-MeHg relationship. Controlled laboratory experiments showed that it was the added sulfate, not pH, that increased Hg methylation rates in these lakes. Slurries with sediments from Lake Clara, WI, were made with added H<sub>2</sub>SO<sub>4</sub> or a molar equivalent amount of sulfate as Na<sub>2</sub>SO<sub>4</sub>. Acidification from neutral slurries to pH 4.5 with H<sub>2</sub>SO<sub>4</sub> decreased methylation by 65%, while an equivalent addition of Na<sub>2</sub>SO<sub>4</sub> did not alter methylation rates; acidification to pH 3.0 almost entirely inhibited methylation ([Steffan et al., 1988](#)). This study also measured demethylation over a range of pH 2.0–8.0. The results showed that demethylation was higher than 2% from pH 4.4–8, while methylation rose above 2% from pH 6.0–8.0, and both processes slowed with decreasing pH ([Steffan et al., 1988](#)). The 2008 ISA correctly identified the correlation between acidic surface water and high rates of MeHg, but the two factors share a common cause, which is increased surface water sulfate concentrations, rather than a direct causal relationship. In the Adirondacks, which have historically experienced high S deposition (see [Appendix 16.2](#)), surface water total Hg, MeHg, and %MeHg were unrelated to pH when all variables were measured across 44 lakes in 2003–2004 ([Yu et al., 2011](#)). However, there were effects of pH on Hg in biota (see [Appendix 12.4](#)). In regions like the Adirondacks, which historically received high S deposition and have not fully recovered from this historical acidification, pH remains an important predictor of Hg in biota.

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### 12.3.3.5 Organic Matter and Methylation Potential

Organic matter is the metabolic substrate of all the microbial methylators, including both the group of organisms responsive to sulfate and the microbial methylators that depend on other metabolic pathways. Organic matter in environments where carbon affects mercury cycling may be quantified as soil organic matter (SOM; as percentage of soil or in g OM/g sediment); total organic carbon (TOC, g carbon/mL pore or surface water) or its components; particulate organic carbon (POC, g C/mL water); and dissolved organic

carbon (DOC, g C/mL water). The 2008 ISA described some of the complex qualitative relationships (stimulatory and/or inhibitory) between DOC and rates of Hg methylation. Organic matter influences the mercury cycle in a number of important ways. Organic matter affects MeHg production through effects on inorganic Hg ion chemistry and availability to microbes, and by serving as a metabolic substrate for SRPs. New studies from lakes, rivers, wetlands, and estuaries have found positive relationships between a range of lower DOC concentrations and MeHg production or concentrations. However, the chemical form of DOC or the salinity of the water body can alter DOC and MeHg relationships.

Certain forms of DOC may serve as a metabolic substrate that increases SRP activity, and by extension, Hg methylation. In wetlands in the Arbutus Lake Watershed, NY, there were strong correlations ( $r^2 = 0.58$  or  $0.60$ ) between Hg and total carbon in the upper 30 cm of peat ([Selvendiran et al., 2008b](#)). In northern Wisconsin lakes, the quantity of DOC derived from wetlands is the strongest (>80% variance) predictor of MeHg ([Watras et al., 2006](#)). In Canadian boreal lakes, there was a positive relationship between methylation rates and DOC ( $r^2 = 0.62$ ). In Little Rock Lake, WI, DOC and S reduction had a complex relationship: in the range of 3.6–7.6 mg C/L (reported as 300–600  $\mu\text{mol/L}$ ), sulfide (a proxy for S reduction) increased linearly with DOC concentration, while S reduction did not occur at DOC less than 3.6 mg C/L, and S reduction did not increase at DOC concentrations above 7.6 mg C/L ([Watras et al., 2006](#)).

In Lake Geneva, Switzerland, mercury methylation rates were an order of magnitude higher in settling particles than in sediments, and analysis of the particles suggested that they were derived from algal biomass ([Gascón Díez et al., 2016](#)).

Sediment organic matter may also increase microbial Hg methylation. At another watershed in the Adirondacks, Sunday Lake, NY, the highest MeHg concentrations were in samples that were more than 20% organic material ([Yu et al., 2010](#)). In prairie potholes in Saskatchewan, surface water [MeHg] increased in a linear relationship with the sediment percentage of organic matter (OM), with a 2.65 ng/L increase in MeHg for every 10% increase in the percentage of OM ([Hoggarth et al., 2015](#)).

In wetlands, rivers, and lakes of the Mississippi River Delta, LA, total Hg dissolved in surface water was positively correlated with DOC concentrations, but negatively correlated with sulfate concentrations. However, this correlation is confounded by ecosystem salinity, because mean sulfate concentrations in surface water were 16 mg/L in freshwater wetlands, 63 mg/L in brackish wetlands, and 909 mg/L in marine wetlands ([Hall et al., 2008](#)). Also, dissolved MeHg in surface water increased linearly with the hydrophobic organic acid fraction of DOC, with dissolved MeHg increasing 1 ng/L (0.000001 mg/L) for each increase of 0.048 mg organic acid/L ([Hall et al., 2008](#)). The

hydrophobic organic acid fraction represents a recalcitrant source of aromatic carbon such as that found in peat, which would account for the high amounts of MeHg in these wetlands. The hydrophobic organic acid fraction of terrestrially derived C also controls Hg export (see paragraph below). Another recent study used controlled incubations of an SRP strain, varying concentrations of Hg, and two well-characterized forms of DOC to quantify the effects of DOC on methylation. DOC typical of terrestrial sources (high aromatic fraction, high molecular weights) increased MeHg production 10–40 times above unamended controls, while aquatic DOC (high aliphatic fraction, low molecular weights) doubled MeHg production ([Graham et al., 2012](#)). The authors hypothesize that DOC increases MeHg production by slowing the growth of Hg-S particles, increasing Hg-S residence time in the water, and enhancing Hg bioavailability ([Graham et al., 2012](#)). The stronger effects of terrestrial DOC on MeHg may explain why MeHg production is particularly high in wetlands, recently flooded reservoirs, and periodically flooded river plains ([Benoit et al., 2003](#)). In estuarine and marine sediments of the Chesapeake Bay, MD, organic C in the sediments had a strong positive correlation ( $r = 0.96$ ) with sediment MeHg concentrations ([Hollweg et al., 2010](#)). In coastal marshes of the Chesapeake such as Kirkpatrick Marsh, MD, there was also a statistically significant positive relationship ( $r^2 = 0.478$ ) between Hg methylation rate and mineralization of organic C, a metric of cellular metabolism within the sediment ([Mitchell and Gilmour, 2008](#)).

Organic matter in surface water can increase the amount of Hg transported throughout a watershed, as well as MeHg production at the watershed scale. DOC can form complexes with Hg ions that facilitate their transport. In lakes and rivers of the St. Louis River, DOC and dissolved Hg were correlated ( $r^2=0.69$ ), as were aromatic DOC and dissolved Hg ( $r^2 = 0.70$ ), indicating that aromatic DOC transports Hg through aquatic ecosystems in this watershed ([Jeremiason et al., 2016](#)). In riparian forest soils in Oak Ridge, TN, flooding resulted in a pulse of both aromatic DOC and MeHg in the soil solution ([Poulin et al., 2016](#)). In the Arbutus Lake watershed in the Adirondack Mountains, NY, the fluxes of Hg and DOC in streams were correlated ( $r^2 = 0.80$ ) across seasons, and the highest fluxes were in June and July ([Selvendiran et al., 2008a](#)). In a study of five watersheds across the U.S., MeHg concentrations in catchment outflows correlated positively with particulate organic matter (POC) in Sleepers River, VT ( $r^2 = 0.93$ ), and in Rio Icacos, Puerto Rico [ $r^2 = 0.83$  ([Shanley et al., 2008](#))]. In three Northeast watersheds, stream export of dissolved Hg correlated positively with DOC, with 0.34 ng Hg/L increase for each 1 mg C/L increase ( $r^2 = 0.87$ ), and hydrophobic organic acid fraction of DOC explained 91% of variation in dissolved Hg ([Dittman et al., 2010](#)). Storm events, which increased water flow through surface soil layers and stream discharger, also increased the export of organic matter and associated Hg ([Dittman et al., 2010](#)). Thus, the evidence

indicates that the amount and form of organic matter will affect Hg transport in watersheds.

DOC affects the partitioning of inorganic Hg between sediment and water, and hence the bioavailability of inorganic Hg to methylating organisms ([Hsu-Kim et al., 2013](#); [Marvin-Dipasquale et al., 2009](#); [Benoit et al., 2003](#)). In Kirkpatrick Marsh on the Chesapeake Bay, MD, linear relationships between methylation rates and absorbance values indicated that Hg methylation rates were higher when the DOC was composed of high molecular weight, aromatic organic compounds ([Mitchell and Gilmour, 2008](#)). There were no correlations between DOC characterization and measures of microbial activity, so the authors suggested that the form of DOC (size and aromaticity of compounds) controls Hg bioavailability rather than serving as a metabolic substrate powering MeHg production ([Mitchell and Gilmour, 2008](#)). However, the relationship between DOC and Hg partitioning is complex [reviewed in [Hsu-Kim et al. \(2013\)](#)], and in an extensive survey of the Alabama River basin around Mobile, AL, there was no relationship across 52 sampling sites between DOC and Hg fractions [total, aqueous, particulate ([Warner et al., 2005](#))].

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### 12.3.3.6 Iron and Methylation Potential

The 2008 ISA briefly identified iron (Fe) as a surface water component that can alter the relationship between SO<sub>x</sub> deposition and MeHg production (as it also interacts with sulfide phytotoxicity and internal eutrophication, see [Appendix 12.2.3](#) and [Appendix 12.2.4](#)). Iron can alter the rates of Hg methylation via abiotic and biotic mechanisms. Iron binds with sulfide produced by SRPs during methylation to precipitate out of solution ([Hellal et al., 2015](#)), preventing the negative feedback of sulfide on sulfate reduction. Iron oxides form surface complexes with inorganic Hg that decrease Hg bioavailability. However, sulfide released by SRPs can react with Fe-Hg complexes to release Hg into the water column ([Hellal et al., 2015](#)). Iron can increase methylation rates directly, by stimulating the activity of iron-reducing bacteria capable of Hg methylation, including *Geobacter* spp. In laboratory incubations mimicking freshwater sediments, iron reduction and sulfate reduction co-occurred in time but at different zones in the sediment ([Hellal et al., 2015](#)). Iron and S reduction also co-occurred in wetlands of the Yolo Bypass, CA (see [Appendix 12.3.4.3](#)).

In Kirkpatrick Marsh on the Chesapeake Bay, MD, there was a positive relationship ( $r^2 = 0.478$ ) between Hg methylation rate and mineralization of organic C and an equally strong positive relationship between Hg methylation rate and the pool of Fe<sup>2+</sup> [ $r^2 = 0.478$  ([Mitchell and Gilmour, 2008](#))]. Although Fe precipitation with Hg-S has been posited as

one of the mechanisms by which Hg is buried in sediments, there was no relationship between iron concentration and partitioning of Hg between water and soil.

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### 12.3.3.7 Nitrate and Methylation Potential

The 2008 ISA did not address the effect of nitrate upon MeHg production. Nitrate ions are energetically favored over sulfate in redox reactions, so N addition can depress Hg methylation by shifting the energetic advantage from SRPs to denitrifiers ([Dev et al., 2015](#)). In Florida Everglades sediment incubations, addition of 1.4 mg N/L as  $\text{NO}_3^-$  to incubations decreased MeHg production by 70% ([Gilmour et al., 1998](#)). In Onondaga Lake, NY, the Syracuse water treatment plant incorporated year-round nitrification in 2004, doubling the nitrate concentrations measured annually in May before the lake stratified ([Todorova et al., 2009](#)). MeHg concentrations decreased exponentially with increasing  $\text{NO}_3^-$  concentrations (estimated pseudo- $r^2 = 0.61$ ) in the 2–3 years following the change in water treatment. This change in N load reduced MeHg accumulation in the hypolimnion by 50% in 2006, and by 93% in 2007 compared to MeHg measured earlier, in 1982, 1992, and 2002 ([Todorova et al., 2009](#)). In summer 2011, a calcium nitrate solution was pumped directly into the hypolimnion of Onondaga Lake thrice weekly, adding 84 MT of N over the course of the season ([Matthews et al., 2013](#)). As a result, hypolimnion N- $\text{NO}_3^-$  remained above 1.0 mg/L during summer stratification, and hypolimnion maximum MeHg concentration decreased 94% compared to 2009. ([Matthews et al., 2013](#)) attributed this to two effects of N: a shift in competitive advantage from SRP to denitrifying bacteria, and increased sorption of MeHg to lake sediments.

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### 12.3.3.8 Salinity and Methylation Potential

Mercury methylation occurs in estuarine and marine ecosystems ([Lehnherr et al., 2011](#); [Benoit et al., 1998](#)), but sulfate concentrations in saline water are generally so high that direct deposition of  $\text{SO}_x$  is unlikely to alter existing MeHg dynamics. An early study on coastal marshes in Georgia showed that both sulfate reduction and MeHg production were at their highest rates in the top 4 cm of the marsh soil ([King et al., 1999](#)). An older study of Hg dynamics in the Patuxent River Estuary, MD, where sulfate concentrations range from 150 to 1,200 mg/L, found no correlation between sediment pore water sulfate concentrations and MeHg fraction in sediments ([Benoit et al., 1998](#)). There was a peak in surface water MeHg fraction of 25% at the mouth of the river, which authors speculated was due to mixing by wind of stratified anoxic water from the Chesapeake Bay with the river water ([Benoit et al., 1998](#)). MeHg sediment fraction across the Patuxent River, MD,

was negatively correlated with sulfide sediment concentrations, presumably because Hg bound to sulfide is unavailable to methylating bacteria ([Benoit et al., 1998](#)).

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## 12.3.4 Mercury Methylation in Sulfur Addition Field Studies

There are a number of ecosystems in which sulfate is elevated by anthropogenic activities. Scientists have added sulfate to ecosystems in order to study S and Hg cycling (see [Appendix 12.3.4.1](#)). S is used as an agricultural amendment in peat soils, and so Hg cycling has been extensively studied in the Everglades Water Conservation Area (see [Appendix 12.3.4.2](#)) and the San Joaquin Delta (see [Appendix 12.3.4.3](#)).

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### 12.3.4.1 Ecosystem Scale and Field Mesocosm Studies

The 2008 ISA found that experimental S addition to aquatic and wetland ecosystems increased MeHg concentrations in surface water (and Hg concentrations in biota, see [Appendix 12.4](#)). Key studies supporting this finding focused on the long-term S acidification (1984–1989) and recovery (1990–present) experiment at Little Rock Lake, WI and the relatively recent (initiated in 2001) experimental S addition experiment at Bog Lake Fen in the Marcell Experimental Forest, MN. This section integrates older published reports and recent papers from S addition experiments that presented quantitative relationships between S addition and Hg mobilization, methylation, and MeHg concentrations in surface water. There is new evidence from the S addition experiment at Bog Lake Fen and from an S addition by warming experiment in a Swedish bog that confirms the relationship reported in the 2008 ISA between increased S loading and environmental increases in MeHg. There is also new evidence that decreases in S addition allow recovery of MeHg toward control conditions, as well as new evidence that climate change (drought, warming) will increase S cycling and increase MeHg concentrations ([Table 12-7](#)).

As reported in the 2008 ISA, experimental S addition increases MeHg production in lake ecosystems, and cessation of S addition results in reductions in MeHg production in lakes. Little Rock Lake, WI was an S addition experiment that ran from 1985–1991. In this experiment, the north and south basins of the lake were artificially isolated by a plastic barrier, and then annual S additions were used to acidify the northern basin, while the unamended south basin served as a control. In 1993, after S addition had ceased but sulfate concentrations in the north treatment basin (4.8 mg/L or 50  $\mu$ M) were still twice that of the reference basin (2.4 mg/L or 25  $\mu$ M), the potential methylation rate was 220% higher in the treatment basin ([Gilmour and Riedel, 1995](#)). In June 1993, when MeHg

fractions were at their highest, the MeHg fraction of total Hg was 30% higher in the treatment basin ([Gilmour and Riedel, 1995](#)). Mercury and S cycling were monitored in the lake through 2003, and elevated sulfate concentrations and acidification persisted in the lake through 1996; the lake was considered recovered from 1998–2003. During acidified years, 25% more of annual Hg<sup>2+</sup> inputs were transformed into water column MeHg than in recovery years ([Watras et al., 2006](#)). Net methylation during the summer was 70% higher in acidified than in recovery years, and summertime MeHg accumulation was 75% higher in the whole lake in acidified years ([Watras et al., 2006](#)). There was a strong positive correlation between summer MeHg accumulation (1990–2003) and the interaction of epilimnion sulfate concentration and epilimnion Hg<sup>2+</sup> concentration. The hypolimnion or the anoxic-oxic boundary were likely the sites of Hg methylation, because the hypolimnion, which was less than 5% of the lake volume, accumulated more than 70% of the total MeHg mass of the lake in acidified years ([Watras et al., 2006](#)). Hypolimnion MeHg was associated with hypolimnion S reduction, as there was a 10.8 ng MeHg/L (0.0000108 mg MeHg/L) increase for each 1 mg/L increase in hydrogen sulfide (H<sub>2</sub>S; reported as 1.71 pmol/L increase in MeHg for each 1 μmol/L increase in H<sub>2</sub>S;  $r^2 = 0.65$ ). Total MeHg in Little Rock Lake, WI increased 14.4 mg for every 1 kg/ha increase in sulfate deposition ([Watras and Morrison, 2008](#)).

**Table 12-7 New studies on mercury methylation in sulfur-amended ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Peat fen	Ambient S deposition: 3 kg S/ha/yr S addition: low S (7 kg S/ha/yr added for total load of 10 kg S/ha/yr) or high S (17 kg S/ha/yr added for total load of 20 kg S/ha/yr) as Na <sub>2</sub> SO <sub>4</sub> , with 0 or 30 kg N/ha/yr as NH <sub>4</sub> NO <sub>3</sub>	At 30-cm depth, total Hg (per peat mass) in warming + high S was 19% lower than in high S plots. <hr/> Low S decreased total Hg in peat methylation hotspots by 25 or 31% on a per-mass or per-volume basis. <hr/> The Hg methylation rate constant increased by 71% in low S and by 400% in high S. <hr/> Peat MeHg concentrations decreased by 22% in low S and increased by 74% in high S.	Degerö Stormyr, Sweden (64° 09' N, 20° 22' E), measured in 2007 and 2008	Peat samples	<a href="#">Akerblom et al. (2013)</a>

**Table 12-7 (Continued): New studies on mercury methylation in sulfur-amended ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Peat fen	Ambient S deposition: 3 kg S/ha/yr S addition: high S (17 kg S/ha/yr added for total load of 20 kg S/ha/yr)	S addition increased pore water MeHg concentrations by 117%. S addition increased the range of MeHg concentrations by 4.3x, and the variance by 22.2x the control variance. <hr/> With S addition, MeHg increased with higher groundwater levels, although there was no relationship in ambient plots. <hr/> Total Hg in the top 5 cm of peat increased by 133% with S addition.	Degerö Stormyr, Sweden (64° 11' N, 19° 33' E), measured in 1999	Pore water in peat	<a href="#">Bergman et al. (2012)</a>

**Table 12-7 (Continued): New studies on mercury methylation in sulfur-amended ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Peatland (poor fen)	<p>Experimental treatment, addition of 32 kg/ha/yr in three simulated rainfall events, 2001–2008</p> <p>Recovery treatment, 32 kg/ha/yr 2001–2006, no added S 2006–2008</p> <p>Deposition = 5.5 kg S/ha/yr (NADP site MN16)</p> <p>Mesocosms installed in ambient, added S, and recovery zones of marsh, pulse of 130 mg Na<sub>2</sub>SO<sub>4</sub> added</p>	<p>In spring 2005, S addition increased %MeHg 387% over control wetland. In fall 2005, S addition increased %MeHg 275%.</p> <p>Following a 9-mo drought, spring 2007 rewetting released internally stored S, the pulse of SO<sub>4</sub><sup>2-</sup> was 78% higher in recovery and 147% higher in experimental than in control wetlands.</p> <p>Following a 9-mo drought and rewetting in spring 2007, peak [MeHg] was 75% higher in recovery and 120% in experimental wetland. Peak %MeHg was 60% higher in recovery and 150% in experimental wetland.</p> <p>Following summer-long drought and rewetting in fall 2007, [SO<sub>4</sub><sup>2-</sup>] was 14% higher in recovery and 165% higher in experimental wetland.</p> <p>Following summer-long drought, the fall 2007 peak [MeHg] was 102% higher in recovery and 301% higher in the experimental wetland. Peak %MeHg was 150% higher in recovery and 350% higher in the experimental wetland.</p> <p>Following summer-long drought, the spring 2008 peak [MeHg] was 62% higher in recovery and 133% higher in the experimental wetland. Peak %MeHg was 146% higher in recovery and 262% higher in the experimental wetland.</p> <p>Experimental water level rise in mesocosms does not affect chemical constituents in control and recovery wetlands, but increased total Hg, SO<sub>4</sub><sup>2-</sup>, MeHg, and %MeHg in the experimental wetland. DOC decreases in the experimental wetland mesocosm.</p>	S6 peatland in Marcell Experimental Forest, MN	<i>Sphagnum</i> spp., herbaceous forbs, ericaceous shrubs, spruce, and tamarack	<a href="#">Wasik et al. (2015)</a>

**Table 12-7 (Continued): New studies on mercury methylation in sulfur-amended ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Bog	Ambient S load: 2.07 kg S/ha/yr as quantified by NADP  S addition: 8.28 kg S/ha/yr (low), or 20.7 kg S/ha/yr (high) as SO <sub>4</sub> <sup>2-</sup> solution	S addition increased pore water MeHg concentrations 219–246%.  High S increased MeHg fraction (MeHg/total Hg) by 117%.  Labile organic C and S additions increased methylation rates (pg MeHg/L/day) by 163% and rates of increasing MeHg fraction (%MeHg/day) by 152% over rates for S-only addition.	Bog Lake Fen, Marcell Experimental Forest, MN	Peat pore water	<a href="#">Mitchell et al. (2008a)</a>
Bog	Ambient S deposition: 5.5 kg/ha/yr (mid 2000s) as quantified by NADP site MN16  S addition: 32 kg S/ha/yr dissolved in pond water and delivered by sprinklers (mimics 4x the 1990s deposition rate)	In pore water, MeHg (ng/L) was increased by 8.8–17.9x the control levels in 2006 and 3.4–11.7x the control levels in 2008. MeHg fraction (MeHg/total Hg) was increased 6.1–13.4x in 2006 and 3.9–11.6x in 2008.  In solid peat, MeHg concentrations and MeHg fraction were 4–9x higher than in controls or 5–6x higher when accounting for annual variability.  3 yr after SO <sub>4</sub> <sup>2-</sup> treatment cessation (recovery treatment), pore water MeHg declined 32%, peat MeHg declined (ng/L) by 62%, and peat MeHg fraction (%) declined 76%.	S6 peatland, bog section, Marcell Experimental Forest, MN	Pore water, peat, and <i>Culex</i> spp. (mosquito) larvae	<a href="#">Wasik et al. (2012)</a>

**Table 12-7 (Continued): New studies on mercury methylation in sulfur-amended ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Lakes: rain-fed LRL, DL drains stream fed by wetland	LRL: [SO <sub>4</sub> <sup>2-</sup> ] = 2.5 mg/L, DL: [SO <sub>4</sub> <sup>2-</sup> ] = 2.8 mg/L, stream feeding DL [SO <sub>4</sub> <sup>2-</sup> ] = 1.6 mg/L S deposition not reported	In LRL during drought years, lake SO <sub>4</sub> <sup>2-</sup> concentrations increased 0.18 mg/L/yr, as MeHg concentrations increased 0.004 ng/L/yr. In stratified basin of LRL, total MeHg increased with increasing S deposition: mg MeHg = 14.368 × (kg S/ha) – 18.494. In stream draining wetland, SO <sub>4</sub> <sup>2-</sup> decreased 80% as MeHg increased 69% over the course of spring and summer.	Little Rock Lake (LRL) and Devils Lake (DL), WI	Lake water	<a href="#">Watras and Morrison (2008)</a>

C = carbon; cm = centimeter; DL = Devils Lake; Ha = hectare; Hg = mercury; kg = kilogram; L = liter; LRL = Little Rock Lake; MeHg = methylmercury; mg = milligram; Na<sub>2</sub>SO<sub>4</sub> = sodium sulfate; NADP = National Atmospheric Deposition Program; ng = nanogram; NH<sub>4</sub>NO<sub>3</sub> = ammonium nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

DL = Devils Lake; ha = hectare; kg = kilogram; L = liter; LRL = Little Rock Lake; LTER = Long Term Ecological Research; MeHg = methylmercury; mg = milligram; ng = nanogram; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Experimental S addition substantially increases MeHg in wetlands. The ELA in Ontario has been the subject of considerable research in Hg cycling (see [Appendix 12.8](#)). An early experiment added pulses of sulfate to peat inside collars installed in a poor fen and monitored changes in MeHg concentrations over 4 days. In one experiment, addition of 14 kg sulfate/ha increased MeHg pore water concentrations (ng/L) at the water table surface 30% above the highest measured MeHg concentrations in the control plot, with a 100% increase in MeHg above control plot concentrations at a 10-cm depth in the water table ([Branfireun et al., 1999](#)). Following a second 14 kg sulfate/ha addition, MeHg at 5-cm depth in the peat water table increased to 130% above maximum MeHg in the control plot. Four days after the first S addition, MeHg at the 5-cm depth remained elevated at 250% above maximum measured MeHg in control plots ([Branfireun et al., 1999](#)). In an experiment the following year, one sulfate addition equivalent to 2.8 kg sulfate/ha was added. After 24 hours, this S addition had increased MeHg pore water concentrations at the water table surface 100% above maximum measured MeHg in the control plot, and at the 10-cm depth below the water table, MeHg increased 20%. This MeHg increase did not persist to 48 hours after addition ([Branfireun et al., 1999](#)).

There is new evidence that addition of labile DOC typical of leachate from a forested watershed enhanced the stimulatory effect of S addition upon MeHg concentrations in wetlands. At the Marcell Experimental Forest, MN, field mesocosms were initiated in Bog Lake Fen to test the effects of S and carbon addition on Hg cycling in an ombrotrophic peat bog. Mesocosms received experimentally added loads of 8.3 kg S/ha/yr or 20.7 kg S/ha/yr, alone or in combination with additions of organic

carbon in different forms ([Mitchell et al., 2008a](#)). S addition increased peat pore water concentrations of MeHg 219–246% above MeHg levels in unamended control plots, with no significant difference between net methylation under 8.3 versus 20.7 kg S/ha addition ([Mitchell et al., 2008a](#)). Adding 20.7 kg S/ha/yr to mesocosms increased the fraction of the total Hg pool that took the form of MeHg, with MeHg 117% higher than in control plots ([Mitchell et al., 2008a](#)). The combined addition of sulfate and organic carbon (as glucose, acetate, or leachate from coniferous leaf litter) increased methylation rates (reported in pg MeHg/L/day) by 163% and increased the fraction of MeHg (%MeHg) by 152% over rates measured in mesocosms that received only S addition ([Mitchell et al., 2008a](#)). This study showed that S addition will increase MeHg in surface water in bogs, particularly when combined with labile C inputs. These results coincide with findings presented elsewhere in the ISA that DOC concentrations are increasing in surface waters ([Appendix 7](#)) as terrestrial ecosystems recover from acidification.

A decade of research at Bog Lake Fen in Minnesota shows that additional S increases MeHg production in this wetland, with consequences for water quality and also for resident organisms (see [Appendix 12.4](#)). Bog Lake Fen is the site of a long-term S addition experiment in which entire sections of the *Sphagnum* peat wetland have received additional S loading in simulated wet deposition. As reported in the 2008 ISA, S addition began in 2001 at a rate of 32 kg S/ha/yr, and increased the levels of MeHg in the bog by 40–190% in the first summer and increased the MeHg export from the bog by 144% in 2002 ([Jeremiason et al., 2006](#)). More recent sampling has confirmed the relationship between S addition and elevated MeHg production and concentrations in the wetland. In peat pore water sampled 5 cm below the water table for 2 weeks after S addition events, S addition increased MeHg concentrations by 880–1,790% in 2006 (0.2–0.3 ng MeHg/L in control, 2.9–4.2 ng/L in S addition plots), and increased MeHg concentrations 340–1,170% in 2008 ([Wasik et al., 2012](#)). Pore water MeHg fraction (percentage of total Hg in MeHg form) increased 610–1,340% over control levels in 2006 and 390–1,160% over control levels in 2008 ([Wasik et al., 2012](#)). Researchers also sampled surface peat and found that S addition altered MeHg concentrations in peat. MeHg concentrations (ng/L) and MeHg fraction (percentage of total Hg as MeHg) were 4–9 times higher in S addition plots than in control plots, although there was no effect of S addition on total Hg in plots ([Wasik et al., 2012](#)). The elevated MeHg in water and peat had consequences for the food chain (see [Appendix 12.4](#)).

There is also evidence of a link between S addition and MeHg production from a European wetland experiment. Degerö Stormyr in Sweden is the site of an experiment that addresses the effects of S and N deposition as well as warming due to climate change. Plots received S loads of 10 kg S/ha/yr or 20 kg S/ha/yr, and a subset of plots was enclosed by greenhouses to raise air temperature by about 4°C and peat temperature

(at the 20-cm depth) by about 2°C. Four years after the 1995 initiation of the experiment, [Bergman et al. \(2012\)](#) measured MeHg production in the control and 20-kg-S/ha/yr plots. S addition increased mean growing season peat pore water MeHg concentrations 117% over MeHg concentrations in control plots ([Bergman et al., 2012](#)). There was higher variation in MeHg in S addition plots (20 kg S/ha/yr), as the range of measured concentrations was 4.3 times the range of measured MeHg in control plots ([Bergman et al., 2012](#)). The experiment was resampled 12 years after initiation, and the Hg methylation constant was 71% higher in methylation hotspots (a hotspot was experimentally defined as the point in each sampled peat profile with the highest Hg methylation rate constant) under addition of 10 kg S/ha/yr compared to control plots, while MeHg concentrations were 22% lower than in control hotspots ([Akerblom et al., 2013](#)). These seemingly contradictory results (higher production, lower concentration) may indicate increased mobilization of MeHg from methylation hotspots (see below) or increased microbial demethylation rates, which were not tested. Under higher S addition of 20 kg S/ha/yr, the Hg methylation rate constant was 400% higher than in the control plots, while the MeHg concentrations were 74% higher than in control plots ([Akerblom et al., 2013](#)). Together, these results indicate that in wetlands an S addition of 10 or 20 kg/ha/yr increases microbial MeHg production and that an S addition of 20 kg/ha/yr increases MeHg concentrations.

S addition also increases the mobilization and transport of Hg and MeHg from peat methylation hotspots into the water column, increasing bioavailability. After 4 years of S addition at Degerö Stormyr in Sweden, plots that received 20 kg S/ha/yr had 133% higher total Hg levels in the top 5 cm of peat than control plots ([Bergman et al., 2012](#)). After 12 years, sampling of Hg methylation hotspots in plots with 10-kg-S/ha/yr addition found total Hg was 25% lower per peat mass or 31% per peat volume than in control plots ([Akerblom et al., 2013](#)). These results indicate that S addition mobilizes Hg stored in deeper parts of the peat profile, resulting in Hg transport to more accessible parts of the peat profile.

Recent work from the experiment at Bog Lake Fen also provides evidence that reduction of experimental S addition to wetlands results in reductions of MeHg concentrations in wetlands. In 2006, after 5 years of elevated S levels, a recovery treatment was initiated in the S6 bog experiment, where S addition was halted in recovery plots. Following the cessation of S addition, pore water MeHg (ng/L) declined by 32% between 2006 and 2008, and peat MeHg concentration and peat MeHg fraction declined by 62 and 76%, respectively ([Wasik et al., 2012](#)).

### 12.3.4.2 Agricultural Systems: The Everglades Water Conservation Area, Florida

There are multiple new studies that relate Hg concentrations in water, periphyton, soil, or fish to sulfate concentrations in the Everglades Water Conservation Area (see [Table 12-8](#)). In the Water Conservation Areas outside Everglades National Park, FL (Class I area), sulfate concentrations were as high as 48 mg/L near the EAA, whereas in pristine areas distant from the EAA, sulfate concentrations were less than 0.5 mg/L. Previous studies noted that Hg methylation was highest in areas of the wetland where sulfate concentrations ranged from 0.7 to 1.9 mg sulfate/L ([Bates et al., 2002](#); [Gilmour et al., 1998](#)). More recently, a study by [Corrales et al. \(2011\)](#), quantified the S budget and determined that atmospheric deposition of S is 15 kg S/ha/yr, 4% of the total S load in the WCAs. MeHg concentrations in surface water in the Florida Everglades increase when sulfate concentrations are above 1 mg/L, which [Corrales et al. \(2011\)](#) recommended as a target level for sulfate reduction efforts ([Figure 12-10](#)).

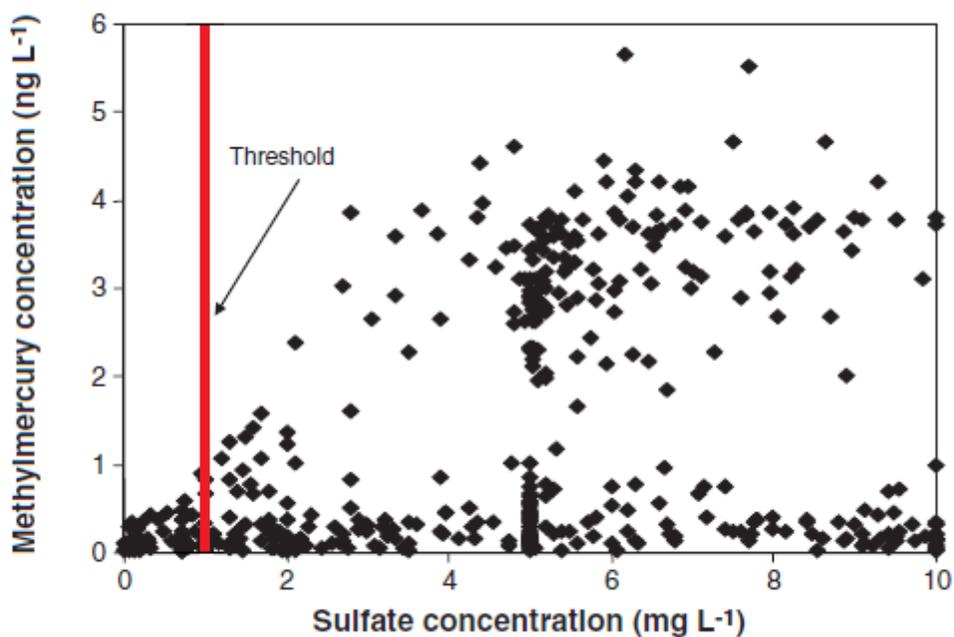
**Table 12-8 New studies on mercury (Hg) and sulfur (S) cycling in the Everglades Water Conservation Areas (WCA).**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Freshwater marsh	W3 pore water [SO <sub>4</sub> <sup>2-</sup> ] ≤4 μM U3 pore water [SO <sub>4</sub> <sup>2-</sup> ] is 39 μM F4 pore water [SO <sub>4</sub> <sup>2-</sup> ] is 74 μM Deposition = not measured	SRB abundance was 6.9x higher in U3 than W3, 16.8x higher in F4. In W3, abundance of SRB and methanogens are not significantly different. In U3, SRB abundance is 80% higher than methanogen abundance. In F4, SRB abundance is 60% higher than methanogens. mcrA copy number correlates positively with mRNA and methane production rates. Acetotrophic methanogens are dominant at W3, while at high S U3 and F4 sites, hydrogenotrophic methanogens are dominant.	F4, U3, and W3 sites in Water Conservation Area, Everglades, FL	Methanogens as quantified by mcrA copies Sulfur reducing bacteria as quantified by dsrB copies	<a href="#">Bae et al. (2015)</a>

**Table 12-8 (Continued): New studies on mercury (Hg) and sulfur (S) cycling in the Everglades Water Conservation Areas (WCA).**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Wetland	Total S load is 110,303 mtons/yr, atm dep is 4% of total, or 15 kg S/ha/yr as measured by US EPA CASNET (FL11 and FL99)	MeHg surface water concentration rises above suggested threshold level of 1 mg/L sulfate in groundwater.	Everglades agricultural area (EAA), FL	Surface and groundwater	<a href="#">Corrales et al. (2011)</a>
Constructed wetlands	Deposition not reported S load as [SO <sub>4</sub> <sup>2-</sup> ] in wetland inflow: 39–110 mg/L	Fish Hg (Y = log mg Hg/kg <i>G. holbrooki</i> ) was negatively correlated with water sulfate (X = log mg SO <sub>4</sub> <sup>2-</sup> /L) concentrations in three treatment wetlands: Y = -2.09X + 2.60; Y = -3.17X + 3.80; Y = -1.09X - 0.01.	Western Palm Beach County, FL	<i>Gambusia holbrooki</i> (eastern mosquitofish) and surface water	<a href="#">Feng et al. (2014)</a>
Wetlands and canals	Deposition not reported S load as [SO <sub>4</sub> <sup>2-</sup> ] in surface water: 0–60 mg/L	Fish Hg (mg Hg/kg or mg Hg/kg/mm for <i>Lepomis</i> ) increased over 0–1 mg/L SO <sub>4</sub> <sup>2-</sup> , and reached peak levels at 1–12 mg/L SO <sub>4</sub> <sup>2-</sup> , and decreased over 12–25 mg/L SO <sub>4</sub> <sup>2-</sup> , to remain flat at SO <sub>4</sub> <sup>2-</sup> concentrations 25–60 mg/L.	Everglades protection area, FL	<i>Gambusia spp.</i> (mosquito-fish), <i>Lepomis spp.</i> (sunfish), and <i>Micropterus salmoides</i> (largemouth bass)	<a href="#">Gabriel et al. (2014)</a>
Constructed wetlands	Deposition not reported S load in surface water as [SO <sub>4</sub> <sup>2-</sup> ]: 39.3–110.1 mg/L (mean 59.5 mg/L)	Between 2000–2004, total Hg and MeHg wetland export were negatively correlated to inflow [SO <sub>4</sub> <sup>2-</sup> ]. tHg: (log ng tHg/L) = -1.22*(log mg SO <sub>4</sub> <sup>2-</sup> /L) + 2.40; MeHg: (log ng MeHg/L) = -1.91*(log [SO <sub>4</sub> <sup>2-</sup> ]) + 3.02. Between 2000–2011, sulfate was negatively correlated with tHg and MeHg as one variable in multivariate models.	Western Palm Beach County, FL	Surface water	<a href="#">Zheng et al. (2013)</a>

atm = atmospheric; CASTNET = Clean Air Status and Trends Network; dep = deposition; EEA = Everglades agricultural area; ha = hectare; Hg = mercury; kg = kilogram; L = liter; MeHg = methylmercury; mg = milligram; ng = nanogram; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; THg = total mercury; yr = year.



L = liter; mg = milligram; ng = nanogram.

Source: adapted from [Corrales et al. \(2011\)](#).

**Figure 12-10 The relationship between surface water sulfate and methylmercury concentrations in the Florida Everglades.**

[Orem et al. \(2011\)](#) suggested that at high surface water sulfate (>20 mg/L) concentrations in the Florida Everglades, sulfide accumulates and inhibits methylation. In treatment wetlands that collect stormwater runoff from the EAA, the concentrations of sulfate are so high that sulfide inhibition of MeHg may occur at the higher end of the sulfate range. [Zheng et al. \(2013\)](#) reported on the water quality parameters, total Hg, and MeHg in the inflow and outflow waters of a constructed treatment wetland in the Everglades WCAs. The wetland was a net source of MeHg to surface water between 2000 and 2004, and during this time, total Hg and MeHg concentrations in water exiting the wetland were negatively correlated with sulfate concentrations of water flowing into the wetland ([Zheng et al., 2013](#)). The range of sulfate concentrations of inflow was 39–110 mg/L sulfate, with mean sulfate of 59.5 mg/L. [Zheng et al. \(2013\)](#) also constructed multivariate models for total Hg and MeHg, and even with other factors such as DOC, pH, and chloride in the model, inflow sulfate remained a strong and negative correlate of outflow

Hg concentrations. The positive relationship between sulfate and MeHg in the Florida Everglades is significant only at low sulfate concentrations (in this study, 39 mg SO<sub>4</sub><sup>2-</sup>/L).

A gradient of nutrient eutrophication (N, P, and S) from agricultural runoff runs from northeast to southwest across the WCA, with sulfate concentrations around 4.8 mg/L (reported as 50 µM) in southern, less disturbed sites ([Gilmour et al., 1998](#)). Sediment Hg increased from north to south by a factor of 3–4, and MeHg sediment concentrations increased across the same gradient by a factor of 25 ([Gilmour et al., 1998](#)). A more recent study in the Everglades suggested that mercury hotspots (elevated Hg in mosquitofish) were correlated with relatively oligotrophic conditions (low soil total phosphorus, TP) and native sawgrass sloughs, while fish Hg was lower in sites with higher soil TP with invasive cattail stands ([Julian et al., 2016a](#)). Surface water sulfate concentrations measured at the same sites ranged from 0.2–35 mg SO<sub>4</sub><sup>2-</sup>/L in the Hg hotspots and 6.5–70 mg SO<sub>4</sub><sup>2-</sup>/L at the nonhotspots ([Julian et al., 2016b](#)). Surface water sulfate and pore water sulfate were correlated, and the ratio of pore water sulfide:pore water sulfate correlated with pore water DOC ([Julian et al., 2016b](#)), suggesting that dissimilatory sulfate reduction (and by extension, a portion of mercury methylation) is controlled by DOC as well as sulfate in these marshes. In addition to the studies described in this section, studies in the Everglades WCA have focused on the microbial mechanisms of mercury methylation (see [Appendix 12.3.2](#)) and Hg loads in wildlife (see [Appendix 12.4](#)).

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#### 12.3.4.3 Agricultural Systems: Rice in the San Joaquin Delta, California

There is evidence from the California Central Valley that microbial Hg methylation occurs in managed agricultural wetlands that produce rice, which suggests a route of MeHg exposure to humans and wildlife. California (particularly the Central Valley where these studies were conducted) is the second largest producer of rice in the U.S., as well as an important stop along a major bird migratory route. The USGS coordinated an intensive research effort on Hg cycling and methylation of Hg in wetlands of the Central Valley of California, focusing on the Yolo Bypass Wildlife Area, located in the northwestern region of the San Francisco Bay delta where there are permanent wetlands dominated by *Typha* spp. (cattails) and *Scirpus* spp. (tule) and also agricultural wetlands in which *Oryza sativa* (white rice) and *Zizania palustris* (wild rice) are cultivated. Rice fields go through annual drying and rewetting cycles. They are flooded in the summer, drained for fall harvesting, and flooded in the winter to speed decomposition of rice straw and organic residue.

In the Yolo Bypass, CA, permanent and agricultural wetlands were sampled over the course of a growing season, June 2007–April 2008. About 10% of the 105 water samples taken over that time period exceeded the U.S. EPA Hg water quality criterion of 50 ng total Hg/L, and total Hg was higher in the center and outflow of agricultural wetlands than in permanent wetlands ([Alpers et al., 2014](#)).

Across the wetlands, all of the water samples taken for MeHg determination exceeded the San Joaquin Delta regulatory total maximum daily load (TMDL) limit of 0.06 ng MeHg/L. In fact, MeHg concentrations in all water samples exceeded 1 ng/L, with maximum measured water MeHg of 37 ng/L at the outlet of wild rice fields during harvest. Water MeHg concentrations were significantly higher, about twice as high, in the agricultural fields as in the permanent wetlands ([Alpers et al., 2014](#)), and sediment MeHg concentrations were also higher in the agricultural wetlands ([Marvin-Dipasquale et al., 2014](#)). The water MeHg fraction ranged from 1–80%, with a median value of 6.4%, and there were seasonal variations in agricultural but not permanent wetlands. In agricultural wetlands, the MeHg fraction increased 20 times between June and August in fields where white or wild rice was grown, and the MeHg fraction increased 5 times in fallow fields over the same time period ([Alpers et al., 2014](#)).

Hg methylation in the permanent and agricultural wetlands of the Yolo Bypass, CA correlated with S, Fe, and manganese (Mn) reduction. The strongest correlations of MeHg fraction in the wetlands were with metrics of Mn reduction, not reduction of Fe or S ([Alpers et al., 2014](#)). Sulfate was not a limiting factor of Hg methylation in the wetlands, although  $\delta^{34}\text{S}$  and sulfate:Cl in outlet waters indicated that sulfate reduction occurred in the wetlands, with at least 20% of the sulfate in the water column reduced ([Alpers et al., 2014](#)). In agricultural wetland sediments, mineralization of C by iron reduction was 2.4 times the mineralization of C by sulfate reduction, indicating that Fe reduction was more important than S reduction in terms of anaerobic decomposition ([Marvin-Dipasquale et al., 2014](#)). Furthermore, addition of sulfate fertilizer in rice fields did not raise measured sulfate reduction rates to the higher levels observed in fallow, unfertilized fields, indicating that sulfate was not a limiting factor on anaerobic microbial activity in the agricultural wetlands ([Alpers et al., 2014](#); [Marvin-Dipasquale et al., 2014](#)).

In the Yolo Bypass, CA, seasonal wetland export of MeHg occurs during the winter as well as the summer. In the summer, newly methylated MeHg is drawn into the root zone of the sediment by plant transpiration, and in winter, diffusion releases MeHg from the sediment into the water column ([Bachand et al., 2014](#)). The short-term storage of MeHg in wetland soils decreases MeHg exports from the wetland, but increases exposure of wetland fish to MeHg ([Windham-Myers et al., 2014b](#)). Also, MeHg in rice seeds were correlated with root MeHg ( $r = 0.90$ ), suggesting that MeHg from the root zone may be

transported through the plant to tissues that are consumed by migrating waterfowl ([Windham-Myers et al., 2014a](#)). Research in other systems has shown that MeHg produced in sediments is transported to rice grains ([Paranjape and Hall, 2017](#)). In a study of rice paddies surrounding industrial emitters of SO<sub>x</sub> and Hg in Hunan Province, China ([Xu et al., 2017a](#)), MeHg and %MeHg in rice grains were positively correlated with soil S, soil MeHg, and atmospheric concentrations of gaseous elemental Hg. MeHg in rice fields and in rice grains may be an important pathway to human and wildlife Hg exposure via rice consumption.

Evidence from fish Hg levels in different wetland types suggests that fluctuating water levels in the agricultural fields, as well as high levels of organic carbon from winter decomposition of rice straw, raise Hg methylation rates in the rice fields above rates in the permanent wetlands. Mercury concentrations of penned *Gambusia affinis* (mosquitofish) rose 12 times over initial concentration in white rice fields, 5.8 times in wild rice fields, and 2.9 over initial fish Hg concentration in the permanent wetlands ([Ackerman and Eagles-Smith, 2010](#)), and these trends were similar to Hg concentration trends in wild mosquitofish and *Menidia audens* (Mississippi silversides) caught in the wetlands. However, trends of Hg concentrations in macroinvertebrates did not follow trends in fish. There was no difference by wetland type (permanent, white rice, wild rice) in Hg concentrations of collected water boatmen, *Corisella* spp., which feed on plant and algal biomass. Hg concentrations in collected backswimmers, *Notonecta* spp., which are predatory, were higher in collections from permanent wetlands than in collections from cultivated rice wetlands ([Ackerman et al., 2010](#)).

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### 12.3.5 Drivers of Mercury Methylation under Ambient Conditions

The 2008 ISA presented evidence that elevated sulfate concentrations increased MeHg concentrations in aquatic and wetland ecosystems. At the time, most studies documenting this relationship were conducted in lakes and wetlands, and sulfate was often added experimentally to test the mechanisms of the relationship. Since then, a number of new studies have shown that increases in ambient sulfate concentrations can produce increased MeHg concentrations in surface water and sediments in lakes and wetlands (as well as increased Hg in wildlife, see [Appendix 12.4](#)). In addition, there is new evidence that increased sulfate in rivers, streams, and watersheds increase Hg methylation. Not all studies include information about the form or relative contribution of S sources in these ecosystems, but the studies provide evidence that current concentrations of surface water sulfate contribute to Hg methylation in a broad range of American aquatic and wetland ecosystems.

The 2008 ISA described watersheds with low pH waters and high wetland cover as sensitive to Hg methylation but did not describe MeHg fraction in the environment as an indicator of Hg methylation. MeHg is bioavailable and bioaccumulates within organisms due to the strong complexes it forms with thiosulfate and sulfhydryl groups in organic molecules. The fraction of total Hg that is in the form of MeHg (or %MeHg) is used as an indicator of bioavailable Hg within an ecosystem. New studies (as well as key older studies) of MeHg fractions in watersheds, streams, lakes, and wetlands show the link between S deposition and MeHg fraction in water and sediments, and confirm the importance of wetlands and nonurban watersheds as sources of MeHg to aquatic ecosystems.

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### 12.3.5.1 Sulfur in Ambient Conditions

Aquatic and wetland ecosystems which have received high loads of S generally have higher MeHg fractions. In sampling of Little Rock Lake and four nearby lakes in Wisconsin, MeHg fractions in lake water ranged from 6–25% MeHg, with no relationship to pH ([Bloom et al., 1991](#)). In the Adirondacks, which have historically experienced high S deposition (see case study), surface water total Hg, MeHg, and %MeHg were unrelated to pH when all variables were measured across 44 lakes in 2003–2004. Surface water MeHg ranged from 0–48% MeHg, with a mean of 6% ([Yu et al., 2011](#)).

At the time of the 2008 ISA, only one paper had considered the links between measures of SO<sub>x</sub> deposition and MeHg concentrations in ecosystems. Since then, two additional papers have been published documenting the effects of SO<sub>x</sub> deposition on Hg levels in water or fish ([Table 12-9](#)). The large scale and scope of these studies include confounding and interacting environmental factors, such as correlated Hg deposition and variations in wetland cover, the full effects of which researchers are unable to fully quantify. Despite this limitation, each of these papers show evidence of temporal or spatial correlations between SO<sub>x</sub> deposition and MeHg concentrations in fish or water.

**Table 12-9 New studies on correlations between sulfur (S) and methylmercury (MeHg) in ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
River and reservoir	S addition or deposition not reported [SO <sub>4</sub> <sup>2-</sup> ] in Rio Grande: pore water: (means) 74–230 mg/L; deep water: (range) 152–342 mg/L [SO <sub>4</sub> <sup>2-</sup> ] in Devils River: pore water: (means) 74–230 mg/L; deep water: (range) 15–168 mg/L	Sediment MeHg (ng/g) correlated negatively with pore water sulfate concentrations. RG had 40% higher THg than DR. DR sediment MeHg was 65% higher than in RG sediment, and DR sediment %MeHg was 65% than in RG sediment.	Rio Grande (RG) and Devils River (DR) branches of Amistad International Reservoir, TX	Sediment, pore water, and deep water; <i>Micropterus salmoides</i> (largemouth bass)	<a href="#">Becker et al. (2011)</a>
Prairie potholes (shallow freshwater marsh)	Lowland ponds, average [SO <sub>4</sub> <sup>2-</sup> ] is 14 mg/L Upland ponds, average [SO <sub>4</sub> <sup>2-</sup> ] is 1,490 mg/L Deposition not reported	In July, surface water [MeHg] was 290% higher in upland ponds than in lowland ponds. In August, surface water [MeHg] was 233% higher in upland ponds. Surface water %MeHg was 185% higher in upland ponds, and sediment %MeHg was 205% higher in upland ponds. Surface water [MeHg] increases with sediment organic matter: MeHg (ng/L) = -2.26 + 0.265 (percentage OM).	St Denis National Wildlife Area, Saskatchewan, Canada	Four lowland ponds with high SO <sub>4</sub> <sup>2-</sup> Five upland ponds with low SO <sub>4</sub> <sup>2-</sup>	<a href="#">Hoggarth et al. (2015)</a>
Wetlands	Deposition not reported Ambient wetland [SO <sub>4</sub> <sup>2-</sup> ] < 5 mg/L Mine-impacted wetlands, [SO <sub>4</sub> <sup>2-</sup> ] > 500 mg/L	Peat %MeHg increased with soil acid volatile sulfide in ambient wetland. In mine-impacted wetlands, peat %MeHg decreased with increasing S reduction.	Two wetlands, St Louis River Watershed, MN One wetland is downstream of a mine and receives high SO <sub>4</sub> <sup>2-</sup> effluent	Peat samples	<a href="#">Johnson et al. (2016b)</a>

**Table 12-9 (Continued): New studies on correlations between sulfur (S) and methylmercury (MeHg) in ecosystems.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Bogs	S addition or deposition not reported Peatland pore water median [SO <sub>4</sub> <sup>2-</sup> ]: 0.1, 0.4, 0.6, 3.0 mg/L	Pore water [SO <sub>4</sub> <sup>2-</sup> ] (mg/L) was positively correlated with pore water MeHg (Spearman <i>R</i> = 0.237) and total Hg (Spearman <i>R</i> = 0.576).	Four peatlands: two in Marcell Experimental Forest, MN; two in Experimental Lakes Area, Ontario	Pore water in peat	<a href="#">Mitchell et al. (2008b)</a>
Upland-peatland interface	S deposition not reported Peat pore water [SO <sub>4</sub> <sup>2-</sup> ] = 0–20 mg/L	MeHg was positively correlated with sulfate (Spearman <i>R</i> = 0.39): ng MeHg/L = 0.037 × (mg SO <sub>4</sub> <sup>2-</sup> /L) + 0.58.	S2 and S6 peatlands, Marcell Experimental Forest, MN	Peat pore water	<a href="#">Mitchell et al. (2009)</a>
Streams	S deposition not reported Monthly [SO <sub>4</sub> <sup>2-</sup> ] means in streams: 4–8 mg/L	During the growing season, MeHg increased with decreasing sulfate concentrations: ng MeHg/L = -0.11 × (mg SO <sub>4</sub> <sup>2-</sup> /L) + 0.88.	Archer Creek, Adirondacks, NY	Stream water	<a href="#">Selvendiran et al. (2008a)</a>
Streams and lakes	Not reported	MeHg was negatively correlated with water sulfate concentrations: ng MeHg/L = 6.67 × (mg SO <sub>4</sub> <sup>2-</sup> /L) - 2.40.	Arbutus Lake and Sunday Lake, Adirondacks, NY	Stream and lake surface water	<a href="#">Selvendiran et al. (2009)</a>

DOM = dissolved organic matter; DR = Devils River; g = gram; ha = hectare; kg = kilogram; L = liter; MeHg = methylmercury; mg = milligram; ng = nanogram; OM = organic matter; RG = Rio Grande; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; THg = total mercury; yr = year.

A study of fish and SO<sub>x</sub> deposition sediment records at Isle Royale in Lake Superior indicated a temporal relationship in this remote location between S deposition and Hg loads in fish. Isle Royale is a Class I area and contains several lakes impacted by S and Hg deposition. Between 1981 and 2006, S deposition in the region fell 40–60% (from about 10 kg S/ha/yr in 1981 to about 6 kg S/ha/yr in 2006 at NADP site MN18 in mainland Minnesota), while Hg deposition remained stable. S deposition on the island between 1985 and 2006 was in the range of 2.3 to 7 kg S/ha/yr with a trend (*p* = 0.09) toward a decline in deposition over that time period ([Drevnick et al., 2007](#)). Fish collections were conducted in eight Isle Royale lakes in 1995–1996 and again in 2004–2006. In six lakes, 1995 collections of northern pike (*Esox lucius*) exceeded the U.S. EPA fish tissue Hg limit (0.3 µg Hg/g wet weight). When these lakes were resampled in 2004–2006, northern pike mean Hg levels were below the U.S. EPA limit,

which the authors attributed to a decline in SO<sub>x</sub> deposition despite steady Hg deposition. This study also used museum collections of fish from Isle Royale (collected in 1905, 1929, 1966) and an analysis of lake sediment cores to test the relationship between historical S loads and fish Hg burdens. The chromium-reducible sulfur (CRS) fraction in sediment cores was determined to closely track known patterns of S deposition since monitoring began in 1985, allowing the inference of S loads to island lakes since the Industrial Revolution in the late nineteenth century. The historical S load data were compared to Hg loads in both the historical and recent fish collections from Isle Royale lakes. The CRS fraction explained 79% of the variation in Hg concentration of northern pike fish fillets. There were similar correlations between sediment reduced S and Hg burden in other fish species, but sample sizes for those species were low and correlations were not statistically significant ([Drevnick et al., 2007](#)). DOC and pH were not directly tested for their relationship with Hg levels in fish, but the authors note that there are no significant trends in DOC or pH in these lakes from 1980–2006. This study showed that Hg fish burdens increased in Isle Royale lakes with increasing SO<sub>x</sub> deposition in the twentieth century, and that Hg fish burdens declined in response to reductions in SO<sub>x</sub> deposition since the 1990s.

The other two studies that find effects of SO<sub>x</sub> deposition are summarized in the following sections. A 12-year study of MeHg and fish Hg in Voyageurs National Park found that declines in SO<sub>x</sub> deposition have resulted in MeHg declines only in lakes where DOC has remained stable (see [Appendix 12.3.5.3](#)). A study that compiled data from reservoir fish sampling in Texas found correlations between geographic variations in SO<sub>x</sub> and Hg deposition and average fish Hg burden over 25 years (see [Appendix 12.3.5.2](#)).

Sampling at small scales within peatlands has shown positive relationships between sulfate concentrations and MeHg concentrations ([Table 12-9](#)). In two peatlands at the Marcell Experimental Forest, MN, researchers monitored water quality at the upland-peatland interface, hypothesized to be an important zone for methylation due to labile carbon inputs in runoff from terrestrial communities to the peatland microbial community. Sulfate peat pore water concentrations ranged from 0–20 mg sulfate/L, and MeHg concentrations increased 0.037 ng/L for each 1 mg/L increase in sulfate ([Mitchell et al., 2009](#)). The relationship between sulfate and MeHg is also significant at a larger spatial scale in the same region. Across four peatlands at the temperate-boreal boundary in Minnesota and Ontario, MeHg was positively correlated with sulfate in peat pore water (Spearman's  $R = 0.237$ ) as well as with pH during the 2005 growing season ([Mitchell et al., 2008b](#)). The range of median sulfate levels in these peat bogs during the course of the study was 0.01–3 mg/L, while the range of MeHg concentrations was 0.35–0.62 ng MeHg/L ([Mitchell et al., 2008b](#)).

The South River in Waynesboro, VA, was contaminated by historical (1929–1950) textile industrial use and release of Hg. In 2008, sediments were collected within the channel at 10 study sites at increasing distances downstream of the historic Hg source. MeHg concentrations in the sediment increased linearly with increasing sediment pore water sulfate concentrations, with a 0.06 ng increase in MeHg per gram of sediment for every 1 mg/L increase in sulfate pore water concentration, with mean pore water sulfate concentrations ranging from 2–16 mg/L ([Yu et al., 2012](#)).

Chemical constituents measured at watershed outflows represent the cumulative microbial and abiotic chemical transformations within the watershed. A watershed in which SRPs are present will therefore have higher MeHg and lower sulfate concentrations in its outflow than an adjacent watershed without active SRPs that experiences the same S and Hg deposition loads. Many of the following studies document inverse relationships between sulfate concentrations and MeHg concentrations in outflows of trunk streams (those that drain an entire watershed) where sulfate and Hg concentrations reflect upstream sulfate stimulation of SRPs and Hg methylation. In a tributary stream draining a wetland in Wisconsin, there were seasonal trends in sulfate and MeHg concentrations indicative of wetland Hg methylation. Sulfate in the stream declined 80% between April and June 2003, indicating S immobilization or reduction in the wetland during the early summer, and MeHg increased 69% over the same time period ([Watras and Morrison, 2008](#)). This increase in MeHg and simultaneous decrease in sulfate in stream water concentrations suggests upstream activity of SRB in Hg methylation.

In streams draining wetlands in the Archer Creek watershed in the Adirondack Mountains, NY, water sulfate concentrations were lower than in streams upstream of the wetlands ([Selvendiran et al., 2008a](#)). Wetland microbial communities reduced sulfate while methylating Hg, which would account for the elevated MeHg concentrations in wetland-draining streams compared to upland streams. There was a negative correlation between sulfate concentrations and MeHg concentrations in streams draining the wetlands where Hg methylation occurred, with a 0.11 ng/L increase in MeHg concentrations in the stream for each mg/L sulfate removed from surface water ([Selvendiran et al., 2008a](#)). [Selvendiran et al. \(2009\)](#) measured and calculated Hg budgets for the adjacent watersheds of Arbutus Lake and Sunday Lake in the Adirondacks, NY, measuring inlet and outlet streams at both water bodies as well as lake surface water at Arbutus. Across both watersheds, MeHg concentrations were inversely correlated with sulfate concentrations. This pattern was driven by the concentrations measured in the streams in Sunday Lake, which drains a watershed that is approximately 20% wetlands ([Selvendiran et al., 2009](#)), indicating that SRB in upstream wetlands may have been reducing sulfate and methylating Hg to impact the measured stream surface water.

Arbutus Lake drains a watershed of which wetlands comprise only 4% of surface area, which may explain the relatively higher sulfate concentrations and the lower mean and variability of MeHg (Selvendiran et al., 2009). In watersheds where S and Hg deposition rates do not differ spatially, negative correlations between sulfate concentrations and MeHg show the link between sulfate reduction and Hg methylation.

Highly elevated sulfate concentrations, as can result from agricultural runoff, can depress SRP activity and Hg methylation, as sulfide produced by SRPs accumulates and downregulates SRP activity. In a sampling study of the Amistad International Reservoir on the Texas-Mexico border, Hg pools in sediment, water, and largemouth bass (for more on this endpoint, see [Appendix 12.4](#)) were quantified and compared between the Rio Grande and Devils River branches of the reservoir. The Rio Grande branch had sulfate concentrations an order of magnitude higher (site with highest sulfate concentration: 230 mg/L sediment pore water), as well as 40% higher total Hg pools in sediments, than did the Devils River branch [site with highest sulfate concentrations: 23 mg/L ([Becker et al., 2011](#))]. However, total Hg and sulfate were negatively correlated with MeHg, and SRB (researchers used techniques to detect bacterial sulfur reducers) were present at all sites. Hg methylation in this system was not limited by Hg supply or biota and was not stimulated by the Rio Grande's high sulfate levels, originating from agricultural land use in the watershed. The Devils River branch had 65% higher MeHg concentrations in sediments, and a 230% higher proportion of total sediment Hg in the form of MeHg ([Becker et al., 2011](#)). [Becker et al. \(2011\)](#) posited that the higher MeHg in Devils River sediments was due to higher DOC in this area of the reservoir and to sulfate concentrations (in sediment pore water, 2.5–23 mg/L) being optimal for the metabolism of SRB.

Two wetlands in the St Louis River Watershed, MN, were the subject of a study of Hg and S because one wetland regularly receives high-sulfate mine effluent ([Johnson et al., 2016b](#)). Peat %MeHg increased with S reduction (quantified as pore water sulfide or soil acid volatile sulfide) in the wetland that did not receive mine effluent, and in which surface water sulfate concentrations averaged less than 5 mg/L. In wetlands that received sulfate mine effluent of >500 mg  $\text{SO}_4^{2-}$ /L, peat %MeHg decreased with increasing S reduction. Together, these results support the model of methylation first proposed for the Everglades [see [Figure 12-7](#), and [Glimour \(2011\)](#)], in which there is a net methylation optimum at low moderate sulfate concentrations (1–10s of mg  $\text{SO}_4^{2-}$ /L) and a suppression of net methylation at high sulfate (100s of mg  $\text{SO}_4^{2-}$ /L) and sulfide (0.6–0.7 mg S/L in pore water) concentrations ([Johnson et al., 2016b](#)).

In contrast, in the St. Denis National Wildlife Area in Saskatchewan, Canada, prairie potholes vary in sulfate concentrations in relation to geology and position in the

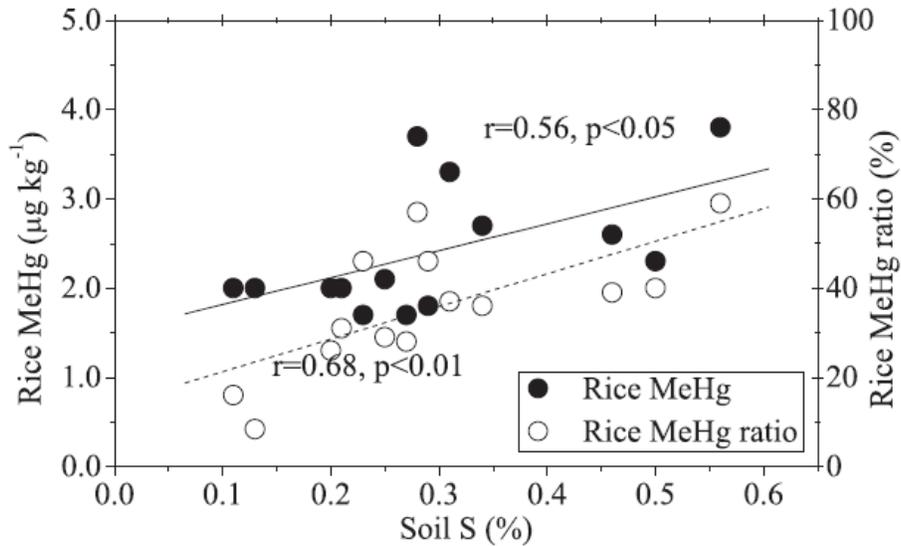
landscape. In a study of water MeHg, five upland ponds had average sulfate concentrations of 1,490 mg/L (S sources are geologic), and four lowland ponds had average sulfate concentrations of 14 mg/L ([Hoggarth et al., 2015](#)). MeHg fraction was 185% higher in surface water and 205% higher in sediments in the upland ponds than in the lowland ponds, which had lower sulfate concentrations ([Hoggarth et al., 2015](#)).

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### 12.3.5.2 Mercury and Sulfur Interactions in Ambient Conditions

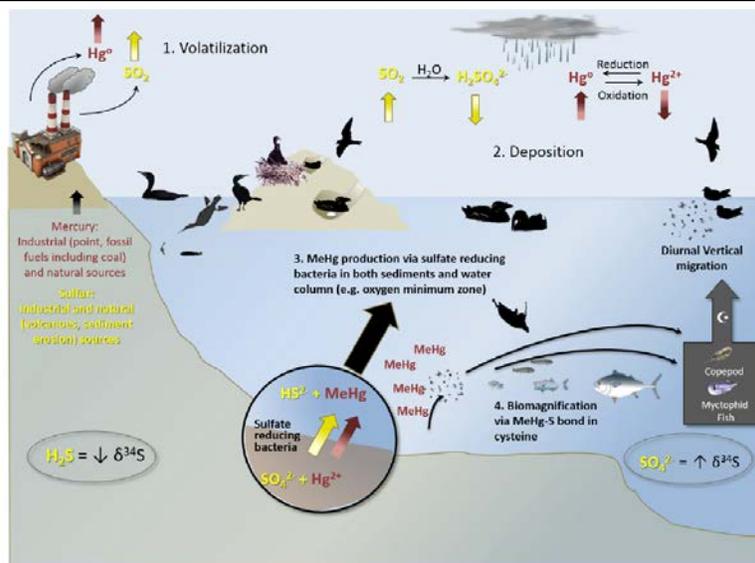
It can be difficult to tease apart the effects of Hg and SO<sub>x</sub> deposition upon mercury methylation rates or concentrations of MeHg in biota, because at some scales, Hg and SO<sub>x</sub> emissions are correlated ([Figure 12-11](#), [Figure 12-12](#), and [Table 12-10](#)). In a small-scale (15 km, single sampling event) gradient study of Hg, MeHg, and S downwind of a coal plant and other industrial sources in China ([Xu et al., 2017a](#)), soil S and gaseous elemental Hg (GEM) were positively correlated, with effects upon cultivated rice. In surrounding rice paddies, MeHg and %MeHg in rice grains were positively correlated with soil S, soil MeHg, and atmospheric concentrations of gaseous elemental Hg ([Figure 12-11](#)).

Regionally, Hg and S depositions were correlated in Texas ([Drenner et al., 2011](#)) and atmospheric reactive Hg and SO<sub>2</sub> were correlated in the Ohio River valley ([Yatavelli et al., 2006](#)). At a national or international spatial scale, different factors govern long-range transport and deposition of SO<sub>x</sub>, PM, and Hg, so S deposition and Hg deposition may not be spatially correlated. However, at a longer temporal scale, Hg and S deposition have declined in concert over the past decades in the U.S. [U.S. emissions of Hg declined 79% and SO<sub>2</sub> emissions declined 73% between 1990 and 2011 ([U.S. EPA, 2017a](#))]. Temporal and spatial correlations between Hg and S emissions and deposition make it difficult to distinguish between Hg and SO<sub>4</sub><sup>2-</sup> as the limiting factor in ecosystems receiving high deposition.



Source: adapted from [Xu et al. \(2017a\)](#).

**Figure 12-11** Concentrations of soil sulfur (S), elevated by sulfur oxides (SO<sub>x</sub>) deposition, correlate with rice grain (methylmercury [MeHg]) and rice grain %MeHg in rice paddies near industrial emitters in China.



Source: [Elliott and Elliott \(2016\)](#).

**Figure 12-12** Interactions between mercury (Hg) and sulfur (S) cycles.

**Table 12-10 New studies on deposition of sulfur (S) and mercury (Hg) and their effect on methylmercury (MeHg).**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Reservoir	NADP quantifies S deposition in 2008 at CT: 7.7 kg SO <sub>4</sub> <sup>2-</sup> /ha, TBP: 8.1 kg SO <sub>4</sub> <sup>2-</sup> /ha, ECTP: 8.1 kg SO <sub>4</sub> <sup>2-</sup> /ha, SCTP: 11.9 kg SO <sub>4</sub> <sup>2-</sup> /ha	Mean Hg fish levels were 61–89% higher in the SCP region (highest S and Hg deposition) than in other regions.	145 reservoirs in four Level 3 ecoregions of eastern Texas: CT, TBP, ECTP, SCTP	<i>Micropterus salmoides</i> (large-mouth bass)	<a href="#">Drenner et al. (2011)</a>
Lake	S deposition not reported	Between 2004–2015, Hg <sup>0</sup> deposition decreased 25%, while Hg <sup>2</sup> deposition remained constant.  Sulfate concentrations in Arbutus Lake declined approximately 40% between 2004–2016. In 2004, sulfate concentrations ranged 4.3–7.0 mg/L, and in 2016, sulfate concentrations ranged 2.4–4.3 mg/L.  Between 2004–2015, lake MeHg and THg concentrations and fluxes decreased statistically significantly (mean changes not reported due to high variability).	Arbutus Lake watershed, Adirondacks, NY	Water samples	<a href="#">Gerson and Driscoll (2016)</a>
Agricultural wetland	S and Hg deposition not recorded	MeHg and %MeHg in rice grains were positively correlated with soil S, soil MeHg, and atmospheric concentrations of gaseous elemental Hg.	Gradient of S and Hg deposition 2–15 km downwind of Yueyang Coal-fired Power Plant, Hunan Province, China	<i>Oryza sativa</i> (rice) grown in paddies	<a href="#">Xu et al. (2017a)</a>

CT = Cross Timber; ECTP = East Central Texas Plains; ha = hectare; kg = kilogram; MeHg = methylmercury; NADP = National Atmospheric Deposition Program; S = sulfur; SCTP = South Central Texas Plains; SO<sub>4</sub><sup>2-</sup> = sulfate; SO<sub>x</sub> = sulfur oxides; TBP = Texas Blackland Prairie; yr = year.

A study that compiled data from reservoir fish sampling in Texas found correlations between geographic variations in SO<sub>x</sub> deposition and average fish Hg burden over 25 years. Largemouth bass (*Micropterus salmoides*) were collected between 1985 and 2009 with heavy sampling between 2004 and 2008 (45% of the samples) from 145 reservoirs in eastern Texas. The samples were grouped and analyzed by Level 3 ecoregions which received varying amounts of Hg and S deposition, increasing from the westernmost Cross Timber region where S deposition was 7.7 kg/ha to the easternmost South Central Plains region where S deposition was 11.9 kg/ha ([Drenner et al., 2011](#)). The South Central Plains region received high deposition of SO<sub>x</sub> and Hg, and also had the highest percentage of land area as wetlands (12%) and the lowest percentage of land area in agriculture of the four regions, all of which are conducive to high methylation rates in aquatic ecosystems. Mean Hg levels in sampled largemouth bass were 61–89% higher in the South Central Plains than in other eastern Texas regions ([Drenner et al., 2011](#)). These results have regional implications because the South Central Plains ecoregion extends into Arkansas, Louisiana, and Oklahoma. This study showed that within Texas, the geographic region with the most wetlands and the highest SO<sub>x</sub> deposition also had fish with the highest Hg burden.

In the Adirondacks, a temporal study of water MeHg, water sulfate concentrations, and mercury deposition reported no correlation between stream sulfate and MeHg (as concentration or as %MeHg) in the summer when SRB are active, in lake data collected in 2004–2005 ([Gerson and Driscoll, 2016](#)). Over the decade in which these data were collected, Hg<sup>0</sup> atmospheric concentration and deposition in the watershed, litter Hg concentration, and sulfate concentrations in streams all declined in this system; [Gerson and Driscoll \(2016\)](#) suggested that decreases in surface water MeHg in the watershed were attributable to decreased Hg deposition, and that surface water sulfate concentration over the entire decade was so high in the lake that it did not control Hg methylation.

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### **12.3.5.3 Organic Matter and Sulfur Interactions in Ambient Conditions**

There is evidence from recent research of interactions between organic matter and sulfur in controlling mercury methylation ([Table 12-11](#)). A 12-year study of MeHg and fish Hg in Voyageurs National Park found that declines in SO<sub>x</sub> deposition have resulted in MeHg declines only in lakes where DOC has remained stable. In lakes in Voyageurs National Park, MN, a Class I area, researchers measured MeHg in the epilimnion of four lakes between 2000 and 2012 and compared trends in lake water Hg concentrations with trends of measured Hg and S deposition ([Brigham et al., 2014](#)). S deposition to the region decreased 48% between 1998 and 2012 based on regression analysis of data measured at

National Atmospheric Deposition Program (NADP) stations MN16 and MN18, and Hg deposition decreased 32%. In two lakes, MeHg surface water concentrations decreased over 12 years of measurement, 50% in Peary Lake and 43% in Ryan Lake ([Brigham et al., 2014](#)), and fish Hg concentrations followed suit (see [Appendix 12.4](#)). In contrast, Brown Lake MeHg concentrations increased 85% over the same time period, which the authors ascribed to increasing inputs from upstream methylating aquatic environments. An alternative explanation may be in the differences between lakes in dissolved organic carbon (DOC) concentrations; in Peary and Ryan Lakes, DOC concentrations remained flat over the decade in which MeHg concentrations decreased, while in Brown Lake, DOC concentrations increased 30% ([Brigham et al., 2014](#)). *Perca flavescens* (yellow perch) were collected between 2000 and 2012 to determine fish Hg levels in comparison with Hg lake water trends and S deposition. Between 2000 and 2012, *P. flavescens* Hg concentrations decreased 37% in Peary Lake and 32% in Ryan Lake, just as S deposition and lake MeHg declined ([Brigham et al., 2014](#)). In Brown Lake, where DOC increased 30% over the same time period, *P. flavescens* Hg increased 80% ([Brigham et al., 2014](#)). In Voyageurs National Park, lakes with stable DOC responded to decreased S deposition with decreasing MeHg in water and Hg concentrations in fish.

There is evidence from recent research that higher sulfate concentrations correspond to higher MeHg concentrations and sulfate reduction rates in prairie potholes. Prairie potholes are shallow wetlands and lakes in depressions created by glaciation, which depend upon snowmelt and precipitation for their water supply and tend to be hydrologically isolated. A survey of prairie pothole wetlands and lakes in Saskatchewan measured Hg levels in water. Surface water MeHg correlated positively with sulfate concentrations and negatively with conductivity and specific ultraviolet absorbance (SUVA; an indicator of aromatic fraction of DOM), such that surface water MeHg increased 0.03 ng/L for each mg/L increase in sulfate concentrations, when all other factors remained constant ([Hall et al., 2009a](#)).

In wetlands in the Allequash Watershed, WI, potential methylation rates in streambed sediments were positively correlated with microbial sulfate reduction (quantified as sediment acid volatile sulfide,  $r^2 = 0.258$ ), DOC, and reduced iron ([Creswell et al., 2017](#)). These correlations reflect the activity of methylating SRB, IRB, and methanogens, which shift in dominance spatially and seasonally across the wetland streams (see [Appendix 12.3.2](#)). Hg concentrations did not correlate with mercury methylation in this system ([Creswell et al., 2017](#)). The total dissolved S and sulfide fraction did not correlate with methylation rate, suggesting that sulfate was not a limiting factor, and that DOC was probably the main driver of methylation in this system.

**Table 12-11 New studies of Interactions between organic matter and sulfur (S) in Controlling methylmercury (MeHg).**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Lakes	6.44 kg S/ha in 1998, 3.35 kg S/ha in 2012 as quantified by NADP sites MN16 and MN18	As SO <sub>x</sub> deposition decreased 48% in 1998–2012, water MeHg decreased 50% in Peary Lake and 43% in Ryan Lake. In Brown Lake, water MeHg increased 85% in 1998–2012.  Between 2000 and 2012, Hg concentration in <i>P. flavescens</i> decreased 37% in Peary Lake and 32% in Ryan Lake, and increased 80% in Brown Lake.	Voyageurs National Park, MN	Surface water and <i>Perca flavescens</i> (yellow perch)	<a href="#">Brigham et al. (2014)</a>
Wetland	Pore water concentrations 0.0 to 59.2 μM SO <sub>4</sub> <sup>2-</sup>	Methylation was correlated with acid volatile sulfide (AVS) ( $r^2 = 0.258$ , $p = 0.001$ ), and stepwise with DOC, and porewater Fe(II), THg, MeHg and dissolved Fe ( $r^2 = 0.5096$ , $p = 0.004$ ).	Allequash Creek, WI	Pore water	<a href="#">Creswell et al. (2017)</a>
Reservoir	Deposition not reported Permanently inundated sediment porewater: 3.8 mg SO <sub>4</sub> <sup>2-</sup> /L Seasonally inundated: 8.2 mg SO <sub>4</sub> <sup>2-</sup> /L	Seasonal inundation increased sediment MeHg and MeHg fraction of total Hg in comparison to permanently inundated sections: Seasonal: 2.70 ng MeHg/g sediment, 0.55% MeHg Permanent: 0.71 ng MeHg/g soil, 0.18% MeHg	Cottage Grove Reservoir, OR.	Sediment, pore water, and surface water	<a href="#">Eckley et al. (2017)</a>
Lakes and wetlands	Not reported	Surface water MeHg was positively correlated with sulfate concentrations: ng MeHg/L = $-2.94 - 0.44$ (conductivity) + $0.303(\text{SO}_4^{2-}) - 0.268$ (aromatic fraction of DOM).	49 lakes and wetlands, prairie pothole region, Saskatchewan, Canada	Lake water	<a href="#">Hall et al. (2009a)</a>
Artificial reservoir	Concentrations ranged from 3–12 mg/ L SO <sub>4</sub> <sup>2-</sup>	Strong correlation noted between sulfate and chlorophyll a ( $r = 0.73$ ), DOC ( $r = 0.92$ ), and conductivity ( $r = 0.83$ )	Reservoirs in South Korea	Surface water	<a href="#">Noh et al. (2016)</a>

Reservoirs have been identified as sources of MeHg. Cottage Grove Reservoir, OR, was built for flood control and experiences large, seasonal fluctuations in water levels. Hg and MeHg dynamics differ between permanently flooded portions of the reservoir and areas that are inundated during summer months ([Eckley et al., 2017](#)). When the reservoir was flooded in the spring, sulfate, inorganic Hg, and DOC were released in high concentrations from previously exposed sediments, creating zones of high mercury methylation in seasonally inundated sediments. Across nine reservoirs in South Korea, algal blooms stimulated methylation of mercury. Algal blooms released large pulses of labile C, as demonstrated by a positive correlation of Chl *a* and DOC [ $r = 0.73$ ; [Noh et al. \(2016\)](#)]. Sulfate concentrations ranged from 3 to 12 mg/L, and also correlated with DOC ( $r = 0.92$ ). Concentrations of MeHg and %MeHg were positively correlated with Chl *a*, DOC, and sulfate across reservoirs.

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#### 12.3.5.4 pH and Sulfur Interactions in Ambient Conditions

Sulfate deposition is not the primary driver of MeHg concentrations in every ecosystem with elevated Hg concentrations in its biota. In Wallowa-Whitman National Forest, OR and ID, fish Hg sampled in high-elevation lakes in 2011 correlated positively with basal area of conifers in the lake catchment and correlated negatively with lake area, surface water  $\text{SO}_4^{2-}$ , and DOC ([Eagles-Smith et al., 2016](#)). This study did not test microbial methylation rates or community composition, but lakes with low  $\text{SO}_4^{2-}$  and low DOC were acidified, as quantified by pH measurements. [Eagles-Smith et al. \(2016\)](#) interpreted model results to show that acidification of lakes had negative effects upon fish condition and resulted in high Hg bioaccumulation, with conifer-forested catchments most at risk. In Kejimikujik National Park, Nova Scotia, regressions and model selection of Hg in biota against  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$  suggested that lake productivity was a stronger driver of Hg in biota than sulfur reduction (indicated by enrichment of  $\delta^{34}\text{S}$ ), which was negatively correlated with Hg in lake biota ([Clayden et al., 2017](#)). The lakes in this study are unstratified, shallow and acidic, with S deposition enriched in  $\delta^{34}\text{S}$  from nearby marine waters, all conditions unfavorable to sulfate-reducing bacteria. [Clayden et al. \(2017\)](#) suggested that microbial methylators not utilizing sulfate are responsible for producing MeHg in these lakes, and that trophic interactions are responsible for variations in Hg in biota across lakes.

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#### 12.3.5.5 Nutrient Enrichment Effects on Methylmercury (MeHg)

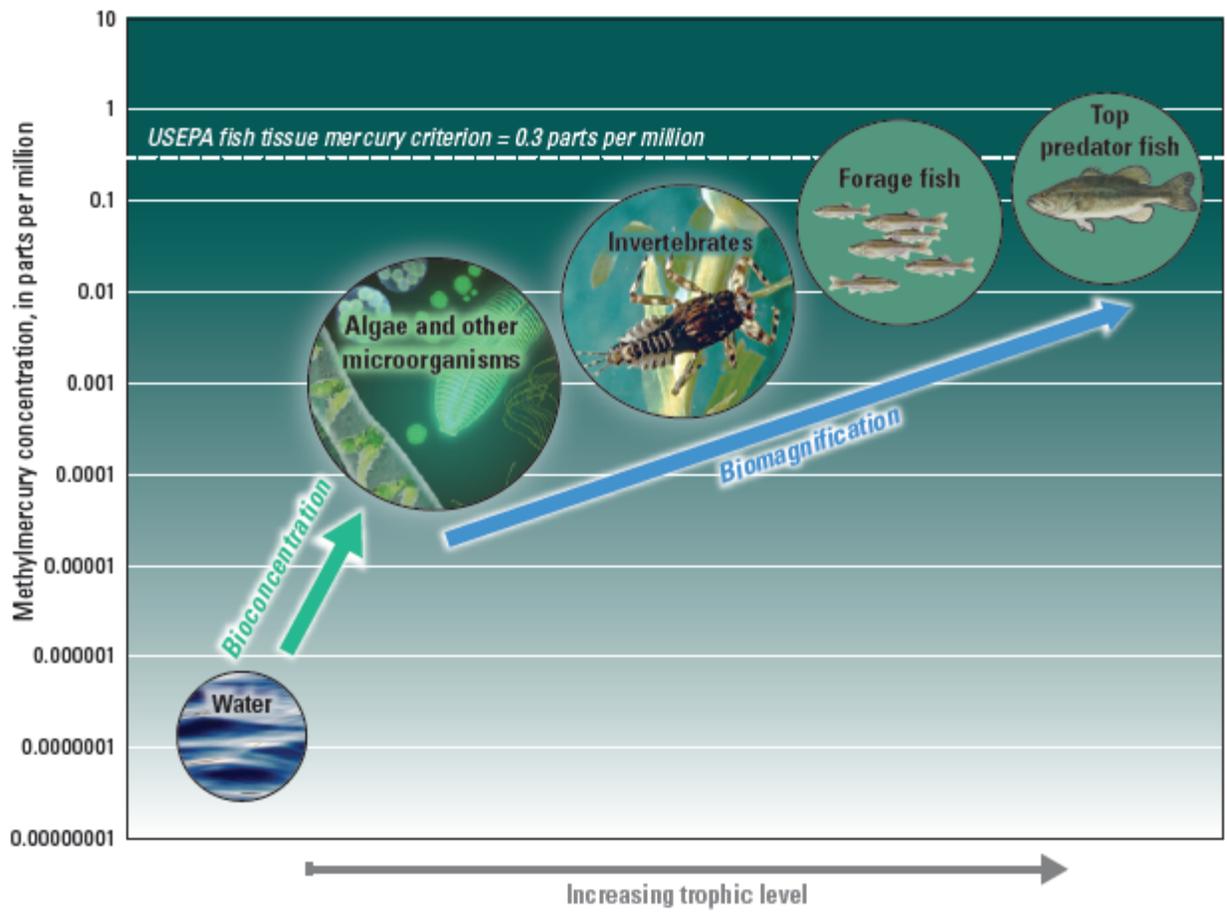
Nutrient availability—the relative availability of nitrogen (N) and P as well as of S—can impact MeHg fraction, with low or intermediate levels of nutrients most conducive to

higher MeHg across two very different nutrient gradients. In seven wetlands across a nutrient gradient in Sweden, total Hg was 113–287 ng/g in soils, MeHg was 3.5–21 ng/g in soils, and the highest MeHg fraction was 16%. Potential methylation rate constants and MeHg fractions were highest in wetlands with an intermediate nutrient status ([Tjerngren et al., 2012](#)). N and P concentrations have also been implicated as contributing to variation in Hg methylation rate in the Everglades (see [Appendix 12.3.4.3](#)).

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## 12.4 Sulfur Impacts on Mercury in Wildlife

Mercury has no known beneficial property in living cells. MeHg is bioconcentrated by living cells, in which it forms strong bonds with thiosulfate and sulfhydryl groups in organic compounds. It is common for MeHg to be present at progressively higher concentrations up the trophic level of food chains, as MeHg consumed is remarkably persistent ([Figure 12-13](#)). A recent report by the USGS reviews the known effects of Hg on wildlife. Fish and birds experience negative physiological and reproductive effects at Hg levels below the 0.3 ppm tissue level set by the U.S. EPA to protect human health ([Wentz et al., 2014](#)). There are a number of new studies on the effects of sulfur upon Hg in wildlife ([Figure 12-12](#)).



Note logarithmic scale of y-axis. The top and bottom of each circle represent the range of measured methylmercury concentrations from streams in Oregon, Wisconsin, and Florida sampled during 2002–2006, and in New York and South Carolina sampled during 2007–2009.

Source: [Wentz et al. \(2014\)](#).

**Figure 12-13** Bioconcentration and biomagnification result in methylmercury concentrations about 1 million times higher in predator fish than in stream water.

**Table 12-12 New studies on sulfur (S) impacts upon mercury (Hg) in wildlife.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
River	S addition or deposition not reported [SO <sub>4</sub> <sup>2-</sup> ] in Rio Grande: pore water: (means) 74–230 mg/L; deep water: (range) 152–342 mg/L [SO <sub>4</sub> <sup>2-</sup> ] in Devils River: pore water: (means) 74–230 mg/L; deep water: (range) 15–168 mg/L	<i>M. salmoides</i> muscle Hg (mg/fish kg) was 38% higher in DR than RG.	Rio Grande (RG) and Devils River (DR) branches of Amistad International Reservoir, TX	Sediment, pore water, and deep water; <i>Micropterus salmoides</i> (largemouth bass)	<a href="#">Becker et al. (2011)</a>
Constructed wetlands	S load as [SO <sub>4</sub> <sup>2-</sup> ] in wetland inflow: 39–110 mg/L	Fish Hg (Y = log mg Hg/kg <i>G. holbrooki</i> ) was negatively correlated with water sulfate (X = log mg SO <sub>4</sub> <sup>2-</sup> /L) concentrations in three treatment wetlands: Y = -2.09X + 2.60; Y = -3.17X + 3.80; Y = -1.09X - 0.01.	Western Palm Beach County, FL	<i>Gambusia holbrooki</i> (eastern mosquitofish) and surface water	<a href="#">Feng et al. (2014)</a>
Wetlands and canals	S load as [SO <sub>4</sub> <sup>2-</sup> ] in surface water: 0–60 mg/L	Fish Hg (mg Hg/kg or mg Hg/kg/mm for <i>Lepomis</i> ) increased over 0–1 mg/L SO <sub>4</sub> <sup>2-</sup> , reached peak levels at 1–12 mg/L SO <sub>4</sub> <sup>2-</sup> , and decreased over 12–25 mg/L SO <sub>4</sub> <sup>2-</sup> , to remain flat at SO <sub>4</sub> <sup>2-</sup> concentrations 25–60 mg/L.	Everglades protection area, FL	<i>Gambusia</i> spp. (mosquitofish), <i>Lepomis</i> spp. (sunfish), and <i>Micropterus salmoides</i> (largemouth bass)	<a href="#">Gabriel et al. (2014)</a>
Lakes	Not reported	Fish Hg is positively correlated (r <sup>2</sup> = 0.928) with lake water SO <sub>4</sub> <sup>2-</sup> (mg/L).	One impoundment and five natural lakes, SD	<i>Sander vitreus</i> (walleye)	<a href="#">Stone et al. (2011)</a>

**Table 12-12 (Continued): New studies on sulfur (S) impacts upon mercury (Hg) in wildlife.**

Type of Ecosystem	Additions or Load (kg S/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Bog	Ambient S deposition: 5.5 kg/ha/yr (mid 2000s) as quantified by NADP Station MN16 S addition: 32 kg S/ha/yr dissolved in pond water and delivered by sprinklers (mimics 4x the 1990s deposition rate)	Hg levels in <i>Culex</i> spp. increased 126%. <i>Culex</i> spp. Hg was 41% lower in recovery treatment than under SO <sub>4</sub> <sup>2-</sup> treatment, but still 34% higher than control.	S6 peatland, bog section, Marcell Experimental Forest, MN	Pore water, peat, and <i>Culex</i> spp. (mosquito) larvae	<a href="#">Wasik et al. (2012)</a>

DR = Devils River; ha = hectare; Hg = mercury; kg = kilogram; L = liter; mg = milligram; NADP = National Atmospheric Deposition Program; RG = Rio Grande; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

S deposition affects the production and net amount of MeHg in water bodies, increasing accumulation of Hg up the food chain ([Table 12-12](#)) but not affecting the rates at which Hg is transferred between trophic levels. Early work by [Bloom et al. \(1991\)](#) in seepage lakes of varying pH in the Northern Highland Lake District, WI, considered whether varying deposition would affect the rates at which MeHg accumulates in biota. The authors sampled five lakes with common geology but a range of pH (5.1–7.2, including the experimentally acidified north basin of Little Rock Lake), which the authors ascribed to varying acidic deposition loads. The fraction of Hg was higher in *Perca flavescens*, yellow perch, than in seston, reflecting bioaccumulation of MeHg at higher trophic levels, but there was no detected effect of pH (and by extension, S deposition load) on relative bioaccumulation across lakes ([Bloom et al., 1991](#)). In Dickie Lake, Ontario, early studies documented the biomagnification of Hg in higher trophic levels of the lake. MeHg concentrations were 0.2 ng/g in sediments; Hg concentrations were 56.5 ng/g in periphyton, 143 ng/g in *P. flavescens*, and 703 ng/g in *Micropterus* spp. [largemouth and smallmouth bass, ([Kerry et al., 1991](#))]. Sulfate effects on biomagnification were not documented in these studies, although sulfate was measured at 6–8 mg/L in lake water, and microbial sulfate reduction and Hg methylation within the lake sediments were demonstrated with sediment slurry incubations ([Kerry et al., 1991](#)). There is evidence from 44 Adirondack lakes sampled in 2003–2004 that the legacy of acidic deposition, low surface water pH, low ANC, and high aluminum concentrations, all correlated with increasing Hg concentrations in zooplankton and Hg body burdens in fish and loons ([Yu et al., 2011](#)). Because these factors did not affect Hg or MeHg concentrations in water, [Yu et al. \(2011\)](#) concluded that acidic lake conditions enhanced bioaccumulation of MeHg.

Experimental S addition studies demonstrate that S addition increases Hg burdens in different trophic levels. Little Rock Lake, WI was the site of a multiyear (1985–1990), progressively acidic S addition study, in which the basins of this lake were separated by a plastic barrier, allowing the northern half to be experimentally acidified while the southern half served as a control. Abiotic compartments and biota of the lake were intensively sampled during the course of the experiment. Aqueous MeHg concentrations were 2 times higher in the treatment basin, while zooplankton MeHg concentrations (ng/g) were 1.8 times higher and microseston MeHg concentrations were 2.75 times higher in the treatment than the control basin ([Frost et al., 1999](#); [Watras and Bloom, 1992](#)). S amendment also affected MeHg in *Perca flavescens* (yellow perch); MeHg concentrations were 12–100% higher in 1-year-old yellow perch from the treatment basin, and the annual mean burden ( $\mu\text{g MeHg/fish}$ ) was 16–214% higher in the treatment basin over 5 of the 6 years of the experiment ([Frost et al., 1999](#); [Wiener et al., 1990](#)).

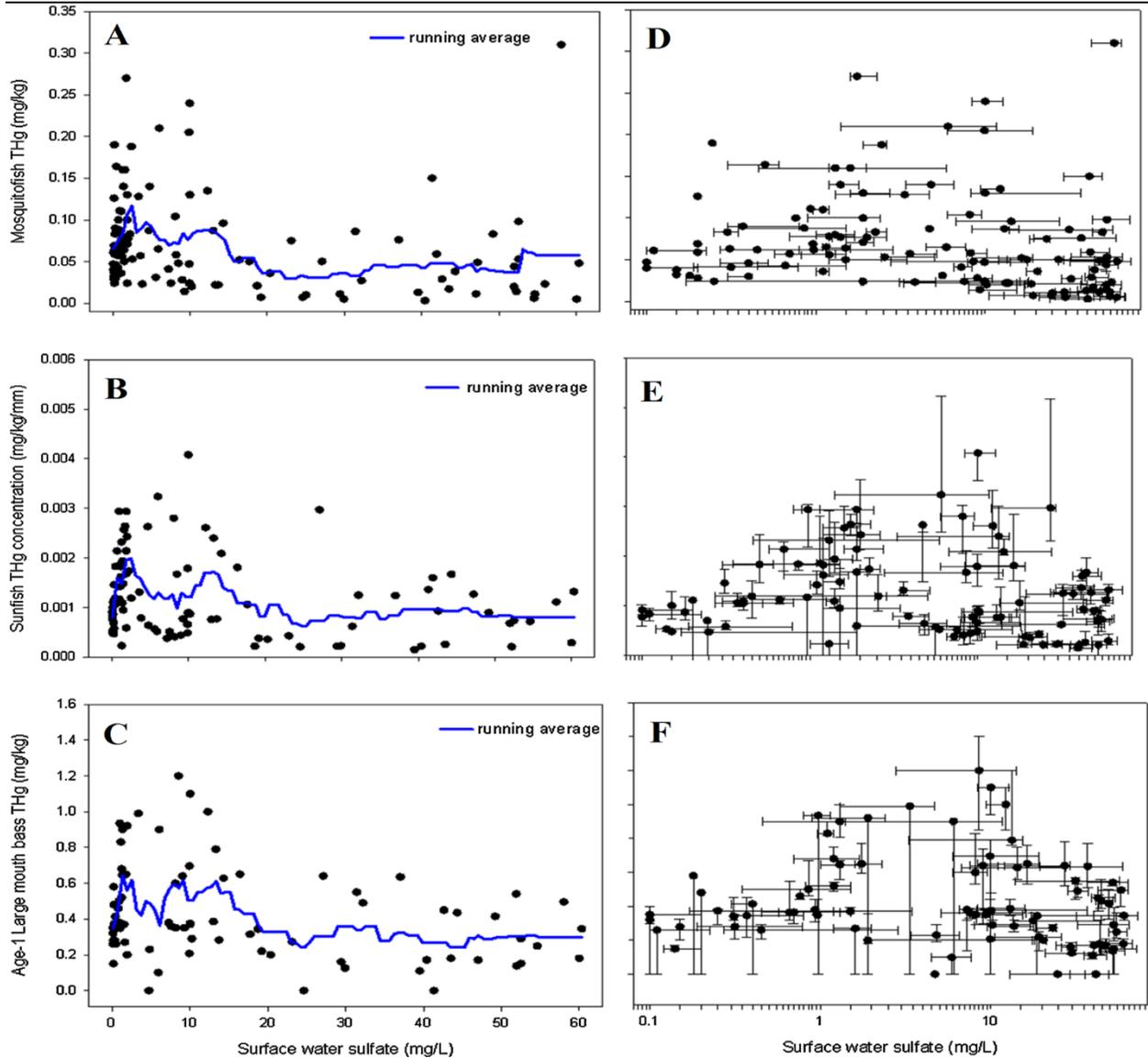
Decreasing S loads result in decreased Hg burdens in biota. The S addition experiment at the Marcell peat bog also shows the effects of S addition on Hg burdens in an animal on a lower trophic level. In the S addition and S recovery experiments at the S6 peat bog, Marcell Experimental Forest, MN, elevated S increased Hg levels in sampled *Culex* spp. (mosquito) larvae. Mosquito larvae are important to consider as a food source because they are widely consumed by invertebrate predators, fish, amphibians, and birds. In spring 2009, mosquito larvae Hg was 126% higher in plots that had received 32 kg S/ha/yr addition for 9 years than in mosquito larvae from the control plots ([Wasik et al., 2012](#)). The recovery plots received 32 kg S/ha/yr from 2001–2006 and no S addition after 2006, and when these plots were sampled in 2009, *Culex* spp. (mosquito) larvae had Hg levels 34% higher in recovery plots than in control plot mosquitoes, indicating legacy effects of past S addition. However, recovery plot mosquito Hg concentrations were 41% lower than in mosquitoes from plots still receiving S additions, indicating that decreases in S addition will decrease biotic Hg concentrations ([Wasik et al., 2012](#)).

In stormwater treatment wetlands draining the EAA in Florida, sulfate concentrations have been elevated by agricultural runoff, and concentrations ranged from 39–110 mg/L between 2000 and 2007. Under these very high sulfate surface water concentrations, Hg levels (mg Hg/kg fish) in bioindicator fish species *Gambusia holbrooki* (mosquitofish) were negatively correlated with inflow water sulfate concentrations ([Feng et al., 2014](#)) because the higher end of the sulfate concentration range reached levels inhibitory to SRPs. In the Everglades Protection Area, where water sulfate concentrations were lower and ranged from 0–60 mg/L in surface water, relationships between sulfate and fish Hg levels were more complicated. *Gambusia* spp. (mosquitofish), *Lepomis* spp. (sunfish), and largemouth bass were sampled annually between 1998 and 2009 ([Gabriel et al.,](#)

2014). In all three fishes, Hg tissue concentrations increased between 0–1 mg sulfate/L in the water, and reached their highest tissue levels between 1 and 12 mg sulfate/L (see [Figure 12-14](#)). Based on these relationships, [Gabriel et al. \(2014\)](#) recommended a sulfate water standard of 1 mg/L. Two papers challenged this analysis and interpretation of the sulfate and fish Hg data. In a commentary, [Julian et al. \(2015\)](#) suggested that the variability in fish Hg levels was too high to correlate with sulfate concentrations, and in analyses of largemouth bass collected between 2005–2011, Hg concentrations in fish correlated with alkalinity, pH, and specific conductance as well as sulfate ([Julian and Gu, 2015](#)). [Gabriel et al. \(2015\)](#) responded to Julian’s commentary by highlighting the similarity of fish Hg patterns to documented MeHg water column concentrations in the Florida Everglades and suggested that sulfate reductions are the most efficient way to reduce Hg loads in fish because about 60% of the Everglades area has sulfate concentrations exceeding 1 mg/L ([Orem et al., 2011](#)). Using structural equation modeling, [Pollman \(2014\)](#) showed that sulfate was second only to periphyton MeHg concentrations in predicting Hg burdens in mosquitofish in the Everglades, although the relationships among predictive factors were complex and involved both direct and indirect effects.

