

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

Disclaimer

This document has been reviewed in accordance with the U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTEGRATED SYNTHESIS

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

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, 1990](#)).¹ 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, 2016a](#)). 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, 2016c](#)), oxides of sulfur ([U.S. EPA, 2016b](#)), 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_y) compounds, including

¹ 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, 2015](#)).

NO, NO₂, and all other oxidized N containing compounds formed from NO and NO₂.¹ Oxides of sulfur² are defined here to include sulfur monoxide (SO), sulfur dioxide (SO₂), sulfur trioxide (SO₃), disulfur monoxide (S₂O), and sulfate (SO₄²⁻). However, SO, SO₃, and S₂O are present at much lower ambient levels than SO₂ and SO₄²⁻ and are therefore not discussed further. Particulate matter is composed of some or all of the following components: nitrate (NO₃⁻), SO₄²⁻, ammonium (NH₄⁺), 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, 2008](#))], 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, 2011](#)) 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 (NO₂) and sulfur dioxide (SO₂) secondary standards to address direct effects of gaseous NO₂ and SO₂ on vegetation. Thus, taken together, the Administrator decided to retain and not revise the current NO₂ and SO₂ secondary standards: an NO₂ standard set at a level of 0.053 ppm, as an annual arithmetic average, and an SO₂ 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_{2.5} concentration of 15 µg/m³, with the 24-hour average PM_{2.5} and PM₁₀ set at concentrations of 35 µg/m³ and 150 µg/m³, respectively.

¹ This ISA reserves the abbreviation NO_x strictly as the sum of NO and NO₂—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_y as the total oxidized nitrogen in both gaseous and particulate forms. The major gaseous and particulate constituents of NO_y include nitric oxide (NO), nitrogen dioxide (NO₂), nitric acid (HNO₃), peroxyacetyl nitrate (PAN), nitrous acid (HONO), organic nitrates, and particulate nitrate (NO₃). This ISA uses the definitions adopted by the atmospheric sciences community.

² 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, 2017a](#))].

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 (NO_Y), which include NO, NO_2 , HNO_3 , PAN, HONO, organic nitrates, and NO_3^- ;
- the major gaseous and particulate constituents of SO_X , which include SO_2 and SO_4^{2-} ; and
- PM composed of some or all of the following components: particulate NO_3^- , particulate SO_4^{2-} , ammonium (NH_4^+), metals, minerals (dust), and organic and elemental carbon (C).

The assessment activities include:

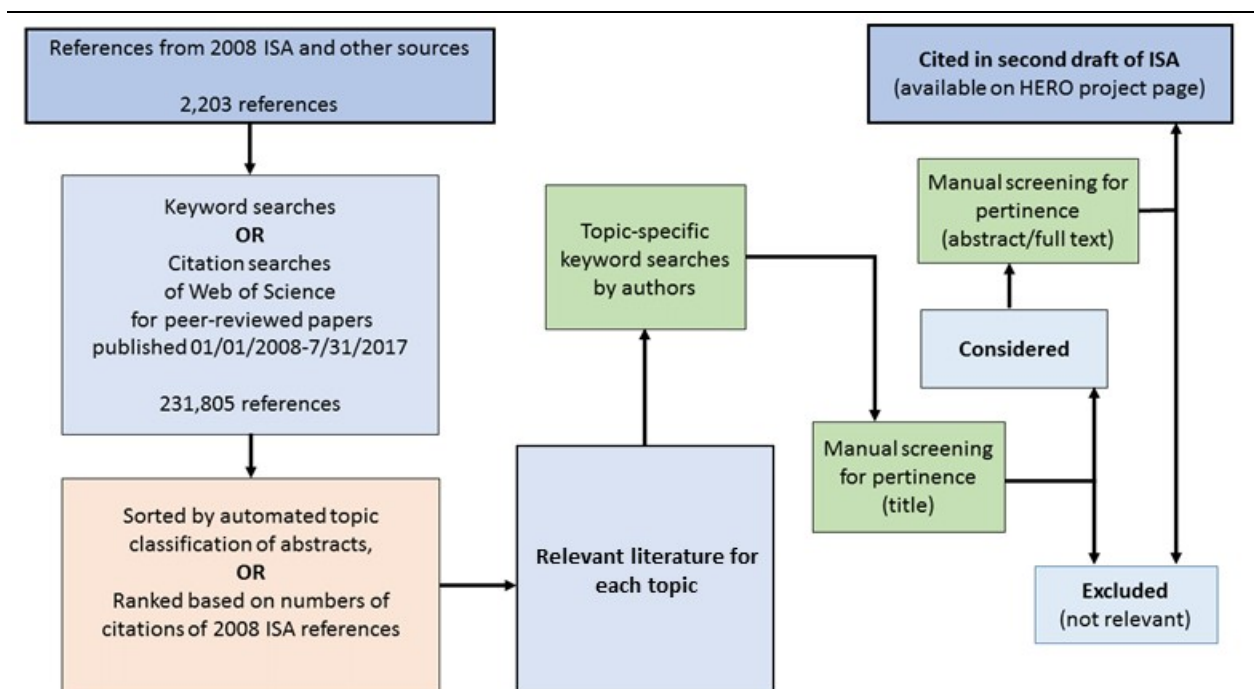
- Identifying policy-relevant literature.
- Evaluating strength, limitations, and consistency of findings.
- Integrating findings across scientific disciplines and across related ecological outcomes.
- Considering important uncertainties identified in the interpretation of the scientific evidence.
- 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, 2017a](#)). 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.

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, 2015](#))]. 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_y, SO_x, 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, 2015](#)), 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) 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, 2015](#)) 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_y, SO_x, 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, 2015](#))], 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

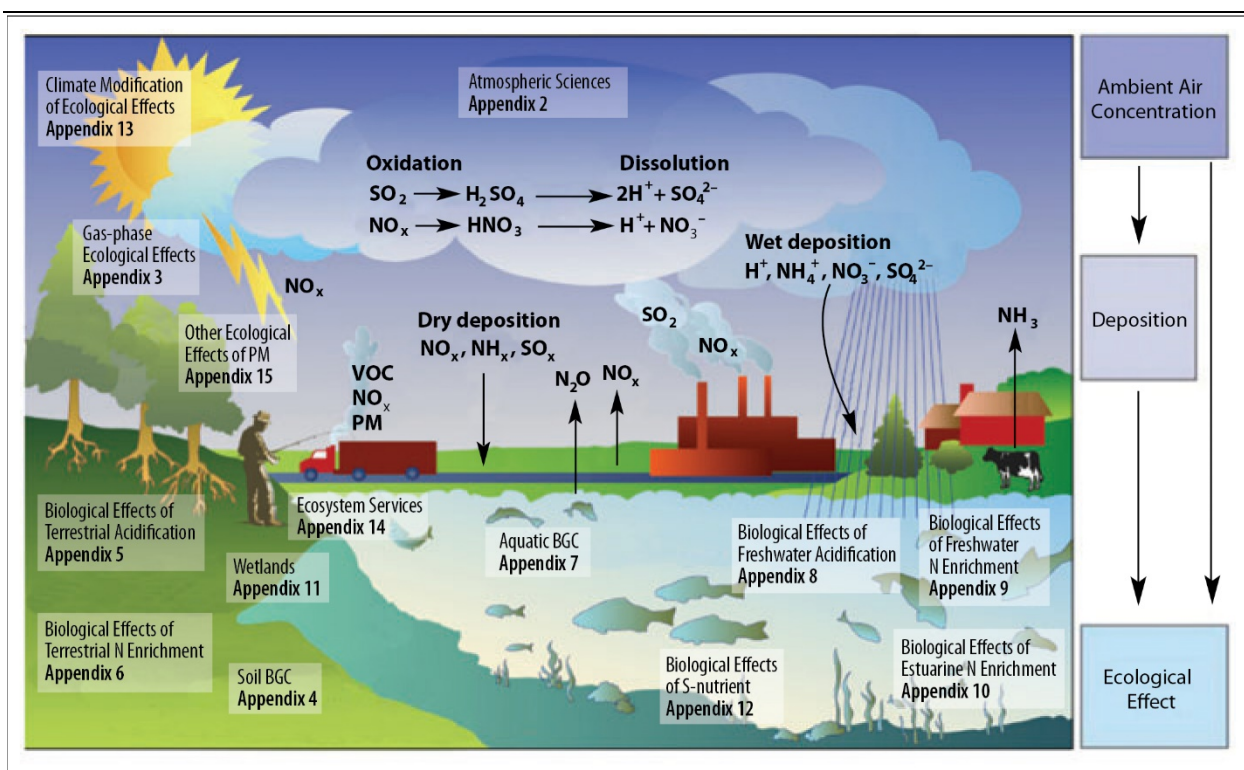
APPENDIX 7 This ISA includes the Preface (legislative requirements and history of the secondary oxides of nitrogen, oxides of sulfur, and particulate matter NAAQS), an Executive Summary, an [Integrated Synthesis](#), and 16 appendices. The general process for developing an ISA is described in a companion document, *Preamble to the Integrated Science Assessments* ([U.S. EPA, 2015](#)). 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_y, SO_x, and PM. Appendix 3 describes direct effects of NO_y and SO_x 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.