A number of studies document Hg burdens in fish without also quantifying contributions of S to methylation, but other relationships between S and MeHg documented in the 2008 ISA suggest that the findings of these studies may be relevant ([U.S. EPA, 2008a](#)). In the Alabama River basin around Mobile, AL, there was no relationship across 52 sites in the watershed between Hg burdens in largemouth bass and MeHg fractions in sediments or water ([Warner et al., 2005](#)). However, a subset of seven of the sites were downstream of wetlands, and in these sites the bass Hg burden was positively correlated with watershed area ( $r^2 = 0.71$ ), indicating that wetlands may contribute to higher Hg burdens in fish as well as to higher MeHg concentrations in water ([Warner et al., 2005](#)). In a study of Hg burdens in South Dakota, [Stone et al. \(2011\)](#) analyzed water quality and fish samples from one impoundment and five natural lakes, and found a positive correlation ( $R^2 = 0.928$ ) between water sulfate measurements and Hg in piscivorous *Sander vitreus* (walleye). However, sulfate concentrations were not reported, and sulfate measurements and fish samples were not collected simultaneously, with a gap of up to 3 years between collection of fish and water samples. In the Amistad International Reservoir, Texas, elevated MeHg in sediments of one branch of the reservoir correlated with Hg accumulation in young (age: 0–3 years) largemouth bass. The Devils River area had elevated sediment MeHg compared to the Rio Grande area of the reservoir (see [Appendix 12.3.5.1](#)), and the length-standardized mean of muscle Hg was 38% higher in Devils River than in Rio Grande bass ([Becker et al., 2011](#)). Of 138 largemouth bass (age >3 years) line-caught at the reservoir in April 2007, 77% exceeded the U.S. EPA recommended human consumption value of 0.3 mg Hg/kg (or 0.3 ppm), and mean fish

Hg was 0.51 mg/kg fish, although fishing site data for these samples were unavailable, preventing assessment of connections between sediment MeHg and Hg levels in these large fish (Becker et al., 2011).



L = liter; kg = kilogram; mg = milligram; mm = millimeter; THg = total mercury.

Panels A–C show the running average of mercury concentrations in (A) *Gambusia* spp. (n = 484), (B) *Lepomis* spp. (n = 2,559), and (C) *Micropterus salmoides* (n = 679). Panels D–F show the same data with sulfate transformed to a log scale to better illustrate the peak in fish Hg concentrations that approximately corresponds to sulfate concentrations of 1–10 mg/L. Samples were collected from 12 fish and 12 sulfate stations within the Everglades, between 1998–2009.

Source: adapted from Gabriel et al. (2014).

**Figure 12-14** Tissue mercury concentrations as a function of surface water sulfate concentrations (n = 2,360 surface water samples) in the Everglades Protection Area.

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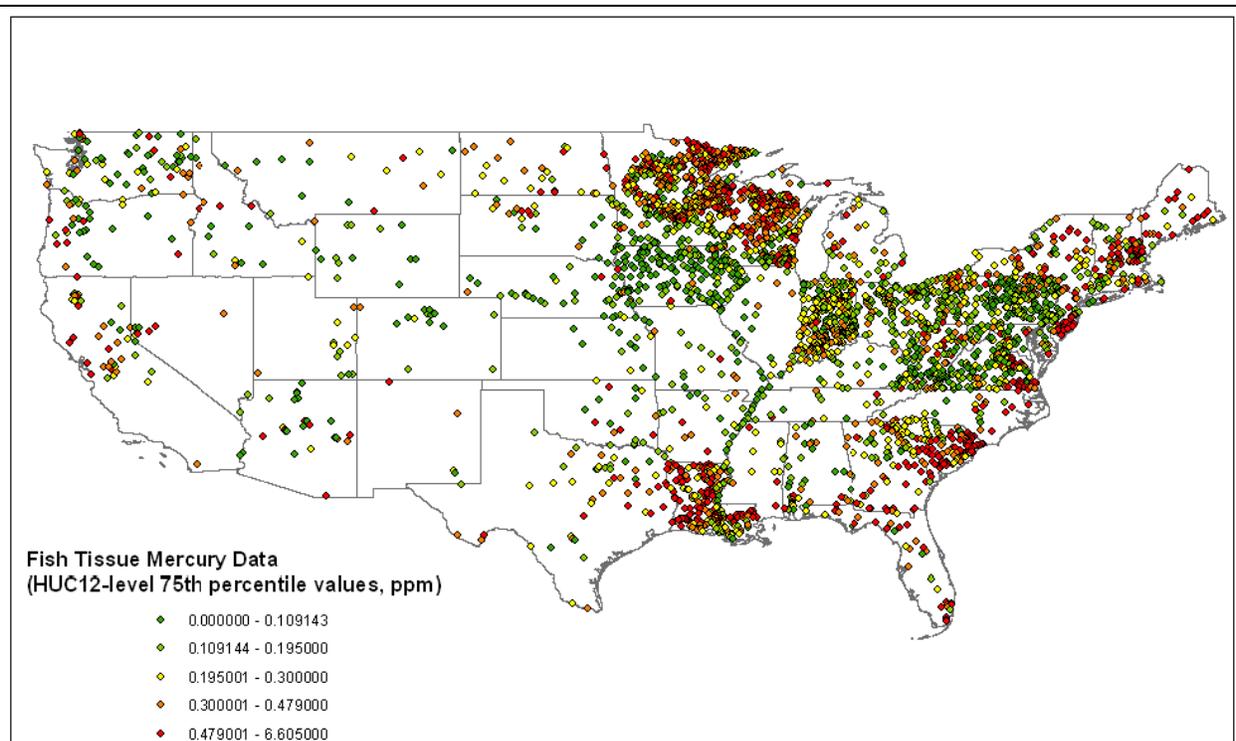
## 12.5 Extent and Distribution of Sensitive Ecosystems

Reservoirs in which water levels fluctuate enough to expose sediments may be particularly susceptible to S deposition effects on MeHg production because mud flats are directly exposed to the atmosphere and then flooded to create conditions favorable to Hg methylation by SRPs. Older work in the ELA, Ontario, showed that reservoir creation leads to a pulse of MeHg production. A small watershed was flooded in 1993, and Hg and MeHg fluxes were measured over the next decade ([St.Louis et al., 2004](#)). Before flooding, 90% of the annual total Hg input and 130% of the annual MeHg was retained by the wetland. In the first 3 years following flooding, 100–170% of the annual total Hg input was exported annually; and in years 5–9, 69–79% of the annual total Hg input was exported annually. MeHg levels were high following flooding, 60–80% in water, and 300–860% of the annual MeHg input was exported annually from the reservoir ([St.Louis et al., 2004](#)). The reservoir creation also affected Hg in the food web: the level of MeHg in zooplankton was 7 to 10 times higher in the first 3 years of flooding, and 14 to 30 times higher years 4–9, than MeHg in pre-flood zooplankton ([St.Louis et al., 2004](#)). Researchers stocked finescale dace (current scientific name, *Chrosomus neogaeus*) annually and found that the Hg body burden of the fish increased 306% following a year in the reservoir ([St.Louis et al., 2004](#)). More recently, at the Cottage Grove Reservoir, OR, elevated MeHg concentrations in the fall outflow (4–13% MeHg fraction compared to 0.5–7% MeHg in the river flowing into the reservoir) were linked to seasonal water fluctuations ([Eckley et al., 2015](#)). The reservoir water level is lowered from September to February to allow the dam to catch and regulate spring flooding, so 50% of the reservoir area is exposed mud flats in the winter. Sulfate was below detection limits (0.005 mg sulfate/g sediment, reported as 5 µg/g) in permanently inundated reservoir sediments, but was 0.0011 mg sulfate/g sediment (11 µg/g) in mudflat sediment. MeHg concentrations were higher at sediment surfaces than in the sediment profile at seasonally inundated sites, indicating that MeHg production was occurring there; in contrast, [MeHg] was constant across sediment depths in the permanently inundated sites, indicating that settling of MeHg into sediments was the only process occurring there ([Eckley et al., 2015](#)).

*The National-Scale Assessment of Mercury Risk to Populations with High Consumption of Self-Caught Freshwater Fish of 2011* ([U.S. EPA, 2011b](#)) compiled fish Hg load data on a national scale, which can be considered a county-wide sampling of ecosystems where Hg loads in fish are high. The assessment did not directly quantify or analyze sulfate effects, but it considered patterns of Hg deposition and Hg concentrations in freshwater fish caught between 2005–2009 by state regulatory agencies, and modeled the

extent to which reductions in Hg deposition would affect subsistence-level human consumers of fish from U.S. water bodies. Fish collections showed that there were elevated fish Hg levels in water bodies across the country, although high fish Hg concentrations were more common in the eastern U.S. [see [Figure 12-15 \(U.S. EPA, 2011b\)](#)]. In this study, 5% of total Hg deposition was attributed to coal and oil-fired electric utility steam generating units (EGUs), but EGUs contributed 9% to fish tissue levels of Hg.

The 2014 USGS's report on mercury in streams ([Wentz et al., 2014](#)) suggests that eastern water bodies, watersheds with high wetland cover, and watersheds with low population densities are linked to higher MeHg concentrations in streams and in stream biota.



HUC12 = 12-digit hydrologic unit code.

Source: [U.S. EPA \(2011b\)](#).

**Figure 12-15 Fish mercury concentrations across the U.S.**

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## 12.6 Critical Loads

There are currently no critical loads for SO<sub>x</sub> deposition related to the nonacidifying effects described in this appendix. There are European critical loads for Hg deposition and Hg effects upon human health and ecosystems. A critical load of 1 µg Hg/L in soil drainage water was set to protect drinking water ([Hettelingh et al., 2015](#)). A critical load of 0.3 mg Hg/kg fresh weight fish tissue was set to protect human health. A critical load to protect soil invertebrates and soil microbial process of 0.5 mg Hg/kg organic material was set for the humus layer of forest soils ([Hettelingh et al., 2015](#)). This source did not report critical loads in terms of areal deposition rates, but did map exceedances based on soil, water, and fish tissue samples, and found that about 59% of European natural areas received Hg deposition in exceedance of these critical loads ([Hettelingh et al., 2015](#)).

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## 12.7 Summary of Nonacidifying Sulfur Effects

Sulfate deposition has a number of effects beyond acidification in ecosystems. In the 2008 ISA, the evidence was sufficient to infer a causal relationship between S deposition and increased methylation of Hg in aquatic environments where the value of other factors was within adequate range for methylation. The 2008 ISA surveyed literature from approximately 1980 to 2008 and described the qualitative relationships between sulfate deposition and a number of ecological endpoints, including altered S cycling, sulfide phytotoxicity, internal eutrophication of aquatic systems, altered methane emissions, increased Hg methylation, and increased Hg loading in animals, particularly fish. New evidence from wetland and freshwater aquatic ecosystems strengthens and extends the causal findings of the 2008 ISA regarding nonacidifying sulfur effects and provides the basis for a new causal determination. [Table 12-13](#) summarizes recent thresholds and quantitative relationships describing effects of sulfate deposition. This new information strengthens the weight of evidence presented in the 2008 ISA, and consistent with the 2008 causal statement, **the body of evidence is sufficient to infer a causal relationship between S deposition and the alteration of Hg methylation in surface water, sediment, and soils in wetland and freshwater ecosystems.** In addition, recent research demonstrates sulfide phytotoxicity under current conditions in North American wetlands, consistent with the 2008 ISA's summary of sulfide phytotoxicity in European wetland and freshwater ecosystems. **The body of evidence is sufficient to infer a causal relationship between S deposition and changes in biota due to sulfide phytotoxicity including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems.**

**Table 12-13 Summary of quantitative effects of nonacidifying sulfur enrichment.**

Section of Nonacidifying Sulfur Effects Appendix	Threshold, Critical Level, or Quantitative Relationship	Reference
<a href="#">12.2.1</a>	2.5–7.9 times higher sulfate reduction in lake with 22.7 mg SO <sub>4</sub> <sup>2-</sup> /L than in lake with 9.0 mg SO <sub>4</sub> <sup>2-</sup> /L	<a href="#">Kleeberg et al. (2016)</a>
<a href="#">12.2.3</a>	34.1 mg S <sup>2-</sup> /L for plant root nutrient uptake	<a href="#">Koch et al. (1990)</a>
<a href="#">12.2.3</a>	48–50 mg SO <sub>4</sub> <sup>2-</sup> /L as a threshold to protect <i>Potamogeton</i> spp. and <i>Utricularia vulgaris</i>	<a href="#">Vermaat et al. (2016); Smolders et al. (2003)</a>
<a href="#">12.2.3</a>	0.3–29.5 mg S <sup>2-</sup> /L for altered growth, productivity, physiology, or mortality of 16 freshwater wetland emergent plant and aquatic submerged macrophyte species native to North America	<a href="#">Lamers et al. (2013)</a>
<a href="#">12.2.3</a>	250 mg SO <sub>4</sub> <sup>2-</sup> /L U.S. EPA aesthetic secondary water quality standard for human consumption	<a href="#">Pastor et al. (2017)</a>
<a href="#">12.2.3</a>	<7.5 mg/L sulfide to preserve growth rate of <i>Cladium jamaicense</i> , sawgrass, in Everglades	<a href="#">Li et al. (2009)</a>
<a href="#">12.2.3</a>	0.165 mg sulfide/L to protect <i>Zizania palustris</i> , wild rice	<a href="#">MPCA (2015a, 2015b)</a>
<a href="#">12.3.2</a>	Sulfate reduction rates increase 0.35 mg (sulfate reduced)/L/day with a 1 mg/L increase in sulfate addition	<a href="#">Kerry et al. (1991)</a>
<a href="#">12.3.3.1</a>	11.1 mg SO <sub>4</sub> <sup>2-</sup> /L added for peak MeHg production in incubation of sediments from Quabbin Reservoir, MA	<a href="#">Gilmour et al. (1992)</a>
<a href="#">12.3.3.1</a>	5.8–23 mg SO <sub>4</sub> <sup>2-</sup> /L added to change incubation of sediments from net demethylating to net demethylating, from Little Rock Lake, WI	<a href="#">Gilmour and Riedel (1995)</a>
<a href="#">12.3.3.1</a>	190 mg SO <sub>4</sub> <sup>2-</sup> /L added to increase MeHg production in incubation of peat from Sunday Lake, NY	<a href="#">Yu et al. (2010)</a>
<a href="#">12.3.3.1</a>	96.1 mg SO <sub>4</sub> <sup>2-</sup> /L increases methylation rates in incubations of sediment from South River, VA (ambient concentrations of 19.2 mg SO <sub>4</sub> <sup>2-</sup> /L)	<a href="#">Yu et al. (2012)</a>
<a href="#">12.3.3.5</a>	<3.6 mg C/L as dissolved organic carbon, microbial sulfate reduction did not occur 3.6–7.6 mg C/L of DOC, microbial sulfate reduction increases linearly with C increase >7.6 mg C/L, microbial sulfate reduction rate does not change	<a href="#">Watras et al. (2006)</a>
<a href="#">12.3.3.5</a>	20% organic material in sediments for peak MeHg concentrations in Adirondacks, NY watersheds	<a href="#">Yu et al. (2010)</a>
<a href="#">12.3.3.5</a>	2.65 ng/L increase in MeHg for every 10% increase in percentage organic matter	<a href="#">Hoggarth et al. (2015)</a>

**Table 12-13 (Continued): Summary of quantitative effects of nonacidifying sulfur enrichment.**

Section of Nonacidifying Sulfur Effects Appendix	Threshold, Critical Level, or Quantitative Relationship	Reference
<a href="#">12.3.3.5</a>	1 ng MeHg/L increase for each increase of 0.048 mg hydrophobic organic acid fraction of DOC/L	<a href="#">Hall et al. (2008)</a>
<a href="#">12.3.3.5</a>	0.34 ng Hg/L increase in Hg exported in streams for each 1 mg C/L increase in DOC from Northeast watersheds	<a href="#">Dittman et al. (2010)</a>
<a href="#">12.3.3.7</a>	1.0 mg N-NO <sub>3</sub> <sup>-</sup> /L in hypolimnion to prevent mercury methylation in Onondaga Lake, NY	<a href="#">Matthews et al. (2013)</a>
<a href="#">12.3.4.1</a>	Addition of 4.8 mg SO <sub>4</sub> <sup>2-</sup> /L increases methylation rate in Little Rock Lake, WI (ambient water concentration, 2.4 mg SO <sub>4</sub> <sup>2-</sup> /L)	<a href="#">Gilmour and Riedel (1995)</a>
<a href="#">12.3.4.1</a>	10.8 ng MeHg/L increase for each 1 mg/L increase in H <sub>2</sub> S in lake water	<a href="#">Watras et al. (2006)</a>
<a href="#">12.3.4.1</a>	14.4 mg total lake MeHg increase for every 1 kg/ha increase in SO <sub>x</sub> deposition	<a href="#">Watras and Morrison (2008)</a>
<a href="#">12.3.4.1</a>	14 kg S/ha increased MeHg concentrations in peat mesocosm	<a href="#">Branfireun et al. (1999)</a>
<a href="#">12.3.4.1</a>	<8.3 kg S/ha addition for pore water MeHg in peatlands	<a href="#">Mitchell et al. (2008a)</a>
<a href="#">12.3.4.1</a>	<32 kg S/ha/yr to control pore water MeHg concentrations and fraction of total Hg in peatlands	<a href="#">Jeremiason et al. (2006)</a>
<a href="#">12.3.4.1</a>	<20 kg S/ha/yr to control pore water total Hg concentrations and MeHg concentrations in peatlands	<a href="#">Bergman et al. (2012)</a>
<a href="#">12.3.4.3</a>	1 mg/L sulfate in surface water to keep MeHg concentrations low in Everglades surface water	<a href="#">Corrales et al. (2011)</a>
<a href="#">12.3.4.3</a>	>20 mg SO <sub>4</sub> <sup>2-</sup> /L inhibits Hg methylation in Everglades due to sulfide accumulation	<a href="#">Orem et al. (2011)</a>
<a href="#">12.3.4.3</a>	>39 mg SO <sub>4</sub> <sup>2-</sup> /L inhibits Hg methylation in Everglades due to sulfide accumulation	<a href="#">Zheng et al. (2013)</a>
<a href="#">12.3.4.3</a>	50 ng total Hg/L, the U.S. EPA water quality criterion	<a href="#">Alpers et al. (2014)</a>
<a href="#">12.3.5.1</a>	<10 kg S/ha/yr, decreases in S deposition result in declining fish Hg concentrations on a decadal time scale in Isle Royale lakes	<a href="#">Drevnick et al. (2007)</a>
<a href="#">12.3.5.1</a>	MeHg concentrations increased 0.037 ng/L for each 1 mg/L increase in sulfate in pore water in peatlands	<a href="#">Mitchell et al. (2009)</a>
<a href="#">12.3.5.1</a>	0.06 ng increase in MeHg per gram of sediment for every 1 mg/L increase in sulfate pore water concentration in South River, VA	<a href="#">Yu et al. (2012)</a>
<a href="#">12.3.5.1</a>	0.11 ng/L increase in stream MeHg concentration for each mg/L sulfate decrease in Archer Creek, NY	<a href="#">Selvendiran et al. (2008a)</a>

**Table 12-13 (Continued): Summary of quantitative effects of nonacidifying sulfur enrichment.**

Section of Nonacidifying Sulfur Effects Appendix	Threshold, Critical Level, or Quantitative Relationship	Reference
<a href="#">12.3.5.1</a>	65% higher MeHg in Devils River branch ( $\text{SO}_4^{2-} \leq 23$ mg/L) than in Rio Grande branch ( $\text{SO}_4^{2-} \leq 230$ mg/L) of Amistad Reservoir, TX	<a href="#">Becker et al. (2011)</a>
<a href="#">12.3.5.1</a>	MeHg increases with S reduction in wetland where average $\text{SO}_4^{2-} \leq 5$ mg/L, but not in wetland where $\text{SO}_4^{2-} \leq 500$ mg/L	<a href="#">Johnson et al. (2016b)</a>
<a href="#">12.3.5.2</a>	11.9 kg S deposition/ha/yr increases Hg levels in largemouth bass compared to ecoregions where deposition was 7.7–8.1 kg S/ha/yr in Texas	<a href="#">Drenner et al. (2011)</a>
<a href="#">12.3.5.2</a>	MeHg decreased in surface water and in <i>Perca flavescens</i> when S deposition decreased from 6.44 kg S/ha/yr (1998) to 3.35 kg S/ha/yr (2012) in two lakes in Voyageurs NP	<a href="#">Brigham et al. (2014)</a>
<a href="#">12.3.5.3</a>	When conductivity and aromatic DOC remain constant, surface water MeHg increases 0.3 ng/L for each mg/L increase in sulfate concentrations	<a href="#">Hall et al. (2009a)</a>
<a href="#">12.4</a>	<32 kg S/ha/yr, for Hg load in larval <i>Culex</i> spp. (mosquitoes) in peatlands	<a href="#">Wasik et al. (2012)</a>
<a href="#">12.4</a>	1 mg/L sulfate in surface water to keep Hg concentrations low in fish: <i>Gambusia</i> spp., <i>Lepomis</i> spp., and <i>Micropterus salmoides</i> , in the Everglades	<a href="#">Gabriel et al. (2014)</a>

C = carbon; DOC = dissolved organic carbon;  $\text{H}_2\text{S}$  = hydrogen sulfide; ha = hectare; Hg = mercury; kg = kilogram; L = liter; MeHg = methylmercury; mg = milligram; ng = nanogram; S = sulfur; yr = year.

### 12.7.1 Terrestrial Sulfur Cycling

The 2008 ISA noted that S is an essential plant nutrient and that S deposition can affect plant protein synthesis by affecting S availability for S-containing amino acids as well by affecting N uptake. Sulfate can be taken up directly by plant roots as well as by soil microbes, or it can adsorb to soil particles. The 2008 ISA reported that watersheds in the Southeast, which retained more S than was deposited during high S loading in the 1980s, received decreasing S deposition over the 1990s but continued to export historically deposited sulfate in streams. In the Northeast, budgets of sites from the 1980s indicated that high S deposition caused high sulfate export in streams. On a national level, S deposition resulted in increased S content in organic matter in soils, and studies suggested that mineralization of this stored S may contribute to elevated sulfate leaching for decades after reductions in S deposition. More recent research confirms that watersheds

in the Northeast continue to leach more S than they currently receive from S deposition, as much as 24–45% more S than the S deposition load ([Mitchell et al., 2011](#)).

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### 12.7.2 Aquatic Sulfur Cycling

The 2008 ISA reported that nonacidifying effects of S in freshwater systems will be affected by water residence times, with larger lakes and beaver ponds providing ample opportunity for SRPs to reduce sulfate and generate acid-neutralizing capacity (ANC). Early work showed that a 1 mg/L increase in sulfate concentration in Dickie Lake, Ontario, increased S reduction rates 0.35 mg S/L/day ([Kerry et al., 1991](#)).

The 2008 ISA reported the role of wetlands in removing sulfate from surface water and storing it in sediments or biomass, but it also highlighted the way drought reverses this capacity to make wetlands sources of S to downstream waters. Specifically, studies reviewed in the 2008 ISA demonstrated that under drought conditions, sulfide in previously saturated moss or sediments is exposed to atmospheric oxygen and reoxidized to sulfate. This resulted in high sulfate concentrations in surface water when the water table rose to its former level, and MAGIC modeling showed that variable water levels due to climate change-induced droughts would delay ANC recovery in the Plastic Lake Watershed, NY ([Aherne et al., 2004](#)). In Little Rock Lake, WI, water level fluctuation due to drought added an additional 5 kg S/ha/yr from internal ecosystem S stores to the lake ([Watras and Morrison, 2008](#)). Recent work confirmed that periods of drought result in elevated water sulfate concentrations during the recovery period following the drought ([Wasik et al., 2012](#)).

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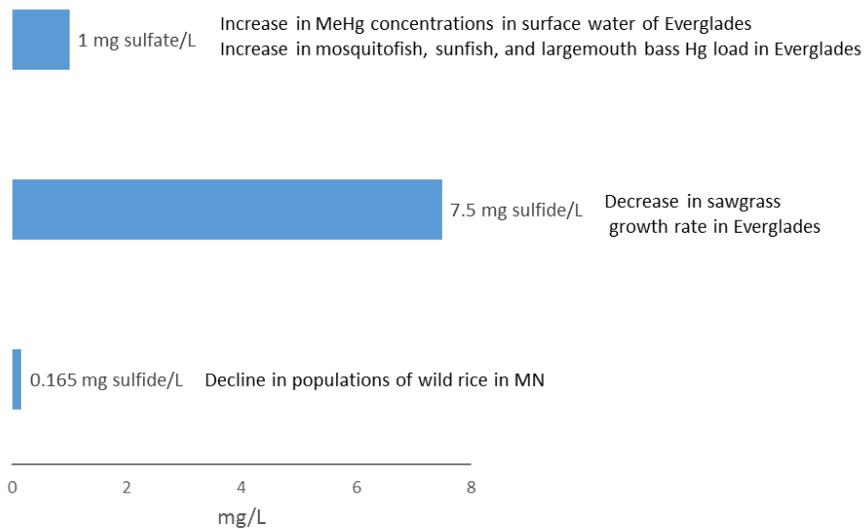
### 12.7.3 Sulfide Toxicity

In aquatic systems or in saturated soils, SRPs convert sulfate into sulfide, which inhibits nutrient uptake in freshwater aquatic and wetland plant species. The 2008 ISA showed that sulfide toxicity reduced biomass of wetland plants and aquatic macrophytes in mesocosms under aquatic S concentrations higher than those that occur in U.S. regions with high S deposition. Recent research has shown sulfide phytotoxicity occurs at ambient aquatic S concentrations within multiple ecosystems in the U.S. ([Figure 12-16](#)). Sulfide decreases total plant cover and cover of dominant species in a New York fen ([Simkin et al., 2013](#)) and decreases the growth rate of Everglades, FL, keystone species *Cladium jamaicense* (sawgrass) at surface water concentrations of 7.5 mg sulfide/L ([Li et al., 2009](#)). The state of Minnesota is also working on a sulfide standard to protect the economically and culturally important *Zizania palustris* (wild rice) and has proposed a

water standard of 0.165 mg sulfide/L to protect the species ([MPCA, 2015a](#)). Additionally, a review by [Lamers et al. \(2013\)](#) reported experimentally-determined sulfide toxicity values between 0.3–29.5 mg S<sup>2-</sup>/L for 16 North American species (see [Table 12-2](#)), and there are sulfate tolerance values for North American fish and macroinvertebrates based on USGS’s NAWQA. This new information shows that sulfide toxicity occurs in North American wetlands under current deposition conditions, and **the body of evidence is sufficient to infer a causal relationship between S deposition and changes in biota due to sulfide phytotoxicity including alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetland and freshwater ecosystems.**

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### Water quality thresholds for non-acidifying S effects



L = liter; Hg = mercury; MeHg = methylmercury; mg = milligram; S = sulfide.

**Figure 12-16** Thresholds of sulfate or sulfide concentrations in water, which cause biological and chemical effects in ecosystems.

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#### 12.7.4 Internal Eutrophication

The 2008 ISA described the contribution of S deposition to internal eutrophication in aquatic systems. In wetland and lake waters, sulfate is reduced to sulfide, which reacts with Fe to form insoluble iron sulfide complexes. In many ecosystems, the iron in this reaction is provided by  $\text{FePO}_4$ , which releases phosphorus as it forms  $\text{FeS}_x$  thus contributing to downstream eutrophication. More recently, internal eutrophication caused by sulfate addition was observed in mesocosms of samples collected from Lake Moshui, China ([Yu et al., 2015](#)).

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#### 12.7.5 Effects on Methane Production

Sulfate deposition can shift microbial community interactions, resulting in lower methane emissions. The 2008 ISA documented the suppression of methane emissions in wetland soils by sulfate addition in several studies and noted that 15 kg S/ha/yr (the lowest S load in experimental treatments) suppressed methane emissions to the same extent as higher S loads ([Gauci et al., 2004](#)). There is no recent research that relates  $\text{SO}_x$  deposition to wetland methane emissions, but recent research has confirmed the underlying microbial mechanisms of this process. Sulfate deposition increases the abundance or metabolic activity of SRPs. In many freshwater water bodies, including wetlands, low primary productivity limits microbially available, labile C during the growing season when higher temperatures favor microbial activity. Recent research documents competition among microbial guilds for labile C, and when SRPs are favored, competing methanogens decline, resulting in suppressed methane emissions ([Bae et al., 2015](#); [He et al., 2015](#); [Paulo et al., 2015](#)). However, there is also evidence of methanogens forming syntrophic associations with SRPs ([Paranjape and Hall, 2017](#)), suggesting that these groups may not always directly compete in all ecosystems.

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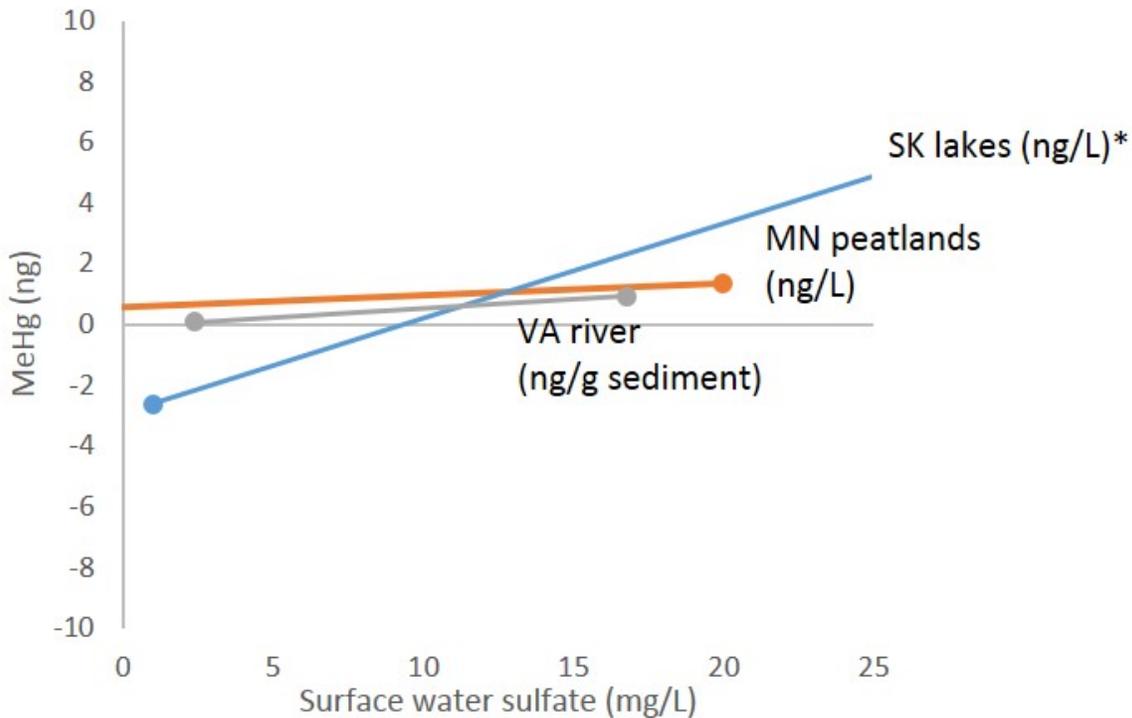
#### 12.7.6 The Role of Microbes in Mercury Methylation

The 2008 ISA identified sulfur-reducing bacteria as responsible for Hg methylation, and identified anoxic wetland and lake bottom sediments as their location within watersheds. More recent research confirms that SRB in these locations methylate Hg, but also shows that the ability to methylate Hg is more broadly distributed in the prokaryotic taxa and across the environment.

Recent research suggests that the *hgcAB* gene pair confers the ability to methylate inorganic Hg. *HgcAB* has been sequenced in lineages within bacteria and archaea, which

is why this document refers to mercury methylators as SRPs rather than the SRB described in the previous ISA ([Gilmour et al., 2013](#)). Experimental work has shown that MeHg production rates vary among prokaryotic strains ([Shao et al., 2012](#)), but also has confirmed that sulfate addition causes Hg methylation in the Everglades ([Goñi-Urriza et al., 2015](#)), as abundant syntrophs (heterotrophs dependent on the metabolic byproducts of other microbes) were responsible for both Hg methylation and sulfate reduction ([Bae et al., 2014](#)).

Recent research shows that the microbial communities responsible for Hg methylation are more widely distributed than in the freshwater lake or wetland bottom sediments described in the 2008 ISA ([Figure 12-17](#)). There is evidence from Sweden, Finland, and the U.S. that disturbances in terrestrial forests stimulate mercury methylation in soils and MeHg export to surface waters ([Kronberg et al., 2016](#); [Poulin et al., 2016](#); [Ukonmaanaho et al., 2016](#)). The *Sphagnum* (moss) mat of wetlands was the most efficient retention site of deposited Hg in a forested watershed in the Adirondacks ([Selvendiran et al., 2008b](#)), as well as an important location of mercury methylation within peat wetlands in New York and Wisconsin ([Yu et al., 2010](#); [Creswell et al., 2008](#); [Selvendiran et al., 2008b](#)). Experiments using samples from rivers or streams in Virginia, Minnesota, or Germany showed that higher sulfate concentrations increased methylation rates or [MeHg] ([Frohne et al., 2012](#); [Yu et al., 2012](#); [Tsui et al., 2008](#)), with a 0.06 ng/L increase in MeHg per gram of sediment for every 1 mg/L increase in sulfate pore water concentration in South River, VA ([Yu et al., 2012](#)). New research shows that SRPs actively methylate Hg within periphyton, the aquatic biofilms attached to substrate or macrophytes in oxic freshwater environments ([Correia et al., 2012](#); [Achá et al., 2011](#)). MeHg production has also been documented in estuarine and marine sediments of the Chesapeake Bay ([Hollweg et al., 2009](#)) and in the marine water columns sampled at 20 to 327 m depths in the Canadian Arctic Archipelago ([Lehnherr et al., 2011](#)).



C = carbon; cm = centimeter; DOM = dissolved organic matter; g = gram; L = liter; MeHg = methylmercury; mg = milligram; mS = millisiemens; ng = nanogram; SK = Saskatchewan;  $\text{SO}_4^{2-}$  = sulfate.

Note: A study of prairie lakes and wetlands in Saskatchewan found that conductivity, aromatic DOM, and sulfate concentrations correlate with water MeHg ( $\text{ng MeHg/L} = -2.94 - 0.44 (\text{conductivity, mS/cm}) + 0.303 (\text{mg SO}_4^{2-}/\text{L}) - 0.268 (\text{aromatic fraction of DOM, L/mg C/cm})$ ). Simple linear regressions relate MeHg to water sulfate concentrations in Minnesota peatlands ( $\text{water ng MeHg/L} = 0.58 + 0.037 \text{ mg SO}_4^{2-}/\text{L}$ ) and in South River, VA ( $\text{riverbed ng MeHg/g sediment} = -0.08 + 0.059 \text{ mg SO}_4^{2-}/\text{L}$ ).

**Figure 12-17 Linear relationships between sulfate and methylmercury concentrations in published studies.**

As a microbial process, Hg methylation is determined not just by sulfate and Hg concentrations, but by other environmental and nutritional requirements of SRPs: pH, temperature, and water quality parameters, and carbon supply. The 2008 ISA identified pH and dissolved organic carbon (DOC) to be major controls on Hg production, with low pH and moderately high DOC correlating with high fish MeHg levels in lakes. The 2008 ISA also identified wetland area or density as an important determinant of MeHg bioaccumulation and export in watersheds. Recent research presented in [Appendix 12.3.3](#) evaluates temperature, total Hg concentration, pH, organic matter in water and sediments, iron, and nitrate for their influence on Hg methylation rates.

The 2008 ISA identified organic C as an important control on microbial sulfate reduction and Hg methylation, and recent research has quantified this relationship. In Little Rock Lake, WI, DOC concentrations had to be at least 3.6 mg C/L to allow microbial sulfate

reduction, and microbial sulfate reduction increased linearly with an increase of C only when DOC was in the range of 3.6–7.6 mg C/L (Watras et al., 2006). Across prairie potholes in Saskatchewan, surface water [MeHg] increased 2.65 ng/L for every 10% increase in percentage organic matter in underlying sediment (Hoggarth et al., 2015). In wetlands, rivers, and lakes of the Mississippi River delta, LA, there was a 1 ng MeHg/L increase in surface water for each additional 0.048 mg hydrophobic organic acid fraction (aromatic carbon typical of peat) of DOC/L (Hall et al., 2008).

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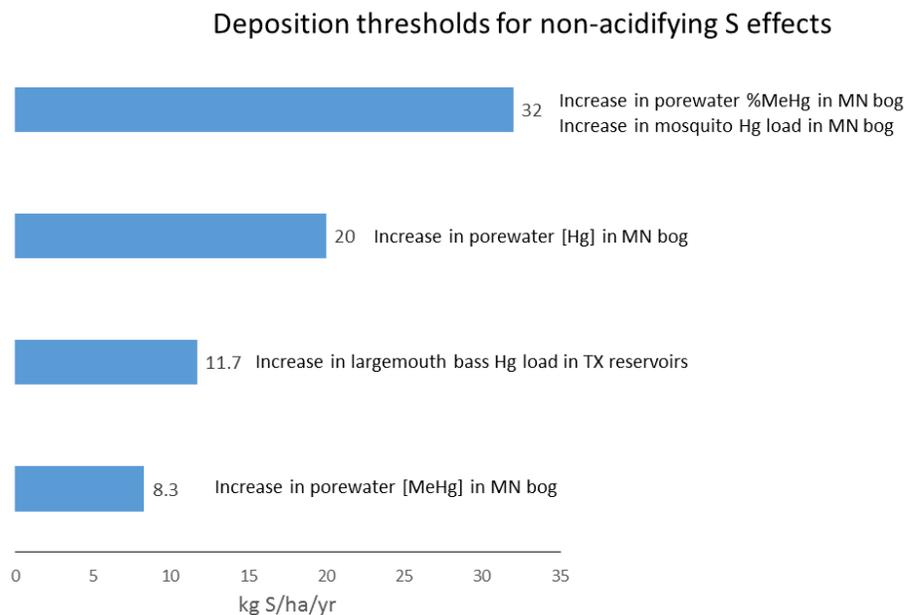
### 12.7.7 Impacts of Sulfur upon Mercury Cycling

Based on experimental evidence, the 2008 ISA identified maximum MeHg production occurring at sulfate concentrations of 200–400  $\mu\text{eq sulfate/L}$  (9.6–19.2 mg  $\text{SO}_4^{2-}/\text{L}$ ) and noted that waters under S deposition in the U.S. have sulfate concentrations in the range of 60–200  $\mu\text{eq sulfate/L}$  (2.9–9.6 mg  $\text{SO}_4^{2-}/\text{L}$ ). More recent research shows that detectable mercury methylation and bioaccumulation occurs at water sulfate concentrations  $>1$  mg/L in the Everglades (Gabriel et al., 2014; Corrales et al., 2011) and at ambient S deposition and water sulfate concentrations within the U.S. There was a positive relationship between sulfate reduction and concentrations of MeHg in the hypolimnion of Little Rock Lake, WI, with a 10.8 ng MeHg/L increase for each mg S/L reduced (Watras et al., 2006). There was also a positive relationship at this site between total lake MeHg and annual  $\text{SO}_x$  deposition, with a 14.4 mg MeHg/lake increase for every 1 kg S/ha/yr increase in  $\text{SO}_x$  deposition (Watras and Morrison, 2008).

There are multiple lines of evidence of a positive relationship between sulfate surface water concentrations and MeHg concentration or production in multiple freshwater systems. Both experimental manipulations and observational studies show that higher sulfate concentrations in peat wetlands increase MeHg concentrations (Figure 12-18). Experimental addition of sulfate to Bog Lake Fen in Minnesota showed that 8.3 kg S/ha increased pore water [MeHg] (Mitchell et al., 2008a), and 32 kg S/ha/yr increased pore water [MeHg] as well as MeHg fraction of total Hg, or %MeHg (Jeremiason et al., 2006). In other bogs sampled in the same region of Minnesota and Ontario, [MeHg] in water increased 0.037 ng/L for each 1 mg sulfate/L increase (Mitchell et al., 2009). These results were confirmed in a peatland S addition experiment in Sweden, which found that 20 kg S/ha/yr addition to the peat increased [MeHg] (Akerblom et al., 2013; Bergman et al., 2012).

Recent work also established positive relationships between sulfate and MeHg in ecosystems other than peat wetlands. In prairie potholes in the West (Hoggarth et al., 2015), with surface water MeHg increasing 0.3 ng/L for each additional mg sulfate/L

where conductivity and aromatic DOC remain constant (Hall et al., 2009a). In a freshwater marsh in the Everglades, water [MeHg] concentrations increased when sulfate concentrations exceeded 1 mg sulfate/L (Corrales et al., 2011), which is also an important threshold value for fish in the Everglades (see below). There are also recent ecosystem-scale studies that show that sulfate reduction and MeHg can be correlated at the landscape level. At the watershed level in the Adirondacks, [MeHg] in stream outflows was negatively correlated with sulfate concentration (Selvendiran et al., 2009), with a 0.11 ng/L increase in stream [MeHg] for each mg sulfate/L removed from surface water (Selvendiran et al., 2008a).



ha = hectare; Hg = mercury; kg = kilogram; MeHg = methylmercury; S = sulfur; yr = year.

**Figure 12-18** Thresholds of sulfate addition or deposition from published studies which affect chemical or biological changes in ecosystems.

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## 12.7.8 Sensitive Ecosystems

The 2008 ISA identified ecosystems in the Northeast as particularly sensitive to Hg methylation in response to S deposition, because many watersheds there have abundant wetlands and freshwater water bodies with high DOC and low pH. Recent analyses confirm that ecosystems east of the Mississippi tend to have higher Hg concentrations in fish ([Wentz et al., 2014](#); [U.S. EPA, 2011b](#)). Recent papers suggest that reservoirs with high water-level fluctuation or high algal productivity also have high methylmercury production or bioaccumulation within fishes ([Eckley et al., 2017](#); [Noh et al., 2016](#); [Eckley et al., 2015](#); [Becker et al., 2011](#)), and that at the ecoregion level, reservoir fish Hg concentrations correlate with both Hg and S deposition ([Drenner et al., 2011](#)).

Recent research in the Yolo Bypass Wildlife Area, CA, indicates that Hg methylation occurs in both permanent and agricultural wetlands and was higher in the agricultural wetlands where rice is grown ([Alpers et al., 2014](#); [Marvin-Dipasquale et al., 2014](#)). Hg methylation in this system was associated with Mn reduction, and then to a lesser extent with Fe reduction, and was only marginally associated with S reduction; sulfate addition did not affect Hg methylation ([Alpers et al., 2014](#); [Marvin-Dipasquale et al., 2014](#)). However, MeHg produced in the sediments where rice grew was highly correlated with MeHg concentrations in rice seeds ([Windham-Myers et al., 2014a](#)), suggesting a route to human exposure, and there were higher MeHg burdens in several animal species collected from agricultural wetlands than from permanent marshes (see below).

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## 12.7.9 Mercury Effects on Animal Species

Mercury is a developmental, neurological, endocrine, and reproductive toxin across animal species. It is transformed by SRPs from inorganic Hg into methylmercury (MeHg), which forms strong complexes with thiosulfate and sulfhydryl groups of organic molecules. This bound MeHg accumulates in biota in successively higher concentrations at ascending trophic levels. The 2008 ISA documented Hg accumulation in four turtle species, songbirds, insectivorous passerines, and the common loon (*Gavia immer*). A recent report by the USGS notes that Hg accumulation has also been documented in insectivorous songbirds and bats ([Wentz et al., 2014](#)). In recent research conducted in the Yolo Bypass, CA, higher water [MeHg] in agricultural rice-producing wetlands than in permanent marshes led to higher MeHg concentrations in mosquitofish (*Gambusia affinis*) and Mississippi silversides (*Menidia audens*) from the agricultural wetland than from the permanent marshes ([Ackerman and Eagles-Smith, 2010](#)).

The 2008 ISA reported that 23 states had issued fish advisories by 2007 in response to the U.S. EPA's fish tissue criterion set to protect human health of 0.3 µg MeHg/g fish, or 0.3 ppm. The 2008 ISA reported on the negative impacts of Hg on development, morphology, survival, or reproduction in the following fish species: walleye (*Stizostedion vitreum*), grayling (*Thymallus thymallus*), mummichog (*Fundulus heteroclitus*), rainbow trout (*Oncorhynchus mykiss*), fathead minnows (*Pimephales promelas*), and zebrafish (*Danio rerio*). However, a recent report on Hg in streams of the U.S. by the USGS summarizes current research that birds, fish, and fish-eating wildlife experience negative effects of Hg at lower concentrations than the 0.3 ppm criteria ([Wentz et al., 2014](#)).

The 2008 ISA reviewed two studies that considered the link between S deposition and Hg levels in fish ([Drevnick et al., 2007](#); [Hrabik and Watras, 2002](#)); both studies showed that decreases in S deposition resulted in decreases in fish MeHg levels. Recent research supports this finding in Voyageurs National Park (a Class I area) in Ryan Lake between 1998–2012 ([Brigham et al., 2014](#)), when decreasing S deposition correlated with decreasing fish Hg. In addition, a survey of fish caught in Texas reservoirs found that fish in the highest deposition region (11.7 kg S/ha/yr) had significantly higher mean Hg levels than fish from other regions ([Drenner et al., 2011](#)). Experimental S addition to the Marcell peat bog in Minnesota demonstrated that 32 kg S/ha/yr increased the Hg concentrations in larval *Culex* spp. (mosquitoes), which are an important food source for both aquatic and terrestrial species ([Wasik et al., 2012](#)).

In addition to the studies that consider S deposition, there are recent studies that consider sulfate concentrations in water in relation to fish Hg concentrations. A study of fish from six lakes in South Dakota found a positive correlation between sulfate water concentrations and walleye Hg concentrations ([Stone et al., 2011](#)). The marshes of the Everglades receive high S loading as agricultural runoff, and recent analysis of Hg loads in mosquitofish, sunfish (*Lepomis* spp.), and largemouth bass (*Micropterus salmoides*) collected from 1998–2009 showed that Hg levels in fish were highest when sulfate concentrations were between 1 and 12 mg sulfate/L; the researchers proposed 1 mg sulfate/L as a water standard ([Gabriel et al., 2014](#)).

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## 12.8 Supplemental Materials: Mercury Cycling

This appendix describes the deposition and cycling of mercury within North American ecosystems. Connections to sulfur cycling are emphasized where such information is available. This appendix provides background information and context for the discussion of nonacidifying sulfur stimulation of mercury methylation in wetland and aquatic ecosystems ([Appendix 12](#)).

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### 12.8.1 Transfer of Mercury from the Atmosphere to Terrestrial Ecosystems

Mercury enters most natural terrestrial and aquatic ecosystems in the U.S. via atmospheric deposition, although both active and historic mining and industrial sites have contaminated soil and water in many ecosystems. Sources and atmospheric processes governing Hg deposition are covered more exhaustively elsewhere ([Wentz et al., 2014](#); [Pirrone et al., 2010](#)). For the purposes of this section, we will focus on the deposition of reactive Hg, which is deposited into ecosystems in the form of free Hg(II), particulate-bound Hg, or as MeHg. In a jack pine/birch forest in the ELA sampled in 1998–1999, wet deposition was 71,000,000 ng/ha/yr (reported as 71 mg total Hg/ha/yr), with dry deposition estimated at 9,000,000 ng/ha/yr [reported as 9 mg/ha/yr in ([St Louis et al., 2001](#))].

Foliage is an important Hg pool in both forested and wetland ecosystems because it can directly absorb Hg deposition as well as store Hg taken up by plant roots. In the Arbutus Lake watershed in the Adirondack Mountains, Hg in the *Alnus* and *Betula* overstory was 3,080 ng Hg/m<sup>2</sup> (3.08 µg Hg/m<sup>2</sup>), and was 9,480 ng/m<sup>2</sup> (9.48 µg/m<sup>2</sup>) in the *Sphagnum* mat of the wetlands ([Selvendiran et al., 2008b](#)). In a 3-year-long Hg tracer isotope annual addition experiment at ELA, upland canopy and ground vegetation retained 40% of added Hg. In a wetland ecosystem, vegetation retained 80% of added Hg ([Harris et al., 2007](#)). Although the wetland ecosystems exported Hg and MeHg to an adjacent lake in the watershed during the course of the study, the Hg was from sources existing before the start of the experiment, indicating that Hg storage in wetland vegetation may have a residence time greater than 1 year ([Harris et al., 2007](#)).

Foliage also represents an important flux of Hg; following senescence, leaf litter becomes the substrate for microbial decomposition, and Hg moves out of plant biomass and into microbial biomass, soil, or water. Flux of total Hg from litter in the ELA, Ontario, was twice that of wet deposition in litter from upland trees and was of a similar magnitude to deposition in litter from wetland shrubs and trees [72,000,000 ng/ha/yr or 72 mg

Hg/ha/yr, and 88,000,000 ng/ha/yr or 88 mg/ha/yr; ([St Louis et al., 2001](#))]. The organic horizon of the soil, where litter and microbial communities are concentrated, was a major sink of Hg within the forested and wetland ecosystems for the 20 years preceding this study, with annual Hg accumulation rates of 130,000,000 ng Hg/ha/yr (reported as 130 mg Hg/ha/yr) for ridgetop soils (160% of total annual deposition), 200,000,000 ng/ha/yr (200 mg/ha/yr) for upland forest (250% of deposition), and 590,000,000 ng/ha/yr (590 mg/ha/yr) in wet soils supporting *Sphagnum* mosses [7.4 times annual deposition; ([St Louis et al., 2001](#))]. In forest catchments, much of the Hg deposition is retained in soil ([St Louis et al., 2001](#); [St. Louis et al., 1996](#)), as confirmed by the Hg tracer isotope addition experiment in ELA, which found that after 3 years of Hg addition, 58% of the added Hg was retained in soil in the upland forest catchment ([Harris et al., 2007](#)). The length of residence within the soil for Hg likely depends on the same factors that control the storage of organic matter, such as soil structure, temperature, precipitation, and timing of disturbances, particularly of wildfire.

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## 12.8.2 Transfer of Mercury from Terrestrial to Aquatic Ecosystems

When Hg is released from plant tissue, detritus, or soil particles into surface water or the soil solution, it becomes available for transport into aquatic systems. In five boreal forest catchments in the ELA, Ontario, measured during the period 1990–1993, the flux of total Hg from the forest into water bodies was estimated to be 14,000,000–21,000,000 ng/ha/yr (reported as 14–21 mg/ha/yr 28–42% of annual Hg input), in response to approximately 47,000,000 ng/ha/yr (47 mg/ha/yr) wet + dry deposition of Hg, and estimated contributions from weathering of granite of as much as 3,000,000 ng/ha/yr [reported as 3 mg/ha/yr in [St. Louis et al. \(1996\)](#)]. On Isle Royale, a large island in Lake Superior and a Class I Area, researchers estimated that lakes received one-third of their annual Hg load directly from atmospheric deposition, and the remaining two-thirds of annual Hg load was mobilized from soils in the watersheds ([Drevnick et al., 2007](#)). In aquatic environments, specialized microbes (SRPs; as well as iron-reducing bacteria) in anoxic zones can methylate inorganic Hg, transforming it into the toxic, persistent MeHg.

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### 12.8.3 Transfer of Mercury from Atmosphere to Aquatic Ecosystems

Total Hg deposited directly to lakes is rapidly incorporated into Hg cycling in abiotic and biotic pools. In a Hg isotope addition experiment at the ELA, Ontario, a spike of isotope  $^{202}\text{Hg}$  was added directly to the lake annually over the course of 3 years. The  $^{202}\text{Hg}$  was detected in the anoxic hypolimnion within days of addition, and in bottom sediments of the lake within 4 weeks ([Harris et al., 2007](#)), and methylated  $^{202}\text{Hg}$  was detected in zooplankton, benthic amphipod *Hyallolella Azteca*, and fish species within 2 months of addition ([Harris et al., 2007](#)), indicating that Hg methylation and movement of MeHg within the food web can occur within a single season in aquatic ecosystems. Estimated residence time of atmospherically deposited  $\text{Hg}^{2+}$  in the water column of Little Rock Lake, WI, was 150 days ([Watras et al., 2006](#)).

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### 12.8.4 Methylmercury Cycling

Methylmercury (MeHg) is produced by sulfur-reducing prokaryotes (SRPs) in the course of sulfate reduction. It is toxic to humans and vertebrate animals, particularly because it biomagnifies up the food chain and bioaccumulates within organisms. The following sections describe transfer of MeHg between ecosystem compartments, as well as characteristics of zones of high MeHg production within the landscape.

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### 12.8.5 Transfer of Methylmercury from Terrestrial to Aquatic Ecosystems

MeHg is a very small component (1%) of Hg atmospheric deposition to ecosystems ([Wentz et al., 2014](#)); most MeHg in ecosystems is microbially produced from inorganic Hg. Much of our knowledge about Hg cycling in natural ecosystems comes from the Experimental Lakes Area (ELA) in northwestern Ontario, Canada, which receives low Hg deposition [47,000,000 ng/ha/yr or 47 mg/ha/yr in 1990–1993; 80,000,000 ng/ha/yr or 80 mg/ha/yr in 1998–1999 ([St Louis et al., 2001](#); [St. Louis et al., 1996](#))]. A small portion of total Hg deposition in the ELA is in the form of MeHg, 900,000 ng/ha/yr (reported as 0.9 mg/ha/yr, or <1.5% of total Hg deposition). MeHg cycles through the terrestrial ecosystem as total Hg does. Leaf litter represents a significant flux of MeHg from the living canopy in upland forest to the detrital food web of 800,000 ng MeHg/ha/yr (reported as 0.8 mg MeHg/ha/yr), a flux of a similar magnitude to atmospheric deposition ([St Louis et al., 2001](#)). In the 20 years preceding the study, 600,000 ng MeHg/ha/yr (reported as 0.6 mg/ha/yr of MeHg) were annually stored in the organic soil pool, and on average 100,000 ng MeHg/ha/yr (reported as 0.1 mg MeHg/ha/yr) was exported from the catchment in stream flow ([St Louis et al., 2001](#)).

In five boreal forest catchments at the ELA, [St. Louis et al. \(1996\)](#) assumed a background MeHg deposition rate of <500,000 ng MeHg/ha/yr (reported as <0.5 mg MeHg/ha/yr). A catchment consisting only of upland forests exported 18% of estimated annual MeHg deposition, indicating that terrestrial ecosystems retain MeHg ([St. Louis et al., 1996](#)), and that aquatic MeHg is produced endogenously.

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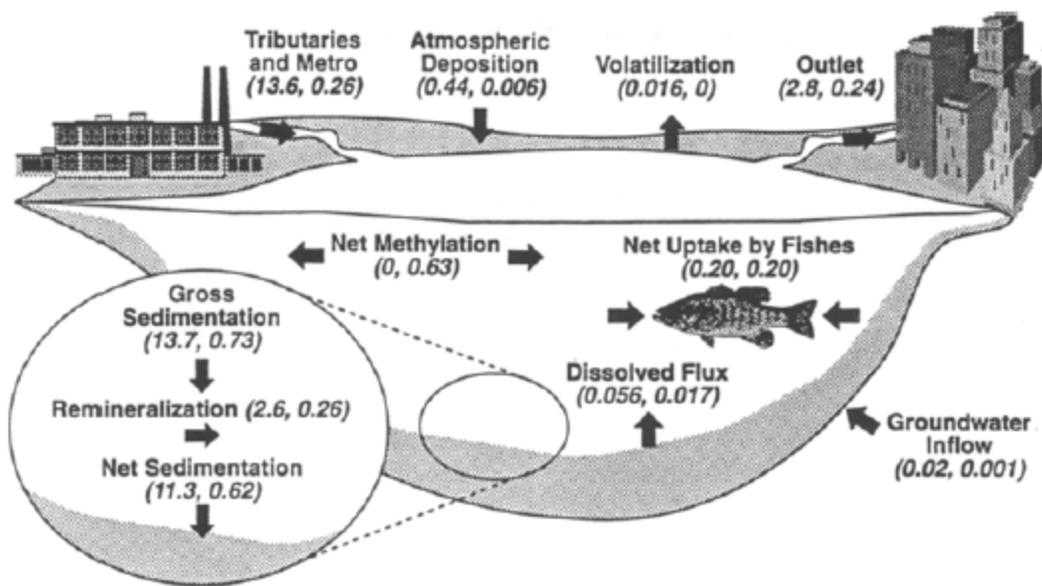
## 12.8.6 Transfer of Methylmercury from Wetlands to Aquatic Ecosystems

At the landscape level, MeHg export from wetlands in streams and rivers is correlated with wetland cover in watersheds. In the ELA in Ontario, a catchment with valley bottom wetlands exported 73% of deposited MeHg in a dry year, but 158–200% of deposited MeHg in a wet year, indicating that the wetlands produced MeHg in wet years. MeHg export was high in catchments with other types of wetlands as well. A catchment with riverine wetland (peatland fed by surface water flow) exported 120–130% of annually deposited MeHg in dry and wet years, and a catchment containing a basin wetland exported 213% MeHg in a dry year and 500–719% annually deposited MeHg in wet years, indicating a strong source of MeHg within the watershed, presumably in the wetlands ([St. Louis et al., 1996](#)). More recent work in the watershed of Arbutus Lake, NY measured Hg and MeHg in streams draining upland and wetland areas; MeHg was 1.7–3.0% of total Hg in upland streams and 7.8% of total Hg in a similarly low-order stream that drained a wetland. In downstream peatlands, MeHg was 5.4–9.5% of total Hg ([Selvendiran et al., 2008a](#)), and the beaver meadow peatland exported 623% of total MeHg input annually, while the riparian wetland exported 8% of total MeHg input ([Selvendiran et al., 2008b](#)). Wetlands with high dissolved organic carbon and fluctuating water levels and anoxic zones are areas of high MeHg production within watersheds, and such wetlands will affect MeHg concentrations in water and biota downstream.

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## 12.8.7 Methylmercury Cycling in Aquatic Ecosystems—Lake Onondaga, NY

Lake Onondaga, NY was the subject of a Hg budget project in 1992 because the eutrophic lake received high Hg loads through the late 1970s from industry [[Figure 12-19](#); ([Henry et al., 1995](#))].



Hg = mercury; kg = kilogram; MeHg = methylmercury; yr = year.  
 Source: [Henry et al. \(1995\)](#).

**Figure 12-19** Mercury and methylmercury mass balance cycle in Lake Onondaga in 1992. The quantities of mercury in each flux are indicated in parentheses by (kg total Hg/yr, kg MeHg/yr).

In 1992, 14.1 kg of total Hg entered the lake, 96% of which was carried into the lake by tributaries, including one that drained a former chlor-alkali plant. The largest sink for Hg within the lake was through sedimentation, which accounted for 11.1 kg of total Hg. In that same year, 2.8 kg of total Hg flowed out of the lake downstream and 0.20 kg Hg (0.1% of total annual Hg load) was incorporated into fish biomass ([Henry et al., 1995](#)).

A budget for Hg methylation was also constructed for the lake, and differs from that of total Hg in several important points ([Figure 12-4](#)). First, only 29% of the annual lake MeHg load of 0.88 kg entered the lake via tributaries (compared to nearly the entire total Hg load). The water column, particularly deep, anoxic water, contributed 0.60 kg or 68% of the annual MeHg load of the lake ([Henry et al., 1995](#)). More than half (about 0.47 kg) of the annual MeHg load was incorporated into sediments, and while sedimentation rates were high, about one- to two-thirds of MeHg in sediments was released back into the water column. Because most of the total Hg in fish is in the form of MeHg, the model calculated that the MeHg in fish biomass was the same amount as total Hg in fish biomass, 0.20 kg, although this value constituted a much higher portion of the annual

MeHg load [23% of annual MeHg; ([Henry et al., 1995](#))]. This early study showed that the majority of MeHg in Lake Onondaga was produced within the lake itself, specifically in the anoxic zone, and that MeHg cycled between the sediments and water column, with a significant amount stored in fish tissue.

Lake Onondaga was resampled in 2006, 2007, and 2009, following industrial remediation projects and incorporation of nitrification treatment in the municipal wastewater plant discharging into the lake ([Todorova et al., 2014](#)). In the 2006–2009 sampling, MeHg concentrations in the epilimnion were significantly lower than in 1992, and total Hg in the epilimnion was half of the total Hg concentrations measured in 1992 ([Todorova et al., 2014](#)). However, in all years there was a significant peak in MeHg concentrations and in MeHg:tHG ratios in the epilimnion in the fall following turnover ([Todorova et al., 2014](#)), indicating that this seasonal event will have significant effects on total MeHg in the food chain of the lake.

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### 12.8.8 Methylmercury in Sediments and Water Column—Lakes

The sediments under shallow, oxygenated lake waters are an important site of Hg methylation. Early literature showed that Hg methylation rates are higher in shallow organic sediments than in deep clay-rich sediments in Southern Indian Lake in Manitoba, Canada, and that the ratio of methylation:demethylation was also higher in organic sediments ([Ramlal et al., 1986](#)). In the Quabbin Reservoir, MA, MeHg fractions in sediments were 3.1–16.3% at 1-m depth, and decreased with increasing lake depth to 0.1–0.2% at a 22 to 23-m depth ([Gilmour et al., 1992](#)). At Lake Clara, WI, Hg methylation rates were sampled in the water column, flocculant surface sediments, and deeper sediments at water depths of 1–10.5 m ([Korthals and Winfrey, 1987](#)). At all sampling depths, methylation and demethylation were detectable in the water column and in the surface sediments. Gross Hg methylation rates were highest in surficial sediments sampled at depths of 5–7.5 m, but the methylation:demethylation ratio was highest (5.5–5.8) in surficial sediments at depths of 1–2 m ([Korthals and Winfrey, 1987](#)).

Larger, deeper lakes stratify during the summer; waters near the surface (epilimnion) of the lake are high in oxygen and primary productivity, while deeper waters (hypolimnion) have low oxygen, lower primary productivity, and high rates of S reduction and MeHg production. In the experimentally acidified Little Rock Lake, WI, MeHg was low (less than 0.1 ng/L) in surface waters during the summer months, but increased at anoxic depths below 4–6 m to 1 ng/L in June, 3 ng/L in July, and 3.5 ng/L in August ([Bloom et al., 1991](#)). In stratified Lake Onondaga, NY, the water column, particularly deep, anoxic water, contributed 0.60 kg or 68% of the annual MeHg load of the lake ([Henry et al.,](#)

[1995](#)). Sampling in Palette Lake, WI, showed that the oxic-anoxic boundary was at 12 m depth in this stratified lake, which was also the location of the sulfate-sulfide transition ([Watras et al., 1995](#)). There were peaks in both sulfate reduction and Hg methylation from 12–13 m depth, right at the top of the hypolimnion, which was enriched in MeHg (20–30%) compared to the epilimnion (5–10% MeHg). There was no sulfate reduction detected in the profundal sediments or deep layers of the hypolimnion. MeHg was transported from the oxic-anoxic boundary and hypolimnion where it was produced to the epilimnion, and the flux of MeHg from the hypolimnion (3,400,000–6,800,000 ng/day, reported as 3.4–6.8 mg/day) was much larger than the flux of MeHg into the epilimnion from the atmosphere [10,500 ng MeHg/day, or 0.0105 mg MeHg/day; ([Watras et al., 1995](#))]. [Eckley and Hintelmann \(2006\)](#) showed that in boreal Canadian lakes, potential methylation is highest approximately 1 m below the oxycline, and this methylation zone moves up the water column as the oxycline rises due to oxygen depletion at depth in the summer ([Eckley and Hintelmann, 2006](#)).

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### 12.8.9 Methylmercury in Sediments and Water Column—Wetlands

In wetlands at Bog Lake Fen in the Marcell Experimental Forest, MN, the highest levels of MeHg production occurred at the upland-peatland interface. When mesocosms installed in the bog interior received additions of labile C and sulfate, MeHg concentrations were similar to MeHg concentrations from the upland-peatland interface, indicating that upland inputs of C may contribute to high methylation rates in the peatland ([Mitchell et al., 2008a](#)). A larger study that sampled peatlands within the Marcell Experimental Forest, MN, as well as at the ELA in Ontario found that %MeHg was highest within 5–10 m of the upland-peatland interface across wetlands, and that sulfate and pH were higher at the interface, and DOC was lower at the interface, than in the interior of the peatlands ([Mitchell et al., 2008a](#)). In peatlands in the Arbutus Lake watershed in the Adirondack Mountains, NY, MeHg and total Hg were higher in pore water near the top of the peat profile, at 20 to 40-cm depth, than at 80 to 100-cm depth ([Selvendiran et al., 2008a](#)), and the total Hg and MeHg were highest in both peat and pore water in the top 15 cm of the peat ([Selvendiran et al., 2008a](#)). The Hg in the top 15 cm of peat was estimated to be about 27% of the total Hg, and MeHg in the top 15 cm was 30% of the total MeHg in a riparian peatland and 50% of the total MeHg in a beaver meadow ([Selvendiran et al., 2008a](#)). In freshwater *Sphagnum* peatlands of the Allequash Creek watershed in the Northern Highland Lake District of Wisconsin, reducing conditions exist below 2-cm depth in the peat, and MeHg concentrations peak at 7-cm depth in the peat ([Creswell et al., 2008](#)).

In wetlands not dominated by *Sphagnum*, Hg methylation occurs in sediments and in periphyton (see [Appendix 12.3](#)). In the freshwater marshes of the Florida Everglades, where periphyton and flocculation often extend the sediment-water interface, methylation rates were highest in the top 6 cm of sediments ([Gilmour et al., 1998](#)). In coastal marsh sediments, such as at Kirkpatrick Marsh on the Chesapeake Bay, MeHg was highest in the top 6 cm of sediment, although total Hg was highest at a depth of 12–15 cm in the sediments ([Mitchell and Gilmour, 2008](#)), and in coastal Georgia marshes, sediment core incubations showed that MeHg production was highest in the top 4 cm of the marsh sediments ([King et al., 1999](#)).

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### 12.8.10 Methylmercury in Sediments and Water Column—Estuarine and Marine Ecosystems

Research shows that Hg methylation occurs in estuaries and in marine sediments. Incubations of samples collected in the Patuxent River and Estuary, MD, showed that net MeHg production in sediments was four times the rate of MeHg accumulation in sediments, suggesting that MeHg in estuary surface waters comes from estuarine sediment sources as well as sources upstream in the watershed ([Benoit et al., 1998](#)). MeHg comprised 5% of surface water particulate Hg (unclassified compounds large enough to be removed by filtration) and 2% of total Hg in surface water, and 0.3% of Hg in estuarine sediments ([Benoit et al., 1998](#)). More recently, surface sediments were sampled from the Chesapeake Bay, from four locations in the main channel, two locations on the continental shelf, and one location on the slope of the continental shelf. Total Hg in the upper bay ranged from 50 to 171 ng Hg/g sediment (reported as 250–850 pmol/g), in the lower bay and continental shelf ranged from 2.0 to 20 ng Hg/g sediment (10–100 pmol/g), and at the single continental slope site was 50–70 ng Hg/g sediment (250–350 pmol Hg/g); ([Hollweg et al., 2009](#)). MeHg was 0.2–1.5% in the top 0–12 cm of sediments across sites, and bottom water salinity was strongly correlated with %MeHg [ $r = 0.814$ ; ([Hollweg et al., 2009](#))], suggesting that MeHg was produced in marine sediments.

An incubation study of water samples collected at depths of 20–327 m in the ocean around the Canadian Arctic Archipelago found measurable rates of Hg methylation at all depths from all five sites sampled. Methylation of inorganic Hg accounted for 47% of the MeHg present in the water column at these locations, and demethylation was also widely observed, indicating that marine MeHg represents marine production of MeHg, not merely transport of MeHg from other systems ([Lehnherr et al., 2011](#)).

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## APPENDIX 13 CLIMATE MODIFICATION OF ECOSYSTEM RESPONSE TO NITROGEN AND SULFUR

The scope of this appendix is to identify key papers describing how climate alters ecosystem response to nitrogen (N) and sulfur (S) addition. N and S loading occurs in many ecosystems concurrently experiencing multiple stressors, including human-driven climate change. Climate change effects on U.S. ecosystems were recently summarized in the U.S. National Climate Assessment ([Galloway et al., 2014](#); [Groffman et al., 2014](#)). Each appendix of the ISA evaluating the effects of N enrichment or acidification includes a section on how climate modifies the ecosystem response to N or N + S deposition. Additionally, in this appendix, we have excerpted text from [Greaver et al. \(2016\)](#), to serve as a foundation for the discussion. This paper, which focuses on empirical observations, provides a current review of how climate (e.g., temperature and precipitation) modifies ecosystem response to N.

Anthropogenic emissions of greenhouse gases are likely to cause a global average temperature increase of 1.5 to 4.0°C and a significant shift in the amount and distribution of precipitation by the end of the 21st century ([Collins et al., 2013](#)). Recent work has focused on the effects of anthropogenic N on the Earth's radiative forcing ([Pinder et al., 2012](#)) and how temperature and precipitation alter ecological responses to N exposure ([Greaver et al., 2016](#)). Most work is conducted on the effects of climate and N or acidifying deposition (N + S). There are only a couple of studies on how climate modifies ecosystem response to S.

Climate effects on ecosystems is a rapidly expanding field. For some processes we are beginning to understand how temperature and precipitation may interact; however, for many biogeochemical pools and processes, data are insufficient to quantify either the direction or magnitude of how climate may alter ecosystem response to N with certainty. Some global-scale earth systems models now incorporate interactions between N and carbon (C) in ecosystems. They are summarized in [Appendix 6. Greaver et al. \(2016\)](#) includes information on terrestrial and surface water ecosystems. A brief summary of climate modification of estuary response to N is also included in [Appendix 13.2](#).

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## 13.1 Climate Modification of Soil Acidification and Nitrogen Enrichment

Climate-driven changes in N cycling may alter the N supply in terms of quantity and timing of N available for uptake by biota. Alteration of N availability relative to a given organism's life cycle or physiological thresholds may alter overall ecosystem function. These effects may be further modified when temperature and precipitation cause direct stress to biota. In the following sections we describe how climate alters the cycling of N and how temperature and precipitation interact with two important mechanisms affected by N availability to taxa: (1) nitrogen-driven eutrophication, which will stimulate the growth of opportunistic plant and animal species, and (2) acidification, which may decrease growth and cause mortality among sensitive species. We describe how these changes in growth will alter C cycling and biodiversity.

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### 13.1.1 Nitrogen Transport and Transformation

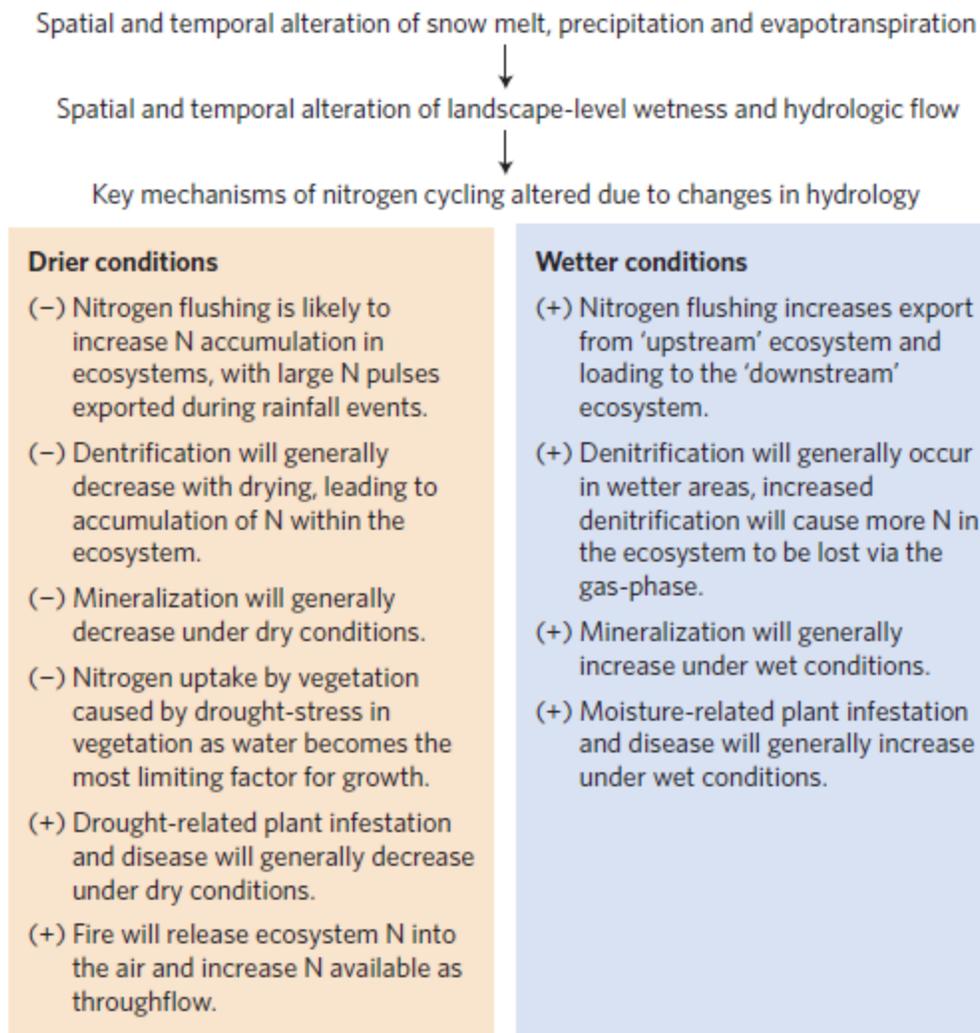
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#### 13.1.1.1 Excerpt from [Greaver et al. \(2016\)](#)

“Although global N cycling is complex, the movement of N through the biosphere can largely be explained by describing a few key transformations ([Figure 13-1](#)). Atmospheric N<sub>2</sub> is converted into reactive N by lightning or by specialized bacteria capable of biological N fixation, in addition to the human activities that create reactive N.

Organisms use reactive N to produce proteins and other essential compounds. Dead organic matter is decomposed by microbial enzymes, producing smaller N containing organic molecules such as amino acids. This organic N is largely converted to mineral forms that are readily assimilated by plants and microorganisms. Where reactive N is present under aerobic conditions, some microorganisms convert ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>), a process termed nitrification. Nitrate is mobile in soils and often leaches into aquatic systems and groundwater. In anaerobic conditions, microorganisms can convert NO<sub>3</sub><sup>-</sup> to gaseous N via denitrification, emitting N back to the atmosphere.

“In nonagricultural terrestrial ecosystems, atmospheric deposition is the dominant source of anthropogenic N. Through changes in precipitation, shifts in atmospheric circulation, and temperature-related effects on the stability of N compounds, climate change is expected to alter the relative contribution of wet and dry forms of N deposition and shift the spatial distribution of N deposition ([Engardt and Langner, 2013](#); [Tagaris et al., 2008](#)). Local N deposition rates are generally predicted to change by 0–20% ([Engardt and Langner, 2013](#); [Tagaris et al., 2008](#)).



N = nitrogen.

Source: [Greaver et al. \(2016\)](#).

**Figure 13-1 Summary of key interactions between nitrogen, anthropogenic-driven climate change, and hydrology.**

“The influence of N addition on reactive N availability within terrestrial and aquatic ecosystems is mediated by microbial transformations and transport within and between ecosystems. Climate change is expected to strongly affect these processes through increasing temperature and through temporal and spatial shifts in temperature and precipitation ([Baron et al., 2012](#)). Warming directly increases the metabolic biokinetics of enzyme activity necessary for microbial N transformation until a temperature [optimum] is reached. Climate change is also expected to cause numerous modifications of the

hydrologic cycle, and moisture availability regulates the biokinetic temperature response ([Borken and Matzner, 2009](#); [Rustad et al., 2001](#)) because water is needed to transport enzymes and substrates and water influences oxygen availability. Warming is predicted to intensify the hydrologic cycle, with heavy rainfall events expected to become more frequent and intense, along with the potential for deepening and lengthening of dry periods, as well as altered snow accumulation and melt and changes in evapotranspiration ([Jiménez Cisneros et al., 2014](#); [Collins et al., 2013](#)). These changes may cause soil conditions for microbial activity to shift between optimal and inhibitory ([Morse et al., 2015b](#)), modifying the link between climate warming and the rate of microbial N transformations such as decomposition, mineralization, nitrification, denitrification, and biological N fixation. Of these transformations, the rates of N fixation may be the most uncertain part of the N cycle ([Vitousek et al., 2013](#)), altering N supply and influencing the C cycle ([Welter et al., 2015](#)).

“Climate-driven changes to the hydrologic cycle will also alter the quantity of N transported through a system via waterborne transport and soil water content-mediated N cycling ([Billen et al., 2013](#)). Alteration of N retention in the soil due to changes in moisture and flushing may be significant enough to determine whether an ecosystem is an N source versus [an] N sink ([Boulton, 2007](#); [Band et al., 2001](#)). Greater precipitation generally increases water flow, which may (1) increase leaching/export of N through terrestrial landscapes, (2) increase terrestrial N inputs to streams and rivers, and (3) increase N transport rates through streams and rivers ([Whitehead et al., 2009](#)), although adaptation by microbes and plants may increase their ability to retain N as flushing increases, thereby potentially limiting some of the overall impact of increased precipitation and flow.

“Under dry conditions, landscapes can become more hydrologically disconnected and N retentive, which can increase N concentrations in subsequent flushing events ([Goodridge and Melack, 2012](#); [Kaushal et al., 2008](#)). Drought can inhibit nitrification and cause N to accumulate in the soil; once precipitation occurs it often results in a pulse of nitrification that produces nitrate and subsequent nitrate leaching ([Lamersdorf et al., 1998](#)). For example, the 2012 droughts in the midwestern U.S. were followed during the spring 2013 by extremely high river nitrate concentrations ([Beeman, 2013](#)). Likewise, longer periods between wet cycles lead to accumulation of nitrate and other acidifying solutes in the soil, causing less frequent, yet more extreme acidification events ([Bayley et al., 1992](#)). Beyond simply the total volume, precipitation intensity influences the rate of N flow through ecosystems. Increased precipitation intensity of cold season frontal storm systems and warm season convective storms would likely increase the frequency of high N loading events to aquatic systems. Due to the limited capacity for in-stream removal of

N during high flow pulse events, most N is transported downstream ([Kaushal et al., 2014](#)).

“Such hydrologic cycle changes are also expected to affect the timing of N transport. Changes in the seasonality of precipitation, and in particular snowmelt, will tend to alter the timing of N flushing through the ecosystem. There has already been widespread earlier snowmelt and increased winter thaws associated with warming over the last few decades ([Collins et al., 2013](#)), but implications for the timing of N export have been assessed in only a few sites ([Casson et al., 2012](#)). Timing changes ultimately can alter the magnitude of N export to downstream water bodies, particularly if the timing of flushing changes relative to the timing of biologically mediated uptake in either terrestrial or aquatic ecosystems ([Baron et al., 2009](#)). Thus, it is possible to have a modification in sink/source behavior in regions where annual or seasonal patterns of water-filled pore space shift with climate change.

“The rate at which denitrification returns reactive N to the atmosphere varies across space and time, with landscape- to micro-scale denitrification hot spots or moments that depend on interactions with hydrologic flow paths, the persistence and variability of low oxygen conditions, and the residence time of water and N, all of which are likely to respond to climate-driven changes in the hydrologic cycle ([Anderson et al., 2015](#); [Weier et al., 1993](#)). Generally, warmer and wetter conditions under climate change would facilitate greater rates of denitrification, whereas warmer and drier areas might experience decreased denitrification or concentrate ‘hot spots’ into smaller areas with higher soil moisture, substrate concentrations, and fluxes ([Duncan et al., 2013](#)). Alternating wet and dry states may promote coupled nitrification/denitrification processes or build-up and flushing of mobile N depending on the ratio of transport to reaction rates. These are general trends associated with moisture availability and transport. Carbon substrate availability and other controls on microbial processes, however, will also be influenced by climate change (discussed below) and can mediate these hydrologic effects.”

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### 13.1.1.2 Additional Considerations

There are considerations to note in addition to the excerpt from [Greaver et al. \(2016\)](#). Additional papers on climate interactions with N and S soil biogeochemistry discussed in [Appendix 4](#) are summarized in [Table 13-1](#). Featured most notably are the effects of precipitation on S cycling, snow on soil N cycling, N addition effects on biogenic GHG flux, and the results of integrating climate parameters into N and S biogeochemistry modeling.

**Table 13-1 Summary on climate modification sulfur and nitrogen cycling in [Appendix 4](#) and [Appendix 6](#) in addition to those in [Appendix 13](#).**

Indicator/Process	T	P	Snow	Reference
<b>Biogeochemical effects (<a href="#">Appendix 4</a>)</b>				
S mineralization	X	X		<b>Empirical:</b> Watershed mass balances of sulfur are increasingly regulated by watershed moisture because high-moisture soil conditions stimulate the net mineralization of soil sulfur pools. <a href="#">Mitchell et al. (2011)</a>
S retention		X		<b>Model:</b> Watersheds with higher runoff ratio tend to convert sooner from net retention to net release of SO <sub>4</sub> <sup>2-</sup> . <a href="#">Rice et al. (2014)</a>
Soil N variables			X	<b>Meta-analysis:</b> Meta-analysis data is from 41 publications based on snow depth manipulation experiments. The general responses of 12 variables related to terrestrial nitrogen (N) pools and dynamics to altered snowpack depth are evaluated. <a href="#">Li et al. (2016c)</a>
N mineralization	X		X	<b>Empirical:</b> More freeze/thaw cycles anticipated with climate warming; supported lower rates of N mineralization. <a href="#">Duran et al. (2016)</a>
N mineralization	X		X	<b>Empirical:</b> Snow-manipulation experiment at Hubbard Brook to evaluate soil freezing later in the season due to prolonged warm season. Freezing likely increases soil NO <sub>3</sub> <sup>-</sup> levels by physical disruption (increased fine root mortality) causing reduced N uptake by plants and reduced competition for inorganic N, allowing soil NO <sub>3</sub> <sup>-</sup> levels to increase even with no increase in net mineralization or nitrification. <a href="#">Groffman et al. (2001)</a>
N mineralization			X	<b>Empirical:</b> N mineralization rates were more strongly related to soil volumetric water content than to root biomass, snow or soil frost, or winter soil temperature. <a href="#">Sorensen et al. (2016)</a>
N effects CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O				<b>Meta-analysis:</b> 313 observations across 109 studies evaluated the effect of N addition on the flux of three major GHGs: CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O. <a href="#">Liu and Greaver (2009)</a>
Soil acidification and N enrichment	X	X		<b>Model:</b> 2009–2100—six climate change simulations of temperature, precipitation, and photosynthesis active radiation (PAR). Without CO <sub>2</sub> fertilization effects, net soil mineralization and nitrification increased, soil and stream acidified, and the percentage of base saturation in soils declined due to increased NO <sub>3</sub> <sup>-</sup> . With CO <sub>2</sub> fertilization effects, the N loss to streams was suppressed due to increased plant uptake. <a href="#">Pourmokhtarian et al. (2012)</a>

**Table 13-1 (Continued): Summary on climate modification of nitrogen (N) effects on nitrogen cycling in Appendix 4 and Appendix 6 in addition to those in Appendix 13.**

Indicator/Process	T	P	Snow	Reference
Soil acidification, N enrichment, and plant community	X	X		<b>Model:</b> The ForSAFE-VEG model simulations show that climate and atmospheric deposition have comparably important effects on N mobilization in the soil, as climate triggers the release of organically bound nitrogen stored in the soil during the elevated deposition period. Climate has the most important effect on plant community composition; thus, climate change cannot be ignored in future simulations of vegetation dynamics. <a href="#">Belyazid et al. (2011a)</a>
Soil acidification and N enrichment	X	X		<b>Model:</b> PnET-BGC modeling found climate change played a larger role in ANC than base cation deposition changes. Temperature had a larger effect than precipitation on decomposition. Net mineralization and nitrification increased faster with climate change than plant NO <sub>3</sub> <sup>-</sup> uptake. <a href="#">Wu and Driscoll (2010)</a>

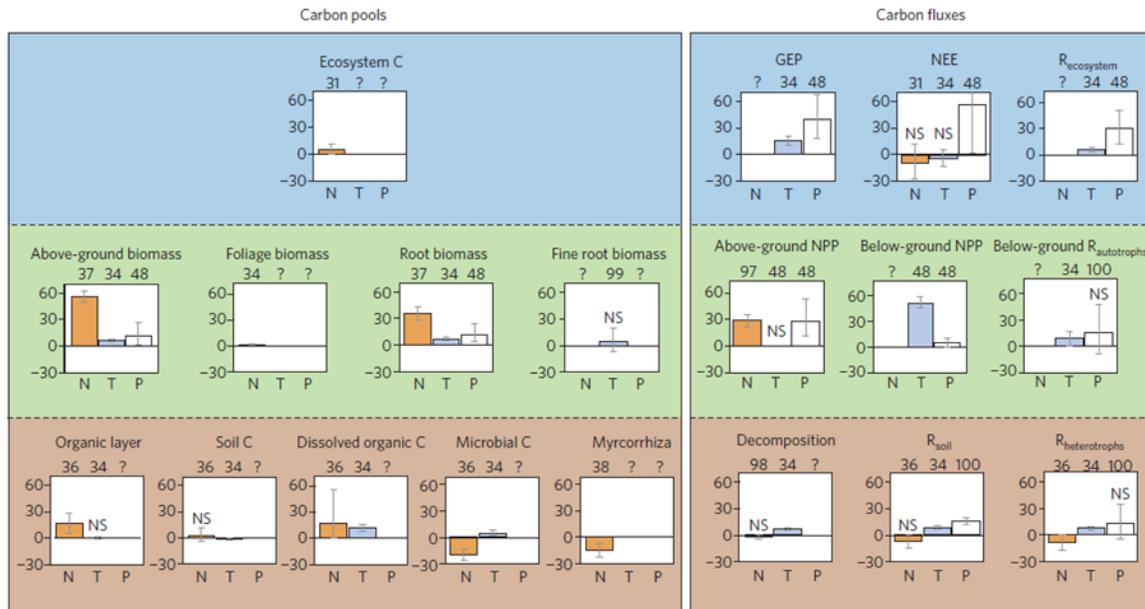
## 13.1.2 Nitrogen, Climate, and Carbon Cycling

### 13.1.2.1 Excerpt from [Greaver et al. \(2016\)](#)

“Changes in N supply alter plant growth and C cycling. The addition of N to terrestrial and aquatic ecosystems can cause eutrophication, a state of high nutrient availability that alters ecosystem function. Autotrophs (plant/algae) capture CO<sub>2</sub> through photosynthesis, storing C in biomass until it is oxidized through respiration or combustion and released back to the atmosphere. In terrestrial systems, N addition usually stimulates autotrophic growth until biotic N demand has been satisfied, although high rates of N addition may increase the concentration of acid anions, which often decreases plant growth (see acidification discussion below). At certain sites, N additions have uneven effects, stimulating growth of some tree species, while impairing the health and growth of others ([Thomas et al., 2010](#)). When considering the net effects on multiple tree species, growth in most forests is stimulated. This additional growth increases the overall amount of C stored in plant biomass; one unit of N input may cause an additional 24.5 to 177 units of forest C uptake ([de Vries et al., 2014a](#); [Liu and Greaver, 2009](#)).

“A number of published meta-analyses evaluate the response of C pools and fluxes to single stressors of N, precipitation, or temperature. To gain insight on stressor interactions from single stressor response studies, we have synthesized existing meta-analyses of terrestrial ecosystem response to additions of N, precipitation, and

temperature (e.g., [see [Figure 13-2](#) in this document]). A recent correlation analysis of growth (in terms of net primary production [NPP]) for 1,247 woody plant communities across global climate gradients confirms that NPP increases with higher temperature and precipitation ([Chu et al., 2016](#)). However, ecological changes along broad natural gradients may differ from the response of ecosystems to comparatively rapid environmental change caused by human activities ([Chu et al., 2016](#)). This latter process may be more accurately characterized by addition experiments, such as those summarized by meta-analysis. Our synthesis of existing meta-analyses indicates that aboveground NPP is highly responsive to N addition and enhanced precipitation, while temperature rise does not increase aboveground NPP. This result is consistent with the basic biokinetic effects of warming on enzyme activity, which would have the counteracting effects of stimulating both plant C capture (photosynthesis) and plant C release (autotrophic respiration). Although there are no meta-analyses on warming and whole-ecosystem autotrophic respiration, [Lu et al. \(2013\)](#) observed in a meta-analysis that temperature increased gross ecosystem production, a metric that does not subtract respiration from gross production (photosynthesis). Therefore, temperature may have larger effects on plant C fluxes than on NPP. Note that precipitation-induced changes in NPP may vary depending on whether there is sufficient enhancement of precipitation to offset increased evapotranspiration in a warmer climate ([Bachelet et al., 2001](#)).



C = carbon; CI = confidence interval; GEP = gross ecosystem photosynthesis; N = nitrogen; NEE = net ecosystem C exchange; NPP = net primary production; NS = nonsignificant effects; P = precipitation;  $R_{\text{autotrophs}}$  = plant/autotroph respiration;  $R_{\text{ecosystem}}$  = ecosystem respiration;  $R_{\text{heterotrophs}}$  = heterotroph respiration;  $R_{\text{soil}}$  = soil respiration; T = temperature; ? = an effect that has not been assessed by meta-analytic review.

Note: Bars indicate response ratios (treatment/control  $\times$  100), and error bars represent 95% confidence intervals for the response. Orange bars indicate the magnitude of response to nitrogen enrichment, blue bars show response to temperature increase, white bars show response to precipitation increase. Blue zone indicates ecosystem carbon inputs and outputs, green zone indicates plant responses, and brown zone indicates soil and microbial responses. The upper confidence interval for the precipitation effect on net ecosystem C exchange is 124.6 and beyond the scale of the chart. The response of aboveground net primary production to warming was stated to be nonsignificant (Wu et al., 2011), but no effect size was given.

Source: Greaver et al. (2016). The number above each bar indicates the published source of the effect size as follows: 1. LeBauer and Treseder (2008); 2. Wu et al. (2011); 3. Lu et al. (2013); 4. Liu and Greaver (2009); 5. Liu and Greaver (2010); 6. Xia and Wan (2008); 7. Knorr et al. (2005); 8. Dieleman et al. (2012); 9. Treseder (2004); 10. Lu et al. (2011b); 11. Liu et al. (2016b).

**Figure 13-2 The effects of increased nitrogen, temperature, and precipitation on terrestrial carbon pools (left panel) and fluxes (right panel) from published meta-analyses.**

“Belowground, initial findings are that N addition tends to increase the C stored in the soil organic layer and in root biomass (Liu and Greaver, 2010; Xia and Wan, 2008), while it tends to decrease mycorrhizae/microbial abundance and heterotrophic respiration (Liu and Greaver, 2010; Treseder, 2004). This offset may result in no net change in soil respiration (Liu and Greaver, 2010); however, this is an active area of research. Consistent with the biokinetic effects of warming, long-term data and meta-analyses show that soil respiration, including decomposition and microbial respiration, is stimulated by increasing temperature (Lu et al., 2013; Bond-Lamberty and Thomson, 2010; Rustad et al., 2001). Most empirical studies show rising temperature stimulates N release by mineralization (Churkina et al., 2010), which may be driven more by

temperature effects on moisture ([Emmett et al., 2004](#)). In some dynamic land models, the additional N from mineralization will stimulate C uptake by plants even more than current N deposition ([Burd et al., 2016](#)). At the same time, increased N from mineralization may cause N induced inhibition of decomposition, a feedback mechanism that might decrease the amount of N released that is currently considered by few models ([Gerber et al., 2010](#)). The mechanisms causing N driven reduction in decomposition are not well understood, but are thought to result from changes in microbial community composition and their production of decomposition enzymes, as well as possible changes in the character and degradability of soil organic matter ([Conant et al., 2011](#); [Janssens et al., 2010](#)). Climate change could also affect decomposition rates by altering both available soil moisture and microscale connectivity among microorganisms, water, and nutrients within the soil matrix that in turn may alter microbial processes ([Xiang et al., 2008](#)). Although there is no consensus about how dissolved organic carbon (DOC) in surface water is regulated overall, increasing N and temperature increase DOC concentrations ([Laudon et al., 2012](#)). While few meta-analyses examine precipitation effects on the soil C cycle, precipitation tends to increase the root C pool (e.g., [see [Figure 13-2](#) in this document]).

“Overall ecosystem C balance is assessed by summing measurements of individual pools to quantify ecosystem carbon (EC) content or by measuring C fluxes to quantify the net ecosystem exchange (NEE) of C. The meta-analysis we identified indicated that temperature did not increase NEE [[Lu et al. \(2013\)](#); positive NEE indicates ecosystem C gain], and as previously mentioned this is likely because the biokinetic effects of warming stimulate respiration that offsets the C capture via stimulation of primary production. Increased precipitation tends to increase NEE ([Wu et al., 2011](#)), likely because water availability increases photosynthesis, while not increasing plant respiratory losses. A meta-analysis of N addition studies indicates that adding N to grasslands had no effect on NEE, but that N addition increased forests EC ([Liu and Greaver, 2009](#)). There may be differences between grasslands and forests in terms of the extent that C gain simulated by N is offset by heterotrophic and autotrophic respiration. Increasing temperature may decrease C storage if the warming causes inhibition of photosystems or enhances evaporation and reduces water availability. A better understanding of these and other contributing processes is needed.

“Traditionally, primary production in freshwater systems was thought to be phosphorous (P) limited, but recent data have shown an increase of limitation by N or colimitation by N and P ([Elser et al., 2007](#)). In N limited fresh waters, N addition enhances rapid growth of nitrophilic algae. This is an important food source to consumer species in the trophic cascade; however, it is unclear if this is an important source of long-term C storage. Sediments are estimated to be the largest pool of long-term C storage ([Cole et al., 2007](#)),

and N stimulates the production of terrestrial biomass that may be transported to aquatic sediments. Nitrogen also stimulates primary production of aquatic algae which contribute to C in sediments ([Kastowski et al., 2011](#)), although few studies have examined this effect. [Gudasz et al. \(2010\)](#) found a strong positive relationship between increasing temperature and organic C mineralization. They conclude future organic C burial in boreal lakes could decrease 4–27% under scenarios of warming due to enhanced temperature-dependent microbial activities. We were unable to identify studies examining precipitation effects, or the combined effects of N, temperature, and precipitation effects, on C storage in freshwater ecosystems. A discussion of biodiversity associated with eutrophication of fresh waters is included in the biodiversity section.”

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### 13.1.2.2 Additional Considerations

There are considerations to note in addition to the excerpt from [Greaver et al. \(2016\)](#). Additional papers on the interacting effects of climate and N on C cycling discussed in [Appendix 4](#) and [Appendix 6](#) are summarized in [Table 13-2](#). Notably there is a new meta-analysis on N and warming interactions and several new papers on the interacting effects of N on plant biomass and precipitation.

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**Table 13-2 Summary on climate modification of nitrogen (N) effects on carbon (C) cycling in [Appendix 4](#) and [Appendix 6](#) in addition to those in [Appendix 13](#).**

Indicator/Process	T	P	Snow	Reference
<b>Biogeochemical effects (<a href="#">Appendix 4</a>)</b>				
19 different C pools and processes within ecosystems	X	X		<b>Synthesis:</b> A synthesis of meta-analyses for single factor experiments on N, T, or P manipulation for 19 different C pools and processes within ecosystems. <a href="#">Greaver et al. (2016)</a>
Soil C	X	X		<b>Meta-analysis:</b> Results showed that the interaction of warming and N deposition greatly increased the soil C input (+49%) compared with the single factor of either warming (+5%) or N deposition (+20%). Soil C loss was not significantly affected by the interaction of N and warming, likely because increases in decomposition due to warming are offset by the decreases by N addition. <a href="#">Ni et al. (2017)</a>
N effects CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O				<b>Meta-analysis:</b> 313 observations across 109 studies evaluated the effect of N addition on the flux of three major GHGs: CO <sub>2</sub> , CH <sub>4</sub> , and N <sub>2</sub> O. <a href="#">Liu and Greaver (2009)</a>

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**Table 13-2 (Continued): Summary on climate modification of nitrogen (N) effects on carbon (C) cycling in Appendix 4 and Appendix 6 in addition to those in Appendix 13.**

Indicator/Process	T	P	Snow	Reference
Decomposition		X		<b>Empirical:</b> Increasing rainfall variability and N addition can stimulate litter decomposition in tall grass prairies in the U.S. <a href="#">Schuster (2016)</a>
<b>Biological effects (<a href="#">Appendix 6</a>)</b>				
Biomass		X		<b>Empirical:</b> Using 1,600 observations, the study authors found that biomass responses to N increased linearly with mean annual precipitation (MAP). <a href="#">Xia and Wan (2008)</a>
Biomass		X		<b>Empirical:</b> Using 126 observations, the study authors found no relationship between biomass and mean annual precipitation (MAP). <a href="#">LeBauer and Treseder (2008)</a>
ANPP	X	X		<b>Empirical:</b> Plant growth response to N increased with precipitation until annual precipitation reached 800 mm/yr. The N response efficiency also peaked with moderate annual temperatures (~8°C) and declined under cooler or warmer conditions. <a href="#">Tian et al. (2016a)</a>
ANPP		X		<b>Empirical:</b> In the Sonoran Desert near Phoenix, AZ, 60 kg N/ha/yr caused little or no increase in production among herbaceous annuals in low precipitation years, moderate N responses with average rainfall, and strong increases in biomass with added N during above-normal rainfall seasons. <a href="#">Hall et al. (2011)</a>
Aboveground biomass and litter production		X		<b>Empirical:</b> Added N was positively correlated with precipitation and was only significant in the high rainfall years. <a href="#">Vourlitis (2012)</a>

### 13.1.3 Climate and Acidification

#### 13.1.3.1 Excerpt from [Greaver et al. \(2016\)](#)

“Atmospheric deposition of acidic N and sulfur (S) compounds (e.g., HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) has directly caused widespread acidification of terrestrial and freshwater ecosystems in many industrial areas. More broadly, other forms of atmospheric N deposition (e.g., NH<sub>x</sub>) can indirectly cause acidification by increasing inorganic N availability enough to induce nitrification. Freshwater and terrestrial ecosystem acidification is well studied and is characterized by decreased pH and elevated aluminum (Al) concentrations/mobility in soils and surface waters that cause plant physiological changes ([Schaberg et al., 2002](#)), tree mortality ([McNulty et al., 2007](#)), aquatic fauna mortality, and decreased aquatic

biodiversity ([Driscoll et al., 2001b](#)). Acidification driven by N (as opposed to N + S) occurs at higher levels of N addition than for initial changes to the C cycle. Often N saturation of the terrestrial ecosystem and subsequent leaching into adjacent aquatic systems is observed in the process of aquatic acidification ([Aber et al., 1998](#)). The threshold for the onset of acidification changes across the landscape, depending on geochemical sensitivity and historical loading of acidifying deposition. Although recent declines in emissions of SO<sub>x</sub> and NO<sub>x</sub> in eastern North America and throughout Europe ([NAPAP, 2011](#)) have led to many improvements in acid-base balances in acid sensitive ecosystems in recent decades, it is unclear whether sensitive ecosystems will continue to improve as emissions decline or whether secondary processes will promote, arrest, or reverse ecosystem recovery as climate changes.

“Potential future changes in the quantity and temporal distribution of precipitation and temperature (and their interactions) is expected to alter the wet-dry cycles that govern the timing and amount of acidic inputs in precipitation, microbial transformation in the soil, and the flush of acid anions from soils to surface waters. If acid anions build up in soil during periods of drought, the eventual flushing likely causes a more potent acidification event ([Mosley, 2015](#); [Whitehead et al., 2009](#)). If the acidification event occurs during a time when sensitive biota or lifestages of biota are present, acidification may cause more adversity to these populations ([Kowalik et al., 2007](#)). Increases in storm frequency associated with global climate change ([Collins et al., 2013](#)) could increase the frequency and severity of acidification driven by high levels of sea salt deposition in coastal regions ([Wright and Schindler, 1995](#)). Although the mechanisms of interaction are unclear, increases in DOC concentrations in aquatic ecosystems across Europe and the U.S. have been linked to acidification, N cycling, and climate change, with important implications for water quality and ecosystem function ([Evans et al., 2008](#)).

“As previously mentioned, warmer temperatures increase decomposition and nitrification. Nitrification will also increase with increased N supply caused by increased weathering or decomposition ([Booth et al., 2005](#)). The process of nitrification generates protons that increase the rate of nitrate and base cation leaching to drainage waters ([Murdoch et al., 1998](#)). The combined increase of NO<sub>3</sub><sup>-</sup> leaching and loss of base cations has the potential to magnify acidification in forest soils ([Fernandez et al., 2003](#)). Soil weathering is typically the key buffer to acidic deposition ([Li and McNulty, 2007](#)), and while weathering is increased by both soil temperature and soil moisture ([Gwiazda and Broecker, 1994](#)), it is unclear whether any future change in the magnitude of temperature and precipitation will be enough to alter base cation supply or influence the acid-base balance of sensitive ecosystems. Furthermore, it is unclear whether increased supply of N in soils from either deposition, increased decomposition, or increased nitrogen fixation may negate the ameliorative effect of enhanced weathering. Some studies show that

climate change will mitigate acidification through increased weathering ([Belyazid et al., 2011a](#)), whereas others show that climate change will aggravate acidification through increased nitrification outpacing enhanced weathering ([Wu and Driscoll, 2010](#)). In general, increased temperature and precipitation will likely enhance inputs of buffering agents from weathering and deposition, but also increase inputs of acidifying agents from deposition and enhanced N cycling. The relative sensitivity of these opposing processes to a given change in climate remains unresolved.