IS.2 Connections, Concepts, and Changes

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_x, SO_x, 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](#).



Ca²⁺ = calcium ion; GHG = greenhouse gas; H⁺ = hydrogen ion; H₂SO₄ = sulfuric acid; HNO₃ = nitric acid; Mg²⁺ = magnesium ion; N₂O = nitrous oxide; N = nitrogen; NH₃ = ammonia; NH₄⁺ = ammonium; NH_x = NH₃ + NH₄⁺ + reduced organic nitrogen compounds; NO = nitric oxide; NO₂ = nitrogen dioxide; NO₃⁻ = nitrate; NO_x = NO + NO₂; PAN = peroxyacetyl nitrate; PM = particulate matter; SO₂ = sulfur dioxide; SO₄²⁻ = sulfate; SO_x = SO₂ + SO₄²⁻; VOC = volatile organic compounds.

The sum of reactive oxidized nitrogen species is referred to as NO_y (NO_y = NO + NO₂ + HNO₃ + 2N₂O₅ + HONO + NO₃⁻ + N₂O 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 \(2008\)](#).

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](#)).

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, 2007](#)). 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, 2008](#)). 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, 2013](#)). 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, 2013](#), [1998](#)).

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 ([Barnhouse 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, 2013](#)). 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 ([Barnhouse 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, 2013](#)). 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 ([Petratis 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.

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.

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 ₃
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO ₄ , NO ₃ , NH ₄	SO ₄ , NO ₃ , NH ₄	SO ₄ , NO ₃ , NH ₄	SO ₄ , NO ₃ , NH ₄	NO ₃ , NH ₄	NO ₃ , NH ₄
8) Critical pollutant load	???	???	???	???	???	???

Al = aluminum; ANC = acid-neutralizing capacity; C = carbon; Ca = calcium; L = liter; µeq = microequivalents; N = nitrogen; NH₄ = ammonium; NO₃ = nitrate; SO₄ = sulfate.

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

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. \(2011\)](#) 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.

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., 2012](#)), 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., 2015](#)) 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.

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 NO_y deposition and increasing 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 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 (NH_3) and 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 (NO_y) or reduced (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 NH_4^+ versus 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).

IS.2.2.6 Aquatic Acidification Index (AAI)

The 2017 IRP ([U.S. EPA, 2017a](#)) 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 (NO_y and SO_x) and noncriteria pollutant (e.g., 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_xSO_x Policy Assessment ([U.S. EPA, 2011](#)), and the equation is described with terms that traditionally define a NAAQS [the indicator,¹ averaging time,² form,³ and level⁴—further described in the 2017 IRP ([U.S. EPA, 2017a](#))].

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, 2017a](#)):

“The AAI, as described in the PA ([U.S. EPA, 2011](#)), 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_x). 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_y and SO_x:

$$AAI = F1 - F2 - F3[NO_y] - F4[SO_x]$$

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_x; and $F3^7$ and $F4^8$ are the

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

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

³ 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.

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

⁵ $F1$ 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 \(2011\)](#), p. 7–37]. The PA described the percentile as an aspect of the form for the standard [[U.S. EPA \(2011\)](#), Section 7.7].

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

⁷ $F3$ is defined as: TNO_y/Q_r , where TNO_y is the transference ratio that converts deposition of NO_y to ambient air concentrations of NO_y [[U.S. EPA \(2011\)](#), p. 7–37].

⁸ $F4$ is defined as: TSO_x/Q_r , where TSO_x is the transference ratio that converts deposition of SO_x to ambient air concentrations of SO_x [[U.S. EPA, 2011](#)], p. 7–37].

transference ratios that convert concentrations of NO_Y and SO_X to related deposition of nitrogen and sulfur [[U.S. EPA \(2011\)](#), Section 7.7].”