“Climate change may alter the sensitivity of biota to acidification, creating the need to adapt to a combination of acidity and climate change stresses. For example, the suitable habitat for brook trout in the Catskills and Adirondack mountains of the northeastern U.S. may be constrained as climate change increases downstream water temperatures, reducing downstream range where the trout can survive, while upstream migration is limited in part by acid conditions in the headwaters. In another example, Al is toxic to many fish and known to be mobilized during acidification events. It is known that the mortality rate of Atlantic salmon exposed to Al increases at higher temperatures ([Poleo and Muniz, 1993](#)); it is unclear how many other aquatic species would experience temperature-dependent toxicity, which could make them more vulnerable to acidification in a warming climate. Overall, there is little knowledge of how the biological thresholds to acidity will be affected by climate change.”

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### **13.1.3.2 Additional Considerations**

There are considerations to note in addition to the excerpt from [Greaver et al. \(2016\)](#). Additional papers on climate interactions with acidification discussed in [Appendix 4](#) and [Appendix 5](#) are summarized in [Table 13-3](#). Most notably, several new studies model the interacting effects of climate and deposition on soil biogeochemistry, plant growth, and plant community composition.

**Table 13-3 Summary on climate modification of acidification in [Appendix 4](#) and [Appendix 5](#) in addition to those in [Appendix 13](#).**

Indicator/Process	T	P	Snow	Reference
<b>Biogeochemical effects (<a href="#">Appendix 4</a>)</b>				
Soil acidification and N enrichment	X	X		<b>Model:</b> 2009–2100—six climate change simulations of temperature, precipitation, and photosynthetically active radiation (PAR). Without CO <sub>2</sub> fertilization effects, net soil mineralization and nitrification increased; soil and stream acidified; and percentage of base saturation in soils declined due to increased NO <sub>3</sub> <sup>-</sup> . With CO <sub>2</sub> fertilization effects, N loss to streams is suppressed due to increased plant uptake. <a href="#">Pourmokhtarian et al. (2012)</a>
Soil acidification, N enrichment, and plant community	X	X		<b>Model:</b> The ForSAFE-VEG model simulations show that climate and atmospheric deposition have comparably important effects on N mobilization in the soil, because climate triggers the release of organically bound nitrogen stored in the soil during the elevated deposition period. Climate has the most important effect on plant community composition, underlining the fact that this cannot be ignored in future simulations of vegetation dynamics. <a href="#">Belyazid et al. (2011a)</a>
Soil acidification and N enrichment	X	X		<b>Model:</b> PnET-BGC modeling found climate change played a larger role in ANC than base cation deposition changes. Temperature had a larger effect than precipitation on decomposition. Net mineralization and nitrification increased faster with climate change than plant NO <sub>3</sub> <sup>-</sup> uptake. <a href="#">Wu and Driscoll (2010)</a>
<b>Biological effects (<a href="#">Appendix 5</a>)</b>				
Growth of red spruce and balsam fir	X	X		<b>Empirical:</b> Tree ring analysis was conducted along an elevation gradient (proxy for climate change). Both species showed increased growth with increased precipitation pH. Red spruce appeared to show increased growth with a warming climate, but balsam fir did not. No changes were noted in the [species?] distribution in the spruce-fir forest, and the authors suggest any such change may be part of a longer term process. <a href="#">Wason et al. (2017)</a>
Growth of red spruce	X	X		<b>Model:</b> The Annual Radial Model used to investigate projected climate change effects and changing air pollution on red spruce growth. High-elevation (<1,700 m) red spruce growth would decline if climate change co-occurred with an increase in air pollution. However, growth would increase under climate change, if air pollution decreased. In contrast, low-elevation red spruce growth would decrease with future climate change regardless of change in air pollution. <a href="#">Koo et al. (2014)</a>

**Table 13-3 (Continued): Summary on climate modification of acidification in Appendix 4 and Appendix 5 in addition to those in Appendix 13.**

Indicator/Process	T	P	Snow	Reference
<b>Biological effects of freshwater acidification (<a href="#">Appendix 8</a>)</b>				
Water DOC	X			<a href="#">Warren et al. (2017)</a> The major stressor affecting native cold-water fish species in the eastern U.S. is shifting from acidification to thermal stress and some lakes recovering from acidification may provide a degree of protection against climate effects. As DOC in the water increases with increasing lake pH in recovering lakes, decreased water clarity may create cooler refuge habitat for fish.

### 13.1.4 Nitrogen, Climate, and Biodiversity

#### 13.1.4.1 Excerpt from [Greaver et al. \(2016\)](#)

“Biodiversity, which contributes to the structure and function of ecosystems, is declining globally ([Rockstrom et al., 2009](#)). Decades of study show that added N reduces autotrophic diversity in terrestrial and aquatic systems, fungal biodiversity in soils, and, although less studied, animal diversity in terrestrial and aquatic systems ([Howarth et al., 2011](#); [Bobbink et al., 2010](#)). As previously mentioned, two mechanisms that contribute to altered biodiversity are eutrophication and acidification. Eutrophication often causes N stimulated growth for opportunistic species, which may cause competitive exclusion of poorer competitors and soil acidification driving cation imbalances and physiological stresses, suppressing seed germination and seedling regeneration ([Sullivan et al., 2013](#); [Roem et al., 2002](#)). In addition, N may alter physiology and/or community properties, increasing the risk to secondary factors such as pests, fire, frost, and drought ([Bobbink et al., 2010](#)). Lastly, direct damage to vegetation from ammonia (NH<sub>3</sub>), nitrogen dioxide (NO<sub>2</sub>), nitrogen monoxide (NO), peroxyacetyl nitrate (PAN), and nitric acid (HNO<sub>3</sub>) exposure is known to occur, but most likely occurs in highly polluted areas and in close proximity to high emission sources ([Greaver et al., 2012](#)). In terrestrial ecosystems, all processes generally reduce local autotroph diversity and homogenize habitats into communities with small numbers of generally fast-growing or acid-tolerant autotrophic species. These changes propagate through the food web, leading to increases of generalist pests, herbivores, and parasitic soil bacteria, and decreases in specialist herbivores and beneficial microbial communities that occur belowground ([de Sassi et al., 2012](#)).

“Biodiversity responses on land may be moderated by the type of climate change occurring and the mechanism of N response. In terrestrial systems that get warmer and wetter, eutrophication may be amplified if endogenous N sources are low or dampened if endogenous sources are high/more liberated to meet community demand. The response of the acidification pathway may depend on whether the change in net fluxes of cations from climate change exceeds the net fluxes of N [i.e., from enhanced deposition of cations and N, decomposition or weathering, and leaching ([Howarth et al., 2011](#); [Roem et al., 2002](#))]. Many of these processes may be dampened in terrestrial systems that are anticipated to get warmer and drier (e.g., southwestern U.S.) due to the drier conditions reducing biological activity ([Bobbink et al., 2010](#)). Colder regions such as montane, alpine, and tundra systems are often strongly N limited and poorly buffered; thus, an extended growing season under climate change will lead to greater opportunities for all operating processes. Climate change may also magnify the effects of secondary stressors in several ways, including increased pest populations under warmer wetter conditions, as well as increasing fire potential and drought vulnerability as more aboveground plant tissue is produced under elevated N ([Dise et al., 2011](#)). Nonetheless, field evidence for interactions between N and climate change under controlled conditions is scarce. The few existing studies find additive effects in Mediterranean California ([Zavaleta et al., 2003](#)), and no interactive effects of precipitation and N addition in Minnesota ([Reich et al., 2014](#); [Reich, 2009](#)). Not all terrestrial ecosystems are anticipated to be equally sensitive to these pressures. In grasslands, many forbs and slow-growing species such as native C4 grasses appear especially vulnerable to added N ([Clark and Tilman, 2008](#); [Zavaleta et al., 2003](#)). In a study of northeastern forests, all three tree species with negative growth responses to N deposition were evergreen conifers (e.g., *Pinus resinosa*, *Picea rubens*, *Thuja occidentalis*), while all five tree species with positive growth responses were broadleaf species with arbuscular mycorrhizal associations [e.g., *Acer rubrum*, *A. saccharum*, *Fraxinus americana*, *Liriodendron tulipifera*, and *Prunus serotina* ([Thomas et al., 2010](#))]. However, contingent factors underly these general patterns, as there were tree species from each group that did follow these generalities.

“In aquatic systems, elevated temperatures and N inputs from increased rain and glacial retreat will likely magnify changes in algal assemblages that can propagate through the food web ([Hobbs et al., 2010](#); [Elser et al., 2009a](#)). In freshwater aquatic biodiversity research, there is a substantial amount of work on lakes investigating the effects of warming via gradient studies (latitude or altitude), warming experiments, time series, and paleoecology ([Jeppesen et al., 2014](#)). Fish community assemblages, size, structure, and dynamics are likely to change with continued global warming, and in some cases the elevated temperatures that have already occurred in the past decades. Fish cannot thermoregulate, but only physically move to areas with appropriate temperatures, if those are accessible. In general, changes in fish composition, particularly in shallow lakes, are

characterized by a decline in abundance of several cold-stenothermal species ([Kangur et al., 2013](#); [Winfield et al., 2010](#)) and in increases in eurythermal species, which exhibit a wide range of thermal tolerance ([Jeppesen et al., 2012](#)). Many fish species are also adapted to specific oxygen concentrations; when temperature increases, oxygen may drop to critical levels as warm water holds less oxygen and the respiration rates increase. Warming effects on the biodiversity of grazing macroinvertebrates and zooplankton is mixed across studies ([Özen et al., 2013](#); [Burgmer et al., 2007](#)). Warming is shown to increase cyanobacteria biomass ([Kosten et al., 2012](#)) and biofilm biomass ([Williamson et al., 2016](#)), while warming effects on phytoplankton show mixed results ([Meerhoff et al., 2012](#); [Feuchtmayr et al., 2009](#)).

“Warming may cause increases in evaporation that will lower water level and increase salinity ([Williams, 2001](#)). Increasing salinity of freshwater systems tends to have a negative effect on phytoplankton, zooplankton, macroinvertebrates, and fish ([Jeppesen et al., 2007](#)). Climate change will alter the transport, availability, and timing of N in ecosystems, and recent data indicates an increase of primary production limitation by N or colimitation by N and P ([Elser et al., 2009a](#)). In N-limited fresh waters, N enrichment enhances rapid growth of nitrophilic algae that outcompete other populations for light and resources such as P and silicon (Si), leading to dominance by a few algal species and a reduction in the nutritional quality of invertebrates as food for fish ([Baron et al., 2012](#); [Hobbs et al., 2010](#); [Elser et al., 2009a](#)). The combination of increasing both N and temperature may be synergistic and sometimes difficult to uncouple ([Kangur et al., 2013](#)), as both may stimulate hypoxic conditions, consequently altering community structure ([Özen et al., 2013](#); [Feuchtmayr et al., 2009](#)) and the frequency, intensity, extent, and duration of harmful algal blooms ([Paerl et al., 2011](#)).

“Presently, there are at least 78 listed or candidate species for threatened or endangered status in North America that have N impacts identified as a primary contributor, and an estimated 15–37% of species may be at risk from climate change ([Hernández et al., 2016](#)). In total, there are numerous pathways whereby these dominant global change factors can interact to impact biodiversity, and it is likely, although not definitive, that N and climate often have additive and potentially amplifying effects on decreasing biodiversity in many systems.”

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#### **13.1.4.2 Additional Considerations**

There are considerations to note in addition to the excerpt from [Greaver et al. \(2016\)](#). Additional papers on climate interactions with N and biodiversity discussed in [Appendix 6](#) are summarized in [Table 13-4](#). Most notably there are several new studies on

the interacting effects of climate and N deposition on plant species richness, and community composition of plants, soil microbes and soil animals.

**Table 13-4 Summary on climate modification of nitrogen (N) effects on biodiversity in [Appendix 6](#) in addition to those in [Appendix 13](#).**

Indicator/Process	T	P	Snow	Reference
Plant species richness	X			<b>Empirical:</b> No significant interaction between N and temperature on plant species richness for closed-canopy systems (deciduous, evergreen, and mixed forests), but significant interaction in open-canopy systems (grasslands, shrublands, and woodlands). In these open-canopy ecosystems, N had a more negative effect on species richness at lower temperatures. <a href="#">Simkin et al. (2016)</a>
Plant community composition	X	X		<b>Model:</b> In the ForSAFE-VEG model projections of plant community composition in three French forests two N reduction scenarios showed that recovery of these plant communities occurred only if climatic factors are held constant at current levels. <a href="#">Rizzetto et al. (2016)</a>
Plant community composition	X	X		<b>Model:</b> Understory plant community composition in northern hardwood forests at Bear Brook Watershed in Maine and Hubbard Brook in New Hampshire: the simulated plant community composition returned toward preindustrial conditions over the next century only in a scenario in which N deposition rates returned to background and climate was kept stable. <a href="#">Phelan et al. (2016)</a>
Soil microbial community		X		<b>Empirical:</b> N additions and lower precipitation interacted to shift microbial community composition in forests soils in northeastern China. <a href="#">Wang et al. (2014c)</a>
Soil microbial community		X		<b>Empirical:</b> N additions and lower precipitation interacted to shift microbial community composition in grassland soils in Inner Mongolia. <a href="#">Li et al. (2016a)</a>
Ectomycorrhizal species composition		X		<b>Empirical:</b> Both changes in precipitation and nitrogen were associated with shifts in ectomycorrhizal species composition in European Scots pine. <a href="#">Jarvis et al. (2013)</a>
Nematode predators, microarthropod herbivores, and taxa richness of nematodes and microarthropods		X		<b>Empirical:</b> In Minnesota grassland, a decline was observed in several categories of biota within a soil food web (numbers of nematode predators, microarthropod herbivores, and taxa richness of nematodes and microarthropods) under increased N, and a decrease in ciliate protists under high N and drought. <a href="#">Eisenhauer et al. (2012)</a>

**Table 13-4 (Continued): Summary on climate modification of nitrogen (N) effects on biodiversity in Appendix 6 in addition to those in Appendix 13.**

Indicator/Process	T	P	Snow	Reference
Algal species composition	X			<a href="#">Rühland et al. (2015)</a> . In regions with no evidence of increased atmospheric nutrient inputs, warming trends are observed to enhance competitiveness of planktonic diatoms like <i>Asterionella formosa</i> , which are typically associated with elevated N, indicating that climate change has significant direct and indirect effects on algal species composition. Climate change may thus enhance the effects observed in areas with nutrient increases alone.

## 13.2 Estuaries

In addition to terrestrial and freshwater systems described above, climate change modifies key processes in estuarine and near-coastal systems linked to nutrient inputs. Atmospheric deposition may represent more than 40% of N in coastal water bodies ([Appendix 7](#)). N sources to near-coastal ecosystems include direct deposition to the water surface and all other N sources upstream. Coastal eutrophication is a process of increasing nutrient over-enrichment indicated by water quality deterioration, resulting in numerous adverse effects including hypoxic zones (water with dissolved oxygen that is too low to support marine life), species mortality, proliferation of phytoplankton and macroalgae (including harmful algal blooms), and decreased coverage of submerged aquatic vegetation [([Bricker et al., 2007](#)); [Appendix 10](#)].

Indicators of nutrient enrichment may be affected by climate-related changes in estuaries including temperature, precipitation, wind patterns, stronger estuary stratification, increased metabolism and organic production, and sea-level rise [see discussion in [Appendix 10](#); ([Altieri and Gedan, 2015](#); [Statham, 2012](#); [Rabalais et al., 2009](#))]. For example, eutrophic conditions and the extent and duration of hypoxia are predicted to increase with changes in temperature and precipitation ([Altieri and Gedan, 2015](#); [Rabalais et al., 2009](#); [Boesch et al., 2007](#)). [Doney et al. \(2012\)](#) reviewed effects of climate change, including coastal hypoxia, on marine biodiversity and reported population-level shifts. In estuaries affected by nutrient enrichment and climate-associated alterations described above, conditions favor a shift in phytoplankton composition toward greater abundance and distribution of toxic cyanobacteria associated with an increased prevalence of harmful algal blooms ([Paerl et al., 2016a](#)). In a meta-analysis of temperature effects on benthic macrofauna, survival times significantly decreased in hypoxic conditions under warmer temperatures ([Vaquer-Sunyer and Duarte,](#)

[2011](#)). Decreases in estuarine biodiversity associated with N loading can be magnified by hydrologic factors. [Glibert et al. \(2014\)](#) observed a regional change in phytoplankton community composition and decreased coverage of submerged aquatic vegetation following a shift from long-term dry to long-term wet conditions in the early 2000s in shallow coastal lagoons along the coast of Maryland and Virginia. Shifts in phytoplankton community structure are known to occur in estuaries due to N enrichment, but climate changes may at times outweigh the impacts of eutrophication ([Paerl et al., 2010](#)). Thus, physical changes caused by climate change should be considered when modeling phytoplankton community response to N enrichment ([Paerl et al., 2014](#)).

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### 13.3 Wetlands

Changes in mean annual temperature and frequency and magnitude of precipitation will affect the responses of all wetlands to N loading ([Appendix 11](#)).

Increasing temperatures may strengthen N effects upon wetland ecosystems. Temperature effects on wetlands have been demonstrated in European bog ecosystems, where increased temperatures increased the cover of woody species and decreased *Sphagnum*. N addition and temperature are known to synergistically depress *Sphagnum* production, with a 1°C increase in summer temperature having an impact on the *Sphagnum* equivalent to an additional 40 kg N/ha/yr ([Limpens et al., 2011](#)).

Hydrologic regimes are important controls on wetland cycling and productivity, so changes in the magnitude and frequency of precipitation can have strong effects on ecosystem N retention and C storage. Increased precipitation is shown to increase *Sphagnum* sensitivity to N addition-induced decreases in production ([Limpens et al., 2011](#)). Experimental mesocosms modeling changes in precipitation to salt marshes found that precipitation delivered in infrequent, heavy storm events decreased N retention and plant productivity, even though storm events delivered a higher N deposition load to the marsh ([Hanson et al., 2016](#); [Oczkowski et al., 2016](#)). Shifts in precipitation towards less frequent, more intense rain events may strengthen N deposition-induced decreases in salt marsh N retention while weakening N deposition-induced increases in plant productivity.

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## APPENDIX 14 ECOSYSTEM SERVICES

This appendix is a review of the state of the science on ecosystem services altered by nitrogen (N) and sulfur (S) deposition. The state of the science in 2008, as presented in the *2008 Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria* (hereafter referred to as the 2008 ISA), is summarized and sets the foundation for the discussion on the new literature (published from 2008–present).

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### 14.1 Introduction

“Ecosystem services” refers to the concept that ecosystems provide benefits to people, directly or indirectly ([Costanza et al., 2017](#)), and that ecosystems produce socially valuable goods and services deserving of protection, restoration, and enhancement ([Boyd and Banzhaf, 2007](#)). The concept of ecosystem services recognizes that human well-being and survival are not independent of the rest of nature, but rather that humans are an integral and interdependent part of the biosphere ([Costanza et al., 2017](#)). In some cases, and in line with more conventional economic thinking, ecosystem services analysis can result in attaching monetary values to ecosystem outcomes. However, because ecosystem services are often public goods their benefits can be difficult to monetize (see case study boxes for lace lichen on page 14-5 and the Chesapeake Bay on 14-10 as examples). We emphasize that this practical difficulty in no way implies that ecosystem service benefits are small or without value. At a minimum, ecosystem services analysis involves discussion and, ideally, quantification of ecological outcomes understood by households, communities, and businesses. Explicitly linking ecosystem services to social and economic welfare measures has proven difficult because of the broad definition of ecosystem services and the numerous types of services that could be affected. An analysis of ecosystem services specifically altered by NO<sub>x</sub>, SO<sub>x</sub>, and PM would translate the effects of ambient concentrations and deposition into biological, physical, or monetary metrics that give insight to public welfare effects.

The 2008 ISA documented the ecosystem services frameworks that were published at that time and provided several examples of how N and S deposition would alter services based on those frameworks. Since the 2008 ISA, new ecosystem services frameworks have been developed and several new approaches have been applied to conduct ecosystem services analysis specifically evaluating outcomes altered by N and S deposition. The conclusions considering the full body of literature published are that (1) there is evidence that N and S deposition has a range of effects on ecosystem services and their social value; (2) there are some economic studies that demonstrate such effects

in broad terms; however, it remains methodologically difficult to derive economic costs and benefits associated with specific regulatory decisions/standards; and (3) new work has identified a large number of scientifically and economically plausible causal relationships that link N and S air pollution to changes in Final Ecosystem Goods and Services (FEGS), defined as the “components of nature, directly enjoyed, consumed or used to yield human wellbeing” ([Boyd and Banzhaf, 2007](#)). The following sections discuss the relevant ecosystem services frameworks ([Appendix 14.2](#)), the studies in the U.S. on ecosystem services altered by acidification and eutrophication ([Appendix 14.3](#)), the studies of ecosystem services analyses conducted in countries outside of the U.S. ([Appendix 14.4](#) and [Appendix 14.5](#)), and a summary ([Appendix 14.6](#)).

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## 14.2 Ecosystem Services Frameworks

Ecosystem services frameworks can help identify causal pathways between specific ecosystem changes and potential human beneficiaries. A single classification system may be desirable to promote standardization and communication. However, classification systems do not by themselves solve the core issue of how to empirically quantify causal relationships between N and S and final ecosystem goods and services. Here an overview of key frameworks is presented to give context on conceptual advances in ecosystem services research.

Several ecosystem services frameworks were published in 2008 and described in the 2008 ISA. These frameworks provided qualitative and/or quantitative metrics by which to identify the services that ecosystems provide to benefit human welfare and society ([WRI, 2000](#); [Costanza et al., 1997](#); [Daily, 1997](#); [Pimentel et al., 1997](#)). It was well documented at that time that some goods and services have explicit market value; however, the value of other services is more difficult to assess ([U.S. EPA, 2008a](#); [Goulder and Kennedy, 1997](#)). The most accepted framework for ecosystem services identified by the 2008 ISA was the 2005 Millennium Ecosystem Assessment (MEA) by [Hassan et al. \(2005\)](#). Since the 2008 ISA, several new ecosystem services frameworks and classification systems have been published. These include The Economics of Ecosystems and Biodiversity [TEEB; [Sukhdev et al. \(2014\)](#)], the Common International Classification of Ecosystem Services [CICES; [Haines-Young and Potschin \(2011\)](#)], U.S. EPA Final Ecosystem Goods and Services Classification System [FEGS-CS; [Landers and Nahlik \(2013\)](#)], and The National Ecosystem Services Classification System [NESCS; [U.S. EPA \(2015d\)](#)].

The goal of the TEEB initiative is to demonstrate the economic value of services provided by species and ecosystems and then capture the value of these services through market- or policy-based approaches ([Sukhdev et al., 2014](#)). The TEEB initiative uses four

primary categories of ecosystem services. Three of the four categories are from the MEA (provisioning, regulating, and cultural services). However, TEEB replaces the MEA's "supporting services" with "habitat services," which emphasizes the provisioning of species and genetic diversity.

The CICES framework was developed in part as a reaction to the increasingly diverse ways that ecosystem services were discussed, categorized, and assessed by different organizations around the world. The CICES program has as a primary goal to create a more uniform approach to assessing ecosystem services ([Haines-Young and Potschin, 2011](#)). The classification approach CICES developed recognizes only final outputs from ecosystems, in other words, "products" that are directly consumed or used by people ([Haines-Young and Potschin, 2011](#)). Thus, the concept of "supporting services" identified by the MEA was dropped under the assumption that these functions would be recognized for their role in facilitating the final outputs. CICES developed a hierarchical structure, beginning with the three broad categories (provisioning, regulating, and cultural), which were broken down into 23 "service groups" and then 59 "service types" ([Haines-Young and Potschin, 2011](#)).

The FECS-CS framework uses the concept of Final Ecosystem Goods and Services (FECS), which are defined as a subset of ecological outcomes, specifically the "components of nature, directly enjoyed, consumed or used to yield human well-being" ([Boyd and Banzhaf, 2007](#)). The U.S. EPA FECS-CS approach defines and classifies 338 unique FECS, each uniquely numbered by a combination of environmental class or subclass and a beneficiary category or subcategory ([Landers and Nahlik, 2013](#)). In addition to FECS-CS, the U.S. EPA also developed NESCS to specifically analyze the human welfare impacts of policy-induced changes to ecosystems ([U.S. EPA, 2015d](#)). The goal of NESCS is to support analysis of changes from baseline conditions, such as cost-benefit analysis, and support systematic accounting of changes in ecosystem services. The NESCS structure defines categories and numeric codes that are designed to help identify flows of services from ecosystems to human beings, while distinguishing between the producers (i.e., "supply-side") and users (i.e., "demand-side") of the service.

Lastly, [Bell et al. \(2017\)](#) developed the Stressor—Ecological Production function—final ecosystem Services (STEPS) framework. STEPS produces "chains" comprised of the biological indicator, the ecological production function (EPF, which uses ecological components to link the biological indicator to a final ecosystem service), and the user group who directly uses, appreciates, or values the component. To this end, STEPS is used in conjunction with other frameworks that identify user groups, like FECS-CS. The framework uses a qualitative score (high, medium, low) to describe the strength of science (SOS) for the relationship between each component in the EPF.

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## 14.3 United States Applications

Among the ecological effects of N and S deposition, the ecosystem services altered by acidification are the most well documented, with several new papers published since 2008 ([Beier et al., 2017](#); [Caputo et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Banzhaf et al., 2016](#); [Office of Air and Radiation, 2011](#); [Chestnut and Mills, 2005](#); [Banzhaf et al., 2004](#); [U.S. EPA, 1999](#); [NAPAP, 1991](#)). In the 2008 ISA, no publications were identified describing how ecosystem services were altered as a result of N driven eutrophication; however, several new comprehensive studies have been published since 2008 ([Clark et al., 2017](#); [Rhodes et al., 2017a](#); [Compton et al., 2013](#); [Birch et al., 2011](#); [Compton et al., 2011](#)). Also new to the literature since 2008 is a group of publications ([Bell et al., 2017](#); [Clark et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Rhodes et al., 2017a](#)) evaluating the FECS altered by four modes of ecological response to N and S deposition (aquatic acidification, terrestrial acidification, aquatic eutrophication, and terrestrial eutrophication). In these analyses critical load (CL) exceedances for N related air pollution were used as a model stressor from which a total of 1,104 unique chains linking stressor to beneficiary were identified. These analyses, built using a holistic STEPS approach, represent a great advance for identifying the wide range of ecosystem processes and types of final ecosystem services affected by N and S deposition. However, it also underscores the many information gaps that exist for quantifying the dose-response relationships between N and S air pollution exposures and final ecosystem services and the values associated with changes in these services.

Two recently published studies ([Jaramillo and Muller, 2016](#); [Holland et al., 2015](#)) have used the Air Pollution Emissions Experiments and Policy (APEEP or AP2) to calculate the value of damages from emissions of SO<sub>2</sub>, VOCs, NO<sub>x</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>, and NH<sub>3</sub>. The model connects changes in emissions to concentrations of several criteria air pollutants. A large majority of the damage estimates are associated with human health impacts and ozone-related damages to crops and forests. A very small portion of damages are linked to forest and recreation impacts from a mix of ambient pollutants including NO<sub>x</sub> and SO<sub>x</sub>, but this portion of the model was developed before 2006, has not been updated, and is not well documented (i.e., the model structure is described but not the estimated parameters).

### How do N deposition impacts on lace lichen affect forest ecosystem services?

Native to the Pacific coast of North America, lace lichen (*Ramalina menziesii* [Ramalinaceae]) grows from Alaska to Baja California. It has a unique morphology that adds to the natural beauty of coastal woodlands along the Pacific Coast ([Hastings Reserve, 2015](#)). It is a food source for browsing mammals, including deer, cows, and squirrels, and is also used as a nesting material for hummingbirds and orioles (Hastings Reserve).



*Photos source: 2016 AQE workshop report.*

Unfortunately, lace lichen abundance is threatened by nitrogen and sulfur pollutants' deposition ([Hernández et al., 2016](#)). It is very sensitive to air pollution, including exposure to nitric acid ([Riddell et al., 2008](#)), and it has been found to contribute to the global uptake of sulfur dioxide, an airborne pollutant ([Gries et al., 1997](#)). Lace lichen was formerly found in the San Jacinto Mountains near Los Angeles and on the surrounding coastal plain but now it only grows at elevations above the smog layer ([Hastings Reserve, 2015](#)).

Declines in lace lichen abundance can reduce ecosystem services to humans in several ways. In addition to reducing the aesthetic benefits provided by lichens, declines in lace lichen may be indirectly contributing to declining populations of the spotted owl, which is an endangered, widely recognized, and charismatic species native to Pacific Northwest forests. This indirect impact may be occurring because the northern flying squirrel, which is an almost exclusive food source for the spotted owl, relies exclusively on forage lichens as a winter time food source.

## **14.3.1 Acidification**

Prior to 2008, ecosystem acidification in the U.S. was evaluated with regard to how ecosystems services respond to lowering NO<sub>x</sub> and SO<sub>x</sub> emissions. Initial monetary valuation of the total annual value for improvements in recreational fishing ([NAPAP, 1991](#)) were improved with updated economic studies and new models for estimating the changes in fish stocks and catch rates in the Adirondacks ([U.S. EPA, 1999](#)). A few years later, [Chestnut and Mills \(2005\)](#) derived new estimates and compared them with the 1990

estimates of the benefits of reducing emissions of NO<sub>x</sub> and SO<sub>x</sub> in Title IV of the Clean Air Act Amendments (CAAA). They concluded that the 1990 quantitative assessment was limited by a lack of measurement units to gauge changes in the quality and quantity of ecosystem services and a lack of dose-response relationships to indicate how quality and quantity may change as a function of changes in pollution exposures. A different approach, that did not rely on dose-response relationships, documented that New York households are willing to pay an average of \$45 to \$100 annually to reduce the number of acidified lakes by 40% and improve forest health in the Adirondacks ([Banzhaf et al., 2004](#)).

Several ecosystem services valuations for acidification published (since 2008) are given in [Table 14-1](#). [Rea et al. \(2012\)](#) paired biogeochemical modeling using the Model for Acidification of Groundwater in Catchment (MAGIC) with two different approaches, one benefit transfer and one random utility, to estimate ecosystem services values for remediation scenarios of acidic deposition on lakes in New York's Adirondack Park. [Beier et al. \(2017\)](#) and [Caputo et al. \(2017\)](#) have also calculated new monetary valuations of acidification effects in the Adirondacks ([Table 14-1](#)). New work in the southern Appalachian region used an approach that wedges biogeochemical (e.g., MAGIC) and economic modeling to evaluate the cost of aquatic and terrestrial acidification ([Banzhaf et al., 2016](#)).

Two new studies used FECS-CS to quantify how many FECS are altered by ecosystem acidification and associated critical load (CL) or total load (TL) exceedance ([Irvine et al., 2017](#); [O'Dea et al., 2017](#)). [O'Dea et al. \(2017\)](#) identified human beneficiary groups for each ecological endpoint affected by aquatic acidification, including effects on otter, mink, loon, aquatic vegetation, shellfish, brook trout, and bass. [Irvine et al. \(2017\)](#) documented the effects of terrestrial acidification on two acid-sensitive tree species, balsam fir (*Abies balsamea*) and white ash (*Fraxinus Americana*; [Table 14-1](#)).

Overall, the new literature since the 2008 ISA includes studies that better characterize ecosystem services valuation by pairing biogeochemical modeling and benefit transfer equations informed by WTP surveys, especially for the Adirondacks and Shenandoah regions. Aside from valuation, the estimate of the total number of ecosystem services affected by N and S deposition is better quantified by the new studies that use FECS-CS. However, for many regions and specific services, poorly characterized dose-response relationships between deposition, ecological effect, and services are the greatest challenge to quantification of the economic benefits of emission reductions ([NAPAP, 2011](#)).

**Table 14-1 Ecosystem services research related to ecosystem acidification.**

Mode	Region	Effect	Reference
Aquatic acidification	Adirondacks	In 1990, the estimates of total annual value for improvements due to lowering NO <sub>x</sub> and SO <sub>x</sub> emissions in recreational fishing were \$12 to \$24 million.	<a href="#">NAPAP (1991)</a>
Aquatic acidification	Adirondacks	Reported estimates of annual value of improvements in conditions for recreational fishing in the Adirondacks of about \$65 million for the reductions in acid deposition as a result of the 1990 CAAA, primarily Title IV.	<a href="#">U.S. EPA (1999)</a>
Aquatic acidification		Compare the actual benefits of reducing emissions of NO <sub>x</sub> and SO <sub>x</sub> in Title IV of the Clean Air Act Amendments (CAAA) by the estimate of benefits made in 1990.	<a href="#">Chestnut and Mills (2005)</a>
Aquatic acidification	Adirondacks	New York households are willing to pay an average of \$45 to \$100 annually to reduce the number of acidified lakes by 40% and improve forest health in the Adirondacks.	<a href="#">Banzhaf et al. (2004)</a>
Aquatic acidification	Adirondacks	Linked NO <sub>x</sub> and SO <sub>x</sub> emissions estimates to CMAQ modeling, MAGIC modeling, then a Random Effects Model that was developed to account for fishing site choices made by recreational fishers based on attributes of sites specifically in the Adirondack region. The difference in economic welfare values between the value of fishable (i.e., not impaired) lakes in the with-CAAA scenario and the without-CAAA scenario represented the benefits to recreational fishing in the Adirondack region associated with the CAAA.	<a href="#">Office of Air and Radiation (2011)</a>
Terrestrial Acidification	Adirondacks	The changes in percent base saturation levels in timber harvest areas were mapped in relation to potential changes in the growth and health of tree species present in these areas and the likely effects of altered tree growth and health on timber harvest rates and volumes. Of the forest types of interest, the paper birch forest type experiences the greatest increase in percent base saturation due to the CAAA, followed by the eastern hemlock and the sugar maple/beech/yellow birch forest types.	<a href="#">Office of Air and Radiation (2011)</a>
Aquatic acidification	Adirondacks (44 lakes)	Biogeochemical modeling (e.g., MAGIC) is combined with a benefit transfer approach based on a stated preference study, which captures ecosystem services values as a whole. Total values range from \$547 million to \$1 billion/yr. In contrast, an approach based on a preference study, which only captures recreation fishing values, estimated benefits ranging from \$7 million to \$9 million/yr.	<a href="#">Rea et al. (2012)</a>
Aquatic and terrestrial acidification	Southern Appalachia (169 sites)	Hypothetical scenarios of lower emissions are coupled with biogeochemical modeling (e.g., MAGIC) and a novel stated preference survey to determine individuals' WTP is used to generate aggregate benefits of about \$3.7 billion, or about \$16/yr/household in the region.	<a href="#">Banzhaf et al. (2016)</a>

**Table 14-1 (Continued): Ecosystem services research related to ecosystem acidification.**

Mode	Region	Effect	Reference
Terrestrial acidification	Adirondacks	Blending regression analysis of tree growth and soil condition with a benefit transfer approach, it was estimated that acid-impaired hardwood forests provide roughly half of the potential benefits of forests on moderate to well-buffered soils—an estimated loss of ~\$10,000 ha <sup>-1</sup> in net present value of wood products, maple syrup, carbon sequestration, and visual quality.	<a href="#">Beier et al. (2017)</a>
Aquatic acidification	Adirondacks (52 study lakes)	Acidic deposition has had little effect on lakes water suitable for drinking in the region. However, as pH declines in lakes, the estimated value of recreational fishing decreases significantly due to loss of desirable fish. The expected value of recreational fishing increased with increasing pH, from a minimum of \$4.41 angler/day in unstocked, acid-impaired lakes to a maximum of \$38.40 angler/day in well-buffered lakes that were stocked with trout.	<a href="#">Beier et al. (2017)</a>
Aquatic acidification	Adirondacks	Analysis of benefit transfer using willingness-to-pay (WTP) for recreational fishing and logistic regression of fish populations demonstrated that under low emissions scenarios combined with fish stocking. These are the same results reported in <a href="#">Beier et al. (2017)</a> .	<a href="#">Caputo et al. (2017)</a>
Aquatic acidification	U.S. national-scale	Using FEGS-CS to quantify the total number of causal relationships between aquatic acidification driven by N and S deposition and beneficiaries. Effects were documented on otter, mink, loon, aquatic vegetation, shellfish, brook trout, and bass.	<a href="#">O'Dea et al. (2017)</a>
Terrestrial acidification	Northeastern U.S.	Using FEGS-CS to identify 160 chains with 10 classes of human beneficiaries for balsam fir and white ash combined, the authors concluded there are resources at risk that the public may value. Estimated ~1,200 chains if all vulnerable tree species are evaluated.	<a href="#">Irvine et al. (2017)</a>

### 14.3.2 Eutrophication

Since the 2008 ISA, several comprehensive studies have been published on the ecosystems services related to N pollution in the U.S. ([Table 14-4](#)). These include an evaluation of services effected by multiple N inputs (including N deposition) to the Chesapeake Bay ([Birch et al., 2011](#)) and syntheses by [Compton et al. \(2011\)](#) and [Compton et al. \(2013\)](#) of the cost-benefits on N loading across the nation for services that included coastal fish harvests, recreational uses of inland and coastal waters, lakefront property values, and water treatment costs. Further expanding on this work, [Sobota et al. \(2015\)](#) calculated the amount of N loading from human activity that is leaked into adjacent ecosystems and the associated effects on ecosystem services. In their work, [Sobota et al. \(2015\)](#) specifically identified the costs of the atmospheric portion of total N

loading. [Baron et al. \(2012\)](#) evaluated the interactions between climate and N, identifying some key services in which a changing climate will modify the response to N.

[Birch et al. \(2011\)](#) examined the spatial and temporal movement of reactive N through multiple ecosystems and media in the Chesapeake Bay watershed and estimated damage costs in several categories ([Figure 14-1](#)). Their analysis estimates the contribution of atmospheric N sources to the total annual N loads delivered to the bay estuary. According to the study, roughly 20% of N related ecosystem services impacts in the estuary are attributable to atmospheric N deposition in the watershed.

Building on the work by [Birch et al. \(2011\)](#), a review and synthesis of the published literature by [Compton et al. \(2011\)](#) compared estimates of the average damage costs/unit of N across a range of affected services. Further building on this work, [Sobota et al. \(2015\)](#) estimated how unintentional N input into the environment (via air/deposition, surface freshwater, groundwater, and coastal zones) alters services. They did this by multiplying watershed-level N inputs (8-digit U.S. Geologic Survey hydrologic unit codes; [HUC8s]) with published coefficients describing nutrient uptake efficiency, leaching losses, and gaseous emissions. [Sobota et al. \(2015\)](#) then applied per-unit damage cost values (\$/N) for a wide variety of ecological effects (based on estimates from various sources, [Table 14-2](#)) to the input estimates.

### Why are aquatic grasses on the path between N deposition and ecosystem services in the Chesapeake Bay?

The Chesapeake Bay is the largest estuary (4,480 sq miles) in the U.S. draining from eight major river basins covering 64,000 sq miles of watershed in six states and a population of 18 million watershed residents. The public's use of the bay is significant with more than 700 public access points on the bay and its tributaries. More than 3,600 species of plants and animals are supported by the bay, including over 80 resident and migratory waterfowl species. About 500 million pounds of seafood is produced annually by the bay (<https://www.chesapeakebay.net>).

Unfortunately, this vital natural resource and estuarine ecosystem are under stress, and nitrogen deposition in the Chesapeake Bay watershed is one of the main contributing sources. The Chesapeake Bay Program reports that one-third of the nitrogen loading to the bay comes from atmospheric deposition, often as nitrogen oxides or ammonia ([https://www.chesapeakebay.net/issues/air\\_pollution](https://www.chesapeakebay.net/issues/air_pollution)). Nitrogen air emission sources include automobiles, fossil fuel-fired electric generating units, and intensive animal operations both within and upwind of the bay watershed.

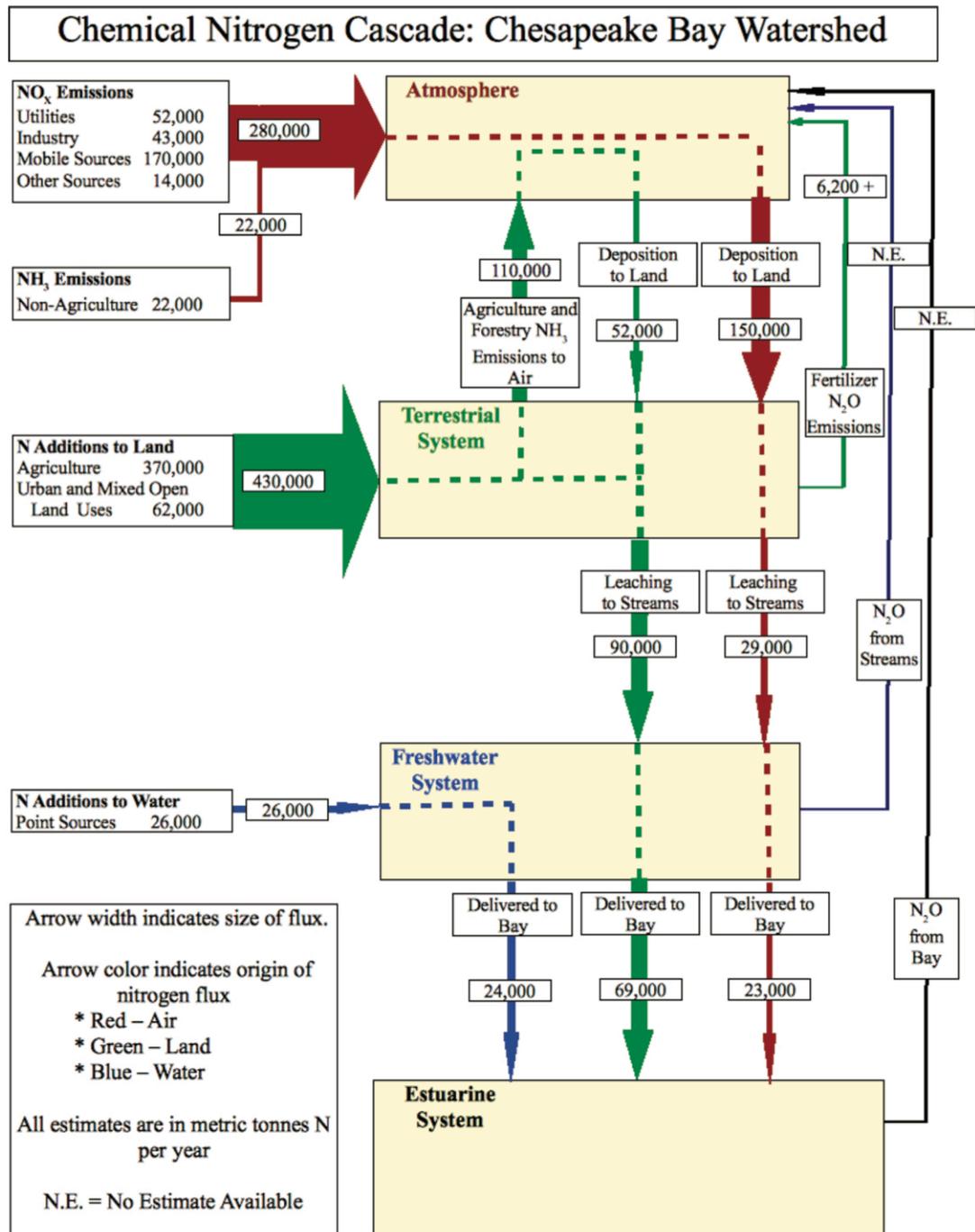
One of the most important indicators of environmental stress to the Chesapeake Bay is the loss of submerged aquatic vegetation (SAV). Nutrient over-enrichment and sediment overloading to the bay has led to SAV loss. Although SAV appears to be recovering as NO<sub>x</sub> emissions have declined in recent decades, the bay still contains only an estimated 53% of the SAV it once supported. The Chesapeake Bay Program's target restoration goal is 185,000 acres ([https://www.chesapeakebay.net/state/underwater\\_grasses](https://www.chesapeakebay.net/state/underwater_grasses)).



Photo courtesy of Chesapeake Bay Program

SAV is a critical indicator of the bay's health in part because of the essential role it plays in supporting a wide range of final ecosystem services to humans. The 80,000 acres of underwater grasses protect and host young and molting blue crabs and juvenile, for example (<https://www.chesapeakebay.net/discover/facts>). SAV supports natural ecosystems in additional ways, including serving as a food source for wildlife, waterfowl, and humans and as habitat (and protection) for wildlife and waterfowl (Barbier et al., 2011; Kemp et al., 2005). In turn, SAV facilitates important recreation, tourism, and commerce, including wildlife and waterfowl watching, fishing, and crabbing. In addition to these valuable indicators of overall WQ and ecosystem health, SAV deters and dissipates wave energy and promotes sedimentation for landowners along the bay, thus, mitigating erosion and protecting and sustaining land value.

The SAV connection is, therefore, one important pathway through which N deposition affects the well-being of human populations in and around the bay.



**FIGURE 1. Chemical Nitrogen Cascade in the Chesapeake Bay Watershed (tonnes/year). See SI for sources and calculations.**

N = nitrogen; N.E. = no estimate available; N<sub>2</sub>O = nitrous oxide; NH<sub>3</sub> = ammonia; NO<sub>x</sub> = nitrogen oxide.

Source: ACS, <https://pubs.acs.org/doi/10.1021/es101472z>, further permissions related to the material excerpted should be directed to the ACS.

**Figure 14-1 Economic nitrogen cascade in the Chesapeake Bay Watershed.**

**Table 14-2 Potential damage costs of nitrogen (N) (\$/kg N; 2008 or as reported) to air, land, and water resources in the conterminous U.S. in the early 2000s as synthesized by [Sobota et al. \(2015\)](#). Low, median, and high costs derive from the specific damage cost reference. Negative values indicate an economic benefit.**

N damage type	System	Cost (\$/kg N)			Reference
		Low	Median	High	
<b>From atmospheric NO<sub>x</sub></b>					
Increased incidence of respiratory disease	Air/Climate	12.88	23.10	38.63	<a href="#">Van Grinsven et al. (2013)</a> ; <a href="#">Birch et al. (2011)</a>
Declining visibility—loss of aesthetics	Air/Climate	0.31	0.31	0.31	<a href="#">Birch et al. (2011)</a>
Increased effects of airborne particulates/increased carbon sequestration in forests (includes benefits)	Air/Climate	-11.59	-4.51	2.58	<a href="#">Van Grinsven et al. (2013)</a>
Increased damages to buildings from acid	Land	0.09	0.09	0.09	<a href="#">Birch et al. (2011)</a>
Increased ozone exposure to crops	Land	1.29	1.51	2.58	<a href="#">Van Grinsven et al. (2013)</a> ; <a href="#">Birch et al. (2011)</a>
Increased ozone exposure to forests	Land	0.89	0.89	0.89	<a href="#">Birch et al. (2011)</a>
Increased loss of plant biodiversity from N enrichment	Land	2.58	7.73	12.88	<a href="#">Van Grinsven et al. (2013)</a>
<b>From atmospheric NH<sub>3</sub></b>					
Increased incidence of respiratory disease	Air/Climate	2.58	4.93	25.75	<a href="#">Van Grinsven et al. (2013)</a> ; <a href="#">Birch et al. (2011)</a>
Declining visibility—loss of aesthetics	Air/Climate	0.31	0.31	0.31	<a href="#">Birch et al. (2011)</a>
Increased effects of airborne particulates/increased carbon sequestration in forests (includes benefits)	Air/Climate	-3.86	-1.93	-1.93	<a href="#">Van Grinsven et al. (2013)</a>
Increased damages to buildings from particulates	Land	0.09	0.09	0.09	<a href="#">Birch et al. (2011)</a>
Increased loss of plant biodiversity	Land	2.58	7.73	12.88	<a href="#">Van Grinsven et al. (2013)</a>

**Table 14-2 (Continued): Potential damage costs of nitrogen (N) (\$/kg N; 2008 or as reported) to air, land, and water resources in the conterminous U.S. in the early 2000s as synthesized by Sobota et al. (2015). Low, median, and high costs derive from the specific damage cost reference. Negative values indicate an economic benefit.**

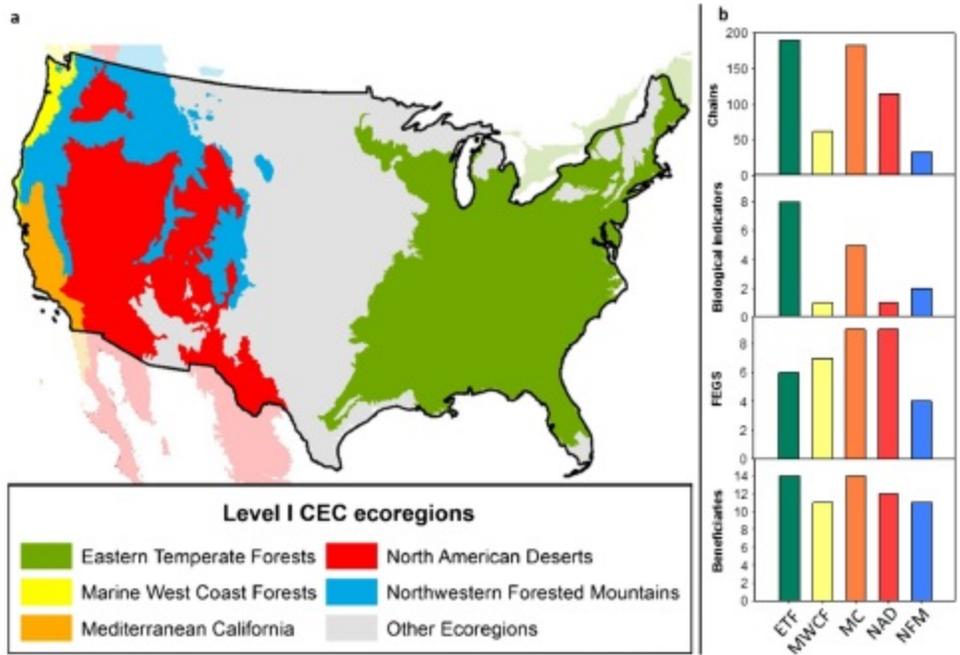
N damage type	System	Cost (\$/kg N)			Reference
		Low	Median	High	
<b>From atmospheric N<sub>2</sub>O</b>					
Increased ultraviolet light exposure from ozone—humans	Air/Climate	1.29	1.33	3.86	<a href="#">Van Grinsven et al. (2013);</a> <a href="#">Compton et al. (2011)</a>
Increased emission of greenhouse gas	Air/Climate	5.15	13.52	21.89	<a href="#">Van Grinsven et al. (2013)</a>
Increased ultraviolet exposure from ozone—crops	Air/Climate	1.33	1.33	1.33	<a href="#">Birch et al. (2011)</a>
<b>From surface freshwater N loading</b>					
Declining waterfront property value	Freshwater	0.21	0.21	0.21	<a href="#">Dodds et al. (2009)</a>
Loss of recreational use	Freshwater	0.17	0.17	0.17	<a href="#">Dodds et al. (2009)</a>
Loss of endangered species	Freshwater	0.01	0.01	0.01	<a href="#">Dodds et al. (2009)</a>
Increased eutrophication	Freshwater	6.44	16.10	25.75	<a href="#">Van Grinsven et al. (2013);</a> <a href="#">Compton et al. (2011)</a>
Undesirable odor and taste	Drinking water	0.14	0.14	0.14	<a href="#">Kusiima and Powers (2010)</a>
Nitrate contamination	Drinking water	0.54	0.54	0.54	<a href="#">Compton et al. (2011)</a>
Increased colon cancer risk	Drinking water	1.76	1.76	5.15	<a href="#">Van Grinsven et al. (2013)</a>
<b>From groundwater N loading</b>					
Undesirable odor and taste	Drinking water	0.14	0.14	0.14	<a href="#">Kusiima and Powers (2010)</a>
Nitrate contamination	Drinking water	0.54	0.54	0.54	<a href="#">Compton et al. (2011)</a>
Increased colon cancer risk	Drinking water	1.76	1.76	5.15	<a href="#">Van Grinsven et al. (2013)</a>

**Table 14-2 (Continued): Potential damage costs of nitrogen (N) (\$/kg N; 2008 or as reported) to air, land, and water resources in the conterminous U.S. in the early 2000s as synthesized by Sobota et al. (2015). Low, median, and high costs derive from the specific damage cost reference. Negative values indicate an economic benefit.**

N damage type	System	Cost (\$/kg N)			Reference
		Low	Median	High	
<b>From coastal N loading</b>					
Loss of recreational use	Coastal zone	6.38	6.38	6.38	<a href="#">Birch et al. (2011)</a>
Declines in fisheries and estuarine/marine habitat	Coastal zone	6.00	15.84 <sup>a</sup>	26.00	<a href="#">Van Grinsven et al. (2013)</a> ; <a href="#">Compton et al. (2011)</a>

<sup>a</sup>Excludes \$56/kg N from submerged aquatic vegetation loss in the Gulf of Mexico from ([Compton et al., 2011](#)).

Still another advance is offered by [Clark et al. \(2017\)](#) and [Rhodes et al. \(2017a\)](#), who synthesized information on N induced terrestrial and aquatic eutrophication, respectively, from the published literature to link the ecological effects of critical load exceedances with human beneficiaries by using STEPS and FECS-CS. [Rhodes et al. \(2017a\)](#) identified that N loading to aquatic ecosystems affects 154 chains that link changes in biological indicators of aquatic eutrophication (a shift in phytoplankton community) to FECS, 13 ecological production functions (EPF) within three different ecosystems (alpine lakes, lakes, and estuaries) and 18 classes of human beneficiaries that potentially will be effected by a change in one of these endpoints. For terrestrial eutrophication, [Clark et al. \(2017\)](#) identified that N critical load exceedances affected beneficiary types through 582 individual chains in the five ecoregions examined (Eastern Temperate Forests, Marine West Coast Forests, Northwestern Forested Mountains, North American Deserts, Mediterranean California) and 66 FECS across a range of final ecosystem services categories (21 categories; e.g., changes in timber production, fire regimes, and native plant and animal communities; [Figure 14-3](#) and [Table 14-3](#)).



Map of (a) Level 1 ecoregions examined and (b) the count of unique chains, biological indicators, Final Ecosystem Goods and Services, and beneficiaries for each ecoregion.

Source: [Clark et al. \(2017\)](#).

**Figure 14-2 Map of ecosystem services altered by nitrogen critical load exceedance.**

**Table 14-3 Numbers of chains, Final Ecosystem Goods and Services (FEGS), and beneficiaries (bens) associated with each initial biological indicator (Clark et al., 2017).**

Biological Indicator	No. Chains	No. FEGS	No. Bens
Increased grass-to-forb ratio and/or increase in total biomass	192	11	12
Decreased lichen biodiversity	62	7	11
Decreased native mycorrhizal diversity	61	5	10
Decreased abundance of ectomycorrhizal fungi	43	3	12
Increased bark beetle abundance	34	4	12
Decreased survival of bigtooth aspen	32	4	11
Decreased survival of scarlet oak	32	4	11
Decreased survival of trembling aspen	32	4	11
Decreased abundance of arbuscular mycorrhizal fungi	25	3	10
Decreased growth of red pine	25	3	10
Increased cover of understory nitrophilic species	18	2	10
Increased bacteria-to-fungi ratio	17	2	9
Change in herbaceous community composition	7	1	7
Increase in N leaching	2	1	2

FEGS = Final Ecosystem Goods and Services.

**Table 14-4 Ecosystem services research related to nitrogen-driven eutrophication.**

Mode	Region	Effect	Reference HERO ID
Estuarine N driven eutrophication	Chesapeake Bay	Recreation and commercial fishing are the main ecosystem services impacts; however, it is difficult to quantify these impacts due to data limitations. The analysis finds that, although atmospheric releases of N are lower than direct releases to land and water, their total damages are larger yet have associated abatement costs that are relatively low.	<a href="#">Birch et al. (2011)</a>
Includes acidification and eutrophication		Damage to services associated with productivity, biodiversity, recreation, and clean water are less certain and although generally lower, these costs are quite variable (<\$2.2–\$56/kg N). In the current Chesapeake Bay restoration effort, for example, the collection of available damage costs clearly exceeds the projected abatement costs to reduce N loads to the bay.	<a href="#">Compton et al. (2011)</a>
Includes acidification and eutrophication	National scale, calculated for 8-digit HUCs	Annual damage costs associated with anthropogenic N leakage range from \$1.94 to \$2,255/ha/yr. Nationally, the total quantifiable damages were estimated to be between \$81–\$144 billion/yr. Between 14–24% of the potential damage costs were associated with fossil fuel combustion. Areas with the largest damage costs corresponded to areas with the largest N inputs and leakages, such as the upper Midwest and central California.	<a href="#">Sobota et al. (2015)</a>
Terrestrial N driven eutrophication	National scale	N critical load exceedances affected beneficiary types through 582 individual and 66 FEGS across a range of final ecosystem services categories.	<a href="#">Clark et al. (2017)</a>
Aquatic N driven eutrophication	National scale	Using STEPS and FEGS-CS, the authors identify 154 chains that link changes in biological indicators of aquatic eutrophication (a shift in phytoplankton community) to FEGS, and 18 classes of human beneficiaries.	<a href="#">Rhodes et al. (2017a)</a>
Terrestrial N driven eutrophication	Indiana	One calculation of the economic value of removing N from the landscape is \$5.91/kg/yr (mean) or \$10.50/kg/yr (high end). These values are based on the estimated cost to remove a kg of N from a community water system using available nutrient removal technologies, as summarized by the <a href="#">U.S. EPA (2008d)</a> .	<a href="#">Wang et al. (2017e)</a>
Includes acidification and eutrophication	Minnesota	The study authors measured the social cost of nitrogen (SCN) in Minnesota. They noted that each kg of N applied to a field generates four compounds: NO <sub>3</sub> <sup>-</sup> , N <sub>2</sub> O, NH <sub>3</sub> , and NO <sub>x</sub> . The total annual damage done by the four compounds measured in dollars/kg of N applied to a field is \$2.62 (mean), \$0.44 (low), and \$10.79 (high). To convert annual values to a net present value, the authors assumed a 20-year time horizon and a 3% rate of discount. This conversion generates values of \$40.15 (mean), \$6.74 (low), and \$165.34 (high)/kg of N applied. All dollar values are in 2010 dollars.	<a href="#">Keeler et al. (2016)</a>
Wetland N eutrophication	Mississippi Alluvial Valley	The study authors estimated an “annualized” value of N mitigation service (\$/kg N) in the Mississippi Delta Region in 2008 as \$25.27 (mean), \$22.82 (low), and \$106.09 (high) with a value of \$1,248/ha/yr for the region.	<a href="#">Jenkins et al. (2010)</a>

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### 14.3.3 Nitrogen and Climate Modification

Some work has discussed the implications of climate change and N loading on ecosystem services such as fish harvests, property values, water treatment, human and wildlife health, ocean acidification, and freshwater diversity ([Baron et al., 2012](#)). The combined effect of N loading and climate change on the economic value of water resources and related products has yet to be evaluated, and even the separate economic effects of N loading or climate change are difficult to determine. However, climate change will modify the effects of N loading on some key ecological services. [Porter et al. \(2013\)](#) and [Compton et al. \(2013\)](#) also identified some effects on the interactions between nitrogen and climate, which include:

- As eutrophication increases with warmer water temperatures, there will be costs associated with upgrades of municipal drinking water treatment facilities, the greater reliance on bottled water, and the health costs of  $\text{NO}_3^-$  in drinking water associated with toxicity and disease ([Compton et al., 2011](#)).
- The U.S. will increasingly rely on groundwater for drinking water under future climate change scenarios ([U.S. Global Change Research Program, 2009](#)), creating a strong potential for increased costs for treating exposure to  $\text{NO}_3^-$ -stimulated disease.
- Increasingly, N enrichment is correlated in waters with pathogen abundance and human and wildlife diseases ([Johnson et al., 2010](#)). Climate warming opens the possibility for more vector-transmitted diseases to migrate to higher latitudes, where N loading may enhance their success ([Johnson et al., 2010](#)).
- Acidification causes direct harm to calcifying shellfish and crustaceans ([Howarth et al., 2012](#)). Changes in climate and the N cycle will intensify ocean acidification, and there are feedbacks from acidification to N cycling ([Doney et al., 2009](#)). [Table 14-5](#) provides a summary of recent studies and findings regarding the economic effects of ocean acidification on U.S. fisheries.

**Table 14-5 Summary of recent literature examining economic impacts of ocean acidification on U.S. fisheries.**

Region	Type of Fish	Key Findings	Reference
Northeast Pacific from northern California to southeast Alaska	Crustaceans (especially shrimp), echinoderms, molluscs, and euphaeids	Ocean acidification alone results in very minor changes in landings relative to the 2060 baseline projections; however, ocean acidification in combination with three other climate change effects (primary productivity, zooplankton community structure, and ocean deoxygenation) reduces landings by about 20%, which suggests that synergies exist.	<a href="#">Ainsworth et al. (2011)</a>
U.S.	Sea scallops	Increased scallop growth rates from warming predicted to outweigh decreasing growth rates from ocean acidification until 2030, at which point the negative influence of ocean acidification will become the dominant effect. After 2030, fewer scallops will attain largest (“U10”) size before they are harvested in current fishing levels are maintained.	<a href="#">Cooley et al. (2015)</a>
U.S.	Various commercial species with a focus on molluscs	Considerable revenue declines, job losses, and indirect economic costs are possible due to ocean acidification broadly damaging marine habitats, altering marine resource availability, and disrupting other ecosystem services. Under a moderate 2% discount rate, U.S. ex-vessel revenue losses are predicted to be \$0.6–\$2.6 billion and broader economic losses are predicted to be \$1.5–\$6.4 billion.	<a href="#">Cooley and Doney (2009)</a>
U.S.	Shellfish	Analysis of sensitivity and adaptive capacity to ocean acidification across 23 regions indicates that the most socially vulnerable communities can be found on the U.S. East Coast and Gulf of Mexico. The East Coast is vulnerable mostly due to economic dependence whereas the Gulf of Mexico is vulnerable because of low adaptive capacity.	<a href="#">Ekstrom et al. (2015)</a>
Washington, Oregon, California	Shellfish	Survey results from a sample of shellfish industry participants (70% owners or managers of hatcheries) indicated that about half had experienced negative impacts from ocean acidification and that more than half the industry felt they would be somewhat or definitely able to adapt to ocean acidification.	<a href="#">Mabardy et al. (2015)</a>
Global, disaggregated by region	Shellfish	The economic cost of mollusc loss estimates for the U.S. are estimated to be roughly \$400 million USD, assuming no change in income but taking into account welfare losses from shellfish price changes.	<a href="#">(Narita et al., 2012)</a>

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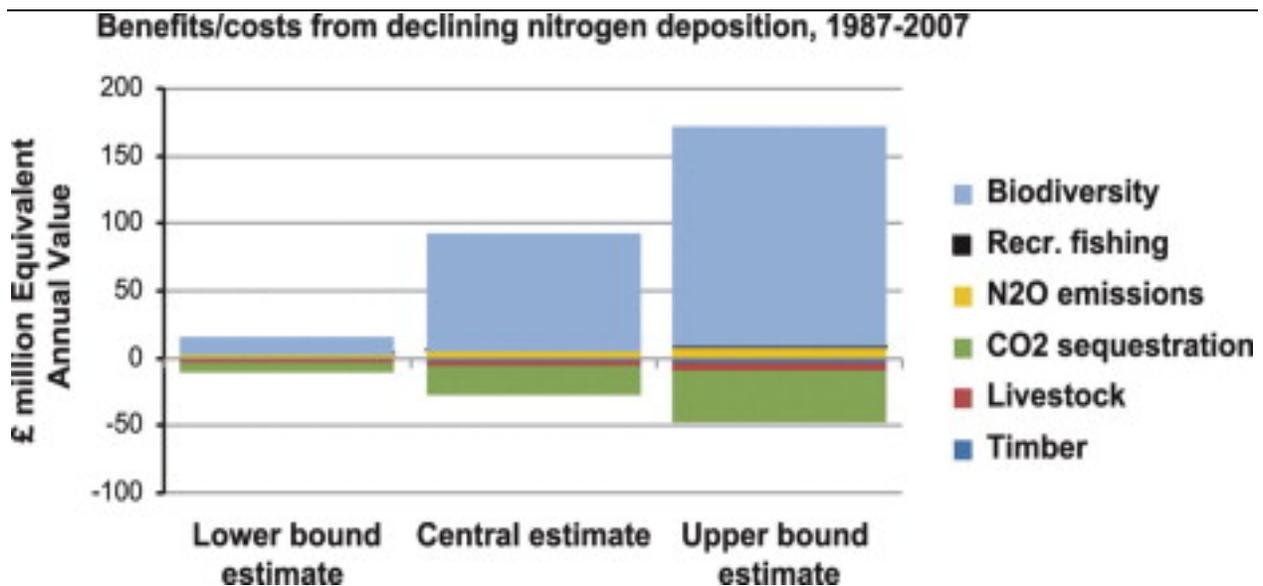
## 14.4 European and Canadian Applications

Since the 2008 ISA, several qualitative and quantitative assessments of either N deposition or the combination of N and S deposition have been conducted in the U.K. ([Jones et al., 2014](#)), across Europe ([de Vries et al., 2014b](#); [de Vries et al., 2014c](#); [Van Grinsven et al., 2013](#)), and Canada ([Aherne and Posch, 2013](#)). Although these assessments have varied considerably in their approaches, all have used simplified methods that intentionally omitted much of the mechanistic and spatial complexity in how deposition affects ecosystem services. Some of the qualitative and conceptual assessments provided descriptions of impacts of N deposition on ecosystems ([de Vries et al., 2014b](#); [de Vries et al., 2014c](#); [Jones et al., 2014](#)).

In Canada, [Aherne and Posch \(2013\)](#) examined critical load exceedances to assess the impacts of N and S deposition on water quality (eutrophication), soil quality (acidification), and plant species diversity. The approach was quantitative but did not assign values for ecosystem services. Instead, the analysis focused on the sources of these emissions and understanding what regions within Canada faced a loss of these services because critical loads had been exceeded.

Studies in Europe found that N deposition has both positive and negative effects on ecosystem services. [de Vries et al. \(2014b\)](#) modeled ecosystem response to N deposition, using the Very Simple Dynamic soil model. The model quantified changes in these services for the 2000–2050 period using three emissions scenarios: 1980 emissions, current legislation, and a scenario where deposition does not exceed critical loads for any ecosystem. The biggest differences among the emission scenarios were that regulations imposed since the 1980s created significant decreases in areas receiving critical N loads for water  $\text{NO}_3^-$  and Al, but also likely decreased  $\text{CO}_2$  uptake by ~20%. A second study by [Van Grinsven et al. \(2013\)](#) conducted economic analysis of the influence of N cycling in Europe and found that most economic impacts were related to atmospheric N emissions. Although there were positive impacts on agricultural production from fertilization, there were large negative impacts of atmospheric N emissions on human health (direct effects on human health are outside the scope of the secondary NAAQS review) and ecosystem function. Overall, the costs of added reactive N (atmospheric and agricultural) in the European Union were between £75 and £485 billion/year. Within the U.K., [Jones et al. \(2014\)](#) conducted a quantitative analysis that focused on six main ecosystem services impact pathways ([Figure 14-3](#)): timber production, livestock production, carbon sequestration, greenhouse gas (GHG) emissions, recreational fishing, and biodiversity appreciation. For the first three pathways, declining N deposition is estimated to result in ecosystem services losses of £27.2 million/year, due to decreased fertilization of woodlands, grasslands, and heathland. For the other three pathways, declining deposition

is estimated to result in ecosystem services gains totaling £93 million/year, due to decreased GHG emissions, improved water quality for recreational fishing, and enhanced nonuse values for biodiversity through habitat protection. The estimated net gains to U.K. society are, therefore, £65.8 million/year, with a 95% confidence interval of £15.1–£123.2 million pounds/year. Because of the large number of assumptions and simplifications, these studies present broad conceptual analyses demonstrating the potential of ecosystem services to quantify the impacts of reactive N in ways that could be valuable for policymakers, rather than as definitive assessments.



CO<sub>2</sub> = carbon dioxide; N<sub>2</sub>O = nitrous oxide; recr = recreational.  
 Source: [Jones et al. \(2014\)](#).

**Figure 14-3 Benefits and costs associated with the 25% decline in nitrogen deposition in the U.K. since 1990.**

## 14.5 Global Perspective

There is one study on ecosystem services with a global perspective published since 2008 and one study published in 2005 not included in the 2008 ISA. [Alcamo et al. \(2005\)](#) modeled global and regional impacts of stressors that included critical load exceedance for acidification and eutrophication on provisions, regulations, support, and cultural ecosystem services. However, these impacts represent the combined effects of eight

drivers (including climate change, land use change, mineral extractions, and N fertilizer use). Consequently, the analysis does not define ecosystem services changes that are specifically attributable to changes in N or S deposition.

[Erisman et al. \(2013\)](#) examined the impact of humans on the global N cycle and how these impacts relate to changes in ecosystem services. They group services into the following categories:

- Drinking water (nitrates),
- Air pollution effects on human health,
- Air pollution effects on crops (due to ozone),
- Freshwater eutrophication [defined as areas where the concentration of nitrate exceeds 1 mg NO<sub>3</sub><sup>-</sup>-N/L; [UNEP \(2007\)](#); [Camargo and Alonso \(2006\)](#); [Vörösmarty et al. \(2005\)](#)],
- Biodiversity loss [they identify the global critical load for biodiversity loss as 5–10 kg/ha/yr; [Bobbink et al. \(2010\)](#)],
- Stratospheric ozone depletion,
- Changes in climate, and
- Coastal dead zones.

It is especially noteworthy that the authors selected thresholds of level of N addition to an ecosystem which begins to cause adverse effects. The paper concludes that better quantitative relationships need to be established between N and the effects on ecosystems at smaller scales, including a better understanding of how N shortages can affect certain populations.

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## 14.6 Summary

Since 2008, several studies have identified a range of ways in which N and S deposition could affect socially valuable ecosystem services. Several new ecosystem services frameworks and classification systems have been published, including The Economics of Ecosystems and Biodiversity [TEEB; [Sukhdev et al. \(2014\)](#)], the Common International Classification of Ecosystem Services [CICES; [Haines-Young and Potschin \(2011\)](#)], and U.S. EPA Final Ecosystem Goods and Services Classification System [FEGS-CS; [Landers and Nahlik \(2013\)](#)].

For acidification, the literature since the 2008 ISA includes studies that better characterize ecosystem services valuation by pairing biogeochemical modeling and benefit transfer equations informed by WTP surveys, especially for the Adirondacks and Shenandoah regions ([Table 14-1](#)). Aside from valuation efforts, studies using the

FED-CS have improved understanding of the numerous causal pathways by which N and S deposition may affect ecosystem services ([Bell et al., 2017](#); [Clark et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Rhodes et al., 2017a](#)). The estimate of the total number of ecosystem services affected by N and S deposition is better quantified by the new studies that use FEG-CS. However, for many regions and specific services, poorly characterized dose-response between deposition, ecological effect, and services are the greatest challenge in developing specific data on the economic benefits of emission reductions ([NAPAP, 2011](#)).

In the 2008 ISA there were no publications specifically evaluating the effects of N deposition on ecosystem services associated with N driven eutrophication. Since the 2008 ISA, several comprehensive studies have been published on the ecosystems services related to N pollution in the U.S. ([Table 14-4](#)). These include an evaluation of services effected by multiple N inputs (including N deposition) to the Chesapeake, a syntheses of the cost/-benefits on N loading across the nation, and analysis of the amount of N leaked from its intended use and the effects on ecosystem services (this work specifically identified the costs of the atmospheric portion of total N loading). Aside from valuation, the estimate of the total number of ecosystem services affected by N is more well quantified by the new studies that use FEG-CS ([Bell et al., 2017](#); [Clark et al., 2017](#); [Irvine et al., 2017](#); [O'Dea et al., 2017](#); [Rhodes et al., 2017a](#)). In these analyses critical load exceedances for N related air pollution were used as a model stressor from which a total of 1,104 unique chains linking stressor to beneficiary were identified.

In the time since the 2008 ISA, several qualitative and quantitative assessments of either N deposition or the combination of N and S deposition have been conducted in the U.K., across Europe, Canada, and at the global scale. Although these assessments have varied considerably in their approaches, all were intentionally simplified to neglect much of the mechanistic and spatial complexity on how N deposition affects ecosystem services. At the global scale, an analysis selected general quantitative thresholds of N loading for the onset of ecologically adverse effects. However, the paper concludes that better quantitative relationships need to be established between N and the effects on ecosystems at smaller scales.

The conclusions considering the full body of literature are that (1) there is evidence that N and S emissions/deposition have a range of effects on U.S. ecosystem services and their social value; (2) there are some economic studies that demonstrate such effects in broad terms; however, it remains methodologically difficult to derive economic costs and benefits associated with specific regulatory decisions/standards; and (3) there is an improved understanding of the number of causal pathways by which N and S deposition

may affect ecosystem services, though most of these causal relationships remain to be quantified.

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## 14.7 Supplemental Materials: Ecosystem Services Profiles of Select Species

Several species profiles have been created to better characterize the ecosystem services provided by species affected by NO<sub>y</sub> and SO<sub>x</sub>. The species included here are identified as threatened and endangered with N identified as a contributing stressor ([Hernández et al., 2016](#)). The species are balsam fir (*Abies balsamea*), eelgrass (*Zostera marina*), green turtle (*Chelonia mydas*), white ash (*Fraxinus americana*), and lace lichen (*Ramalina menziesii*). These profiles identify the geographic distribution within the U.S., ecological function, Class I areas, FEGS, and cultural importance; information on economic valuation is presented when available.

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### 14.7.1 Balsam Fir

**Scientific Name:** *Abies balsamea*.

- **Family:** Pinaceae (pine).

**Symbolic Role:** NA.

**Federal or State Threatened or Endangered Species Listing Status:** Endangered species in Connecticut.

**Geographic Range/Distribution:**

- **Native and Current Range:** The range of balsam fir is North America, including most of eastern Canada. In the U.S., it extends from Minnesota to Maine and south into central Pennsylvania and the mountains of Virginia and West Virginia. Of the two main varieties—*balsamea* and *phanerolepis*—it is the latter that is found in Virginia and West Virginia.

**Overlap with Class I Areas:**

- <http://www.epa.gov/visibility/maps.html>.
- [http://www.epa.gov/ttn/oarpg/t1/fr\\_notices/classimp.gif](http://www.epa.gov/ttn/oarpg/t1/fr_notices/classimp.gif).

**Habitat:** Grows best in areas characterized by cool temperatures and moist soils. In the U.S., it is most commonly found in mixed stands, where associates include red spruce, black spruce, paper birch, aspen, and red maple ([Uchytil, 1991](#); [USDA, 1990b](#)).

### Primary Threats:

- **Related to N or S Deposition:** None.
- **Other:** Balsam fir are particularly vulnerable to insect damage from spruce budworms ([Uchytil, 1991](#)) and from decay caused by the red heart fungus [*Haematostereum sanguinolentum*; [USDA \(1990b\)](#)].

### Ecosystem Role and Function:

- **Nutrition:** Provides some nutrition for mice, voles, red squirrels, and grouse ([USDA, 1990b](#)).
- **Cover:** Provides winter cover to ungulates, including white-tailed deer and moose, and to grouse and songbirds ([Uchytil, 1991](#)). Also provides cover for small mammals including martens and snowshoe hares ([Darveau et al., 2001](#); [de Bellefeuille et al., 2001](#); [Darveau et al., 1998](#)).
- **Other:** As with other tree species in general, balsam fir trees provide a number of other intermediate ecosystem services that are indirectly valued by humans including nutrient cycling, carbon sequestration, soil stabilization and erosion control, water regulation and filtration, and air pollutant filtration ([Krieger, 2001](#)).

### Final Ecosystem Services:

- **Direct Human Uses:**
  - **Raw material in wood products and other industries:** Used as pulpwood and lumber for a variety of products. Oleoresin from balsam fir bark blisters has various uses including as a medium for mounting microscopic specimens and cement for optical systems ([USDA, 1990b](#)). It is also used in developing fragrances ([Zerbe et al., 2012](#)).
  - **Energy/fuel source:** Wood wastes for producers using balsam fir wood or pulp are sometimes used for energy ([USDA, 1990b](#)).
  - **Cultural and human health:** Balsam fir are commonly grown and used as Christmas trees and as material for wreath-making. In 2009 they accounted for 7% of Christmas tree sales in the U.S. ([USDA, 2010](#)). A large number of ethnobotanical uses of balsam fir by Native Americans has also been documented. The Native American Ethnobotany database maintained by [University of Michigan \(2015\)](#) references documents citing 87 specific uses by 13 different tribes, including a wide variety of medicinal uses (e.g., dermatological and venereal aid; cold and cough remedy) and uses as a material for rugs and bedding, sewing, and canoe waterproofing.

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## 14.7.2 Eel Grass

**Scientific Name:** *Zostera marina* (Zosteraceae).

**Symbolic, Federal, or State Threatened or Endangered Species Listing Status:** Listed as a conservation species of least concern.

**Geographic Range/Distribution:**

- **Native Range:** Eelgrass is native to coastal regions of both the Pacific and Atlantic Oceans along the coast of North America.
- **Current Range:** Eelgrass is currently found in coastal regions in the Pacific Ocean along the western U.S. and Canada. It is also found along the eastern coast of North America from Canada to the Mid-Atlantic region in the U.S. ([USDA, 2015a](#)). Seagrasses have been disappearing from their native range at an average rate of 110 km<sup>2</sup>/year since 1980 ([Waycott et al., 2009](#)) and are especially sensitive to changes in temperature along the southern limits of their current range in North America ([Kaldy, 2014](#)).

**Overlap with Class I Areas:**

- <http://www.epa.gov/visibility/maps.html>.
- [http://www.epa.gov/ttn/oarpg/t1/fr\\_notices/classimp.gif](http://www.epa.gov/ttn/oarpg/t1/fr_notices/classimp.gif).

**Habitat:** Coastlines in both the Atlantic and Pacific oceans. It can be found in bays, estuaries, lagoons, and beaches.

**Primary Threats:**

- **Related to N or S Deposition:** [Hernández et al. \(2016\)](#).
- **Other:** Threats to eelgrass include dredging for coastal development, overfishing of predator species that lead to losses of herbivores that clean the leaves, and sediment and nutrient loading from coastal development ([Waycott et al., 2009](#); [Orth et al., 2006](#)). More broad changes in climate, such as temperature and sea-level rise also contribute to the loss of seagrasses ([Kaldy, 2014](#); [Douglass et al., 2010](#)).

**Ecosystem Role and Function:** Eelgrass are an important marine species for primary productivity ([Duarte, 2013](#)), and provides a suitable reproductive habitat and nursery grounds for many species of fish and shellfish ([Barbier et al., 2011](#)). Birds, invertebrates, green turtles, and manatees use eelgrass as a food source. Some commercially viable fish species like pacific salmon, pacific herring, and Dungeness crabs rely on eelgrass to provide cover and habitat ([Plummer et al., 2013](#); [Orth et al., 2006](#)). Another function of eelgrass is its ability to improve water quality through nutrient uptake and particle deposition. Eelgrass is an important species for coastal erosion protection because it helps control wave attenuation ([Barbier et al., 2011](#)). Eelgrass also provides indirect human benefits through carbon sequestration because it uses dissolved carbon in seawater to grow, and at the end of its lifecycle, the carbon is buried and stored as detritus ([Barbier et al., 2011](#)).

### Final Ecosystem Services:

- **Direct Human Uses:**
  - **Cultural:** Native Americans used dried eelgrass to bake into cakes and also for smoking deer meat ([Felger and Moser, 1985](#)). Native Americans consume the roots of the plant or use it to flavor other foods ([University of Michigan, 2015](#)).
  - **Raw Material:** Eelgrass is used to pack crabs to keep them moist during transport in the Mid-Atlantic region of the U.S. ([Barbier et al., 2011](#)).

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### 14.7.3 Green Turtle

**Scientific Name:** *Chelonia mydas* (Cheloniidae).

**Symbolic Role:** Green sea turtles are symbols of guidance and protection in Hawaiian culture.

**Federal or State Threatened or Endangered Species Listing Status:** Listed as an endangered species ([Seminoff, 2004](#)).

#### Geographic Range/Distribution:

- **Native Range:** Green sea turtles have distinct native populations in both the Pacific and Atlantic oceans.
- **Current Range:** In the North American Atlantic, nesting sites are found in coastal regions in Florida, as well as Georgia, South Carolina, and North Carolina ([USFWS, 2015](#)). In the Pacific, green turtles nest along the French Frigate Shoals in the northwestern Hawaiian Islands ([NOAA Fisheries Pacific Islands Regional Office, 2015a](#)).

#### Overlap with Class I Areas:

- <http://www.epa.gov/visibility/maps.html>.
- [http://www.epa.gov/ttn/oarpg/t1/fr\\_notices/classimp.gif](http://www.epa.gov/ttn/oarpg/t1/fr_notices/classimp.gif).

**Habitat:** Mature green sea turtles are found in shallow coastal regions with large seagrass beds such as bays, reefs, and inlets. Green turtles nest on open beaches with minimal disturbance ([USFWS, 2015](#)).

#### Primary Threats:

- **Related to N or S Deposition:** [Hernández et al. \(2016\)](#).
- **Other:** Other major threats to green sea turtles include entanglement in fishing gear, incidental bycatch, and collisions with fishing boats or jet skis. Green turtles also face threats from illegal human harvesting and habitat loss and degradation

due to human development along coastal areas and reefs ([Malama na Honu, 2015](#)).

**Ecosystem Role and Function:** Green sea turtles are herbivores that mostly feed on seagrasses and algae in near-shore marine ecosystems. Green sea turtle eggs are a food source for many coastal species like ghost crabs or marine birds, as well as other scavenging animals. Tiger sharks are the only nonhuman predator for large juvenile and mature turtles ([NOAA Fisheries Pacific Islands Regional Office, 2015b](#)). Green sea turtles are valued for their natural beauty, and several conservation groups are dedicated to increasing sea turtle populations ([Komoroske et al., 2011](#)). Turtles can also be a source of ecotourism ([Campbell, 2002](#)).

**Final Ecosystem Services:**

- **Direct Human Uses:**
  - **Cultural:** Some native Hawaiians consider the green turtle to be a personal or family deity, which should not be harmed. The green turtle is featured in Hawaiian culture through depictions in petroglyphs ([NOAA Fisheries Pacific Islands Regional Office, 2015a](#)).

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#### 14.7.4 White Ash

**Scientific Name:** *Fraxinus americana*.

- **Family:** Oleaceae (olive).

**Symbolic Role:** NA.

**Federal or State Threatened or Endangered Species Listing Status:** No special status.

**Geographic Range/Distribution:**

- **Native Range:** Most of eastern North America from southern Canada to northern Florida and as far west as Minnesota ([Griffith, 1991](#)).
- **Current Range:** In addition to its native range, white ash is cultivated in other areas, including Hawaii ([Griffith, 1991](#)).

**Overlap with Class I Areas:**

- <http://www.epa.gov/visibility/maps.html>.
- [http://www.epa.gov/ttn/oarpg/t1/fr\\_notices/classimp.gif](http://www.epa.gov/ttn/oarpg/t1/fr_notices/classimp.gif).

**Habitat:** Usually found mixed with other hardwoods (not the dominant species) in various topographic conditions. It can grow in a wide variety of soil types but does best

in soils with high nitrogen and calcium content, as well as moist and well-drained soils ([USDA, 1990a](#)).

#### **Primary Threats:**

- **Related to N or S Deposition:** [Hernández et al. \(2016\)](#).
- **Other:** White ash has experienced extensive dieback and mortality in its native range since the 1920s, due to a variety of factors, including ash yellows (AshY phytoplasma), canker fungi, viruses, drought ([Hibben and Silverborg, 1978](#)), and more recently, invasions of the emerald ash borer [*Agrilus planipennis*; [Poland and McCullough \(2006\)](#)]. White ash has also been found to be sensitive to ground level ozone exposures ([Chappelka et al., 1988](#)).

#### **Ecosystem Role and Function:**

- **Nutrition:** Samaras (seeds) are good forage for wood ducks, northern bobwhites, purple finches, pine grosbeaks, fox squirrels, mice, and many other birds and small mammals. It is browsed by white-tailed deer and cattle, and its bark is occasionally used as food by beavers, porcupines, and rabbits ([Griffith, 1991](#)).
- **Cover:** It provides cover to primary cavity nesters, such as red-headed, red-bellied, and pileated woodpeckers, and to secondary nesters such as wood ducks, owls, nuthatches, and gray squirrels ([Griffith, 1991](#)).
- **Other:** As with other hardwood tree species in general, white ash trees provide a number of other intermediate ecosystem services that are indirectly valued by humans, including nutrient cycling, carbon sequestration, soil stabilization and erosion control, water regulation and filtration, and air pollutant filtration ([Krieger, 2001](#)).

#### **Final Ecosystem Services:**

- **Direct Human Uses (Final Ecosystem Services)**
  - **Raw material in wood products and related industries:** White ash trees provide a dense, shock resistant, and durable wood that is used in a variety of products, including baseball bats, tool handles, furniture, cabinets, canoe paddles, snowshoes, and railroad ties ([USDA NRCS, 2011](#)).
  - **Energy/fuel source:** Used for fuel wood ([USDA NRCS, 2011](#)).
  - **Human health:** Leaves from the white ash have purported beneficial uses, including the relief of swelling and itching from mosquito bites and as a deterrent to snake bites ([Griffith, 1991](#)).
  - **Cultural:** A large number of ethnobotanical uses of white ash by Native Americans has been documented. The Native American Ethnobotany database maintained by [University of Michigan \(2015\)](#) references documents citing 38 specific uses by 9 different tribes, including a wide variety of medicinal uses (e.g., gastrointestinal, dermatological, and gynecological aids) and uses as a material for snow gear, basketry, furniture, canoes, hunting, and fishing.

- **Aesthetic:** Provides attractive and vivid fall foliage, including combinations of orange, yellow, maroon, and purple. For landscaping uses, it is also considered to be a good and relatively quick-growing shade tree ([University of Kentucky, 2015](#)).
- **Nonuse value:** Survey-based economic studies have found evidence of nonuse values among the general population for protecting white ash from air pollution in the Adirondacks region ([Banzhaf et al., 2006](#)).

### 14.7.5 Lace Lichen

**Scientific Name:** *Ramalina menziesii* (Ramalinaceae).

**Federal or State Threatened or Endangered Species Listing Status:** Listed as a conservation species of least concern.

**Geographic Range/Distribution:**

- **Native Range:** Lace lichen is native to the western coast of North America; in the past it was found in the San Jacinto Mountains near Los Angeles and on the surrounding coastal plain but now only grows at elevations above the smog layer ([Hastings Reserve, 2015](#)).
- **Current Range:** Lace lichen grows along the Pacific Coast of North America from Alaska to Baja California. It grows at elevations up to 3,500 feet ([Werth and Sork, 2008](#)).

**Overlap with Class I Areas:**

- <http://www.epa.gov/visibility/maps.html>.
- [http://www.epa.gov/ttn/oarpg/t1/fr\\_notices/classimp.gif](http://www.epa.gov/ttn/oarpg/t1/fr_notices/classimp.gif).

**Habitat:** Grows on tree species in coastal areas with enough moisture from fog and strong winds ([Egan and Holzman, 2003](#)).

**Primary Threats:**

- **Related to N or S Deposition:** [Hernández et al. \(2016\)](#).
- **Other:** Other threats to lace lichen include changes in climate. This species requires a good amount of moisture and a temperate climate to survive; it is absent from drier areas within its range ([Egan and Holzman, 2003](#)).

**Final Ecosystem Services:**

- **Direct Human Uses:**
  - **Aesthetic:** Lace lichen has a unique morphology that adds to the natural beauty of coastal woodlands along the Pacific Coast ([Hastings Reserve, 2015](#)).

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## APPENDIX 15 OTHER ECOLOGICAL EFFECTS OF PARTICULATE MATTER

Evidence for effects of particulate matter (PM) on ecological receptors include direct effects of airborne PM on radiative flux and both direct and indirect effects of deposited particles. In addition to nitrogen (N) and sulfur (S) and their transformation products (discussed in [Appendix 3–Appendix 12](#)), other PM components such as trace metals and organics are deposited to ecosystems and may subsequently impact biota. Direct effects include alteration of leaf processes from deposition of PM (“dust”) to vegetative surfaces ([Appendix 15.4.1](#)). Indirect effects encompass physiological responses associated with uptake of PM components and alterations to ecosystem structure and function. Exposures can occur directly to surfaces of vegetation (leaves, bark, twigs), by ingestion, or via soil or water through uptake by roots or other biological tissues. Bioaccumulation and biomagnification of PM components can lead to effects at higher trophic levels. Direct and indirect effects of PM on vegetation, fauna, and the soil environment, and evidence for effects at higher levels of biological organization (communities, ecosystems) from PM deposition are evaluated in the context of what was known from previous PM assessments ([U.S. EPA, 2009a, 2004](#)) and newly available studies.

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### 15.1 Introduction

PM-associated components include N and S and their transformation products, trace metals, organics, base cations, and salts. Base cations (especially  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$ ) from atmospheric deposition can help ameliorate the effects of acidic deposition associated with oxides of N and S, although under very high base cation deposition, plant health can be adversely affected ([U.S. EPA, 2009a](#)). Particulate salt may be added to an ecosystem from deicing salt ([U.S. EPA, 2009a](#)). The focus of this appendix is on the PM effects not associated with N and S components that are covered elsewhere in this ISA. The primary non-N and S components covered in this appendix include trace metals ([Appendix 15.3.1](#)) and organics ([Appendix 15.3.2](#)).

Effects of PM on ecological receptors can be both chemical and physical ([U.S. EPA, 2009a, 2004](#)). As described in the *2009 Integrated Science Assessment for Particulate Matter* (2009 PM ISA), particulates that elicit direct and indirect effects on ecological receptors vary in terms of size, origin, and chemical composition. Particle composition is attributed to ecological outcomes to a greater extent than particle size ([Grantz et al., 2003](#)). PM-associated metals and organics are linked to responses in biota; however, the heterogeneous nature of PM composition and distribution coupled with variability

inherent in natural environments confound assessment of the ecological effects of particulates.

Ecological effects evaluated in the 2009 PM ISA included direct effects on metabolic processes of plants, the contribution of PM to total metal loading which alters soil biogeochemistry and microbiology, the effects on plant and animal growth and reproduction, and the contribution to total organics loading resulting in trophic transfer.

Newly available information on the ecological effects of PM published since the 2009 PM ISA is summarized in the following sections along with key studies from previous PM assessments ([U.S. EPA, 2009a](#), [2004](#)). Studies conducted in the U.S. are the focus of this review, but research from other countries is included if it has advanced the study of PM effects on biota. Such studies may include those providing documentation of additional physiological effects of PM toxicity, new techniques for PM assessment, and further characterization of effects on communities and ecosystems. Together with the information available in the 2009 PM ISA, **the body of evidence is sufficient to infer a likely causal relationship between deposition of PM and a variety of effects on individual organisms and ecosystems.**

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## 15.2 Direct Effects of Particulate Matter on Radiative Flux

The direct effects of particles suspended in the atmosphere on radiative flux and subsequent effects on vegetation were described in previous PM assessments ([U.S. EPA, 2009a](#), [2004](#)). Briefly, increased atmospheric particulates and aerosols can alter radiative flux by both radiation attenuation and by changing the efficiency of radiation interception in the vegetation canopy by converting direct radiation to diffuse radiation ([Hoyt, 1978](#)). Diffuse radiation is more uniformly distributed throughout the vegetation canopy and can reach leaves more evenly than direct radiation, increasing canopy photosynthetic productivity. In a study reviewed in the 2009 PM ISA, decreased crop yield in China was associated with reduction in solar radiation due to regional haze ([Chameides et al., 1999](#)).

More recent studies provide additional evidence of the role of PM in altering radiative flux and plant response. In an assessment of aerosol effects on plant productivity in the eastern U.S., increased canopy photosynthesis due to increases in diffuse radiation, despite a simultaneous decrease in direct radiation due to light scattering by aerosols, was observed on a regional scale ([Matsui et al., 2008](#)). Surface downwelling solar radiation was reduced by 14.9 W/m<sup>2</sup> in 2000 and 16.0 W/m<sup>2</sup> in 2001, while photosynthesis and stomatal conductance increased simultaneously. In a recent study from Beijing, China, the expression of plant proteins important to photosynthesis were shown to be directly impacted by presence of aerosols and PM in the air column ([Yan et al., 2014](#)). Expression

of plant ribulose 1,5-biphosphate carboxylase/oxygenase (RuBisCO), a key enzyme involved in plant photosynthesis, increased in areas with strong diffuse solar radiation, (identified by measurement of aerosol optical depth and particles with diameters of 0.1 to 1.0  $\mu\text{m}$ ). In the same areas, light-harvesting complex II protein and oxygen-evolving enhancer protein decreased. These enzymes play a role in plant responses to direct solar radiation when photosynthesis capacity is exceeded.

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## 15.3 Particulate Matter Deposition to Ecosystems

Once airborne PM is deposited to aquatic or terrestrial systems, it can elicit additional effects on ecosystem receptors. Large particles tend to be deposited near their sources, such as along roadsides or next to mining, smelting, and other industrial operations, while smaller particles can be transported long distances ([Grantz et al., 2003](#)). Deposition to ecosystems can be in the form of wet, dry, or occult deposition ([U.S. EPA, 2009a](#); [Grantz et al., 2003](#)). Once deposited, PM-associated components may remain on biological surfaces or be transferred between environmental compartments (e.g., water, soil, sediment, biota).

More often, the chemical constituents drive the ecosystem response to PM, rather than size class ([U.S. EPA, 2009a](#); [Grantz et al., 2003](#)). Exposure to a given mass concentration of PM may lead to widely differing phytotoxic and other environmental outcomes depending upon the particular mix of PM constituents involved. Deposition of the metal and organic constituents of PM are discussed below; however, a rigorous assessment of each chemical constituent (e.g., polyaromatic hydrocarbons [PAHs], mercury [Hg], cadmium [Cd]) is not given. An overview of trace metals and organics and their depositional effects in ecosystems was provided in the previous PM assessments ([U.S. EPA, 2009a, 2004](#)) and only summarized below.

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### 15.3.1 Metals

All but 10 of the 90 elements that comprise the inorganic fraction of the soil occur at concentrations of <0.1% (1,000  $\mu\text{g/g}$ ) and are termed “trace” elements or trace metals. Trace metals with a density greater than 6  $\text{g/cm}^3$ , referred to as “heavy metals” (e.g., Cd, copper [Cu], lead [Pb], chromium [Cr], Hg, nickel [Ni], zinc [Zn]), are of particular interest because of their potential toxicity to plants and animals. For example, plant toxicity to trace metals is most frequently associated with Cu, Ni, and Zn ([U.S. EPA, 2004](#)). Some metals such as Zn, manganese (Mn), Cu, and iron (Fe) play important physiological roles in trace quantities; however, other metals such as Hg, Cd, Cr, and Pb

have no known biological function. Although some trace metals are essential for vegetative growth or animal health, they are all toxic in large quantities. Trace metals are naturally found in small amounts in soils, groundwater, and vegetation. They may enter the ecosystems as both fine and coarse particles. Heavy metals tend to be associated with fine particles. Trace elements exist in the atmosphere in particulate form as metal oxides ([Ormrod, 1984](#)). Aerosols containing trace elements derive predominantly from industrial activities. Once deposited to biological surfaces, metals can be taken up by biota, accumulate in tissues, and elicit toxic effects ([Gall et al., 2015](#)). These responses are highly variable across organisms. Only the bioavailable fraction is available for uptake by biota. In plants, metal uptake is generally via soil to root transfer ([Mcbride et al., 2013](#)), although recent studies reviewed in [Appendix 15.4](#) provide evidence for foliar transfer of metals following atmospheric deposition. The ecological effects of atmospherically deposited Pb, a metal associated with PM, are included in the ISA for Pb ([U.S. EPA, 2013b](#)).

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### 15.3.2 Organics

Organic compounds can be in the gas phase or in association with particles ([Grantz et al., 2003](#)). Organic compounds that may be associated with deposited PM include persistent organic pollutants (POPs), pesticides, semivolatile organic compounds (sVOCs), PAHs, and flame retardants, among others ([U.S. EPA, 2009a](#)). Dry deposition of organic materials is often dominated by the coarse fraction, but fine PM may act as a carrier for materials such as pesticides. PAHs are widespread in the environment. Of the anthropogenically derived PAHs, 8 are considered carcinogenic and 16 have been classified by the U.S. EPA as priority pollutants. In general, high molecular weight PAHs are more toxic and have a greater tendency to be associated with PM ([Mesquita et al., 2014a](#)). Derived from vehicular traffic and other sources, they are common air pollutants in metropolitan areas. PAHs and other organics can be transferred to higher trophic levels. Some atmospheric contaminants like POPs, polybrominated diphenyl ethers (PBDEs), and other brominated flame retardants have been shown to accumulate in biota in polar regions and at other remote locations where they are carried by long-range atmospheric transport from lower latitudes ([U.S. EPA, 2009a](#)). The Western Airborne Contaminants Assessment Project (WACAP) summarized in the 2009 PM ISA provided evidence for airborne transfer and bioaccumulation of organics to remote national parks and Class I areas ([Landers et al., 2008](#)), and newer studies from this project have added to this information ([Pritz et al., 2014](#); [Landers et al., 2010](#)). Seven ecosystem compartments (air, snow, water, sediments, lichens, conifer needles, and fish) were analyzed for a suite of contaminants to determine where the pollutants were accumulating, identify ecological

indicators, and assess the source of the air masses most likely to have transported the contaminants to the parks. Overall, semivolatile organic compounds and metals were detected throughout park ecosystems, and biomagnification of organics through the food web indicated contaminants were present at multiple trophic levels.

As reviewed in previous PM assessments, vegetation itself is an important source of hydrocarbon aerosols ([U.S. EPA, 2009a, 2004](#)). Terpenes, particularly  $\alpha$  pinene,  $\beta$  pinene, and limonene, released from tree foliage may react in the atmosphere to form submicron particles. These naturally generated organic particles contribute significantly to the blue haze aerosols formed naturally over forested areas ([U.S. EPA, 2004](#); [Geron et al., 2000](#)).

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## 15.4 Effects of Particulate Matter on Vegetation

Particles deposited to foliar surfaces may lead to both structural and functional alterations in plants. PM may physically obstruct processes associated with the leaf surface or be taken up across the cuticle and into the plant tissues where it affects plant metabolic activities. This section first considers direct impacts of PM deposition to vegetative surfaces. Next, effects following uptake of PM components into plant tissue across leaf surfaces or root uptake via soils are described. Uptake by plants can occur at the soil/plant interface and at the air/plant interface ([Krupa et al., 2008](#)). Once uptake occurs, plant physiological responses may include decreased gas exchange, altered metabolism and photosynthesis, altered pigment and mineral content, and altered enzyme activity ([Naidoo and Chirkoot, 2004](#)). There is some evidence that metals reduce frost hardiness and impair nutrition ([Taulavuori et al., 2005](#); [Kim et al., 2003](#)).

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### 15.4.1 Vegetative Surfaces

As described in the 2009 PM ISA, foliar surfaces are covered with a waxy cuticle layer that helps reduce moisture loss and ultraviolet (UV) radiation stress ([U.S. EPA, 2009a](#)). This epicuticular wax consists largely of long chain esters, polyesters, and paraffins, which accumulate lipophilic compounds. Organic air contaminants in the particulate or vapor phase can be adsorbed to, and accumulate in, the epicuticular wax of leaf surfaces. Low solubility limits foliar uptake and direct heavy metal toxicity because trace metals must be brought into solution before they can enter leaves or bark of vascular plants ([U.S. EPA, 2009a](#)). Particles embedded in waxes may remain for extended periods of time and remain associated with the leaf while other particles may be removed via precipitation, wind, or leaf-fall. Particle capture efficiency varies by plant species, and the role of vegetative surface characteristics in trapping PM, especially in polluted urban

environments, is extensively reviewed in the literature. PM trapping by vegetation depends on distance from source, leaf shape, canopy structure, leaf surface wettability, presence of hairs, properties of the epidermal layer, and phyllotaxy ([Popek et al., 2015](#); [Popek et al., 2013](#); [Saebo et al., 2012](#)).

The 2009 PM ISA also reviewed studies that show effects of direct deposition of particulates to aboveground plant organs. These effects include altered plant metabolism and photosynthesis by the blocking of sunlight, obstruction of stomatal apertures, increasing leaf temperature, and leaf surface injury ([U.S. EPA, 2009a](#); [Naidoo and Chirkoot, 2004](#); [Grantz et al., 2003](#)). Leaf surface pH can be altered by deposition of alkaline particles, which can hydrolyze epicuticular surfaces ([Grantz et al., 2003](#)). The diverse composition of ambient PM and the effects of other air pollutants confound characterization of the direct effects of PM on foliar surfaces ([Grantz et al., 2003](#)).