Several other key scientific considerations are included in the AAI that were discussed in the 2011 NO_XSO_X Policy Assessment ([U.S. EPA, 2011](#)).

- 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 NO_XSO_X Policy Assessment ([U.S. EPA, 2011](#)) 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.

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 NO_X , 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 NO_X than NH_X emissions, and higher levels of uncertainty are associated with agricultural emissions, which contribute more to NH_X than NO_X emissions.

A better understanding of the relationship between atmospheric concentration and deposition has resulted from advances in understanding bidirectional exchange of NH_3 and 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 NO₂ and SO₂ 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 SO₂, NO₂, NO, peroxyacetyl nitrate (PAN), HNO₃, and injury to vegetation ([Table IS-1](#)), but research that tests plant response to the lower exposure levels that represent current atmospheric NO_y and SO_x concentrations is limited. Therefore, little evidence is available to help determine whether current monitored concentrations of gas-phase NO_y and SO_x are high enough to injure vegetation.

It is clear that the criteria pollutants NO_y, SO_x, and PM, in addition to the noncriteria pollutant NH₃, 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_x/SO_x 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 _x /SO _x ISA	Current ISA
Gas-phase direct phytotoxic effects		
Gas-phase SO ₂ and injury to vegetation Section IS.3 and Appendix 3.6.1	Causal relationship	Causal relationship
Gas-phase NO, NO ₂ , and PAN and injury to vegetation Section IS.3 and Appendix 3.6.2	Causal relationship	Causal relationship
Gas-phase HNO ₃ and injury to vegetation ^a Section IS.3 and Appendix 3.6.3	Causal relationship	Causal relationship
N and acidifying deposition to terrestrial ecosystems		
N and S deposition and alteration of soil biogeochemistry in terrestrial ecosystems ^b Section IS.5.1 and Appendix 4.1	Causal relationship	Causal relationship
N deposition and the alteration of the physiology and growth of terrestrial organisms and the productivity of terrestrial ecosystems ^c Section IS.5.2 and Appendix 6.6.1	Not included	Causal relationship
N deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems ^c Section IS.5.2 and Appendix 6.6.2	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 ^d Section IS.5.3 and Appendix 5.7.1	Not included	Causal relationship
Acidifying N and S deposition and the alteration of species richness, community composition, and biodiversity in terrestrial ecosystems ^d Section IS.5.3 and Appendix 5.7.2	Causal relationship	Causal relationship
N and acidifying deposition to freshwater ecosystems		
N and S deposition and alteration of freshwater biogeochemistry ^e Section IS.6.1 and Appendix 7.1.7	Causal relationship	Causal relationship

Table IS-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO_x/SO_x 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 _x /SO _x 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 ^f Section IS.6.3 and Appendix 8.6	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 ^g Section IS.6.2 and Appendix 9.6	Causal relationship	Causal relationship
N deposition to estuarine ecosystems		
N deposition and alteration of biogeochemistry in estuarine and near-coastal marine systems Section IS.7.1 and Appendix 7.2.10	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 ^h Section IS.7.2 and Appendix 10.7	Causal relationship	Causal relationship
N deposition to wetland ecosystems		
N deposition and the alteration of biogeochemical cycling in wetlands Section IS.8.1 and Appendix 11.10	Causal relationship	Causal relationship
N deposition and the alteration of growth and productivity, species physiology, species richness, community composition, and biodiversity in wetlands Section IS.8.2 and Appendix 11.10	Causal relationship	Causal relationship
S deposition to wetland and freshwater ecosystems		
S deposition and the alteration of mercury methylation in surface water, sediment, and soils in wetland and freshwater ecosystems ⁱ Section IS.9.1 and Appendix 12.7	Causal relationship	Causal relationship

Table IS-1 (Continued): Causal determinations for relationships between criteria pollutants and ecological effects from the 2008 NO_x/SO_x 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 _x /SO _x 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 Section IS.9.2 and Appendix 12.7	Not included	Causal relationship
	2009 PM ISA	Current Draft ISA
Other ecological effects of PM (course and fine particles, without regard to chemical speciation)		
PM and a variety of effects on individual organisms and ecosystems Section IS.10 and Appendix 15.7	Likely to be a causal relationship	Likely to be a causal relationship

C = carbon; Hg = mercury; HNO₃ = nitric acid; ISA = Integrated Science Assessment; N = nitrogen; NO = nitric oxide; NO₂ = nitrogen dioxide; PAN = peroxyacetyl nitrate; S = sulfur; SO₂ = sulfur dioxide.