A number of recent studies published since the 2009 PM ISA have examined the effects of PM deposition to vegetative surfaces. For example, some have further characterized the effects of particle size and composition on leaf surface processes. Following 60-day experimental application of urban dust collected from roadsides in India to common annual plant species (*Abelmoschus esculentus*, *Celosia cristata*, *Coleus blumei*, *Cyamopsis tetragonolobus*, *Gomphrena globosa*, *Impatiens balsamina*, *Ocimum sanctum*, *Phaseolus vulgaris*, *Solanum melongena*, *Zinnia elegans*), scanning electron micrographs of leaf surfaces indicated that larger particles piled up around the stomata, while finer particles clogged the stomatal openings ([Rai et al., 2010](#)). In the applied dust, about 75% was in the 2.5 to 10  $\mu\text{m}$  size fraction, with particles greater than 10  $\mu\text{m}$  composing approximately 10% of PM and ultrafines (less than 2.5  $\mu\text{m}$ ) comprising 15%. Experimental application of PM (monometallic PM oxides: cadmium oxide [CdO], antimony trioxide [Sb<sub>2</sub>O<sub>3</sub>], and zinc oxide [ZnO] and process PM enriched with Pb) to cabbage (*Brassica oleracea*) and spinach (*Spinacia oleracea*) leaves resulted in a coverage rate of particles on the leaf surface estimated at approximately 2% following washing ([Xiong et al., 2014](#)). Most of the particles were concentrated in stomatal apertures, with up to 12% of the area occupied. The presence of PM in the stomata was correlated to particle size and solubility of the associated metal oxides. Newer studies ([Oguntimehin et al., 2010](#); [Oguntimehin et al., 2008](#)) support observations of visible foliar injury reported in previous PM assessments, with some suggesting that drought may affect the particle capture efficiency of trees, and other studies report that deposited particles on leaf surfaces possibly leads to decreased drought tolerance ([Burkhardt and Pariyar, 2015, 2014](#); [Rasanen et al., 2014](#)).

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## 15.4.2 Foliar Uptake of Particulate Matter

As reported in the 2009 PM ISA, fine PM has been shown to enter the leaf through the stomata and penetrate into the mesophyll layers where it alters leaf chemistry and physiology ([Da Silva et al., 2006](#); [Naidoo and Chirkoot, 2004](#)). Organic compounds can be deposited as particles on the leaves or be taken up through the cuticle or stomata in the gas phase, although these pathways are not well characterized for most trace organics ([Oguntimehin et al., 2010](#)). As reviewed in the 2009 PM ISA, for lipophilic POPs, such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated biphenyls (PCBs), the air/plant response route generally dominates ([Lee et al., 2003](#); [Thomas et al., 1998](#)), but uptake through aboveground plant tissue also occurs. The pathways depend on the chemical and its physical properties, such as lipophilicity, water solubility, vapor pressure, and Henry's law constant. Environmental conditions can also be important, including temperature and organic content of soil, plant species, and the foliar surface area and lipid content.

([Eichert et al., 2008](#)) demonstrated hydrophilic particle penetration into the substomatal cavity of faba bean (*Vicia faba*) leaves. Since the 2009 PM ISA, development and refinement of techniques such as micro x-ray fluorescence, scanning electron microscopy coupled with energy dispersive x-ray microanalysis, and secondary ion mass spectrometry have been applied toward characterizing particulate transfer from foliar surfaces to the interior of the plant ([Schreck et al., 2014](#); [Burkhardt et al., 2012](#); [Schreck et al., 2012](#)). Repeated deliquescence and efflorescence of soluble PM may have the effect of slowly advancing solutes into the stomatal pore where they may become bioavailable ([Burkhardt et al., 2012](#)). Recently, stomatal uptake of aqueous solutions was confirmed by environmental scanning electron microscopy ([Burkhardt et al., 2012](#)). Deposited aerosols on leaf surfaces may alter surface tension and hydrophobicity, enabling stomatal liquid water transport and facilitating foliar uptake. Several studies provide additional evidence of particles entering plant tissues through stomata openings ([Schreck et al., 2012](#); [Uzu et al., 2010](#)). [Schreck et al. \(2014\)](#) observed particles in stomata and damage to guard cells from Pb-rich particles from a Pb recycling factory. Other pathways of deposited metals to vegetative surfaces may include diffusion across the cuticle ([Schreck et al., 2012](#); [Uzu et al., 2010](#)). Nonstomatal uptake of atmospheric Hg into plant leaves has recently been demonstrated in addition to stomatal pathways ([Stamenkovic and Gustin, 2009](#)). Biogeochemical transformations were observed in metal-rich PM at the leaf surface ([Schreck et al., 2012](#)). The role of the phyllosphere (i.e., the microbial communities on foliar surfaces) on the uptake and chemical transformation of deposited particles and in promoting plant growth is an emerging area of study; however, interactions associated with PM are not well characterized at this time ([Weyens et al., 2015](#); [Xiong et al., 2014](#)).

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### 15.4.3 Particulate Matter Impacts on Gas Exchange Processes

In earlier assessments of ecological effects of PM, deposition of particles to vegetation was known to interfere with gas exchange processes such as photosynthesis, respiration, and transpiration ([U.S. EPA, 2009a, 2004](#)). Several new studies support observations from previous PM reviews on the exchange of oxygen and carbon dioxide across the leaf surface. Most studies involve the application of dust to leaves. A greenhouse study with lettuce (*Lactuca serriola*) leaves showed decreased gas-exchange parameters (net photosynthetic rate and stomatal conductance) and a change in transpiration rate following PM (dust from vehicular traffic with a dominance of fine particles) application to leaves ([Pavlík et al., 2012](#)). Fly ash dusting of 0.5 to 1.5 g/m<sup>2</sup>/day to rice reduced photosynthesis, stomatal conductance, and transpiration ([Raja et al., 2014](#)). Photosynthesis, transpiration rate, and water use efficiency was decreased in peach (*Prunus persica*) leaves dusted with cement kiln dust, and to a lesser extent with soil dust ([Maletsika et al., 2015](#)). Exposure of the leaves of *Prunus padus* to PM in Poland resulted in decreased photosynthesis and chlorophyll fluorescence, but similar effects on the photosynthetic apparatus were not found in *Prunus serotina* ([Popek et al., 2017](#)). In a study of native and non-native plant species in Argentina, [Gonzalez et al. \(2014\)](#) reported that gas-exchange parameters, including maximum assimilation rate, stomatal conductance, and transpiration rate, were significantly decreased in most plant species by ambient dust accumulation on leaf surfaces compared with those parameters in plants from which deposited dust had been removed. Similarly, decreased photosynthesis rate, increased stomatal resistance, and lower chlorophyll content was observed with increased PM accumulation in plant species growing in the city center of Warsaw, Poland compared to a moderately clean environment ([Przybysz et al., 2014](#)). The photosynthetic apparatus of the lichen species *Evernia prunastri* was significantly affected by dust enriched by calcium (Ca), Fe, and titanium (Ti) near a quarry and cement factory in Slovakia ([Paoli et al., 2015](#)). Photosynthetic rate and chlorophyll content were significantly reduced in cherry tomatoes (*Lycopersicon esculentum*) misted with fluoranthene for 30 days to represent atmospheric wet deposition to the leaf surface ([Oguntimehin et al., 2010](#)).

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### 15.4.4 Plant Physiology

In the 2009 PM ISA, particulates were associated with phytotoxic responses, including induction of phytochelatins, alteration of pigments, and changes in mineral content and enzyme activity ([U.S. EPA, 2009a](#)). Newly available studies support these findings. Chlorophyll content as well as specific leaf area and relative water content of selected tree species was significantly reduced by the greater dust load associated with a polluted

site in India compared to a low pollution location ([Chaturvedi et al., 2013](#)). Decreased leaf chlorophyll and increased phenol content was also observed in peach leaves with accumulated cement or soil dust ([Maletsika et al., 2015](#)). In lettuce leaves, PM application caused a depletion in amino acids that are metabolized during photosynthesis as well as an increase in proline ([Pavlík et al., 2012](#)). Proline and malondialdehyde concentrations were elevated in maize leaves treated with Hg ([Niu et al., 2014](#)). Recently, the use of foliar fatty acid composition as an indicator of foliar (and root) metal uptake was demonstrated with lettuce leaves exposed to PM from smelter emissions ([Schreck et al., 2013](#)).

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#### 15.4.5 Uptake of Particulate Matter by Plants from Soils

Plants can also uptake PM that has been deposited to soils. As reviewed in the 2009 PM, ISA uptake from soils varies by the PM component and plant species ([U.S. EPA, 2009a](#)). There was some evidence that shallow-rooted plant species are most likely to take up metals from the soil ([Martin and Coughtrey, 1981](#)). The ability of plants to take up contaminants from soil and water has been applied toward environmental cleanup efforts, a process known as phytoremediation ([Hooda, 2007](#); [Padmavathiamma and Li, 2007](#); [Clemens, 2006](#)). Plants that are hyperaccumulators of metals are especially useful in phytoremediation efforts ([Prasad and DeOliveira, 2003](#)).

Plants respond to high concentrations of metals in soil through a variety of mechanisms, and plant species differ substantially in their response to heavy metal exposure. As reviewed in the 2009 PM ISA, mechanisms of metal tolerance included exclusion, excretion, genetics ([Yang et al., 2005](#); [Patra et al., 2004](#)), mycorrhizal interactions ([Gohre and Paszkowski, 2006](#)), storage capability and accumulation ([Clemens, 2006](#)), various cellular detoxification mechanisms ([Gratao et al., 2005](#); [Hall, 2002](#)), and chelation with phytochelatins ([Memon and Schroder, 2009](#)).

Since the 2009 PM ISA, additional studies have focused on the use of vegetation to remediate sites with both organic and inorganic contaminants and the use of mycorrhizal fungi and bacteria to promote phytoremediation ([Appendix 15.5.4](#)). In addition, soil-bound PAHs associated with soil organic matter, historically thought to be generally not easily available for root uptake, have been shown in recent studies to be readily adsorbed to root surfaces, with some evidence showing translocation to the shoots ([Desalme et al., 2013](#)).

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## 15.4.6 Effects on Plant Growth and Reproduction

PM effects on plant growth reviewed in the 2009 PM ISA include reduced vigor and impaired root development ([U.S. EPA, 2009a](#)). In general, plant biomass is negatively correlated with organics ([Desalme et al., 2013](#)) and metal concentrations ([Audet and Charest, 2007](#)). Inhibition of aboveground biomass was observed in lettuce leaves with traffic-associated PM applied directly to vegetation ([Pavlík et al., 2012](#)). Increased trace metal concentration along with the decrease in biomass was measured in the treated leaves. Decreased primary root elongation and shoot and root rates were observed in tomatoes (*Solanum lycopersicum*) grown for 18 days with growth solution in a quartz fiber particulate matter filter with particles with a nominal mean aerodynamic diameter less than or equal to 10 µm (PM<sub>10</sub>) collected from an urban background site in Italy ([Daresta et al., 2014](#)). Decreased chlorophyll *a* and increased carotenoids in the exposed plants were noted along with increased reactive oxygen species production in roots from the PM<sub>10</sub> substrate. Phenanthrene, a common PAH in air, applied to soils via simulated atmospheric deposition in an exposure chamber was shown to significantly decrease root length and shoot biomass of leek (*Allium porrum*) seedlings ([Desalme et al., 2012](#)). In a similar study, shoot biomass of red clover (*Trifolium pratense*) exposed to atmospheric phenanthrene decreased by around 30% while ryegrass (*Lolium perenne*) was unaffected ([Desalme et al., 2011a](#)). No effects on root biomass were observed in either plant. With phenanthrene exposure to red clover, more carbon (C) was retained in leaves with decreased C allocation to stems and roots ([Desalme et al., 2011b](#)).

Daily application of urban dust to common annual plant species for 60 days showed reduction in plant growth, number of leaves, and leaf area ([Rai et al., 2010](#)). Growth and yield of rice was significantly influenced at higher rates of fly ash deposition due to increased heat load and reduced intracellular carbon dioxide (CO<sub>2</sub>) concentration ([Raja et al., 2014](#)). Following dusting of the plants by fly ash at 0.5, 1.0, and 1.5 g/m<sup>2</sup>/day, a significant decrease in grain yield of 12.3, 15.7, and 20.2%, respectively, was observed.

[Farahat et al. \(2016\)](#) studied the effects of dust deposition from a rock quarry on old-growth eastern hemlock (*Tsuga canadensis*) in Quebec, Canada. Mean radial growth declined 43% after the construction of the quarry compared with growth rates before construction. Major changes in the hemlock occurred 3–16 years after the quarry was established, indicating that the effect on growth may be indirect through the alteration of soil pH in this forest. In a study from Beijing, China, application of local road dust to *Sophora japonica* seedlings significantly affected growth characteristics such as leaf N, shoot biomass, root-shoot ratio, photosynthesis, and total chlorophyll ([Bao et al., 2016](#); [Bao et al., 2015](#)).

Recently, the effect of air pollutants on the timing and budburst of vegetation has been assessed in several studies ([Jochner et al., 2015](#); [Kozlov et al., 2007](#)). The timing of full flowering of hazel (*Corylus avellana*) was found to be significantly related to PM in ambient air in urban areas of Munich, Germany ([Jochner et al., 2015](#)).

These effects on phenological onset were also observed with ozone (O<sub>3</sub>), nitrogen dioxide (NO<sub>2</sub>), and nitrate (NO<sub>3</sub>) in hazel and additional tree species in the same study. In a field and greenhouse study in Russia with mountain birch (*Betula pubescens*), no impacts of air pollution on phenology were observed between trees surveyed in proximity to a Ni-Cu smelter and trees at further distance from the emission source ([Kozlov et al., 2007](#)).

Some studies have examined the effects of PM on plant reproduction. Some potential effects demonstrated were those in flowering phenology and timing ([Jochner et al., 2015](#); [Rai et al., 2010](#); [Honour et al., 2009](#)). [Jaconis et al. \(2017\)](#) examined the effect of PM on stigmatic clogging in *Cichorium intybus* on roadsides in Cincinnati, OH. The authors reported no relationship between PM levels and pollen germination across all of the roads studied.

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## 15.5 Effects of Particulate Matter on the Soil Environment

As described in the 2009 PM ISA, the soil is one of the most dynamic environments of biological interaction in nature ([U.S. EPA, 2009a](#)). The upper soil layers where deposited particles accumulate are typically active sites of litter decomposition and plant root uptake. Processes within the rhizosphere, the soil around plant roots that mineral nutrients must pass through, may be affected by PM components. Soil-associated microbial communities of bacteria and fungi such as actinomycetes and basidiomycetes, respectively, break down organic matter for nutrient cycling and make elements available for plant uptake. Soil mycorrhiza, (fungi that colonize plant roots) form a symbiosis to provide nutrients in exchange for carbon from the plant. The effects of PM-associated organics and metals on the soil environment is largely dictated by bioavailability to soil microflora and plant roots.

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### 15.5.1 Bioavailability in Soils

Soils are heterogeneous and the effects of PM deposition and subsequent bioavailability of PM components depend on soil characteristics (e.g., pH, organic content). PM-associated organics partition between the soil and the atmosphere based on soil properties, such as organic matter content, moisture, porosity, texture, and structure, as

well as the physiochemical properties of the pollutant, including vapor pressure and water solubility ([U.S. EPA, 2009a](#)). These compounds may be taken up by roots or be associated with organic matter ([Fismes et al., 2002](#)). For heavy metals, accumulation in soil is influenced by a variety of soil characteristics, including pH, Fe and aluminum oxide content, amount of clay and organic material, and cation exchange capacity [CEC; ([Hernandez et al., 2003](#))]. Bioavailability depends on metal speciation, soil pH, and degree of binding to dissolved organic matter [DOM; ([Sauvé, 2001](#))].

In the 2009 PM ISA, several models, isotopic studies, and sequential extraction methods for determining metal bioavailability in soils were reported ([Feng et al., 2005](#); [Collins et al., 2003](#); [Shan et al., 2003](#)). However, actual measurement of biological effects is generally regarded as the preferred criterion to assess bioavailability ([Almas et al., 2004](#)). Since the 2009 PM ISA, Biomet biosensors have been used to assess bioavailability of metals in contaminated topsoils and subsoils ([Almendras et al., 2009](#)). Biomet biosensors use genetically engineered bacteria that give off light when exposed to heavy metals that are bioavailable. [Almendras et al. \(2009\)](#) also used sequential extraction to determine solubility. At three sites near a smelter in Chile, they found that Cu and Zn had the greatest solubility, arsenic (As) had less solubility, and Pb and Fe were the least soluble of those heavy metals. Further, as was determined to be the most bioavailable, while Cu and Zn were less bioavailable. The authors were unable to determine bioavailability of Pb using the same technique.

The mobility of heavy metals, an indicator of potential bioavailability, was determined in surface soil using sequential extraction ([Svendsen et al., 2011](#)). In five sites at decreasing distances from a smelter in Norway, Cd was determined to be most mobile and Cu the least mobile ([Svendsen et al., 2011](#)). Zn and Pb were moderately mobile. These results were in contrast to the results of ([Almendras et al., 2009](#)).

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## 15.5.2 Soil Nutrient Cycling

In previous PM reviews, toxicity of metals, especially Zn, Cd, and Cu, to soil microflora was found to reduce decomposition processes in soils and interfere with nutrient cycling ([U.S. EPA, 2009a](#)). In previous PM reviews, changes to microbial enzymatic activity, soil basal respiration rate, and soil microbial biomass were all associated with increased metal content in soils. Studies reviewed in the 2009 PM ISA report increased leaf litter accumulation near point sources.

Since the 2009 PM ISA, many studies showing the deleterious effects of PM on nutrient cycling have been published. The effect of PM on the microbial coefficient of soils contaminated by atmospheric emissions from an active mining and smelting complex was

determined in one study. The microbial coefficient, which is the ratio of microbial biomass carbon to total organic carbon, was negatively correlated with metal concentrations ([Shukurov et al., 2014](#)). The microbial coefficient gives a measure of substrate bioavailability.

A recent study demonstrated the role of atmospheric deposition of particulate heavy metals in inhibiting C cycling. In this study, a cropping system was exposed to atmospheric deposition while a similar cropping system was designed to exclude it by using a greenhouse. Total organic carbon and water soluble organic carbon increased in the exposed plots and decreased in the greenhouse plots; slow decomposition in soils polluted with heavy metals could have caused the increased levels of total organic carbon and water soluble organic carbon observed in the open plots ([Pandey and Pandey, 2009](#)).

New studies show decreases in enzyme activity and varying sensitivity of enzymes to metal pollution. Soil dehydrogenase activity was diminished in polluted soils compared to control soils ([Bojarczuk and Kieliszewska-Rokicka, 2010](#)). High soil dehydrogenase activity indicates a living microbial community; additionally, dehydrogenase activity increases with microbial biomass C, organic matter levels, and basal respiration ([Bojarczuk and Kieliszewska-Rokicka, 2010](#)). In another study, enzyme activities of alkaline phosphatase and fluorescein diacetate were greater in greenhouse treatments than in open treatments exposed to deposition over the study period, showing that the potential for hydrolysis was elevated in the greenhouse treatments ([Pandey and Pandey, 2009](#)). As a result, organic C was mineralized to carbon dioxide and released from the soil more quickly than it was in the treatments exposed to deposition. [Qu et al. \(2011\)](#) found that enzyme activity was higher at sites farther from an active mining operation than those close to it. However, urease activity was more affected by heavy metals than dehydrogenase and phosphatase activity. Dehydrogenase contributes to many oxidative activities, which degrade soil organic matter ([Qu et al., 2011](#)). Phosphatase conducts hydrolysis to convert organic phosphorus compounds into inorganic phosphorus compounds, and urease converts urea into carbon dioxide and ammonia through hydrolysis ([Qu et al., 2011](#)).

A new study compared soil functional activity measured by the bait-lamina assay and by the Biolog assay. Feeding activity was increased at the less polluted site compared to the more polluted site ([Boshoff et al., 2014](#)). Substrate utilization rate and richness of used substrates were decreased in the more polluted site compared with the less polluted site after 2 and 6 days. On the other hand, diversity of used substrates at all plots resembled one another by the end of the experiment. Feeding activity, substrate utilization rate, richness of used substrates, and diversity of used substrates all decreased as As, Cu, and Pb concentrations increased. The Biolog assay was a better indicator of soil functional

activity than the bait-lamina assay ([Boshoff et al., 2014](#)). The bait-lamina assay indicates the feeding activity of soil fauna; the Biolog assay measures the metabolic use pattern of the culturable microbial community.

The effects of PM on microbial activity and biomass have been widely studied in the literature since the release of the 2009 PM ISA. Additions of Cr and Zn to soils have been found to reduce microbial respiration ([Åkerblom et al., 2007](#)). The highest concentrations of Pb and molybdenum (Mo) decreased respiration, as did higher levels of Ni and Cd. On the other hand, low levels of Ni and Cd increased microbial respiration. In this study, metals were added in low, medium, and high doses to soil from the humus layer of a Swedish forest ([Åkerblom et al., 2007](#)). Similarly, in another study, microbial activity (for all metals except Cu) decreased with increasing metal concentrations, and a negative correlation was also determined between metal concentrations and microbial biomass ([Anderson et al., 2009a](#)). Notably, microbial biomass levels were all similarly reduced among contaminated sites compared to the control site, even though metal concentrations among the contaminated sites varied. At the same time, microbial activity and biomass increased with increasing concentrations of physicochemical variables (such as nitrate, magnesium [Mg], and potassium [K]). Microbial activity, indicated by the amount of carbon substrates used, was measured using the Biolog assay ([Anderson et al., 2009a](#)). Using similar methods, ([Anderson et al., 2009b](#)) found that microbial activity and biomass in polluted sites were reduced compared to activity and biomass in the control site, prior to the experiment, which consisted of adding metals to soils from the sites. Microbial activity and biomass were lower at all sites after metal addition ([Anderson et al., 2009b](#)). In [Azarbad et al. \(2013\)](#), basal respiration and substrate-induced respiration increased with organic matter and pH and decreased as the toxicity index (an indicator of heavy metal contamination) increased. The toxicity index was more important in explaining effects of heavy metal contamination on substrate-induced respiration than basal respiration. In the same study, microbial biomass, represented by total phospholipid fatty acids (PLFAs), increased as toxicity index decreased ([Azarbad et al., 2013](#)). [Chodak et al. \(2013\)](#) found that microbial biomass and basal respiration were affected mainly by environmental variables, such as total nitrogen and organic carbon, and heavy metals impacted them much less. In another study, microbial biomass C and substrate-induced respiration were lower in open treatments exposed to atmospheric deposition than in greenhouse treatments as time progressed ([Pandey and Pandey, 2009](#)).

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### 15.5.3 Soil Community Effects

At the time of the 2009 PM ISA, toxicity of heavy metals to soil-associated microbes were well characterized in laboratory studies, but less was known about the relative

sensitivity of fungi, bacteria, and actinomycetes and community-level changes. New techniques described in the 2009 PM ISA, such as the use of phospholipid and nucleic-acid biomarkers ([Joynt et al., 2006](#)), have enabled researchers to better characterize microbial community composition and biodiversity. In a recent study, tolerance of microbial communities to heavy metal PM has been shown to vary with ecosystem type. Culturable bacterial communities in contaminated meadow soils experienced greater tolerance to pollution, but the culturable communities in contaminated forest soils did not ([Stefanowicz et al., 2009](#)). The authors suggested that similarities between the degree of heavy metal contamination in control and polluted forest soils, caused by increased pH in polluted soils, may have contributed to the lack of tolerance of bacterial communities in forest soils because pH influences bioavailability of metals. Additionally, the absence of increased tolerance in forest soils might have been caused by a lack of variation in metal sensitivity of bacterial species.

The impact of metal-associated PM on the abundance of microbes has been studied in recently published papers. Total numbers of silver birch (*Betula pendula*) seedling root tips colonized by mycorrhizae decreased in seedlings grown in polluted soils relative to those in control soil ([Bojarczuk and Kieliszewska-Rokicka, 2010](#)). In another study, culturable bacteria were more abundant at the sites farther from an active mining operation than at the sites close to it ([Qu et al., 2011](#)). [Lenart-Boron and Wolny-Koladka \(2015\)](#) found no correlation between metal concentrations and abundance of microbial groups (mesophilic bacteria, fungi, actinomycetes, and *Azotobacter* spp.). The effects of PM from heavy metals on the metabolic quotient of soils that were contaminated by an active mining and smelting complex in Uzbekistan have been studied recently in the literature. Metabolic quotient, an indicator of the influence of environmental variables on microbial communities, increased with increasing heavy metal concentrations ([Shukurov et al., 2014](#)).

Recently published studies show that the response of soil-associated microbial community structure and function to heavy metal PM varies. ([Åkerblom et al., 2007](#)) found that most metals altered community structure in a similar way. Phospholipid fatty acids (PLFAs) can indicate microbial community structure, and different PLFAs are associated with different groups of microbes [e.g., fungi, bacteria; ([Åkerblom et al., 2007](#))]. Relative abundance of PLFAs associated with Gram-positive bacteria had a positive relationship with metal concentrations, but relative abundance of PLFAs associated with Gram-negative bacteria had a negative relationship with metal concentrations. The relative abundance of actinomycetes PLFAs had a positive relationship with metal concentrations. The reaction of the relative abundance of certain PLFAs found in Gram-negative bacteria varied depending on exposure to particular metals, and the reaction differed most between Cr and Cd. Relative abundance of a fungal

PLFA increased with increasing Cr and Zn concentrations ([Åkerblom et al., 2007](#)). [Likar and Regvar \(2009\)](#) determined that ascomycetes fungi were more common in polluted plots, and ectomycorrhizal ascomycetes mainly comprised one taxonomic group. On the other hand, basidiomycetes fungi were more common in control plots and in plots that were less contaminated, and ectomycorrhizal basidiomycetes were more diverse than ectomycorrhizal ascomycetes, comprising several taxonomic groups. Dark septate endophytes in the ascomycete group were common in polluted plots and comprised several taxonomic groups ([Likar and Regvar, 2009](#)). The increased number of DNA sequences from a particular dark septate endophyte genus (*Phialophora*) in plots that contained greater concentrations of Cd and Pb suggests that this genus could help goat willow (*Salix caprea*) take up more nutrients under metal stress ([Likar and Regvar, 2009](#)); however, the authors did not actually measure nutrient uptake of plants in this study. [Anderson et al. \(2009b\)](#) found that before the experiment, which consisted of adding metals to soils with varying levels of initial contamination by an abandoned smelter in Anaconda, MT, the structure and function of the microbial community from each site differed from one another, and after the experiment, the communities remained structurally and functionally different.

In another study, diversity and evenness of soil fungi communities in forest litter and those of arbuscular mycorrhizal fungi communities in forest litter were lower in a site polluted by emissions from an active copper smelter than they were in the reference site; community structure of soil fungi in the polluted site was not similar to that in the control site ([Mikryukov et al., 2015](#)). Spatial autocorrelations existed in both the control and polluted sites for soil fungi communities, but the spatial structure of the communities in the two sites did not resemble one another. Arbuscular mycorrhizal fungi (AMF) community structures at control and polluted sites did resemble one another. Spatial autocorrelation only existed in the polluted sites for arbuscular mycorrhizal fungi communities ([Mikryukov et al., 2015](#)). Spatial heterogeneity tended to be greater in contaminated areas than in uncontaminated areas ([Mikryukov et al., 2015](#)). [Qu et al. \(2011\)](#) found that microbial community diversity increased as distance from an active mining operation increased. In a different study, ecophysiological index values at two long-term contaminated sites were substantially high for oligotrophs and copiotrophs ([Margesin et al., 2011](#)). Both sites contained bacterial communities with high Shannon diversity index values (a common index used to characterize species diversity), and the metabolically active groups at both sites were Proteobacteria and Actinobacteria ([Margesin et al., 2011](#)).

Recent studies have shown the effects of environmental variables in comparison to the effects of heavy metal associated PM. In a study by [Anderson et al. \(2009a\)](#), microbial species richness was influenced by physicochemical characteristics (Mg, CEC, Ca,

ammonium [NH<sub>4</sub><sup>+</sup>]), but was not affected at all by metal concentrations; however, community structure in polluted sites was altered by metal concentrations compared to control sites. In a different study, toxicity index, which represents the degree of heavy metal pollution, had a positive impact on functional diversity of fungi, and nutrient status had a negative impact on functional diversity of fungi ([Azarbad et al., 2013](#)). On the other hand, toxicity index did not influence functional diversity of bacteria, but functional diversity increased as acidity decreased. PLFAs that represent Gram-positive bacteria increased with toxicity index, while the PLFA associated with fungi decreased as toxicity index increased. The level of organic matter and pH were factors that influenced PLFAs as well as degree of metal contamination ([Azarbad et al., 2013](#)). [Chodak et al. \(2013\)](#) determined that pH had the largest impact on bacterial community diversity, but heavy metals also modulated diversity. Bacterial community structure was mainly affected by pH. Although pH was the main factor controlling microbial community structure, heavy metals also influenced microbial community structure ([Chodak et al., 2013](#)).

In addition to soil microbial communities, the effects of metal-associated PM on other soil fauna have been recently published. [Shukurov et al. \(2014\)](#) found that abundance of nematodes was greater at the plots further from the emission source; similarly, the abundance of nematodes, number of bacterivorous nematodes, and number of omnivorous predator nematodes were negatively correlated with heavy metal concentrations.

The harmful effects of organic PM on soil microbes have been published in recent studies. AMF infectivity in the top soils was reduced compared to control soils when exposed to phenanthrene for 2 weeks ([Desalme et al., 2012](#)). In this study, phenanthrene was pumped into an exposure chamber containing soils to simulate atmospheric exposure. However, in another study using a similar experimental setup, mycorrhizal symbiosis in red clover was similar in control and polluted chambers, and mycorrhizal symbiosis in both treatments remained efficient ([Desalme et al., 2011a](#)). In the same study, *Rhizobium* nodule (bacteria) symbiosis in clover was lower in the upper layer of polluted soil than in the upper layer of control soil ([Desalme et al., 2011a](#)).

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#### **15.5.4 Soil Microbe Interactions with Plant Uptake of Particulate Matter**

In the 2009 PM ISA, the role mycorrhiza in modulating toxicity of deposited metals was reported. This role includes improving nutrient uptake and decreasing metal uptake ([Vogelmikus et al., 2006](#); [Nogueira et al., 2004](#); [Berthelsen et al., 1995](#)) in the plant by acting as a sink for metals ([Carvalho et al., 2006](#); [Berthelsen et al., 1995](#)), often preventing the metals in the roots from allocating to shoots ([Soares and Siqueira, 2008](#);

[Zhang et al., 2005](#); [Kaldorf et al., 1999](#)). In contrast, other studies reviewed in the 2009 PM ISA showed that mycorrhizae may facilitate accumulation of metals in plants and enhance the translocation of metals from the root to the shoot ([Zimmer et al., 2009](#); [Citterio et al., 2005](#); [Vogel-Mikus et al., 2005](#)). There was limited evidence for bacteria and mycorrhiza working together to improve plant tolerance to metals ([Vivas et al., 2006](#); [Vivas et al., 2003](#)).

Since the 2009 PM ISA, additional studies show mycorrhizae modulates metal uptake in plants. Seedlings grown in polluted soil with mycorrhizae preferentially sequestered heavy metals (Cu and Pb) to the roots instead of the shoots ([Bojarczuk and Kieliszewska-Rokicka, 2010](#)). The ratio of mycorrhizal fine roots to nonmycorrhizal fine roots was lower for silver birch seedlings grown in polluted soils (mixture and fully polluted soil near a copper foundry in Poland) than for tree seedlings grown in control soil; however, the mycorrhizae were still able to affect metal uptake by the plants.

Nonmycorrhizal microbes (e.g., bacteria, fungal hyphae, spores from saprobes) may also decrease metal uptake by plants. In a greenhouse experiment using soils collected at varying distances from abandoned smelters in the U.S., wavy hairgrass (*Deschampsia flexuosa*) plants grown in soils with high amounts of contamination and treated with nonmycorrhizal microbial wash accumulated less Zn in the shoots compared to plants without the nonmycorrhizal microbial wash ([Glassman and Casper, 2012](#)). In contrast, although there was an AMF treatment in this experiment, AMF did not impact the amount of Zn in the shoots of plants.

AMF and nonmycorrhizal microbes such as plant growth promoting bacteria can contribute to phytoremediation of polluted soils; much new research on these topics has been published since the release of the previous ISA ([Cabral et al., 2015](#); [Meier et al., 2012](#); [Gamalero et al., 2009](#)).

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### 15.5.5 Effects of Particulate Matter on Physical Properties of Soils

PM can affect physical properties of soils, such as bulk density, porosity, and water holding capacity. Changes in these properties can decrease plant growth and yield. This topic was not discussed in the previous PM ISA. However, new studies on the effects of PM on physical properties of soils have been published since the release of the previous ISA. [Pandey and Pandey \(2009\)](#) found that bulk density was elevated during the study period in an experimental cropping system open to deposition. Porosity and water holding capacity in the open system were diminished over the same time period. The opposite was the case for the experimental cropping system closed to deposition. The authors suggested that the influx of deposition of particulate matter during the study

period caused a rise in bulk density, and the elevated bulk density caused the decrease in porosity and water holding capacity ([Pandey and Pandey, 2009](#)).

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## 15.6 Effects of Particulate Matter on Fauna

Toxicity of PM to fauna varies depending upon the PM composition, concentration, bioaccessibility and bioavailability, biological species sensitivity, and organism lifestage. The bioavailability or bioaccessibility of PM-associated trace metals and organics is dependent upon the physical, chemical, and biological conditions under which an organism is exposed at a particular geographic location. Organisms may have detoxification mechanisms that increase tolerance to stressors. Pathways of PM exposure to aquatic and terrestrial organisms include ingestion, absorption, and trophic transfer. Several types of studies have been used to assess the effects of PM on terrestrial and aquatic organisms, including laboratory bioassays and field studies.

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### 15.6.1 Laboratory Bioassays

The use of ecotoxicity assays to screen and assess PM effects on biota has expanded considerably since the 2009 PM ISA. All but one of the new studies used PM from outside of the U.S., so the pollutant mix may not be representative of exposures occurring in the U.S. These studies are reported below. However, several caveats must be noted in correlating effects in these studies to natural environments. Extracts of PM from air filters may not be representative of exposure routes and conditions in aquatic and terrestrial habitats ([Kováts et al., 2012](#)). Bioavailability of PM in the natural environment is affected by many factors not represented in bioassay techniques. Furthermore, because these studies include a mix of PM constituents, it may be difficult to identify the active component(s). Results from toxicity assays using PM extracts (such as dichloromethane, methanol, or water extracts) should be interpreted with caution because additional compounds might remain unextracted, underestimating or overestimating the whole PM toxicity to aquatic organisms ([Mesquita et al., 2014a](#); [Kováts et al., 2012](#)).

Recently the *Vibrio fischeri* bioluminescence inhibition test (Microtox<sup>®</sup>) has been applied as an ecotoxicological screening tool for PM ([Roig et al., 2013](#); [Kováts et al., 2012](#)). In this bioassay, the rate of inhibition of light emission from the bacteria is measured after exposure to a pollutant. In aqueous PM extracts from air filters from urban, rural, and industrial areas of Catalonia, Spain, no correlation was observed between inhibition of light emission in the in vitro test and PM<sub>10</sub> concentration ([Roig et al., 2013](#)). Metals (except Cr) and PCDD/F congeners in the samples were significantly correlated to the

bioassay results, indicating that PM composition, rather than concentration, explains the experimental observations.

Toxicity of PM extracts to aquatic biota have been assessed in several studies published since the 2009 PM ISA. Acute (24-hour) toxicity of ambient PM with a nominal mean aerodynamic diameter less than or equal to 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) extracted from air filters in Atlanta, GA to the freshwater rotifer *Brachionus calyciflorus* was assessed by ([Verma et al., 2013](#)). The toxicity of methanol extracts was much higher than that of water extracts, and there were no conclusive associations of rotifer toxicity with PM chemical composition. In zebrafish (*Danio rerio*) embryos exposed to organic extracts of PM samples from coal-burning particles in a semirural area in Italy, cytochrome P4501A gene expression was significantly induced ([Olivares et al., 2013](#)). In another zebrafish study, urban PM had adverse developmental effects (spinal deformations, malformation of swim bladder, etc.) on embryos ([Mesquita et al., 2014b](#)). These observations correlated with PAH content of the PM samples. In a comparison of PM in rural and urban air particles collected in Spain, induction of AhR signaling pathway correlated with PAH concentrations in all locations ([Mesquita et al., 2015](#)). The greatest dioxin-like activity and embryotoxicity was observed in the finest PM fraction ( $<0.5 \mu\text{m}$ ). During the winter, maximal assay activity occurred in the rural samples due to biomass-burning emissions.

A series of in vivo studies on the effects of  $\text{PM}_{2.5}$  exposure on the nematode *Caenorhabditis elegans* indicated a suite of responses in this organism. [Zhao et al. \(2014b\)](#) observed altered development, lifespan, reproduction, locomotion, and defecation behavior associated with long-term exposure to  $\text{PM}_{2.5}$  collected from a traffic-dense area in Beijing, China. PM components included S, Cd, Pb, Zn, Cu, and PAHs. The insulin signaling pathway was identified as a possible molecular target of the traffic-related  $\text{PM}_{2.5}$  in nematodes ([Yang et al., 2016](#); [Yang et al., 2015](#)). In nematodes exposed to  $\text{PM}_{2.5}$  in coal ash, altered functioning of neurons that control defecation behavior and gene expression patterns required for control of oxidative stress were reported, as were effects on development, reproduction, locomotion behavior, lifespan, and susceptibility to metal toxicity ([Wu et al., 2017](#); [Sun et al., 2016](#); [Sun et al., 2015b](#)). Elemental analysis of the PM from coal combustion indicated Fe, Zn, and Pb were the most common metals followed by As, Cd, Cr, Cu, and Ni. Fluoranthene, pyrene, and 12 additional PAHs were detected in the  $\text{PM}_{2.5}$  in the coal ash.

Earthworms often constitute a large percentage of soil animal biomass and are considered to be relatively sensitive bioindicators of soil contamination by metals and organics. Several studies in the 2009 PM ISA reported uptake of trace metals and organics by earthworms ([Hobbelen et al., 2006](#); [Parrish et al., 2006](#)), while fewer studies reported responses due to atmospheric deposition of PM ([Massicotte et al., 2003](#)). Earthworms can

also modify PM bioavailability and bioaccessibility in soils through bioturbation. For example, the presence of earthworms has been shown to significantly increase soil-to-plant transfer of metals via modifications to soil and increased bioaccessibility of metals to roots ([Leveque et al., 2014](#)).

In a recent study, earthworms (*Eisenia andrei*), directly exposed to powder from PM<sub>10</sub> quartz filters (24.9 mg/g PM<sub>10</sub> and 14 µg/g PAHs) in artificial soil for a range of final concentrations from 15 to 30 µg/g PM<sub>10</sub>, showed genotoxic effects ([Vernile et al., 2013](#)). DNA damage measured by comet assay was observed starting at 22.5 µg/g PM<sub>10</sub> (0.012 µg/g PAHs) in samples collected from an urban site in Italy.

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### 15.6.2 Wildlife as Biomonitors of Particulate Matter

The 2009 PM ISA reviewed several studies in which resident biota was used to biomonitor urban air pollution including PM. For example, snails (*Helix* spp.) accumulate trace metals and agrochemicals and can be used as effective biomonitors for urban air pollution ([Regoli et al., 2006](#); [Viard et al., 2004](#); [Beeby and Richmond, 2002](#)). Biological effects that have been demonstrated include oxidative stress, growth inhibition, impairment of reproduction, and induction of metallothioneins, which are involved in metal detoxification ([Regoli et al., 2006](#); [Gomot-De Vaufleury and Kerhoas, 2000](#)). Biomonitoring of aquatic species was also reported. For example, [Coelho et al. \(2006\)](#) investigated Hg concentrations in *Scrobicularia plana*, a long-lived, deposit-feeding bivalve in southern Europe. The use of sentinel species to detect the effects of complex mixtures of air pollutants is of particular value because the chemical constituents are difficult to characterize, exhibit varying bioavailability, and are subject to various synergistic effects.

New biomonitoring studies of PM effects on biota include vertebrate and invertebrate organisms. Use of the land snail *Helix aspersa* as a biomonitor for PAHs associated with atmospheric particles in Porto Alegre, Brazil indicated, in general, that higher genotoxicity in this indicator organism was associated with PM size fractions <PM<sub>2.5</sub> ([Janistcki et al., 2009](#)). Various biomarkers of oxidative stress were induced in *Helix* monitored in Kafr El-Zayet, Egypt in response to heavy metals from industrial sources and vehicular traffic ([Abdel-Halim et al., 2013](#)).

Recent biomonitoring studies of PM components include several studies using wild pigeons. Genotoxic endpoints (percentage DNA migrated, tail moment, and damage index), evaluated in pigeons (*Columba livia*) in the city of Milan, Italy showed significant differences when compared with control pigeons living indoors, and the highest values were observed in summer ([Sicolo et al., 2010](#)). In a companion study, porphyrin patterns

in excreta were always higher in the wild urban pigeon population, while methemoglobin levels in blood showed significant differences from season to season, but values in the indoor birds were significantly lower only in summer and autumn ([Sicolo et al., 2009](#)). The authors chose this model because pigeons have a small habitat and high metabolic rate, and the main route of exposure to urban air is through inhalation and intake of contaminated food particles. Assay results were compared with measurements of contaminants in the urban air (carbon monoxide [CO], PM<sub>10</sub>, NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub>, benzene [C<sub>6</sub>H<sub>6</sub>], PAHs in PM<sub>2.5</sub>), and a positive correlation with PAH and protoporphyrin was observed along with a positive correlation between O<sub>3</sub> and DNA damage index ([Sicolo et al., 2010](#); [Sicolo et al., 2009](#)). Feathers, lung, liver, and kidney tissues were sampled from pigeons in two urban areas in the U.S. (Glendora, CA and Midland, TX) to evaluate Hg exposure ([Cizdziel et al., 2013](#)); however, no significant differences were observed between the two locations. In another study in two atmospherically polluted sites in North Texas, Hg was found in the blood and feathers of eastern bluebird (*Sialis sialis*), Carolina wren (*Thryothorus ludovicianus*), wood duck (*Aix sponsa*), great egret (*Ardea alba*), and great blue heron [*Ardea Herodias*; [Schulwitz et al. \(2015\)](#)]. Levels reported in these birds may be high enough to affect fitness ([Schulwitz et al., 2015](#)).

Several species have been evaluated as indicators of metal pollution from a long-term monitoring site near a former Cu-Ni smelter in Harjavalta, Finland. Metal concentrations in bird feces were quantified at the site to measure exposure via atmospheric deposition; however, measured decreases in the excrement did not directly reflect emission patterns ([Berghlund et al., 2015](#)). The authors suggest this is due to uptake of metals from food items in contact with contaminated soils. Plasma carotenoid levels measured in the birds on the site were not directly correlated to metal pollution or nesting survival ([Eeva et al., 2012](#)). Leg deformities of oribatid mites were also evaluated as a biomonitor but determined to be an unreliable indicator of heavy metals in soil at the site ([Eeva and Penttinen, 2009](#)).

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### 15.6.3 Biomagnification

Biomagnification of PM-associated metals and organics was reviewed in the 2009 PM ISA and are summarized here. The basic understanding of the process of biomagnification has not appreciably changed since the previous assessment. As reported in the 2009 PM ISA, biomagnification is the progressive accumulation of chemicals with increasing trophic level ([Leblanc, 1995](#)). At the time of the 2009 PM ISA, biomagnification had been demonstrated for a few trace metals in terrestrial and aquatic systems ([U.S. EPA, 2009a](#)). Plant uptake is often the first step for a metals to enter higher levels of the food web. Consumers of vegetation may often receive heavy loading of

metals from their diets. Metals may also bioaccumulate in some species, and tissue concentrations are magnified at the higher trophic levels. Organic Hg is the most likely metal to biomagnify, in part because organisms can efficiently assimilate methylmercury and are slow to eliminate it [(Croteau et al., 2005; Reinfelder et al., 1998); [Appendix 12](#)]. There is also evidence that the trace metals Cd, Pb, Zn, Cu, and selenium (Se) biomagnify.

Biomagnification of organics has been extensively documented in aquatic and terrestrial ecosystems, and these compounds are detected in biota at remote locations due to long-range atmospheric transport processes ([U.S. EPA, 2009a](#)). Organics, such as PAHs, can be transferred to higher trophic levels, including fish, and this transfer can be mediated by aquatic invertebrates in the fish diet ([U.S. EPA, 2009a](#)). In high mountain lakes, atmospheric inputs dominate as sources of contamination. In addition, such lakes tend to have relatively simple food webs. In a study reviewed in the 2009 PM ISA, ([Vives et al., 2005](#)) investigated PAH content of brown trout (*Salmo trutta*) and their food items. Total PAH concentrations tended to be highest in organisms that occupy littoral habitats, and lowest in pelagic organisms.

The study of trophic transfer and biomagnification is limited by the difficulty in discriminating food webs and the uncertainty associated with assigning trophic position to individual species ([Croteau et al., 2005](#)). Use of stable isotopes can help establish linkages. However, it is difficult to determine the extent to which biomagnification occurs in a given ecosystem without thoroughly investigating physiological biodynamics, habitat, food web structure, and trophic position of relevant species. Thus, developing an understanding of ecosystem complexity is necessary to determine which species are at greatest risk from toxic metal exposure ([Croteau et al., 2005](#)).

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## 15.7 Effects of Particulate Matter on Ecological Communities and Ecosystems

Evidence for PM effects on higher levels of biological organization is primarily from field studies conducted in proximity to point sources, such as smelters, mining, and other industrial sources. These areas where PM deposition decreases from the source have been assessed through ecological gradient studies. Several long-term monitoring studies have been conducted on ecosystem responses to atmospheric deposition of metals, including the Harjavalta smelter in Finland where metal-rich dust emissions have decreased by 99% during the 23-year study period ([Eeva and Lehikoinen, 2015](#)). Additional evidence for PM effects on ecological communities include studies from urban areas and model microecosystems.

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## 15.7.1 Gradient Effects near Smelters

The 2009 PM ISA reviewed multiple studies conducted near a Cu-Ni smelter in Harjavalta, Finland. These studies documented effects on multiple species operating at different trophic levels ([Kiikkilä, 2003](#); [Helmisaari et al., 1999](#); [Malkönen et al., 1999](#); [Pennanen et al., 1996](#)). The species composition of vegetation, insects, birds, and soil microbiota changed, and tree growth was reduced 4 km from the smelter. Within 1 km, very few organisms were documented ([Kiikkilä, 2003](#)).

Since the 2009 PM ISA, additional studies have been published from the long-term monitoring of the ecological communities near the Cu-Ni smelter site in Harjavalta, Finland. Several studies in passerine birds (pied flycatcher [*Ficedula hypoleuca*] and great tit [*Parus major*]) show some biological recovery and a reduction in metal concentration with decreased atmospheric emissions over time, even though metal levels in tissues remain high in birds near the smelter, likely due to contamination of soils and food items ([Berglund et al., 2012](#); [Berglund et al., 2011](#)). Similarly, tissue levels in pied flycatchers remained high near a smelter in Northern Sweden even after a 93 to 99% reduction in metal emissions ([Berglund and Nyholm, 2011](#)). With decreased metal pollution at Harjavalta, breeding parameters in pied flycatchers and great tits have improved since the 1990s. However, clutch size and fledgling number remain below those of birds from a reference area ([Eeva and Lehikoinen, 2015](#); [Eeva et al., 2009](#)). Interruption of egg laying was assessed in passerine birds at the Harjavalta Smelter site and was attributed to both cold weather and pollution ([Eeva and Lehikoinen, 2010](#)). These laying gaps occurred with greater frequency, and most commonly at the beginning of the laying sequence, close to the smelter. The authors suggested that heavy metals at the site interfere with Ca availability and metabolism during the breeding season when extra Ca is needed for eggshell formation and growth.

[Eeva et al. \(2010\)](#) sampled land snail shells from pied flycatcher nests along the Harjavalta smelter pollution gradient to assess effects of air pollution on shell mass, abundance, and diversity of land snail communities. The snails represent an important source of Ca for the birds, especially for eggshell formation and development of nestlings. Shell size decreased near the smelter, indicating snail growth was also impacted at the most highly polluted areas. The highest diversity, largest size, and greatest abundance of snail populations were observed in the moderately polluted areas compared to snails in the vicinity of the smelter and in remote unpolluted areas.

Recent literature continues to show a gradient of response in vegetation to trace metal deposition from smelting operations including evidence from the U.S. The forest surrounding two historical Zn smelters in Palmerton, PA has been used as a study site to assess ecological response and recovery following historic emissions. A portion of this

forest includes the Appalachian National Scenic Trail, and a barren area of approximately 600 to 800 ha remains where Zn, Mn, and Cd were once emitted ([Beyer et al., 2013](#)). Operation at the smelter ceased in 1980, but effects from the contaminated soils persist. In a greenhouse study using seedlings of native tree species, as little as 10% of soil collected in proximity to the smelter site and mixed with reference soil caused reduced growth or mortality of the tree seedlings ([Beyer et al., 2013](#)). Red maple (*Acer rubrum*) was most sensitive, followed by gray birch (*Betula populifolia*), northern red oak (*Quercus rubra*), chestnut oak (*Quercus prinus*), and eastern white pine (*Pinus strobus*). In a field survey relating Zn soil concentrations to forest response, canopy closure and shrub cover was decreased to half at approximately 2,060 mg/kg Zn, while tree-seedling density was reduced by 80% at 1,080 mg/kg Zn ([Beyer et al., 2011](#)). Vegetative communities near the Nikel smelter in Russia near the border with Finland and Norway showed varied response to deposition of heavy metals ([Myking et al., 2009](#)). Epiphytic lichens were most affected followed by decreased abundance and species richness of lichens and bryophytes closer to the smelter. No effects on tree crown condition or growth were observed.

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## 15.7.2 Urban Environments

Resident biota in urban areas are affected by PM along with other stressors associated with the built environment such as increased temperature due to heat island effects ([Pickett et al., 2011](#)). [McDonnell et al. \(1997\)](#) observed differences in urban forest structure and function compared to rural and suburban areas of New York. Oak forests near the city were characterized by reduced soil fungal and invertebrate populations, elevated soil metals (presumably from air pollution), and lower quality of leaf litter. The removal of PM by urban vegetation to mitigate air pollution has been extensively reviewed, but few of these studies consider ecological impacts of PM ([Escobedo et al., 2011](#); [Pataki et al., 2011](#)).

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## 15.7.3 Aquatic Ecosystems

In the 2009 PM ISA, PM components in aquatic ecosystems were primarily considered in the context of aquatic food web transfer of organic contaminants ([U.S. EPA, 2009a](#)). In another study reviewed in the 2009 PM ISA, bioassay procedures with green algae were used to provide an initial screening of ambient PM toxicity from two urban/industrial and one rural site near Lake Michigan ([Sheesley et al., 2004](#)). Results suggested that toxicity was not related to the total mass of PM in the extract but to the chemical components of the PM. In a study of the effects of contaminated tunnel wash water runoff in Norway,

growth of sea trout (*Salmo trutta*) was significantly reduced in the stream receiving the wastewater ([Meland et al., 2010](#)). The contaminated wash water had elevated concentrations of traffic-related contaminants including metals, PAHs, and road salt from combustion and highway runoff. Fractionation of water samples indicated some of the metals and PAHs were highly associated with particles. Size ratios of detected PAHs suggested that sources included tire wear and incomplete combustion.

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#### 15.7.4 Experimental Microecosystems

Since the 2009 PM ISA, several studies have employed a microecosystem to assess effects of air pollutants at the community level of biological organization to see how microbial communities living on terrestrial mosses (bryophytes) respond to atmospheric deposition of PM components (metals, PAHs, NO<sub>2</sub>). In a series of bioindicator studies conducted in France, species-specific responses to PM components and effects on total biomass were observed in the associated microbial communities ([Meyer et al., 2010a](#); [Meyer et al., 2010b](#)). Primary producers, decomposers, and predators responded differently to the pollutants ([Meyer et al., 2010a](#); [Meyer et al., 2010b](#)). Testate amoebae are especially sensitive to changes in atmospheric pollution in these microsystems and were proposed as a biomonitoring tool ([Meyer et al., 2012](#)). Total testate amoebae abundance and the abundance of five species of testate amoebae decreased with increased deposition of the PAH phenanthrene in the experimental microecosystem ([Meyer et al., 2013](#)).

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### 15.8 Summary of Ecological Effects of Particulate Matter

Since publication of the 2009 PM ISA, new literature builds upon the existing knowledge of ecological effects associated with PM components, especially metals and organics. In some instances, new techniques have enabled further characterization of the mechanisms of PM on soil processes, vegetation, and effects on fauna. New studies provide additional evidence for community-level responses to PM deposition, especially in soil microbial communities. However, uncertainties remain due to the difficulty in quantifying relationships between ambient concentrations of PM and ecosystem response. Overall, **the body of evidence is sufficient to infer a likely causal relationship between deposition of PM and a variety of effects on individual organisms and ecosystems**, based on information from the previous review and new findings in this review.

In regard to direct effects of PM on radiative flux, a newly available research method links changes in expression of proteins involved in photosynthesis to changes in radiation

associated with aerosols and PM. Although this method has not been widely applied, it may represent an important way to study mechanistic changes to photosynthesis in response to more diffuse radiation resulting from PM in the air column.

In general, new studies on PM deposition to vegetation support findings in previous PM reviews on altered photosynthesis, transpiration, and reduced growth. Additional characterization of PM effects at the leaf surface since the 2009 PM ISA has led to a greater understanding of PM foliar uptake. Alterations in leaf fatty acid composition are associated with metals transferred to plant tissues from PM deposition on foliar surfaces ([Schreck et al., 2013](#)).

Several studies published since the 2009 PM ISA show PM effects on soil physical properties and nutrient cycling. Previous findings in the PM ISA of changes to microbial respiration and biomass are further supported by new studies. Microbial community responses to PM vary in tolerance to heavy metals and organics.

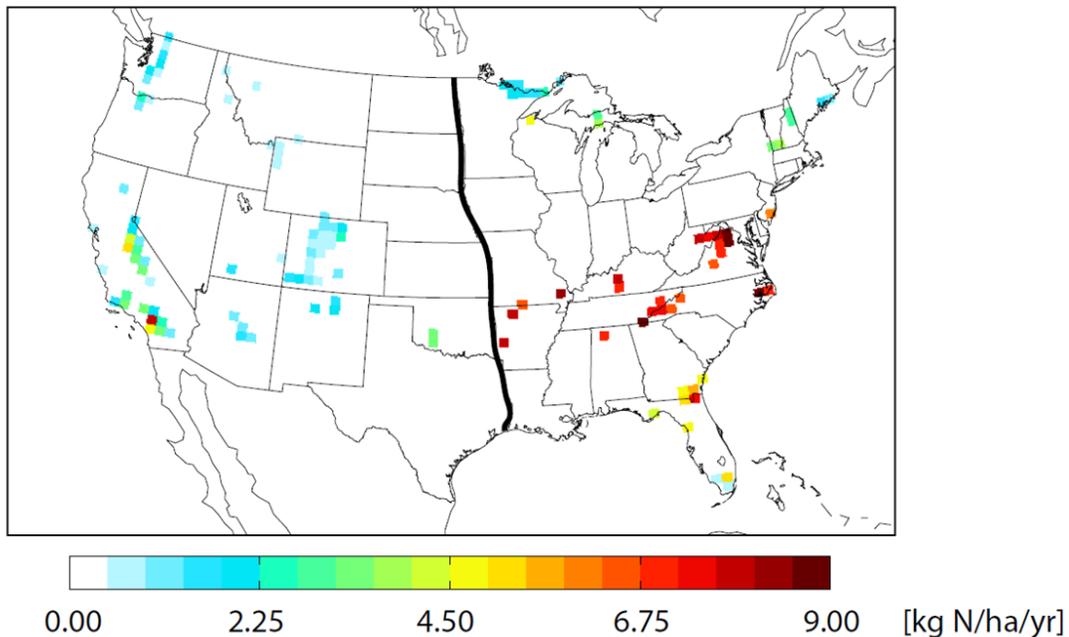
In fauna, results from ecotoxicity assays with PM extracts using bacteria, rotifers, nematodes, zebrafish, and earthworms support findings in the 2009 PM ISA that toxicity is not related to the total mass of PM in the extract, but to the chemical components of the PM. In nematodes exposed to PM from air filters, the insulin-signaling pathway was identified as a possible molecular target. Use of wildlife as PM biomonitors has been expanded to new taxa since the last PM review. Several studies in invertebrates and birds report physiological responses to air pollutants, including PM.

For ecosystem-level effects, a gradient of response with increasing distance from PM source was reported in the 2009 PM ISA. Newly available studies from long-term ecological monitoring sites provide limited evidence for recovery in areas such as those around former smelters due to the continued presence of metals in soils after operations ceased. A novel experimental microecosystem using microbial communities living in terrestrial mosses indicates that PM deposition alters responses of primary producers, decomposers, and predators.

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## APPENDIX 16 CASE STUDIES

This appendix includes six case studies which are meant to identify the ecological effects of nitrogen (N) and sulfur (S), with a specific focus on national parks, other protected areas, and areas with long-term research. The locations of these case studies were chosen because they are areas for which a substantial amount of published work on ecological response to N and/or S deposition is available. The locations include the northeastern U.S., Adirondack State Park, southeastern Appalachia, Tampa Bay, Rocky Mountain National Park, and southern/central California. These case studies identify current acidification and nutrient status, as well as empirical and modeled critical loads. A recent model of reactive N deposition to Federal Class I areas suggests that reactive nitrogen (Nr) deposition exceeds the most sensitive critical loads in many of these areas [Figure 16-1, from (Lee et al., 2016)]. The scientific characterizations of ecological responses to N and S in these case studies set the scientific foundation for further analysis of risk and exposure.



Notes: color indicates magnitude of the reactive N exceedance. The size of Class I areas is not represented. Air quality model grid cells containing Class I areas are shown as colored regardless of the fraction of grid cell area the Class I area covers. Bold line divides Western and Eastern U.S.

Source: Figure 9 from [Lee et al. \(2016\)](#).

**Figure 16-1      Critical loads (CL) exceedance in Class I areas.**

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## **16.1 Northeastern U.S. Case Study: Acadia National Park, Hubbard Brook Experimental Forest, and Bear Brook Watershed**

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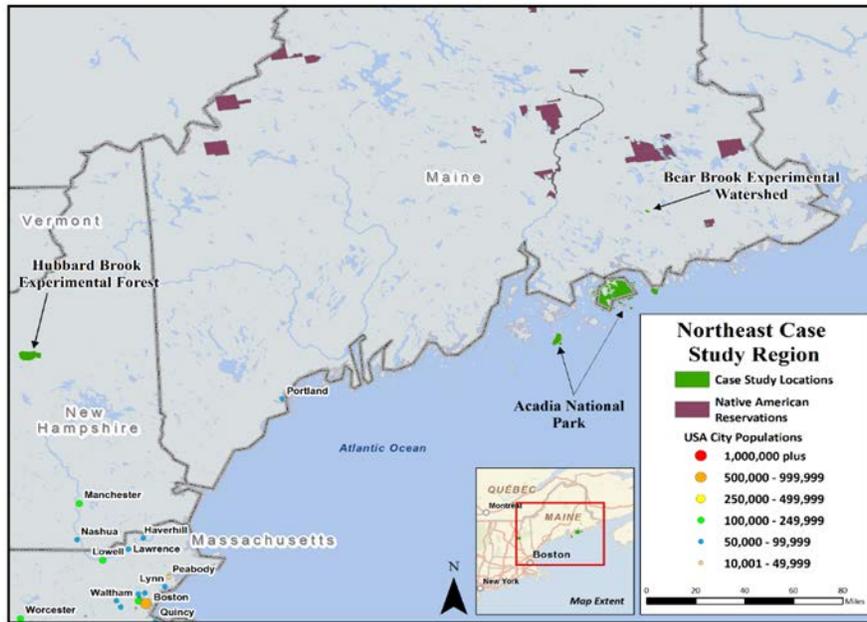
### **16.1.1 Background**

This case study is meant to identify effects of N and S in the northeastern U.S., with a specific focus on national parks and areas with long-term research data. It identifies current acidification and nutrient status and empirical and modeled critical loads (CLs). The 2008 NO<sub>x</sub>-SO<sub>x</sub> ISA included another case study of acidification in the Adirondack region of New York [Section 3.2.2.4 of 2008 ISA ([U.S. EPA, 2008a](#))]. The case study reported here is considered as a supplement to that earlier case study. Further information about the Adirondack region can be found in [Appendix 4](#) and [Appendix 5](#).

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#### **16.1.1.1 Description of Case Study Region**

Acadia National Park (ACAD) in coastal Maine, the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire, and the Bear Brook Watershed (BBW) in southeastern Maine were chosen for this case study to represent northeastern U.S. ecosystems known historically to be sensitive to acidification and nutrient enrichment from atmospheric S and N deposition ([Figure 16-2](#), [Table 16-1](#)). In this case study, we highlight multiple decades of research and monitoring at these locations to provide insights into the ecosystems' responses to S and N deposition and look for any indications of recovery.



**Figure 16-2** Locations of northeastern U.S. case study areas and nearby human population centers.

**Table 16-1** Selected characteristics of northeastern case study areas.

Case Study Area	Elevation	Geology	Dominant Vegetation	Focus
ACAD	0 to 466 m	Granitic	Red spruce, mixed forest	National Park
HBEF	183 to 1,002 m	Metamorphic	Northern hardwood forest, mixed forest, spruce-fir forest	Experimental forest, site of diverse biogeochemical research and monitoring
BBW	172 to 450 m	Metamorphic	Northern hardwood forest	Site of watershed manipulation experiment

ACAD = Acadia National Park; BBW = Bear Brook Watershed; m = meters; HBEF = Hubbard Brook Experimental Forest.

#### 16.1.1.1 Acadia National Park

Acadia National Park is located at the interface between northern coniferous forests and temperate deciduous woods and hosts plant species from two distinct regions

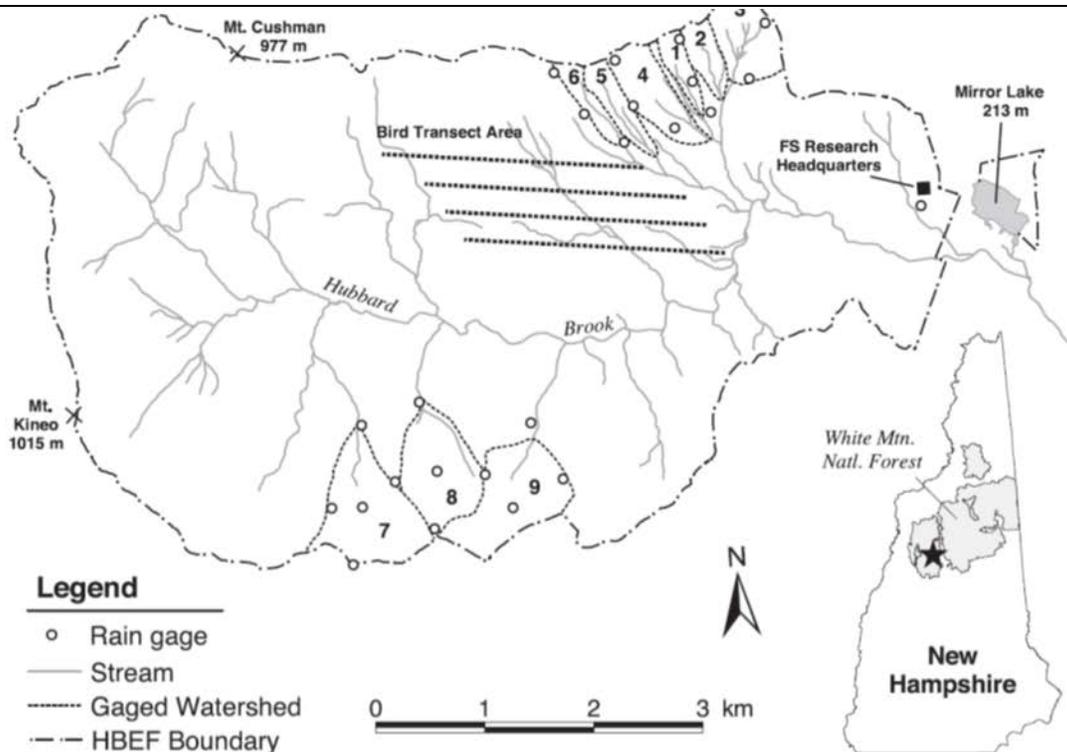
(<https://www.nps.gov/acad/>). ACAD extends over 45,000 acres on two islands and a mainland peninsula on Maine's coast. It receives about 140 cm/year of rainfall (Nielsen and Kahl, 2007). Geologically, the park consists of granite mountains with surrounding sedimentary and metamorphic rock. The soils have low buffering capacity, and steep slopes at high elevations make soil and runoff susceptible to acidification. The park's ecosystems include alpine heath, stunted growth woodlands, jack pine forests that include pitch pine, rocky woodlands of black spruce and heaths, mature spruce, and fir. Red spruce and sugar maple are the predominant tree species.

Eighty freshwater plant species have been documented in ACAD with another 12 semiaquatic shorelines species. Seven of the aquatic and semiaquatic plants are listed or proposed for inclusion on Maine's List of Endangered and Threatened Species. Another 30 of these species are considered "locally rare" (<https://www.nps.gov/acad/learn/nature/plants.htm>).

#### **16.1.1.1.2 Hubbard Brook Experimental Forest**

Hubbard Brook Experimental Forest is located in the southern portion of the White Mountain National Forest in central New Hampshire (Figure 16-3). The Atlantic Ocean is about 116 km to the southeast. Most of the surrounding land is also within the National Forest. The area is hilly and steep in places with coarse-textured acidic soils. The bedrock is dominated by metamorphosed igneous and sedimentary rocks. Bedrock is covered by about 2 m of glacial till.

Northern hardwood forests occupy lower elevation slopes with spruce-fir occurring on upper elevation slopes. Annual average precipitation is about 140 cm (one-third to one-quarter of which falls as snow).



FS = Forest Service; HBEF = Hubbard Brook Experimental Forest; km = kilometer; m = meter; Mt = mount; Mtn = mountain; Natl = national.

Notes: shown are the network of rain gauges, experimental watersheds (1-9), and Mirror Lake.

Source: [Campbell et al. \(2007\)](#).

**Figure 16-3 Site map of Hubbard Brook Experimental Forest in the White Mountains of New Hampshire.**

Glacier-deposited materials vary greatly in degree of sorting and grain size, with thicknesses ranging from zero on ridgetops and in stream valleys to 50 m near Mirror Lake. The principal soils are acidic (pH about 4.5 or less) and relatively infertile. The 20- to 200-mm-thick forest floor allows rapid infiltration of water and acts as insulation to prevent soil freezing before snow accumulates. Streams vary from small ephemeral channels to as large as perennial 5th order. Up to about 60 to 80% of storm precipitation flows by stream. HBEF is entirely forested, predominately with deciduous northern hardwoods including sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and yellow birch (*Betula allegheniensis*). High-elevation conifers include red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white birch (*Betula papyrifera*). Logging operations ended from around 1915 to 1917. The second-growth forest is about 80 to 90% hardwoods and 10 to 20% conifers. HBEF hosts more than 90 species of birds.

Snowshoe hare, moose, fox, black bear, beaver, and white-tailed deer are also present (<http://www.hubbardbrook.org/overview/sitedescription.shtml>).

HBEF ornithological studies have found that the abundance of birds decreased from more than 200 individuals per 10 ha in the early 1970s to 70 to 100 per 10 ha during the period from the early 1990s to the present. This decrease is unexplained (R.T. Holmes publications—Bird Abundances—<http://www.hubbardbrook.org/data/dataset.php?id=81> and).

#### **16.1.1.1.3 Bear Brook Watershed**

The BBW hosts a long-term, gaged, forested, first-order paired stream watershed. It is located about 40 km from the Atlantic Ocean on the southeast slope of Lead Mountain. It has a total relief of 210 m and a maximum elevation of 450 m. Two nearly perennial, low dissolved organic carbon (DOC), low acid neutralizing-capacity (ANC) streams (East and West Bear Brook [EB and WB]) drain 10.3 and 11.0 ha contiguous watersheds, respectively. BBW is covered predominantly by hardwoods (*Fagus grandifolia*, *Acer rubrum*, *Acer saccharum*, *Betula alleghaniensis*, *Betula papyrifera*, and *Acer pensylvanicum*) and red spruce. Soils are coarse, loamy, mixed, frigid Typic Haplorthods developed on till averaging 1 m in thickness. Bedrock is mainly quartzites and metapelites with local granitic intrusions.

West Bear Brook has received bimonthly additions of ammonium nitrate since November 1989 (~1,800 eq/ha/year—a 300% increase over ambient N deposition at the beginning of the study). East Bear Brook has received no additions and serves as a reference [see [Norton et al. \(1999\)](#)]. BBW has been a research site for three decades with a focus on increasing decadal-scale understanding about northern forested ecosystems' response to chemical and physical change, including whole ecosystem acidification, nitrogen enrichment, and climate change. BBW research has focused on: alterations to nitrogen dynamics, base cation decline, carbon cycling, phosphorus controls on nitrogen cycling, response to decreasing ambient sulfate deposition, sustained elevated experimental sulfate deposition, and changes in forest growth (<https://umaine.edu/bbwm/research/environmental-research/>).

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#### **16.1.1.2 Class I Areas**

In an effort to preserve pristine atmospheric conditions, the Clean Air Act (42 USC 7470) authorized Class I areas to protect air quality in national parks over 6,000 acres in size and national wilderness areas over 5,000 acres.

Class I areas are subject to the “prevention of significant deterioration (PSD)” regulations under the Clean Air Act. (42 USC 7470). PSD preconstruction permits are required for new and modified existing air pollution sources, and air regulatory agencies are required to notify federal land managers (FLMs) of any PSD permit applications for facilities within 100 km of a Class I area.

ACAD is a PSD Class I Area. HBEF is not in a Class I area, but is near two New Hampshire Class I areas, the Great Gulf and the Presidential Range—Dry River Wilderness Areas. BBW is located southwest of the Moosehorn Wilderness Area in Maine.

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### 16.1.1.3 Regional Land Use and Land Cover

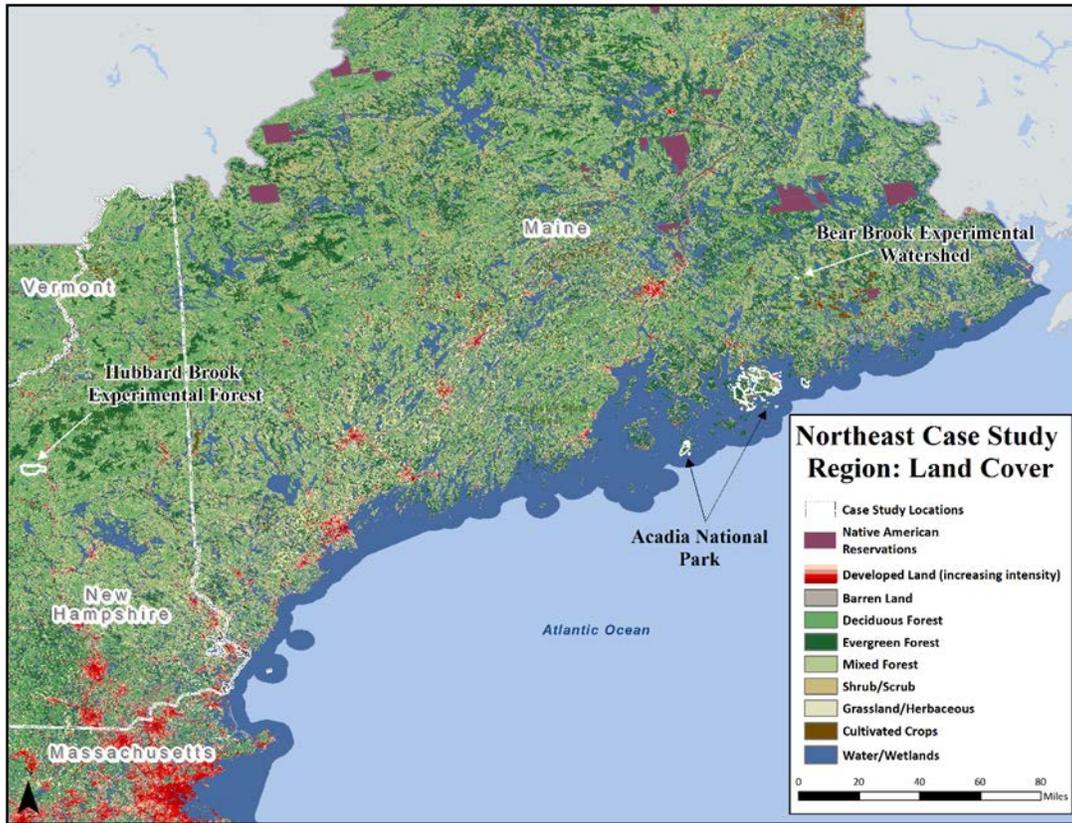
No large population centers are located near HBEF or BBW. Several small towns are interspersed with ACAD lands, including Bar Harbor (pop. 5,235), Southwest Harbor (pop. 1,765), and Trenton (pop. 1,481). The populations of these towns increase substantially with tourists during summer. Bangor (pop. 32,000) lies about 40 miles north from Mount Desert Island. All three study areas are mostly forested, as is much of the Northeast region ([Table 16-2](#), [Figure 16-4](#)).

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**Table 16-2 Land use/land cover for northeastern case study areas.**

Land Cover	Area Covered (km <sup>2</sup> )		
	ACAD	HBEF	BBW
Developed and barren	83.82	2.96	0.00
Hardwood forest	76.84	159.53	6.64
Conifer forest	592.56	61.88	0.60
Mixed forest and shrubland	300.27	111.49	2.53
Meadow/herbaceous	26.33	0.50	0.00
Wetland	137.05	1.47	0.16

ACAD = Acadia National Park; BBW = Bear Brook Watershed; HBEF = Hubbard Brook Experimental Forest; km = kilometer.



**Figure 16-4** Land cover in the Northeast case study region.

#### 16.1.1.4 Organization of This Case Study

Because this case study addresses the condition of three discrete locations in the Northeast (ACAD, HBEF, and BBW), we developed [Table 16-3](#) to summarize the primary post-2000 research reported in the case study. In addition, we cite relevant research in other areas of the northeastern region. [Appendix 16.1.2](#) presents information about N and S deposition in the Northeast. Discussions of critical load or dose-response research ([Appendix 16.1.3](#)) are each organized around the three case study areas and the Northeast region. [Appendix 16.1.4](#) presents information available on long-term ecological monitoring, and [Appendix 16.1.5](#) contains information on the current status and forecasts for recovery in the case study areas. Key research literature since January 2008 is highlighted in [Table 16-4](#).

**Table 16-3** Literature cited by Northeast U.S. case study area.

**Table 16-3 (Continued): Literature cited by northeast U.S. case study area.**

Variable	Acadia	BBW	HBEF	Northeast Regional
<b>Summary of studies from NE case study for acidification</b>				
Base cation		<a href="#">Elvir et al. (2006)</a>		
BAI		<a href="#">SanClements et al. (2010)</a>		
Mineralization		<a href="#">Fernandez et al. (2003)</a>		
Stream dissolved SO <sub>4</sub> <sup>2-</sup> , pH, ANC, Al <sup>+</sup>		<a href="#">Norton et al. (2004)</a>		
Base cation, Ca, Mg		<a href="#">Norton et al. (2004)</a>	<a href="#">Gbondo-Tugbawa and Driscoll (2003)</a> , <a href="#">Gbondo-Tugbawa and Driscoll (2002)</a>	
<b>Summary of studies from NE case study for nutrient status</b>				
Aquatic N cycling		<a href="#">Mineau et al. (2014)</a> , <a href="#">Simon et al. (2010)</a>		
Soil N cycling		<a href="#">Mineau et al. (2014)</a> , <a href="#">Jefts et al. (2004)</a>		
Ca addition			<a href="#">Battles et al. (2014)</a>	
N addition		<a href="#">Bethers et al. (2009)</a> , <a href="#">Hunt et al. (2008)</a>		
N retention + multiple disturbances			<a href="#">Aber et al. (2002)</a>	
N retention climate/freezing			<a href="#">Gronffman et al. (2011)</a> , <a href="#">Judd et al. (2011)</a> , <a href="#">Campbell et al. (2010)</a>	
N retention and fire	<a href="#">Nelson et al. (2007)</a> <a href="#">Campbell et al. (2004b)</a>			
N deposition effect on wetlands	<a href="#">Calhoun et al. (1994)</a>			
N loading to coastal waters	<a href="#">Nielsen and Kahl (2007)</a>			
N addition to lakes	<a href="#">Saros (2014)</a>			

**Table 16-3 (Continued): Literature cited by northeast U.S. case study area.**

Variable	Acadia	BBW	HBEF	Northeast Regional
<b>Summary of studies from NE case study for terrestrial critical load or dose-response</b>				
Dose-response trees	<a href="#">Ellis et al. (2013)</a>	<a href="#">Elvir et al. (2006)</a> , <a href="#">Elvir et al. (2003)</a>		<a href="#">Pardo et al. (2011c)</a> , <a href="#">Thomas et al. (2010)</a> , <a href="#">McNulty et al. (2005)</a>
Dose-response herbs				<a href="#">Pardo et al. (2011c)</a> , <a href="#">Hurd et al. (1998)</a>
Dose-response soil		<a href="#">SanClements et al. (2010)</a> , <a href="#">Fernandez et al. (2003)</a>	<a href="#">Gbondo-Tugbawa and Driscoll (2002)</a>	<a href="#">Pardo et al. (2011c)</a>
Dose-response surface water			<a href="#">Gbondo-Tugbawa and Driscoll (2002)</a>	
Modeling climate, acid-base chemistry, changes in plants		<a href="#">Phelan et al. (2016)</a>	<a href="#">Phelan et al. (2016)</a> , <a href="#">Campbell et al. (2009)</a>	
<b>Summary of studies from NE case study for aquatic critical load or dose-response</b>				
Macroinvertebrate production				<a href="#">Chadwick and Huryn (2005)</a>
Shift from deposition to climate influence				<a href="#">Mitchell and Likens (2011)</a>
Flow volume and peak flows				<a href="#">Kim et al. (2010)</a>
NO <sub>3</sub> <sup>-</sup> concentration				<a href="#">Aber et al. (2003)</a>
N limitation				<a href="#">Baron et al. (2011a)</a>
NO <sub>3</sub> <sup>-</sup> leaching				<a href="#">Driscoll et al. (2003a)</a>
DOC				<a href="#">SanClements et al. (2012)</a>
Climate effects on pools, concentrations, and fluxes of major elements				<a href="#">Pourmokhtarian et al. (2012)</a>
pH				<a href="#">Quimet et al. (2006)</a> , <a href="#">Dupont et al. (2005)</a> , <a href="#">Quimet et al. (2001)</a>

**Table 16-3 (Continued): Literature cited by northeast U.S. case study area.**

Variable	Acadia	BBW	HBEF	Northeast Regional
ANC				<a href="#">Sutherland et al. (2015)</a> , <a href="#">Nierzwicki-Bauer et al. (2010)</a> , <a href="#">Tominaga et al. (2010)</a> , <a href="#">Ouimet et al. (2006)</a> , <a href="#">Dupont et al. (2005)</a> , <a href="#">Ouimet et al. (2001)</a>

Al<sup>+</sup> = aluminum; ANC = acid neutralizing capacity; BAI = basal area increment; BBW = Bear Brook Watershed; Ca = calcium; DOC = dissolved organic carbon; HBEF = Hubbard Brook Experimental Forest; Mg = magnesium; N = nitrogen; NE = northeastern; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>4</sub><sup>2-</sup> = sulfate.

**Table 16-4 Key recent research literature focused on the case study region.**

<b>Publication</b>	<b>Focus</b>
<a href="#">Baron et al. (2011a)</a>	Regional patterns in N limitation
<a href="#">Battles et al. (2014)</a>	Ca addition at HBEF
<a href="#">Bethers et al. (2009)</a>	Effects of S and N on sugar maple foliar chemistry
<a href="#">Campbell et al. (2009)</a>	Influence of climate on biogeochemical cycling
<a href="#">Campbell et al. (2010)</a>	Monitoring of climate conditions at HBEF
<a href="#">Cho et al. (2009)</a>	Response of stream high-flow chemistry to Ca addition at HBEF
<a href="#">Ellis et al. (2013)</a>	Empirical critical loads
<a href="#">Elvir et al. (2010)</a>	Tree growth and foliar chemistry at BBW
<a href="#">Fernandez and Norton (2010)</a>	Overview of BBW study
<a href="#">Fernandez et al. (2010)</a>	Responses to experimental acidification at BBW
<a href="#">Groffman et al. (2011)</a>	Soil freezing at HBEF
<a href="#">Hunt et al. (2008)</a>	N and P content of leaves
<a href="#">Judd et al. (2011)</a>	Soil freezing at HBEF
<a href="#">Kim et al. (2010)</a>	Stream flow at BBW
<a href="#">Laudon and Norton (2010)</a>	Episodic stream chemistry at BBW
<a href="#">Lawrence et al. (2012)</a>	Recovery of soil base status
<a href="#">Long et al. (2009)</a>	Sugar maple decline
<a href="#">Mineau et al. (2014)</a>	Enzyme activity in soil and leaf litter
<a href="#">Mitchell and Likens (2011)</a>	S budget at HBEF
<a href="#">Mitchell et al. (2011)</a>	S mass balances for HBEF and BBW

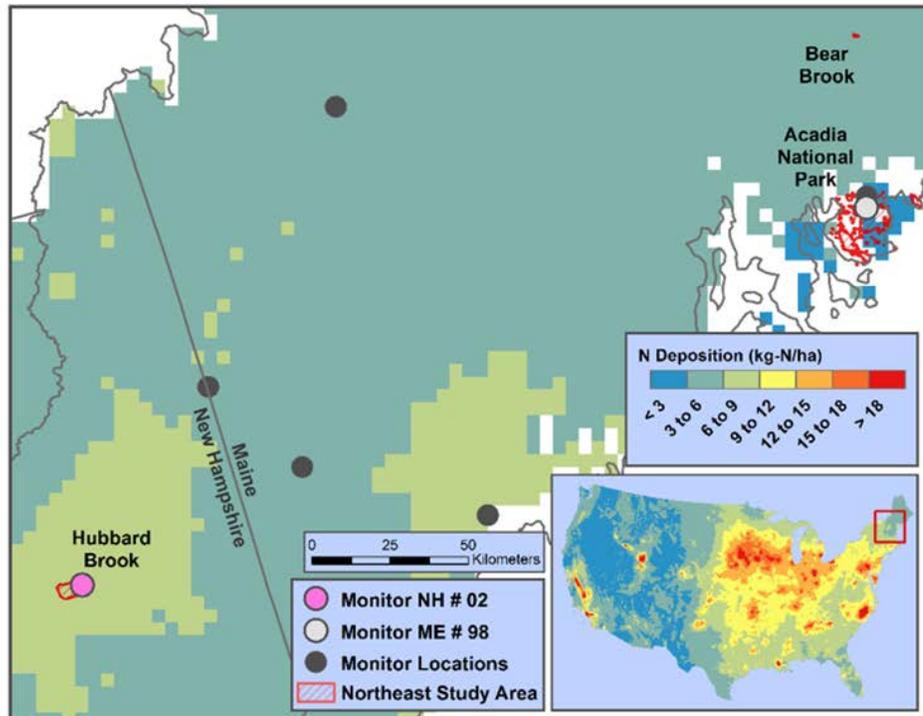
BBW = Bear Brook Watershed; Ca = calcium; HBEF = Hubbard Brook Experimental Forest; N = nitrogen; P = phosphorus; S = sulfur.

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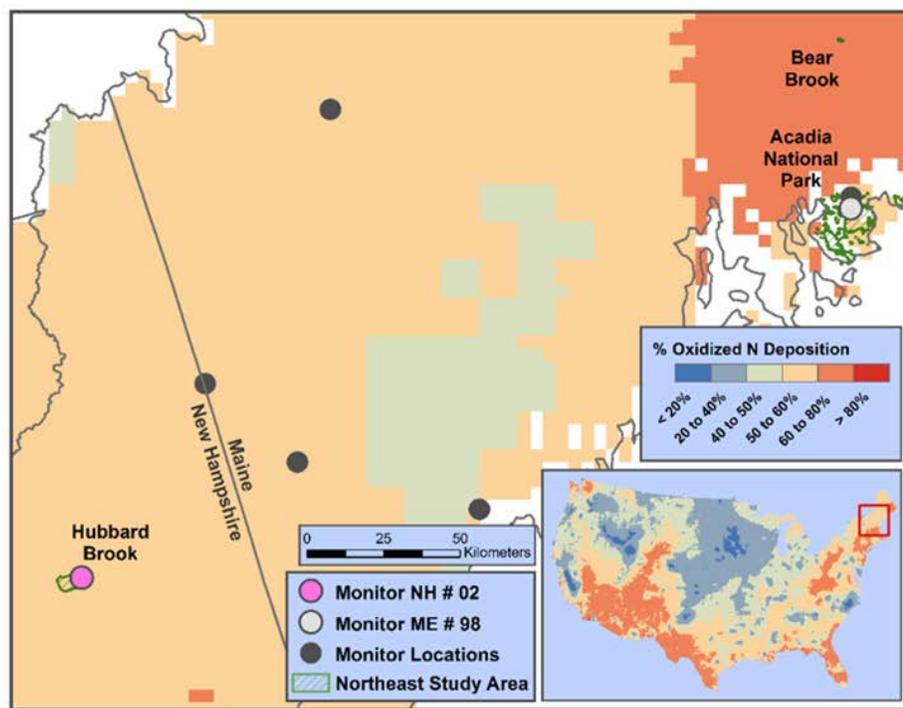
## 16.1.2 Deposition

Characteristics of nitrogen and sulfur deposition affecting the ACAD, HBEF, and BBW in the study area are shown in [Figure 16-5](#) and [Figure 16-6](#). [Figure 16-5A](#) and [Figure 16-6A](#) show 3-year average total deposition of N and S for 2011–2013; [Figure 16-5B](#) shows the partitioning between oxidized and reduced N; [Figure 16-6B](#) shows the 25-year-long time series for wet deposition for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  obtained at the NADP/NTN (National Atmospheric Deposition Program/National Trends Network) monitoring site at HBEF (NH02). Surrounding areas in Maine and New Hampshire and inserts showing the coterminous U.S. (CONUS) are shown to place the depositional environment in context. See [Appendix 2.4](#), [Appendix 2.5](#), and [Appendix 2.6](#) for more information on deposition in the U.S. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

Data shown in the map [Figure 16-5](#) and [Figure 16-6A](#) were obtained from the hybrid modeling/data fusion product, TDEP (Total Deposition, <http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/> and described in [Appendix 2.7](#)). However, the time series of wet deposition is taken directly from data on the NADP/NTN ([Figure 16-6B](#)). This was done to track changes in deposition since the passage of the Clean Air Act Amendment (CAAA) because the Community Multiscale Air Quality (CMAQ) model simulations used in TDEP extend back only to 2000.



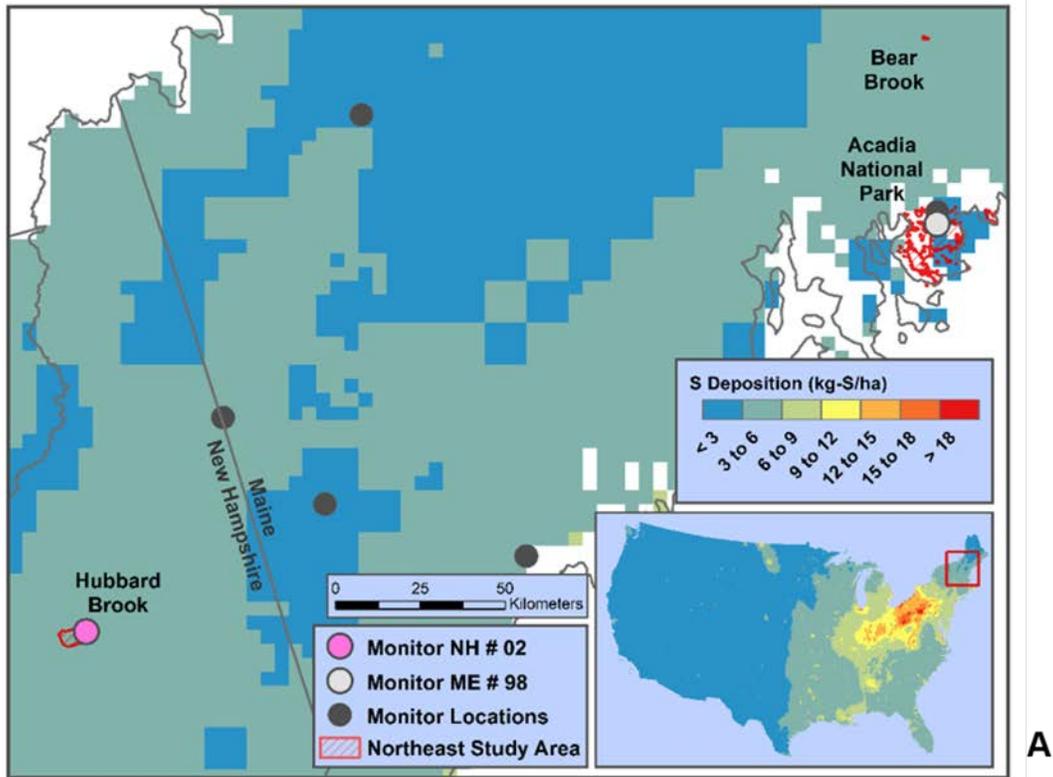
A



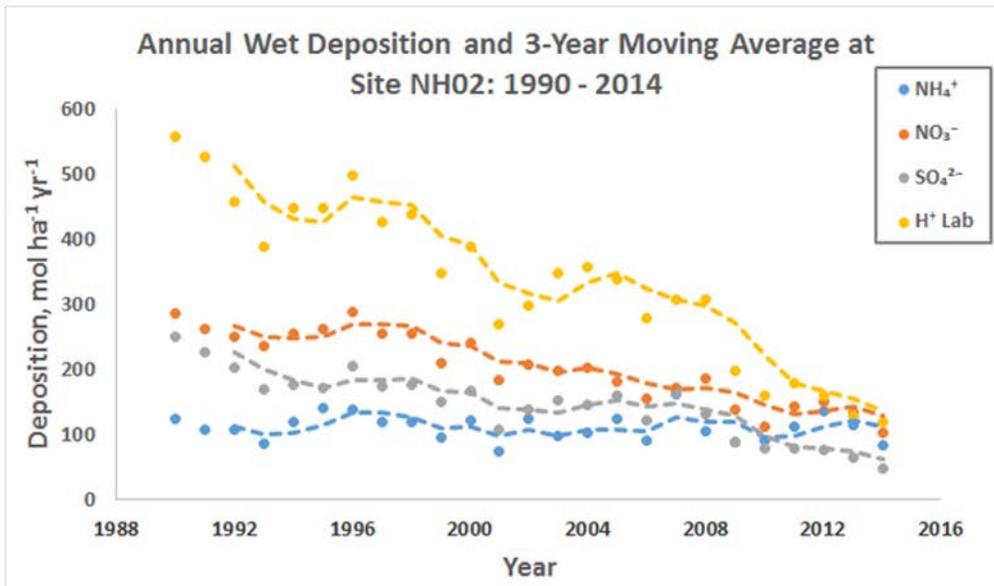
B

ha = hectare; kg = kilogram; N = nitrogen.

**Figure 16-5** Total nitrogen deposition (A) and percentage of oxidized nitrogen deposition (B) for the Northeast case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee.



A



B

H<sup>+</sup> = hydrogen ion; ha = hectare; kg = kilogram; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

**Figure 16-6** Total sulfur deposition (A) for the Northeast case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. Time series of wet deposition (B) from the National Atmospheric Deposition Program/National Trends Network in the Hubbard Brook Experimental Forest, NH.

Comparison of [Figure 16-5A](#) and [Figure 16-6A](#) indicates that the general pattern of deposition of N and S is broadly similar; deposition tends to be higher near the coast and decreases inland. Deposition at ACAD is an exception, with lower values along the coast than elsewhere. As seen in [Figure 16-5A](#), total deposition of N is relatively uniform within the three portions of the study area. In addition, the area surrounding the three sites shows a high degree of regional homogeneity but with higher values in New Hampshire. Deposition of N is not as high as in many areas of the central U.S. or the rest of the Northeast. Deposition of S is considerably lower than along the Ohio River Valley.

[Figure 16-5B](#) shows that the deposition of nitrogen is estimated to be mostly in oxidized form throughout the entire domain. Although most of the area is subject to N deposition in oxidized form with highest percentages surrounding ACAD and BBW, there are areas, principally in central Maine, where N is deposited mostly in reduced form. In [Figure 16-6B](#), wet deposition of all species shows that downward trends in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  are consistently found over the past 25 years, although the rate of decrease has been variable. In general, wet deposition typically exceeds dry deposition of N and S in this case study area.

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## 16.1.3 Critical Loads and Other Dose-Response Relationships

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### 16.1.3.1 Terrestrial

This section presents post-2000 ACAD, HBEF, and BBW findings on the dose-response relationships of N and S to terrestrial ecology, as well as the critical N and S loads for maintaining ecosystem health. Additional relevant information for the northeastern region is summarized. The section presents findings on both empirical research and modeling analyses.

#### 16.1.3.1.1 Empirical Studies

Post-2000 findings from empirical studies of terrestrial dose-response relationships and critical loads are summarized in this section. [Table 16-5](#) summarizes the body of empirical and modeling research identified.

**Table 16-5 Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the northeastern U.S.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Primary productivity	NA	PnET-BGC Model. Predicted increase due to future longer growing season	Not specified	1999–2099	HBEF	<a href="#">Campbell et al. (2009)</a>
Base cation Ca and Mg depletion	NA	PnET-BGC Model. Historical forest cutting had little impact on exchangeable cation soil pools	Not specified	1850–1995	HBEF	<a href="#">Gbondo-Tugbawa and Driscoll (2003)</a>
Base cation	Sugar maple, American beech, red spruce	American beech and red spruce had lower foliar Ca, Mg, Zn concentrations; nutrient imbalance may offset potential photosynthesis benefits Sugar maple had higher photosynthesis rates; no decrease in Ca, Mg, Zn concentrations	N addition: 8.4 (wet + dry) (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> addition: WB 25.2	1989–2003	BBW	<a href="#">Elvir et al. (2006)</a>
Tree growth	Northern hardwoods	+	8.4 N (wet + dry)/ +25 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–2002	BBW	<a href="#">Pardo et al. (2011c)</a>
Mortality		ND				
Foliar %N		+				
Foliar %Ca		0				
NO <sub>3</sub> <sup>-</sup> leaching		+				
Cation loss		+				
Soil C:N		0				
N mineralization		+				
Nitrification		–				
Soil respiration		0				
Microbial biomass		0				

**Table 16-5 (Continued): Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the northeastern U.S.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Tree growth	Red spruce	0	8.4 N (wet + dry)/+25 kg (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–2002	BBW	<a href="#">Pardo et al. (2011c)</a>
Mortality		ND				
Foliar %N		+				
Foliar %Ca		–				
NO <sub>3</sub> <sup>-</sup> leaching		+				
Cation loss		+				
Soil C:N		–				
N mineralization		+				
Nitrification		+				
Soil respiration		ND				
Microbial biomass		ND				
Base cation	Sugar maple	Little evidence of BC depletion but confounded by ice storm litter mineralization	8.4 N (wet + dry) + 25 kg (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Not specified	BBW	<a href="#">SanClements et al. (2010)</a>
Mineralization	Not specified	Storm caused increased litterfall, accelerated mineralization, and obstructed temporal trends in soil chemistry (17 yr)	8.4 (wet + dry)/+25 (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–1998	BBW	<a href="#">Fernandez et al. (2003)</a>
Soil base saturation	Not specified	ForSAFE-VEG model. Expected future climate change was simulated to cause increase, especially at BBW.	Not specified	Not specified	BBW and HBEF	<a href="#">Phelan et al. (2016)</a>
Soil acid-base chemistry	Not specified	ForSAFE-VEG model. Simulated future climate had a lesser effect at HBEF than BBW, likely due to the overwhelming influences of high S and N deposition.	Not specified	Not specified	BBW and HBEF	<a href="#">Phelan et al. (2016)</a>

**Table 16-5 (Continued): Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the northeastern U.S.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Plant communities and N enrichment	Not specified	ForSAFE-VEG model. Climate futures predicted by the IPCC of increased temperature and precipitation will change plant communities and N enrichment, counteracting the acidifying impacts of S and N deposition on soil acid-base chemistry.	Not specified	Not specified	BBW and HBEF	<a href="#">Phelan et al. (2016)</a>
NO <sub>3</sub> <sup>-</sup> leaching	NA	PnET-BGC Model. Increase due to enhanced net mineralization and nitrification	Not specified	1999–2099	NE	<a href="#">Campbell et al. (2009)</a>
Mineral weathering	NA	PnET-BGC Model. Slight decrease due to reduced simulated soil moisture (negative effect) and increased temperature (positive effect)	Not specified	1999–2099	NE	<a href="#">Campbell et al. (2009)</a>
NO <sub>3</sub> <sup>-</sup> leaching, GHG sequestration, ecosystem C pools	Not specified	DayCent-Chem model. Simulated future high N deposition under climate scenarios had increased ecosystem GHG sequestration. High N increased stream NO <sub>3</sub> <sup>-</sup> fluxes and ecosystem C pools.	Simulated N deposition 3.9 to 9.6 kg/ha/yr for HBEF and 4 to 11.3 kg/ha/yr for ACADr	2001–2075	ACAD and HBEF	<a href="#">Hartman et al. (2014)</a>

BBW = Bear Brook Watershed; BC = base cation; C = carbon; Ca = calcium; ForSAFE-VEG = Soil Acidification in Forest Ecosystems; ha = hectare; GHG = greenhouse gas; HBEF = Hubbard Brook Experimental Forest; IPCC = Intergovernmental Panel on Climate Change; kg = kilogram; Mg = magnesium; N = nitrogen; NA = not applicable; ND = no data; NE = northeastern; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; PnET-BGC = Photosynthesis and Evapotranspiration-Biogeochemical; S = sulfur; WB = West Bear Brook; yr = year; Zn = zinc.

#### 16.1.3.1.1.1 Acadia National Park

[Ellis et al. \(2013\)](#) estimated the CL exceedance for nutrient-N deposition to protect the most sensitive ecosystem receptors in 45 national parks, based on CL ranges compiled by [Pardo et al. \(2011c\)](#). [Ellis et al. \(2013\)](#) estimated the N CL for ACAD in the range of 3–8 kg N/ha/yr to protect hardwood forests and a similar range to protect lichens.

[Cleavitt et al. \(2015\)](#) conducted surveys and used FIA assessments of lichen species in the Northeast, with particular focus on the four Class I wilderness areas in the region (Lye Brook, VT; Great Gulf, NH; Presidential Range—Dry River, NH; and Acadia National Park, ME). In general, cumulative N and S deposition over the course of the modeled period (2000–2013) was a more powerful explanatory factor than annual N or S load for the lichen data. This work determined a critical load of 4.3–5.7 kg total N (oxidized + reduced N)/ha/yr based on lichen species richness, the abundance of sensitive species (higher species richness of cyanolichens and fruticose lichens below CL), and thallus condition. Cumulative S and N deposition were both equally powerful predictors of thallus condition, but no S critical load was determined ([Cleavitt et al., 2015](#)).

[Pardo et al. \(2011c\)](#) estimated that ambient N deposition in parts of ACAD was higher than estimated empirical CL values. Thus, these data suggest the possibility of exceedance of nutrient-N CL in ACAD (see [Table 16-6](#)).

**Table 16-6 Empirical critical loads for nitrogen in Acadia National Park, by receptor, from [Pardo et al. \(2011c\)](#).**

NPS Unit	Ecoregion	N Deposition (kg/ha/yr)	Critical Load (kg/ha/yr)				
			Mycorrhizal Fungi	Lichen	Herbaceous Plant	Forest	Nitrate Leaching
Acadia NP	Eastern Temperate Forests	5.2	5 to 12	4 to 8	17.5	3 to 8	8

ha = hectare; kg = kilogram; N = nitrogen; NP = national park; NPS = National Park Service; yr = year.

Ambient N deposition reported by [Pardo et al. \(2011c\)](#) is compared to the lowest critical load for a receptor to identify potential exceedance. A critical load exceedance suggests that the receptor is at increased risk for harmful effects.

#### 16.1.3.1.1.2 Hubbard Brook Experimental Forest

[Gbondo-Tugbawa and Driscoll \(2002\)](#) used the PnET-BGC model to simulate the responses of soil and surface water chemistry at the reference watershed at HBEF to future emissions controls. Model performance was assessed using the normalized mean absolute error and the efficiency as objective statistical criteria. The focus was on comparing simulated chemistry with observed values between 1980 and 1998. Results showed good agreement for stream Ca and  $\text{SO}_4^{2-}$ . However, stream  $\text{NO}_3^-$  and Al concentrations and soil solution Ca:Al ratios were over-predicted after 1990. Simulation results suggested that emissions controls required by the CAAA will likely not result in

substantial changes in the future in “critical indicators such as soil base saturation, soil solution Ca:Al, or stream ANC and Al concentrations.”

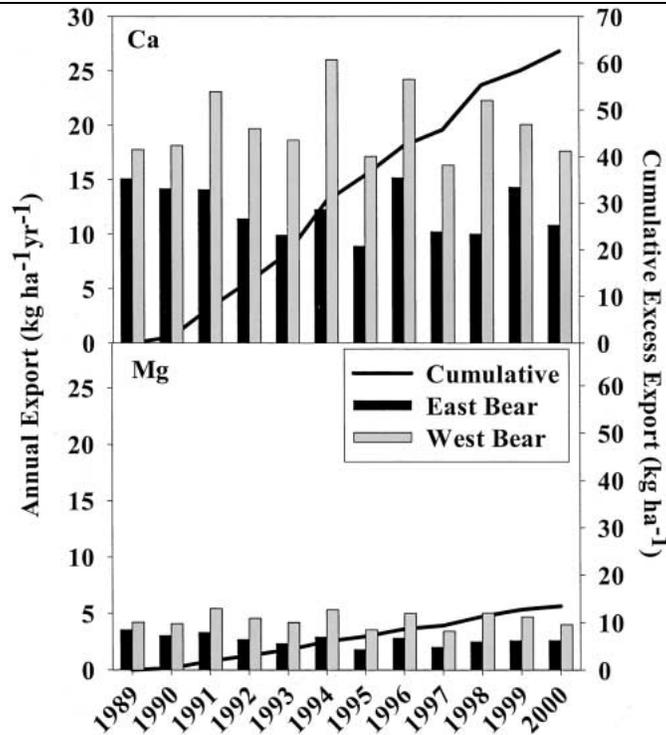
#### 16.1.3.1.1.3 Bear Brook Watershed

[Elvir et al. \(2006\)](#) investigated the effects of increased N deposition on photosynthesis and foliar nutrient content of sugar maple, American beech, and red spruce at the BBW. Trees in the treated WB watershed (an addition of 25 kg N/ha/yr as  $[\text{NH}_4]_2\text{SO}_4$ ) had higher foliar N concentrations than EB reference trees. American beech and red spruce displayed significantly lower foliar concentrations of Ca, Mg, and Zn. Sugar maple did not show decreases in these nutrients and was the only species to have significantly higher photosynthetic rates in the treated watershed as compared with the reference. This result suggested that nutrient imbalances in American beech and red spruce in the treatment watershed may have offset any potential photosynthetic benefits to these species from higher N availability ([Elvir et al., 2006](#)).

During the first 7 years of treatment at WB, sugar maple basal area increment (BAI) was higher in WB compared with EB. After 8 years of treatment, however, the initial higher sugar maple growth rate in WB decreased ([Elvir et al., 2010](#)).

In the WB catchments, the BAI of sugar maple was enhanced 13 to 104% by the addition of 25 kg N/ha/yr as  $(\text{NH}_4)_2\text{SO}_4$ . The BAI of red spruce was not significantly affected ([Elvir et al., 2003](#)).

[Fernandez et al. \(2003\)](#) reported results of quantitative soil excavations in 1998 that measured soil pools of exchangeable base cations after 9 years of treatment at WB. The treated watershed had lower concentrations of exchangeable Ca and Mg in all soil horizons, with greater nutrient cation depletion in the O-horizon as compared with the mineral soil. Depletion was also greater in conifer, as opposed to hardwood, stands. The importance of treatment-caused base cation depletion was reinforced by MAGIC model simulations. Estimates of watershed-wide exchangeable Ca and Mg (66 and 27 kg/ha) were roughly comparable to the total cumulative excess stream Ca and Mg export in WB after 9 years of treatment (55 and 11 kg/ha, respectively; [Figure 16-7](#)).



Ca = calcium; ha = hectare; kg = kilogram; Mg = magnesium; yr = year.  
 Source: [Fernandez et al. \(2003\)](#).

**Figure 16-7 Annual stream calcium and magnesium export (paired bars), and cumulative excess export in West Bear Brook compared with East Bear Brook (line), over the study period 1989–2000 at the Bear Brook Watershed experiment.**

**16.1.3.1.1.4 Other Northeastern Regions**

[Pardo et al. \(2011c\)](#) compiled data on empirical CLs for protecting sensitive resources in Level I ecoregions across the CONUS against nutrient enrichment effects caused by atmospheric N deposition. Available data on empirical CL of nutrient-N in the Northeast suggested that the lower end of estimates of the CL for resource protection was 3 kg N/ha/yr. Values at or above this level of deposition loading are considered to have increased risk of harmful effects for mycorrhizal fungi, lichens, and forest vegetation ([Table 16-7](#)). Keeping levels below this value also helps prevent NO<sub>3</sub><sup>-</sup> leaching into drainage water.

**Table 16-7 Critical loads of nutrient nitrogen for the Northern Forests ecoregion.**

Ecosystem Component	Critical load or N deposition (kg/ha/yr)	Reliability	Response	Comment	Reference
Tree	>3	#	Decreased growth of red pine, and decrease survivorship of yellow birch, scarlet and chestnut oak, quaking aspen, and basswood	None	<a href="#">Thomas et al. (2010)</a>
Lichens	4 to 6	(#)	Community composition shift	Application of model developed for marine West Coast forest to northern forests	<a href="#">Geiser et al. (2010)</a>
Ectomycorrhizal fungi	5 to 7	#	Change in fungal community structure	None	<a href="#">Lilleskov et al. (2008)</a>
Herbaceous species cover	>7 and <21	#	Loss of prominent species	Response observed in low-level fertilization experiment	<a href="#">Hurd et al. (1998)</a>
Northern hardwood and coniferous forest	8	##	Increased surface water NO <sub>3</sub> <sup>-</sup> leaching	None	<a href="#">Aber et al. (2003)</a>
Tree growth and mortality	>10 and <26	#	Decreased growth and/or induced mortality	Response observed in low-level fertilization experiment in old-growth montane red spruce	<a href="#">McNulty et al. (2005)</a>
Arbuscular mycorrhizal fungi	<12	(#)	Biomass decline and community composition change	Observed along a Michigan N gradient	<a href="#">Pardo et al. (2011c)</a>

ha = hectare; kg = kilogram; N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate; yr = year.

Reliability rate: ## reliable—a number of published papers show comparable results; # fairly reliable—the results of some studies are comparable; (#) expert judgment—few empirical data are available, Critical Load based on expert judgment of those ecosystems.

Source: [Pardo et al. \(2011c\)](#).

[Thomas et al. \(2010\)](#) analyzed Forest Inventory Analysis (FIA) data in the Northeast to determine tree growth in response to a gradient of atmospheric N deposition from about 3 to 11 kg N/ha/yr. Some tree species showed increased growth across the N input gradient (yellow poplar [*Liriodendron tulipifera*], black cherry [*Prunus serotina*], and white ash [*Fraxinus americana*]). Some showed highest growth at intermediate levels of N deposition (quaking aspen [*Populus tremuloides*] and scarlet oak [*Quercus coccinea*]). Red pine (*Pinus resinosa*) exhibited growth decline across the gradient of increasing N

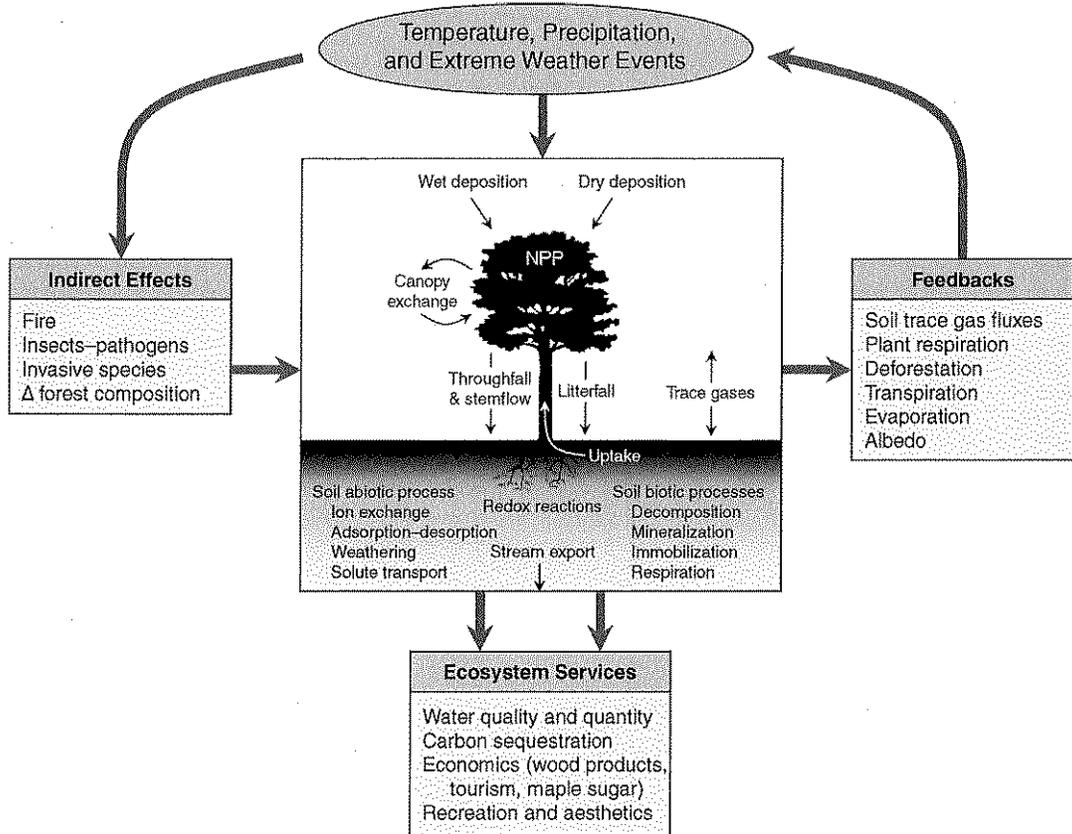
deposition ([Thomas et al., 2010](#)). Thus, it appeared that N deposition at ambient levels can have both positive and negative effects on tree growth, depending on species and deposition level.

In a high-elevation red spruce-balsam fir (*Abies balsamea*) forest in the Northeast, N fertilization over 14 years led to a decrease in live basal area (LBA) with increasing N additions. In control plots, LBA increased by 9% over the course of the study, while LBA decreased by 18 and 40% in plots treated with 15.7 kg N/ha/yr and 31.4 kg N/ha/yr, respectively ([McNulty et al., 2005](#)).

There is little information available regarding the effects of N deposition on herbaceous plants within northern hardwood forests in the Northeast. However, [Hurd et al. \(1998\)](#) reported the results of experimental studies that added N at two and four times the ambient N deposition level at several sites in the Adirondack Mountains. Herbaceous plant coverage decreased after 3 years of fertilization, largely in response to shading caused by enhanced growth of ferns. Additionally, information has been recently published by [Simkin et al. \(2016\)](#) and is discussed in [Appendix 6.2](#) of this ISA.

#### **16.1.3.1.2 Modeling Studies**

Evidence from research in northeastern forests indicates that direct and indirect effects of climate change will cause changes in N and other biogeochemical cycling by altering plant physiology, forest productivity, and soil processes. [Campbell et al. \(2009\)](#) reviewed these relationships ([Figure 16-8](#)) and applied the PnET-BGC model in a northern hardwood forest ecosystem at HBEF to test assumptions about interactions regarding climate change. Model results suggested an increase in primary productivity due to a longer growing season in the future, an increase in  $\text{NO}_3^-$  leaching due to enhanced net mineralization and nitrification, and a slight decrease in mineral weathering due to reduced simulated soil moisture (negative effect) and increased temperature (positive effect).



NPP = net primary production.  
 Source: [Campbell et al. \(2009\)](#).

**Figure 16-8** Conceptual diagram showing the direct and indirect effects of changes in temperature and precipitation on biogeochemical processes in forests and on the services forests provide. Also shown are feedbacks that further influence climatological effects.

### 16.1.3.2 Aquatic

This section presents post-2000 research findings at ACAD, HBEF, and BBW on the dose-response relationships of N and S to aquatic ecology, as well as the critical N and S loads for maintaining ecosystem health. Additional relevant information for the Northeast region is summarized. Both empirical and modeling studies of aquatic dose-response relationships and critical loads are included in this section.

### 16.1.3.2.1 Empirical Studies

Post-2000 findings from empirical studies of aquatic dose-response relationships and critical loads are summarized in this section. [Table 16-8](#) compiles the body of empirical research identified.

**Table 16-8 Aquatic empirical research on the response of nitrogen and sulfur deposition for the northeastern U.S.**

Variable	Response	Deposition	Addition	Years	Site	Reference
Fish community including brook trout ( <i>Salvelinus fontinalis</i> )	Shift in the upper mainstem of HBEF from the presence of at least three fish species to only brook trout ( <i>Salvelinus fontinalis</i> )	Not specified	0	1960s–2007	HBEF	<a href="#">Warren et al. (2008)</a>
SO <sub>4</sub> <sup>2-</sup>	W6 had a 32% decline in the annual volume-weighted concentration (–1.1 µeq/L/yr)	Not specified	0	1963–1994	HBEF	<a href="#">Driscoll et al. (2001b)</a> <a href="#">Likens et al. (2001)</a>
SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup>	W6 had declines in stream concentrations of strong acids (–1.9 µeq/L/yr)	Not specified	0	1963–1994	HBEF	<a href="#">Driscoll et al. (2001b)</a>
Sum of base cations	–1.6 µeq/L/yr	Not specified	0	1963–1994	HBEF	<a href="#">Driscoll et al. (2001b)</a>
pH	Small but significant increases in stream pH, from 4.8 to 5.0	Not specified	0	1963–1994	HBEF	<a href="#">Driscoll et al. (2001b)</a>
SO <sub>4</sub> <sup>2-</sup>	Biogeochemical control of SO <sub>4</sub> <sup>2-</sup> export from forested watersheds has shifted from atmospheric S deposition to climatic factors that regulate soil moisture.	Not specified	0	1965–2008	HBEF	<a href="#">Mitchell and Likens (2011)</a>
pH and ANC	Decrease	Not specified	1,800 eq/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	7 yr acidification treatment	BBW	<a href="#">Norton et al. (2004)</a>

**Table 16-8 (Continued): Aquatic empirical research on the response of nitrogen and sulfur deposition for the northeastern U.S.**

Variable	Response	Deposition	Addition	Years	Site	Reference
Stream dissolved SO <sub>4</sub> <sup>2-</sup>	Decreased	Not specified	1,800 eq/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–2007	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>
Base cations	Decreased	Not specified	1,800 eq/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–2007	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>
Al <sup>+</sup>	Increased	Not specified	1,800 eq/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1989–2007	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>
ANC	Regional surface water ANC did not change significantly in New England during the 1990s	Not specified	0	NA	NE	<a href="#">U.S. EPA (2003)</a> <a href="#">Evans and Monteith (2001)</a>
Release of S from internal storage pools to drainage water	Increased	Not specified	0	1965–2008	General	<a href="#">Mitchell and Likens (2011)</a>

Al<sup>+</sup> = aluminum; ANC = acid neutralizing capacity; BBW = Bear Brook Watershed; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; L = liter; µeq = microequivalents; eq = equivalents; NE = northeastern; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; W6 = Watershed 6; yr = year.

#### 16.1.3.2.1.1 Acadia National Park

No empirical aquatic critical loads or dose-response studies have been identified in the literature for the ACAD case study area since 2000.

#### 16.1.3.2.1.2 Hubbard Brook Experimental Forest

The cycling of N, S, and other elements in the Northeast is closely linked with aspects of climate. Many recent studies have explored some of those linkages, and many of the empirical studies of aquatic dose-response relationships have included aspects of climate change. The potential for a shift from atmospheric deposition to climatic regulation of watershed S biogeochemistry at HBEF was examined by [Mitchell and Likens \(2011\)](#). More than four decades of continuous long-term data collected from four watersheds were used to evaluate S budgets. “Analyses focused on the role of changing water availability in affecting the amount of S mobilized from internal watershed sources and the resultant changes in the S budget discrepancies over time...The biogeochemical

controls on annual  $\text{SO}_4^{2-}$  export in stream water [appear to have] shifted from atmospheric S deposition to climatic factors that affect soil moisture.”

With declining inputs of atmospheric S, the higher outputs of  $\text{SO}_4^{2-}$  in drainage waters relative to precipitation inputs appear to be driven by the S stored in the soil. These biogeochemical responses at the HBEF might be amplified with further climate change, resulting in greater annual stream discharge and watershed wetness. Such climatic change will potentially increase  $\text{SO}_4^{2-}$  mobilization and hence may slow the recovery of both aquatic and terrestrial ecosystems from acidification.

#### **16.1.3.2.1.3 Bear Brook Watershed**

[Chadwick and Huryn \(2005\)](#) assessed the effects of N additions on secondary stream macroinvertebrate production in BBW. Production did not vary between streams (reference and treatment) but was 35% higher for both streams in the second year of the study. Results suggested that patterns of litter input and channel drying, rather than N input, controlled secondary production in these intermittent streams by altering resource availability and invertebrate community structure. It appeared that these variables overrode the effects of N supply, perhaps because N is not limiting.

Ongoing climate change will likely affect a wide range of biogeochemical processes in northeastern forested ecosystems. Of particular interest are the effects on flow volumes and peak flows. [Kim et al. \(2010\)](#) analyzed a nearly two-decades-long stream flow record at EB and a longer record for the Narraguagus River (a proximate watershed to the BBW). The focus was on improving understanding of high-flow events that have a disproportionate impact on biogeochemical processes and fluxes. A moving window analysis to evaluate the changing flood potential over time suggested upward trends in the occurrence of high-flow events during recent decades.

#### **16.1.3.2.1.4 Other Northeastern Regions**

Considering trends across the Northeast, [Aber et al. \(2003\)](#) found that surface water  $\text{NO}_3^-$  concentrations exceeded  $1 \mu\text{eq/L}$  mainly in northeastern watersheds receiving more than about 9 to 13 kg N/ha/yr deposition. Above this range, mean  $\text{NO}_3^-$  export increased linearly with increasing deposition at a rate of about 0.85 kg  $\text{NO}_3^-$ -N/ha/yr for every 1 kg N/ha/yr increase in deposition, although at higher rates of deposition there was considerable variability in N retention among watersheds ([Aber et al., 2003](#)).

N limitation across the Northeast was evaluated by [Baron et al. \(2011a\)](#) who estimated that 34% of 4,361 New England lakes represented in the Eastern Lakes Survey were

likely to be N limited, based on having dissolved inorganic N (DIN):total P (TP) ratio (by weight) less than 4. Although eutrophication is a concern, there is no published evidence that eutrophication is occurring to any appreciable extent in the lakes in ACAD.

Dissolved organic matter (DOM) is important to a range of processes critical to aquatic ecosystem functioning, including providing a microbial food source, attenuating light, buffering pH, binding metals, and controlling the cycling of C, N, Hg, and P. Shifts in the quality of DOM may affect aquatic ecosystem functioning. A chemical signature of terrestrial DOM was used by [SanClements et al. \(2012\)](#) to support the hypothesis that increased dissolved organic carbon (DOC) concentrations in surface water in the Northeast since about 1993 have been driven mainly by decreasing acidic deposition and increasing solubility of soil organic matter. Fluorescence spectroscopy was used to characterize the quality of DOM of archived samples from nine acid-sensitive lakes in Maine. Decadal decreases in  $\text{SO}_4^{2-}$  in lake water were correlated with increased DOC concentrations and a shift from microbial to terrestrially derived DOM during ecosystem recovery from prior acidification.

Aquatic biota in the Northeast have been affected by acidification at virtually all levels of the food web. Some species and some lifestages are especially sensitive. Decreases in ANC and pH and increases in inorganic Al concentration contributed to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish as documented in the Adirondacks ([Sutherland et al., 2015](#); [Nierzwicki-Bauer et al., 2010](#); [Keller and Gunn, 1995](#); [Schindler et al., 1985](#)). Although some species are favored by increased acidity, the overall species richness typically decreases as surface water acidity increases.

#### **16.1.3.2.2 Modeling Studies**

Post-2000 findings from modeling studies of aquatic dose-response relationships and critical loads are summarized in this section. [Table 16-9](#) compiles the body of research identified.

**Table 16-9 Critical and target load and exceedance modeling studies in the northeastern U.S.**

Reference	Location	Model	Focus
<a href="#">Dupont et al. (2005)</a>	NE region	SSWC	CLs for acidity to protect aquatic biota to pH 6.0
<a href="#">SanClements et al. (2010)</a>	BBW	PnET-BGC	Interactions between climate change parameters and atmospheric deposition
<a href="#">Phelan et al. (2016)</a>	BBW and HBEF	ForSAFE-VEG	Atmospheric deposition to northern hardwood forests
<a href="#">Tominaga et al. (2010)</a>	HBEF	MAGIC, PnET-BGC, SAFE, VSD	Model output comparison
<a href="#">Pourmokhtarian et al. (2012)</a>	HBEF	PnET-BGC	N cycling and climate change

BBW = Bear Brook Watershed; CL = critical load; ForSAFE-VEG = Soil Acidification in Forest Ecosystems; HBEF = Hubbard Brook Experimental Forest; MAGIC = Model of Acidification and Groundwater in Catchments; N = nitrogen; NE = northeastern; PnET-BGC = Photosynthesis and Evapotranspiration-Biogeochemical; SAFE = Soil Acidification in Forest Ecosystems; SSWC = Steady-State Water Chemistry; VSD = Very Simple Dynamic.

#### 16.1.3.2.2.1 Acadia National Park

No modeling studies on aquatic critical loads for ACAD have been identified in the literature.

#### 16.1.3.2.2.2 Hubbard Brook Experimental Forest

[Tominaga et al. \(2010\)](#) evaluated the performance and prediction uncertainty of four dynamic process-based watershed acidification models: MAGIC, PnET-BGC, SAFE, and VSD. Model output was assessed by systematically applying each of the models to data from the HBEF. The models were used to assess future soil and stream chemistry response to reduced levels of atmospheric S deposition. Both hindcast and forecast predictions were qualitatively similar across the four models. Nevertheless, the temporal patterns of projected stream ANC and soil base saturation differed. [Tominaga et al. \(2010\)](#) concluded that these differences can be accommodated by employing multiple models. Nevertheless, these results have implications for individual model applications.

[Pourmokhtarian et al. \(2012\)](#) used “the PnET-BGC model to evaluate the effects of potential future changes in temperature, precipitation, solar radiation, and atmospheric

CO<sub>2</sub> on the pools, concentrations, and fluxes of major elements at the HBEF.” The climate projections were based on downscaled climate output from atmospheric-ocean general circulation models. These climate projections indicated that the average air temperature will likely increase at the HBEF site by 1.7 to 6.5°C over the 21st century, with simultaneous increase in annual average precipitation ranging from 4 to 32 cm above the long-term mean. The PnET-BGC model simulations under expected future climate showed shifts in hydrology from later snowpack development, earlier snowmelt, increased evapotranspiration, and a slight increase in the annual water yield. The model results suggested that net soil N mineralization and nitrification will markedly increase under elevated temperature. This increase resulted in simulated acidification of soil and stream water, altering the quality of water draining from the forested watershed.

#### **16.1.3.2.2.3 Bear Brook Watershed**

No aquatic critical loads modeling studies have been identified for BBW in the literature since 2000.

#### **16.1.3.2.2.4 Other Northeastern Regions**

Studies in the Northeastern region have used a variety of steady-state and dynamic modeling approaches. The Conference of the New England Governors and Eastern Canadian Premiers (NEG/ECP) sponsored a modeling assessment of steady-state CLs for protection of forest soils and lakes against acidification in the Northeast region and in eastern Canada ([Ouimet et al., 2006](#); [Dupont et al., 2005](#); [Ouimet et al., 2001](#)). [Dupont et al. \(2005\)](#) reported the SSWC steady-state aquatic CLs of acidity and associated exceedances for lakes. Atmospheric acid loads were assessed based on atmospheric deposition of both S and N, using a critical limit of pH 6 to protect aquatic biota. This pH level approximately corresponds with ANC = 40 µeq/L in this region ([Small and Sutton, 1986](#)). Estimated S critical loads were exceeded in 2002 for 12.3% of all studied lakes. Lakes having lowest calculated CLs included many in southern Vermont, eastern and northern Maine, northern New Hampshire, and Cape Cod. Exceedances of CLs, based on estimated acidic deposition in 2002, were highest in central and coastal Massachusetts, southern Vermont, much of Maine, and portions of New Hampshire. Eastern Maine and southern Vermont were notable “hot spots” where ambient S + N deposition exceeded CLs by more than 10 meq/m<sup>2</sup>/year ([Dupont et al., 2005](#)).

### 16.1.3.3 Integration

[Table 16-10](#) contains a list of northeastern U.S. critical load determinations by multiple researchers, ranging from 3–8 kg N/ha/yr (forests) to 17.5 kg N/ha/yr (herbaceous plants).

**Table 16-10 Empirical and modeled nitrogen critical loads applicable to the northeastern U.S.**

Critical Load (kg N/ha/yr)	Ecosystem Component	Response	N Deposition (kg/ha/yr)	Site	Reference
5 to 12	Eastern temperate forest	Mycorrhizal Fungi	5.2	ACAD	<a href="#">Pardo et al. (2011c)</a>
4 to 8	Lichens	Epiphytic lichen community change	5.2	ACAD	<a href="#">Pardo et al. (2011c)</a>
17.5	Herbaceous Species	Increases in nitrophilic species, declines in species-richness	5.2	ACAD	<a href="#">Pardo et al. (2011c)</a>
3 to 8	Hardwood forest	Not specified	5.2	ACAD	<a href="#">Pardo et al. (2011c)</a> <a href="#">Ellis et al. (2013)</a>
8	Eastern hardwood forests	Increased surface water NO <sub>3</sub> <sup>-</sup> leaching	5.2	ACAD	<a href="#">Pardo et al. (2011c)</a> <a href="#">Ellis et al. (2013)</a>
ANC crucial concentration = 20 µeq/L Soil base saturation critical level of 10%	Not specified	Current legislated emissions (= 13% reduction of SO <sub>4</sub> <sup>2-</sup> by 2015) results in limited response recovery Maximum feasible technology reductions (= 78% reduction of SO <sub>4</sub> <sup>2-</sup> by 2015) results in a more rapid and greater extent of chemical recovery	Not specified	HBEF	<a href="#">Tominaga et al. (2010)</a>

**Table 16-10 (Continued): Empirical and modeled nitrogen critical loads applicable to the northeastern U.S.**

Critical Load (kg N/ha/yr)	Ecosystem Component	Response	N Deposition (kg/ha/yr)	Site	Reference
CO <sub>2</sub> fertilization plateau of 600 ppm	Not specified	N cycling and climate change. "Under elevated temperature, net soil N mineralization and nitrification markedly increase, resulting in acidification of soil and stream water...Invoking CO <sub>2</sub> fertilization effect on vegetation under climate change substantially mitigates watershed N loss...Showed recovery of up to 1 pH unit (assuming pH of 6.0 as steady-state value) and...ANC of 6.9 to 15.5 µeq/L in comparison to -3.4 µeq/L mean annual measured values (1988-2000)"	Not specified	HBEF (year 2070-2100)	<a href="#">Pourmokhtarian et al. (2012)</a>
Not specified	Eastern temperate forest	Interactions among climate change parameters and atmospheric deposition	Not specified	BBW	<a href="#">SanClements et al. (2010)</a>
Not specified	Eastern temperate forest	Atmospheric deposition to northern hardwood forests	Not specified	BBW and HBEF	<a href="#">Phelan et al. (2016)</a>
Not specified	NE watersheds	Surface water NO <sub>3</sub> <sup>-</sup> concentrations exceeded 1 µeq/L and mean NO <sub>3</sub> <sup>-</sup> export increased linearly with increasing deposition	9 to 13	NE	<a href="#">Aber et al. (2003)</a>
<20 kg/ha/yr S + N (= 9.6 kg SO <sub>4</sub> <sup>2-</sup> /ha/yr)	Aquatic biota	Protect aquatic biota to pH 6.0	Not specified	NE	<a href="#">Dupont et al. (2005)</a>

ACAD = Acadia National Park; ANC = acid neutralizing capacity; BBW = Bear Brook Watershed; CO<sub>2</sub> = carbon dioxide; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; L = liter; µeq = microequivalents; N = nitrogen; NE = northeastern; NO<sub>3</sub><sup>-</sup> = nitrate; ppm = parts per million; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

### 16.1.4 Long-Term Ecological Monitoring

This section summarizes research on the long-term effects of S and N deposition in the case study areas. The focus is primarily on research published since about the year 2000. The acidification and nutrient enrichment subsections are each organized by three case study areas followed by relevant information for the overall Northeast region. Key publications are summarized in [Table 16-11](#).

**Table 16-11 Summary table of observed terrestrial and aquatic acidification long-term trends in Hubbard Brook Experimental Forest and Bear Brook Watershed.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
C:N	NA	Significant increase over 25 yr	Not specified	Not specified	HBEF	<a href="#">Campbell et al. (2007)</a>
Biomass	Sugar maple	Decrease	Not specified	Not specified	HBEF	<a href="#">Campbell et al. (2007)</a>
Al <sup>+</sup>	NA	Decrease	Not specified	Not specified	HBEF	<a href="#">Campbell et al. (2007)</a>
Base cation Ca and Mg depletion	NA	Historical forest cutting had little impact on exchangeable cation soil pools	Not specified	Not specified	HBEF	<a href="#">Gbondo-Tugbawa and Driscoll (2003)</a>
SO <sub>4</sub> <sup>2-</sup>	NA	Watershed 6, had a 32% decline in the annual volume-weighted concentration (-1.1 µeq/L/yr)	Not specified	Not specified	HBEF 1963–1994	<a href="#">Driscoll et al. (2001b)</a> <a href="#">Likens et al. (2001)</a>
SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup>	NA	Declines in stream concentrations of strong acids (-1.9 µeq/L/yr)	Not specified	Not specified	HBEF 1963–1994	<a href="#">Driscoll et al. (2001b)</a>
Sum of base cations	NA	-1.6 µeq/L/yr	Not specified	Not specified	HBEF 1963–1994	<a href="#">Driscoll et al. (2001b)</a>
pH	NA	Small but significant increases in stream pH, from 4.8 to 5.0	Not specified	Not specified	HBEF 1963–1994	<a href="#">Driscoll et al. (2001b)</a>
Fish community	Slimy sculpin ( <i>Cottus cognatus</i> ), blacknose dace ( <i>Rhinichthys atratulus</i> ), and brook trout ( <i>Salvelinus fontinalis</i> )	Shift in the upper mainstem of Hubbard Brook from the presence of at least three fish species (slimy sculpin [ <i>Cottus cognatus</i> ], blacknose dace [ <i>Rhinichthys atratulus</i> ], and brook trout [ <i>Salvelinus fontinalis</i> ]) to only brook trout	Not specified	Not specified	HBEF (1960s–2007)	<a href="#">Warren et al. (2008)</a>

**Table 16-11 (Continued): Summary table of observed terrestrial and aquatic acidification long-term trends in Hubbard Brook Experimental Forest and Bear Brook Watershed.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
Base cation	Sugar maple, American beech, red spruce	American beech and red spruce had lower foliar Ca, Mg, Zn concentrations; nutrient imbalance may offset potential photosynthesis benefits Sugar maple higher photosynthesis rates/no decrease in Ca, Mg, Zn concentrations	8.4 N (wet + dry)	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Elvir et al. (2006)</a>
Base cation	Sugar maple, American beech, red spruce	Little evidence of BC depletion but confounded by ice storm litter mineralization	18.5 (1980) 4.74 (2010) Wet SO <sub>4</sub> <sup>2-</sup> 2.8 Inorganic N	WB 25.2 kg (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">SanClements et al. (2010)</a>
Mineralization	Sugar maple, American beech, red spruce	Storm caused increased litterfall and accelerated mineralization, obstructing temporal trends in soil chemistry (17 yr)	Not specified	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Fernandez et al. (2003)</a>
pH and ANC	NA	Decrease	Not specified	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Norton et al. (2004)</a>
Stream dissolved SO <sub>4</sub> <sup>2-</sup>	NA	Decrease	Not specified	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>
Base cation export in runoff	NA	Increased BC export. Export rates declined after 7 yr treatment.	Not specified	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>

**Table 16-11 (Continued): Summary table of observed terrestrial and aquatic acidification long-term trends in Hubbard Brook Experimental Forest and Bear Brook Watershed.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
Al <sup>+</sup>	NA	Increase	Not specified	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Norton et al. (2004)</a> <a href="#">Fatemi et al. (2012)</a>
Release of S from internal storage pools to drainage water	NA	Increased	Not specified	0	General (1972–2008)	<a href="#">Mitchell and Likens (2011)</a>
SO <sub>4</sub> <sup>2-</sup>	NA	Biogeochemical control of SO <sub>4</sub> <sup>2-</sup> export from forested watersheds in HBEF has shifted from atmospheric S deposition to climatic factors that regulate soil moisture	Not specified	0	General	<a href="#">Mitchell and Likens (2011)</a>
Critical loads	Varied	Varied	Not specified	Not specified	NE	<a href="#">Pardo et al. (2011c)</a>
ANC	NA	Regional surface water ANC did not change significantly in New England during the 1990s	Not specified	0	NE	<a href="#">U.S. EPA (2003)</a>

Al<sup>+</sup> = aluminum; ANC = acid neutralizing capacity; BC = base cation; BBW = Bear Brook Watershed; C = carbon; Ca = calcium; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; L = liter; µeq = microequivalents; Mg = magnesium; N = nitrogen; NA = not applicable; NE = northeastern; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; W6 = Watershed 6; WB = West Bear Brook; yr = year; Zn = zinc.

Acadia National Park is not a federally funded long-term monitoring study area.

#### 16.1.4.1 Long-Term Monitoring of Acidification

Acidic deposition has been shown to be an important factor causing decreases throughout much of the Northeast region in concentrations of exchangeable base cations in soils, which were naturally low historically. Base saturation values less than 12% predominate in the B-horizon in portions of the region where soil and surface water acidification from acidic deposition have been most pronounced ([Sullivan et al., 2006a](#); [Bailey et al., 2004](#); [David and Lawrence, 1996](#)).

[Mitchell et al. \(2011\)](#) evaluated S mass balances for 15 watersheds in the northeastern U.S. and southeastern Canada, including watersheds at HBEF, BBW, and Cone Pond in New Hampshire, for the period 1985 to 2002. Most study watersheds showed evidence of internal watershed sources of  $\text{SO}_4^{2-}$ , likely from mineralization of organic S stored from decades of high S deposition. Mobilization of the mineralized S contributed an estimated 1–6 kg S/ha/yr to the stream fluxes of  $\text{SO}_4^{2-}$ . This mobilization has affected the observed rates of recovery from acidification as S deposition has declined.

Surface water chemistry in the northeastern U.S. has been characterized, surveyed, resurveyed, and monitored in many studies conducted over the last several decades ([Table 16-12](#)).

**Table 16-12 Example surface water acidification chemistry studies in the Northeast case study region.**

Focus	Results	Deposition	Addition	Time Period	Site	Reference
N export	An unburned study watershed exported 10 to 20 times more inorganic N than the burned watershed; in addition, retention of inorganic N was 96% in the burned watershed vs. 72% in the unburned watershed.	Not specified	Not applicable	Pre- vs. post-1947 fire	ACAD	<a href="#">Nelson et al. (2007)</a>
N export	Total N + P exported by watersheds entirely within ACAD were significantly lower than exports in watersheds that were partly or completely outside the park.	Not specified	Not applicable	Not specified	ACAD	<a href="#">Nelson et al. (2007)</a>
Reference stream chemistry	Decline in stream $\text{SO}_4^{2-}$ ( $-1.1 \mu\text{eq/L/yr}$ ) Decline in $\text{SO}_4^{2-} + \text{NO}_3^-$ in stream ( $-1.9 \mu\text{eq/L/yr}$ )	Not specified	Not specified	1963–1994	HBEF	<a href="#">Driscoll et al. (2001b)</a>
S budget	Biogeochemical control of $\text{SO}_4^{2-}$ export has switched from atmospheric deposition to climate factors that regulate soil moisture.	Not specified	Not specified	1965–2008	HBEF	<a href="#">Mitchell and Likens (2011)</a>

**Table 16-12 (Continued): Example surface water acidification chemistry studies in the northeast case study region.**

Focus	Results	Deposition	Addition	Time Period	Site	Reference
Stream trends for reference and treatment catchments	Stream dissolved $\text{SO}_4^{2-}$ , pH, and ANC decrease Base cation and $\text{Al}^+$ increase	Not specified	1,800 eq/ha/yr $(\text{NH}_4)_2\text{SO}_4$	1987–2000	BBW	<a href="#">Norton et al. (2004)</a>
Low-flow and high-flow stream chemistry of reference and treatment catchments	Base cation, $\text{NH}_4^+$ and $\text{Cl}^-$ unchanged	Not specified	1,800 eq/ha/yr $(\text{NH}_4)_2\text{SO}_4$	1987–2006	BBW	<a href="#">Navrátil et al. (2010)</a>
Chronic stream chemistry for reference and treatment catchments	Increased BC export; declined after 7 yr of treatment. Decrease pH and alkalinity Increased dissolved $\text{Al}^+$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$	Not specified	1,800 eq/ha/yr $(\text{NH}_4)_2\text{SO}_4$	1987–2007	BBW	<a href="#">Norton et al. (2010)</a>
Episodic stream chemistry for reference and treatment catchments	“18 yr of N and S addition have not affected the natural drivers of episodic acidification. The contribution of $\text{SO}_4^{2-}$ to the ANC decline in WB has been increasing linearly since the beginning of watershed treatment while the role of $\text{NO}_3^-$ has remained relatively constant after an initial increase.”	Not specified	1,800 eq/ha/yr $(\text{NH}_4)_2\text{SO}_4$	1988–2006	BBW	<a href="#">Laudon and Norton (2010)</a>
Lake resurvey	Ubiquitous decreases in the concentration of inorganic Al across the region. Organic monomeric Al also declined region-wide in New England. In 2001, only seven study lakes (representing 130 lakes in the Northeast region) that had Al <sub>i</sub> above the toxic threshold of 2 $\mu\text{M}$ , compared with 20 sampled lakes (representing 449 lakes in the population) in 1986.	Not specified	Not specified	1986 and 1998	NE region	<a href="#">Warby et al. (2009)</a>

**Table 16-12 (Continued): Example surface water acidification chemistry studies in the northeast case study region.**

Focus	Results	Deposition	Addition	Time Period	Site	Reference
Chronic and episodic lake and stream chemistry	Rates of change for individual water bodies ranged from about -1.5 to -3 µeq/L/yr.	Not specified	Not specified	1990–2000	NE and Appalachian Mtns.	<a href="#">U.S. EPA (2003)</a>
Regional lake trends	NO <sub>3</sub> <sup>-</sup> concentrations in New England and the Adirondack Mountains, which had no trend prior to 2000, declined at a rate of -0.05 µeq/L/yr	Not specified	Not specified	2000–2010	New England and Adirondacks	<a href="#">Strock et al. (2014)</a>
Response to deposition reduction	Oa-horizon BS decreased from 56.2 to 33.0% and almost equivalent changes in carbon-normalized exchangeable Ca and exchangeable Al	Not specified	Not specified	1984 to 2001	NE region	<a href="#">Warby et al. (2009)</a>
	Suggested a nascent recovery of soil acid-base chemistry at some locations in the Northeast where six red spruce stands sampled. Exchangeable Al in the Oa-horizons decreased ( $p < 0.05$ ) by 20 to 40% at all New England sites. Evidence of base cation depletion and decreased Ca:Al ratio	Not specified	Not specified	1992–1993 vs. 2003–2004	General	<a href="#">Lawrence et al. (2012)</a>

ACAD = Acadia National Park; Al = aluminum; ANC = acid neutralizing capacity; BBW = Bear Brook Watershed; BC = base cation; BS = base saturation; Ca = calcium; Cl<sup>-</sup> = chloride; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; L = liter; µeq = microequivalents; µM = micromole; N = nitrogen; NE = northeastern; NH<sub>4</sub><sup>+</sup> = ammonium; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; Oa = well decomposed humus; P = phosphorus; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; WB = West Bear Brook; yr = year.

These studies have focused on both chronic and episodic responses of reference and (in the case of BBW and HBEF) experimentally treated catchments.

The U.S. EPA's Long-Term Monitoring (LTM) Program has been collecting monitoring data since the early 1980s for many lakes and streams in acid-sensitive areas of the U.S., including within the Northeast region. These data allow evaluation of trends and variability in key components of lake and stream water chemistry prior to, during, and subsequent to 1990 CAAA Title IV implementation. Throughout the Northeast region, the concentration of SO<sub>4</sub><sup>2-</sup> in surface waters has decreased substantially, often by one-third to one-half, subsequent to the 1990 CAAA. These declines in lake and stream

SO<sub>4</sub><sup>2-</sup> concentrations were considered consistent with observed declines in S wet deposition and have been corroborated by other studies showing that SO<sub>4</sub><sup>2-</sup> concentrations in northeastern lakes have decreased steadily since about the late 1970s [e.g., [Driscoll et al. \(1995\)](#); [U.S. EPA \(2003\)](#)]. Regional surface water ANC did not change significantly in New England during the 1990s ([U.S. EPA, 2003](#)).

The impact of the 1990 CAAA relevant to aluminum releases to surface waters was assessed by [Warby et al. \(2008\)](#), who surveyed 113 lakes in the Northeast that had been sampled in 1986 and again in 2001. They “found ubiquitous decreases in the concentration of inorganic Al across the region.” In 2001, there were only 7 study lakes (representing 130 lakes in the Northeast region) that had inorganic Al above the toxic threshold of 2 µM, compared with 20 sampled lakes (representing 449 lakes in the population) in 1986.

[Strock et al. \(2014\)](#) analyzed recent trends in wet deposition and lake chemistry using long-term monitoring data for lakes in New England and the Adirondack Mountains. From 2000 to 2010, lake NO<sub>3</sub><sup>-</sup> concentrations decreased at a rate of -0.05 µeq/L/year (no trend before 2000). There was a shift to nontoxic organic Al. Both ANC and pH exhibited variable trends.

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#### 16.1.4.2 Long-Term Monitoring of Nitrogen Enrichment

[Table 16-13](#) summarizes the effects of N deposition on watershed nutrient in the three case studies areas and relevant Northeastern regional studies.

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**Table 16-13 Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
N export	Not specified	An unburned study watershed exported 10 to 20 times more inorganic N than the burned watershed.	Wet deposition only (value not specified)	Not specified	ACAD (pre- vs. post-1947 fire)	<a href="#">Nelson et al. (2007)</a>

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**Table 16-13 (Continued): Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
N mass balance	Sugar maple, American Beech, yellow birch	Stream water export decrease from 4 to 1 kg N/ha/yr Shift to a net N sink storing ~8 kg N/ha/yr; unclear whether N is accumulating or being lost through denitrification.	~7 kg N/ha/yr	0	HBEF	<a href="#">Yanai et al. (2013)</a>
DIN loss	Sugar maple, American Beech, yellow birch	In W6, "losses were elevated in 1960s by a combination of recovery from extreme drought and a significant defoliation event. N deposition alone, in the absence of other disturbances, would have increased DIN losses by 0.35 g N/m <sup>2</sup> /yr."	"0.13 g/m <sup>2</sup> /yr is 20% of wet + dry deposition"	0	HBEF	<a href="#">Aber et al. (2002)</a>
Biogeochemical process	Sugar maple, American Beech, yellow birch	Modeled soil freeze-thaw to year 2100. "Shortened frost covered period has biogeochemical process implications."	Not specified	0	HBEF	<a href="#">Campbell et al. (2010)</a>

**Table 16-13 (Continued): Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
Biogeochemical process	Sugar maple, American Beech, yellow birch	"A relatively mild freezing event induced significant increases in N mineralization and nitrification rates, solute leaching, and soil N <sub>2</sub> O production and caused significant decreases in soil methane uptake. Soil freezing events may be major regulators of soil biogeochemical processes and solute delivery to streams in forested watersheds."	Not specified	0	HBEF	<a href="#">Groffman et al. (2011)</a>
NO <sub>3</sub> <sup>-</sup> export in 2006	Sugar maple, American Beech, yellow birch	NO <sub>3</sub> <sup>-</sup> retention greater than expected. "Changes over last five decades have reduced impacts of frost events on watershed NO <sub>3</sub> <sup>-</sup> export."	~6 kg N/ha/yr (1999–2008)		HBEF	<a href="#">Judd et al. (2011)</a>
NPP and photosynthetic surface area	Sugar maple, American Beech, yellow birch	Ca nutrition promoted higher aboveground NPP and increased photosynthetic surface area.	Not specified	0	HBEF (15-yr study)	<a href="#">Battles et al. (2014)</a>
Nitrification		Showed greatest response to N treatments.	8.4 kg N/ha/yr (wet + dry)	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Jefts et al. (2004)</a>

**Table 16-13 (Continued): Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
$\beta$ -1,4 glucosidase $\beta$ -1,4-N-acetylglucosaminidase	Sugar maple, American beech, Red spruce	“Greatest leaf N + P contents can increase short-term decomposition, accelerate production of more humic-like water extractable organic matter and thereby potentially influence the distribution of organic matter within the soil C pool.”  Not affected by long-term N enrichment in aquatic and terrestrial habitats.	Not specified	25.2 N since 1989	BBW	<a href="#">Hunt et al. (2008)</a> <a href="#">Mineau et al. (2014)</a>
WB vs. EB streams: Leaf breakdown	Not specified	Little difference found	Not specified	Not specified	BBW	<a href="#">Simon et al. (2010)</a>
WB vs. EB streams: Invertebrate production	Not specified	“Virtually identical”	Not specified	Not specified	BBW	<a href="#">Simon et al. (2010)</a>
WB vs. EB streams: Nutrient uptake	NA	N uptake responsive	Not specified	Not specified	BBW	<a href="#">Simon et al. (2010)</a>
Base cation	Sugar maple, American beech, red spruce	American beech and red spruce lower foliar Ca, Mg, Zn concentrations; nutrient imbalance may offset potential photosynthesis benefits.  Sugar maple higher photosynthesis rates; no decrease in Ca, Mg, Zn concentrations.	8.4 kg N/ha/yr (wet + dry)	WB 25.2 kg N/ha/yr (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> WB 28.8 S	BBW	<a href="#">Elvir et al. (2006)</a>

**Table 16-13 (Continued): Summary of observed terrestrial and aquatic nutrient enrichment long-term responses in Acadia National Park, Hubbard Brook Experimental Forest, Bear Brook Watershed, and other northeastern regions.**

Variable	Species	Response	Deposition (kg/ha/yr)	Addition (kg/ha/yr)	Site	Reference
Watershed N retention	Varied	Varies widely. Not directly related to N loading.	Wet deposition 1.8 to 5.5 NO <sub>3</sub> <sup>-</sup> 0.9 to 2.4 NH <sub>4</sub> <sup>+</sup>	0	Mid-Atlantic and NE forests	<a href="#">(Campbell et al., 2004b)</a>
Net nitrification	<i>Picea rubens</i>	<i>Picea rubens</i> density influences net nitrification.	Not specified	0	NE: Ranch Brook Watershed, Vermont	<a href="#">Ross and Wemple (2011)</a>
BAI	Sugar maple, black cherry	Varied species with acid deposition impact on soil nutrient status. Maple responds (growth) to lime (Ca) addition.	Not specified	Not specified	NE (7 sites) (1937–1996)	<a href="#">Long et al. (2009)</a>
SOC response	Hardwood red pine	Increased cumulative O-, A-, and B-horizons C stocks of 211 g C/m <sup>2</sup> .	0.9 g N/m <sup>2</sup> /yr	5 to 15 g N/m <sup>2</sup> /yr	NE: Harvard Forest	<a href="#">Tonitto et al. (2014)</a>

ACAD = Acadia National Park; BAI = basal area increment; BBW = Bear Brook Watershed; C = carbon; Ca = calcium; DIN = dissolved inorganic nitrogen; EB = East Bear Brook; g = gram; ha = hectare; HBEF = Hubbard Brook Experimental Forest; kg = kilogram; m = meter; Mg = magnesium; N = nitrogen; N<sub>2</sub>O = nitrous oxide; NA = not applicable; NE = northeastern; NH<sub>4</sub><sup>+</sup> = ammonium; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; NPP = net primary production; P = phosphorus; S = sulfur; SOC = soil organic carbon; W6 = Watershed 6; WB = West Bear Brook; yr = year; Zn = zinc.

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## 16.1.5 Recovery

Research to measure and predict recovery in the Northeast indicates that while emission control legislation has resulted in reduced S and N emissions from some stationary and mobile sources, recovery of sensitive northeastern watersheds, including those located at HBEF, BBW, and ACAD, has been limited. From 2000 to 2010, lake  $\text{NO}_3^-$  concentrations in New England and the Adirondack Mountains, which had no trend prior to 2000, declined at a rate of  $-0.05 \mu\text{eq/L/year}$  (Strock et al., 2014). Research by Warby et al. (2008) in the Northeast suggested a nascent recovery of soil acid-base chemistry at some locations where red spruce stands were sampled. In BBW, SanClements et al. (2010) found little evidence of continued depletion or recovery of soil exchangeable base cations. Mitchell and Likens (2011) observed that with declining inputs of atmospheric S, the higher outputs of  $\text{SO}_4^{2-}$  in drainage waters relative to precipitation inputs appear to be driven by the S stored in the soil.

To simulate the future responses of soil and surface water chemistry to potential future emissions controls at the reference watershed at HBEF, Gbondo-Tugbawa and Driscoll (2002) used the PnET-BGC (Photosynthesis and Evapotranspiration-Biogeochemical) model. Simulation results suggested that emissions controls required by the CAAA will likely not result in substantial future changes in critical indicators, such as soil base saturation, soil solution Ca:Al, or stream ANC and Al concentrations. Tominaga et al. (2010) assessed model outputs of four ecosystem models by systematically applying each of the models to data from the HBEF. They predicted that current legislated emissions reductions (13% reduction of  $\text{SO}_4^{2-}$  by 2015) would result in limited recovery and that maximum feasible technology reductions (78% reduction of  $\text{SO}_4^{2-}$  by 2015) would result in a more rapid and greater extent of chemical recovery.

The recovery of sensitive northeastern watersheds appears to be influenced by climate change, which has become increasingly important to consider in understanding the potential for recovery from decades of S and N deposition. For example, climatic change, which increases annual stream discharge and watershed wetness, will potentially increase  $\text{SO}_4^{2-}$  mobilization and hence may slow the recovery of both aquatic and terrestrial ecosystems from acidification (Mitchell and Likens, 2011). Predictive modeling of recovery should, therefore, consider climate change. Two modeling studies reported in this case study are noteworthy for improving scientific understanding of recovery in the Northeast. To test assumptions about interactions that are influenced by climate change, Campbell et al. (2009) applied the PnET-BGC model in a northern hardwood forest ecosystem at HBEF. Results suggested an increase in primary productivity due to a longer growing season in the future, an increase in  $\text{NO}_3^-$  leaching due to enhanced net

mineralization and nitrification, and a slight decrease in mineral weathering. In addition, this warmer climate has contributed to significant declines in snow depth, snow-water equivalents, and snow cover duration. This change has important implications for forest ecosystem processes, such as tree phenology and growth, hydrological flow paths during winter and spring, and soil biogeochemistry. Expected future climate change was also simulated using ForSAFE-VEG (Soil Acidification in Forest Ecosystems model) and found to cause an increase in soil base saturation, especially at BBW ([Phelan et al., 2016](#)). The authors observed that climate had a lesser effect on simulated soil acid-base chemistry at HBEF, likely due to the overwhelming influences of high S and N deposition. They suggested that climate futures predicted by the Intergovernmental Panel on Climate Change (IPCC) of increased temperature and precipitation will change plant communities and N enrichment, counteracting the acidifying impacts of S and N deposition on soil acid-base chemistry.

Finally, increasing attention is being given to developing and implementing practices to restore forest productivity lost to impacts from acidification. Practices such as calcium addition may increase recovery rates in northeastern forests. For example, [Battles et al. \(2014\)](#) added calcium silicate to the HBEF paired watershed to determine whether Ca lost from leaching due to acidification can be restored. Their results suggested tree biomass recovery and reversal of forest decline through greater aboveground net primary production and increased photosynthetic surface area. CO<sub>2</sub> fertilization associated with climate change is also being evaluated for its role in helping mitigate N loss in watersheds ([Pourmokhtarian et al., 2012](#)).

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## 16.2 Adirondack Case Study: Adirondack Region of New York

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### 16.2.1 Background

This case study is meant to identify the effects of nitrogen (N) and sulfur (S) in the Adirondack region and the Adirondack state park in New York. This case study identifies current acidification and nutrient status and empirical and modeled critical loads (CLs). It is a supplement to the case study of acidification in the Adirondack region of New York included in the 2008 NO<sub>x</sub>-SO<sub>x</sub> ISA [Section 3.2.2.4 of 2008 ISA ([U.S. EPA, 2008a](#))]. Further information about the effects in the Adirondack region can be found in [Appendix 4](#), [Appendix 5](#), [Appendix 7](#), and [Appendix 8](#).

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### 16.2.1.1 Description of Case Study Region

The Adirondack Mountains are in northeastern New York State and are densely forested, have abundant surface waters, and have 46 peaks that extend up to 1,600 m in elevation ([Figure 16-9](#)). This area includes the headlands of five major drainage basins: Lake Champlain and the Hudson, Black, St. Lawrence, and Mohawk rivers. There are more than 2,800 lakes and ponds, and more than 1,500 miles of rivers that are fed by an estimated 30,000 miles of brooks and streams. The Adirondack Park has long been a nationally important recreation area for fishing, hiking, boating, and other outdoor activities.

The Adirondacks, particularly the southwestern Adirondacks, are sensitive to acidifying deposition because they receive high precipitation, have shallow base-poor soils, and are underlain by igneous bedrock with low weathering rates. The Adirondacks are among the most severely acid-affected regions in North America ([Driscoll et al., 2003a](#); [Landers et al., 1988](#)) and have long been used as an indicator of the response of forest and aquatic ecosystems to U.S. policy on atmospheric emissions of SO<sub>2</sub> and NO<sub>x</sub> ([NAPAP, 2011](#); [U.S. EPA, 1995a](#)).

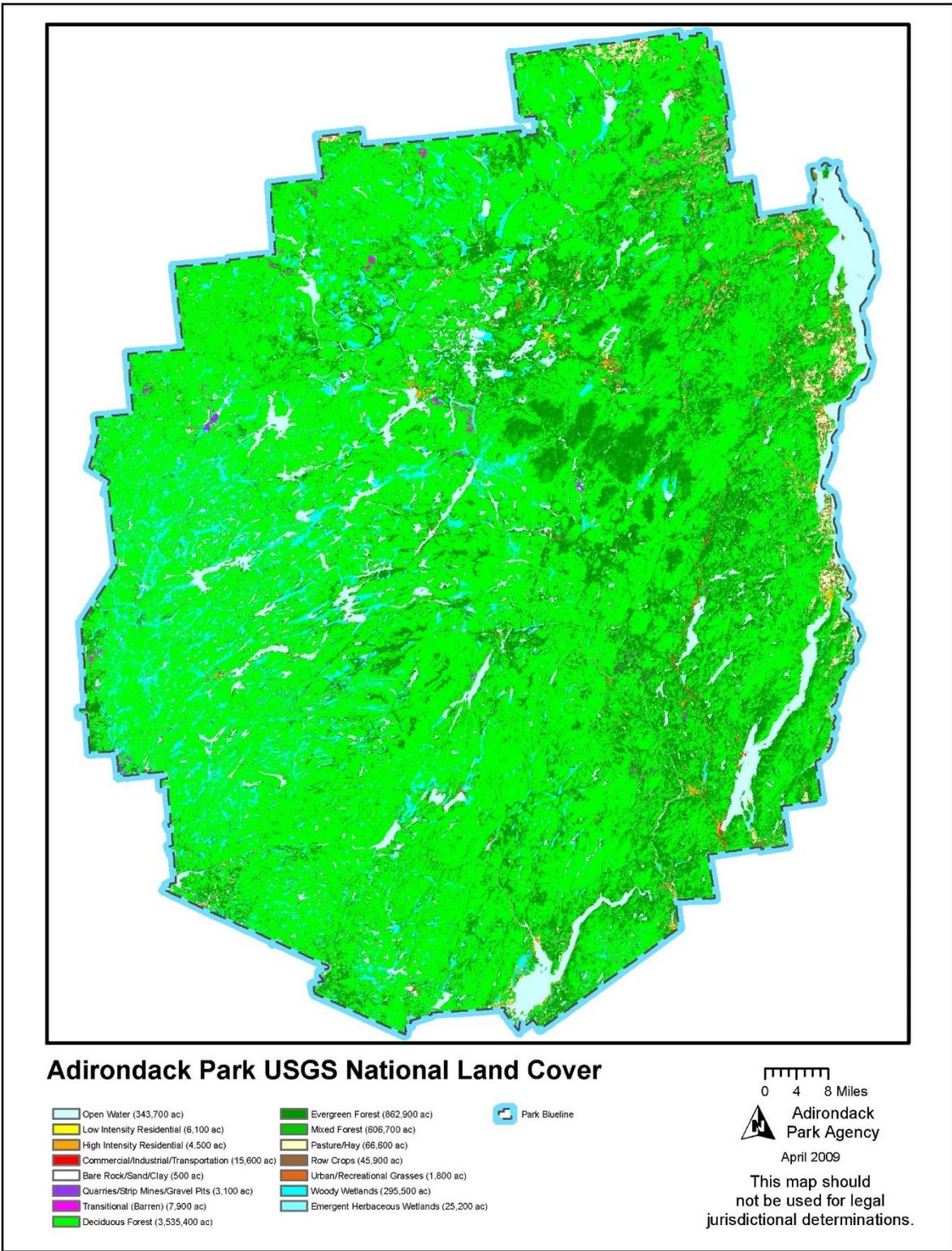


Figure 16-9 Map of Adirondack park land cover.

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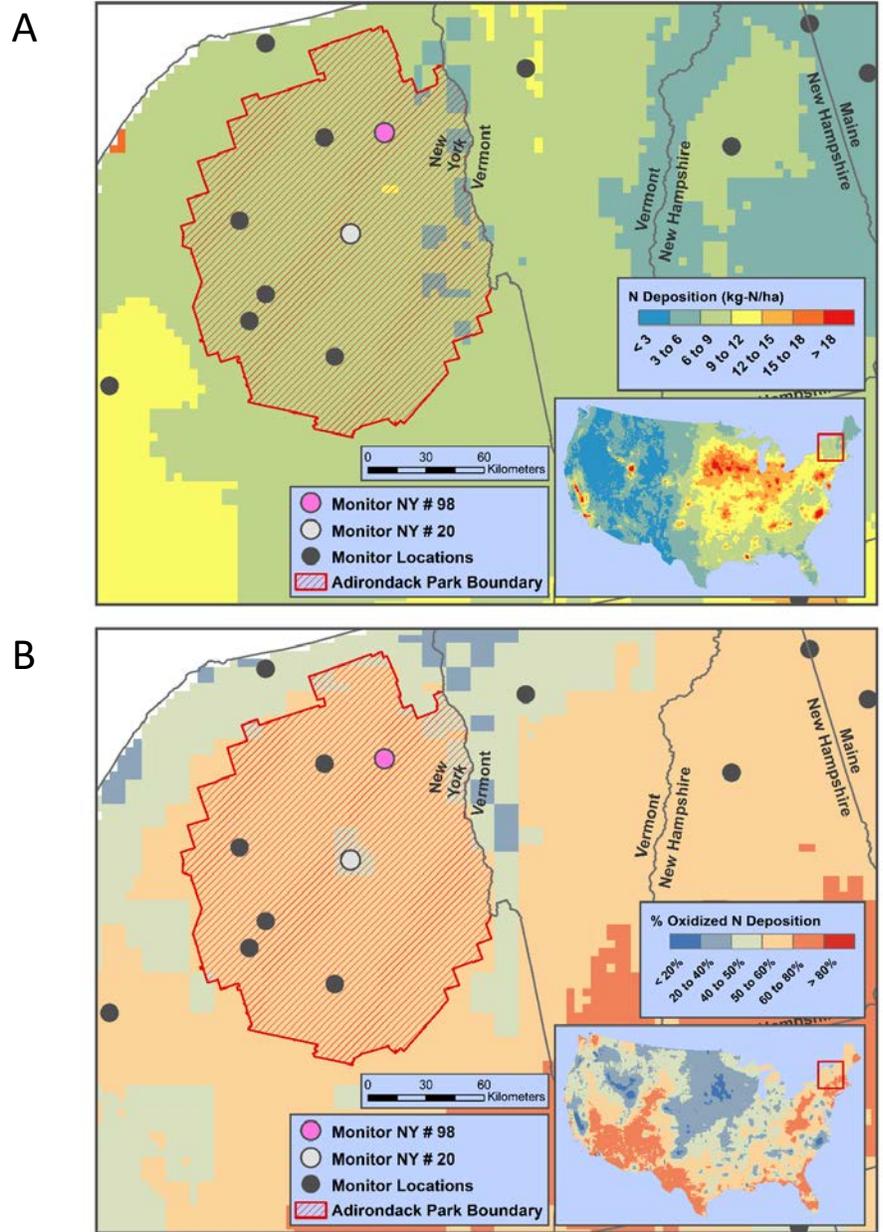
## 16.2.2 Deposition

Characteristics of nitrogen and sulfur deposition affecting the Adirondack region are shown in [Figure 16-10](#) and [Figure 16-11](#). [Figure 16-10A](#) and [Figure 16-11A](#) show 3-year average total deposition of N and S for 2011–2013; [Figure 16-10B](#) shows the partitioning between oxidized and reduced N; [Figure 16-11B](#) shows the 25-year-long time series for wet deposition for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  obtained at the NADP/NTN (National Atmospheric Deposition Program/National Trends Network) monitoring site at Whiteface Mountain, NY (NY98). Surrounding areas in Vermont and New Hampshire and inserts showing the coterminous U.S. (CONUS) are shown to place the depositional environment in context. See [Appendix 2.4](#), [Appendix 2.5](#), and [Appendix 2.6](#) for more information on deposition in the U.S. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

Data shown in the map [Figure 16-10](#) and [Figure 16-11A](#) were obtained from the hybrid modeling/data fusion product, TDEP (Total Deposition, <http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/> and described in Annex 2, Section 2.8). The time series of wet deposition is taken directly from data on the NADP/NTN ([Figure 16-11B](#)). This was done to track changes in deposition since the passage of the Clean Air Act Amendment (CAAA) because the Community Multiscale Air Quality (CMAQ) model simulations used in TDEP extend back only to 2000.

Comparison of [Figure 16-10A](#) and [Figure 16-11A](#) indicates that the general pattern of deposition of N and S is broadly similar; deposition estimates tend to be uniform throughout the Adirondack Park. In addition, the area surrounding the park shows a high degree of regional homogeneity but with higher values to the Southwest. Deposition of N is not as high as in many areas of the central U.S. Deposition of S is considerably lower than along the Ohio River Valley.

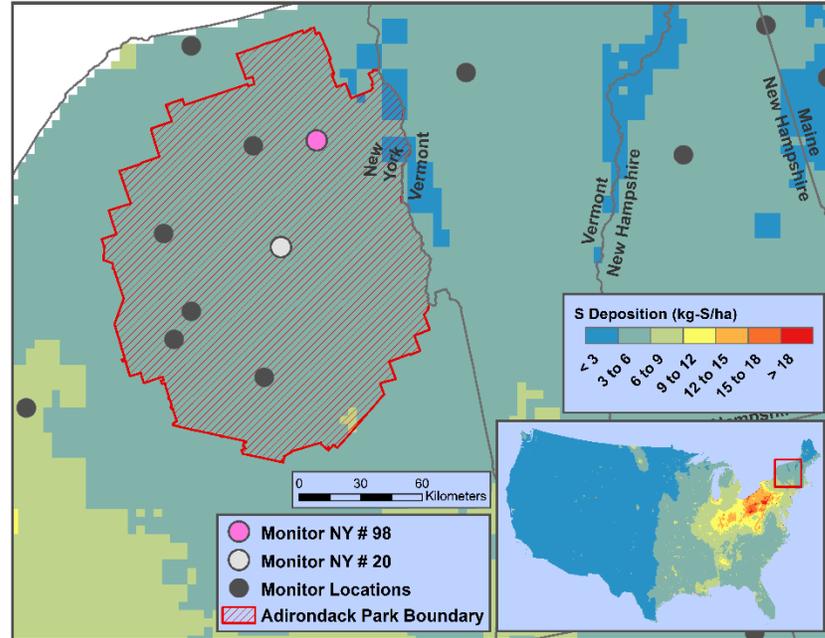
[Figure 16-10B](#) shows that the deposition of nitrogen is estimated to be mostly in oxidized form throughout the entire park. In [Figure 16-11B](#), wet deposition of all species shows that downward trends in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  are consistently found over the past 25 years, although the rate of decrease was variable. In general, wet deposition typically exceeds dry deposition of N and S in this area.



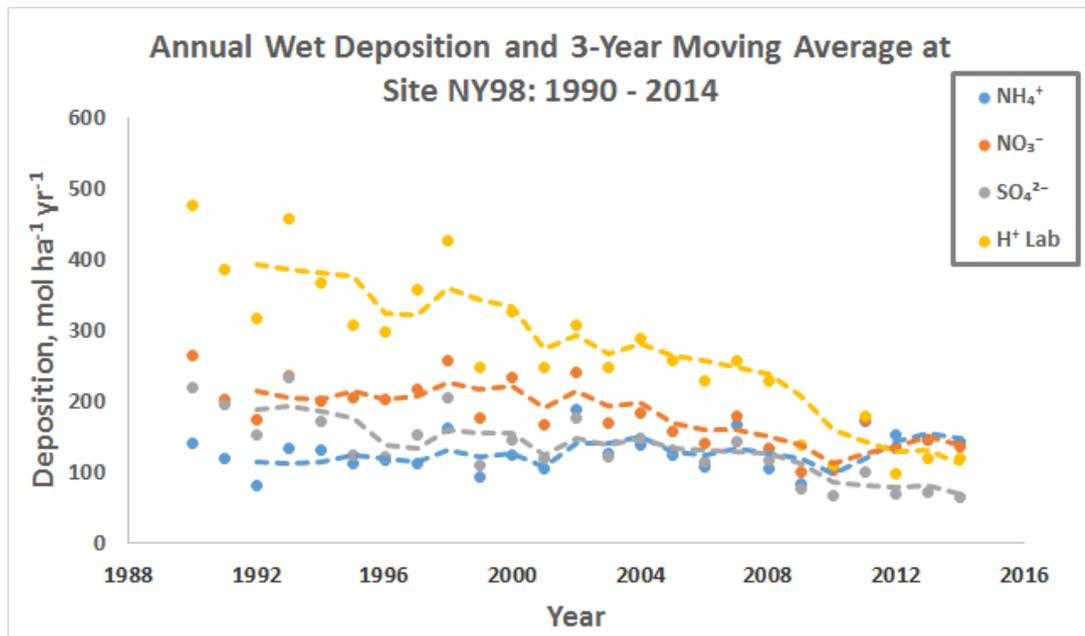
ha = hectare; kg = kilogram; N = nitrogen.

**Figure 16-10** Total nitrogen deposition (A) and percentage of oxidized nitrogen deposition (B) for the Adirondack case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee.

A



B



H<sup>+</sup> = hydrogen ion; ha = hectare; kg = kilogram; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

**Figure 16-11** Total sulfur deposition (A) for the Adirondack case study area estimated by the National Atmospheric Deposition Program Total Deposition Science committee. Time series of wet deposition (B) from the National Atmospheric Deposition Program/National Trends Network Whiteface Mountain, NY.

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## 16.2.3 Critical Loads and Other Dose-Response Relationships

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### 16.2.3.1 Terrestrial

This section presents post-2008 Adirondack area findings on the dose-response relationships of N and S to terrestrial ecology, as well as the critical N and S loads for maintaining ecosystem health. Additional relevant information for the Adirondack region is summarized. The section presents findings on both empirical research and modeling analyses.

#### 16.2.3.1.1 Empirical and Modeling Studies

Post-2000 findings from empirical and modeling studies of terrestrial dose-response relationships and critical loads are summarized in this section. [Table 16-14](#) summarizes the body of empirical and modeling research identified.

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**Table 16-14 Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the Adirondack Mountains.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Community richness and abundance, live biomass	Redback salamanders, calciphilic species of snails	Increasing trends in snail community richness and abundance, live biomass of salamanders, with increasing soil Ca.	14.57 to 19.7 kg/ha/yr as wet NO <sub>3</sub> <sup>-</sup> ; 17.44 to 29.09 kg/ha/yr as wet SO <sub>4</sub> <sup>2-</sup> , modeled ( <a href="#">Ito et al., 2002</a> ) 1990–1999	2009	12 upland hardwood forests	<a href="#">Beier et al. (2012)</a>
Canopy tree basal area	Sugar maple	Sugar maple basal area was positively correlated to forest floor and mineral soil (B-horizon)	14.57 to 19.7 kg/ha/yr as wet NO <sub>3</sub> <sup>-</sup> ; 17.44 to 29.09 kg/ha/yr as wet SO <sub>4</sub> <sup>2-</sup> , modeled ( <a href="#">Ito et al., 2002</a> ) 1990–1999	2009	12 upland hardwood forests	<a href="#">Beier et al. (2012)</a>

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**Table 16-14 (Continued): Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the Adirondack Mountains.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Tree basal area	Sugar maple, black cherry, American beech, red maple, and yellow birch	Sugar maple basal area was positively correlated with mineral soil pH, and yellow birch basal area was positively correlated with mineral soil exchangeable Ca. Sugar maple basal area was also negatively correlated with stream water DOC.	NA	2008	Ha De-Ron-Dah Wilderness Area in Adirondack Mountains	<a href="#">McEathron et al. (2013)</a>
Tree basal area	Sugar maple, American beech, American basswood, and white ash	Relative basal areas of sugar maple and American basswood were positively correlated with mineral soil exchangeable Ca; American beech was negatively correlated; white ash was not correlated.	NA	2004–2005	Adirondack Park	<a href="#">Page and Mitchell (2008)</a>
Sugar maple regeneration	Sugar maple	Plots with lower soil base saturation did not have sugar maple regeneration (these same plots also received higher N and S deposition levels); proportion of sugar maple seedlings dropped substantially at base saturation levels less than 20%.	750 to 1,120 eq/ha/yr as N + S (NADP wet, CASTNET dry)	2009	Adirondack Park	<a href="#">Sullivan et al. (2013)</a>
Canopy vigor and tree growth	Sugar maple	Canopy vigor was positively correlated with soil pH and exchangeable Ca and Mg. Mean growth rates (BAI) were positively correlated with exchangeable Ca and base saturation at the watershed level.	750 to 1,120 eq/ha/yr as N + S (NADP wet, CASTNET dry)	2009	Adirondack Park	<a href="#">Sullivan et al. (2013)</a>

**Table 16-14 (Continued): Terrestrial empirical and modeling research on the response of nitrogen and sulfur deposition for the Adirondack Mountains.**

Variable	Species	Response	Deposition/ Addition (kg N/ha/yr)	Years	Site	Reference
Tree basal area and woody biomass increments	All major trees	Significant positive overall effect of N deposition on tree growth from 1984–2004, but positive growth effects only for red maple, balsam fir, and red spruce at the species level.	Gradient of 3.5–7 kg N/ha/yr	1984–2004	Adirondack Park	<a href="#">Bedison and McNeil (2009)</a>
NO <sub>3</sub> <sup>-</sup> leaching	NA	PnET-BGC Model. Increase due to enhanced net mineralization and nitrification	Not specified	1999–2099	NE	<a href="#">Campbell et al. (2009)</a>
Mineral weathering	NA	PnET-BGC Model. Slight decrease due to reduced simulated soil moisture (negative effect) and increased temperature (positive effect)	Not specified	1999–2099	NE	<a href="#">Campbell et al. (2009)</a>

BBW = Bear Brook Watershed; BC = base cation; C = carbon; Ca = calcium; ForSAFE-VEG = Soil Acidification in Forest Ecosystems; ha = hectare; HBEF = Hubbard Brook Experimental Forest; IPCC = Intergovernmental Panel on Climate Change; kg = kilogram; Mg = magnesium; N = nitrogen; NA = not applicable; ND = no data; NE = northeastern; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> = ammonium sulfate; NO<sub>3</sub><sup>-</sup> = nitrate; PnET-BGC = Photosynthesis and Evapotranspiration-Biogeochemical; S = sulfur; WB = West Bear Brook; yr = year; Zn = zinc.

#### 16.2.3.1.1.1 Critical Loads

Target loads of S deposition were calculated for 44 watersheds and extrapolated to 1,320 acid-sensitive watersheds in the Adirondacks using MAGIC and different soil chemical indicator and thresholds of base saturation (5 and 10%), soil solution Bc:Al, and Ca:Al [1.0 and 10.0; [Sullivan et al. \(2011a\)](#)]. In a comparison of target loads (out to years 2050 and 2100) and the 2002 deposition, only 11.6 to 13.5% of the watersheds were simulated to be in exceedance of target loads to protect soil base saturation to 5%. For target loads to protect soils to a base saturation of 10%, 79.7 to 87.5% of the watersheds were in exceedance. For soil solution Bc:Al, 7.8 and 98.1% of watersheds were exceeded by the 2002 deposition for target loads to protect soil solution ratios of 1.0 and 10.0, respectively. For soil solution Ca:Al, 44.1 to 58.2% of watersheds experienced

exceedances of target loads associated with a soil solution ratio of 1.0, and 98.1% of watersheds with target loads to protect Ca:Al ratios of 10.0 were exceeded. Further investigations revealed that 58.2, 85.7, and 93.6% of watersheds could not obtain threshold values of 10% base saturation, Bc:Al = 10, or Ca:Al = 10, respectively, even if acidic deposition was held at zero, thereby demonstrating that these chemical indicator threshold values were not useful for target load calculations using MAGIC in the Adirondack Mountains.

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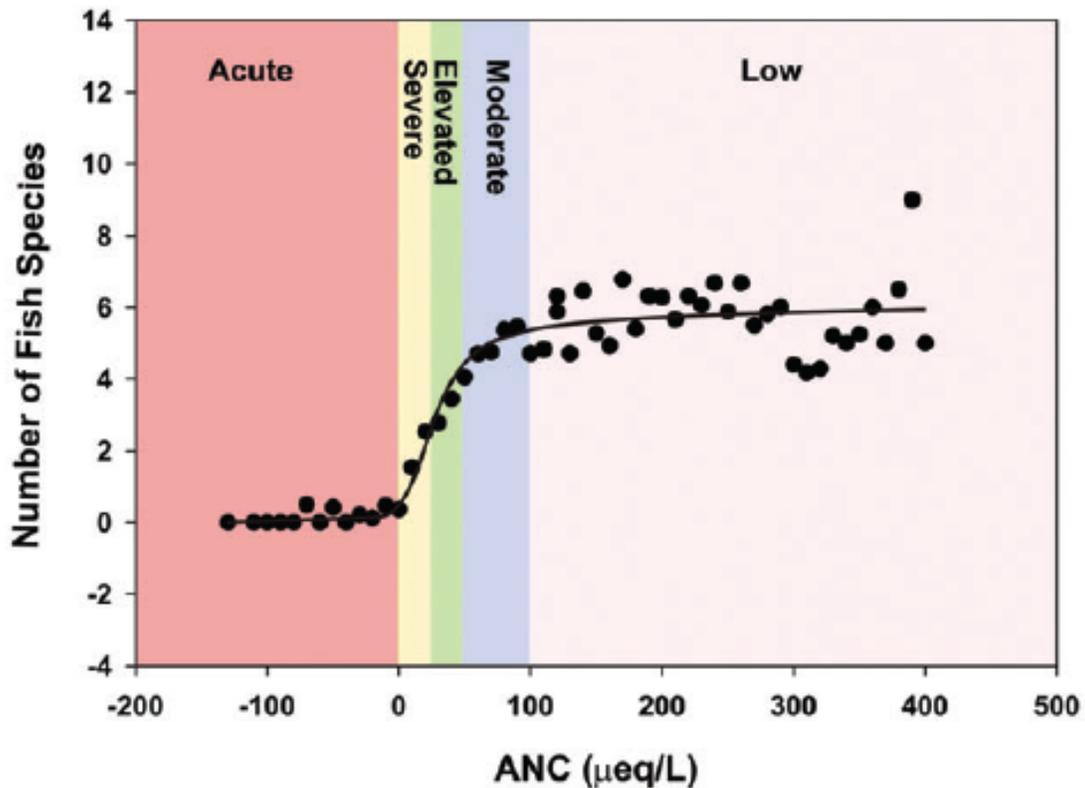
### 16.2.3.2 Aquatic

This section presents research findings at Adirondack Mountains on the dose-response relationships of N and S to aquatic ecology, as well as the critical N and S loads for maintaining ecosystem health. Additional relevant information for the Adirondack region is summarized. Both empirical and modeling studies of aquatic dose-response relationships and critical loads are included in this section.

#### 16.2.3.2.1 Empirical Studies

Studies in the Adirondack Mountains reviewed in the 2008 ISA demonstrated the effect of acidification on fish species richness. Of the 53 fish species recorded in Adirondack lakes, about half (26 species) were absent from lakes with pH below 6.0. Those 26 species included important recreational species plus ecologically important minnows that serve as forage for sport fish ([Baker et al., 1990b](#)). There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100  $\mu\text{eq/L}$  ([Cosby et al., 2006](#); [Sullivan et al., 2006a](#); [Driscoll et al., 2003b](#); [Bulger et al., 1999](#)).

As summarized in the 2008 ISA, lakes and streams having an ANC < 0  $\mu\text{eq/L}$  generally do not support fish ([Figure 16-12](#)). The analysis shown in this figure suggests that there could be a loss of fish species with decreases in ANC below a threshold of approximately 50 to 100  $\mu\text{eq/L}$  ([Sullivan et al., 2006a](#)).



ANC = acid neutralizing capacity; L = liter;  $\mu\text{eq}$  = microequivalent.

Notes: the data are presented as the mean (filled circles) of species richness within 10  $\mu\text{eq/L}$  ANC categories, based on data collected by the Adirondacks Lakes Survey Corporation.

Source: Modified from [Sullivan et al. \(2006a\)](#).

**Figure 16-12** Number of fish species per lake and acidity status, expressed as acid neutralizing capacity, for Adirondack lakes.

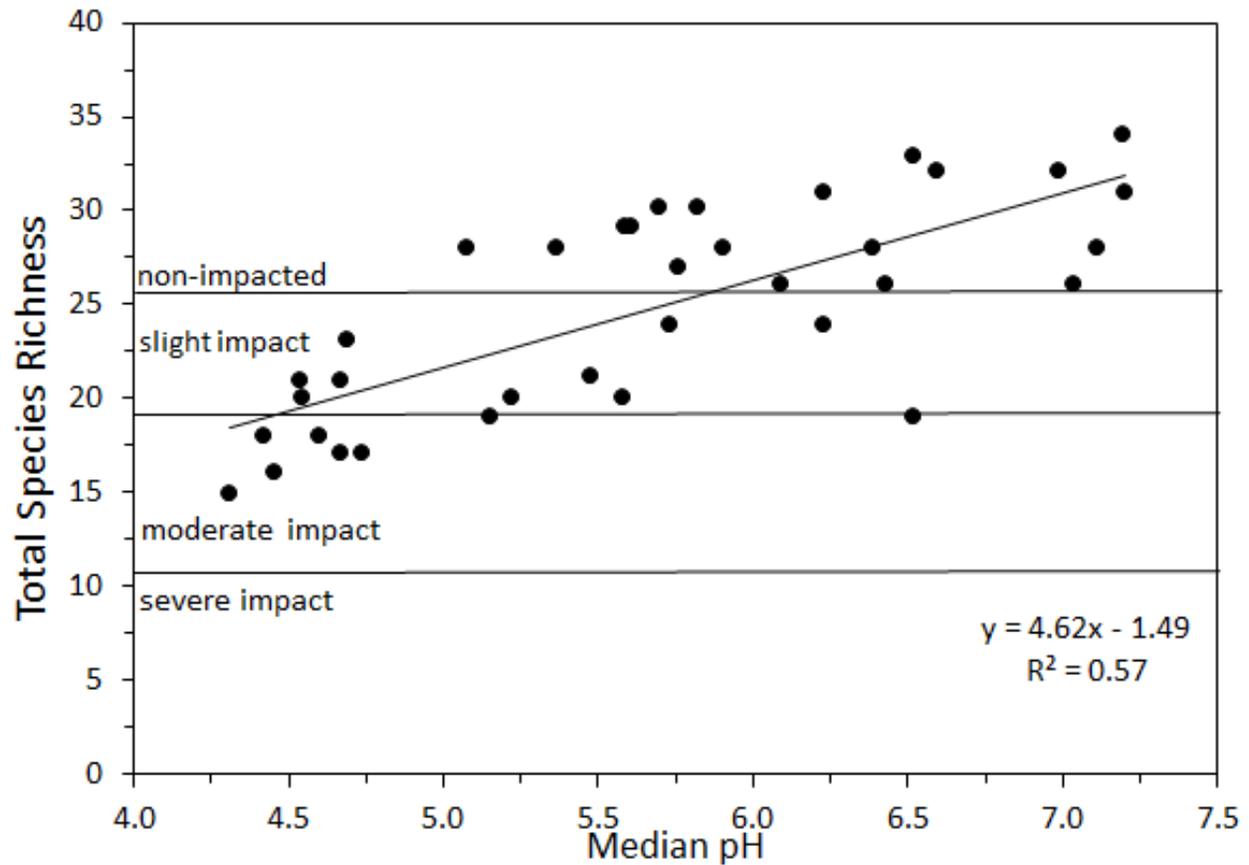
Work by [Baldigo et al. \(2009\)](#) assessed the effects of acidification on benthic macroinvertebrate community dynamics in the southwestern Adirondack Mountains. Water chemistry and benthic macroinvertebrates were surveyed in 36 streams with different levels of acidity to characterize community response and identify thresholds for biological effects ([Figure 16-13](#)). In the study streams, macroinvertebrate assemblages were severely impacted at  $\text{pH} < 5.1$ , moderately impacted at  $\text{pH}$  from 5.1 to 5.7, slightly impacted at  $\text{pH}$  from 5.7 to 6.4 and usually unaffected above  $\text{pH}$  6.4. Inorganic Al concentrations reached potentially toxic levels in two-thirds of the study streams. The authors applied the Acid Biological Assessment Profile [acidBAP] index, which is based on percentage mayfly richness and percentage acid tolerant macroinvertebrate taxa ([Burns et al., 2008b](#)). The acidBAP was strongly correlated with  $\text{pH}$ , ANC, BCS, and the concentration of inorganic Al, indicating the loss of mayflies in the stream as the surface

water's pH declines from pH 7.0 to 4.2. A loss of about 12 species occurred in streams that had a pH between 7 and 4.2. Regression across all 36 streams showed a loss of 4.6 species per unit pH decrease ([Figure 16-13](#)). Inorganic Al toxicity was likely the main cause of the loss of macroinvertebrates. The Al concentration is strongly correlated with surface water pH (as pH decreases, the solubility of inorganic Al increases) and acid-base balance as measured by BCS.

Studies in the Adirondacks have considered effects of species assemblages associated with acid-impacted water bodies. [Nierzwicki-Bauer et al. \(2010\)](#) presented baseline midsummer chemistry and community composition of phytoplankton, bacteria, rotifers, crustaceans, macrophytes, and fish in 30 lakes of the southwestern Adirondacks ([Figure 16-14](#)). Species richness in the lakes was correlated with acid-base chemistry at all trophic levels except bacteria. The decrease in number of taxa per unit pH was similar among groups and ranged from 1.75 (crustaceans) to 3.96 (macrophytes).

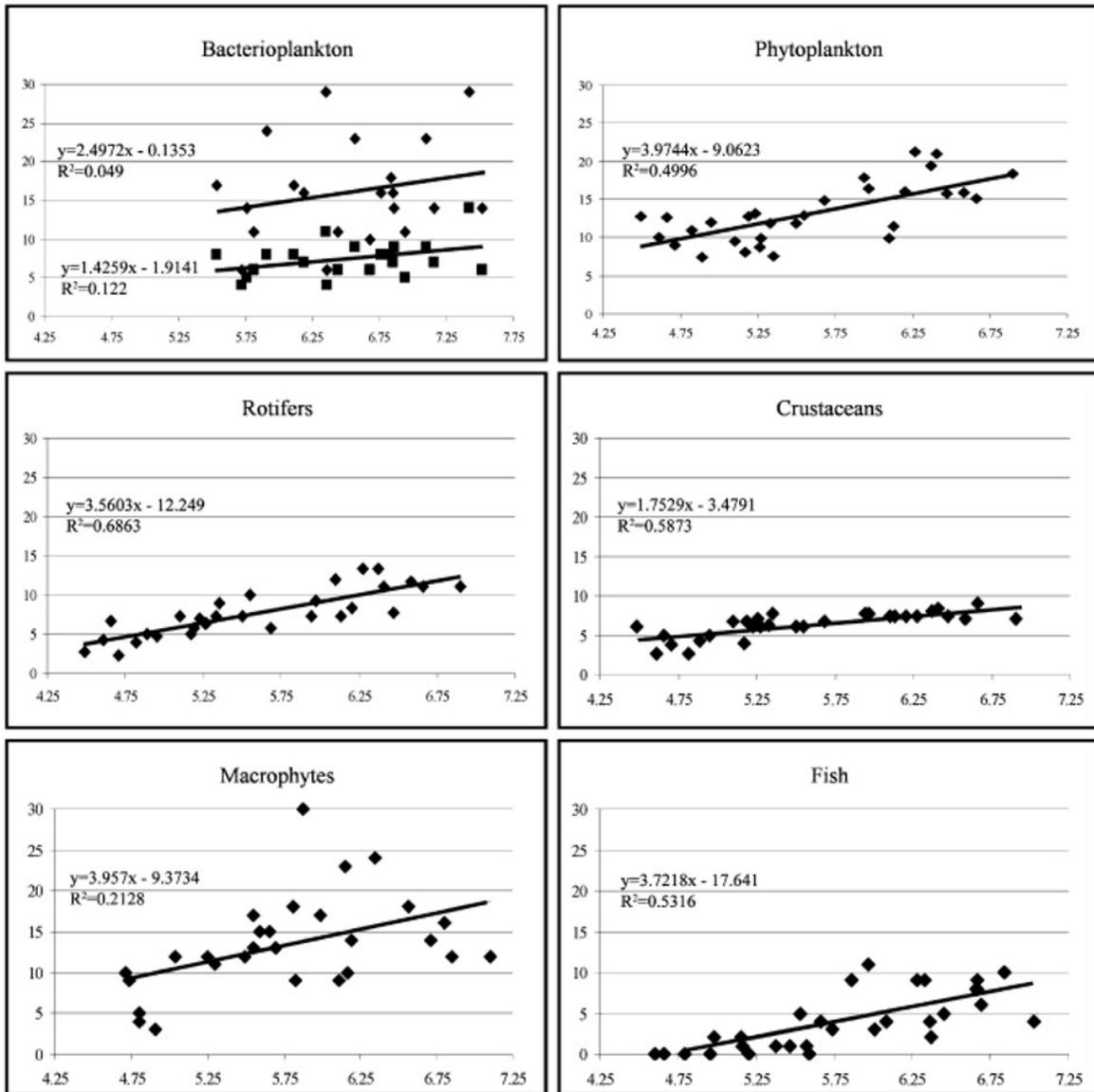
[Percent et al. \(2008\)](#) assessed bacterioplankton community diversity and structure in 18 Adirondack lakes across a range of acid-base chemistry using sequencing and amplified ribosomal DNA restriction analysis of constructed rRNA gene libraries. Based on principal components analysis, pH was positively correlated with bacterioplankton community richness and diversity. The richness of several bacterial classes, including Alphaproteobacteria, was directly correlated with pH. However, other environmental factors, such as lake depth, hydraulic retention time, dissolved inorganic C, and nonlabile (organically bound) monomeric Al, were also important in explaining bacterioplankton community richness and diversity, suggesting that acidity is only one factor that controls community composition.

Post-2008 findings from empirical studies of aquatic dose-response relationships and critical loads are summarized in this section. [Table 16-15](#) compiles the body of empirical research identified.



Source: Modified from [Baldigo et al. \(2009\)](#).

**Figure 16-13** Total macroinvertebrate species (community) richness as a function of median pH in 36 streams sampled in the western Adirondack Mountains of New York, 2003–2005; the four standard (New York State) impact categories for species richness are defined.



## Lake pH

Notes: the y-axis denotes number of groups (bacteria), taxa (phytoplankton) or species (rotifers, crustaceans, macrophytes, fish). The x-axis denotes the pH range that occurred in the 30 study lakes. In the bacterioplankton graph, two regressions were run on the basis of genera (diamonds) and classes (squares).

Source: [Nierzwicki-Bauer et al. \(2010\)](#).

**Figure 16-14** Species richness of biotic groups in 30 Adirondack study lakes relative to midsummer epilimnetic pH during sample years.

**Table 16-15 Aquatic empirical research on the response of nitrogen and sulfur deposition for the Adirondacks.**

Study	Time Period	Focus	Notable Results
<b>Changes to Acidity</b>			
<a href="#">Strock et al. (2014)</a>	1980–2010	Trends in recovery for lakes in the Northeast, including 43 sites in the Adirondack Mountains.	SO <sub>4</sub> <sup>2-</sup> concentration decreased slightly faster in the 2000s than the 1990s—possibly the result of a decline in S emissions that was twice as large in the 2000s than it was in the previous decade. NO <sub>3</sub> <sup>-</sup> concentration did not significantly fall in the 1990s (a decade which had more modest N emissions reductions) but did significantly fall in the 2000s, which saw large N emission reductions.
<a href="#">Mitchell et al. (2013)</a>	1984–2010	S deposition response in 16 Adirondack long-term monitoring Lakes.	SO <sub>4</sub> <sup>2-</sup> concentration has declined significantly along with total S deposition. However, there is a discrepancy in the balance of deposition inputs and discharge outputs. The authors conclude that internal S supplies are likely contributing to high sulfur concentrations and the slow recovery of lakes in the region, and that internal S will become a more important factor as emissions decline.
<a href="#">Waller et al. (2012)</a>	1991–2007	The effectiveness of the Acid Rain Program and Nitrogen Budget Program in the 1990 CAAA in reducing Adirondack lake acidity for 42 lakes.	Sulfate concentration declined by 23.47% over the study period, but nitrate concentration did not significantly decline. ANC has increased over the study period, with the number of lakes with ANC <0 dropping by 46%. ANC <sub>G</sub> was higher than ANC <sub>calc</sub> , suggesting contribution to acidity from naturally occurring organic acids that are not factored into ANC <sub>calc</sub> .
<a href="#">Baron et al. (2011b)</a>	1997–2006	Empirical N loads in 216 northeastern U.S. lakes including Adirondack lakes.	Minimally disturbed Northeast lakes were estimated to have thresholds of 3.5–6.0 kg N/ha/yr for avoidance of acidic episodes.
<a href="#">Lawrence et al. (2011)</a>	1985–2008	Focuses on 12 Adirondack streams rather than lakes.	The pH in streams with lower ANC was more responsive to the 50% reduction in S deposition over the study period than pH in streams with high ANC. Authors noted “a more muted recovery response” in streams compared to what has been reported in lakes.
<a href="#">Inamdar and Mitchell (2008)</a>	2002–2004	Point Peter Brook watershed in Western New York and fluxes of sulfate following storms.	Results suggested that groundwater sources have greater impact on changes to sulfate flux in observed lakes than does deposition through precipitation.
<a href="#">Warby et al. (2008)</a>	1986–2001	Speciation and concentration of Al in 113 northeastern U.S. lakes (including the Adirondacks) and the effect of decreased acid deposition.	The Adirondack lakes had the largest decline in Al concentration of all lakes studied (Adirondacks: 2.01 μmol/L; all: 0.44). For reference, the decline in SO <sub>4</sub> <sup>2-</sup> deposition in the Adirondacks was about the same as the decline in the region as a whole.

**Table 16-15 (Continued): Aquatic empirical research on the response of nitrogen and sulfur deposition for the Adirondacks.**

Study	Time Period	Focus	Notable Results
<b>Changes to Biota</b>			
<a href="#">Sutherland et al. (2015)</a>	1984–2012	Brooktrout Lake acidification and biotic recovery.	Likely as a result of the 1990 Clean Air Act Amendments, $\text{SO}_4^{2-}$ concentrations have dropped 56% or 2 $\mu\text{equiv/L/yr}$ since the 1980s. Plankton species richness has also blossomed, though crustacean species richness has had less impressive growth (possibly due to pressures exerted by the predator-free glassworm, <i>Chaoborus</i> ). Brook trout ( <i>Salvelinus fontinalis</i> ) are now successfully surviving and reproducing after their reintroduction in 2005.
<a href="#">Josephson et al. (2014)</a>	1960–2011	Honnedaga Lake watershed recovery.	There has been significant decline in $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ since 2001, when consistent measurements in surface water chemistry began. There were no notable trends in zooplankton species richness as lake acidity dropped over the observation period, but there was a significant resurgence of adult brook trout in the 2000s compared to catches in the 1970s (a nearly sixfold increase). The authors noted the relationship between acidity and aluminum toxicity for fish. Recovery of adult trout could be improved by lower acidity tributaries that would make a friendlier environment for young-of-year trout.
<a href="#">Yu et al. (2011)</a>	2003–2004	Focused on Hg concentrations in biota of 44 lakes (not $\text{NO}_x\text{SO}_x$ but relevant to acidity).	Lower ANC in surface water was correlated with higher Hg concentrations in the tissues of fish, loons, and zooplankton.
<a href="#">Nierzwicki-Bauer et al. (2010)</a>	1994–2006	Correlation between species richness and acid-base chemistry of 30 Adirondack lakes.	For each unit of pH (toward increased acidity), species richness dropped from 1.4–1.8 (bacterial classes, crustaceans) to above 3.5 (fish, rotifers, phytoplankton, macrophytes). Authors classified species into a system of brackets describing acid sensitivity or tolerance, with most fish species being considered acid sensitive.
<a href="#">Baldigo et al. (2009)</a>	2003–2005	Macroinvertebrate response to acidification of 36 streams in the Adirondack region.	Species richness was measured by acid bioassessment profile (acidBAP) scores. In about half of streams, acidBAP scores were moderately or severely impacted (44%) from low pH—this increased to about two-thirds of streams when including slight impacts (69%).
<a href="#">Percent et al. (2008)</a>	2002–2002	Acidity and bacterial communities in 18 Adirondack lakes.	Authors reported a significant decline in bacterial species richness and species diversity with increasing acidity. However, they did not find the overall bacterial community composition to be significantly affected.

Notes: ANC = acid neutralizing capacity.

### 16.2.3.2.2 Modeling Studies

Post-2008 findings from modeling studies of aquatic dose-response relationships and critical loads are summarized in this section. [Table 16-16](#) compiles the body of research identified.

**Table 16-16 Critical and target load and exceedance modeling studies in Adirondack Mountains.**

Reference	Model	Focus	Notable Results
<a href="#">Sullivan et al. (2012a)</a>	MAGIC and regional extrapolation of model	TL for lakes in 2050 and 2100	To achieve ANC = 50 µeq/L in 2100, about 30% of lakes had simulated TL of S deposition <500 eq/ha/yr and about 600 lakes were in exceedance.
<a href="#">Zhou et al. (2015b)</a>	PnET-BGC	TL link to fish and zooplankton richness	The magnitude of simulated historical acidification represented by ANC loss ranged from about 26 to 100 µeq/L. The amount of historical acidification of the lakes was related to the total ambient deposition of SO <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> , the Ca weathering rate, and the simulated preindustrial ANC in the year 1850. Adirondack lakes have lost fish and total zooplankton species richness beginning with the onset of acidic deposition. Modeling results suggested that complete recovery to preindustrial conditions may not be possible for most acidified lake ecosystems.
<a href="#">Zhou et al. (2015c)</a>	PnET-BGC	Effects of biophysical factors on the TL in lakes	Model simulations suggested that future decreases in SO <sub>4</sub> <sup>2-</sup> deposition would be more effective in increasing the lake water ANC than equivalent decreases in NO <sub>3</sub> <sup>-</sup> deposition. The difference was a factor of 4.6 during the period 2040 to 2050 but decreased to a factor of 2 by the year 2200. Lakes that had longer hydrologic residence exhibited less historical acidification and therefore could achieve a higher ANC in response to chemical recovery compared with lakes that had short hydrologic residence times.
<a href="#">Fakhraei et al. (2014)</a>	PnET-BGC	TMDLs for 128 acid-impaired lakes	Model simulations suggested that an S TL equal to 79 eq S/ha/yr (representing a 60% decrease from ambient deposition) would lead to ANC recovery at a rate of 0.18 µeq/L/yr through 2050, with reduced rate of recovery thereafter.

**Table 16-16 (Continued): Critical and target load and exceedance modeling studies in Adirondack Mountains.**

Reference	Model	Focus	Notable Results
<a href="#">NAPAP (2011)</a>	SSWC	Combined deposition load of S and N to which a stream and its watershed could be subjected and still have a surface water concentration ANC of 50 µeq/L on an annual basis	To achieve ANC = 50 µeq/L on average, critical load of sulfur and nitrogen for lakes in the Adirondack Mountains is 1,620 eq/ha/yr
<a href="#">Sullivan (2015)</a>	MAGIC and regional extrapolation of model	Development and application of tools to document and quantify TL and their exceedances	To achieve ANC values of 50 and 20 µeq/L in the year 2050 and 2100, the TL to protect against acidification of surface waters was exceeded throughout the Adirondack Mountains.

ANC = acid neutralizing capacity; CL = critical load; ForSAFE-VEG = Soil Acidification in Forest Ecosystems; MAGIC = Model of Acidification and Groundwater in Catchments; N = nitrogen; PnET-BGC = Photosynthesis and Evapotranspiration-Biogeochemical; S = sulfur; SSWC = Steady-State Water Chemistry; TL = target load; TMDL = total maximum daily load; VSD = very simple dynamic.

## 16.2.4 Long-Term Monitoring

This section summarizes research on the long-term effects of S and N deposition in the Adirondacks.

### 16.2.4.1 Long-Term Monitoring of Acidification

Acidic deposition has been shown to be an important factor causing decreases throughout much of the Northeast region in concentrations of exchangeable base cations in soils, which were naturally low historically. Base saturation values less than 12% predominate in the B-horizon in portions of the region where soil and surface water acidification from acidic deposition have been most pronounced ([Sullivan et al., 2006a](#); [Bailey et al., 2004](#); [David and Lawrence, 1996](#)).

At the time of the 2008 ISA, the region of the U.S. most thoroughly studied to ascertain changes in acid-base surface water chemistry over time was the Adirondack Mountains. This has not changed. Several new studies are highlighted here that focused on Adirondack surface waters, three on lakes and one on streams. The Adirondack Lakes Survey Corporation (ALSC) has been monitoring Adirondack lakes for about 30 years. This work has mainly focused on acid-base chemistry but has also involved some fish monitoring and measurement of parameters relevant to nutrient enrichment. Monitoring

data have shown some chemical recovery from lake acidification, reflected in increased pH and ANC and decreased inorganic Al concentrations.

A mass balance study by [Mitchell et al. \(2011\)](#) for 15 watersheds located in the northeastern U.S. and southeastern Canada suggested substantial sources of  $\text{SO}_4^{2-}$  in watershed soils. The internal S sources were attributed mainly to mineralization of S stored in soils in response to decades of atmospheric S deposition. [Mitchell et al. \(2013\)](#) studied 16 of the original Adirondack Long-Term Monitoring lakes that were monitored between 1984 and 2010. Total S deposition significantly declined in all of the study lake watersheds during the monitoring period. Correspondingly, significant decreases were observed over time ( $-2.14 \mu\text{mol/L/year}$ ) in lake  $\text{SO}_4^{2-}$  concentrations. The authors observed discrepancies in the calculated S mass balances that were associated with discharge. These results suggested that internal S sources have become more important to the watershed S budget as atmospheric S deposition has decreased. The watershed supply of  $\text{SO}_4^{2-}$  was lower in those watersheds that contained lakes that had lower ANC. Limited contributions from internal sources of  $\text{SO}_4^{2-}$  to the low-ANC lakes will allow ANC recovery. [Mitchell et al. \(2013\)](#) further concluded that the effects of future increases in precipitation might become more important in regulating the amount of  $\text{SO}_4^{2-}$  mobilized from internal watershed sources.

Surface water ANC and pH recovery has been documented by [Lawrence et al. \(2013\)](#) and [Lawrence et al. \(2011\)](#) in studies of Adirondack streams and lakes. [Lawrence et al. \(2011\)](#) reported results of Adirondack Mountain stream monitoring from the early 1980s to 2008. During that period, there was an approximate 50% reduction in atmospheric deposition of S in the Adirondack region. On average, the pH increased by only 0.28 pH units and ANC by  $13 \mu\text{eq/L}$  in 12 streams that were monitored over a period of 23 years. Larger increases in ANC and pH occurred in the monitored streams that had lower initial ANC. In the north tributary of Buck Creek that had a relatively high DOC concentration, the  $\text{SO}_4^{2-}$  concentration decreased between 1999 and 2008 at a rate of  $2 \mu\text{mol/L/year}$ . In the adjacent south tributary, which had a lower DOC concentration, the decrease in  $\text{SO}_4^{2-}$  concentration was substantially smaller, only  $0.73 \mu\text{mol/L/year}$ . [Driscoll et al. \(2016\)](#) observed increases in ANC and pH and marked decreases in dissolved inorganic Al in 45 of 48 study lakes in the Adirondack region from 1982 to 2015, corresponding to decreases in acidifying deposition.