^aThe 2008 ISA causality statements for gas-phase HNO₃ was phrased as “changes in vegetation.”

^bThe 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.”

^cThe 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.”

^dThe 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.”

^eThe 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.”

^fThe 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.”

^gThe 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.”

^hThe 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.”

ⁱThe 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												
		Biodiversity												
	Population	Individual	Growth rate											
			Physiological alteration, stress or injury											
	Geochemistry	Soil or sediment chemistry												
		Surface water chemistry												

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, NO₂, HNO₃, SO₂, 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_x and NO_y 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.

IS.3 Emissions and Atmospheric Chemistry

The atmospheric chemistry from emission to deposition discussed in this ISA is for the criteria pollutants NO_Y , SO_X , and PM. In addition to gas-phase indicators like SO_2 and 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). NH_X ($\text{NH}_X = \text{NH}_3 + \text{NH}_4^+$) includes both the PM component NH_4^+ and gas-phase NH_3 . The contribution of 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, NH_3 is discussed in the ISA along with 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 NO_Y , SO_X , and NH_X all contribute to atmospheric wet and dry deposition. The major components of particulate matter in the U.S. are NO_3^- , SO_4^{2-} , 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 NO_3^- , SO_4^{2-} , and NH_4^+ . Of these, SO_4^{2-} and NO_3^- are also components of total oxides of sulfur and nitrogen, respectively. NO_3^- , SO_4^{2-} , and NH_4^+ usually have a strong influence on acid deposition. NO_3^- and 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 NH_3 and 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 NO₂, SO₂, and NH₃ (Appendix 2.6).

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 H₂SO₄, HNO₃, and NH₄⁺, which are formed from precursor emissions of SO₂, NO_x (NO + NO₂), and NH₃ (Appendix 2.2). Gaseous emissions of NH₃ 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 SO₂ emissions are from by electricity-generating units (EGUs), mainly coal-fired power plants. Notably, SO₂ emissions from EGUs have been decreasing. NO_x emissions have a wider distribution of sources, with substantial contributions from highway and off-highway vehicles, lightning, and EGUs. Primary PM_{2.5} and PM₁₀ emissions are dominated by dust and fires, but much of the PM_{2.5} mass in the U.S. is produced by reactions that form secondary PM_{2.5} from gas phase precursor N and S species. Because of these processes, a sharp decrease in SO₂ emissions and smaller, but substantial decreases in NO_x emissions have occurred since the passage of the Clean Air Act Amendments in 1990. Emissions of NO_x in the U.S. declined 61% between 1990 and 2017 ([U.S. EPA, 2020](#)), while nationwide annual average 98th percentile NO₂ concentrations decreased by 53% from 1990 to 2017 ([U.S. EPA, 2016c](#)). Total emissions of SO₂ decreased by 89% from 1990 to 2017 ([U.S. EPA, 2020](#)), resulting in a decrease in SO₂ concentrations of 89% in the eastern U.S. and 45% in the western U.S. (Appendix 2.6.5). National annual NH₃ emissions have fluctuated as a result of changes in both emissions and methods of estimating emissions. However, no clear trend is evident for national NH₃ emissions, with estimates for 1990 and 2017 differing by less than 1% ([U.S. EPA, 2020](#)). National NH₃ monitoring is too recent for evaluating long-term concentration trends, although more limited studies of NH₃ emissions, concentrations and deposition each suggest slight increases may have occurred (Appendix 2.6.4).

Major components of particulate N and S include NH₄⁺, NO₃⁻, and SO₄²⁻, which are primarily derived from gaseous precursors NH₃, NO_x, and SO₂ (Appendix 2.3). Together, NO₃⁻, SO₄²⁻, and NH₄⁺ make up a large fraction of PM_{2.5} 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.