[Michelena et al. \(2016\)](#) reported changes in the water chemistry of 30 Adirondack lakes, in response to reductions in acidic deposition from 1994 to 2012. The water quality of the study lakes generally improved during the study period, but the responses were sporadic and complex. Lake pH values increased until about 2002 and then fluctuated. Inorganic Al concentrations generally decreased throughout the period of record. During the early

years of monitoring, the average pH increased dramatically from about 5.5 to 6.0. This increase was followed by a period of reacidification for about 5 years, followed by another period of increased pH. This 5-year cycle was then repeated to a muted extent, even though acidic deposition continued to decline.

Chemical recovery from surface water acidification, and associated CL exceedance, in the Adirondack Mountains has been accompanied by increasing concentrations of DOC and organic acids, which have complicated and restricted recovery from acidification. [Lawrence et al. \(2013\)](#) reported the chemistry of 42 Adirondack lakes from samples collected between 1994 and 2011. They evaluated long-term changes in DOC and BCS (which reflects the calculated ANC and includes an adjustment for strong organic acid anions). Increases in DOC concentration during the study period contributed to organic complexation of Al. This reduced the fraction of monomeric Al that was in the inorganic (and potentially toxic) form from 57% in 1994 to 23% in 2011. Thus, the higher DOC found during the latter sampling period increased the organic acidity of the lake water and limited ANC recovery, but at the same time it decreased the toxicity of dissolved Al to aquatic biota. Similarly, [Strock et al. \(2014\)](#) reported trends in recovery from acidification of northeastern U.S. surface waters associated with Al chemistry. They analyzed recent trends in lake chemistry using long-term data from lakes in the Adirondack Mountains and New England. During the 2000s, the wet deposition of  $\text{NO}_3^-$  declined more than 50%. The lake  $\text{NO}_3^-$  concentration, which showed no trend prior to 2000, declined subsequent to 2000 at a rate of  $-0.05 \mu\text{eq/L/year}$ . There was a shift to nontoxic (organic) forms of Al. Despite the Al recovery, both the ANC and pH in the study lakes failed to show evidence of appreciable chemical recovery; rather, the lakes continued to exhibit variable trends in ANC and pH.

[Waller et al. \(2012\)](#) also evaluated the response of lake watersheds in the Adirondack Mountains to changes in  $\text{SO}_2$  and  $\text{NO}_x$  emissions and deposition, in this case using data from the TIME monitoring program collected during the period 1991 to 2007. The percentage of Adirondack lakes that were acidic decreased from an estimated 15.5 to 8.3%. Decreases in lake water  $\text{SO}_4^{2-}$  concentrations, and to a lesser extent  $\text{NO}_3^-$  concentrations, generally were accompanied by increases in lake ANC. However, the calculated ANC increased more than twice as much as the Gran titrated ANC. This discrepancy is important for assessing lake recovery from acidification. It appeared to be due mainly to increases in DOC (and associated organic anions) that accompanied decreases in concentrations of the strong mineral acid anions,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . The difference between calculated ANC and Gran titrated ANC was generally consistent with trends of increasing DOC. [Waller et al. \(2012\)](#) concluded that assessments of surface water recovery from previous acidification should consider differences in DOC concentration and in the manner in which ANC is calculated and quantified.

Interpretation of long-term trends in Adirondack surface water chemistry, as summarized above, has also been augmented by results of repeated surveys of the chemistry of lakes initially surveyed several decades previously. [Warby et al. \(2008\)](#) resurveyed 113 lakes throughout the Northeast in 2001 that had previously been sampled by the U.S. EPA in 1986 to assess chemical recovery from lake acidification. Decreases in total Al and inorganic Al concentrations were widespread and largest in the Adirondack Mountains (−2.59 to −4.60  $\mu\text{mol/L}$ ). In 2001, only 7 study lakes (representing 130 lakes in the population) had inorganic Al concentrations above a toxic limit of 2  $\mu\text{mol/L}$ , compared with 20 sampled lakes (representing 449 lakes in the population) in 1986. Thus, it was estimated that in 2001 more than 300 northeastern lakes no longer had summer inorganic Al concentrations at levels considered harmful to aquatic biota.

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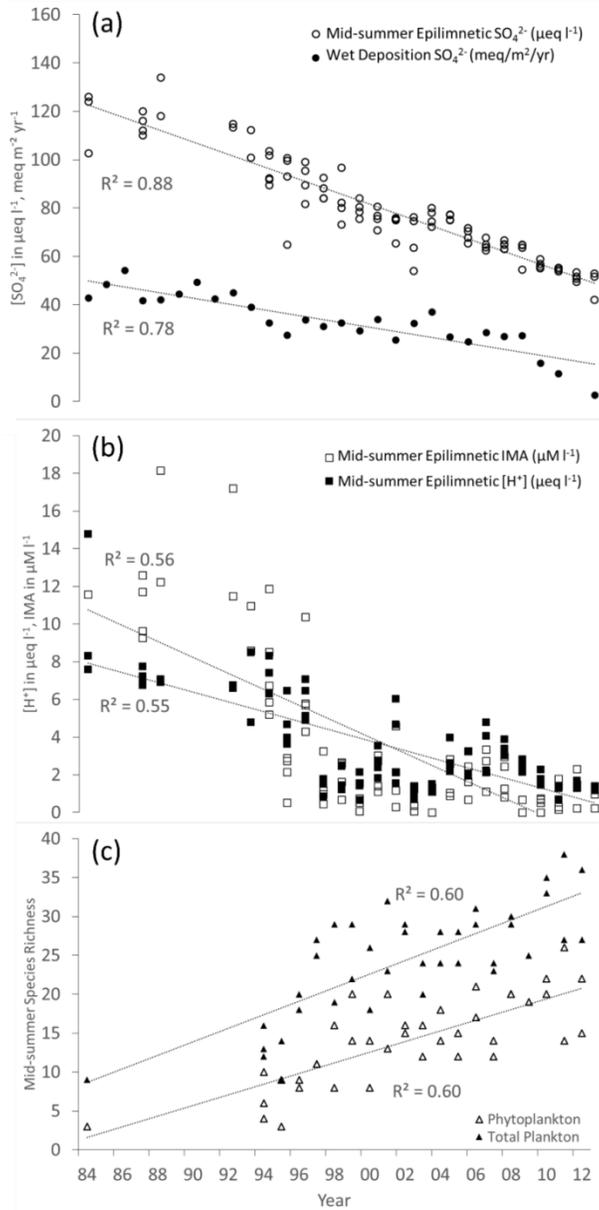
#### 16.2.4.2 Recovery

Biological recovery from past acidification is a process affected by chemical, climatic, biological, and hydrologic influences over time. It may, under certain conditions, follow chemical recovery of such water quality constituents as pH, ANC, and the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , inorganic Al, and DOC. Both chemical and biological recovery can, and often does, lag behind changes in the levels of S and/or N emissions and deposition because of chemical, hydrological, and biological processes and constraints. Studies at Honnedaga Lake and Brooktrout Lake in the Adirondacks show evidence for return of biota to levels approaching preacidification levels ([Sutherland et al., 2015](#); [Josephson et al., 2014](#)). In Brooktrout Lake, biological recovery of the food web structure has begun, in part, due to reintroduction and re-establishment of brook trout in the lake. However, ongoing biological recovery cannot necessarily be expected to conclude with the return of the biological community to preacidification conditions. The reason is due to factors such as differences in the rate of recovery of aquatic organisms, permanent loss of some acid-sensitive species, and irreversible chemical and physical alterations to aquatic environments during acidification ([NAPAP, 2011](#)).

Since the 2008 ISA, some paleolimnological studies have been conducted that documented historical acidification and subsequent recovery (see [Appendix 8](#)). In one study from the U.S., diatom shifts were linked to historical changes in pH at Brooktrout Lake in the Adirondacks. *Fragilariforma acidobiontica*, a diatom that is often abundant at pH <5.0, was present in lake sediments deposited since the 1950s, and shifts in *Mallomonas* and *Synura* were also observed ([Sutherland et al., 2015](#)). In this study, phytoplankton and rotifer taxonomic richness showed substantial increases ([Figure 16-15](#)) in association with pronounced decreases in lake  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and inorganic Al concentrations. In contrast, species richness of crustaceans changed little. [Sutherland](#)

[et al. \(2015\)](#) suggested that the absence of crustacean recovery may have been due to the severity of the initial stress and continuing toxic pH conditions during some seasons, and/or to a large population of predatory *Chaoborus* larvae present since the early 1980s when fish were absent from the lake. In another study, [Arseneau et al. \(2016\)](#) concluded that Adirondack lakes that were not previously acidified by acidic deposition will likely not recover to predisturbance chrysophyte community structure because of the influence of other stressors, including changes in climate.

Despite observed reductions in acidic deposition and improvement in water quality of New York lakes, [Baldigo et al. \(2016\)](#) found no evidence of widespread or substantial biological recovery of brook trout populations or broader fish communities in the Adirondack Mountains. The study focused on 43 lakes sampled by the Adirondack Lakes Survey Corporation during three time periods (1984–1987, 1994–2005, and 2008–2012). Metrics reflecting fish species richness, abundance of fish species, and abundance of brook trout did not change significantly over the 28-year period across the group of study lakes despite a significant average ANC increase and a decrease in inorganic Al over time. Fish species richness and catch of all fish species per net-night were positively related to lake chemistry reflecting some limited degree of biological recovery. The authors speculated that additional time may be needed for fish recolonization.



H<sup>+</sup> = hydrogen ion; IMA = inorganic monomeric aluminum;  $\mu\text{eq}$  = microequivalent;  $\mu\text{M}$  = micromolar; m = meter;  $\text{SO}_4^{2-}$  = sulfate; yr = year.

Source: [Sutherland et al. \(2015\)](#).

**Figure 16-15 (A) Midsummer sulfate concentration in the epilimnion of Brooktrout Lake (○) and in annual wet deposition (●) at local National Atmospheric Deposition Program/National Trends Network Station NY52 from 1984–2012. (B) Midsummer epilimnetic concentrations of inorganic monomeric aluminum (□) and hydrogen ion (■) in Brooktrout Lake from 1984–2012. (C) Midsummer phytoplankton (Δ) and total plankton (phytoplankton, rotifers, crustaceans) (▲) species richness in Brooktrout Lake from 1984–2012.**

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## 16.3 Southeastern Appalachia Case Study

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### 16.3.1 Background

This case study focuses on the Great Smoky Mountain National Park and on several closely located Class I areas in North Carolina (Joyce Kilmer Forest, Linville Gorge, Shining Rock). These areas are representative of the southern Appalachian region and also have been the focus of research on the ecological impacts of historical and current NO<sub>x</sub> and SO<sub>x</sub> deposition. The case study summarizes literature published since 2008, although older studies are included when relevant (e.g., conducted in Class I areas for the purpose of investigating critical loads). The southern Appalachians are in the Eastern Temperate Forests ecoregion, so critical loads for the broader Level I ecoregion are also presented.

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#### 16.3.1.1 Description of Case Study Region

This case study focuses on the southern Appalachian Mountains, with special emphasis on Great Smoky Mountains National Park (GRSM), located on the border between eastern Tennessee and western North Carolina. The park consists of 2,100 km<sup>2</sup> of mountain ridges and valleys and ranges over an elevation of 267 to 2,025 m ([Thornberry-Ehrlich, 2008](#)), with peaks at the highest elevations in the eastern U.S. The wide range in elevation, annual precipitation [140 cm in valleys and 215 cm on ridges and peaks; [Thornberry-Ehrlich \(2008\)](#)], and temperature [growing season temperatures are 10–15°C cooler on ridge tops and peaks than in valleys; [Lesser and Fridley \(2016\)](#)] within the park has allowed distinct terrestrial and aquatic communities to form at different elevations.

Geologically, the park is in the Blue Ridge physiographic province, where Cambrian crystalline quartzite forms ridges, and Precambrian metamorphic rocks underlie the valleys, particularly in the eastern part of the park. Carbonates and shales of the Valley and Ridge province underlie valleys in the western part of the park where deposits of dolomite provide substantial base cations to drainage water. The Anakeesta Formation sits at the highest elevation of the Great Smoky Group, which forms the crest of the mountains. The Anakeesta Formation contains iron sulfide minerals that contribute to soil solution and surface water sulfate; it has outcroppings at Clingmans Dome, Newfound Gap, and Chimney Tops, as well as at other high-elevation locations in the north-central section of the park.

Soils of the Blue Ridge tend to be thin and shallow, overlying steep terrain ([Thornberry-Ehrlich, 2008](#)). Park soils are highly weathered and, particularly on mountain tops and ridges, have substantial soil S adsorption capacity and limited base cation supply ([Elwood, 1991](#)). Linville Gorge Wilderness is also within the Blue Ridge Province, with soils that formed with low Ca, Mg, and K concentrations, in which base cation concentrations have further declined in response to acid deposition ([Elliott et al., 2013](#)).

There are 3,200 km of streams within the park's boundaries ([Nichols and Langdon, 2007](#)). Streams in the park are first through sixth order, and their chemistry is strongly influenced by geology and storm events, as well as by acidic deposition. In 2006, Tennessee listed 12 streams (67 km stream length) within GRSM as impaired under the Clean Water Act Section 303d, because mean stream pH was below 6.0 ([Fakhraei et al., 2016](#)). Streams in GRSM that have ANC between 50 and 200  $\mu\text{eq/L}$  (41%) are mostly influenced by limestone weathering and tend to be located in the western portion of the park ([Neff et al., 2009](#)). Most stream ANCs in the park (54.2%) are in the 0–50  $\mu\text{eq/L}$  range. Streams that have ANC near or below 0  $\mu\text{eq/L}$  (2.4%) are influenced by weathering of the Anakeesta Formation and are mainly located in the north-central portion of the park ([Neff et al., 2009](#); [Flum and Nodvin, 1995](#)). Within the park, hindcasting by PnET-BGC model simulations suggested that ANC in park streams in 1850 ranged from 28 to 107  $\mu\text{eq/L}$ , with lower ANC at higher elevations ([Zhou et al., 2015a](#)). In the broader southern Blue Ridge province, MAGIC model simulations hindcasted to 1860 suggested that 66 modeled streams had preindustrial ANC > 30  $\mu\text{eq/L}$ ; in 2005, 30% of the streams had ANC below that level ([Sullivan et al., 2011c](#)). Streams in the Blue Ridge region with ANC < 20  $\mu\text{eq/L}$  were underlain by siliceous bedrock, including sandstone and quartzite ([Sullivan et al., 2007b](#)).

Storm events cause episodic acidification in streams, with decreases in pH of 0.5 to 1.6 pH units in streams with ANC of <20  $\mu\text{eq/L}$  under high-flow conditions ([Lawrence et al., 2015b](#); [Deyton et al., 2009](#)). Stream chemistry responses to storm events varies by elevation within the park. At high elevations, stream pH decreased by as much 0.5–2.0 pH units during storm events in 1990–2008 ([Neff et al., 2009](#); [Cook et al., 1994](#)), and streams above 975 m in elevation had significantly lower pH and ANC and higher nitrate concentrations during storm events than did lower elevation streams ([Neff et al., 2013](#)). High-elevation streams (823–966 m elevation) in the Little Pigeon River watershed had lower ANC and pH during storm events and higher sulfate, nitrate, and organic acid anion concentrations than at low flow ([Deyton et al., 2009](#)). Streams in watersheds influenced by the Anakeesta Formation also had significantly lower pH and higher Al concentrations during storm flow ([Neff et al., 2013](#)).

GRSM historically received some of the highest deposition loads of NO<sub>x</sub> and SO<sub>x</sub> in the U.S. In the late 1980s, a monitor at 1,740 m elevation within the park estimated S deposition of approximately 2,200 kg S/ha/yr, about half of which was occult deposition ([Johnson and Lindberg, 1992](#)); long-term trends in deposition from a monitor placed at a lower elevation within the park are shown in [Figure 16-18](#) and [Figure 16-19](#). Much of the historically deposited N and S remains stored within park ecosystems, with N stored in soils, biomass, and coarse woody debris ([Cai et al., 2011b](#); [Creed et al., 2004](#)), and S adsorbed to soil ([Fakhraei et al., 2016](#); [Cai et al., 2011b](#)). The capacity of these compartments for storing N and S are not infinite, and the capacity to retain N has been exceeded in some areas (ecosystems have reached N saturation), as evidenced by increased nitrate leaching and acidification of some surface waters. This suggests that ecosystems are impaired by N deposition, and that there may be a lag time in ecosystem recovery if deposition is reduced ([Fakhraei et al., 2016](#); [Cai et al., 2011a](#)).

The range of elevation and precipitation within the park has allowed distinct terrestrial and aquatic communities to form at different elevations, making the park one of the most biologically diverse areas in North America. Furthermore, because the park remained unglaciated during recent ice ages, it served as a refugium for northern plant and animal species, as well as an evolutionary generator of new species. The All Taxa Biodiversity Initiative is an ongoing project that seeks to document all species within the park's boundaries, and as of March 2016, there were 19,260 species across all domains documented within the park (<https://www.dlia.org/smokies-species-tally>).

Land cover in this case study region is mostly hardwood forest; coniferous forest occurs primarily at the higher elevations in and around GRSM ([Figure 16-17](#)). Distributed in elevational zones from highest elevation to lowest, forest types in the park include spruce-fir forest, beech-yellow birch forest, pine-oak forest, hemlock forest, and cove hardwood forest. Different forest types may support endemic animal, plant, fungal, and lichen species, as well as more broadly distributed species. There are 831 species of lichens documented within the park (<https://www.dlia.org/smokies-species-tally>); lichens are some of the most sensitive organisms in terrestrial ecosystems to atmospheric deposition (see [Appendix 6.3.7](#)), and work in Eastern Temperate forests ([Cleavitt et al., 2015](#); [Will-Wolf et al., 2015](#)) suggests that high atmospheric deposition can negatively impact their condition, species richness, and community composition. The forests in the park support rich understory plant communities, which are sensitive to deposition effects such as shifts in mycorrhizal communities, competitive exclusion, and increases in herbivory, all of which can lead to declines in herbaceous species richness ([Simkin et al., 2016](#)).

A number of threatened and endangered species occur within the park ([Table 16-17](#)). GRSM is a key preserve for North American amphibian species ([Nickerson et al., 2002](#); [Hyde and Simons, 2001](#)), including salamander species which have seen their North American populations decline over the past half century ([Caruso and Lips, 2013](#)). The park's high biodiversity has been recognized by its designation as a UNESCO World Heritage Site and International Biosphere Reserve. The broader Tennessee-Cumberland region contains the highest diversity of freshwater mussel and crayfish species and the highest levels of aquatic species endemism in North America ([Abell et al., 1999](#)). Within the park, sampling between 1993 and 2001 found 90–168 genera of benthic macroinvertebrates in 13 different streams ([Milner et al., 2016](#)). A national analysis of federally listed species identified 49 aquatic and 4 terrestrial threatened or endangered species impacted by anthropogenic N in the U.S. Fish and Wildlife Service Region 4, which encompasses 10 southeastern states, including Tennessee and North Carolina ([Hernández et al., 2016](#)).

**Table 16-17 Species in the Southeast case study region that are listed as threatened or endangered or as a species of concern.**

Threatened and endangered species known or believed to occur in Great Smoky Mountains NP
<b>Mammals</b>
<ul style="list-style-type: none"> <li>• <i>Myotis septentrionalis</i>, northern long-eared bat—threatened</li> <li>• <i>Myotis sodalis</i>, Indiana bat—endangered</li> <li>• <i>Glaucomys sabrinus coloratus</i>, Carolina northern flying squirrel—endangered</li> </ul>
<b>Birds</b>
<ul style="list-style-type: none"> <li>• <i>Picoides borealis</i>, red-cockaded woodpecker—endangered</li> </ul>
<b>Fish</b>
<ul style="list-style-type: none"> <li>• <i>Etheostoma sitikuense</i>, Citico darter—endangered</li> <li>• <i>Noturus baileyi</i>, smoky madtom—endangered</li> <li>• <i>Noturus flavipinnis</i>, yellowfin madtom—threatened</li> </ul>
<b>Arthropods</b>
<ul style="list-style-type: none"> <li>• <i>Microhexura montivaga</i>, spruce-fir moss spider—endangered</li> </ul>

**Table 16-17 (Continued): Species in the southeast case study region that are listed as threatened or endangered or as species of concern.**

Threatened and endangered species known or believed to occur in Great Smoky Mountains NP
<b>Plants</b>
<ul style="list-style-type: none"> <li>• <i>Geum radiatum</i>, spreading avens—endangered</li> <li>• <i>Spiraea virginiana</i>, Virginia spiraea—threatened</li> <li>• <i>Gymnoderma lineare</i>, rock gnome lichen—endangered</li> </ul>
<b>Species believed to have been extirpated from the park</b>
<ul style="list-style-type: none"> <li>• <i>Canis lupus</i>, gray wolf—endangered mammal</li> <li>• <i>Canis rufus</i>, red wolf—endangered mammal</li> <li>• <i>Felis concolor cougar</i>, eastern puma or cougar—endangered mammal</li> <li>• <i>Erimonax monachus</i>, spotfin chub—threatened fish</li> </ul>
<b>Federal Species of Concern found in the park</b>
<b>Mammals</b>
<ul style="list-style-type: none"> <li>• <i>Myotis leibii</i>, eastern small-footed bat</li> <li>• <i>Sorex palustris</i>, water shrew</li> <li>• <i>Sylvilagus obscurus</i>, Appalachian cottontail</li> </ul>
<b>Birds</b>
<ul style="list-style-type: none"> <li>• <i>Ammodramus henslowii</i>, Henslow's sparrow</li> <li>• <i>Contopus cooperi</i>, olive-sided flycatcher</li> <li>• <i>Dendroica cerulea</i>, cerulean warbler</li> <li>• <i>Loxia curvirostra</i>, red crossbill</li> <li>• <i>Poecile atricapillus</i>, black-capped chickadee</li> <li>• <i>Sphyrapicus varius</i>, yellow-bellied sapsucker</li> <li>• <i>Vermivora chrysoptera</i>, golden-winged warbler</li> </ul>
<b>Amphibians</b>
<ul style="list-style-type: none"> <li>• <i>Cryptobranchus alleganiensis</i>, eastern hellbender</li> <li>• <i>Desmognathus aeneus</i>, seepage salamander</li> <li>• <i>Eurycea junaluska</i>, Junaluska salamander</li> </ul>
<b>Fish</b>
<ul style="list-style-type: none"> <li>• <i>Percina squamata</i>, olive darter</li> <li>• <i>Phoxinus tennesseensis</i>, Tennessee dace</li> </ul>

**Table 16-17 (Continued): Species in the southeast case study region that are listed as threatened or endangered or as species of concern.**

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Threatened and endangered species known or believed to occur in Great Smoky Mountains NP
<b>Plants</b>
<ul style="list-style-type: none"><li>• <i>Abies fraseri</i>, Fraser fir</li><li>• <i>Calamagrostis cainii</i>, Cain's reed-bent grass</li><li>• <i>Cardamine clematitidis</i>, mountain bittercress</li><li>• <i>Glyceria nubigena</i>, Smoky Mountain manna grass</li><li>• <i>Silene ovata</i>, Blue Ridge catchfly</li></ul>

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NP = national park.

Source: National Park Service <https://home.nps.gov/grsm/learn/nature/te-species.htm>.

A number of disturbances in the park can interact with acidic deposition to affect biodiversity. Invasive species alter the distribution of native species within the park; for example, native brook trout (*Salvelinus fontinalis*) have been displaced from approximately 75% of their historical range within park streams by rainbow trout (*Oncorhynchus mykiss*) introduced to the park in the early twentieth century for recreational fishing (Kanno et al., 2017). Recent eradication campaigns of rainbow trout and reintroduction of brook trout within a set of park streams showed that brook trout quickly re-established populations (Kanno et al., 2016). Both introduced and native pathogens are also changing plant communities within the park. Fraser fir is endemic to the Southeast and sensitive to acidic deposition, and 74% of remaining Fraser fir (*Abies fraseri*) forests are within GSMNP boundaries (Kaylor et al., 2017). The invasive balsam woolly adelgid (*Adelges piceae*) killed mature stands of Fraser fir which historically dominated the highest elevations of the park (Kaylor et al., 2017; Van Miegroet et al., 2007). The most recent survey of Fraser fir was conducted in the park in 2010 and found the highest elevation stands regenerating despite the continuing presence of the adelgid, suggesting some population recovery following reductions in acid deposition (Kaylor et al., 2017). Ongoing damage from the invasive hemlock woolly adelgid (*Adelges tsugae*) may kill the mature hemlock (*Tsuga* spp.) stands which grow along streams in the park and which regulate stream temperature by the dense shading they provide (Martin and Goebel, 2012). Recent research suggests that N deposition may alter beech (*Fagus grandifolia*) bark chemistry, making the trees more susceptible to mortality caused by beech bark disease (attack by beech scale, *Cryptococcus fagisuga*, followed by infection by fungal pathogens in the *Neonectria* genus), which was first detected in the park in 1993 (Cale et al., 2017). In addition to disturbances caused by plant pathogens, shifting wildfire frequency affects the distribution of plant communities within the park and the wider region. In late November 2016, a fire burning at Chimney Tops spread rapidly

north across the park and into the nearby cities of Gatlinburg and Pigeon Forge. The fire, aided by drought conditions and strong winds, burned 17,140 acres (<https://www.nps.gov/grsm/learn/chimney-tops-2-fire.htm>). Wildfire suppression was the policy of the Park from its founding in 1931 until 1996, when a program of prescribed burns was instituted in order to regenerate forests of fire-dependent oak and pine species on dry ridges ([Schwartz et al., 2016](#)).

Precipitation and temperature alter the responses of terrestrial and aquatic ecosystems to N and S deposition. Between 1900 and 2011, annual precipitation increased 10 cm while there was no overall trend in temperature over the same period of time at stations within GSMNP ([Lesser and Fridley, 2016](#)). At nearby Grandfather Mountain, NC, summer temperature increased by more than 1.4°C between 1956 and 2011 ([Soulé, 2011](#)). Changes in temperature may alter species distributions. For example, native brook trout inhabit about 970 km of stream length in GRSM, most of which is above 900 m elevation ([Neff et al., 2009](#)). Brook trout have disappeared from six high-elevation streams in the Little Pigeon River watershed ([Deyton et al., 2009](#); [Neff et al., 2009](#)). Simulation modeling by [McDonnell et al. \(2015\)](#) showed that acidification of streams may hinder the movement of southern Appalachian aquatic species (including brook trout) to colder, higher elevation habitats if stream temperatures rise.

Like GSMNP, Linville Gorge Wilderness (LGW) contains plant communities structured by elevation. LGW comprises 43.9 km<sup>2</sup> of mountain ridges and gorges that range over an elevation of 426 to 1,250 m. Forest cover in the gorge is 43% coniferous tree species and 55% deciduous tree species, in plant communities from low to high elevation of acidic cove, mesic oak-hickory, and xeric pine-oak or oak heath zones ([Kantola et al., 2016](#)). Soils in LGW formed from parent material with very low concentrations of Ca, Mg, and K; and historic acidic deposition has further depleted these nutrients while decreasing soil pH and increasing soluble aluminum ([Elliott et al., 2013](#)). Experimental addition of dolomitic limestone resulted in transient improvements in soil Ca:Al ratios, while wildfire, which can release base cations from biomass into the soil, had no measurable impact on Ca pools in soils ([Elliott et al., 2013](#)). Between 1992 and 2011, forest structure in LGW shifted towards trees in younger age classes, as outbreaks of beetles and hemlock wooly adelgid, drought, and wildfire caused mortality in older and larger age classes of trees ([Hagan et al., 2015](#)).

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### 16.3.1.2 Legal Authorities

GRSM is a Prevention of Significant Deterioration (PSD) Class I Area. The CAA (42 USC 7470) authorized Class I areas to protect air quality in national parks over

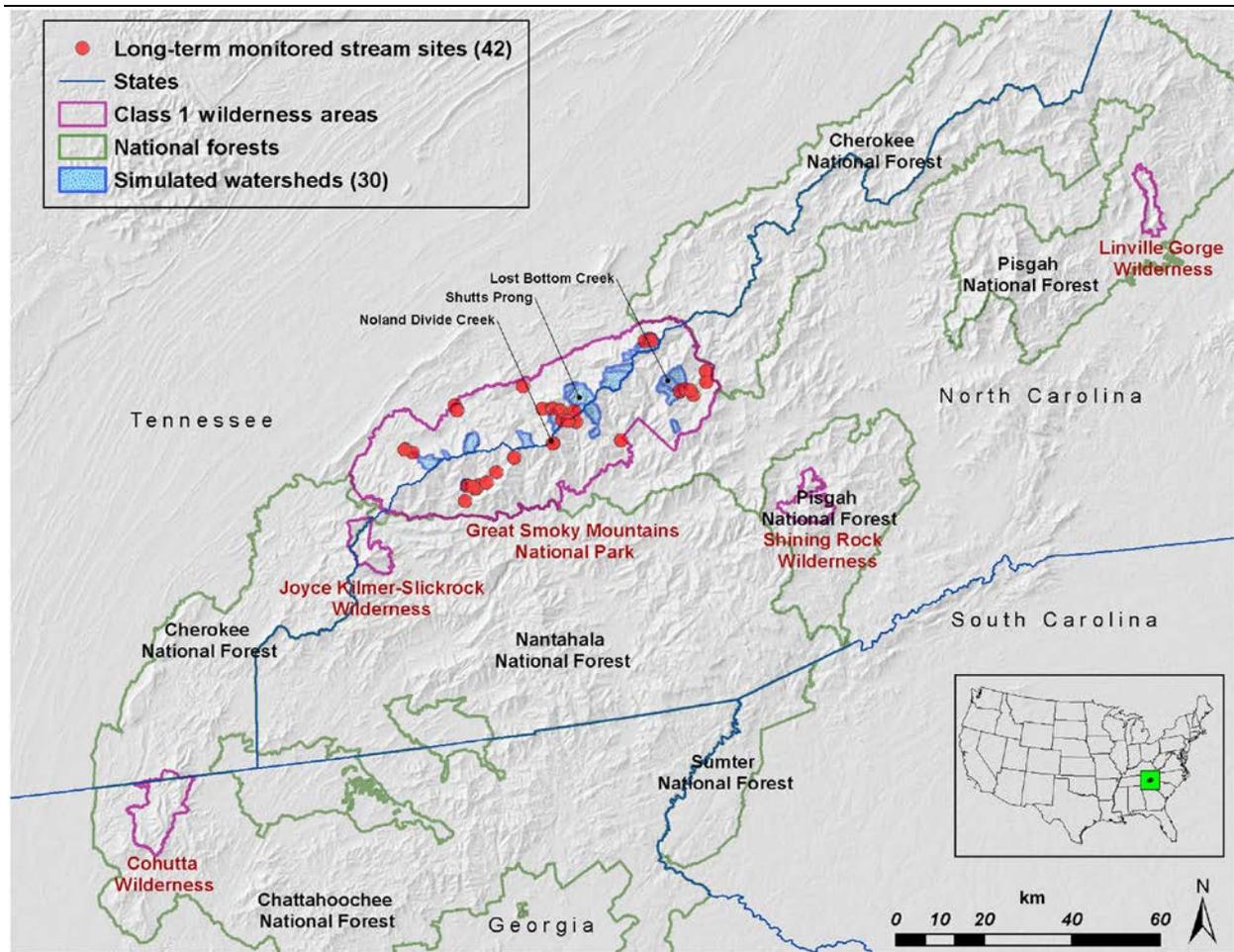
6,000 acres and national wilderness areas over 5,000 acres in an effort to preserve pristine atmospheric conditions and air quality related values (AQRVs).

Wilderness areas in North Carolina located in the vicinity of GRSM that also have been designated PSD Class I include Shining Rock, Linville Gorge, and Joyce Kilmer Memorial Forest. All are managed by the USDA's U.S. Forest Service. Shining Rock consists of 74 km<sup>2</sup> of high elevation (1,450–1,550 m) hardwood forests dominated by yellow birch and red maple on soils formed in gneissic bedrock. Linville Gorge is 43.9 km<sup>2</sup> of acidic cove and slope forests at intermediate elevations (1,090–1,160 m) dominated by chestnut oak and red maple on quartzite parent material. Joyce Kilmer Memorial Forest is 68.1 km<sup>2</sup> of low elevation (250–450 m) cove hardwoods, dominated by tulip poplar, oaks, and eastern hemlock stands, on metasandstone parent material. Additional information on these three wilderness areas is in [Elliott et al. \(2008\)](#). The geography of the Class I wilderness areas described in this case study are shown in [Figure 16-16](#); further details on this study can be found in [Appendix 16.2.3.2](#).

Class I areas are subject to the PSD regulations under the CAA. PSD preconstruction permits are required for new and modified existing air pollution sources. Air regulatory agencies are required to notify federal land managers (FLMs) of any PSD permit applications for facilities within 100 km of a Class I area.<sup>1</sup> The FLMs are entitled to review and comment on PSD Class I permit applications with the authorized permitting agency. Information on air quality monitoring by NPS within GRSM is available at the GRSM Air Quality website (<https://www.nps.gov/grsm/learn/nature/air-quality.htm>).

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<sup>1</sup> <http://webcam.srs.fs.fed.us/psd>.

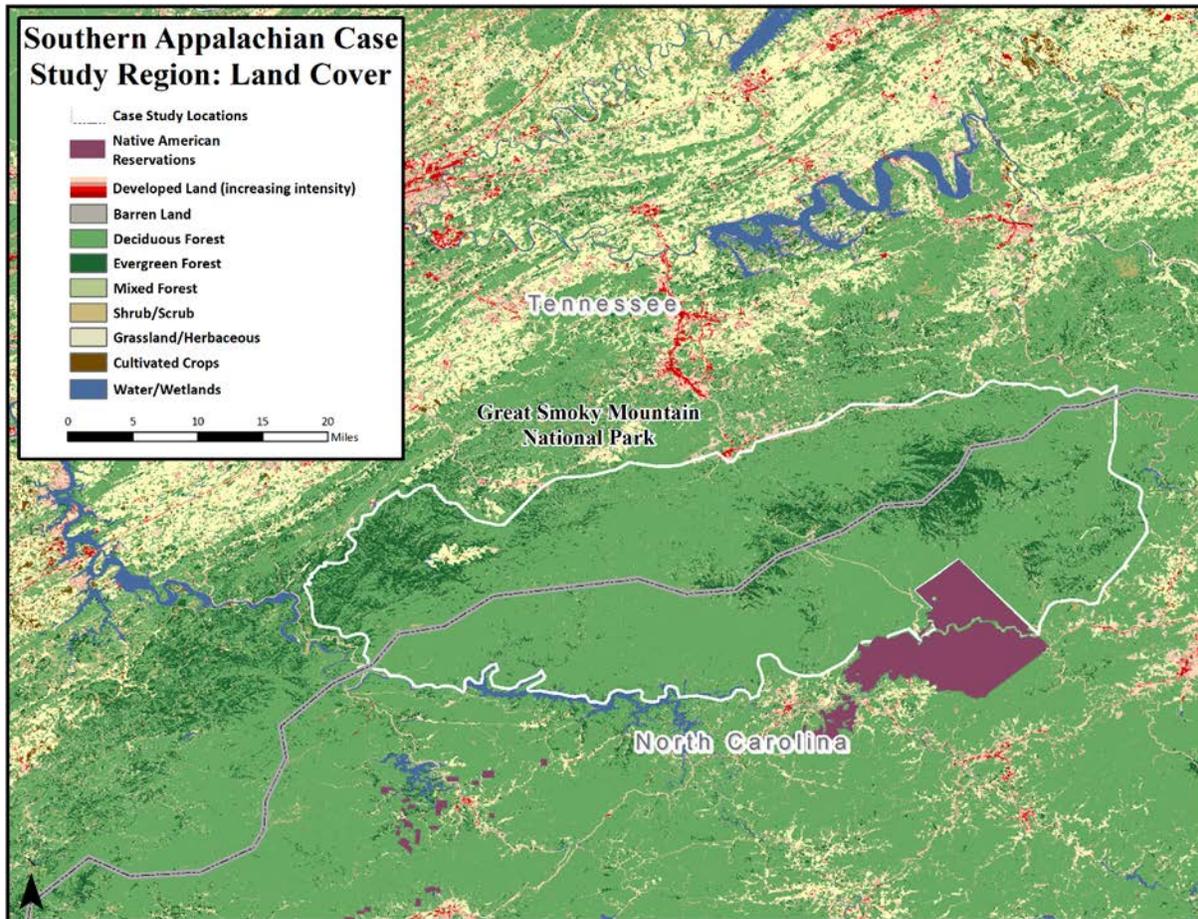


Source: [Fakhraei et al. \(2016\)](#).

**Figure 16-16** Great Smoky Mountains National Park and nearby Class I wilderness areas, with emphasis on water sampling locations within GSMNP and critical loads for watersheds described in [Appendix 16.2.3.2](#).

### 16.3.1.3 Regional Land Use and Land Cover

Land cover in this case study region is mostly hardwood forest; coniferous forest occurs primarily at the higher elevations in and around GRSM ([Figure 16-17](#)). Although located generally downwind of populous areas, GRSM has only a few human population centers of any magnitude nearby. They include Knoxville, TN, 30 mi from the park (pop. 181,000); Asheville, NC, 30 mi (pop. 87,000); Johnson City, TN, 70 mi (pop. 64,000); and Greenville, SC, 90 mi (pop. 61,188).



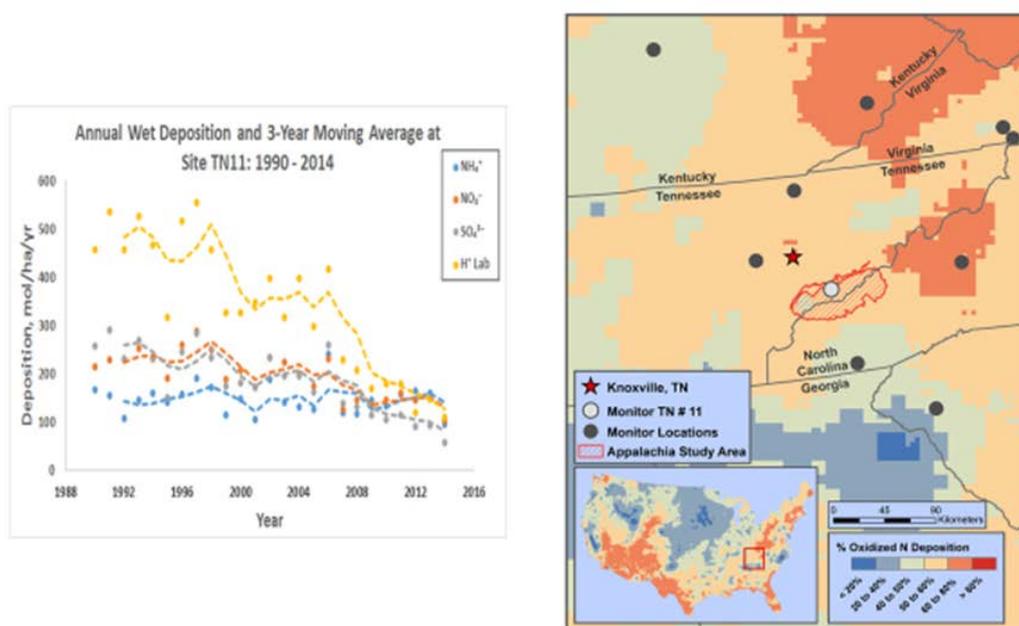
**Figure 16-17** Land cover in the southern Appalachian Mountains case study region.

### 16.3.2 Deposition

The highest elevations of the park have received some of the highest rates of acidic deposition in the U.S. (Weathers et al., 2006; Herlihy et al., 1993) due largely to the location of upwind power plants, major agricultural regions, and the substantial amount of annual precipitation.

Characteristics of nitrogen and sulfur deposition affecting the Great Smoky Mountains Study Area are shown in [Figure 16-18](#)–[Figure 16-21](#). Data shown in [Figure 16-18](#)–[Figure 16-23](#) were obtained from the hybrid modeling/data fusion product, TDEP, <http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/> and described earlier in

[Appendix 2.7](#). However, the time series of wet deposition is taken directly from data on the NADP/NTN website. This was done to use the long-term record of wet deposition to illustrate trends in deposition since the passage of the Clean Air Act Amendment, because the CMAQ dry deposition simulations involved in estimating TDEP total deposition extend back only to 2000. [Figure 16-18](#) shows the 25-year-long time series for wet deposition for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  measured at the NADP/NTN monitoring site Great Smoky Mountain NP (TN11), as well as the partitioning between oxidized and reduced N Deposition of nitrogen, which is estimated to be mostly in oxidized form in the study area. Although most of the area in [Figure 16-18](#) is subject to N deposition in oxidized form, there are areas, principally in northern Georgia, where N is deposited mainly in reduced form. The graph of wet deposition of all chemical species shows that downward trends in  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  are consistently found over the past 25 years, although the rate of decrease has been irregular, with occasional increases.



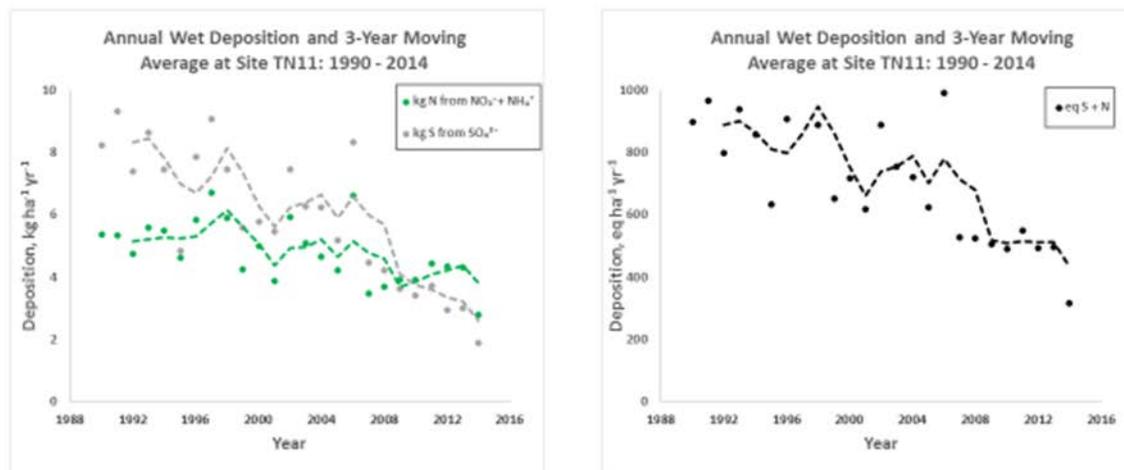
$\text{H}^+$  = hydrogen ion; ha = hectare; mol = mole; N = nitrogen;  $\text{NH}_4^+$  = ammonium;  $\text{NO}_3^-$  = nitrate;  $\text{SO}_4^{2-}$  = sulfate; yr = year.

Notes: on the left, trends in wet deposition, 1990–2014. On the right, partitioning between reduced and oxidized forms of N in deposition in 2011–2013.

Source: NCEA based on data from TDEP.

**Figure 16-18 Deposition over Great Smoky Mountain National Park.**

[Figure 16-19](#) shows the 25-year-long time series for wet deposition of N and S in terms of units commonly used to determine critical loads within GSMNP. Critical loads for eutrophication are commonly expressed in terms of kg N/ha/yr. Critical loads for acidification are commonly expressed in terms of kg S/ha/yr, or because both N and S deposition can contribute to acidification, in terms of eq/ha/yr.



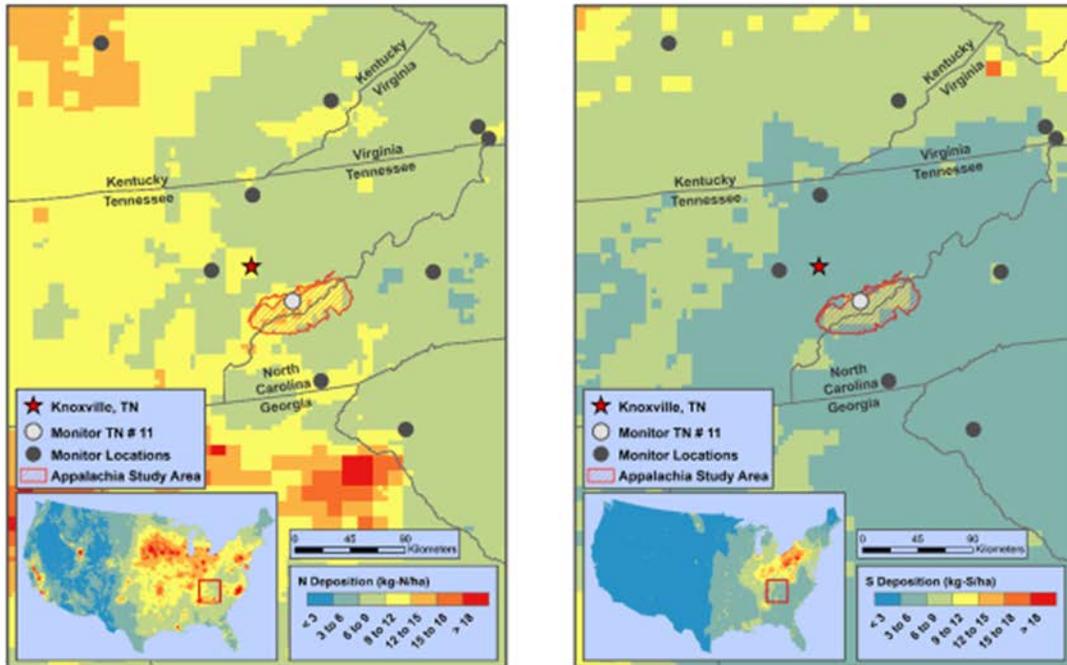
eq = H<sup>+</sup> equivalents; ha = hectare; kg = kilogram; N = nitrogen; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Notes: On the left, N and S deposition are shown in units of kg/ha/yr of N or S. On the right, N and S deposition are combined into units of acidifying deposition, eq/ha/yr of S + N.

Source: NADP/NTN.

**Figure 16-19 Trends in wet deposition of nitrogen and sulfur in Great Smoky Mountain National Park, 1990–2014.**

[Figure 16-20](#) shows the 3-year average total deposition of N and S for 2011–2013. Surrounding areas in southern states and inserts showing the coterminous U.S. are shown to place the depositional environment in context. Comparison of maps indicates that the general pattern of deposition of N and S is broadly similar, with higher values within the study area than outside of it. Current rates of deposition of S are considerably lower than along the Ohio River Valley, which might be expected given that the Ohio River Valley is a major industrial region, and GRSM is a national park. Wet and dry deposition of S were roughly equal across the study area. See [Appendix 2.4](#), [Appendix 2.5](#), and [Appendix 2.6](#) for more information on deposition in the U.S. Other maps showing the contributions of individual species to dry and/or wet deposition, based on TDEP are given in [Appendix 2.7](#).

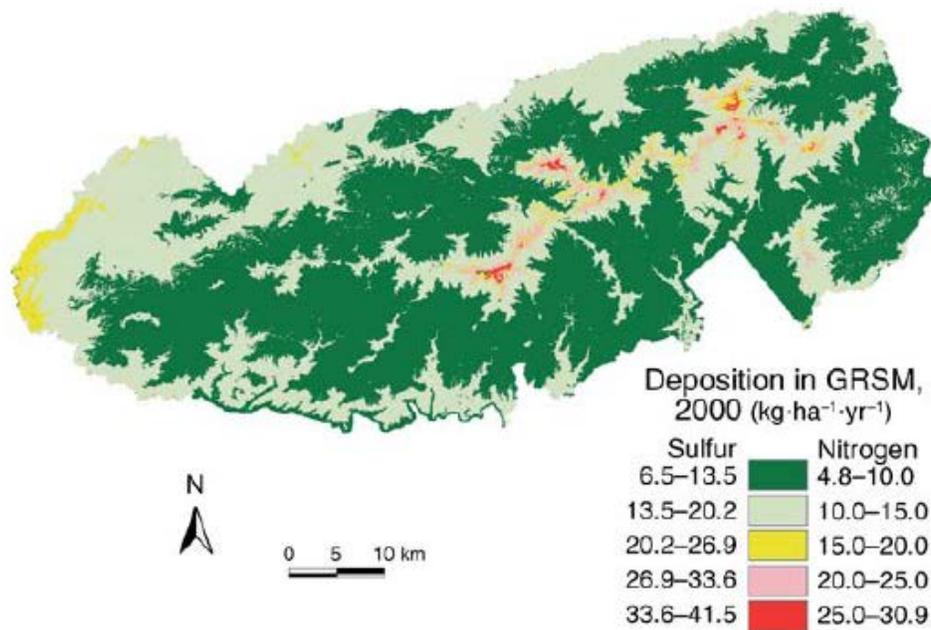


ha = hectare; kg = kilogram; N = nitrogen; S = sulfur.

**Figure 16-20** Total nitrogen deposition on left, total sulfur deposition on right, for the 3-year average, 2011–2013 in Great Smoky Mountain National Park.

The Great Smoky Mountain National Park NADP/NTN monitoring site (TN11) was chosen to characterize long-term wet deposition of N and S species in the study area. [Figure 16-18–Figure 16-20](#) are based on data for wet deposition from the TN11 monitor, which is located in low-elevation hardwood forest within the park. [Weathers et al. \(2006\)](#) mapped deposition in 2000 in the park at a finer scale and showed that deposition rates at higher elevations (see [Figure 16-21](#)) were roughly two to five times higher than at the low-elevation NADP monitor site.

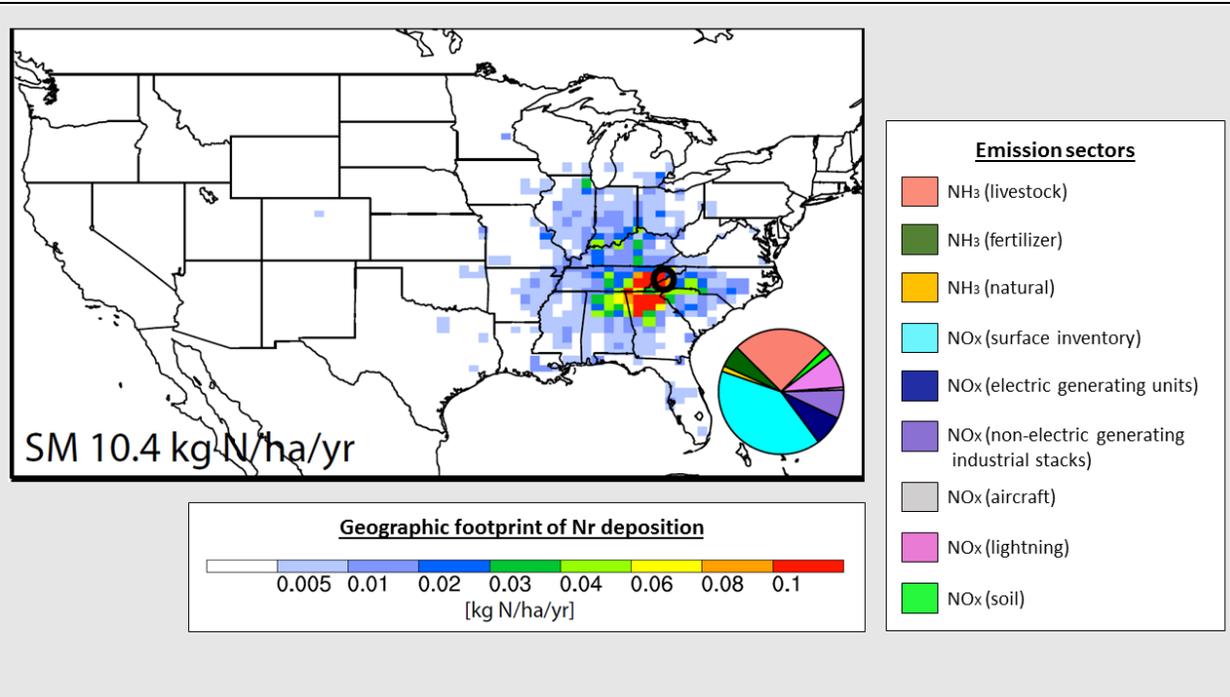
A recent modeling study of Class I areas, including GSMNP, used a GEOS-Chem adjoint model to identify the geographic sources of reactive N deposition, as well as the emission sector sources of reactive N deposition within the park ([Lee et al., 2016](#)). Emissions of Nr that affect GSMNP originate as far as 1,500 km from the park, and mobile sources of NO<sub>x</sub> are the major emission source (40%) to N deposition within GSMNP (see [Figure 16-22](#)).



GRSM = Great Smoky Mountain National Park; ha = hectare; kg = kilogram; yr = year.

Source: [Weathers et al. \(2006\)](#).

**Figure 16-21 Modeled sulfur and nitrogen deposition to the Great Smoky Mountain National Park for the year 2000.**



Source: Adapted from Figure 5 in [Lee et al. \(2016\)](#).

**Figure 16-22. Annual-averaged monthly footprint of reactive N deposition in Great Smoky Mountain National Park (10.4 kg N/ha/yr), and pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model.**

### 16.3.3 Critical Loads and Other Dose-Response Relationships

The following sections describe critical loads determined for the Great Smoky Mountains National Park, for the larger southern Appalachian region, or for the Level I ecoregion in which the park resides, the Eastern Temperate Forests.

#### 16.3.3.1 Empirical Studies

Thresholds of deposition are quantified for GRSM and the broader region. Sampling of soil and streams at high elevations in the park in the mid-1990s found elevated extractable inorganic N concentrations at high elevations ([Garten, 2000](#)), as well as substantial nitrate leaching in streams from these watersheds ([Van Miegroet et al., 2001](#)). Because NO<sub>x</sub> deposition was determined by [Van Miegroet et al. \(2001\)](#) in the watersheds

to be 32 kg N/ha/yr, [Gilliam et al. \(2011a\)](#) stated that the nitrate leaching critical load would be <32 kg N/ha/yr. Additional water quality critical loads for the park are based on models (see below). The comparable critical load set for leaching in the Eastern Temperate Forests is 8 kg N/ha/yr, which is lower than the [Gilliam et al. \(2011a\)](#) value. This critical load is set to protect hardwood forest soils from NO<sub>3</sub><sup>-</sup> leaching to surface water and is based on a synthesis of data across northeastern forests ([Aber et al., 2003](#)). This quantity is in agreement with an earlier recommendation for Class I wildernesses in the Forest Service's eastern region that N deposition should not exceed 5–8 kg N/ha/yr to protect terrestrial biota ([Adams et al., 1991](#)). That report also recommended an annual load for total sulfur deposition not to exceed 5–7 kg S/ha/yr to protect terrestrial biota ([Adams et al., 1991](#)). The critical loads set by [Adams et al. \(1991\)](#) were based on observations across Class I wildernesses in the Forest Service eastern region; the deposition limits were based on the deposition loads of three Class I areas where eutrophication and acidification were not observed.

A number of additional empirical critical loads have been set for the Eastern Temperate Forests ecoregion based on protection of sensitive biota from the effects of nitrogen deposition ([Gilliam et al., 2011a](#); [Pardo et al., 2011a](#)). A critical load of >3 kg N/ha/yr protects growth rates or survivorship of sensitive tree species, including red pine, yellow birch, scarlet and chestnut oaks, quaking aspen, and basswood. A critical load of 4–8 kg N/ha/yr was set for Eastern Temperate Forests based on extrapolation from data collected in Northwest forests to preserve sensitive lichen species and prevent lichen community composition shifts towards more eutrophic species. A critical load of 5–10 kg N/ha/yr protects ectomycorrhizal fungi associated with coniferous tree species from community composition change. A critical load of <12 kg N/ha/yr protects arbuscular mycorrhizal fungi associated with hardwood tree species from decreases in abundance and community composition change. A critical load of <17.5 kg N/ha/yr protects forest understory communities from herbaceous species loss and shifts in plant community composition. These critical loads (3–17.5 kg N/ha/yr) represent protection for a broad range of sensitive terrestrial species within the Eastern Temperate Forest ecoregion ([Gilliam et al., 2011a](#); [Pardo et al., 2011a](#)).

Two more recent studies document empirical critical loads for the broad Eastern Temperate Forest ecoregion. [Cleavitt et al. \(2015\)](#) conducted surveys and used FIA assessments of lichen species in the Northeast, with particular focus on the four Class I wilderness areas in the region (Lye Brook, VT; Great Gulf, NH; Presidential Range—Dry River, NH; and Acadia National Park, ME). In general, cumulative N and S deposition over the course of the modeled period (2000–2013) was a more powerful explanatory factor than annual N or S load for the lichen data. This work determined a critical load of 4.3–5.7 kg total N (oxidized + reduced N)/ha/yr based on lichen species richness, the

abundance of sensitive species (higher species richness of cyanolichens and fruticose lichens below CL), and thallus condition. Cumulative S and N deposition were both equally powerful predictors of thallus condition, but no S critical load was determined (Cleavitt et al., 2015). A study by Simkin et al. (2016) used FIA data to determine critical loads for herbaceous species in a national assessment. The critical load for this analysis was placed to prevent any loss of herbaceous species richness and was determined to be 7.8–19.3 kg N/ha/yr for closed-canopy forest herbaceous communities in the Eastern Temperate Forest ecoregion. The critical load determined for open-canopy (grassland, shrubland, and woodland) herbaceous communities in this ecoregion was lower, 6.6–9.7 kg N/ha/yr (Simkin et al., 2016). These critical load estimates may be too high for GRSM, as Simkin et al. (2016) determined that critical loads tended to decrease under conditions of low soil pH, high precipitation, and high temperatures, all of which affect park ecosystems (Appendix 6.2.3.2).

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### 16.3.3.2 Modeling Studies

Some of the critical loads modeled for GSMNP are aimed to protect terrestrial ecosystems from N saturation and associated acidification. The Integrated Forest Study sampled forests across North America, and several plots were located at high elevations within GSMNP. A critical load of 2.5–9 kg N/ha/yr was determined for the park using SMB modeling (Oja and Arp, 1998). A decade later, Pardo and Duarte (2007) used SMB and data from GRSM to determine critical loads for different forest types within the park. Critical loads of 2.7–2.8 kg N/ha/yr to prevent terrestrial ecosystem eutrophication were determined for low- and mid-elevation hardwood forests within the parks, while the critical load for high-elevation spruce-fir forests was 3.4–7 kg N/ha/yr. Pardo and Duarte (2007) also developed critical loads to protect GSMNP forests from acidification based on pH, Al, and base cation threshold values. In low-elevation hardwood forests, the most protective critical load was 1,080 eq S + N/ha/yr; in mid-elevation hardwood forest, the most protective critical load was 1,650 eq S + N/ha/yr; and in high-elevation spruce-fir forest, the most protective critical load was 2,000 eq S + N/ha/yr (Pardo and Duarte, 2007).

Critical loads of N and S deposition to protect aquatic ecosystems depend upon underlying geology, elevation, and sensitivity of streams (i.e., preindustrial ANC) in the southern Appalachian Mountains (Sullivan et al., 2011b). A recent application of the PnET-BGC model was used to determine target loads to protect aquatic ecosystems in 12 streams within GSMNP from acidification. The target load to achieve a target ANC of 50 µeq/L by 2050 was deposition of 270–1,400 eq (S + N)/ha/yr in streams at <1,000 m elevation and which did not drain watersheds within the Anakeesta Formation (Zhou et

[al., 2015a](#)). In an acid-sensitive, high-elevation watershed with drainage from the Anakeesta Formation, no reduction in deposition was sufficient to reach a target of ANC = 50  $\mu\text{eq/L}$ , but a target load of 270 eq (S + N)/ha/yr resulted in ANC recovery to 0 by 2050 ([Zhou et al., 2015a](#)). In a follow-up analysis, [Fakhraei et al. \(2016\)](#) and [Fakhraei et al. \(2017a\)](#) determined total maximum daily loads of acid deposition for each of the twelve 303(d)-listed stream watersheds at high elevations within the park. The target date for recovery to pH of 6.0 was 2150 for these model runs, and critical loads ranged between 240 and 960 eq/ha/yr of  $\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$  deposition to eight of the twelve watersheds. For the remaining four watersheds, no reduction in deposition was sufficient to achieve pH of 6 by 2150; recovery in these streams is projected to take centuries ([Fakhraei et al., 2017a](#)). These target loads are in good agreement with critical loads set for S only deposition based on MAGIC and Steady-State Water Chemistry (SSWC) modeling for the broader southeastern Appalachian region ([McDonnell et al., 2014b](#)). The S only critical load was based on achieving a target stream ANC of 50  $\mu\text{eq/L}$ , and for high elevations in the park, the critical load was 0–250 eq S/ha/yr. Most of the low-elevation area within the park had a critical load of 250–500 eq S/ha/yr by this method ([McDonnell et al., 2014b](#)).

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#### 16.3.4 Characterization and Long-Term Monitoring

The majority of studies conducted in this case study region have evaluated the effects of acidification on ecosystems rather than the effects of eutrophication (see [Table 16-18](#)). Acidification has been considered to be the dominant result of air pollution stress in the region. Biogeochemical processes that govern watershed responses to acidification are generally similar between the Northeast and the southern Appalachian Mountains in most respects. The major exception is that soils in the southern Appalachians are unglaciated and therefore more weathered, with greater sulfate adsorption capacity, than soils in northeastern forests. [Cai et al. \(2010\)](#) used long-term monitoring data to generate an input-output budget to identify processes that have influenced stream pH and ANC at the Noland Divide watershed in Great Smoky Mountains NP during the period 1991–2006. The majority (about 61%) of the net  $\text{SO}_4^{2-}$  entering the watershed was retained, confirming that S adsorption on soil is an important biogeochemical process in this watershed. However, during large precipitation events,  $\text{SO}_4^{2-}$  in wet deposition moved more directly and rapidly to streams, contributing to episodic stream acidification. [Fakhraei et al. \(2016\)](#) projected that GRSM streams in watersheds with a low capacity to adsorb  $\text{SO}_4^{2-}$  and low N retention will respond positively (increase stream pH and ANC) to additional reductions in S and N deposition, while streams in watersheds with high  $\text{SO}_4^{2-}$  adsorption and low N retention (typically higher elevation watersheds) are less

responsive (or unresponsive) to reduced S and N deposition. In these watersheds, increases in soil pH due to reduced deposition are projected to increase desorption of accumulated  $\text{SO}_4^{2-}$  from soils, resulting in a  $\text{SO}_4^{2-}$  pulse to streams that will slow recovery of stream ANC and pH (Fakhraei et al., 2016). Monitoring data from the Great Smoky Mountains NP indicated that the high S absorption in watershed soils delayed recovery from previous stream acidification. Stream chemistry at 42 monitoring sites in the park did not show substantial changes over the recent period of long-term monitoring, 1991–2014 (Fakhraei et al., 2016).

**Table 16-18 Example soil, terrestrial biota, and surface water acidification characterization and long-term monitoring studies in the southern Appalachian Mountains region.**

Study (HERO ID)	Location	Time Period	Focus	Results
<b>Soil studies</b>				
<a href="#">Rice et al. (2014)</a>	Southeastern U.S.	2006–2021	Sulfate mass balances for 27 forested watersheds to estimate cross-over years (change from retaining to releasing $\text{SO}_4^{2-}$ ).	Documented extensive S adsorption on soils
<a href="#">Lawrence et al. (2015b)</a>	AT corridor, including through GRSM	2010–2012	Soil sampling along AT corridor and compilation of other existing soil chemistry data	Documented occurrence of low soil base saturation along the AT corridor, including within GRSM
<a href="#">Cai et al. (2011a)</a>	Noland Divide, GRSM	2008	Laboratory soil columns and in situ lysimeters to determine response of soil solution to reduced acidic deposition.	Recovery of soil water, as represented by renewed $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ retention, was estimated to occur at S deposition reduction of 61% of ambient.
<a href="#">Cai et al. (2012)</a>	Noland Divide, GRSM	2009	Four sites along elevational gradient.	Base saturation values <7% and Ca:Al ratio <0.01 indicated high acid sensitivity.
<a href="#">Elliott et al. (2008)</a>	Three FS Class I areas in North Carolina		NuCM model	Low Ca:Al (~0.3) in A-horizon at Shining Rock and Linville Gorge suggested stress to forests from soil acidification.

**Table 16-18 (Continued): Example soil, terrestrial biota, and surface water acidification characterization and long-term monitoring studies in the southern Appalachian Mountains region.**

Study (HERO ID)	Location	Time Period	Focus	Results
<b>Terrestrial biota studies</b>				
<a href="#">Hames et al. (2002)</a>	Assessment of 650 study sites across the range of the wood thrush in the eastern U.S.	1995–1999	Wood thrush breeding success	Low breeding success in the wood thrush strongly correlated with low soil pH
<a href="#">McNulty and Boggs (2010)</a>	Western North Carolina	1999–2002	Red spruce and southern pine beetle	CL for protecting forest ecosystems may not accurately reflect risk to ecosystem health due to multiple stresses, including climate change, insect infestation, and N supply.
<b>Surface water studies</b>				
<a href="#">Scheffe et al. (2014)</a>	U.S., including southern Appalachian Mts. region		Critical load by ecoregion, as reflected in AAI	AAI model
<a href="#">Sullivan et al. (2004); Sullivan et al. (2002)</a>	SAMI region		MAGIC model	Streams exhibited broad range of responses to changes in future S deposition, including pronounced base cation depletion. Recovery from past acidification expected to be slow and gradual.
<a href="#">Sullivan et al. (2007b)</a>	Southern Appalachian Mts.	~2,000	Delimited high-interest area for water acidification based on geology and elevation, which included almost all known low-ANC ( $\leq 20 \mu\text{eq/L}$ ) streams in the region.	Lithology and elevation explained locations of low-ANC streams.
<a href="#">Sullivan et al. (2011b)</a>	Southern Appalachian Mts.		MAGIC model	Estimate target loads of S deposition to protect stream ANC to multiple levels (0, 20, 50, 100 $\mu\text{eq/L}$ ) at multiple points in time (2020, 2040, 2100). TLs ranged from 0 to values many times higher than ambient S deposition.

**Table 16-18 (Continued): Example soil, terrestrial biota, and surface water acidification characterization and long-term monitoring studies in the southern Appalachian Mountains region.**

Study (HERO ID)	Location	Time Period	Focus	Results
<a href="#">Sullivan et al. (2011c)</a>	Southern Blue Ridge province of southern Appalachian Mts. region		MAGIC model	Modeled 66 stream watersheds, all of which were simulated to have had preindustrial ANC > 30 µeq/L. In 2005, 30% of streams had ANC below this level. Median stream lost 25 µeq/L of ANC between 1860 and 2005.
<a href="#">Hoos and McMahon (2009)</a>	Southeastern U.S.		SPARROW model	Examined N transport relative to landscape characteristics. N transport coincided with Level III ecoregion boundaries. Lower fraction of N input delivered to stream at locations where primary flow path is shallow.
<a href="#">Cai et al. (2011b)</a>	Noland Divide, GRSM	1991–2007	Stream water chemistry trends.	Volume-weighted NO <sub>3</sub> <sup>-</sup> concentration decreased 0.56 µeq/L/yr; stream pH and SO <sub>4</sub> <sup>2-</sup> concentration did not change.
<a href="#">Cai et al. (2010)</a>	Noland Divide, GRSM	1991–2007	Developed input-output budget.	About 61% of incoming SO <sub>4</sub> <sup>2-</sup> was retained; during rain events, SO <sub>4</sub> <sup>2-</sup> moved more readily to streams.
<a href="#">Lawrence et al. (2015b)</a>	AT corridor, including through GRSM	2010–2012	Sampled more than 200 streams along the AT corridor, including under both high- and low-flow conditions.	Documented wide variability in stream ANC along the AT corridor.
<a href="#">Robinson et al. (2004)</a>	Noland Divide, GRSM	1990–1999	Developed MLR model of water chemistry.	Showed decrease in ANC over time.
<a href="#">Robinson et al. (2008)</a>	GRSM	1993–2002	Conducted trends analysis for 90 stream sites, which showed decreases in pH and SO <sub>4</sub> <sup>2-</sup> concentrations.	Extrapolation over 50 yr suggested pH <6.0 for nearly all study streams in the future.
<a href="#">Neff et al. (2013)</a>	GRSM	2008–2009	Examined relationships between stream chemistry at base flow and storm flow vs. basin characteristics.	Following precipitation, pH decreased and AI increased.

**Table 16-18 (Continued): Example soil, terrestrial biota, and surface water acidification characterization and long-term monitoring studies in the southern Appalachian Mountains region.**

Study (HERO ID)	Location	Time Period	Focus	Results
<a href="#">Deyton et al. (2009)</a>	Little Pigeon River watersheds, GRSM	2006–2007	Characterized chemistry of three high-elevation streams during episodes.	During storm flow, stream pH and ANC decreased: $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , and organic acids increased.

AAI = Aquatic Acidification Index; Al = aluminum; ANC = acid neutralizing capacity; AT = Appalachian Trail; Ca = calcium; CL = critical load; FS = Forest Service; GRSM = Great Smoky Mountains National Park; L = liter;  $\mu\text{eq}$  = microequivalents; MAGIC = Model of Acidification of Groundwater in Catchments;  $\text{Mg}^{2+}$  = magnesium; MLR = Multiple Linear Regression models; N = nitrogen;  $\text{NO}_3^-$  = nitrate; NuCM = Nutrient Cycling Model; S = sulfur; SAMI = Southern Appalachian Mountains Initiative;  $\text{SO}_4^{2-}$  = sulfate; SPARROW = Spatially Referenced Regressions on Watershed Attributes; TL = target load; yr = year.

## 16.4 Tampa Bay Case Study

### 16.4.1 Background

This case study provides an overview of the Tampa Bay estuary’s ecology and research related to nutrient impairments and nitrogen (N) deposition. It also reports on the improvements to the bay’s ecology being realized from strategies to reduce nutrient loading to the bay. Years of historical data going back to the 1950s and unique partnerships among government, industry, and citizen groups make Tampa Bay an interesting example of the varied issues involved in monitoring and managing water quality and N loading in an urban estuary. During the 1970s and early 1980s eutrophic conditions were commonly observed in Tampa Bay. Contrary to many other estuaries suffering from eutrophication worldwide, Tampa Bay appears to be recovering since the mid-1980s as a result of the nutrient management strategy defined by the community ([Greening et al., 2014](#); [Morrison et al., 2011](#)). These approaches have included upgraded sewage treatment, reduction of atmospheric N emissions, and controls on stormwater and point sources. Atmospheric deposition continues to be a source of N to Tampa Bay and, with the decreases in N loading from point sources, represents a greater proportion of total N loading to the bay ([Greening et al., 2014](#)). Estimates from both modeling and measurement indicate that direct atmospheric N deposition to Tampa Bay is between 14 and 30% while total (direct plus indirect) atmospheric deposition is between 35 and 71% ([Poor et al., 2013b](#); [Poor et al., 2013a](#); [Greening and Janicki, 2006](#)).

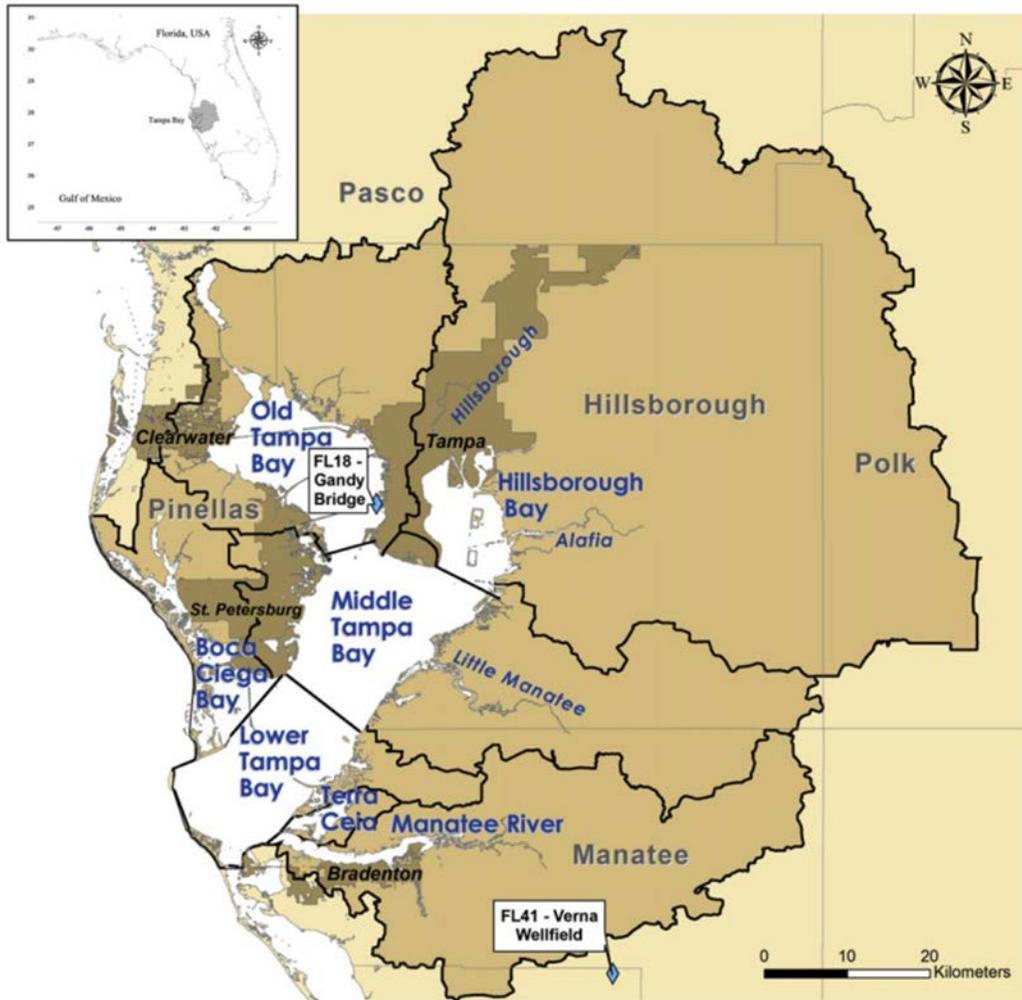
Information regarding sulfur deposition is not included in this case study because N is a primary contributor to nutrient enrichment and the focus of the monitoring studies used to compile this case study.

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#### 16.4.1.1 Description of Case Study Region

The Tampa Bay estuary ([Figure 16-23](#)) is located on the eastern shore of the Gulf of Mexico in Florida. At more than 1,000 km<sup>2</sup>, it is Florida's largest open water estuary, with an average water depth of just 4 m and annual average rainfall rate of more than 125 cm ([TBEP, 2015](#); [Poor et al., 2013a](#); [TBEP, 2012b](#)). It lies in the Northern Gulf of Mexico marine ecoregion near the South Florida/Bahamian Atlantic marine ecoregion ([Wilkinson et al., 2009](#)). This transition zone between warm-temperate and tropical ecoregions, combined with its shallow waters, large size, and gradient of fresh water to salt water, allows the bay to support a diversity of organisms and habitats ([Greening et al., 2014](#); [USGS, 2011](#); [USFWS, 1990, 1988](#)).

Seagrass, a type of submerged aquatic vegetation (SAV), and mangrove forests are the most prominent estuarine habitats within Tampa Bay ([TBEP, 2015](#)). Tidal marshes and mud flats are also found throughout the estuary ([USGS, 2011](#)). Collectively, these habitats support a large biodiversity of flora and fauna and play a role in nutrient cycling. Seagrasses stabilize sediments, are a food source for wildlife, provide habitat, and serve as a nursery for large numbers of fish and shellfish species ([Greening et al., 2014](#)). Mangrove roots help to stabilize the shoreline and provide nursery habitat for important fishery species. Mud flats and salt marshes in the bay provide habitat for wading birds, while oyster reefs near river mouths serve to naturally filter the water and attract recreational fish species, making them popular fishing spots ([TBEP, 2015](#)). Federally endangered West Indian manatees (*Trichechus manatus*), a migratory species, visit Tampa Bay seasonally to feed in the seagrass meadows. Other endangered species in the bay documented to be impacted by N enrichment include green turtle (*Chelonia mydas*) and Atlantic sturgeon [*Acipenser oxyrinchus*; [Hernández et al. \(2016\)](#)]. Three national wildlife refuges (Egmont Key, Passage Key, and Pinellas) are located in Tampa Bay and support populations of nesting birds.



Source: [Poor et al. \(2013a\)](#).

**Figure 16-23 Tampa Bay mainstem segments and watershed. Also shown are the National Atmospheric Deposition (NADP) National Trends Network wet deposition monitoring site FL41 at Verna wellfield in Sarasota County and the NADP Atmospheric Integrated Research Monitoring Network site FL18 in Hillsborough County.**

The Tampa Bay watershed, located in the Eastern Temperate Forest ecoregion, is highly urbanized. It is now the second largest metropolitan area in Florida with a population of over 2 million people ([TBEP, 2015](#)). Pinellas, Hillsborough, and Manatee counties border directly on Tampa Bay while Pasco, Polk, and Sarasota counties are also within the estuary's 6,000-km<sup>2</sup> watershed ([Poor et al., 2013a](#)). Activities in Tampa Bay linked to the local and regional economy include shipping, tourism, and commercial and recreational fishing ([Poor et al., 2013a](#); [TBEP, 2006](#); [Tomasko et al., 2005](#)). More than 80 miles of

deep-water shipping channels carry water traffic to the three seaports along the bay's borders, in Tampa, St. Petersburg, and in northern Manatee County. The largest of these, the Port of Tampa, consistently ranks among the busiest ports in the nation.

Mangroves, salt marshes, and SAV habitats in Tampa Bay have all experienced significant reductions in extent since the 1950s, due to physical disturbance (dredge and fill operations) and water quality degradation ([TBEP, 2015](#)). Excess N enrichment in the bay is one of the main factors impacting water clarity and quality. The excess N leads to increased algal biomass and reduced light availability for shallow-water (less than a 3-m depth) SAV ([TBEP, 2015](#)). Numerous studies have shown that the waters of Tampa Bay are strongly N limited, due to a high concentration of phosphorus (P) from natural leaching and from active P mining in the watershed ([Greening et al., 2014](#)). Therefore, the primary focus for managing eutrophication in Tampa Bay has been the reduction of N loading to the bay ([Greening et al., 2014](#)).

Tampa Bay was designated an “estuary of national significance” by Congress in 1990. In 1998, the Tampa Bay National Estuary Program (TBNEP) partnership (consisting of the Florida Department of Environmental Protection [FDEP]; the U.S. Environmental Protection Agency; the counties of Hillsborough, Manatee, and Pinellas; the cities of Tampa, St. Petersburg, and Clearwater; and the Southwest Florida Water Management District) signed a formal Inter-local Agreement in support of a Comprehensive Conservation and Management Plan (CCMP) for Tampa Bay. Upon adoption of the Inter-local Agreement, the TBNEP became simply the Tampa Bay Estuary Program (TBEP). TBEP continues to finance research projects in support of the CCMP and coordinates the overall protection and restoration of the bay with assistance and support from its many formal and informal partners ([TBEP, 2015](#); [Morrison et al., 2011](#)). TBEP also coordinates the Tampa Bay N Management Consortium (TBNMC), a public-private partnership working to reduce nitrogen loading to the bay and whose members include local governments (Tampa, St. Petersburg, and others) along with key industries bordering the bay, such as electric utilities, fertilizer manufacturers, and agricultural operations.

The Tampa Bay watershed's human population is expected to increase over the next decade and a 7% increase in N loading is projected to occur ([TBEP, 2012a](#)). To account for these increases, the TBEP and TBNMC have adopted a new 17-ton/year reduction target for total N loading, to offset expected increases in total nitrogen (TN) loading and maintain TN loading rates at average annual rates for 1992–1994.

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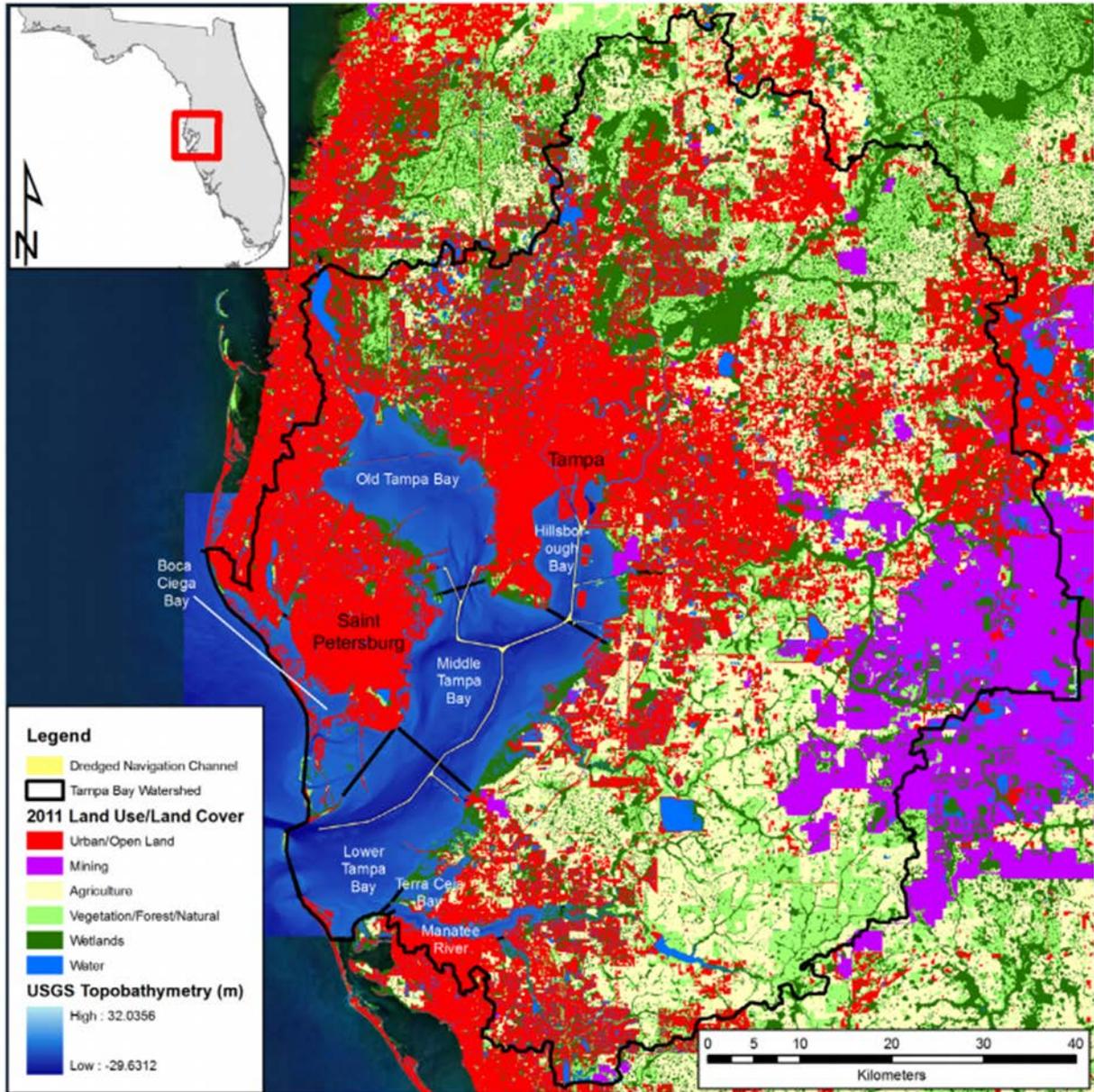
#### **16.4.1.2 Class I Areas**

The Tampa Bay area is not a Clean Air Act Prevention of Significant Deterioration (PSD) Class I area.

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#### **16.4.1.3 Regional Land Use and Land Cover**

Land use within the Tampa Bay watershed is mixed among undeveloped, agricultural, urban, and mining uses, including phosphate mining and fertilizer manufacturing. [Figure 16-24](#) shows the land coverage within the bay's border communities and watershed.

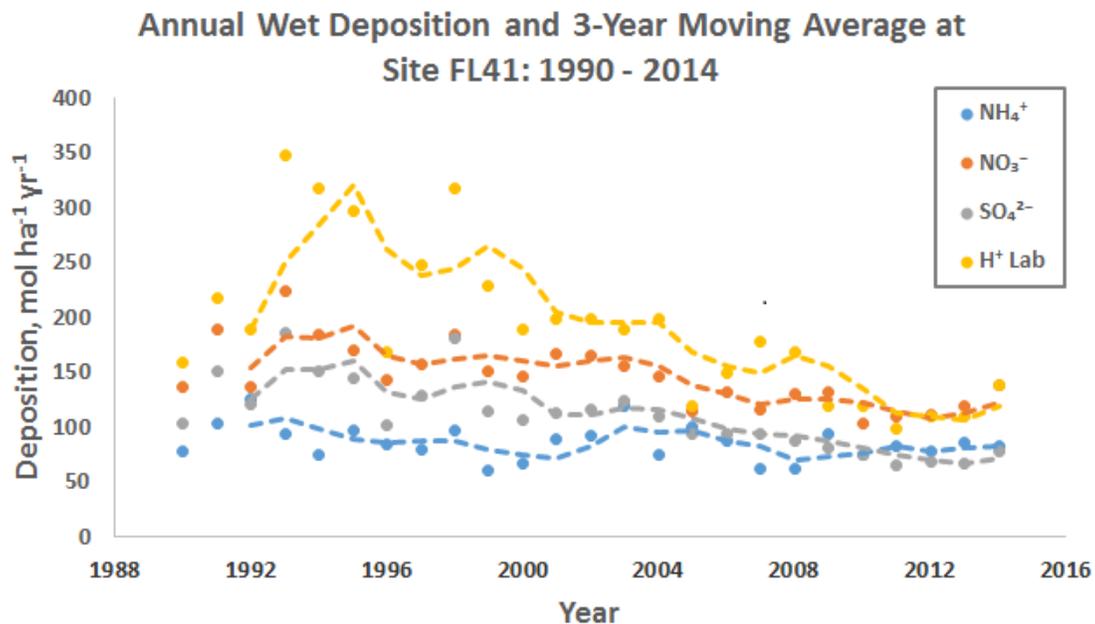


Source: [Sherwood et al. \(2016\)](#).

**Figure 16-24** Tampa Bay overview map highlighting watershed development and land use.

## 16.4.2 Deposition

Both direct atmospheric deposition of N to surface waters and indirect deposition to the watershed with subsequent transport to the Tampa Bay represent important sources of N to the case study area. In a 25-year time series with deposition data from the nearest National Atmospheric Deposition Program (NADP) National Trends Network (NTN) monitoring site ([Figure 16-23](#), Verna wellfield in Sarasota, FL), wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  show strong interannual variability, but downward trends in wet deposition of all these species are consistently found over the past 25 years ([Figure 16-25](#)).



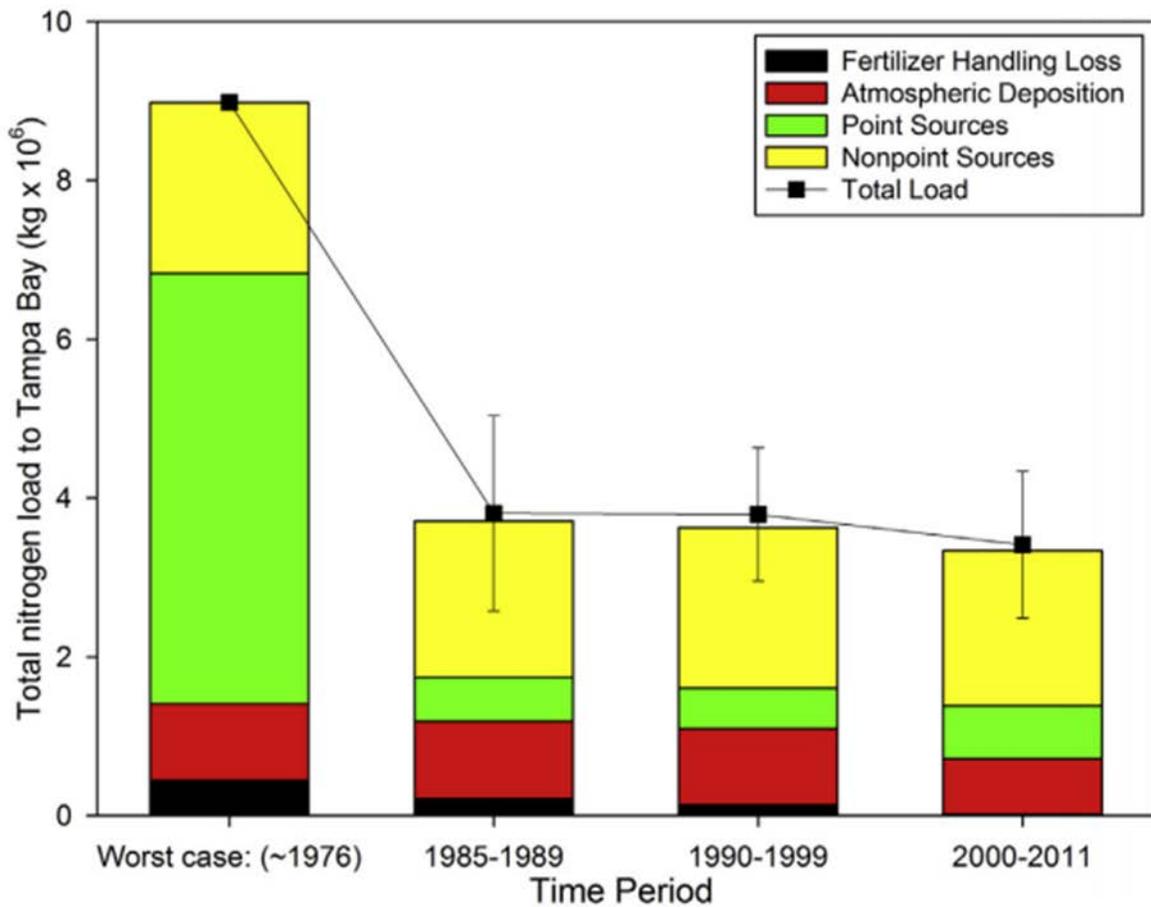
$\text{H}^+$  = hydrogen ion; ha = hectare; mol = mole;  $\text{NH}_4^+$  = ammonium;  $\text{NO}_3^-$  = nitrate;  $\text{SO}_4^{2-}$  = sulfate; yr = year.

Source: National Center for Environmental Assessment, U.S. EPA.

**Figure 16-25 Annual wet deposition of ammonium, nitrate, sulfate, and acidity at the National Atmospheric Deposition National Trends Network monitoring site closest to the Tampa Bay case study area.**

Between 2002 and 2007, U.S. EPA and Tampa Bay area scientists conducted an air quality modeling and measurement project called the Bay Region Atmospheric Chemistry Experiment (BRACE) in order to improve estimates of atmospheric N deposition to Tampa Bay ([Poor et al., 2013a](#); [Atkeson et al., 2007](#)). This project was also

established to identify sources of N deposition in the local Tampa Bay area and assess the impact of air quality regulations (Poor et al., 2013a). Although total nitrogen (TN) loading to Tampa Bay has trended downward over the past 20 years, the percentage of N from different sources has fluctuated. Direct atmospheric deposition has accounted for a greater average percentage of the TN loading in recent years (from 2007–2011) than in previous years [Greening et al. (2014); Poor et al. (2013a); Figure 16-26]. Mainstem segments of the bay vary widely in the percentage of total N loading attributable to direct atmospheric deposition (Janicki Environmental, 2013).



Source: [Greening et al. \(2014\)](#).

**Figure 16-26** Estimated annual loads of total nitrogen from various sources to Tampa Bay summarized from 1976 to 2011.

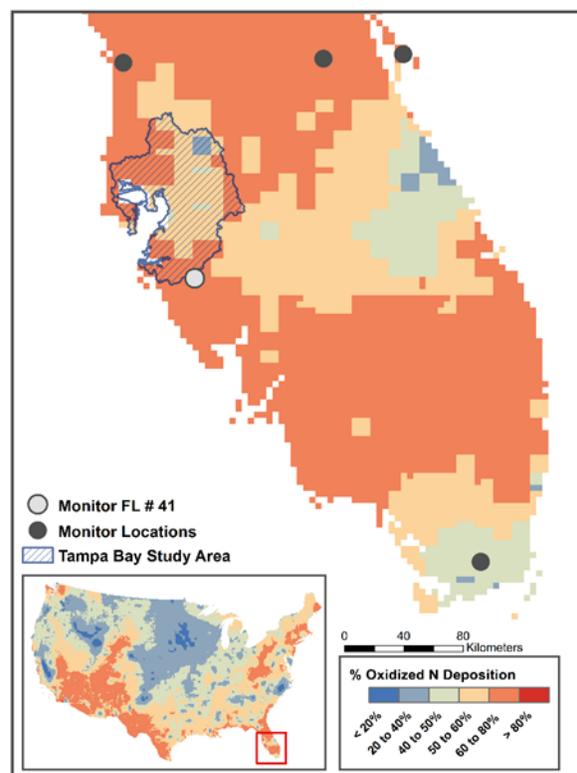
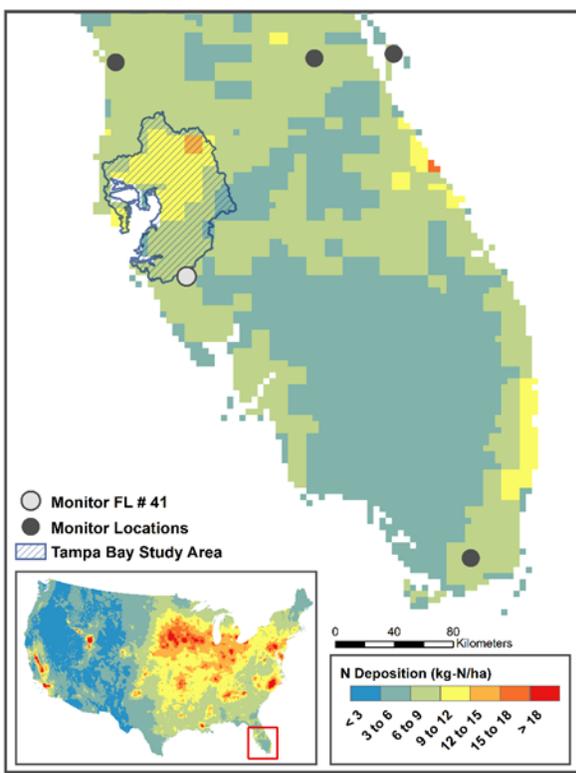
BRACE also investigated the primary sources of N deposition to the bay, which included power plants and mobile sources such as cars and trucks. Power plants had recently reduced N emissions through upgrades made as a result of TBEP's work with the TBNMC ([Poor et al., 2013a](#)). The sensitivity results suggested that, per unit of emission, mobile sources had a disproportionately higher contribution than power plant sources to atmospheric N deposition to Tampa Bay (over the watershed, the mobile NO<sub>x</sub> emissions were responsible for four times more oxidized-N deposition than the power plant emissions; over the bay, the mobile NO<sub>x</sub> emissions were responsible for twice as much oxidized-N deposition as the power plants). According to BRACE, reductions in N emissions from mobile sources must be a part of the strategy to reduce N loading to the bay, and that control of atmospheric N emissions both within and outside the Tampa Bay watershed is important to restore and maintain good water quality and a healthy ecosystem within the bay ([Poor et al., 2013a](#)).

The U.S. EPA recently modeled atmospheric deposition in Tampa Bay using TDEP with monitoring data from 2000 to 2013 (see [Appendix 2.7](#)). The general pattern of wet + dry deposition of N (NO<sub>y</sub> and NH<sub>x</sub>) for 2011–2013 shows that fluxes are higher in the northern half of the study area than the southern half ([Figure 16-27A](#)). The deposition of N varies by roughly a factor of two across the study area with higher deposition of N to the north and west of Tampa Bay and a maximum in the northeast corner of the study area. Fluxes are typically higher than those for the rest of Florida. However, they are not as high as in many areas of the central and northeastern U.S. Dry deposition of NO<sub>2</sub> accounts for approximately 1/6 of total deposition of oxidized N. At Tampa Bay (and some other NADP sites), dry fluxes are directed upward using the Community Multiscale Air Quality (CMAQ) model, due to the implementation of bidirectional exchange of NH<sub>3</sub>. (However, the net flux of NH<sub>x</sub> in CMAQ is still directed downward from wet deposition.).

Most N deposition in the case study area except for the northeastern corner is estimated to be mostly in oxidized form throughout the study area and in most of Florida, which is consistent with many areas in the eastern and southern U.S. ([Figure 16-27B](#)). This is generally in agreement with findings from BRACE modeling where oxidized forms of N made up 60% of the total atmospheric loading to Tampa Bay, compared to 40% for reduced forms such as ammonia [NH<sub>3</sub>; [Poor et al. \(2013a\)](#); [TBEP \(2012b\)](#)]. In the study area dry deposition dominates over wet deposition of N, which contrasts with many areas in southern Florida where wet deposition dominates ([Poor et al., 2013a](#)).

**A. Total Wet and Dry N Deposition in Southern Florida 2011-2013 (12 km resolution)**

**B. Percent Oxidized N Deposition in Southern Florida 2011-2013 (12 km resolution)**



ha = hectare; kg = kilogram; km = kilometer; N = nitrogen.

Notes: the Verna Wellfield National Atmospheric Deposition Program/National Trends Network monitoring site, FL41, was chosen to characterize long-term wet deposition of N species, because it is closest to the Tampa Bay study area. The site is located at the southern edge of the study area in Sarasota, FL and is shown as the grey dot on the maps.

Source: Data shown in the figures were obtained from the hybrid modeling/data fusion product, total deposition, <http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>, and described earlier in [Appendix 2.7](#).

**Figure 16-27 (A) Wet and dry nitrogen deposition in Tampa Bay and the surrounding area. (B) Percentage of oxidized nitrogen deposition in Tampa Bay and the surrounding area.**

**16.4.3 Long-Term Ecological Monitoring**

Tampa Bay has been intensively studied over the years due to its significance as a natural resource and its susceptibility to degradation from eutrophication. There is monthly ambient water quality data going back to 1972 ([Sherwood et al., 2016](#)). Phytoplankton biomass and primary production have been assessed regularly in the bay from the 1980s

and benthic organisms since 1993 ([Greening et al., 2014](#)). Aerial photography of the Tampa Bay shoreline is available from the early 1950s showing the extent of seagrass coverage prior to rapid human population increases in the watershed ([Greening et al., 2014](#)). A consistent monitoring program of seagrass extent (every 2 years) was started in 1988 ([Greening et al., 2014](#)).

Eutrophication symptoms were observed in Tampa Bay as early as the 1970s. These included phytoplankton and macroalgal blooms and areas of low dissolved oxygen ([Greening et al., 2014](#)). According to [Bricker et al. \(2007\)](#), algal blooms were common in the 1970s and caused foul odors and aesthetic impairment. In the late 1970s, hypoxic and anoxic conditions along the shoreline of the most urbanized segment of Tampa Bay caused extensive mortality of benthic organisms in the late summer months ([Greening et al., 2014](#)). Fish kills have also been observed in and near Tampa Bay. Historically, the most obvious symptom of eutrophication in Tampa Bay was the loss of light at depth due to elevated algal biomass. The loss of SAV from reduced light availability was dramatic. In 1950, approximately 16,000 hectares of SAV were present. By the early 1980s, over half of this area had been lost [[Figure 16-28](#); [Bricker et al. \(2007\)](#); [Haddad \(1989\)](#)].

Tampa Bay is somewhat unique in that the bay waters have historically exhibited a high level of P from local phosphate deposits, P mining, and fertilizer manufacturing and shipping operations. The high phosphorus concentrations have resulted in an unusually low N:P ratio in comparison to other estuaries, making N the limiting nutrient for phytoplankton growth ([Greening et al., 2014](#); [Greening and Janicki, 2006](#)). Numerous nutrient limitation studies using natural Tampa Bay phytoplankton populations and cultured test organisms have confirmed N limitation ([Greening et al., 2014](#)).



km = kilometer; mi = mile.

Notes: Red indicates area of submerged aquatic vegetation lost from 1950 to 1990.

Source: [Bricker et al. \(2007\)](#).

**Figure 16-28** Submerged aquatic vegetation cover loss in Tampa Bay.

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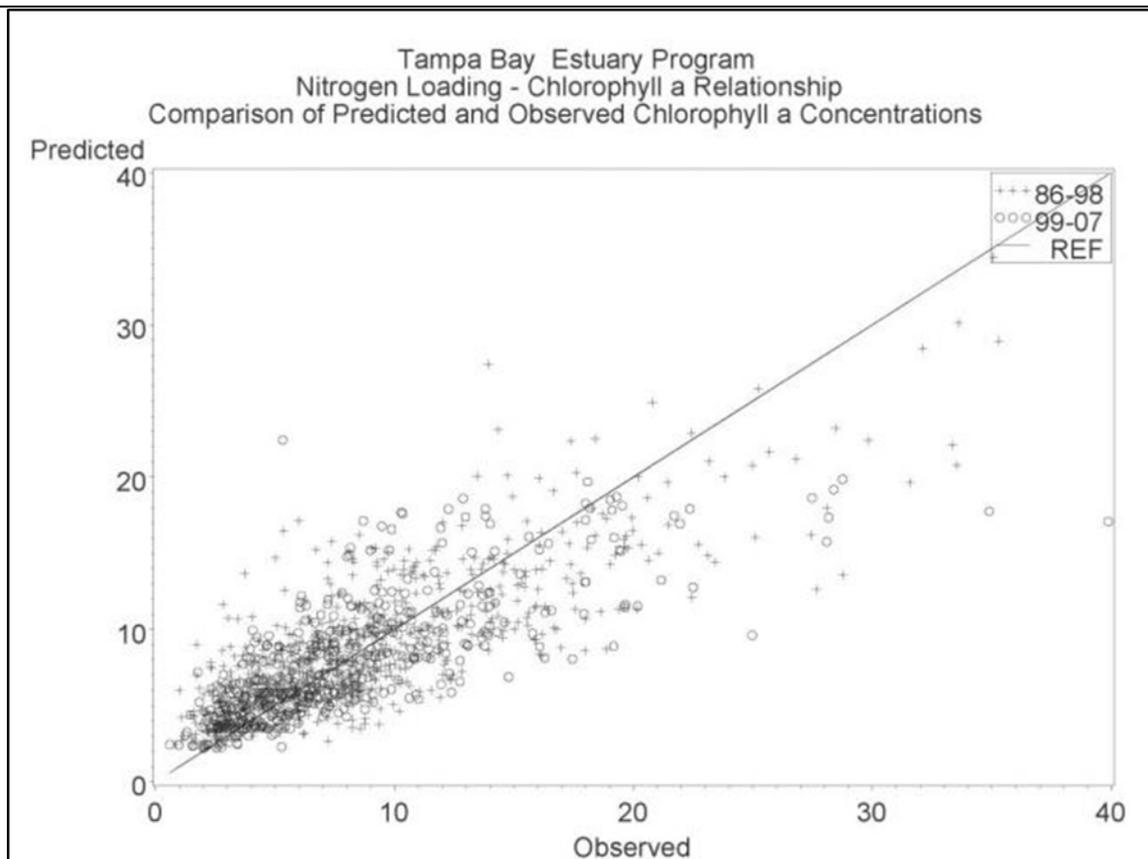
### 16.4.3.1 Indicators of Enrichment and Eutrophication in Tampa Bay

Indicators of historical water quality trends in the bay include chlorophyll *a* concentration and seagrass coverage ([Greening et al., 2014](#)).

### 16.4.3.1.1 Chlorophyll *a*

Phytoplankton biomass as measured by chlorophyll *a* concentration is one of the most effective indicators of eutrophication in the bay ([Sherwood et al., 2016](#)). Chlorophyll *a* is directly linked to nutrient inputs and has been measured in the bay since 1972. Increased algal biomass results in reduced light penetration in the water, thereby harming seagrass and ultimately resulting in the loss of SAV area.

The TBEP has developed water quality models to quantify linkages between N loads and bay water quality. N is generally the primary limiting nutrient, and chlorophyll *a* variation in the bay responds most significantly to watershed TN loads [[Figure 16-29](#); [Greening and Janicki \(2006\)](#)].



Source: [Janicki Environmental \(2011\)](#).

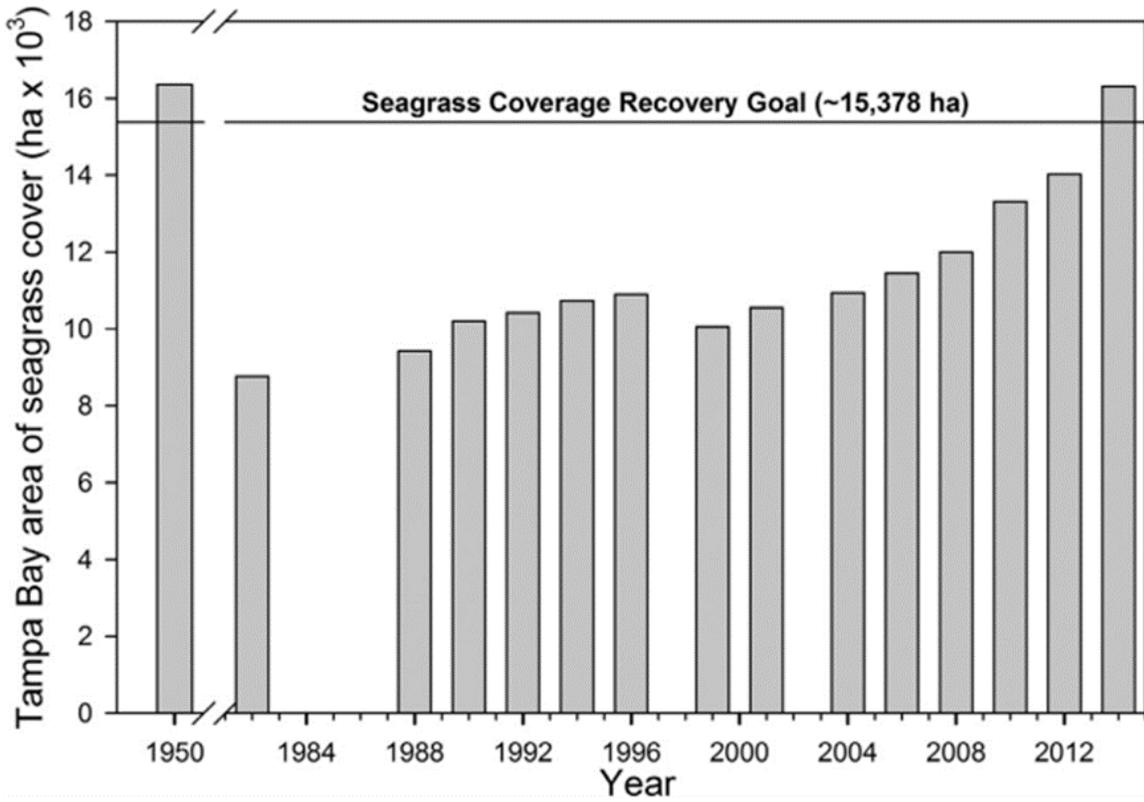
**Figure 16-29 Comparison of observed chlorophyll *a* and that predicted from the total nitrogen load—chlorophyll *a* relationships for all four mainstem Tampa Bay segments, for 1986–1998 and 1999–2007.**

Data show that, with the exception of the Old Tampa Bay segment in 2009 and 2011, chlorophyll *a* thresholds were not exceeded in all four major bay segments over the 2007–2011 period ([TBEP, 2012a](#)). The chlorophyll *a* threshold values are used as indicators of impairment and vary slightly for each different segment of the bay, ranging from 5.1 µg/L for Lower Tampa Bay, to 8.5 µg/L for Middle Tampa Bay, 9.3 µg/L for Old Tampa Bay, and 15 µg/L for Hillsborough Bay [expressed as annual averages; [TBEP \(2012a\)](#)].

#### 16.4.3.1.2 Seagrass Coverage

Five species of seagrasses, turtle grass (*Thalassia testudinum*), manatee grass (*Syringodium filiforme*), shoal grass (*Halodule wrightii*), star grass (*Halophila engelmannii*), and widgeon grass (*Ruppia maritima*), are found in Tampa Bay ([USGS, 2011](#)). These shallow-water grasses need sufficient light for photosynthesis and are sensitive to reduced water clarity associated with increased algal growth. Scientists have been tracking seagrass coverage as far back as the 1950s in Tampa Bay. Between the 1950s and 1980s seagrass coverage declined by about 50% or 9,000 ha in conjunction with decreased water quality and physical impacts to the bay such as dredging and filling ([Poor et al., 2013a](#); [Haddad, 1989](#)). Between 1999 and 2010, bay water clarity improved, chlorophyll *a* concentrations decreased, and seagrass coverage area steadily increased, coinciding with the reductions to N inputs to the bay [[Figure 16-30](#); [Greening and Janicki \(2006\)](#); [Poor et al. \(2013a\)](#); [TBEP \(2011\)](#); [TBEP \(2015\)](#)]. The most recent surveys of seagrasses (2014) exceeded the recovery goal set in 1995 [95% of estimated seagrass coverage of the 1950s; [Sherwood et al. \(2016\)](#)].

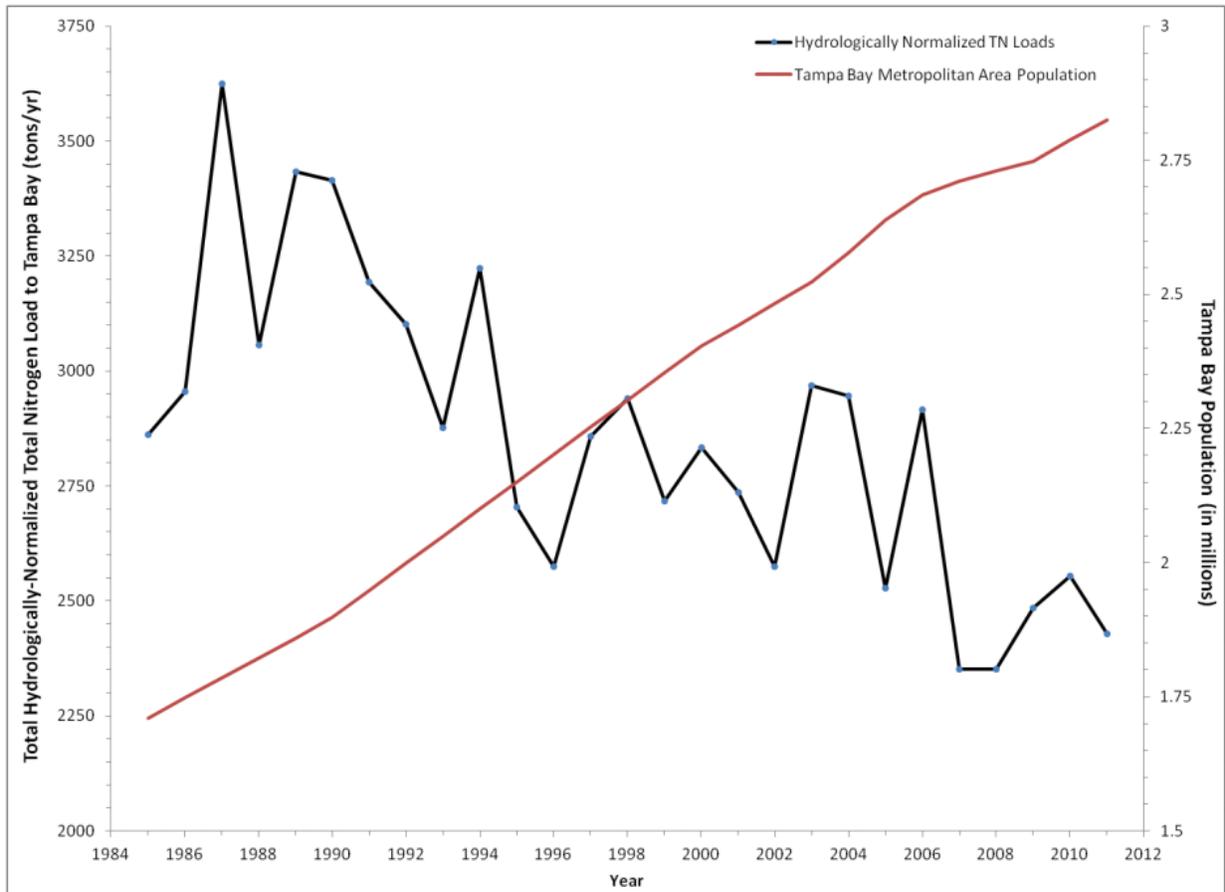
Through management actions, including an agreement with a power company to install air pollution control systems and the completion of more than 250 projects to reduce N inputs from the watershed, TN loadings to the bay have declined from previous annual average estimates despite an ever-increasing population in the Tampa Bay metropolitan area ([Figure 16-31](#)). Data compiled by the TBNMC indicate that continuing efforts to reduce N loading are resulting in more-than-sufficient water quality for the expansion of seagrasses ([TBEP, 2012a](#)).



ha = hectare.

Source: [Sherwood et al. \(2016\)](#).

**Figure 16-30 Total seagrass coverage in Tampa Bay circa 1950 through 2014.**



TN = total nitrogen; yr = year.

Source: [TBEF \(2012a\)](#).

**Figure 16-31** Trend in hydrologically normalized total nitrogen load to Tampa Bay relative to population increases in the Tampa Bay metropolitan area.

[Russell and Greening \(2015\)](#) estimated a potential relative cost savings of \$22 million per year in avoided wastewater treatment plant costs due to nutrient reductions associated with restoration and recovery of seagrass, marsh, and mangrove habitats in Tampa Bay. Ecosystem services benefits of over \$365 million estimated over an 18-year period from 1990 to 2008 include C sequestration and nutrient reductions via denitrification.

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## 16.4.4 Nitrogen Management

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### 16.4.4.1 Numeric Nutrient Criteria

In 1998, the U.S. EPA published the *National Strategy for the Development of Regional Nutrient Criteria* to promote the use of nutrient concentration levels in state water quality standards ([U.S. EPA, 1998b](#)). Historically, Florida had a narrative nutrient water quality criterion in place to protect waters against nutrient enrichment. In 2011, the state adopted the first set of statewide numeric nutrient standards for Florida's waters. By 2015, almost all of the remaining waters in Florida had numeric nutrient standards. Numeric nutrient criteria in Florida are established for all estuary segments and include criteria for TN, total phosphorus (TP), and chlorophyll *a*. For open ocean coastal waters, numeric criteria are derived from satellite remote sensing techniques and established for chlorophyll *a* only. Numeric nutrient criteria covering all of the mainstem segments and estuarine segments in Tampa Bay were approved by the U.S. EPA in November 2012 ([U.S. EPA, 2012c](#)). A map of the bay segments is provided in [Figure 16-23](#). The numeric nutrient criteria for chlorophyll *a* for the mainstream segments of Tampa Bay are shown in [Table 16-19](#).

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**Table 16-19 Numeric nutrient criteria for chlorophyll *a* for the four mainstem segments of Tampa Bay adopted by the Florida Department of Environmental Protection.**

Bay Segment	Chlorophyll <i>a</i> (µg/L)
Old Tampa Bay	9.3 as annual mean
Hillsborough Bay	15.0 as annual mean
Middle Tampa Bay	8.5 as annual mean
Lower Tampa Bay	5.1 as annual mean

L = liter; µg = microgram.

Modified from [Sherwood et al. \(2016\)](#).

Tampa Bay's numeric nutrient criteria for TN ([Table 16-20](#)) is expressed as tons/million cubic meters of water as an annual total not to be exceeded more than once in a 3-year period and represents an unorthodox approach to developing nitrogen nutrient criteria

([Florida DEP, 2016](#); [Sherwood et al., 2016](#)). These values are based on previously adopted total maximum daily loads (TMDLs) or nutrient targets developed by TBEP. Usually, the U.S. EPA’s numeric nutrient criteria are expressed as a concentration, but TMDLs are typically expressed as loads. The N management strategy for Tampa Bay linked seagrass growth to external N loadings based on evidence that TN loads, resultant chlorophyll and light attenuation, and seagrass response were closely correlated ([Sherwood et al., 2016](#); [Janicki Environmental, 2011](#)). The TBNMC also found that when freshwater inputs are greater, TN moves through the system more quickly; therefore, residence time was an important consideration. TN loads and hydrologic loads affect both the chlorophyll within the bay, and the amount of TN delivered per unit water was used to set the numeric nutrient criteria for Tampa Bay. The FDEP and the U.S. EPA both agreed that this framework, although unique for numeric nutrient criteria, would provide reasonable assurance that the state water quality criteria would be met in Tampa Bay ([Sherwood et al., 2016](#); [Greening et al., 2014](#)).

**Table 16-20 Numeric nutrient criteria for total nitrogen for the four mainstem segments of Tampa Bay.**

Segment	Nitrogen Delivery Ratio Threshold (tons/million m <sup>3</sup> )
Old Tampa Bay	1.08
Hillsborough Bay	1.62
Middle Tampa Bay	1.24
Lower Tampa Bay	0.97

m = meter; TBEP = Tampa Bay Estuary Program; TN = total nitrogen.

TBEP estuarine numeric nutrient criteria expresses as nitrogen delivery ratio (tons TN per million m<sup>3</sup> hydrologic load) based on 1992–1994 conditions.

Source: [Florida DEP \(2016\)](#), [Janicki Environmental \(2011\)](#).

#### **16.4.4.2 Nitrogen Management Consortium Efforts**

The TBEP was established in 1992 as a part of the U.S. EPA’s National Estuary Program ([Sherwood et al., 2016](#)). TBEP coordinates TBNMC, a public-private partnership working to reduce N loading to the bay and whose members include 40+ local governments (Tampa, St. Petersburg, and others) along with key industries bordering the bay, such as electric utilities, fertilizer manufacturers, and agricultural operations.

In recent years, one focus of the TBNMC's strategy has been to allocate N loads for major point and nonpoint sources in order to meet state and federal requirements. The governments and industries participating in the TBNMC voluntarily committed to cap their N loads at average annual levels recorded in 2003–2007, which also meets the 1998 federally recognized TMDL for N. These capped allocations have been adopted by the state of Florida and incorporated into NPDES discharge permits ([TBEP, 2014](#)). One example of the Consortium's work is the reconfiguration of coal-fired plants in the Tampa Bay watershed to reduce NO<sub>x</sub> emissions ([Poor et al., 2013a](#)).

Every 5 years, the TBNMC must submit a Reasonable Assurance Update document to FDEP for approval to document progress toward water quality and seagrass management goals. The most recent reasonable Assurance Update (2012) presented data to show that reasonable progress has been made towards the attainment of designated uses of Tampa Bay. Based on this conclusion, FDEP upgraded Hillsborough Bay and Old Tampa Bay segments to assessment Category 4b for nutrients (adequate management in place) from Category 5 (impaired), and segments in Lower Tampa Bay were moved from Category 4b to Category 2 (attains standards), signifying the state's recognition of significant improvements in water quality and seagrass expansion ([TBEP, 2014](#)). The Consortium members share the cost of the data collection and analysis to prepare the Reasonable Assurance Update document, and the next update will cover progress made during the 2013–2017 time period.

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#### **16.4.4.3 Response to Nitrogen Management Strategies**

A recent paper reviewing the response of Tampa Bay to N management strategies presented evidence of the ecosystem's recovery constituting a "regime shift" trajectory ([Duarte et al., 2015](#); [Duarte et al., 2009](#)). Since the mid-1980s Tampa Bay has shifted back to a clear water seagrass system from a phytoplankton-dominated system that was characteristic of the bay under previously eutrophic conditions. Following recovery from an El Niño heavy rainfall period (1997–1998), water clarity in Tampa Bay increased significantly, and seagrass expanded at a rate significantly different than before the event, suggesting a feedback mechanism observed only in a few other systems. The authors observed that too often these estuarine ecosystems are not able to recover even when eutrophication stressors are mitigated because of the concurrent changes in environmental conditions, that affected ecosystem dynamics occurring over the time period from the onset of eutrophication to the reduction of nutrient levels. [Greening et al. \(2014\)](#) noted four specific elements of the Tampa Bay management strategy that have resulted in a successful recovery trajectory: (1) development of numeric water quality targets in consultation with stakeholders, (2) citizen involvement in calling for action from

regulatory agencies, (3) collaborative actions such as the TBNMC, and (4) state and federal regulatory programs. BRACE scientists concluded that declines in atmospheric N deposition to the estuary and its watershed were likely part of the historical improvement in water clarity and increases in seagrass acreage ([Poor et al., 2013a](#); [TBEP, 2011](#)).

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## 16.5 Rocky Mountain National Park Case Study

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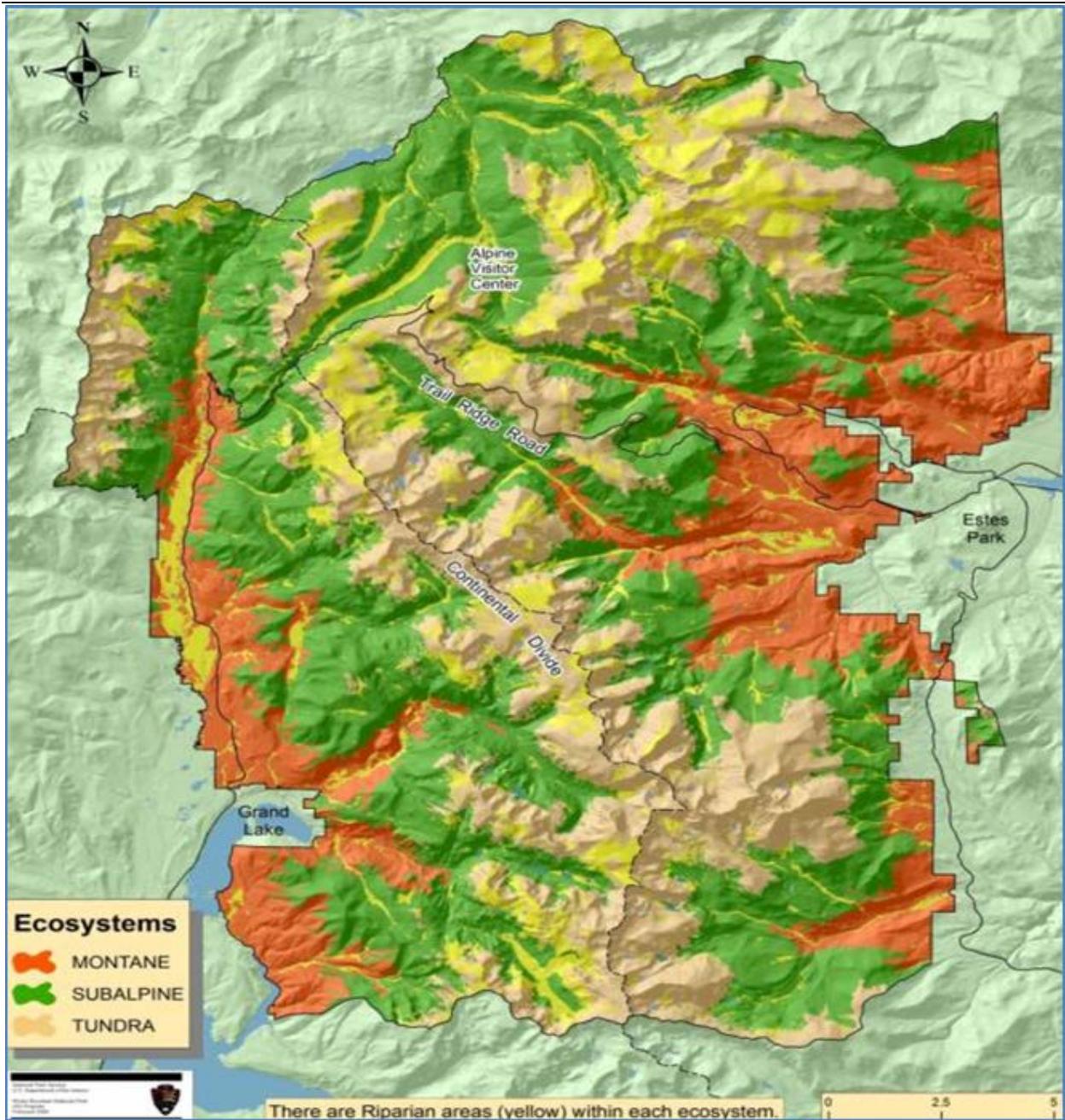
### 16.5.1 Background

This case study describes the environment and ecology of Rocky Mountain National Park (ROMO) and summarizes research that provides insight into the impacts of atmospheric nitrogen and sulfur deposition on terrestrial and aquatic ecosystems in ROMO. This includes atmospheric deposition research from within ROMO, the surrounding area of the Rocky Mountains, as well as other portions of the Northwestern Forested Mountains ecoregion. Although the focus is on research published since 2008, publications prior to 2008 are used to establish context and identify long-term trends.

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#### 16.5.1.1 Description of Case Study Region

Rocky Mountain National Park (ROMO) was established by Congress in 1915 and is located in the Front Range of the Rocky Mountains in north-central Colorado, about 80 km northwest of Denver. Straddling the Continental Divide, the western side of ROMO serves as the headwaters for the Colorado River and eastern slope feeding the South Platte River Basin ([Wolfe et al., 2003](#)). The land within ROMO contains steep elevation gradients and diverse ecosystem types, ranging from talus slopes at high elevations and permanent glaciers above 4,000 m to grassy meadows at 2,400 m. Over 25% of ROMO is above the tree line (about 3,500 m), and ROMO contains large areas of alpine tundra. In addition, there are more than 60 peaks above 3,600 m in elevation ([Porter and Johnson, 2007](#)). Ecologically, ROMO is part of the Northwestern Forested Mountains ecoregion ([Figure 16-32](#)).



Source: [Clarke \(2013\)](#).

**Figure 16-32 Rocky Mountain National Park ecosystems.**

The ecoregion hosts extremely diverse vegetation and well-defined community zones along elevation gradients. Winter snow cover averages 1.5 m annually in the Rocky Mountains, and is a strong determinant of both plant and soil biodiversity ([Clow et al., 2016](#)). More than 1,000 species of vascular plants have been documented in ROMO ([NPS, 2013](#)). Within the alpine tundra, plant communities contain willow (*Salix* spp.) and a variety of grasses, sedges, and forbs such as alpine sunflower (*Rydbergia grandiflora*) and alpine forget-me-nots (*Polemonium viscosum*). The subalpine zone is composed primarily of forests, dominated by Engelmann spruce (*Picea engelmannii*), subalpine fir (*Abies lasiocarpa*), and limber pine (*Pinus flexilis*), whereas forests in the montane zone vary from lodgepole pine (*Pinus contorta*) at cold high elevation sites, trembling aspen (*Populus tremuloides*) in moist sites, and Douglas fir (*Pseudotsuga menziesii*) and ponderosa pine (*Pinus ponderosa*) at more moderate and xeric sites, respectively ([Beidleman et al., 2000](#)).

More than 270 species of birds, including migratory species, have been reported in this area over the last 100 years. Many are unique to mountainous habitats—aspens, ponderosa pine, high-elevation willow, and spruce-fir vegetation types—found in the southern Rocky Mountains. Seven native fish and four exotic fish inhabit the aquatic systems of ROMO. Sixty-seven mammal species are known to be native to the area, but grizzly bears (*Ursus arctos*), gray wolves (*Canis lupus*), and bison (*Bison bison*) were locally extirpated in the 19th and early 20th centuries. The lynx (*Lynx canadensis*) and wolverine (*Gulo gulo*) are either extirpated or extremely rare. Moose (*Alces alces*) are now common but were not historically recorded as part of this area of the Rocky Mountains. A select group of four amphibian and two reptile species survive the high elevations and cold temperatures in ROMO. They are all considered species of concern due to apparent low numbers, lack of information about their status, and/or declining population trends. There are 141 confirmed species of butterflies, but arthropod (insects, spiders, centipedes, etc.) communities in ROMO have not been as well documented as other taxonomic groups.

The NPS maintains a list of species known to occur in ROMO that are considered endangered, threatened, or candidates for protection by the Endangered Species Act ([NPS, 2013](#)):

- Boreal toad (*Bufo boreas boreas*)—candidate
- Yellow-billed cuckoo (*Coccyzus americanus*)—candidate
- Canada lynx (*Lynx canadensis*)—threatened
- Greenback cutthroat trout (*Oncorhynchus clarki stomias*)—threatened

[Pardo et al. \(2011c\)](#) reported that responses to elevated N deposition in the Northwestern Forested Mountains ecoregion include alteration of soil carbon:nitrogen (C:N) ratios, base cation composition, and accelerated N cycling rates, including increased

mineralization and nitrification. Further changes described in this case study and in other Appendices include plant, lichen, and algal chemistry; surface water chemistry (including N concentration and acid neutralizing capacity); catchment N leaching rate; and changes in the community composition of plants, lichens, and phytoplankton.

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### **16.5.1.2 Class I Areas**

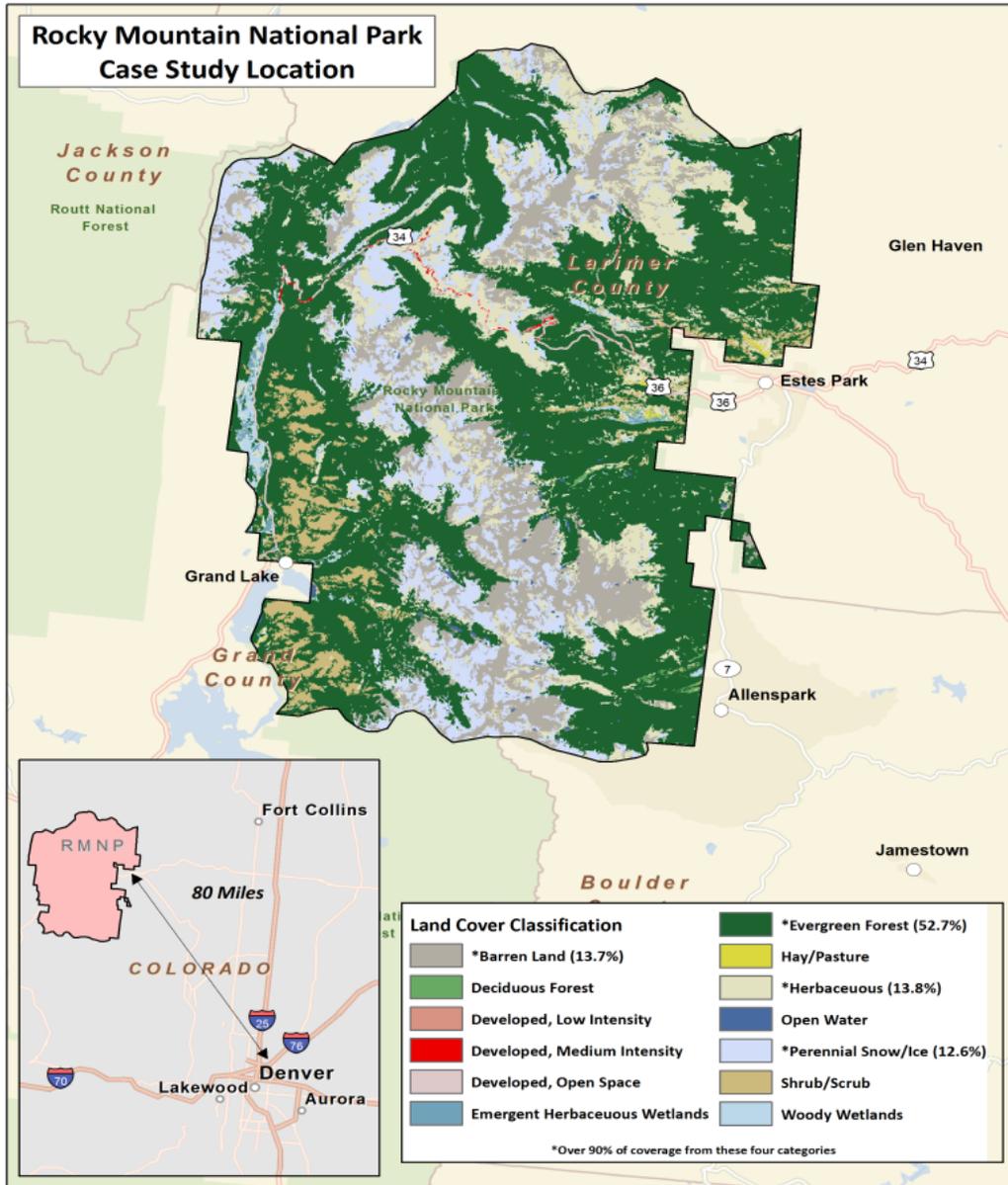
Rocky Mountain National Park is designated as a federal Class I area. The Clean Air Act (42 USC 7470) authorized these Class I areas to protect air quality in national parks over 6,000 acres and national wilderness areas over 5,000 acres in an effort to preserve pristine atmospheric conditions. Class I areas are subject to the “prevention of significant deterioration (PSD)” regulations under the Clean Air Act (42 USC 7470). New and modified existing air pollution sources are required to have PSD preconstruction permits and air regulatory agencies are required to notify federal land managers (FLMs) of any PSD permit applications for facilities within 100 km of a Class I area.

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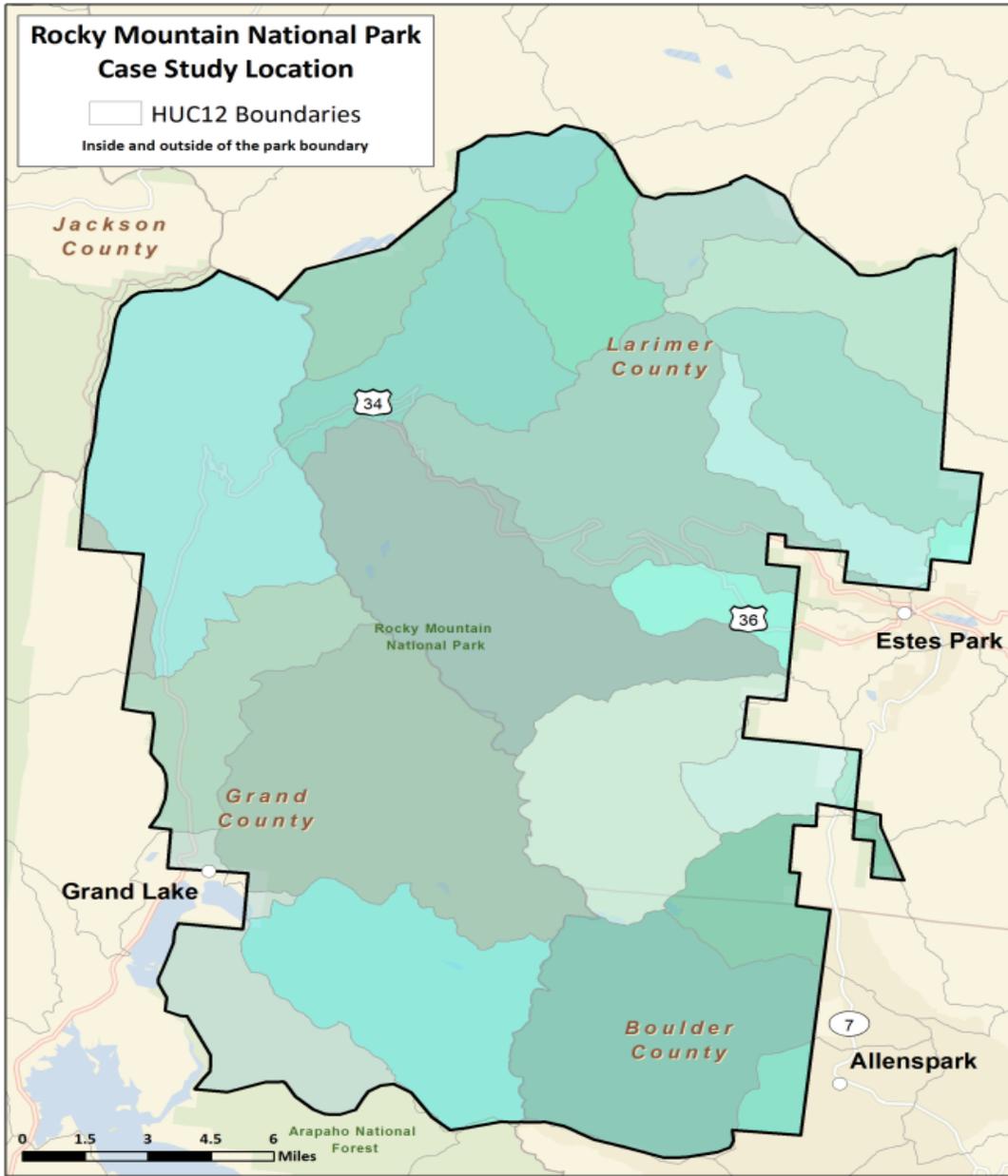
### **16.5.1.3 Regional Land Use and Land Cover**

The land area within the ROMO region falls predominantly into four land cover classifications: evergreen forest, barren land, herbaceous cover, and perennial snow/ice ([Figure 16-33](#)). The remainder of the land coverage categories account for less than 7% of the total area. The area immediately surrounding ROMO is largely forested. Regionally, the land to the north, west, and south of ROMO is predominantly forested, with some grasslands used as grazing land. The region to the east and southeast contains more grassland, agricultural, and urban land use. The smaller towns of Estes Park, Allenspark, and Grand Lake are close to the boundaries of ROMO ([Figure 16-34](#)), while the larger population centers of Fort Collins and the Denver metropolitan area are further to the east and southeast, respectively ([Figure 16-33](#) inset).

There are 29 total watersheds at the U.S. Geological Survey level-12 hydrological unit code (HUC12s) scale that fall completely or partially inside ROMO ([Figure 16-34](#)).



**Figure 16-33 Rocky Mountain National Park land coverage using the land cover classifications as mapped by the National Land Cover Dataset. Percentage of cover is shown for the four dominant cover types.**



HUC = hydrologic unit code.

**Figure 16-34 Rocky Mountain National Park hydrologic unit code 12 watersheds.**

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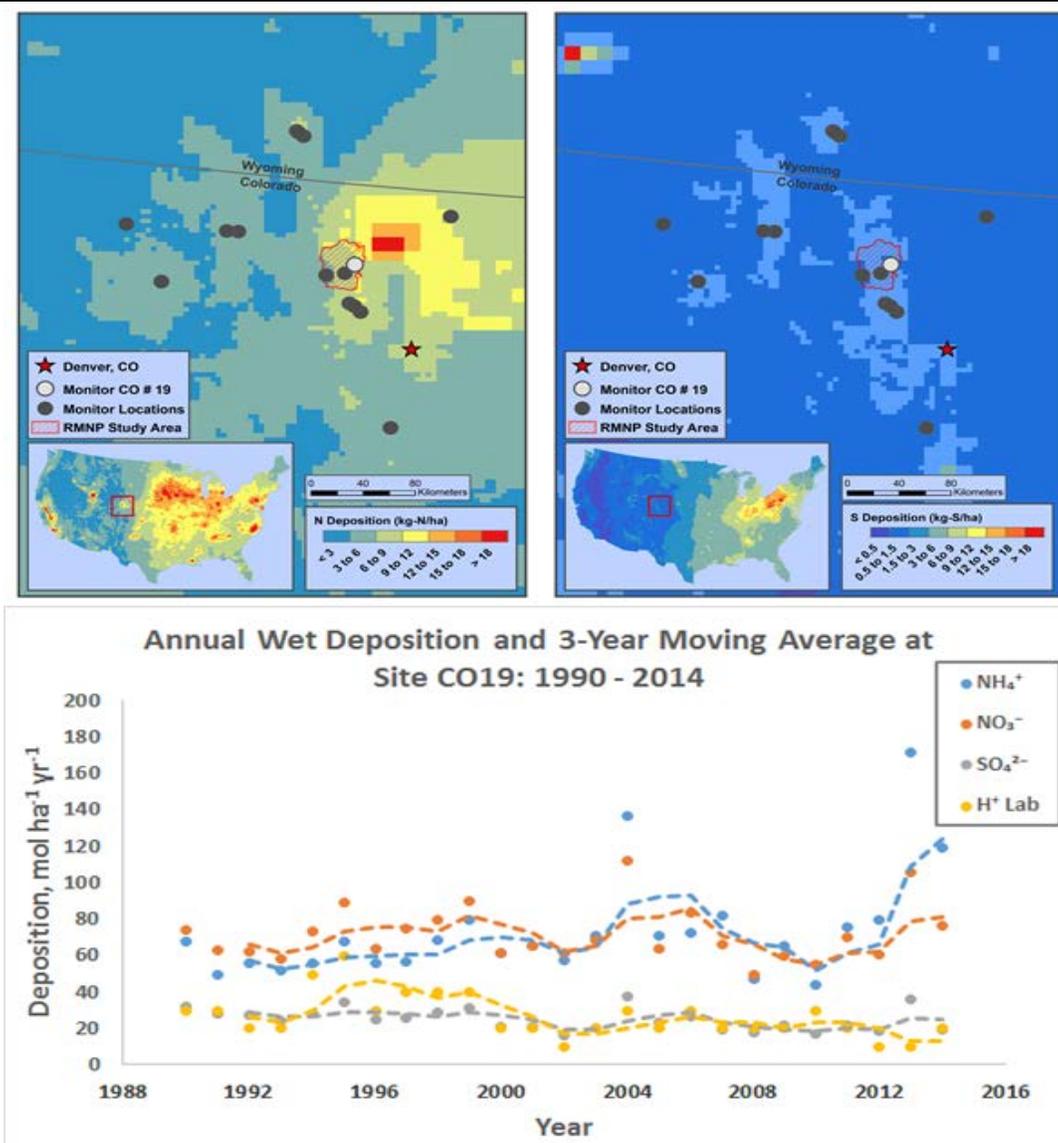
## 16.5.2 Deposition

Based on TDEP calculations (see [Appendix 2](#) of the ISA), most of ROMO is estimated to receive deposition between 3–9 kg N/ha/yr and 3–6 kg S/ha/yr ([Figure 16-35](#)). In contrast to the low rates observed throughout much of the western U.S., rates of N deposition within ROMO are relatively high, and areas to the east of ROMO experience deposition rates similar to areas in the north-central U.S. (see [Figure 16-35](#) N deposition inset). However, the estimated rates of S deposition are consistent with the low rates observed elsewhere in the western U.S. and considerably lower than the S deposition rates observed within the Ohio Valley. Within these TDEP estimates, the inorganic N deposition in ROMO is relatively evenly balanced between oxidized and reduced forms, with the northeastern portion of the region receiving predominantly reduced forms of N ([Figure 16-36](#)). There are three National Atmospheric Deposition Program (NADP) measurement sites within ROMO ([Figure 16-36](#)), including measurements stretching back more than 30 years at the Loch Vale and Beaver Meadows sites. Over the past 25 years, sulfate ( $\text{SO}_4^{2-}$ ) and hydrogen ion ( $\text{H}^+$ ) deposition have declined slightly at the Beaver Meadows site (CO19), whereas deposition of ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) has been relatively constant ([Figure 16-35](#)). See [Appendix 2.4](#), [Appendix 2.5](#), and [Appendix 2.6](#) for more information on deposition in the U.S. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

Atmospheric N deposition generated from anthropogenic sources is a significant influence on many ecosystems within ROMO ([Wolfe et al., 2003](#); [Baron et al., 2000](#); [Williams and Tonnessen, 2000](#); [Williams et al., 1996a](#); [Caine, 1995](#)). For this reason, atmospheric N deposition has been the focus of considerable research, including the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study ([Beem et al., 2010](#)). The RoMANS study was designed to characterize the sources as well as the transport, transformation, and deposition processes of oxidized S and oxidized and reduced forms of N ([Beem et al., 2010](#)).

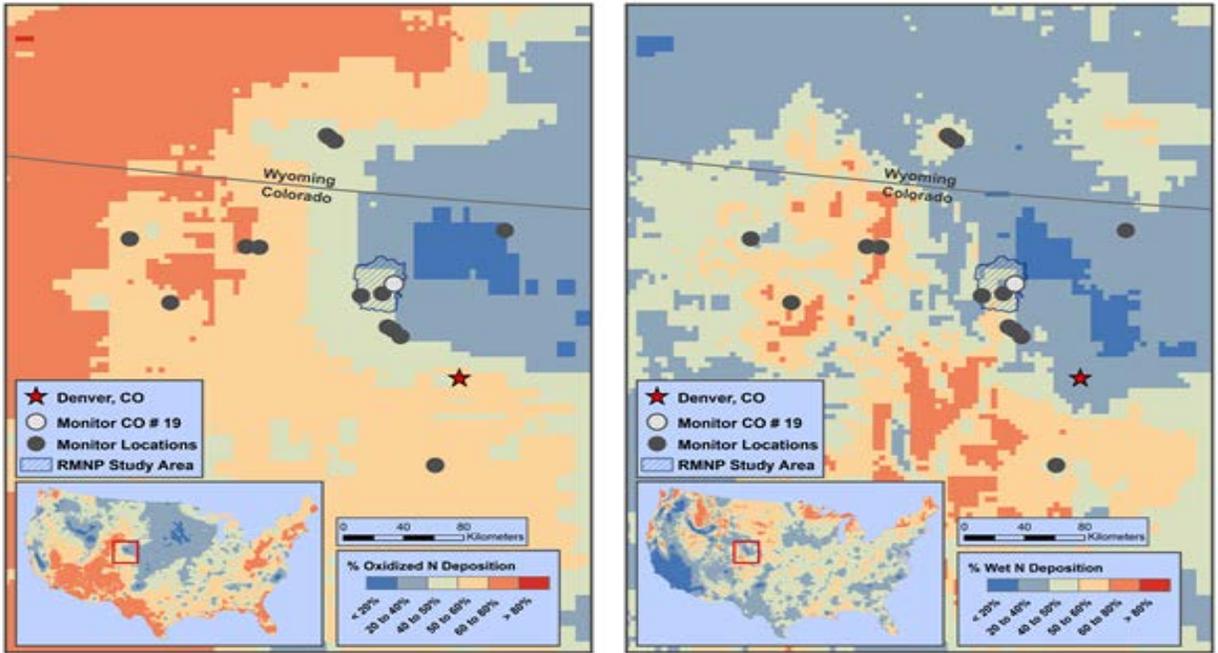
Primary atmospheric transport to ROMO is from the west and northwest. However, atmospheric circulation patterns along the Colorado Front Range can be complex, and significant quantities of precipitation can fall on the east side of ROMO when easterly upslope events occur ([Porter and Johnson, 2007](#); [Mast et al., 2003](#); [Baron and Denning, 1993](#)). For instance, although prevailing pattern of atmospheric circulation brings relatively clean air from west of ROMO, anthropogenic N can be transported to ROMO from urban and agricultural areas along the Front Range when convective heating over the plains produces easterly upslope winds ([Figure 16-37](#)). Higher than 3,000 m above sea level (masl), westerly air flow dominates over the upslope pollution ([Sievering et al.,](#)

1996), but coal-fired power plants located in Hayden and Craig, CO approximately 150 km west of ROMO, emit NO<sub>x</sub> that may reach ROMO with prevailing westerly winds.



H<sup>+</sup> = hydrogen ion; ha = hectare; kg =kilogram; mol = mole; N = nitrogen; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; RMNP = Rocky Mountain National Park; S = sulfur; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

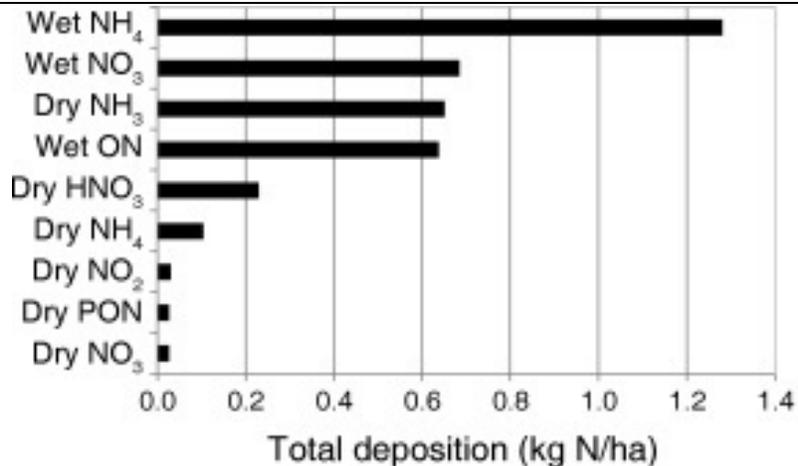
**Figure 16-35** Total atmospheric nitrogen and sulfur deposition in the Rocky Mountain National Park region based on TDEP calculations averaged from 2011–2013 (see [Appendix 2](#)) and long-term trends in wet atmospheric deposition from the Beaver Meadows National Atmospheric Deposition Program Monitoring site within Rocky Mountain National Park.



N = nitrogen; RMNP = Rocky Mountain National Park.

**Figure 16-36** Percentage of atmospheric nitrogen deposited in oxidized forms and through wet deposition in the Rocky Mountain National Park region based on TDEP calculations averaged from 2011–2013 (see [Appendix 2](#)).





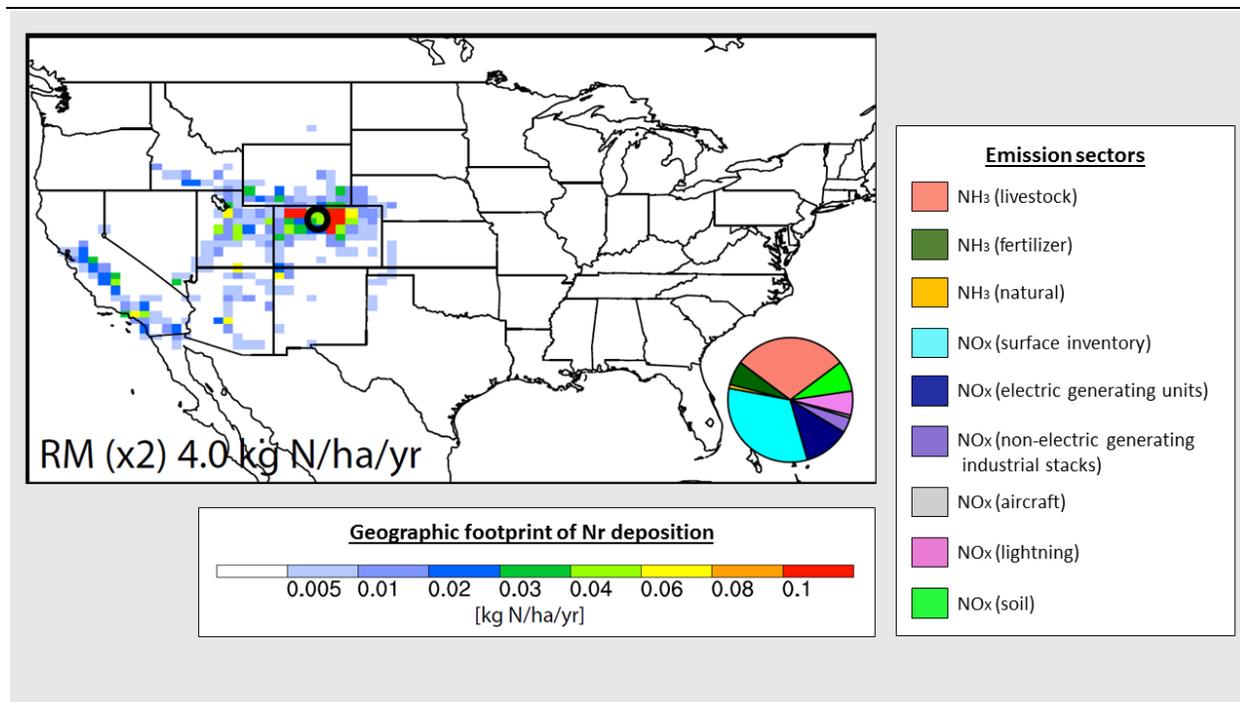
ha = hectare; HNO<sub>3</sub> = nitric acid; kg = kilogram; N = nitrogen; NH<sub>3</sub> = ammonia; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>2</sub> = nitrogen dioxide; NO<sub>3</sub><sup>-</sup> = nitrate; ON = organic nitrogen; PON = particulate organic nitrogen.

Source: [Benedict et al. \(2013\)](#).

**Figure 16-38 National Park from November 2008 to November 2009, including organic nitrogen and particulate organic nitrogen.**

Modeling conducted by [Gebhart et al. \(2011\)](#) suggests that the majority of the ammonia measured in ROMO during the RoMANS study was emitted within Colorado. Modeling conducted by [Lee et al. \(2016\)](#) suggested that reduced N deposition comes mostly from sources east of the park, and oxidized N deposition comes primarily from sources west of the park. Major emission sources of N to deposition in ROMO include ammonia from livestock and oxidized N from mobile sources ([Figure 16-39](#)).

Aeolian dust deposition from the Colorado Plateau mitigates some of the acidifying effects of S and N deposition in ROMO. Between 1993 and 2014, dust deposition increased by as much as 81% in the southern Rocky Mountains. [Clow et al. \(2016\)](#) estimated that deposition of dust has altered snowpack chemistry by increasing its alkalinity (annual change of 0.32 μeq Ca<sup>2+</sup>/L/year) over the same time period in which smaller magnitude decreases in acid deposition to the snowpack (annual changes of -0.10 μeq SO<sub>4</sub><sup>2-</sup>/L/year and -0.07 μeq NO<sub>3</sub><sup>-</sup>/L/year) have occurred.



Source: Adapted from Figure 5 in [Lee et al. \(2016\)](#).

**Figure 16-39 Annual-averaged monthly footprint of reactive N deposition in Rocky Mountain National Park(4.0 kg N/ha/yr), and pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model.**

### 16.5.3 Critical Loads and Other Dose-Response Relationships

This section focuses on studies that describe dose-response functions and/or critical loads (CL) for atmospheric deposition effects on ecological endpoints. Terrestrial effects are discussed first, followed by aquatic effects and a discussion on integration.

#### 16.5.3.1 Terrestrial Critical Loads and Dose-Response Relationships

Among terrestrial ecosystems impacted by N deposition, alpine ecosystems are particularly sensitive to increased availability of N due to inherently low rates of N cycling, low rates of primary production, and thin, poorly weathered soils ([Fenn et al., 1998](#)). Among taxonomic groups in this ecoregion, the impact of atmospheric deposition

on epiphytic lichens is concerning because their strong dependence on atmospheric deposition for nutrients and unique symbiotic physiology makes them highly vulnerable to N and S pollution and because lichens are important contributors to ecosystem services (Brodo et al., 2001). Among lichens, the structure and physiology of oligotrophic species makes them especially important components of winter food webs, hydrologic and nutrient cycles, and wildlife habitat (McCune and Geiser, 1997).

**16.5.3.1.1 Empirical Studies**

In the Pardo et al. (2011c) critical loads assessment, most of the studies examining the responses of alpine ecosystems were conducted in the Colorado Front Range of the Rocky Mountains, either in ROMO or in adjacent ecosystems such as the Niwot Ridge Long-Term Ecological Research site. Critical load values for these alpine ecosystems ranged from 1.2 to >20 kg N/ha/yr, excluding two values from Fenn et al. (2008) which were determined for southwestern forested ecosystems in California (Table 16-21).

**Table 16-21 Terrestrial empirical critical loads of nutrient nitrogen for the Northwestern Forested Mountains ecoregion.**

CL (kg N/ha/yr)	Species	Response	Method	Deposition/ Addition	Site	Reliability in Pardo et al. (2011c)	Reference
1.2 to 3.7	Epiphytic lichens (150 species)	Lichen community change in mixed-conifer forests	Application of western Oregon and Washington model	Total deposition: 0.8 to 8.2 kg N/ha/yr (CMAQ)	Coastal Alaska	(#)	<a href="#">Geiser et al. (2010)</a>
2.5 to 7.1	Epiphytic lichens Fenn: <i>Letharia vulpina</i> Geiser: 150 species	Lichen community change in mixed-conifer forests	Fenn: empirical CLs and DayCent modeling Geiser: application of western Oregon and Washington model	Fenn: Inorganic N throughfall: 1.4 to 71.1 kg N/ha/yr Geiser: Total deposition: 0.8 to 8.2 kg N/ha/yr (CMAQ)	Sierra Nevada and San Bernardino Mountains	##	<a href="#">Fenn et al. (2008)</a> <a href="#">Geiser et al. (2010)</a>

**Table 16-21 (Continued): Terrestrial empirical critical loads of nutrient nitrogen for the Northwestern Forested Mountains ecoregion.**

CL (kg N/ha/yr)	Species	Response	Method	Deposition/ Addition	Site	Reliability in Pardo et al. (2011c)	Reference
4	Subalpine forest (Engelmann spruce [ <i>Picea engelmannii</i> ])	Increase in organic horizon N, foliar N, potential net N mineralization, and soil solution N, initial increases in N leaching below the organic layer	Baron: CENTURY model Rueth and Baron: field sampling east and west slope forests	Baron: modeled total deposition: 0.2 to 16.0 kg N/ha/yr Rueth and Baron: total deposition: 3.2 to 5.5 kg N/ha/yr (for 1992–1997)	ROMO east and west of Continental Divide	##	<a href="#">Baron et al. (1994)</a> , <a href="#">Rueth and Baron (2002)</a>
4 to 10	Alpine dry meadow ( <i>Carex</i> spp., including <i>Carex rupestris</i> )	Plant species composition change	N addition experiment	Ambient: 6 kg N/ha/yr; Addition: 20, 40, or 60 kg N/ha/yr	Niwot Ridge, CO	##	<a href="#">Bowman et al. (2006)</a>
4	<i>Carex rupestris</i>	Increase in vegetation cover	N addition experiment	Total deposition: 6 kg N/ha/yr N additions: 20, 40, or 60 kg N/ha/yr	Niwot Ridge, CO	##	<a href="#">Bowman et al. (2006)</a>
5 to 10	Ectomycorrhizal fungi (~40 species)	Ectomycorrhizal fungi community structure change in spruce ( <i>Picea</i> ) forests	Expert judgment extrapolated from marine west coast spruce forest	2002: bulk N deposition across five sampling sites ranged from 0.15 to 2.3 kg/ha/60 days 2008: Wet deposition 2.8 to 7.9 kg N/ha/yr	Kenai Peninsula, AK	(#)	<a href="#">Lilleskov (1999)</a> , <a href="#">Lilleskov et al. (2001)</a> , <a href="#">Lilleskov et al. (2002)</a> , <a href="#">Lilleskov et al. (2008)</a>
>20	Alpine terrestrial	Soil NO <sub>3</sub> <sup>-</sup> leaching and N fluxes	N addition	Total deposition: 6 kg N/ha/yr N additions: 20, 40, or 60 kg N/ha/yr	Niwot Ridge, CO	#	<a href="#">Bowman et al. (2006)</a>

CL = critical load; CMAQ = Community Multiscale Air Quality model; ha = hectare; kg = kilogram; N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate; ROMO = Rocky Mountain National Park; yr = year.

Reliability rating: ## = highly reliable—a number of published papers show comparable results; # fairly reliable—the results of some studies are comparable; (#) expert judgment—few empirical data are available, Critical Load based on expert judgment of those ecosystems.

Source: [Pardo et al. \(2011c\)](#).

Since the publication of [Pardo et al. \(2011c\)](#) assessment, there have been several new studies on terrestrial CLs ([Table 16-22](#)). New studies find CLs for soil N concentration changes and leaching at 9.0–14.0 kg N/ha/yr, CLs to protect lichens at 4.0–4.1 kg N/ha/yr, and CLs to protect vascular plant biodiversity (species richness, abundance, or community composition) at 1.0–8.7 kg N/ha/yr.

**Table 16-22 Montane forest and alpine ecosystem critical loads for nitrogen deposition research published since the critical load assessment by [Pardo et al. \(2011c\)](#).**

CL (kg N/ha/yr)	Vegetation	Response	Method	Deposition/Addition	Site	Reference
1.0	Composite montane plant communities	5% change in alpine and subalpine plant community composition	ForSAFE-VEG modeled change in future (to 2500) vegetation	Deposition: ~4 kg N/ha/yr, 1 kg S/ha/yr	Northern and central Rocky Mountains region	<a href="#">Sverdrup et al. (2012)</a>
1.9	<i>Salix candida</i> , <i>Carex</i> spp., <i>Abies lasiocarpa</i> , <i>Geum rossii</i>	10% change in tree-line (sub/alpine) plant community composition	ForSAFE-VEG modeled change in future (to 2100) vegetation	Deposition: 3.5 kg N/ha/yr	Loch Vale watershed, ROMO	<a href="#">McDonnell et al. (2014a)</a>
3.0	<i>Carex rupestris</i>	Alpine vegetation abundance	Field addition study	Ambient deposition: 4 kg N/ha/yr Addition: 5, 10, and 30 kg N/ha/yr.	ROMO	<a href="#">Bowman et al. (2012)</a>
4.0	Epiphytic lichens	Degradation of lichen communities	Empirical CLs	1.83 to 3.45 kg N/ha/yr (CMAQ)	Northern Rocky Mountains	<a href="#">McMurray et al. (2015)</a>
4.1	Epiphytic lichens <i>L. vulpina</i> <i>U. lapponica</i>	Poorer thallus condition	Empirical CLs	Throughfall <0.9 to 4.1 kg N/ha/yr	Wind River Range, WY, including the Class I Bridger Wilderness	<a href="#">McMurray et al. (2013)</a>
8.7	Forbs and grasses—open canopy ecosystem	Species richness loss	Empirical CLs from vegetation surveys	1 to 19 kg N/ha/yr, wet (NADP) + dry (CMAQ) deposition.	Over 15,000 plots over the continental U.S.	<a href="#">Simkin et al. (2016)</a>
9.0	Alpine dry meadow	Soil solution NO <sub>3</sub> <sup>-</sup> concentrations	Field addition study	Ambient deposition: 4 kg N/ha/yr Addition: 5, 10, and 30 kg N/ha/yr	ROMO	<a href="#">Bowman et al. (2012)</a>
14.0	Alpine dry meadow	Soil dissolved inorganic N concentrations	Field addition study	Ambient deposition: 4 kg N/ha/yr Addition: 5, 10, and 30 kg N/ha/yr	ROMO	<a href="#">Bowman et al. (2012)</a>

CL = critical load; CMAQ = Community Multiscale Air Quality model; ForSAFE-VEG = a dynamic forest ecosystem model; ha = hectare; kg = kilogram; N = nitrogen; NADP = National Atmospheric Deposition Program; NO<sub>3</sub><sup>-</sup> = nitrate; ROMO = Rocky Mountain National Park; S = sulfur; yr = year.

### 16.5.3.1.2 Modeling Studies

Elevated lake and stream  $\text{NO}_3^-$  concentrations have been observed in ROMO since the mid-1980s. To understand the source of these elevated  $\text{NO}_3^-$  concentrations and the role of atmospheric N deposition, [Baron et al. \(1994\)](#) used the CENTURY terrestrial biogeochemistry model to estimate N uptake by plants and soils in alpine forest and subalpine tundra within the Loch Vale watershed in ROMO. Based on the model output, N uptake in the subalpine tundra was considerably lower than in the alpine forest. Increased export of  $\text{NO}_3^-$  into stream water occurred at low N deposition rates (3 to 4 kg N/ha/yr) because much of this atmospheric N was deposited in the tundra or on exposed rock surfaces, providing little N uptake. This work by [Baron et al. \(1994\)](#) was the first N deposition CL research within the Northwestern Forested Mountains ecoregion and aside from two CL estimates for lichens ([Geiser et al., 2010](#)), the CL estimate produced from this research is the lowest among the CL estimates reviewed by [Pardo et al. \(2011c\)](#) for this ecoregion ([Table 16-21](#)).

Terrestrial biogeochemistry models have also played a role in the development of some CL estimates for the ROMO region published since the [Pardo et al. \(2011c\)](#) assessment. [Sverdrup et al. \(2012\)](#) and [McDonnell et al. \(2014a\)](#) used the ForSAFE-VEG model to evaluate potential long-term effects of climate change and atmospheric N deposition on alpine/subalpine ecosystems. Critical loads in both studies were defined as the rate of N deposition at which plant diversity was protected from a change of 5 to 10 Mondrian units (Mu; i.e., 5–10% change in plant species cover). [Sverdrup et al. \(2012\)](#) focused on a “generalized” alpine/subalpine site, with vegetation composition constructed from plant community data from ROMO and other national parks in the northern and central Rocky Mountains region. [Sverdrup et al. \(2012\)](#) simulated plant responses to a future climate (IPCC A2) and four levels of N and S deposition (preindustrial background, Clean Air Act [CAA] controls, no CAA controls, and no CAA controls + high deposition). Soil base saturation and soil solution base cation (Bc)-to-aluminum (Al) ratios (Bc:Al) were predicted to decrease to less than 1% and less than 10% after year 2100, respectively, with the scenarios of no CAA emission controls and no CAA controls + high deposition (indicating soil acidification). Future plant species coverages were predicted to change in successively greater amounts in response to the altered climate, CAA emission controls, no CAA emission controls, and no CAA emission controls + high deposition. Calculated CLs (based on a change of 5 Mu) for N deposition were 1 kg N/ha/yr. Critical loads related to S deposition were not discussed. All future N deposition scenarios (except preindustrial background N) resulted in CL exceedance.

The approach of [McDonnell et al. \(2014a\)](#) was similar to that of [Sverdrup et al. \(2012\)](#) because both applied the ForSAFE-VEG model to a subalpine ecosystem to determine

CLs for long-term vegetation composition shifts caused by climate change and atmospheric N deposition. The former study differed from the latter by using the Loch Vale watershed within ROMO as the study area and also back-projecting the model to 1900. [McDonnell et al. \(2014a\)](#) estimated that the N deposition CL to avert a 10% (5 Mu) change in future (2010–2100) plant biodiversity was 1.9 to 3.5 kg N/ha/yr, which had already been exceeded. Future air temperature increases were predicted to further change plant community composition and exacerbate changes caused by N deposition alone. In the simulations between 1900 and 2010, the authors found that subalpine fir (*Abies lasiocarpa*) sapling coverage had increased by more than 25%, graminoid response was mixed, and forbs generally had decreased in abundance ([Table 16-23](#)). By 2010, *Geum rossii* was reduced by more than 50% of its simulated historical cover. In scenarios using ambient N deposition and 0.5 times ambient N deposition, pronounced increases in the abundance of the moss *Aulacomnium palustre* would occur in 2065 and 2080, respectively, while the dominant graminoid (*Carex rupestris*) decreased. They also found that higher total N deposition scenarios would suppress moss cover near the end of the simulation period. Projected future tree responses were similar between the lowest two and highest three total N deposition scenarios. Future forb and *Carex rupestris* cover remained relatively constant under higher total N deposition rate scenarios.

**Table 16-23 Hindcast absolute and percentage changes in species abundance between 1900 and 2010 in response to historical reconstructions of nitrogen deposition ([Sullivan et al., 2005](#)) and historical climate change ([IPCC, 2007b](#)).**

Growth Form	Species	Relative Abundance %		Absolute Change	% Change
		1900	2010		
Tree	<i>Abies lasiocarpa</i>	6.3	8.4	2.1	33.3
Shrubs	<i>Salix candida</i>	15.4	25.5	10.1	65.6
	<i>Rubus parviflorus</i>	0.0	4.4	4.4	—
Graminoids	<i>Carex rupestris</i>	6.8	16.4	9.6	141.2
	<i>Carex elynoides</i>	25.1	12.8	-12.3	-49.0
	<i>Festuca ovina</i>	1.7	3.2	1.5	88.2
	<i>Calamagrostis purpurascens</i>	4.3	3.0	-1.4	-32.6
	<i>Poa abbreviata</i>	3.2	2.3	-0.9	-28.1
Forbs	<i>Geum rossii</i>	19.7	8.9	-10.8	-54.8
	<i>Aquilegia caerulea</i>	4.6	4.8	0.2	4.3
	<i>Antennaria rosea</i>	1.5	2.0	0.5	33.3
	<i>Arenaria fendleri</i>	4.7	1.8	-2.9	-61.7
	<i>Minuartia obtusiloba</i>	3.7	1.6	-2.0	-54.1
	<i>Zigadenus elegans</i>	0.0	2.2	2.2	—
Moss	<i>Aulacomnium palustre</i>	3.0	2.6	-0.5	-16.7

Source: [McDonnell et al. \(2014a\)](#).

### 16.5.3.2 Aquatic Critical Loads

Nitrogen limitation of algal productivity is widespread in remote and undisturbed freshwater lakes, such as the high-elevation lakes located throughout the Rocky Mountains ([Baron et al., 2011b](#)). Based on surveys conducted in the 1980s that quantified the ratio of dissolved inorganic N to total phosphorus, alpine lakes in the Rocky Mountains region are predominantly N limited (45% of lakes) or colimited by both N and

P [22% of lakes; [Pardo et al. \(2011c\)](#)]. This may underestimate the previous extent of N limitation in these systems because lake sediment records indicate that N deposition began impacting biogeochemistry in some alpine lakes during the 1950s ([Das et al., 2005](#); [Wolfe et al., 2003](#); [Wolfe et al., 2001](#)). [Pardo et al. \(2011c\)](#) summarized CLs for ROMO surface waters ([Table 16-24](#)) with empirical and modeled CL estimates ranging from 1.5 to 2.5 kg N/ha/yr. Within ROMO, eastern slope surface waters commonly have higher dissolved inorganic N (DIN) than western slope surface waters ([Wolfe et al., 2001](#); [Baron et al., 2000](#)).

While the majority of ROMO aquatic research since 2000 focused on eutrophication, [Vertucci and Corn \(1996\)](#) and [Wolfe et al. \(2003\)](#) described the potential for aquatic acidification in the Colorado Rocky Mountains. Neither [Vertucci and Corn \(1996\)](#) nor [Wolfe et al. \(2003\)](#) found evidence for acidification, citing the influence of catchment sources of base cation neutralization. However, [Wolfe et al. \(2003\)](#) suggested that persistent N deposition threatened to cause chronic surface water acidification, particularly given that episodic declines of pH and acid neutralizing capacity (ANC) have been well documented in east slope headwaters of the Front Range ([Williams and Tonnessen, 2000](#); [Williams et al., 1996b](#)). [Vertucci and Corn \(1996\)](#) found that although episodic acidification occurred during snowmelt, at no point was  $ANC < 0$  in the northern Colorado and southern Wyoming lakes and streams that were sampled. Importantly, the observed acidification episodes did not coincide with the presence of amphibian embryos, meaning that amphibians in the region were not threatened by acidification (including the boreal toad, a candidate species for Endangered Species Act protection).

**Table 16-24 Critical loads for nitrogen for eutrophication for surface water (high-elevation lakes) in the Rocky Mountains.**

CL kg N/ha/yr	Species	Response	Method	Deposition/ Addition	Site	Reference
1.5	Diatom community composition	Eutrophication	Used exponential equations correlating with NO <sub>x</sub> emissions from CO and 11 western U.S. states to reconstruct historic N deposition. 1950–1964 wet N deposition correlated with alteration of ROMO diatom assemblages.	Wet deposition 2.94 kg N/ha/yr Dry deposition 0.94 kg N/ha/yr	Southern Rockies/ Loch Vale ROMO	<a href="#">Bowman et al. (2006)</a>
1.5	<i>F. crotonensis</i> <i>A. formosa</i>	Eutrophication	Paleolimnological—analyzed diatom fossil records of four lakes in the Beartooth Mountains. Small <i>Fragilaria</i> species declined while <i>Fragilaria crotonensis</i> , <i>Asterionella formosa</i> , and multiple <i>Cyclotella</i> spp. increased	Not specified	Northern Rockies/ Beartooth Mountains, WY	<a href="#">Saros et al. (2003)</a>
2.0	Not applicable	Eutrophication	Used CENTURY model to discern if high lake and stream N measurements are attributed to alpine tundra and subalpine forest N saturation	Modeled total deposition of 0.2 to 16.0 kg N/ha/yr	Southern Rockies/ Loch Vale ROMO	<a href="#">Baron et al. (1994)</a>
2.5	Chlorophyll a	Eutrophication, N and P colimitation	Compared oligotrophic lake chemical and chlorophyll a data in 42 European and North American regions to inorganic N deposition data	Wet DIN deposition 2.5 to 3.5 kg N/ha/yr for regions 26 to 29 (Rocky Mountains in area of ROMO)	Rocky Mountains	<a href="#">Bergström and Jansson (2006)</a>
3.0	Not applicable	Increases in lake nitrate concentration	Compared observations of nitrate concentrations in 285 lakes to observations to N deposition estimates derived from NADP and PRISM	Modeled total deposition of 1.5 to 7.5 kg N/ha/yr	Rocky Mountains	<a href="#">Baron et al. (2011b)</a>

CL = critical load; CO = carbon monoxide; DIN = dissolved inorganic nitrogen; ha = hectare; kg = kilogram; N = nitrogen; NADP = National Atmospheric Deposition Program; NO<sub>x</sub> = NO + NO<sub>2</sub>; P = phosphorus; PRISM = a model for spatial climate data; ROMO = Rocky Mountain National Park; yr = year.

Source: [Baron et al. \(2011b\)](#), [Pardo et al. \(2011c\)](#), [Williams and Tonnessen \(2000\)](#).

### 16.5.3.2.1 Empirical Studies

[Pardo et al. \(2011c\)](#) compiled a list of N deposition studies in high-elevation lakes that have observed changes in the growth, biomass, or composition of phytoplankton ([Table 16-25](#)). Within these studies, there was a relatively narrow range of lake water nitrate concentrations at which these phytoplankton responses were observed ([Table 16-25](#)). In paleolimnological studies of alpine lakes in this region that experienced increased rates of deposition, there were pronounced shifts in the composition and productivity of phytoplankton communities that occurred around 1950 ([Table 16-26](#)).

**Table 16-25 Lake water nitrate concentrations in nitrogen deposition studies observing phytoplankton responses.**

N Conc. (mg NO <sub>3</sub> <sup>-</sup> -N/L)	Species	Response	Deposition/Addition	Site	Reference
0.9	<i>A. formosa</i> , <i>F. crotonensis</i>	Stimulation of <i>A. formosa</i> , <i>F. crotonensis</i>	Wet deposition <2 kg N/ha/yr; N addition of 18 µmol N as NaNO <sub>3</sub> ; N + P enrichment, 18 µmol N + 5 µmol P as NaH <sub>2</sub> PO <sub>4</sub>	Beartooth Mountains, WY	<a href="#">Saros et al. (2005)</a>
0.9	Chlorophyll a	Increasing biomass	Wet DIN deposition 1.3 to 11 kg N/ha/yr; total N deposition <0.1 kg N/ha/yr to >15 kg N/ha/yr	Sweden	<a href="#">Bergström et al. (2005)</a>
0.9	Chlorophyll a	Increasing biomass	Wet DIN deposition 2.5 to 3.5 kg N/ha/yr for regions 26 to 29 (Rocky Mountains in an area of ROMO)	European and N. American lakes, including Rocky Mountains	<a href="#">Bergström and Jansson (2006)</a>
1.0	Chlorophyll a	Shift in species composition	Ambient deposition not specified; single pulse N treatment of 1,000 µg/L NO <sub>3</sub> <sup>-</sup> -N as KNO <sub>3</sub>	Snowy Range, WY	<a href="#">Nydic et al. (2004)</a>
1.1	Chlorophyll a	Diatom spp. growth stimulation	Ambient deposition of 3.5 kg N/ha/yr; N treatment of ambient NO <sub>3</sub> <sup>-</sup> -N plus 1 mg NO <sub>3</sub> <sup>-</sup> -N/L	Colorado Front Range (Loch Vale)	<a href="#">Lafrancois et al. (2003a)</a>

conc. = concentration; DIN = dissolved inorganic nitrogen; ha = hectare; kg = kilogram; KNO<sub>3</sub> = potassium nitrate; L = liter; µg = microgram; mg = milligram; N = nitrogen; NaH<sub>2</sub>PO<sub>4</sub> = monosodium phosphate; NaNO<sub>3</sub> = sodium nitrate; NO<sub>3</sub><sup>-</sup>-N = nitrate N; P = phosphorus; ROMO = Rocky Mountain National Park; yr = year.

Source: [Pardo et al. \(2011c\)](#).

**Table 16-26 Paleolimnological biological responses in Rocky Mountain lakes exposed to anthropogenic nitrogen deposition.**

Species	Response	Deposition/ Addition	Site	Year(s) of Shift	Reference
<i>A. formosa</i>	Increased microbial activity, greater primary production, change in species composition	Not specified	Colorado Rocky Mountains	1950	<a href="#">Enders et al. (2008)</a>
<i>A. formosa</i> , <i>F. crotonensis</i>	Greater primary production, stimulation of <i>A. formosa</i> and <i>F. crotonensis</i> , shift in species assemblages	Inorganic N deposition 4 kg N/ha/yr	Eastside ROMO lakes compared to remote Colorado Rocky Mountains wilderness lake	1950	<a href="#">Das et al. (2005)</a>
<i>A. formosa</i> , <i>F. crotonensis</i>	Greater primary production, stimulation of <i>A. formosa</i> and <i>F. crotonensis</i> , shift in species assemblages	Wet inorganic N deposition 2 to 4 kg N/ha/yr Dry deposition: 0.9 kg N/ha/yr	Colorado Rocky Mountains	1950	<a href="#">Wolfe et al. (2001)</a> , <a href="#">Wolfe et al. (2003)</a>
<i>A. formosa</i> , <i>F. crotonensis</i>	Greater primary production, stimulation of <i>A. formosa</i> and <i>F. crotonensis</i> , shift in species assemblages after 1995	Not specified	Beartooth Mountain Range, WY (Yellowstone NP region)	1995	<a href="#">Saros et al. (2003)</a>

ha = hectare; kg = kilogram; N = nitrogen; NP = national park; ROMO = Rocky Mountain National Park; yr = year.

Source: ([Pardo et al., 2011c](#)).

Since the [Pardo et al. \(2011c\)](#) CLs synthesis, [Baron et al. \(2011b\)](#) synthesized aquatic N cycling research for lakes in several regions of the U.S., including alpine lakes in the Rocky Mountains. Using existing water chemistry measurements and modeled estimates of wet and dry N deposition, [Baron et al. \(2011b\)](#) observed that lake nitrate concentrations increased where N deposition exceeded 2.0 kg N/ha/yr. This threshold was similar to previous CLs of 1.5–4 kg N/ha/yr for lakes in this region ([Table 16-24](#)). ([Baron et al., 2011b](#)) also sought to develop a CL for N driven episodic aquatic acidification, but found little data apart from that used to generate the [Williams and Tonnessen \(2000\)](#) CL estimate of 4.0 kg N/ha/yr. Using phytoplankton biomass N to P limitation shifts as the basis for CL calculations, [Williams et al. \(2017b\)](#) determined an empirical CL of 4.1 kg/TN/ha/yr for remote high-elevation lakes across the western U.S. The CLs were calculated as the total (wet + dry) N deposition rate at which point below the CL, N limitation is more likely than P limitation and above the CL, P limitation is more likely than N limitation. DIN:TP and DIN response categories yielded an average critical load of 3.8 kg/TN/ha/yr for the lakes.

### 16.5.3.2.2 Modeling Studies

In addition to the empirical estimates of aquatic CLs, [Sullivan et al. \(2005\)](#) and [Hartman et al. \(2007\)](#) modeled CL estimates for aquatic acidification in ROMO. [Sullivan et al. \(2005\)](#) used the MAGIC model to evaluate the sensitivity of two water bodies in the Loch Vale watershed within ROMO—the Loch and Andrews Creek—to N and S deposition based on ANC. [Hartman et al. \(2007\)](#) also modeled deposition scenarios for changes in ANC at Andrews Creek, but used the DayCent-Chem model. Beginning with 1996 deposition rates of 2.2 kg S/ha/yr and 4.2 kg N/ha/yr, [Sullivan et al. \(2005\)](#) estimated CLs for N or S in order to reach ANC of 0, 20, or 50  $\mu\text{eq/L}$  by 2046 in the Loch and Andrews Creek, which had 1996 ANC values of 53 and 34, respectively. Acidification of the watershed to ANC to 0 or 20 by 2046 in either water body would require doubling of either N or S deposition ([Sullivan et al., 2005](#)). However, increasing ANC to 50 in Andrews Creek was not achievable by 2046 in any deposition scenario considered by [Sullivan et al. \(2005\)](#). [Hartman et al. \(2007\)](#) took a somewhat different approach, modeling 47-year scenarios beginning in 2000 where N deposition increased at rates that were low (+60%), moderate (+120%), and high (+240%) relative to the contemporary deposition rate. In these scenarios, episodic acidification (ANC = 0  $\mu\text{eq/L}$ ) of Andrews Creek occurred at 6.3–7.1 kg N/ha/yr. Estimates for persistent (chronic) changes in ANC of Andrews Creek were similar to those of [Sullivan et al. \(2005\)](#), within 1 kg N/ha/yr for ANC = 20  $\mu\text{eq/L}$  and within 3 kg N/ha/yr for ANC = 0  $\mu\text{eq/L}$  ([Table 16-27](#)). Notably, the Loch does not represent the most acid-sensitive lakes in the Front Range, with approximately 1/5th of the alpine lakes in the Colorado Front Range having a similar or lower ANC ([Eilers et al., 1989](#)). [Williams et al. \(2017b\)](#) modeled CLS for remote high-elevation lakes across the Western U.S. based on nutrient limitation shift thresholds. Modeled critical loads ranged from 2.8 to 5.2 kg/TN/ha/yr and correctly predicted exceedances in 69% of lakes using  $\text{NO}_3^-$ -N.

**Table 16-27 Critical loads of nitrogen or sulfur for surface water acidification Rocky Mountain National Park and other high-elevation lakes in the Rocky Mountains.**

CL kg/ha/yr of N or S	Species	Response	Method	Deposition/ Addition	Site	Reference
4.0 (N)	Not applicable	Episodic freshwater acidification (ANC < 0 µmol/L)	1995 synoptic survey of 9 high-elevation lakes: headwater catchments experienced episodic acidification due to inorganic N in wetfall (ANC < 0 µmol/L in surface waters during snowmelt).	NADP DIN wetfall at 23 sites. >2,500 masl: 2.5 to 3.5 kg N/ha/yr <2,500 masl: <2.5 kg N/ha/yr	Central Rockies/ Colorado Front Range	<a href="#">Williams and Tonnessen (2000)</a>
5.8 (N)	Not applicable	Freshwater acidification (ANC = 50 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>
6.3 to 7.1 (N)	Not applicable	Episodic freshwater acidification (ANC < 0 µeq/L)	DayCent-Chem model for 2000 to 2047 of four N deposition (current, +60% increase, +120% increase, +240% increase)	Deposition: 2.7 kg S/ha/yr, 3.5 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Hartman et al. (2007)</a>
7.1 (N)	Not applicable	Freshwater acidification (ANC = 20 µeq/L)	DayCent-Chem model for 2000 to 2047 of four N deposition (current, +60% increase, +120% increase, +240% increase)	Deposition: 2.7 kg S/ha/yr, 3.5 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Hartman et al. (2007)</a>
7.8 (N)	Not applicable	Freshwater acidification (ANC = 20 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Sullivan et al. (2005)</a>
12.2 (N)	Not applicable	Freshwater acidification (ANC = 0 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Sullivan et al. (2005)</a>
14.7 (N)	Not applicable	Freshwater acidification (ANC = 20 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>
14.6 to 15.3 (N)	Not applicable	Chronic freshwater acidification (ANC < 0 µeq/L)	DayCent-Chem model for 2000 to 2047 of four N deposition (current, +60% increase, +120% increase, +240% increase)	Deposition: 2.7 kg S/ha/yr, 3.5 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Hartman et al. (2007)</a>
20.6 (N)	Not applicable	Freshwater acidification (ANC = 0 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>

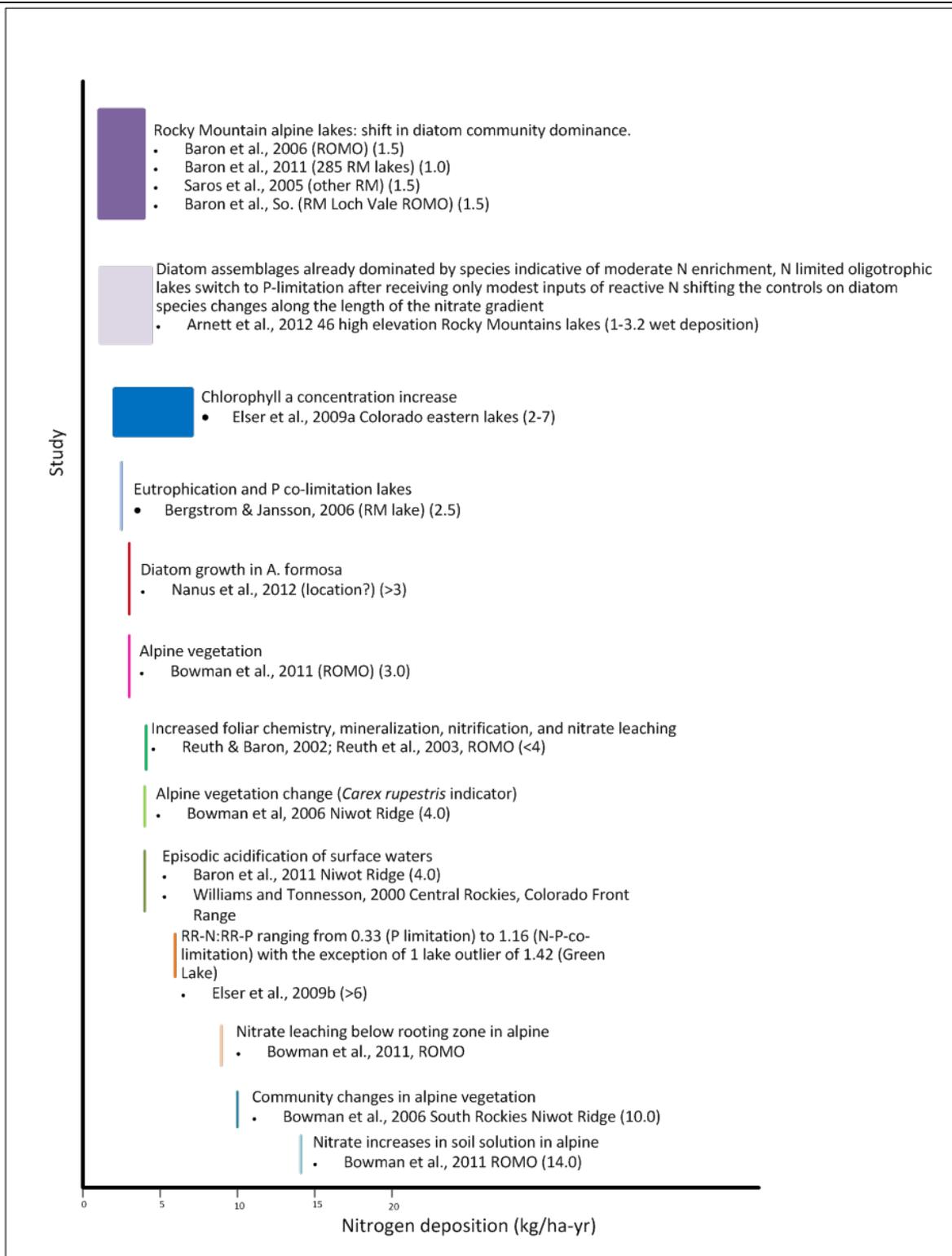
**Table 16-27 (Continued): Critical loads of nitrogen or sulfur for surface water acidification Rocky Mountain National Park and other high-elevation lakes in the Rocky Mountains.**

CL kg/ha/yr of N or S	Species	Response	Method	Deposition/ Addition	Site	Reference
2.8 (S)	Not applicable	Freshwater acidification (ANC = 50 µeq/L)	AGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>
4.6 (S)	Not applicable	Freshwater acidification (ANC = 20 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Sullivan et al. (2005)</a>
7.8 (S)	Not applicable	Freshwater acidification (ANC = 20 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>
8.1 (S)	Not applicable	Freshwater acidification (ANC = 0 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	Andrews Creek (ROMO)	<a href="#">Sullivan et al. (2005)</a>
11.1 (S)	Not applicable	Freshwater acidification (ANC = 0 µeq/L)	MAGIC model scenario for 1996 to 2046	Deposition: 2.2 kg S/ha/yr, 4.2 kg N/ha/yr	The Loch (ROMO)	<a href="#">Sullivan et al. (2005)</a>

ANC = acid neutralizing capacity; CL = critical load; DIN = dissolved inorganic nitrogen; ha = hectare; kg = kilogram; L = liter; µeq = microequivalent; µmol = micromole; MAGIC = a biogeochemical process model; masl = meters above sea level; N = nitrogen; NADP = National Atmospheric Deposition Program; ROMO = Rocky Mountain National Park; S = sulfur; yr = year.

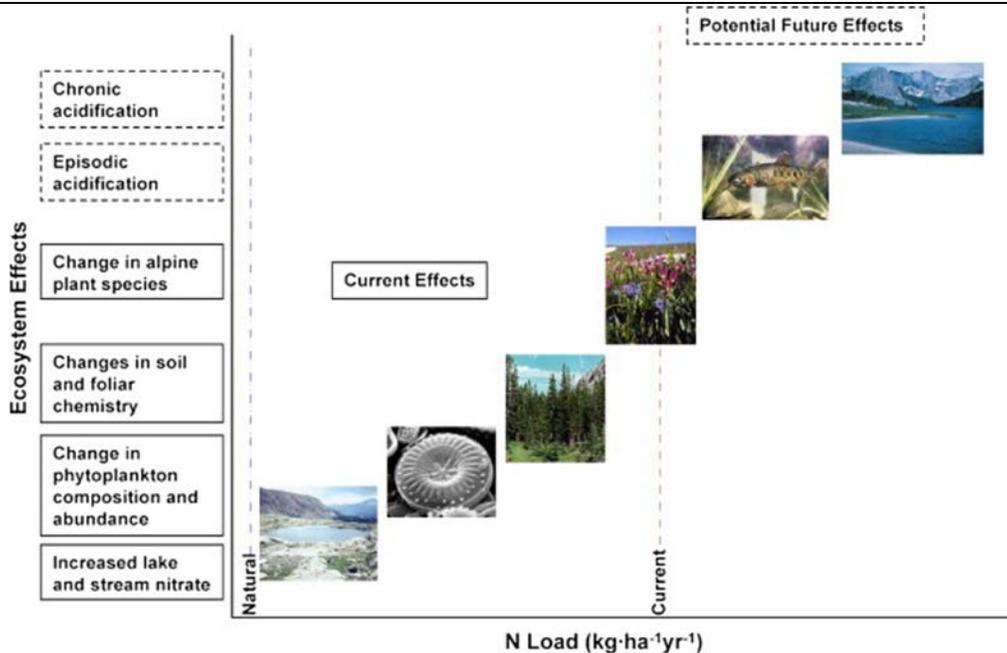
### 16.5.3.3 Integration

Together, there is a considerable amount of research available on the effects of atmospheric N deposition on ecological processes and characteristics within ROMO. Assembled together, the CL estimates developed in and around ROMO ([Figure 16-40](#)) show a continuum of effects as atmospheric N loads increase from natural background rates (0.2 kg N/ha/yr) to levels several times greater than the current estimates of 3–9 kg N/ha/yr ([Figure 16-35](#)). Broadly, the chemistry and biota of aquatic systems appear to be the most sensitive to N deposition, followed by alpine plant communities ([Figure 16-39](#)). It is notable that many of the published CLs ([Table 16-21](#), [Table 16-22](#), and [Table 16-24](#)) are near or below the rates of atmospheric N deposition currently observed in ROMO. Thus, there is considerable evidence that current rates of atmospheric N deposition are influencing the composition and function of aquatic and terrestrial ecosystems within ROMO [[Figure 16-41](#); [Porter and Johnson \(2007\)](#); [RMNP Initiative \(2014\)](#)].



ha = hectare; kg = kilogram; N = nitrogen; P = phosphorus; RM = Rocky Mountain; ROMO = Rocky Mountain National Park; RR = relative response to changes in N or P; yr = year.

**Figure 16-40 The continuum of ecological sensitivity to nitrogen deposition.**



ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Notes: Current rates of N deposition impact terrestrial and aquatic ecosystems and relatively small increases in deposition may cause further ecological change.

Source: [Porter and Johnson \(2007\)](#).

**Figure 16-41 Critical load thresholds for current and possible future biogeochemical and biological effects of nitrogen deposition.**

## 16.5.4 Highlights of Additional Research Literature and Federal Reports since January 2008

A number of studies documenting the effects of N or S deposition on terrestrial and aquatic systems in ROMO or the ROMO region have been published since 2008. We discuss these studies briefly here but refer readers to the appropriate portion of the main body of the ISA for a more detailed review of this work.

### 16.5.4.1 Terrestrial

A number of the studies reviewed in [Appendix 4](#) and [Appendix 6](#) of the current NO<sub>x</sub>-SO<sub>x</sub> ISA as part of the body of terrestrial N deposition research published since 2008 were conducted in and around ROMO. [Farrer et al. \(2013\)](#) and [Bowman et al. \(2012\)](#) both conducted N addition studies in alpine tundra ecosystems to understand the response of

plants to N deposition. [Farrer et al. \(2013\)](#) did not find an increase in net primary productivity, but found both positive and negative effects on the aboveground biomass of individual plant species. [Bowman et al. \(2012\)](#) did not find any significant overall effect on aboveground plant biomass, plant tissue N concentration, or plant diversity; but the abundance of an important sedge (*Carex*) species almost quadrupled. This contrasts with [Farrer et al. \(2015\)](#) and [Yuan et al. \(2016\)](#), who found that N additions decreased plant species diversity. In mixed grass meadows near ROMO, an experiment that recreated historical, low N deposition conditions (soil N availability reduced by 63%, winter precipitation reduced 50%) reduced biomass of invasive cool-season grass *Bromus tectorum* ([Concilio et al., 2016](#)).

There are no published CLs for changes in soil microbial communities in the ROMO area, but several studies in alpine tundra ecosystems have quantified microbial responses to N additions ranging from 8 to 288 kg N/ha/yr. [Dean et al. \(2014\)](#) observed decreased ericoid fungi abundance and decreased richness and diversity of root-associated fungi, while [Farrer et al. \(2015\)](#) and [Boot et al. \(2016\)](#) observed decreased microbial biomass, fungal biomass, and bacterial biomass. [Farrer et al. \(2013\)](#), [Nemergut et al. \(2008\)](#), and [Yuan et al. \(2016\)](#) documented shifts in microbial community composition.

[Lieb et al. \(2011\)](#) found that a decade of N additions to alpine ecosystems lowered soil acid buffering capacity, decreased concentrations of base cation  $Mg^{2+}$ , and increased concentrations of  $Mn^{2+}$  and  $Al^{3+}$ . After 15 years of N additions, [Boot et al. \(2016\)](#) found that N addition reduced soil pH, soil percentage of C, and soil C:N in the O-horizon.

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#### 16.5.4.2 Aquatic

As with terrestrial ecosystems, there have been a number of new studies quantifying the effects of N deposition on aquatic ecosystems in the Rocky Mountains since 2008 ([Table 16-28](#)). [McCrackin and Elser \(2012\)](#) measured denitrification in sediments of alpine lakes in the Colorado Rocky Mountains that received elevated (5–8 kg N/ha/yr) or low (<2 kg N/ha/yr) N deposition inputs. In high-deposition lakes, the  $NO_3^-$ -N concentration was significantly higher than in low-deposition lakes, but there was also evidence that denitrifying bacteria could remove a meaningful portion of N inputs to the lakes. While current levels of N deposition have not saturated the microbial capacity for denitrification, the abundance of denitrifying bacteria has not increased in response to additional N.

**Table 16-28 Summary of freshwater eutrophication studies in the Rocky Mountains since 2008.**

Species	Response	Method	Deposition/ Addition	Site	Reference
Not applicable	Diatom assemblages already dominated by species indicative of moderate N enrichment	Diatom calibration from surface sediment samples	Wet deposition: 1 to 3.2 kg N/ha/yr	46 high-elevation lakes in the Rocky Mountains	<a href="#">Arnett et al. (2012)</a>
Not applicable	Average lake DIN:TP of 16.3 + 2.76, suggesting widespread N saturation, but unclear if this is a new or historical condition	Mesocosms amended with NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , or PO <sub>4</sub> <sup>3-</sup> + NO <sub>3</sub> <sup>-</sup>	Ambient deposition not specified Addition: 930 mg/L NO <sub>3</sub> <sup>-</sup>	Colorado Front Range	<a href="#">Gardner et al. (2008)</a>
Chlorophyll a	Greater N deposition increased the N:P ratio in lakes. Phytoplankton growth P limited in high N deposition lakes (~7 kg N/ha/yr), but N limited in low-N deposition lakes (~2 kg N/ha/yr)	N and P enrichment bioassay experiments in high- and low-deposition lakes	Deposition: 2 to 7 kg N/ha/yr	14 eastern Colorado alpine lakes	<a href="#">Elser et al. (2009a)</a>
Chlorophyll a	Chl a conc. increase. Responses indicated a range from P limitation to N-P colimitation with one N limited outlier lake.	Enrichment bioassay	Wet deposition >6 kg N/ha/yr	14 eastern Colorado alpine lakes	<a href="#">Elser et al. (2009b)</a>
<i>A. formosa</i>	Maximum diatom growth rate at 0.5 μM of NO <sub>3</sub> <sup>-</sup>	Growth kinetics experiments	Total deposition >3 kg N/ha/yr	Rocky Mountains	<a href="#">Nanus et al. (2012)</a>

Chl a = chlorophyll a; DIN = dissolved inorganic nitrogen; ha = hectare; kg = kilogram; L = liter; μM = micromolar; mg = milligram; N = nitrogen; NO<sub>3</sub><sup>-</sup> = nitrate; P = phosphorus; PO<sub>4</sub><sup>3-</sup> = phosphate; TP = total phosphorus; yr = year.

[Mast et al. \(2011\)](#) examined trends in precipitation chemistry and other factors that influence long-term changes in chemistry of high-elevation lakes in three Colorado wilderness areas. [Mast et al. \(2011\)](#) observed that sulfate concentrations in precipitation decreased at rates of -0.15 to -0.55 μeq/L/year during the years 1985 through 2008 at 10 monitoring stations in Colorado. In high-elevation lakes where SO<sub>4</sub><sup>2-</sup> was primarily derived from atmospheric sources, the lake SO<sub>4</sub><sup>2-</sup> concentrations decreased by -0.12 to -0.27 μeq/L/year. In lakes where watershed sources were the dominant source of SO<sub>4</sub><sup>2-</sup>, the SO<sub>4</sub><sup>2-</sup> concentrations in lake water increased during this time period. [Mast et al. \(2011\)](#) attributed this trend to the effects of climate warming on pyrite weathering. Similarly, [Heath and Baron \(2014\)](#) observed increases in summer (June–August) fluxes and concentrations of cations, SiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, inorganic N, and ANC in stream water from

1984–2010 within the Loch Vale watershed in ROMO and attributed these trends to climate change effects on nitrification, mineral weathering, and the release of elements entrained in snow and ice. In comparison, wet N deposition rates were relatively constant and wet  $\text{SO}_4^{2-}$  deposition decreased.

[Mast et al. \(2014\)](#) measured long-term changes in stream  $\text{NO}_3^-$  concentration over three decades at the Loch Vale watershed in RMNP. The concentrations of  $\text{NO}_3^-$  in stream water increased during the early 1990s, peaked in the mid-2000s, and then declined by more than 40%. [Nanus et al. \(2012\)](#) developed a surface water  $\text{NO}_3^-$  threshold for growth of the diatom *A. formosa* for high-elevation lakes in the Rocky Mountains. [Arnett et al. \(2012\)](#) tried to develop a CL for diatom community composition change along a gradient of 46 high-elevation lakes receiving 1 to 3.2 kg N/ha/yr in wet deposition, but observed that diatom communities were dominated by a species associated with moderate N enrichment even in lakes where  $\text{NO}_3^-$  concentrations were at the detection limit (<1  $\mu\text{g/L}$ ).

New information on relative  $\text{NO}_3^-$  inputs from glacial versus snowpack meltwaters indicate water of glacial origin has higher  $\text{NO}_3^-$ , which may influence interpretation of biological data from high-altitude lakes and streams in some regions of the U.S., including the Rocky Mountains ([Slemmons et al., 2015](#); [Slemmons et al., 2013](#); [Saros et al., 2010](#); [Baron et al., 2009](#)). In the central Rockies and Glacier National Park, fossil diatom richness in snowpack-fed lakes was found to be higher relative to lakes fed by both glacial and snowpack meltwaters ([Saros et al., 2010](#)). Sedimentary diatom analysis of alpine lakes in the Rocky Mountains indicated that increases in *A. formosa* occurred at least a century ago in glacially fed lakes whereas shifts in the planktonic diatom communities occurred after 1970 in snow-fed lakes ([Slemmons et al., 2017](#)).