IS.3.2 Measurement and Modeling Techniques

Monitoring networks across the U.S. measure NO_y , SO_x , and 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 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. 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 NO_3^- and 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 NO_2 concentration has limited utility for quantifying NO_y deposition rates in areas with less urban influence. Because NO_y is composed of diverse chemical species with a wide range of deposition velocities and physical properties, concentrations of unmeasured component species of NO_y in general and of all NO_y species in data-sparse regions must be provided by regional models. For NO_2 and 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 $\text{PM}_{2.5}$, SO_4^{2-} , NO_3^- , and NH_4^+ , but are subject to uncertainties in their treatment of turbulence, surface interactions, and in particular, seasonal variability in NO_3^- deposition, mainly because of uncertainties in NH_3 emissions. Consequently, dry deposition rates (and ratios of wet-to-dry deposition) continue to be uncertain.

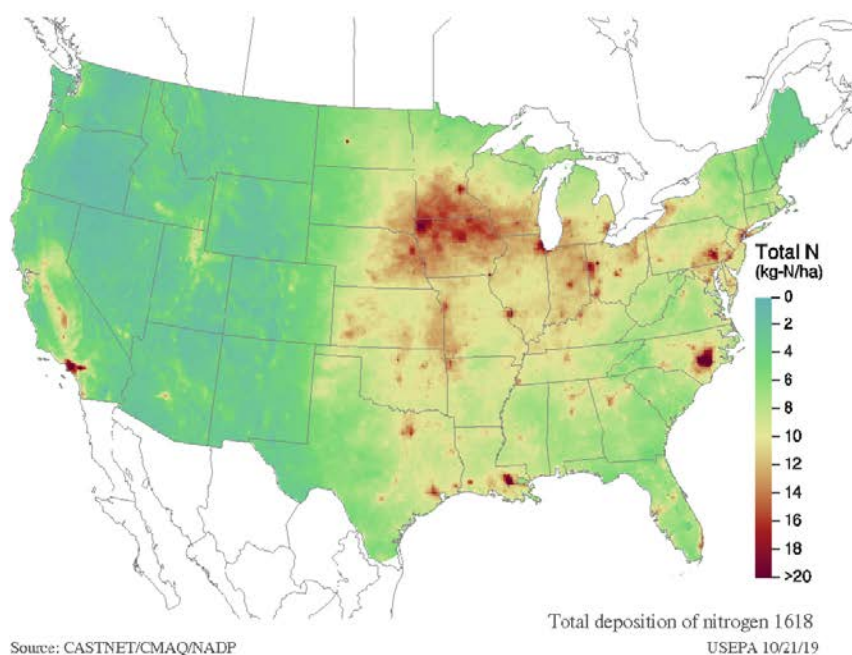
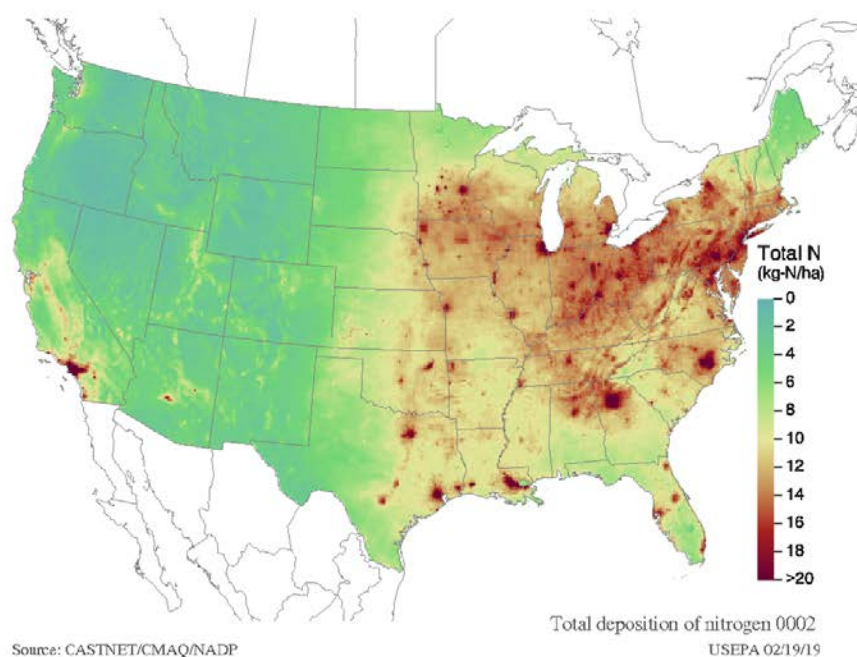
IS.3.3 Spatial and Temporal Variability in Deposition

Overall deposition of total N (oxidized + reduced N) has decreased slightly over the past since 2000 (Appendix 2.6.2). This is because although NO_y deposition has declined considerably in the contiguous U.S., deposition of 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 NO_y and 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, 2014](#)) 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.