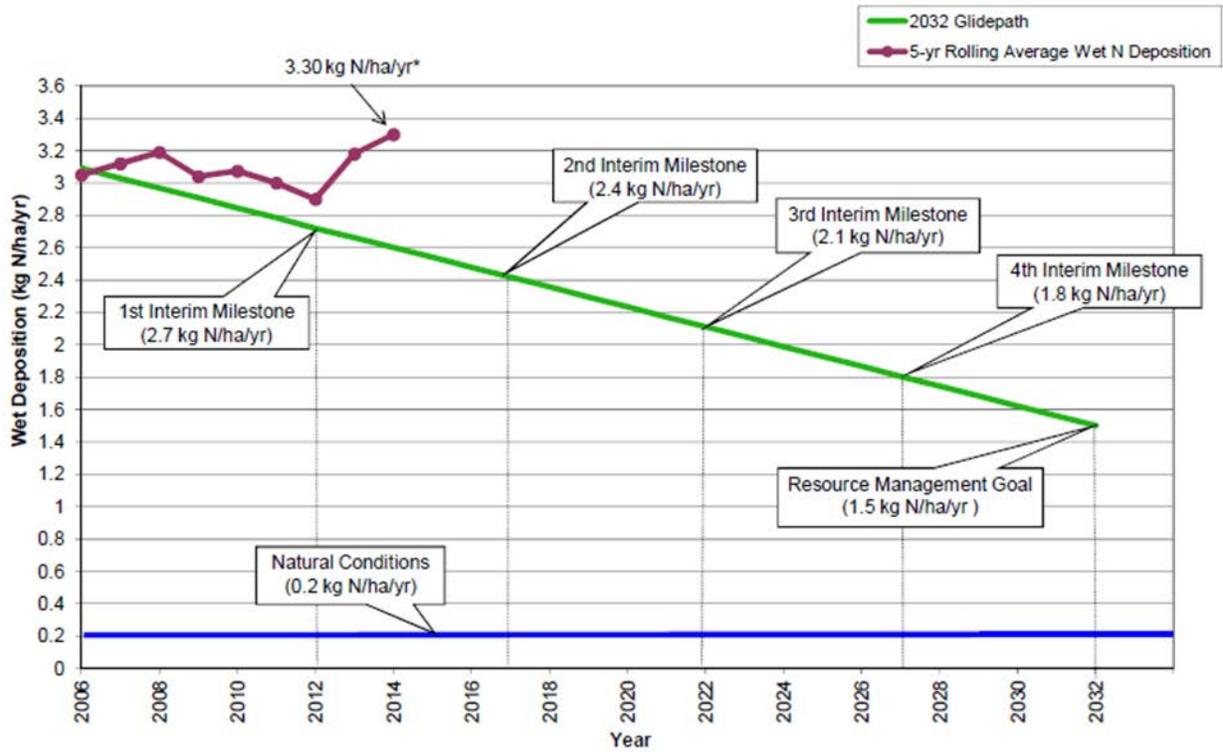
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### 16.5.5 Rocky Mountain National Park Initiative

The large body of research on the effects of atmospheric deposition on terrestrial and aquatic ecosystems in ROMO and the relatively low CLs has led the National Park Service (NPS) to partner with the Colorado Department of Public Health and Environment and the U.S. EPA to develop a plan in 2005 to decrease atmospheric N pollution within ROMO ([Porter and Johnson, 2007](#)). Formally, this collaboration is organized as the Rocky Mountain National Park Initiative (RMNPI). The goal of the collaboration is to understand the impacts of N deposition in ROMO and the sources of N emissions, and resolve the N deposition issue in ROMO ([RMNP Initiative, 2014](#)). The three agencies developed the Nitrogen Deposition Reduction Plan, which intended to

decrease N wet deposition in ROMO from a 2006 baseline of 3.1 kg N/ha/yr to a 2032 target of 1.5 kg N/ha/yr.

The Nitrogen Deposition Reduction Plan aims for a linear decrease in deposition between 2006 and 2032, with interim milestones of 0.3 kg N/ha reductions in annual deposition every 5 years. In 2012, the 5-year rolling average of wet deposition was 2.9 kg N/ha/yr, a number that was 0.2 kg N/ha/yr above the interim milestone target, but also reflective of a 4-year trend toward decreased wet N deposition ([RMNP Initiative, 2014](#)). However, in the most recent status report ([Morris, 2016](#)), the 5-year rolling average has increased in each of the last 2 years and is now 3.3 kg N/ha/yr ([Figure 16-42](#)), well above the intended target. There has been no overall trend in wet N deposition or nitrate deposition since 2007, but the ammonium concentration has increased at four of the five monitoring sites since 2009. Within the nine-county Denver Metropolitan and Northern Colorado Front Range region, the two largest estimated sources of ammonia emissions were livestock (75% of emissions) and fertilizer use [14%; [RMNP Initiative \(2015\)](#)]. However, considerable uncertainty remains in ammonia emissions and transport estimates, and the members of RMNPI have dedicated resources to research ammonia in the region. The agency partners within the RMNPI are working with the agricultural industry in Colorado to decrease ammonia emissions by adopting a set of best management practices for agricultural N ([Figure 16-43](#)).

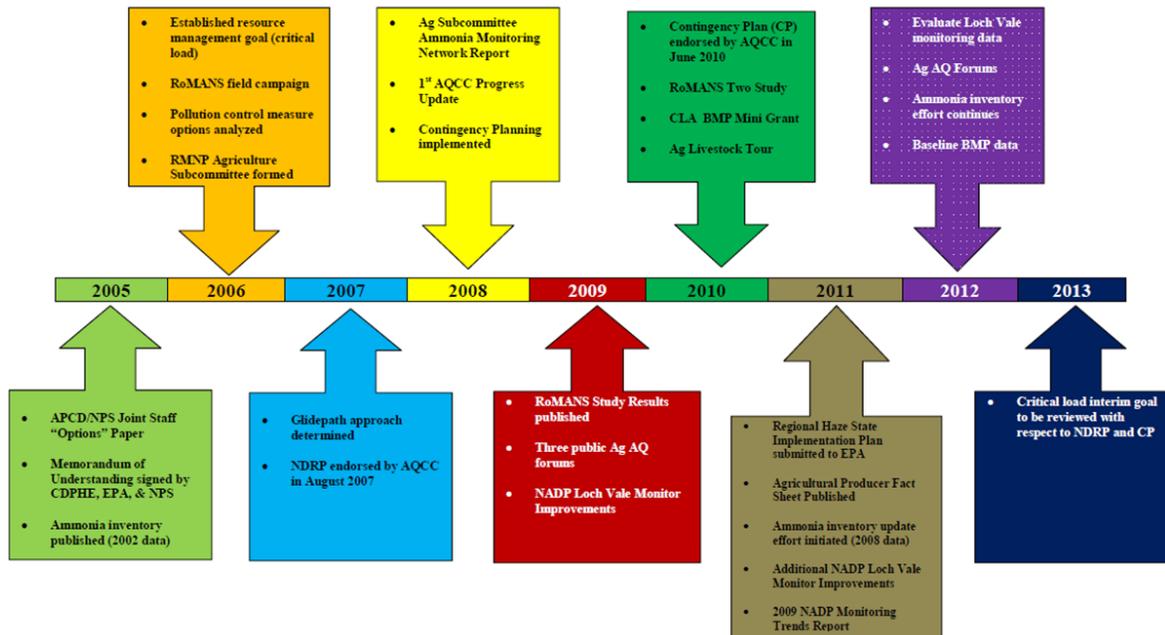


ha = hectare; kg = kilogram; N = nitrogen; yr = year.

Source: [Morris et al. \(2014\)](#).

**Figure 16-42 Rocky Mountain National Park Initiative glidepath and current wet nitrogen deposition at Loch Vale in Rocky Mountain National Park.**

RMNP INITIATIVE ACCOMPLISHMENT TIMELINE



Ag = agriculture; APCD = Air Pollution Control District; AQ = air quality; AQCC = Air Quality Control Commission; BMP = best management practice; CDPHE = Colorado Department of Public Health and Environment; CLA = Colorado Livestock Association; CP = Contingency Plan; EPA = U.S. Environmental Protection Agency; NADP = National Atmospheric Deposition Program; NPS = National Park Service; NDRP = Nitrogen Deposition Reduction Plan; RMNP = Rocky Mountain National Park; RoMANS = Rocky Mountain Atmospheric Nitrogen and Sulfur.

Source: CDPHE (2012). [https://www.colorado.gov/pacific/sites/default/files/AP\\_PO\\_ROMO-Initiative-Accomplishment-Timeline.pdf](https://www.colorado.gov/pacific/sites/default/files/AP_PO_ROMO-Initiative-Accomplishment-Timeline.pdf).

Figure 16-43 Rocky Mountain National Park Initiative accomplishment timeline.

### 16.5.6 Interactions between Nitrogen Deposition, Precipitation, and Large-Scale Ecological Disturbances

Precipitation patterns have changed over the past decades in ROMO, with consequences for biodiversity responses to N deposition. Spring snowfall has diminished over the last two decades (Clow et al., 2016), while winter snowfall has increased over the last century (Concilio et al., 2016). As a consequence, snowmelt occurs 7–18 days earlier than in 1993 (Clow et al., 2016), which extends the growing season. In a review of Niwot Ridge research, Bowman et al. (2014) suggested that N additions tend to have the opposite effect that high snowpack has on soil properties and processes (i.e., if N deposition accelerates soil N cycling, higher snowpack slows soil N cycling). Long-term trends in decreasing snowpack caused by changes in temperature and dust deposition (Clow et al., 2016), will intensify the effects of N deposition upon biodiversity.

Most forests within ROMO are composed of lodgepole pine or a mixture of Engelmann spruce and subalpine fir. Historically, these forests have been vulnerable to two natural mortality agents: bark beetles and wildfire ([Ehle and Baker, 2003](#)). Bark beetles can kill more than 90% of mature trees in heavily infested areas ([Rhoades et al., 2013](#)), while wildfires in these types of forests tend to burn at high intensities and kill trees across large landscapes ([Sibold et al., 2006](#); [Buechling and Baker, 2004](#); [Veblen et al., 1994](#); [Romme and Knight, 1981](#)). The large number of trees killed in these disturbances radically alters many ecological processes, including N cycling.

After tree mortality events, the decrease in biotic demand for N results in higher levels of inorganic N in the soil and increased concentrations of N in the leaves of surviving or recolonizing plants ([Dijkstra and Adams, 2015](#); [Mikkelsen et al., 2013](#); [Rhoades et al., 2013](#)). These changes in N cycling are similar to those caused by N deposition ([Fenn et al., 1998](#)) and those in experiments in and near ROMO simulating N deposition ([Rueth et al., 2003](#)). Although these disturbances increase N availability, beetle epidemics or wildfires in Rocky Mountain lodgepole pine and spruce-fir forests have not historically caused large increases in soil nitrate leaching or high concentrations of N in stream water ([Dunnette et al., 2014](#); [Morris et al., 2013](#); [Rhoades et al., 2013](#)), processes associated with excess N availability and the state of “N saturation” that occurs in ecosystems receiving large amounts of N deposition ([Fenn et al., 2003a](#)). However, there is concern that N deposition along the Colorado Front Range will enhance N availability to the point where disturbances will lead to large N leaching losses ([Rhoades et al., 2013](#)). This means that there is potential for N deposition to interact with bark beetles and wildfire to increase stream and lake water N content and degrade ecosystem function.

Nitrogen deposition can increase insect attack on plants ([Throop and Lerdau, 2004](#)) and there is some evidence that bark beetle activity and the bark beetle-caused tree mortality can be increased by N deposition ([Jones et al., 2004](#)). Unlike in other parts of the western U.S. where N deposition has allowed fires to occur more frequently by increasing fuels through greater plant growth ([Fenn et al., 2003a](#)), there is unlikely to be a large effect of N deposition on fire occurrence in ROMO. Fires in ROMO occur mostly during extreme weather conditions and are not as directly influenced by the amount of fuel available ([Sibold et al., 2006](#)). Notably, warm climate conditions increase fire frequency in lodgepole pine and spruce-fir forests in the Rocky Mountains ([Westerling et al., 2006](#)) and support bark beetle outbreaks in these forests ([Bentz et al., 2010](#); [Hebertson and Jenkins, 2008](#)).

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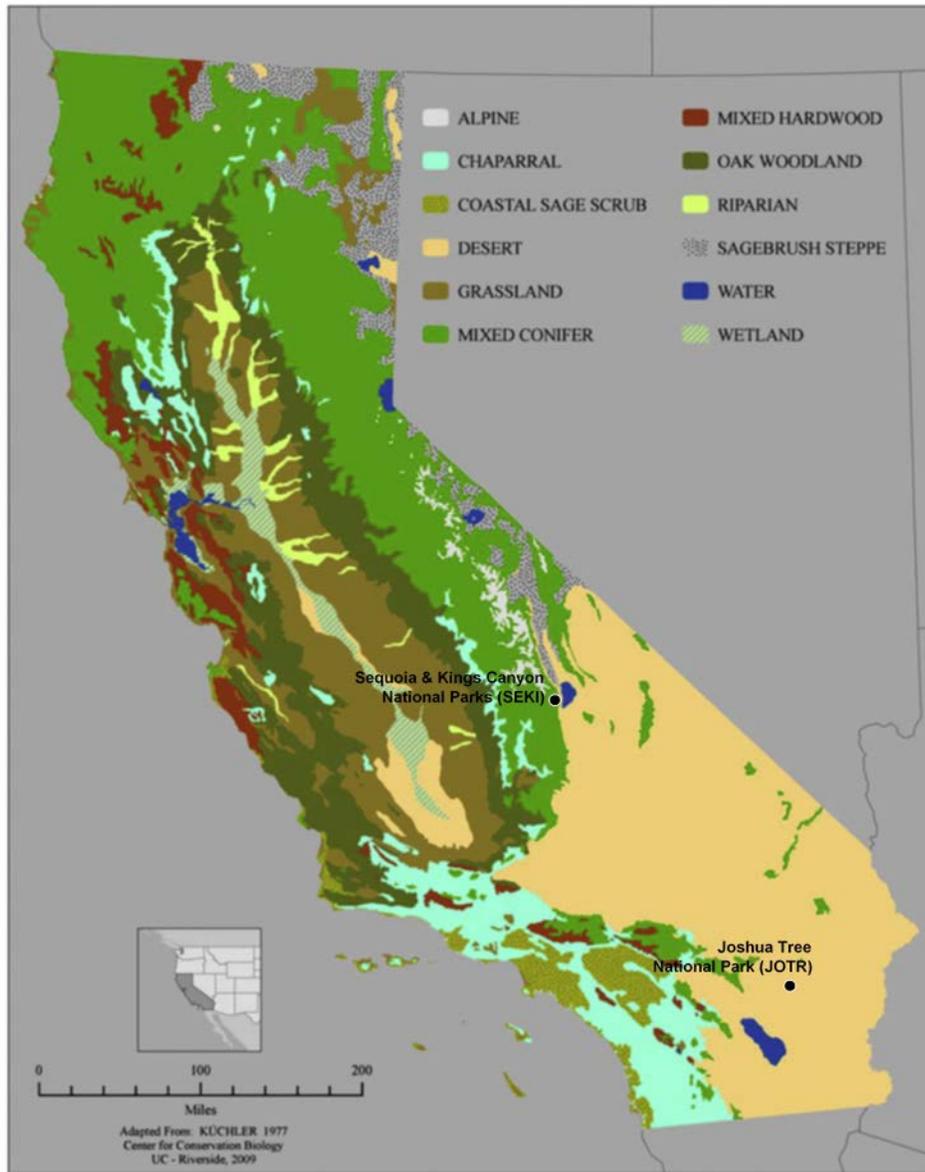
## 16.6 Southern and Central California

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### 16.6.1 Background

This case study focuses on the impact of N and S deposition on aquatic and terrestrial ecosystems in southern and central California. Two areas are considered that have abundant information on ecological effects: the Sierra Nevada and southern California arid land ecosystems. Here we focus on the national parks located in both of these ecosystems, the Sequoia and Kings Canyon national parks (SEKI), located in the southern Sierra Nevada Mountains in central California, and Joshua Tree National Park (JOTR), located in the desert to the southeast ([Figure 16-44](#)). SEKI and JOTR were selected to emphasize Class I areas in the Sierra Nevada (SEKI) and southern California arid land ecosystems (JOTR). In addition, research from surrounding ecoregions relevant to these ecosystems is included because more work has been conducted within the surrounding areas than within the park boundaries.

The majority of the information provided in this case study represents the Sierra Nevada Mountains/SEKI. Limited research conducted in JOTR was found in the peer-reviewed literature. Yosemite National Park (YOSE) to the north shares many commonalities with SEKI regarding air pollution exposure, sensitivities, and impacts. Thus, research conducted in YOSE is relevant and included here. Background information is provided below, including a general description of the region, protected status designation (e.g., Class I, Wilderness Area), and regional land use. This case study includes atmospheric deposition to the parks and surrounding areas, dose-response relationships, and critical loads.



Notes: Land cover presented in this figure represents potential natural vegetation before urbanization and modern agricultural development.

Source: [Reclamation et al. \(1996\)](#); from [Fenn et al. \(2010\)](#). Adapted to show case study locations.

**Figure 16-44 Map of the distribution of vegetation types and land cover in California.**

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### 16.6.1.1 Description of Case Study Region

Sequoia and Kings Canyon national parks are located in the Mediterranean California ecoregion (Level I Omernick classification) and are part of the Sierra Nevada Mountains. These parks are known for exceptionally large trees, high mountain peaks and ridges, and deep canyons and include the highest point in the contiguous U.S. (CONUS), Mount Whitney at 14,494 ft (4,418 m) above sea level. There are more than 200 marble caverns, many with endemic cave invertebrates. Sequoia National Park was originally created in 1890 to protect the giant sequoia trees (*Sequoiadendron giganteum*) from logging. It was the second national park, and the first formed to protect a particular living organism. In 1940, Congress created the contiguous Kings Canyon National Park to include the glacially formed Kings Canyon. These parks have increased in size to encompass 1,353 mi<sup>2</sup> (3,504 km<sup>2</sup>); 97% is designated and managed as wilderness.

Ecosystems in SEKI include chaparral vegetation at low elevation, extending up to alpine areas in the high mountains. Mycorrhizae, lichens, and herbaceous species communities are susceptible to declines in species richness/biodiversity due to the effects of N deposition. Likewise, high-elevation lakes and streams as well as low-order streams are susceptible to eutrophication and acidification driven by N deposition. Five rivers begin in SEKI, and past and present glaciers contributed to more than 3,000 lakes (many at high elevation) and 2,000 miles of streams, generally of low Strahler order ([Boiano et al., 2005](#)). Landscape variation contributes to diverse habitats that contain various assemblages of terrestrial, aquatic, and subterranean biota. As of 2005, of the more than 1,500 taxa of vascular plants in SEKI, 138 were deemed special status; 24 were listed by the California Native Plant Society as rare, threatened, or endangered. Fifty-one taxa of the parks' 312 terrestrial and aquatic vertebrate species had special status designations. Five extant native vertebrate species were federally listed in 2005: Sierra Nevada bighorn sheep (*Ovis canadensis sierrae*), bald eagle (*Haliaeetus leucocephalus*), Little Kern golden trout (*Oncorhynchus mykiss whitei*), mountain yellow-legged frog (*Rana muscosa*), and Yosemite toad (*Anaxyrus canorus*). As of 2005, the state listed the peregrine falcon (*Falco peregrinus*), great gray owl (*Strix nebulosa*), and willow flycatcher (*Empidonax traillii*) as endangered and the red fox (*Vulpes vulpes*), wolverine (*Gulo gulo*), and Swainson's hawk (*Buteo swainsoni*) as threatened. Forty extant native vertebrate species were listed as sensitive, including: white-tailed jackrabbit (*Lepus townsendii*), fisher (*Martes pennanti*), ring-tailed cat (*Bassariscus astutus*), Townsend's big-eared bat (*Corynorhinus townsendii*), western mastiff bats (*Eumops perotis*), merlin (*Falco columbarius*), northern harrier (*Circus cyaneus*), California spotted owl (*Strix occidentalis*), California legless lizard (*Anniella pulchra*), western pond turtle (*Actinemys marmorata*), Mount Lyell salamander (*Hydromantes platycephalus*), San Joaquin roach

fish (*Lavinia symmetricus*), and Kern River rainbow trout [*Oncorhynchus mykiss gilberti*; [Boiano et al. \(2005\)](#)].

Joshua Tree National Park is in the North American Desert ecoregion (Level I ecoregion by Omernick classification). The park was initially dedicated as a U.S. National Monument in 1936 and later declared a national park in 1994 when the U.S. Congress passed the California Desert Protection Act (Public Law 103-433). The park covers 1,235 mi<sup>2</sup> (3,200 km<sup>2</sup>), more than half designated as wilderness. It straddles the San Bernardino County/Riverside County border, including parts of two deserts: the higher, wetter Mojave Desert and the lower, drier Colorado Desert. The Little San Bernardino Mountains cross the southwestern edge of the park. JOTR is covered primarily by semiarid and arid vegetation types, including Joshua tree (*Yucca brevifolia*) woodlands. While rainfall is less than 10 cm/year, JOTR's groundwater supplies 200 surface water sources (e.g., springs, oases, ephemeral streams, or washes).

Joshua Tree National Park was preserved to protect the natural resources found at the junction of three California ecosystems. The Colorado Desert is a western extension of the Sonoran Desert. It occupies the southern and eastern portions of the park and is characterized by ocotillo (*Fouquieria splendens*) shrubs and cholla (*Opuntia* spp.) cacti. The Mojave Desert crosses the northern portions of the park and contains Joshua tree woodlands. The third ecosystem type in JOTR is a community of California juniper (*Juniperus californica*) and pinyon pine (*Pinus* spp.) located in the westernmost portion of the park, above 1,220 m elevation, in the Little San Bernardino Mountains.

There are several threatened and endangered species found within JOTR. Plant species include the triple-ribbed milkvetch (*Astragalus tricarinatus*) and Coachella Valley milkvetch (*A. lentiginosus* var. *coachellae*), which are federally endangered; as well as the Parish's daisy (*Erigeron parishii*), which is federally threatened. The desert tortoise (*Gopherus agassizii*), California's state reptile, is on both California's and the federal threatened lists. Twenty-six other species are listed as "special concern." JOTR was originally inhabited by the Serrano, the Chemehuevi (sometimes called the Southern Paiutes), and the Cahuilla people, and the park contains over 500 archaeological sites. (<https://www.nps.gov/jotr/index.htm>).

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### 16.6.1.2 Class I Areas

The 1964 Wilderness Act and the NPS Organic Act are both used as tools to protect SEKI and JOTR from air pollution impacts. SEKI and JOTR (as well as nearby YOSE) are also Prevention of Significant Deterioration (PSD) Class I areas. They receive the highest level of protection under the Clean Air Act (CAA) against air pollution

degradation. The CAA (42 USC 7470) authorized designation of Class I areas to protect air quality in national parks (over 6,000 ac [2,428 hectares]) and national wilderness areas (over 5,000 ac [2,023 hectares]) in an effort to preserve pristine atmospheric conditions and air quality-related values (AQRVs). Class I areas are subject to the PSD regulations under the CAA. PSD preconstruction permits are required for new and modified existing air pollution sources. Air regulatory agencies are required to notify federal land managers (FLMs) of any PSD permit applications for facilities within 100 km of a Class I area.<sup>1</sup> The FLMs are authorized to review and comment on PSD Class I permit applications with the permitting agency.

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### 16.6.1.3 Regional Land Use and Land Cover

Land cover in SEKI is largely forested and mountainous terrain in and near the Sierra Nevada Mountains. The westernmost portions of the park are covered by mixed conifer and chaparral vegetation. Further to the west is a zone of intensive agriculture ([Table 16-29](#)).

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**Table 16-29 Land coverages of Sequoia, Kings Canyons, and Joshua Tree national parks.**

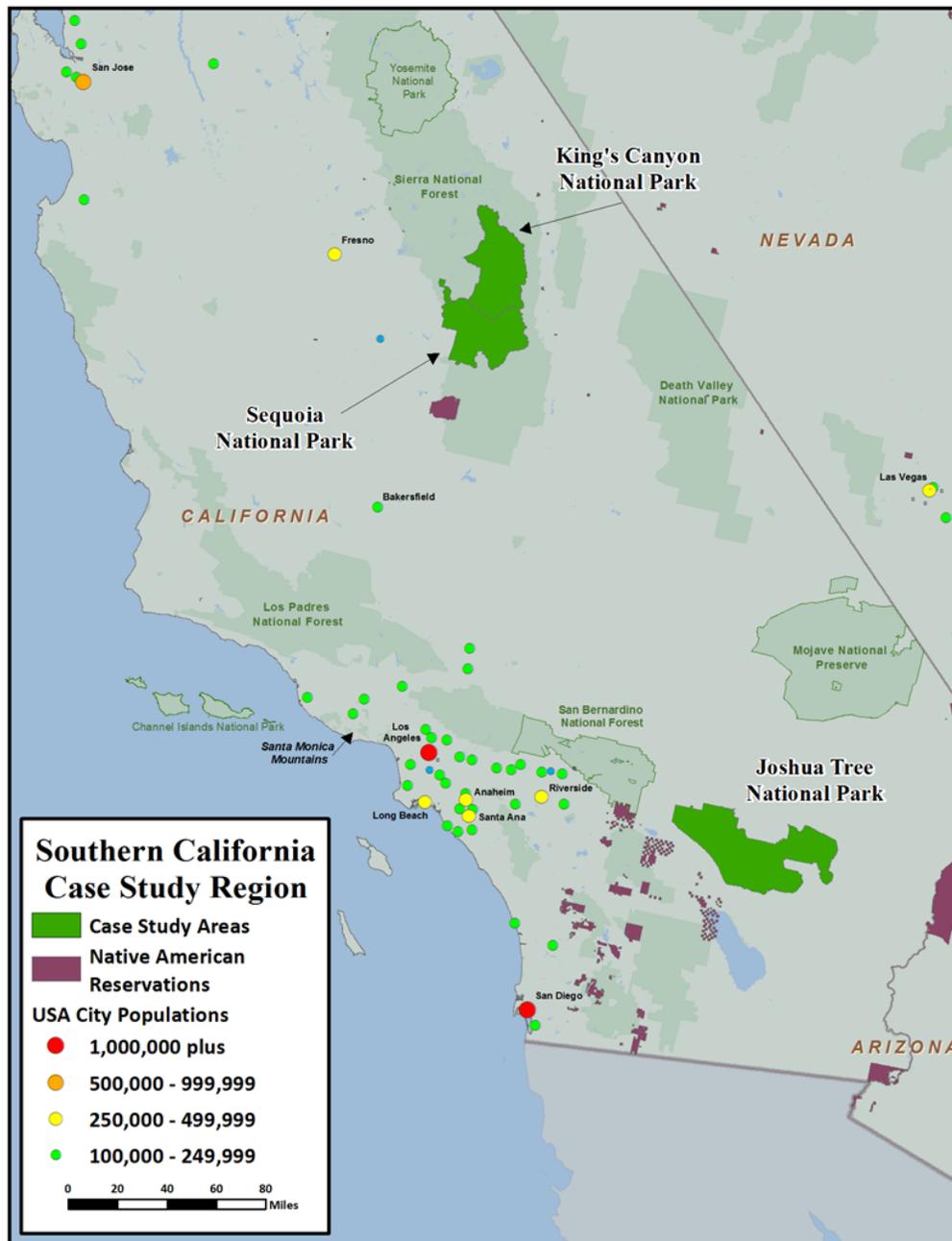
Land Cover Category	Sequoia National Park (km <sup>2</sup> )	Joshua Tree National Park (km <sup>2</sup> )	Kings Canyon National Park (km <sup>2</sup> )
Developed	5	7	4
Barren land and exposed rock	416	207	690
Deciduous forest	12	0	2
Evergreen forest	736	5	519
Mixed forest	8	0	1
Shrub/scrub	390	2,936	516
Grassland/herbaceous	68	54	100
Wetland	2	0	2

km = kilometer.

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<sup>1</sup> <http://webcam.srs.fs.fed.us/psd>.

Land cover in JOTR is largely desert and semiarid land ([Table 16-29](#), [Figure 16-44](#)). Nearby human population centers ([Figure 16-45](#)) include the Coachella Valley (~350,000 people, including the cities of Palm Springs and Indio), as well as the towns of Twentynine Palms (25,600 people) and Joshua Tree (7,400).



**Figure 16-45** Southern and central California case study region showing locations of human population centers.

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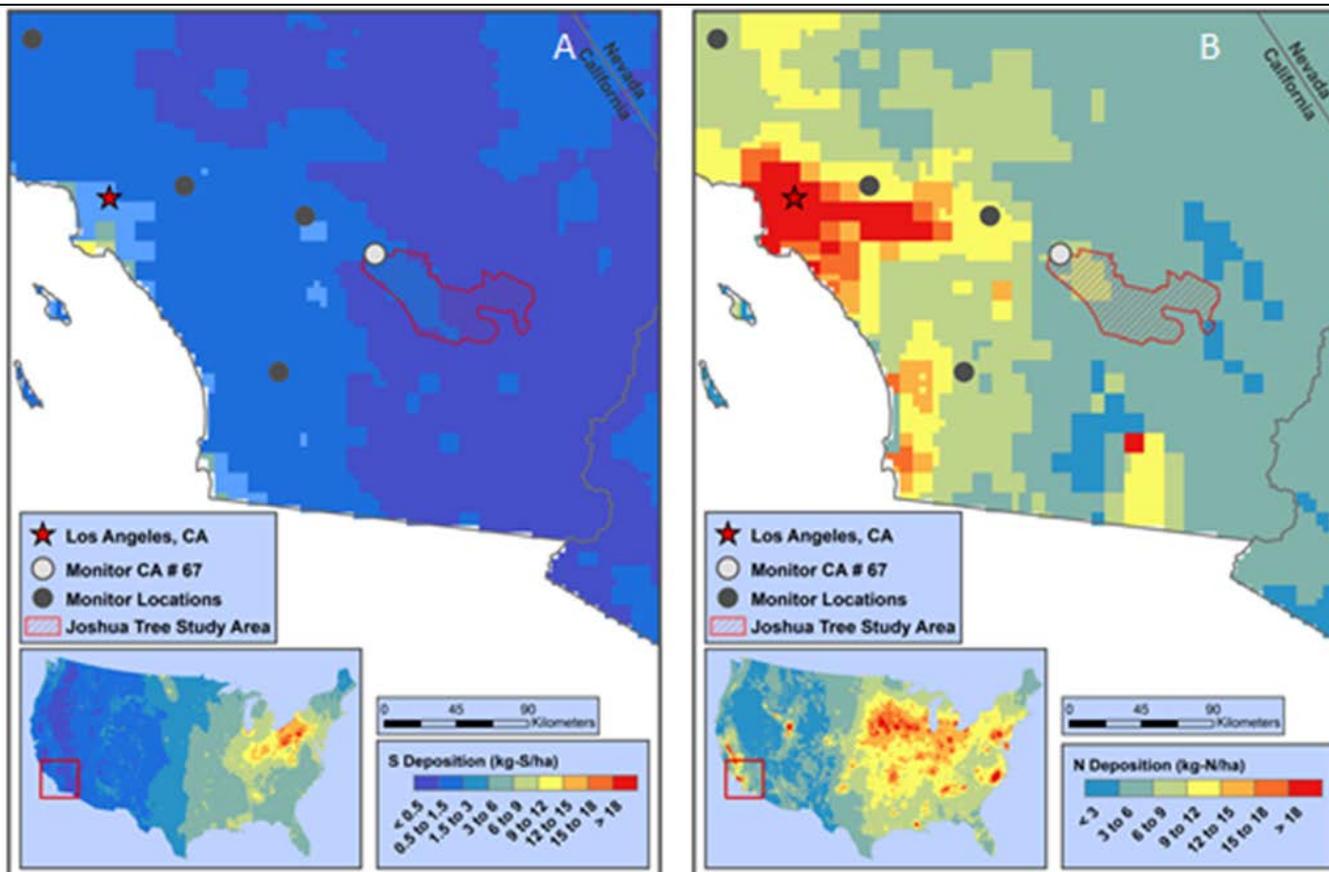
## 16.6.2 Deposition

Characteristics of N and S deposition are shown in [Figure 16-46](#) through [Figure 16-48](#) for JOTR and [Figure 16-49](#) through [Figure 16-51](#) for SEKI. Data shown in the figures were obtained from the hybrid modeling/data fusion product, TDEP (<http://nadp.slh.wisc.edu/committees/tdep/tdepmaps/>), and described earlier in [Appendix 2](#). However, the time series of wet deposition is taken directly from data on the NADP/NTN website. This was done to track changes in deposition since the passage of the Clean Air Act Amendment because the CMAQ simulations involved in TDEP extend back only to 2000. See [Appendix 2.4](#), [Appendix 2.5](#), and [Appendix 2.6](#) for more information on deposition in the U.S. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

[Figure 16-46](#) indicates that the general pattern of deposition in JOTR of N and S is broadly similar, tending to be higher near the NADP site located in the NW corner of the study area and decreasing inland. As expected, N deposition is highest in and surrounding Los Angeles. The park is often subject to transport of emissions from the Los Angeles Basin. However, as can be seen from [Figure 16-46B](#), this influence decreases substantially towards the southeast. In addition, the area surrounding JOTR shows a high degree of regional heterogeneity. Deposition of S is consistent with the rest of the western U.S., but is considerably lower than in the eastern U.S.

As shown in [Figure 16-47A](#), deposition of N in JOTR is estimated by TDEP to be mostly in oxidized forms. NADP measurements of wet deposition at the park as seen in [Figure 16-48](#) are inconsistent with these simulation results. Although wet deposition is small in the arid environment of JSTOR, the difference suggests that processes occurring at spatial scales below that of TDEP may result in localized conditions different from those depicted in [Figure 16-47](#). In [Figure 16-48](#), wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$ , apart from being lower than at many other sites, has not shown consistent trends over the past 25 years. Comparison of [Figure 16-46](#) and [Figure 16-47](#) suggests that dry deposition dominates over wet deposition of N and S in the JOTR study area.

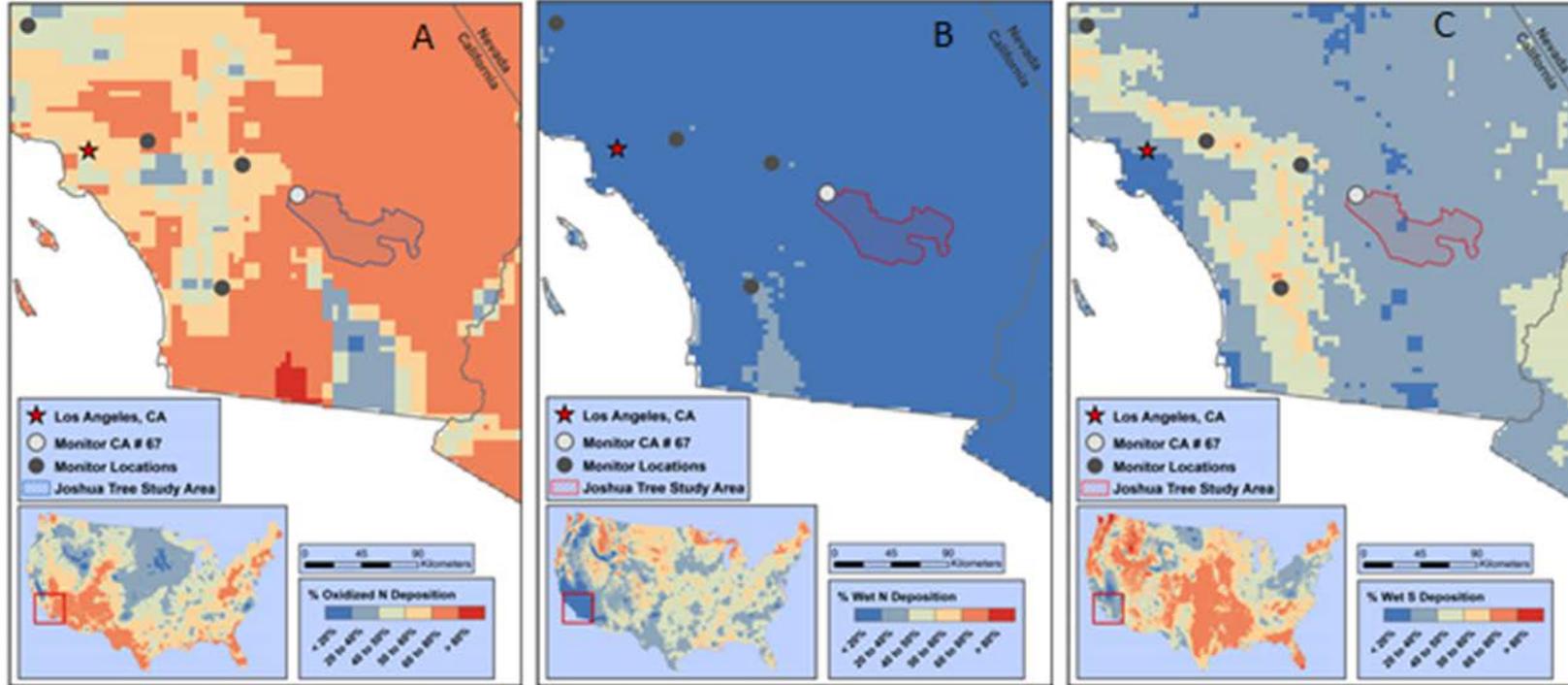
In SEKI, [Figure 16-49](#) shows a 3-year average total deposition of N and S for 2011–2013; [Figure 16-50](#) shows the partitioning between oxidized and total N; [Figure 16-51](#) shows the 25-year time series for wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  obtained at the NADP/NTN monitoring sites near SEKI.



CONUS = contiguous U.S.; ha = hectare; kg = kilogram; N = nitrogen; S = sulfur.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

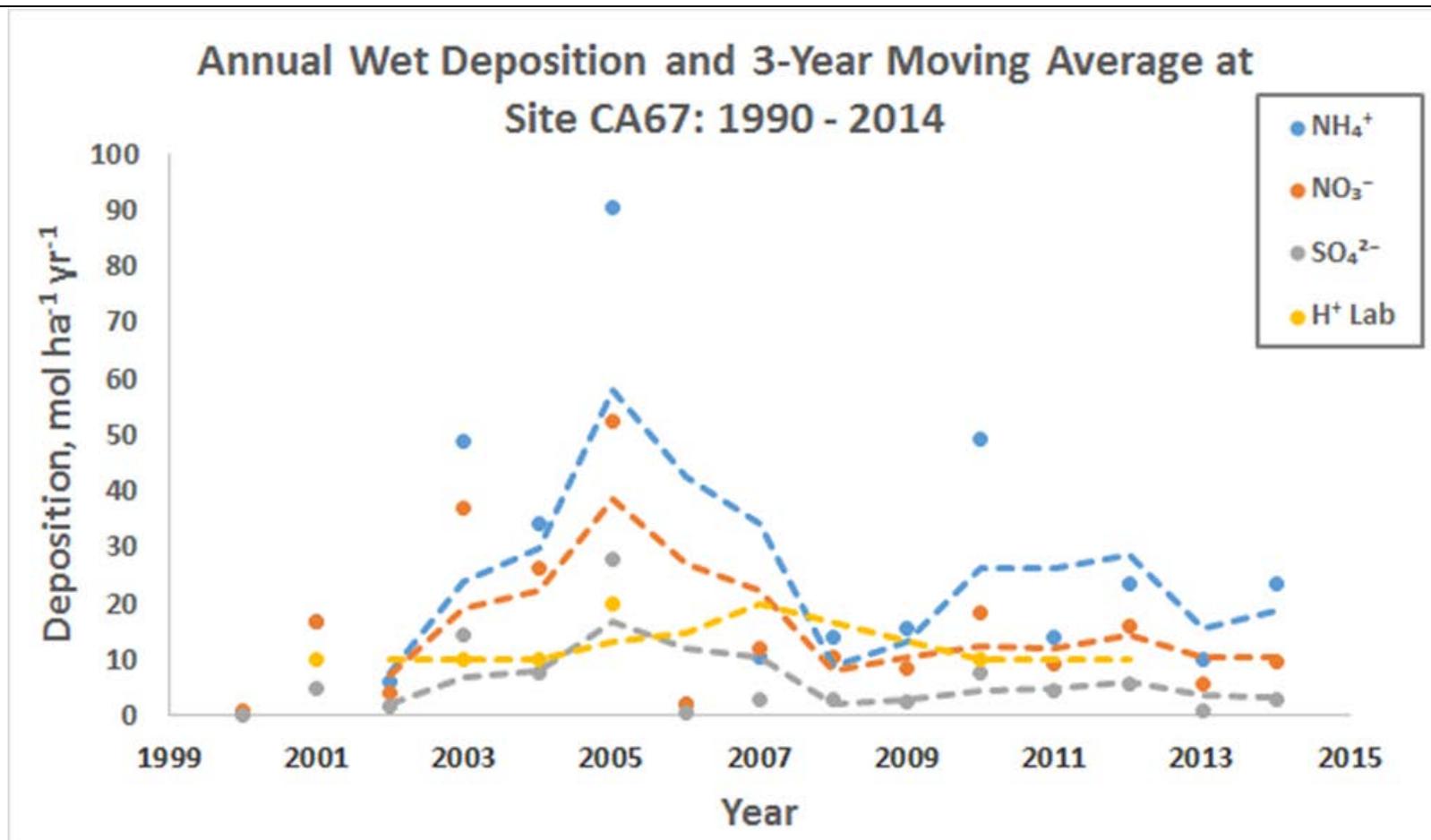
**Figure 16-46** Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. A and B show the 3-year average total deposition of nitrogen and sulfur for 2011–2013



CONUS = contiguous U.S.; N = Nitrogen, S = Sulfur.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

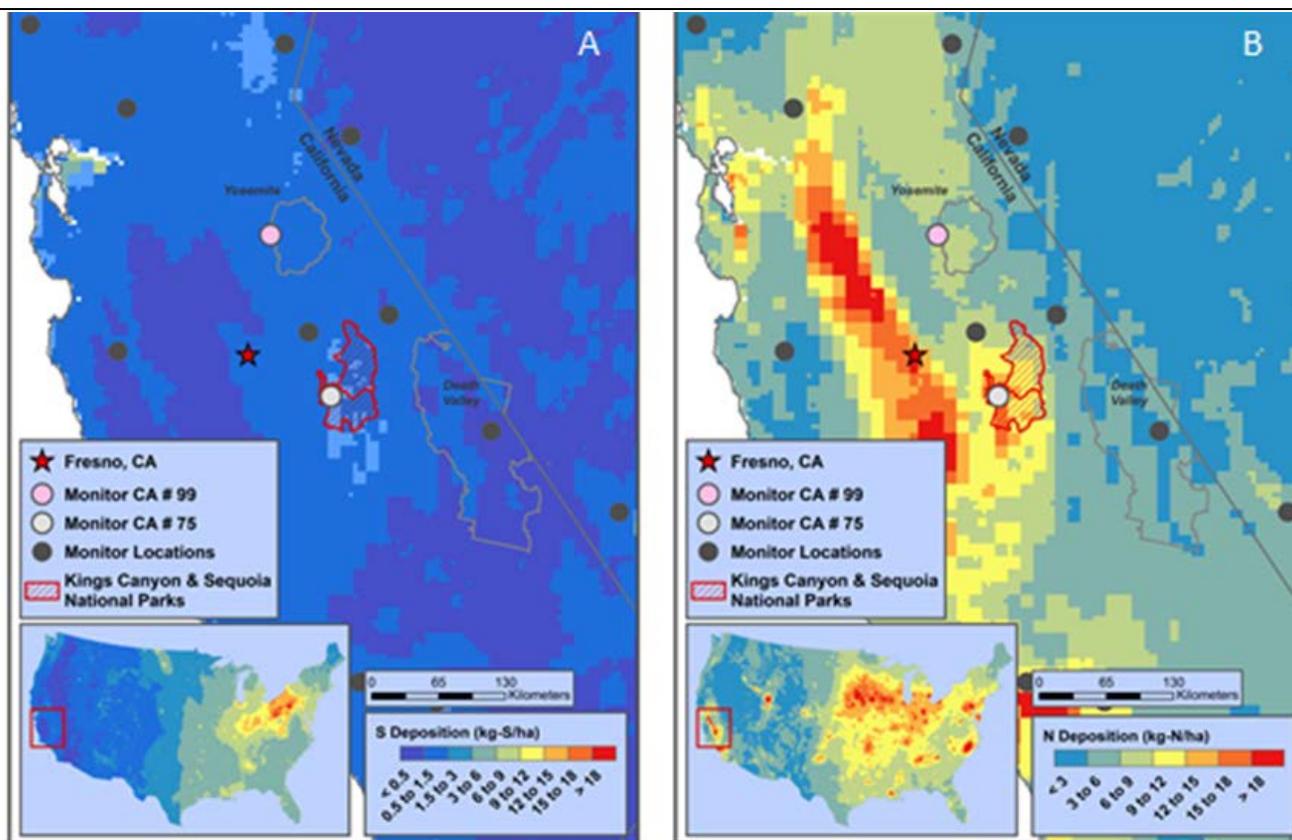
**Figure 16-47** Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. A shows the partitioning between oxidized and reduced nitrogen; B and C show the 3-year average total percentage of wet deposition of nitrogen and sulfur for 2011–2013.



H<sup>+</sup> = hydrogen ion; ha = hectare; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

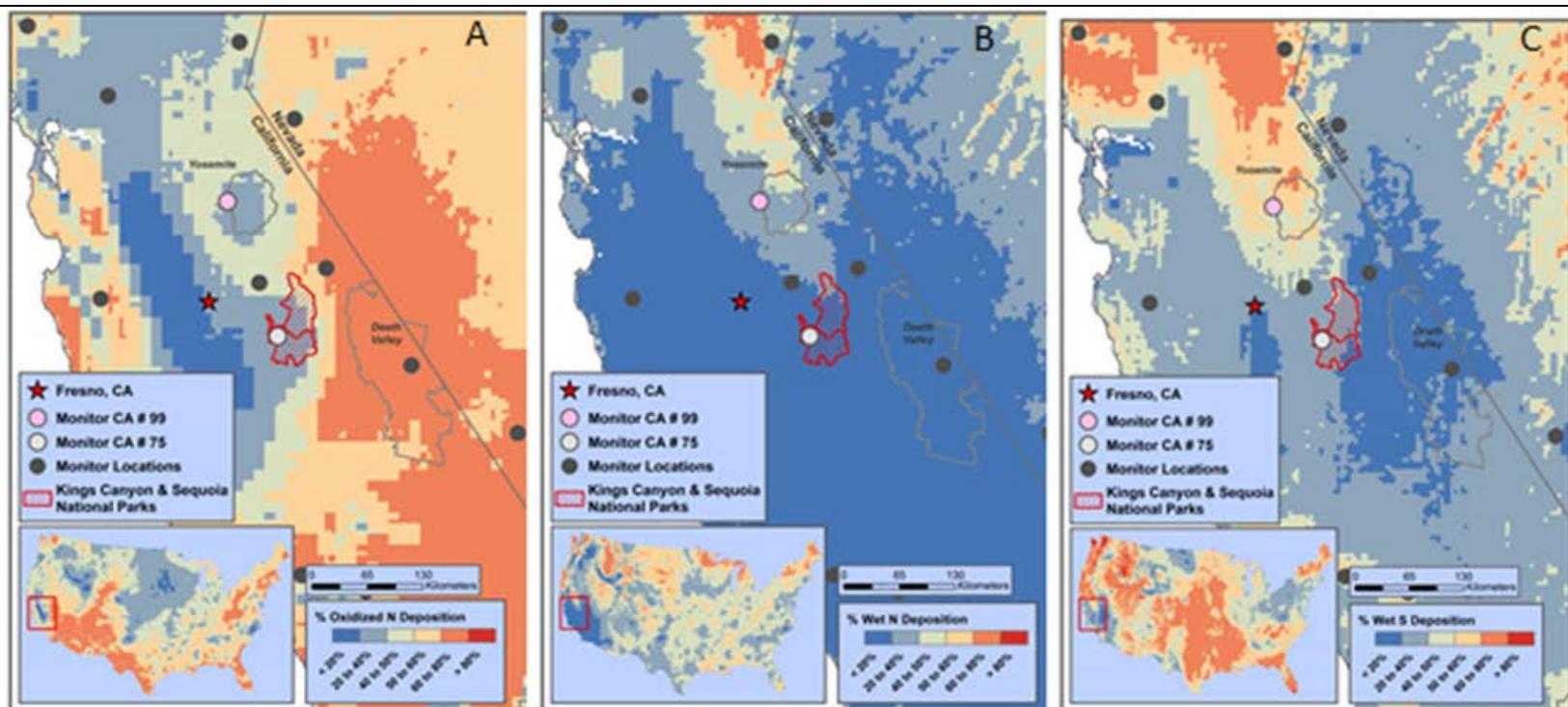
**Figure 16-48** Patterns and temporal trends of nitrogen and sulfur deposition in Joshua Tree National Park and surrounding region in California. The 25-year time series for wet deposition of nitrate, ammonium, sulfate, and hydrogen ion obtained from the National Atmospheric Deposition Program/National Trends Network monitoring site CA67.



CONUS = contiguous U.S.; H<sup>+</sup> = hydrogen ion; ha = hectare; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

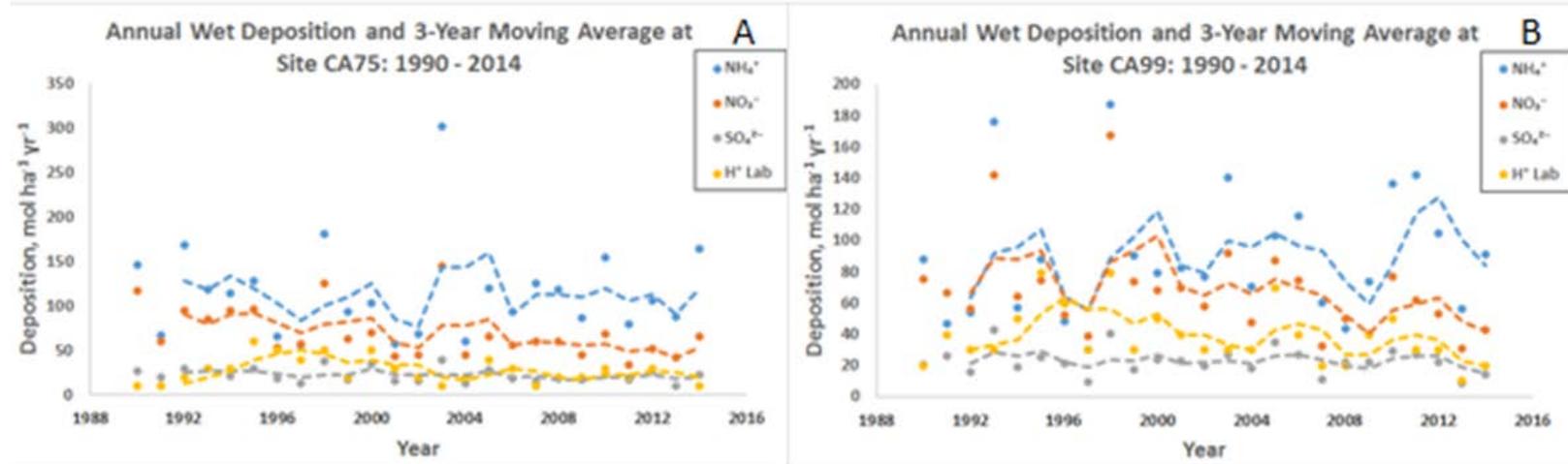
**Figure 16-49** Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons national parks and surrounding region in California. A and B show the 3-year average total deposition of nitrogen and sulfur for 2011–2013.



CONUS = contiguous U.S.; H<sup>+</sup> = hydrogen ion; ha = hectare; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

**Figure 16-50** Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons national parks and surrounding region in California. A shows the partitioning between oxidized and reduced nitrogen, indicated as the fraction of total nitrogen which is oxidized; B and C show the 3-year average total percentage of wet deposition of nitrogen and sulfur for 2011–2013.



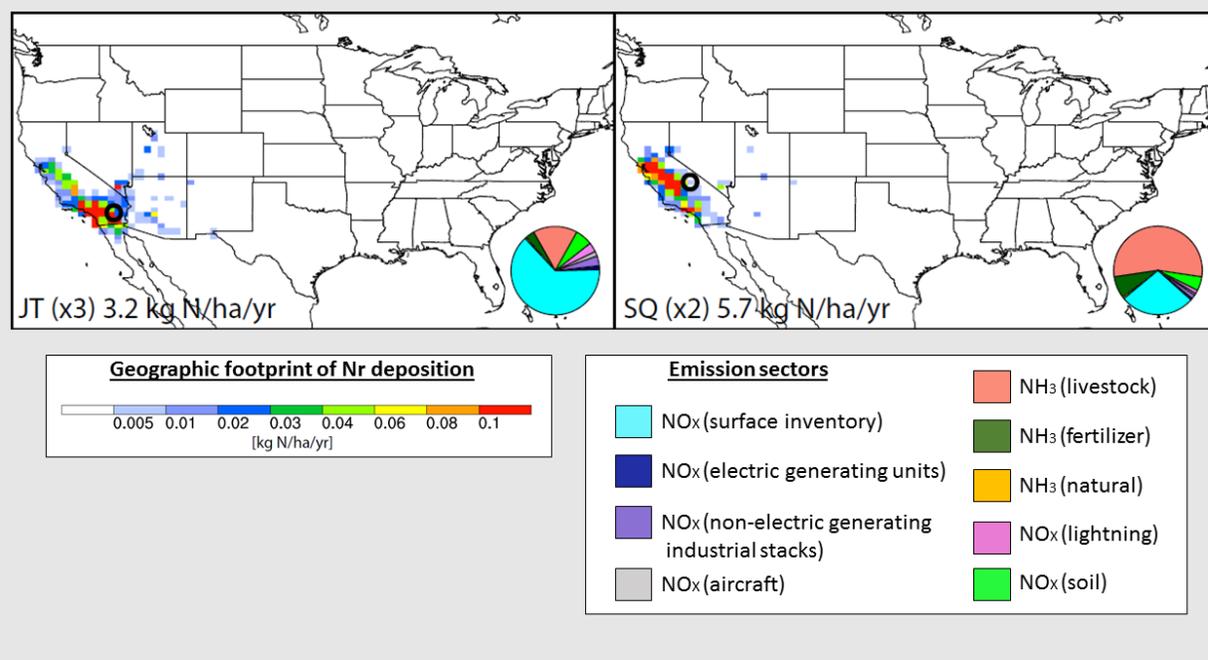
CONUS = contiguous U.S.; H<sup>+</sup> = hydrogen ion; ha = hectare; mol = mole; NH<sub>4</sub><sup>+</sup> = ammonium; NO<sub>3</sub><sup>-</sup> = nitrate; SO<sub>4</sub><sup>2-</sup> = sulfate; yr = year.

Surrounding areas in California and Nevada and inserts showing the whole CONUS are shown to place the depositional environment for both portions of the study area in context. Other maps showing the contributions of individual species to dry and/or wet deposition are given in [Appendix 2.7](#).

**Figure 16-51** Patterns and temporal trends of nitrogen and sulfur deposition of Sequoia and Kings Canyons and in Yosemite national parks and surrounding regions in California. A and B show the 25-year time series for wet deposition of nitrate, ammonium, sulfate, and hydrogen obtained from the National Atmospheric Deposition Program/National Trends Network monitoring sites CA99 and CA75.

As modeled by TDEP simulations, which may carry additional uncertainty when considered at smaller spatial scales, deposition of N is much higher in SEKI than JOTR, and its spatial variability is greater in SEKI than JOTR. On the other hand, S deposition is similar in magnitude between the two sites; S is also characterized by relatively low spatial variability at the two sites. In contrast to JOTR, deposition of N is estimated by TDEP simulations to be mostly in reduced forms in SEKI (see [Figure 16-50](#)), although this is not consistent with the wet portion of deposition measured by NADP at sites within those respective parks. Given the proximity of SEKI to the San Joaquin Valley, however, a higher proportion of reduced as opposed to oxidized N at that park would be expected. There is considerable variability in the percentage of N deposition as either in oxidized or reduced forms. Wet deposition of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$  is larger over SEKI than over JOTR, but still lower than at some NADP sites in the eastern U.S. Similar to JOTR, dry deposition dominates over wet deposition of both N and S in SEKI.

A recent modeling study of Class I areas, including SEKI and JOTR, used a GEOS-Chem adjoint model to identify the geographic sources of reactive N deposition, as well as the emission sector sources of reactive N deposition within the parks ([Lee et al., 2016](#)). Ninety percent of emissions of  $\text{N}_r$  that affect SEKI originate within 400 km of the park, with livestock ammonia as the major emission source (>50%) of N deposition within SEKI (see [Figure 16-52](#)). At JOTR, 90% of N emissions originate within 600 km of the park, and mobile sources of  $\text{NO}_x$  are the major emission source (>60%) of N deposition to JOTR (see [Figure 16-52](#)).



Source: Adapted from Figure 5 in [Lee et al. \(2016\)](#).

**Figure 16-52** Annual-averaged monthly footprint of reactive N deposition in Joshua Tree National Park (3.2 kg N/ha/yr) and Sequoia National Park (5.7 kg N/ha/yr). Also shown for each park is a pie chart of fractional contribution from emission sectors, as estimated by GEOS-Chem adjoint model.

## 16.6.3 Critical Loads and Other Dose-Response Relationships

### 16.6.3.1 Terrestrial

The communities of terrestrial species with well-documented effects caused by N deposition include lichens, mycorrhizae, grasses, and trees. While well studied ecosystems include mixed conifer forest, alpine/subalpine, and chaparral/semiarid shrubland.

Data on the effects of N deposition on mixed conifer forest ecosystems in the Mediterranean California ecoregion (Omernick Level I), including the Sierra Nevada region, are well summarized by [Fenn et al. \(2011b\)](#). A more recent overview of empirical

and modeled CLs for mixed conifer forests was provided by [Fenn et al. \(2015\)](#). Nitrate leaching from soil in combination with high evapotranspiration rates lead to high nitrate concentrations in surface waters in this area.

In general, the alpine and subalpine plant communities, such as those found in SEKI and YOSE, are sensitive to eutrophication, an observation based largely on research conducted in alpine ecosystems in the Rocky Mountains ([Bowman et al., 2006](#)). Alpine and subalpine communities are high-elevation plant communities that have developed under conditions of low nutrient supply, in part because soil-forming processes tend to be poorly developed at high elevations. This contributes to N sensitivity. Consequently, changes in alpine plant productivity and species composition have been reported in response to increased N inputs ([Bowman et al., 2006](#); [Vitousek et al., 1997](#)).

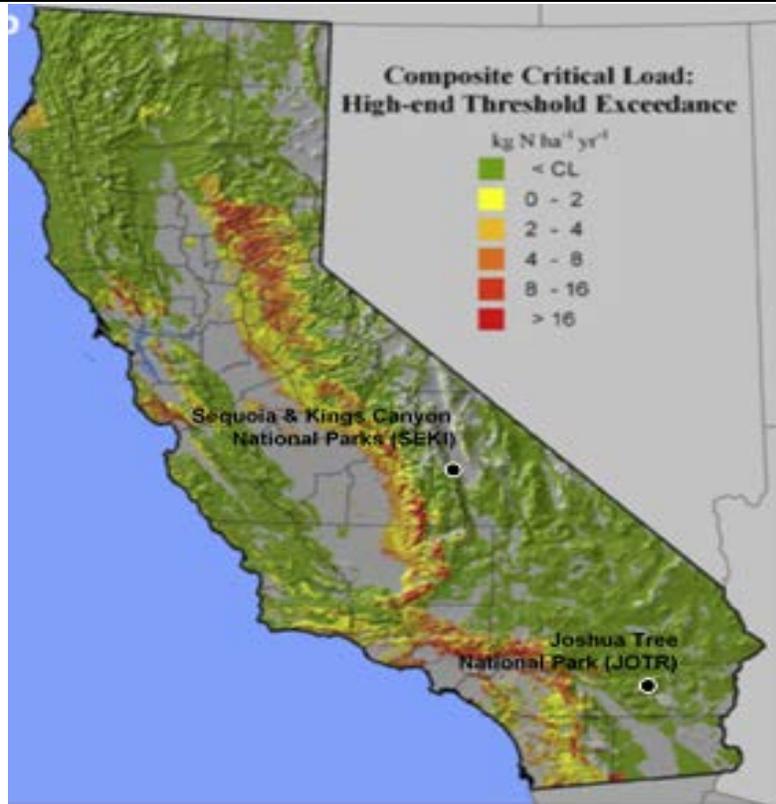
In chaparral and other semiarid shrublands in southern California, nitrogen enrichment can contribute to an increase in net primary productivity; however, water availability is often limiting to growth ([Vourlitis, 2012](#)). Arid ecosystems represent an extreme in terms of water availability and water is the principal limiting resource. Therefore, long-term (many years) experiments and the potential for interactions among water, fire, and nutrient supply in governing plant responses to N additions should be considered. Based on N addition experiments, [Vourlitis and Pasquini \(2009\)](#) suggested that dry-season addition of N significantly changes the community composition of coastal sage scrub (CSS) vegetation, but not chaparral. The impacts of such changes on the plant community may magnify over time. It has been proposed that the increase in the growth of invasive annual forbs and non-native grasses induced by nitrogen deposition leads in turn to greater fire frequency and destructiveness, particularly in arid ecosystems including JOTR ([Rao et al., 2010](#)). [Talluto and Suding \(2008\)](#) on the other hand proposed that increases in both fire frequency and N deposition over the last several decades in southern California may have promoted the conversion of CSS land to non-native grasslands. Both empirical and modeling studies suggest that loss of biodiversity in response to N input and climate change can be greater than the effects of either stressor alone ([Porter et al., 2013](#)).

#### **16.6.3.1.1 Empirical Studies**

A number of empirical studies (N gradient and N experimental additions) have been conducted to identify tipping points and to define areas of CL exceedance. Key studies conducted in the southern and central California case study region are listed in [Table 16-30](#).

[Fenn et al. \(2010\)](#) reported empirical CL exceedance maps for seven major vegetation community types in California ([Figure 16-53](#)). Thirty-five percent of the land area covered by these vegetation types (100,000 km<sup>2</sup>) was estimated to be in exceedance of the nutrient-N CLs (3–8 kg N/ha/yr) that were estimated for mixed conifer forests, chaparral, and oak woodlands. Nearly half of the area covered by CSS (54%) and grasslands (44%) was judged by the authors to be in exceedance of the CLs for protecting the ecosystem against changes associated with invasive grasses. Substantial chaparral (53%) and oak woodland (41%) cover was estimated to be in exceedance for impacts on epiphytic lichens. About 30% of the desert area investigated was in exceedance, based on the presence of invasive grasses and increased fire risk. An estimated 30% of the mixed conifer forest, based on lichens, was in exceedance of the CL. Forested and chaparral communities were less sensitive. Only 3–15% of the forested and chaparral areas were estimated to be in exceedance of the CL for NO<sub>3</sub><sup>-</sup> leaching. By combining the exceedance areas of the seven vegetation types, [Fenn et al. \(2010\)](#) estimated that 25% of the land area of the vegetation types included in the study were in exceedance for protecting against nutrient enrichment.

[Pardo et al. \(2011c\)](#) conducted a synthesis study that evaluated published data to identify the empirical CLs for N in Level I ecoregions across the U.S. The authors estimated CL values as low as 3 kg N/ha/yr to protect sensitive resources in the southern and central California case study area. [Table 16-30](#) lists the CLs identified by [Pardo et al. \(2011c\)](#) for North American Desert and Mediterranean California ecoregions (Omernick Level I) and new studies published after [Pardo et al. \(2011c\)](#). If deposition exceeds the CL, the risk of harmful effects increases.



CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; yr = year.

When CLs based on two different N responders were used within a given vegetation type (e.g., lichen effects and nitrate leaching), only the more sensitive responder was used (lowest CL). The higher value of two CLs, when two values were available, was used in the case of coastal sage scrub, mixed conifer forest (lichen community effects), desert scrub and pinyon-juniper, and the lichen effects CL was used for chaparral.

Source: [Fenn et al. \(2010\)](#). Adapted to show case study locations.

**Figure 16-53** Composite critical load exceedance maps for all seven vegetation types included in the study of [Fenn et al. \(2010\)](#) showing the combined exceedance areas and the level of exceedance (kg N/ha/yr).

**Table 16-30 Summary of recent empirical dose-response and critical load studies focused on the southern/central California case study area and published since [Pardo et al. \(2011c\)](#).**

Study	Terrestrial	Aquatic	Location	Focus	CL/Exceedance
<b>Mediterranean California Ecoregion Level I (Omernick)</b>					
<a href="#">Pardo et al. (2011a)</a>	•		Mediterranean California Ecoregion Level I (Omernick); mixed conifer forest ecosystem	Lichen chemistry and community changes, nitrate leaching, soil acidification, reduced fine root biomass	3.1–39 kg N/ha/yr The lowest critical load is 3.1 based on lichen tissue chemistry above the clean site threshold. Nitrate leaching and fine root biomass critical load is 17, soil acidification is 26 kg N/ha/yr, and susceptibility to beetle infestation is 39 kg N/ha/yr
<a href="#">Pardo et al. (2011a)</a>	•		Mediterranean California Ecoregion Level I (Omernick); chaparral ecosystem	Nitrate leaching and changes in the lichen community	3.1–14 kg N/ha/yr 3.1 kg N/ha/yr is a modeled value for lichens, while 10 kg N/ha/yr is the value for nitrate leaching
<a href="#">Pardo et al. (2011a)</a>	•		Mediterranean California Ecoregion Level I (Omernick); coastal sage scrub ecosystem	Exotic invasive grass cover, native forb richness, arbuscular mycorrhizal richness	7.8–10 kg N/ha/yr
<a href="#">Pardo et al. (2011a)</a>	•		Mediterranean California Ecoregion Level I (Omernick); serpentine grassland ecosystem	Annual grass invasion replacing native herbs	6 kg N/ha/yr
<a href="#">Clark et al. (2013)</a>	•		Mediterranean California and North American Desert	Loss of herbaceous plant species	Species loss 1–30%
<a href="#">Ellis et al. (2013)</a>	•		SEKI and YOSE	Protection of lichens	Estimated CL 2.5 to 7.1 kg N/ha/yr

**Table 16-30 (Continued): Summary of recent empirical dose response and critical load studies focused on the southern California case study area and published since Pardo et al. (2011c).**

Study	Terrestrial	Aquatic	Location	Focus	CL/Exceedance
<a href="#">Cox et al. (2014)</a>	•		Mediterranean California Ecoregion Level I (Omernick); coastal sage scrub ecosystem	Conversion from coastal sage scrub to annual grassland	Estimated CL 11 kg N/ha/yr to conserve coastal sage shrub vegetation
<a href="#">Bytnerowicz et al. (2015)</a>	•		Mediterranean California Ecoregion Level I (Omernick); chaparral ecosystem	Lichens in chaparral, San Bernardino Mountains	Exceedances of CL = 5.5 kg N/ha/yr for lichens occurred mostly in western and northern portions of the study area
<a href="#">Bytnerowicz et al. (2015)</a>	•		Mediterranean California Ecoregion Level I (Omernick); mixed conifer forest ecosystem	Mixed conifer forest	Exceedances of CL = 3.1 kg N/ha/yr for mixed conifer forest covered much of San Bernardino Mountains
<a href="#">Allen et al. (2016)</a>	•		Mediterranean California Ecoregion Level I (Omernick); coastal sage scrub ecosystem	Rapid decline in mycorrhizal biodiversity	CL = 11 kg N/ha/yr
<b>North American Desert Ecoregion Level 1 (Omernick)</b>					
<a href="#">Pardo et al. (2011a)</a>	•		North American Desert Ecoregion Level I (Omernick)	Protect herbaceous plants and shrubs	CL 3 to 8.4 kg N/ha/yr
<a href="#">Simkin et al. (2016)</a>	•		North American Desert Ecoregion Level I (Omernick)	Grass and forb decreasing species richness	CL open canopy: 8.3–9.9 (mean = 9.2, n = 240) CL closed canopy: 13.5–17.0 (mean = 16.5, n = 32)
<a href="#">Clark et al. (2013)</a>	•		Mediterranean California and North American Desert	Loss of herbaceous plant species	Species loss 1–30%

CL = critical load; ha = hectare; kg = kilogram; N = nitrogen; SEKI = Sequoia and Kings Canyons National Parks; YOSE = Yosemite National Park; yr = year.

Data compiled by [Pardo et al. \(2011c\)](#) suggested that ambient N deposition is higher than the lower limit of the expected CL to protect against nutrient enrichment effects in some of the national parks in the Sierra Nevada, mainly SEKI, and to a lesser extent, YOSE. Potential CL exceedances were reported for the protection of mycorrhizal fungi, lichens, herbaceous plants, and forest vegetation, and also to restrict  $\text{NO}_3^-$  leaching in drainage waters. [Fenn et al. \(2010\)](#) estimated low CL values (3–8 kg N/ha/yr) for mixed conifer forests, chaparral, and oak woodlands. These low critical load estimates were driven by the presence of highly N sensitive species (lichens) and N poor vegetation (annual grasslands and desert scrub plant communities). [Fenn et al. \(2010\)](#) concluded that N deposition at or above these critical load values might cause vegetation community changes because the increased availability of N tends to favor invasion by non-native grasses into arid land ecosystems.

[Clark et al. \(2013\)](#) estimated the loss of herbaceous plant species caused by atmospheric N deposition based on a national CL database. Using the lower and more conservative estimates of CLs, the ambient N deposition was judged to be in exceedance of nutrient N CLs over extensive portions of the Mediterranean California and North American Desert ecoregions. Estimated plant species losses ranged from less than 1 to 30%, but variability was high and uncertainty in these estimates was substantial.

#### **16.6.3.1.2 Modeling Studies**

Dynamic and steady-state models have been used to estimate critical or target loads in the southern/central California case study region. Key studies, highlighted in [Table 16-31](#), have focused on CLs of nutrient N and acidity.

**Table 16-31 Terrestrial critical and target load and exceedance modeling studies in southern/central California.**

Study	Location	Model	Focus
<b>Mixed Conifer</b>			
<a href="#">Hurteau et al. (2009)</a>	Teakettle Experimental Forest and YOSE	STELLA <sup>®7</sup>	Modeled how changing precipitation and N deposition levels affect shrub and herb biomass production. Herb cover growth rate greater at 12 kg N/ha/yr than 24 kg N/ha/yr. Precipitation was more important driver for shrub cover.
<a href="#">Fenn et al. (2015)</a>	Sierra Nevada and San Bernardino Mts.	DayCent	Modeled CL to protect against NO <sub>3</sub> <sup>-</sup> leaching; CL ranged from 17 to 30 kg N/ha/yr.
<b>Semiarid</b>			
<a href="#">Li et al. (2006)</a>	SEKI	DayCent	Simulated N deposition of 7.7 kg N/ha/yr; increased loss of N to NO <sub>3</sub> <sup>-</sup> export and gaseous NO.
<a href="#">Rao et al. (2010)</a>	JOTR	DayCent	Effects on fire risk in creosote bush and pinyon-juniper vegetation types. CL = 3.2 kg N/ha/yr (creosote bush) and 3.9 kg N/ha/yr (pinyon-juniper). Wet areas having low soil clay (6–14%) may have CL as low as 1.5 kg N/ha/yr.
<a href="#">Rao et al. (2010)</a>	JOTR	DayCent	Modeled CL was determined as the N deposition load at which fire risk began to increase exponentially above the background fire risk. The CL for creosote bush scrub was 2.1 kg N/ha/yr and for pinyon-juniper woodland was 3.6 kg N/ha/yr.

CL = critical load; ha = hectare; JOTR = Joshua Tree National Park; kg = kilogram; Mts. = mountains; N = nitrogen; NO = nitric oxide; NO<sub>3</sub><sup>-</sup> = nitrate; SEKI = Sequoia and Kings Canyons National Parks; YOSE = Yosemite National Park; yr = year.

#### 16.6.3.1.2.1 Mixed Conifer

[Hurteau et al. \(2009\)](#) developed and tested a model to determine how changes in precipitation and N deposition might affect shrub and herb biomass in mixed conifer forests in Teakettle Experimental Forest (located between SEKI and YOSE) and YOSE. They estimated the prescribed fire intervals needed to counteract high fuel loads. Increased understory (especially grass) biomass enhances fuel connectivity and fosters larger and more severe fires. Under a model scenario that specified higher interannual variability in precipitation and increased N deposition, model results suggested that implementing fire treatments at an interval approximately equivalent to the historical

range (15–30 years) would likely be needed to maintain understory vegetation fuel loads at levels comparable to the control.

Based on 28 streams draining California mixed conifer forests studied by [Fenn and Poth \(1999\)](#), [Fenn et al. \(2015\)](#) estimated that peak  $\text{NO}_3^-$  concentrations in runoff were usually less than  $14.3 \mu\text{eq/L}$ ; therefore, this level of  $\text{NO}_3^-$  leaching was identified as the likely critical threshold value to identify watersheds that exhibit signs of N saturation. [Fenn et al. \(2015\)](#) specified the empirical CL for protecting against  $\text{NO}_3^-$  leaching in California mixed conifer forests equal to the N deposition level at which this identified critical surface water  $\text{NO}_3^-$  concentration is exceeded ([Fenn et al., 2015](#); [Fenn et al., 2008](#)). The CL was derived using linear regression of stream water  $\text{NO}_3^-$  concentrations during the winter high flow period and annual throughfall N deposition at 11 locations in the southern Sierra Nevada and San Bernardino mountains. The calculated CL to protect against  $\text{NO}_3^-$  leaching at the sites (6–71 kg N/ha/yr deposition) was 17 kg N/ha/yr (95% CI 15–19 kg N/ha/yr).

#### 16.6.3.1.2.2 Semiarid Shrublands

[Li et al. \(2006\)](#) used the DayCent model to quantify water, C, and N fluxes for a chaparral ecosystem in SEKI that received about 7.7 kg N/ha/yr of atmospheric N deposition. Simulated  $\text{NO}_3^-$  export and gaseous N emissions (mostly as nitric oxide [NO]) generally agreed with observations. The model projections suggested that increased N deposition would likely increase the flux of N from terrestrial ecosystems as  $\text{NO}_3^-$  in streams and gaseous NO. The authors concluded that the representations within the DayCent model of N mineralization, runoff, and  $\text{NO}_3^-$  export in chaparral or similar semiarid vegetation needed improvement.

[Rao et al. \(2010\)](#) used DayCent to estimate CLs of N deposition in JOTR, with focus on the effects of N input on fire risk in creosote bush (*Larrea tridentata*) and pinyon-juniper vegetation communities. Fire risk was expressed as the probability that annual biomass production would exceed the risk threshold of 1,000 kg/ha of biomass available for burning. Critical load was calculated as the N deposition at the point along the deposition gradient where modeled fire risk began to increase exponentially. Mean estimated CLs across multiple soil types, receiving precipitation of less than 21 cm/year, were 3.2 and 3.9 kg N/ha/yr for creosote bush and pinyon-juniper plant communities, respectively. Critical loads decreased (more nutrient-sensitive) with decreasing soil clay content and increasing precipitation. The wettest areas that had low clay content (6 to 14%) had estimated low CLs, as low as 1.5 kg N/ha/yr ([Rao et al., 2010](#)). These values fall at the lower end of the CL range identified by [Pardo et al. \(2011c\)](#) and [Pardo et al. \(2011a\)](#) for herbaceous vegetation in North American Deserts. Fire risks in the two vegetation types

were highest under moderately high N deposition (9.3 and 8.7 kg N/ha/yr, respectively); above those deposition levels, modeled fire risk was influenced more by precipitation amount than by N supply.

#### 16.6.3.1.2.3 Arid/Semiarid

DayCent modeling results suggested a CL less than 8.2 kg N/ha/yr for low-elevation desert containing invasive Mediterranean grass (*Schismus barbatus*) and less than 5.7 kg N/ha/yr at higher elevation sites containing non-native red brome [*Bromus rubens*; [Rao et al. \(2010\)](#)]. Invasive non-native grass production in JOTR was simulated under varying levels of N input and precipitation. Results suggested changing fire frequency. Simulated fire risk was higher when N deposition was above 3 kg N/ha/yr, but then stabilized at N deposition above 5.7 kg N/ha/yr in pinyon-juniper and at 8.2 kg N/ha/yr in creosote bush scrub plant communities ([Rao et al., 2010](#)). Model results of this study also suggested that fire risk is controlled more by precipitation than by grass productivity ([Allen and Geiser, 2011](#)).

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### 16.6.3.2 Aquatic

This section highlights recent monitoring, dose-response, and critical load studies of N and S deposition to aquatic systems in SEKI, JOTR, and similar southern and central California ecosystems.

#### 16.6.3.2.1 Acidification

In the Sierra Nevada, both S and N deposition can contribute mobile acid anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) to watershed soil solution, streams, and lakes. Many aquatic and terrestrial ecosystems in the Sierra Nevada are generally sensitive to acidification. Lakes in these mountains are highly sensitive to impacts from acidic deposition because of the granitic bedrock, thin acidic soils, large amounts of precipitation, coniferous trees, and dilute surface waters ([Melack and Stoddard, 1991](#); [Melack et al., 1985](#); [McColl, 1981](#)). Because the levels of acidic deposition at the higher elevations have been relatively low, however, acidification effects to date have been minimal.

During the fall of 1985, about one-third of the lakes sampled by the Western Lake Survey (WLS) in and near SEKI had acid neutralizing capacity (ANC) < 50  $\mu\text{eq/L}$ , and two of the lakes in the park had ANC < 20  $\mu\text{eq/L}$  ([Landers et al., 1987](#)). The possibility of recovery from lake acidification during the period 1985–1999 was evaluated by another

chemical survey conducted by the U.S. Geological Survey (USGS) during the fall of 1999 (Clow and Sueker, 2000). Clow et al. (2003) reported that the resampled lakes were generally low in ionic strength and had pH between about 6.0 and 7.0; the median ANC was 59  $\mu\text{eq/L}$  in SEKI and 32  $\mu\text{eq/L}$  in YOSE located to the north. The observed lake chemistry further confirmed the high sensitivity to acidification.

Key acidification characterization and monitoring studies conducted in the Sierra Nevada are listed in Table 16-32. None of these studies are recent (post-2008) other than the study of Clow et al. (2010) in YOSE. The current condition of these waters is probably similar to what was found during previous decades with no additional recovery.

The weight of evidence suggests that many high-elevation lakes in SEKI have in the past received N deposition high enough to cause some chronic  $\text{NO}_3^-$  leaching. This can contribute to both acidification and eutrophication. Widespread chronic lake or stream acidification has not occurred to any degree, although Sullivan (2000) concluded that some episodic acidification has likely occurred. Acid anion concentrations (mainly  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) in most high-elevation lakes were low during summer and fall, but higher during spring when there are commonly pulses of high  $\text{NO}_3^-$  concentrations in surface waters during snowmelt (Melack et al., 1989), which is seldom sampled due to logistical and safety constraints. Acid-base chemistry is not expected to have changed appreciably in recent years.

**Table 16-32 Example surface water acidification studies in Sequoia and Kings Canyons National Parks and other Sequoia and Kings Canyons National Parks—relevant areas in the southern/central California case study region.**

Study	Location	Time Period	Focus
<a href="#">Clow et al. (2003)</a> <a href="#">Clow and Sueker (2000)</a>	National parks in western U.S., including SEKI	1999	Resurvey of WLS lakes
<a href="#">Clow et al. (2003)</a>	Sierra Nevada region	1985 and 1999	Decrease in ANC in lakes in SEKI partly due to climatic differences at time of sampling
<a href="#">Clow et al. (2010)</a>	YOSE	2003	Multiple linear regression modeling to predict $\text{NO}_3^-$ concentrations and ANC in lakes across the park

ANC = acid neutralizing capacity;  $\text{NO}_3^-$  = nitrate; SEKI = Sequoia and Kings Canyons National Parks; WLS = Western Lake Survey; YOSE = Yosemite National Park.

The hydrology of alpine and subalpine ecosystems in the Sierra Nevada is controlled by snowmelt because more than 90% of the annual precipitation in this region falls as snow. The relatively small loads of acidic deposition can contribute to moderately high concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in lakes and streams during the early phase of snowmelt ([Stoddard, 1995](#)). Potential biological effects of acidic deposition on surface waters in the Sierra Nevada are most likely caused by acidification attributable to high  $\text{NO}_3^-$  concentrations, which tend to be episodic rather than chronic ([Wigington et al., 1990](#)).

Climatic fluctuations that control the amount and timing of precipitation, melting of the snowpack, growth of plants, depth to groundwater, and concentration by evaporation of constituents in solution all influence soil and surface water chemistry. These factors regulate interactions between air pollutants and the aquatic and terrestrial biological receptors. Because conditions vary over time, many years of data might be required to establish the existence of trends in episodic surface water chemistry ([Sullivan, 2000](#)).

Effects of acidification on vertebrate animals in the Sierra Nevada have not been documented. However, declines and elimination of frogs and toads due to uncertain causes have been documented throughout the western U.S., including in the national parks in California. Possible impacts of air pollution on aquatic amphibians is noteworthy because amphibians are especially sensitive to environmental change or degradation ([Bradford and Gordon, 1992](#); [Blaustein and Wake, 1990](#)).

Arid and semiarid ecosystems in southern California are generally not known to be sensitive to acidification from either S or N deposition. Precipitation to these ecosystems is limited. There are relatively few surface waters, and it appears that they have appreciable acid buffering capacity. However, semiarid chaparral soils under very high N deposition in the San Gabriel Mountains have decreased considerably in pH between the 1970s and 1990s, and so have soils of mixed conifer forests in the San Bernardino Mountains ([Fenn et al., 2011a](#); [Pardo et al., 2011c](#)).

#### **16.6.3.2.1.1 Empirical Studies**

Empirical studies have shed light on dose-response relationships in lakes and streams of southern/central California. Several new studies are addressed here. [Heard et al. \(2014\)](#) investigated CLs to protect against lake acidification in the Sierra Nevada. An experimental study by [Kratz et al. \(1994\)](#) investigated responses of macroinvertebrates. Earlier studies of effects of N deposition in this region (mainly before 2008) addressed aspects of water chemistry and the response of algae to nutrient addition. More recent

publications include the reviews of [Baron et al. \(2011a\)](#), [Pardo et al. \(2011c\)](#), and [Fenn et al. \(2015\)](#).

[Heard et al. \(2014\)](#) investigated the likelihood that paleoreconstructed changes in ANC in lakes of the Sierra Nevada had been caused by atmospheric deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  during the 20th century. The deposition estimates suggested that the CL at Moat Lake was exceeded in about 1920 and the chemical recovery started in about 1970. The initial inferred decline in the ANC of Moat Lake occurred between 1920 and 1930. This time period corresponded with estimated acidic deposition ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) equal to about 74 eq/ha/yr. This was taken by [Heard et al. \(2014\)](#) to be the critical load (CL) to protect this lake against acidification. Diatom-reconstructed ANC values changed from near 100  $\mu\text{eq/L}$  before 1920 to near 60  $\mu\text{eq/L}$  during the 1970s. Recovery of ANC after 1970 was attributed by [Heard et al. \(2014\)](#) to decreased deposition of S. In addition, during the late 20th century, warmer air temperatures may have contributed to higher ANC via increased weathering rates.

#### 16.6.3.2.1.2 Modeling Studies

Some limited work has been conducted on modeling of aquatic critical loads using steady-state approaches for acidity. Data from over 12,500 streams and lakes were used by the Critical Loads of Atmospheric Deposition (CLAD) science committee of the NADP (<http://nadp.slh.wisc.edu/committees/clad/>) to model steady-state CLs for acidity of surface waters based on multiple approaches for estimating base cation weathering. [Shaw et al. \(2014\)](#) used the Steady-State Water Chemistry (SSWC) model to estimate the steady-state CL of acidity for 208 Sierra Nevada lakes. Study lakes were generally dilute (mean specific conductance 8  $\mu\text{S/cm}$ ) and had relatively low ANC (mean 57  $\mu\text{eq/L}$ ). Most were located in Forest Service wilderness areas, some in proximity to Sierra Nevada national parks. Using a critical ANC limit of 10  $\mu\text{eq/L}$  to protect aquatic biota from effects caused by water acidification, the model predicted a CL of 149 eq/ha (14.9  $\text{meq/m}^2$ ) of acidity for Sierra Nevada watersheds situated on granitic bedrock. More than one-third of the study lakes received acidic deposition that was in exceedance of the estimated CL. The median study lake showed a CL exceedance of about 80 eq/ha (8  $\text{meq/m}^2/\text{year}$ ). Based on these CL calculations, [Shaw et al. \(2014\)](#) concluded that high-elevation lakes in the Sierra Nevada have not fully recovered from effects of acidifying deposition despite large decreases in S and N air pollution and reduced S deposition over the last several decades.

### 16.6.3.2.2 Aquatic Nutrient Enrichment

There have been several studies of water chemistry dose-response relationships that pertain to nutrient enrichment in the Sierra Nevada case study area. These have included studies of N retention and release, critical loads, and N saturation. A meta-analysis of lakes from 42 regions of Europe and North America concluded that atmospheric N deposition has caused higher concentrations of  $\text{NO}_3^-$  in lake water and increased phytoplankton biomass ([Bergström and Jansson, 2006](#)). [Bergström et al. \(2005\)](#) found N limitation in lakes that received N deposition below approximately 2.5 kg N/ha/yr, limitation of N and P at N deposition between ~2.5 and 5.0 kg N/ha/yr, and P limitation in lakes that had N deposition higher than about 5.0 kg N/ha/yr. These findings may be relevant to remote lakes in the Sierra Nevada, including those in SEKI.

[Sickman et al. \(2002\)](#) reported yields and retention of dissolved inorganic N (DIN) at 28 high-elevation lakes, including those within SEKI. Net DIN retention was 1.2 kg N/ha/yr, an estimated 55% of annual DIN loading. [Sickman et al. \(2001\)](#) calculated that the annual yield of N from the Emerald Lake watershed varied by a factor of 8 (0.4 to 3.2 kg N/ha/yr), which explained 89 and 74% of the variation in DIN and organic N, respectively. The N content of runoff was higher during years that experienced high runoff and was lower during dry years. Increases in  $\text{NO}_3^-$  concentration were larger during years with deep, late-melting snowpacks. Therefore, it is expected that climate warming, with associated earlier snowmelt, might increase N retention in high-elevation watersheds ([Sickman et al., 2001](#)).

Nutrient enrichment of Sierra Nevada lakes is not solely a function of N inputs. Atmospheric P deposition can also be important. [Sickman et al. \(2003\)](#) proposed that atmospheric P deposition and enhanced cycling of P due to climate change were the most likely sources of the observed increase in P loading to the Sierra Nevada lakes. It is not known why atmospheric deposition of P to these lakes has increased over time. Possibilities include increased use of organo-phosphate pesticides ([Kegley et al., 2000](#)) and wind-blown transport of soils and dust that are high in P from the agricultural San Joaquin Valley to the mountains ([Sickman et al., 2003](#); [Lesack and Melack, 1996](#); [Bergametti et al., 1992](#)).

Based on results of bioassay experiments and application of coarse nutrient limitation indices, [Sickman et al. \(2003\)](#) concluded that phytoplankton growth in Emerald Lake in SEKI during the early 1980s was limited by P supply. During subsequent years, in response to increased atmospheric P input, the nutrient balance shifted into a pattern of colimitation by N + P, and finally N limitation. [Sickman et al. \(2003\)](#) observed that the total P concentration in the lake doubled from 1983 to 1999. Particulate C concentration in the lake in 1999 was four times higher than the average during the period 1983–1998.

Together with the observed increase in total P in lake water, this suggested that eutrophication had occurred during that time ([Sickman et al., 2003](#)). It was proposed that increased P loading to Sierra Nevada lakes decreased  $\text{NO}_3^-$  concentration in lake water and promoted N limitation. The increased P loading may have been due to increased emissions and deposition of P and/or accelerated internal P cycling that might be caused by changes in climatic conditions and the timing of snowmelt and runoff ([Sickman et al., 2003](#); [Johnson, 1998](#); [Dettinger and Cayan, 1995](#)).

[Baron et al. \(2011a\)](#) synthesized CLs of N deposition for protecting against nutrient enrichment of high-elevation lakes. Relationships between  $\text{NO}_3^-$  concentrations and N deposition suggested a CL near 2 kg N/ha/yr to prevent  $\text{NO}_3^-$  leaching to lakes in the Sierra Nevada. [Fenn et al. \(2011a\)](#) also summarized data reflecting the relationship between atmospheric N deposition and stream  $\text{NO}_3^-$  concentration, in this case for chaparral vegetation in the San Dimas Experimental Forest in the San Gabriel Mountains ([Meixner et al., 2006](#); [Riggan et al., 1994](#); [Riggan et al., 1985](#)), Devil Canyon watershed in the western San Bernardino Mountains ([Meixner and Fenn, 2004](#); [Fenn and Poth, 1999](#)), and Chamise Creek in SEKI ([Fenn et al., 2003a](#); [Fenn et al., 2003c](#)). Stream water  $\text{NO}_3^-$  concentrations in streams draining chaparral vegetation were among the highest reported in North America, with concentrations in some streams higher than 200  $\mu\text{eq/L}$  ([Fenn et al., 2011a](#); [Fenn et al., 2003a](#); [Fenn et al., 2003c](#); [Fenn and Poth, 1999](#); [Riggan et al., 1994](#); [Riggan et al., 1985](#)). Evaluation of N saturation in chaparral must also consider the prevalence of fire in this ecosystem type because the stand-replacing fire interval is only about 40 to 60 years ([Minnich and Bahre, 1995](#)). Much of the atmospherically deposited N that has accumulated in the litter and aboveground vegetation over the intervening years is released suddenly to the atmosphere during fire. In contrast, much of the accumulated N in the mineral soil generally remains on-site after a fire ([Fenn et al., 2011a](#)), and fire contributes to increased  $\text{NO}_3^-$  concentrations in stream water ([Riggan et al., 1994](#); [Anderson and Poth, 1989](#)).

The recent work that has been conducted on aquatic ecosystems has focused mostly on the Sierra Nevada region. Analogous nutrient enrichment work has not been conducted in or around JOTR, in part, because there are few surface waters in that region.

#### **16.6.3.2.2.1 Algae**

Changes in nutrient supply can affect aquatic biota at all trophic levels, but algae are perhaps most likely to show eutrophication effects from N deposition. Studies have shown an increase in lake phytoplankton biomass in response to increases in N deposition in the Sierra Nevada region ([Sickman et al., 2003](#)), Wyoming ([Lafrancois et al., 2003b](#)), Sweden ([Bergström et al., 2005](#)), and across Europe ([Bergström and Jansson, 2006](#)).

Increases in algal biomass have been associated with changes in algal assemblages that favor certain species over others. A widespread increase in the relative abundance of *Asterionella formosa* and *Fragilaria crotonensis* occurred in oligotrophic lakes across the western U.S.; these changes have been documented from both lake sediment cores and limnological surveys ([Saros et al., 2003](#); [Wolfe et al., 2001](#); [Interlandi et al., 1999](#); [Goldman, 1988](#)). In Lake Tahoe to the north of YOSE, there has been an increase since about 1950 in the ratio of araphidinate pennate diatoms to centric diatoms. This was largely due to increased abundance of *Fragilaria crotonensis*. This change in diatom relative abundance was associated with higher N loading to the lake ([Goldman, 1988](#)). [Jassby et al. \(1994\)](#) showed that atmospheric deposition supplies most of the N to Lake Tahoe.

Because high-elevation lakes in the Sierra Nevada tend to be highly oligotrophic, small changes in nutrient supply can affect algal productivity ([Sickman et al., 2003](#)). Chamise Creek in SEKI was reported to have high NO<sub>3</sub><sup>-</sup> leaching in response to throughfall N deposition near 10 kg N/ha/yr, suggesting N saturation ([Fenn et al., 2003a](#); [Fenn et al., 2003c](#)). The U.S. Forest Service has suggested a policy threshold of 2 µeq/L for stream NO<sub>3</sub><sup>-</sup> concentration in N limited ecosystems in the western U.S. This load has been suggested as a tipping point to trigger management concern for possible over-enrichment of aquatic ecosystems with N ([Fenn et al., 2011b](#)).

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#### 16.6.4 Highlights of Additional Research Literature and Federal Reports since January 2008

Key research literature published since January 2008 is highlighted in [Table 16-33](#).

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**Table 16-33 Key recent research literature focused on the case study region.**

Publication	Focus
<a href="#">Allen and Geiser (2011)</a>	N addition experiment in JOTR
<a href="#">Allen et al. (2009)</a>	Soil N along depositional gradient in JOTR
<a href="#">Baron et al. (2011a)</a>	Critical load and dose-response review
<a href="#">Bowman et al. (2011)</a>	Critical loads for high-elevation vegetation
<a href="#">Bytnerowicz et al. (2015)</a>	Empirical N critical loads in San Bernardino Mts.
<a href="#">Clow et al. (2010)</a>	Lake acid-base chemistry characterization in YOSE

**Table 16-33 (Continued): Key recent research literature focused on the case study region.**

<b>Publication</b>	<b>Focus</b>
<a href="#">Clark et al. (2013)</a>	Loss of herbaceous plant species in response to N deposition
<a href="#">Cox et al. (2014)</a>	Conversion from coastal sage scrub to grassland
<a href="#">Ellis et al. (2013)</a>	Empirical critical loads
<a href="#">Esque et al. (2010)</a>	N dynamics after fire in Mojave Desert shrubs
<a href="#">Fenn et al. (2008)</a>	Effects of N on epiphytic lichens and stream nitrate leaching
<a href="#">Fenn et al. (2010)</a>	Empirical critical loads and exceedances
<a href="#">Fenn et al. (2011a)</a>	Critical loads review
<a href="#">Fenn et al. (2015)</a>	Critical loads review
<a href="#">Geiser et al. (2010)</a>	Effects of N on lichens
<a href="#">Grulke et al. (2008)</a>	Forest susceptibility to wildfire in San Bernardino Mts.
<a href="#">Heard et al. (2014)</a>	Critical loads for lakes
<a href="#">Hurteau and North (2009)</a>	Effects of N on a sensitive herbaceous plant species
<a href="#">Johnson et al. (2011)</a>	Soil acid-base chemistry in mixed conifer watersheds
<a href="#">Jovan (2008)</a>	Response of lichens to N
<a href="#">Kimball et al. (2014)</a>	Effects of water and N on CSS following fire
<a href="#">McCalley and Sparks (2009)</a>	Soil temperature effects on N loss in Mojave Desert
<a href="#">Pardo et al. (2011c)</a>	Critical load and exceedance for nutrient N enrichment
<a href="#">Pasquini and Vourlitis (2010)</a>	Net primary production in chaparral
<a href="#">Rao et al. (2009)</a>	Effects of N deposition on mineralization
<a href="#">Rao et al. (2010)</a>	N and fire effects on semiarid plant communities
<a href="#">Rao et al. (2011)</a>	Critical loads for desert vegetation
<a href="#">Shaw et al. (2014)</a>	Critical loads for lakes in Sierra Nevada
<a href="#">Stark et al. (2011)</a>	Effects of N deposition and climate on Mojave Desert vegetation
<a href="#">Talluto and Suding (2008)</a>	Conversion of CSS to grassland
<a href="#">Vamstad and Rotenberry (2010)</a>	Changes in plant species composition after fire
<a href="#">Vourlitis (2012)</a>	Response of semiarid vegetation to N and climate

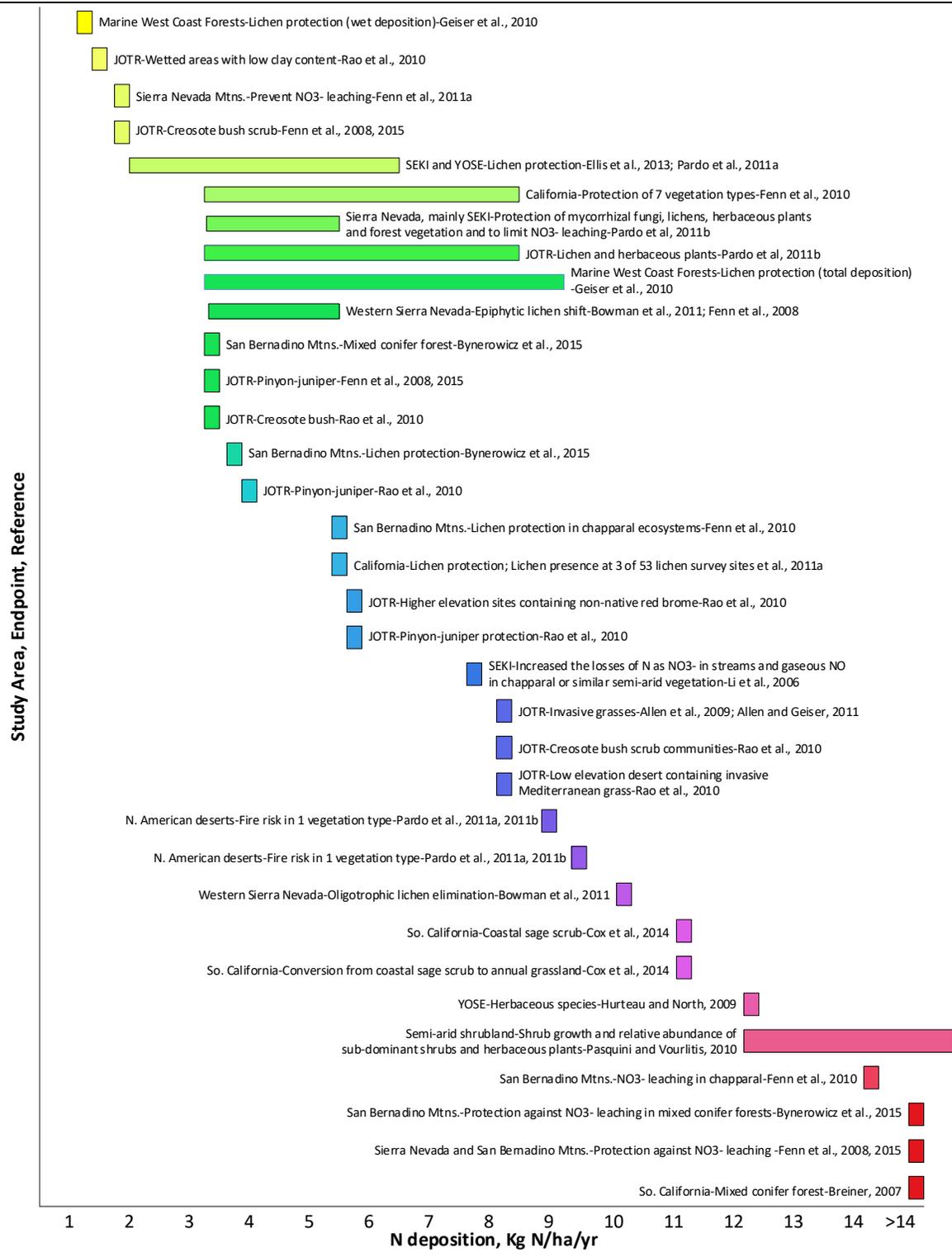
**Table 16-33 (Continued): Key recent research literature focused on the case study region.**

Publication	Focus
<a href="#">Vourlitis and Fernandez (2012)</a>	N response to N input in semiarid shrublands
<a href="#">Vourlitis and Pasquini (2008)</a>	C and N dynamics in pre- and post-fire chaparral
<a href="#">Vourlitis and Pasquini (2009)</a>	Dry season addition of N to CSS and chaparral

C = carbon; CSS = coastal sage scrub; JOTR = Joshua Tree National Park; Mts = mountains; N = nitrogen; YOSE = Yosemite National Park.

### 16.6.5 Summary

This case study focuses on the ecosystems found in two national parks in southern/central California, SEKI, and JOTR. SEKI largely consists of forested and mountainous terrain in and near the Sierra Nevada Mountains. JOTR is covered largely by desert and semiarid land. Both are generally downwind of air pollution (mainly N) sources. The majority of the information provided in this case study is applicable to ecosystems found within SEKI. Limited research conducted in JOTR was found in the peer-reviewed literature. A summary of studies relevant to evaluating CLs is shown by [Figure 16-54](#).



ha = hectare; JOTR = Joshua Tree National Park; kg = kilogram; Mtns. = mountains; N = nitrogen; N. = north; NO = nitric oxide; NO<sub>3</sub><sup>-</sup> = nitrate; SEKI = Sequoia and Kings Canyons National Parks; So = southern; YOSE = Yosemite National Park; yr = year.

**Figure 16-54 Continuum of critical loads in southern/central California case study area and relevant surrounding region.**

The Sierra Nevada Mountains, in which SEKI is located, contain many acid-sensitive aquatic resources. Limited monitoring studies indicated that the current condition of these waters is probably similar to that found during previous decades with no additional recovery. Aquatic acidification effects to date on SEKI's condition have been minimal at higher elevations due to low acidic deposition, and widespread lake or stream acidification has not occurred to any degree, although some episodic acidification has likely occurred. There are expectations for N retention in high-elevation watersheds as snowmelt changes temporally due to climate warming. Small changes in nutrient supply to high-elevation, oligotrophic lakes in the Sierra Nevada can affect algal productivity and increase abundance of *Asterionella formosa* and *Fragilaria crotonensis* ([Saros et al., 2003](#)). Amphibian decline and the possible association with air pollution is noteworthy. However, one of the most pronounced effects of N deposition in the Sierra Nevada has been shown to be an alteration of the lichen community which has CLs ranging from 3.1 to 5.2 kg N/ha/yr ([Bowman et al., 2011](#); [Fenn et al., 2008](#)).

JOTR's arid and semiarid ecosystems are not known to be sensitive to acidification because there is limited precipitation, few surface waters, and high acid buffering capacity. N deposition may increase productivity of invasive grasses after fire, and deposition and climate change may promote an altered fire cycle that does not allow sufficient time for Joshua tree woodlands to re-establish between fires. It has been suggested that N deposition may have already exceeded JOTR's critical load of 8.4 kg N/ha/yr for terrestrial plant communities ([Pardo et al., 2011c](#)).

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