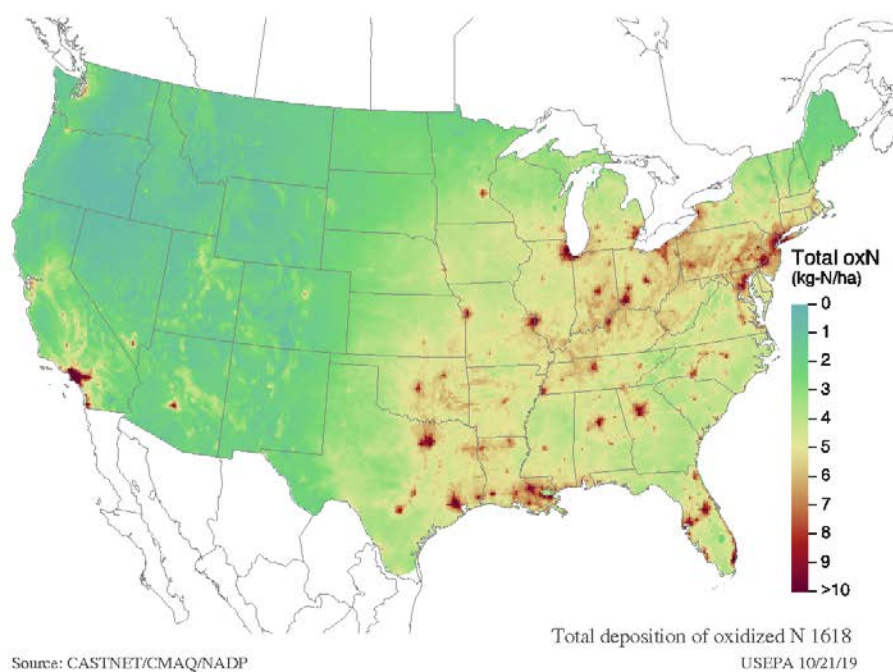
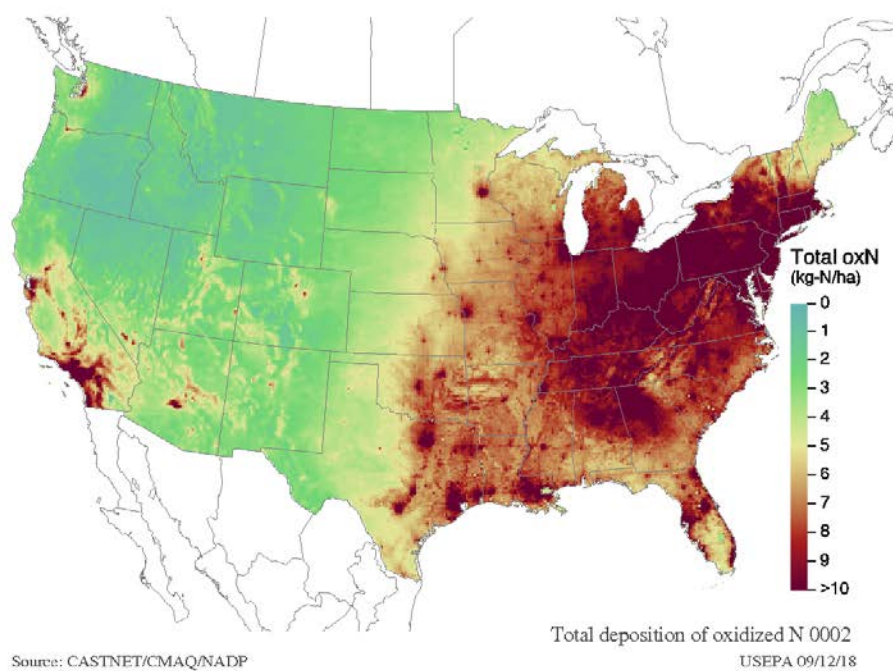
In general, wet deposition of reduced N exceeds that of oxidized N across the contiguous U.S. According to estimates based on CASTNET and NADP data and CMAQ modeling results (Figure 2-16), deposition of N nationwide occurs mainly by dry deposition of HNO_3 and NH_3 (with NH_3 dominant) and wet deposition of NH_4^+ and NO_3^- (with NH_4^+ dominant). Hybrid satellite/modeling and CMAQ results indicate that dry deposition of 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 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.

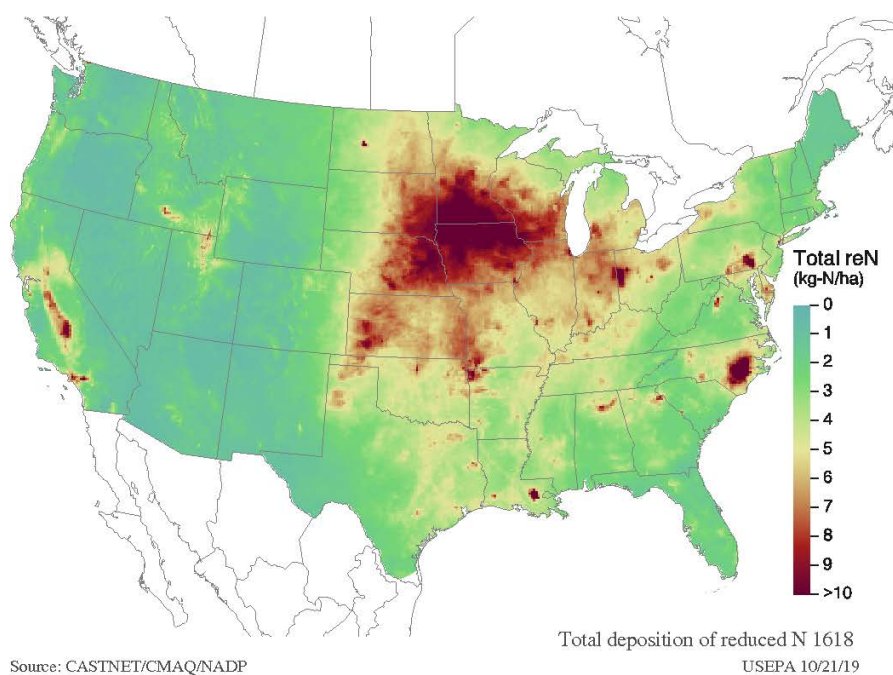
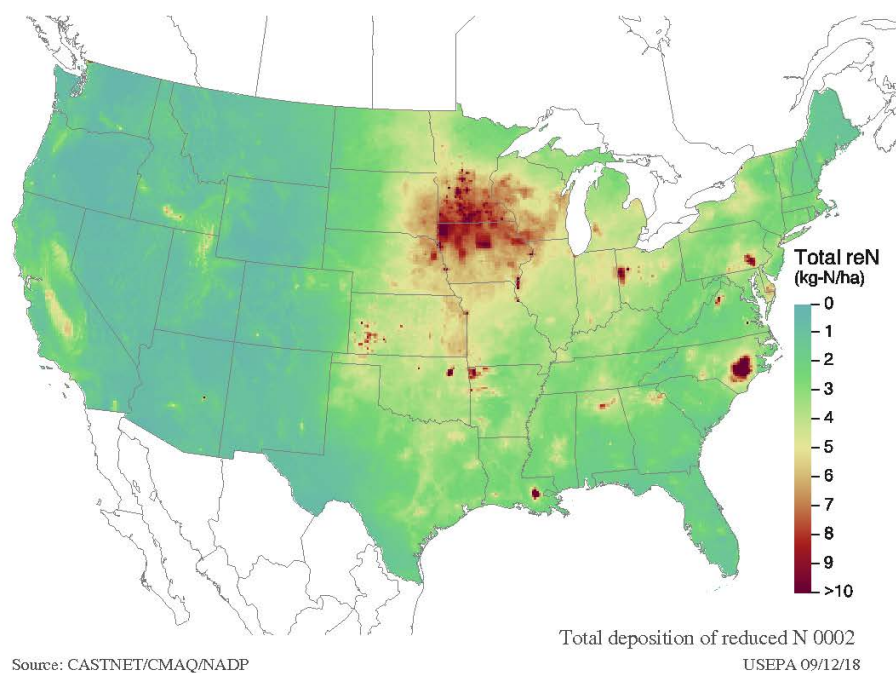
**Figure IS-5 Wet plus dry deposition of total nitrogen over 3-year periods.
Top: 2000–2002; Bottom: 2016–2018.**



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.



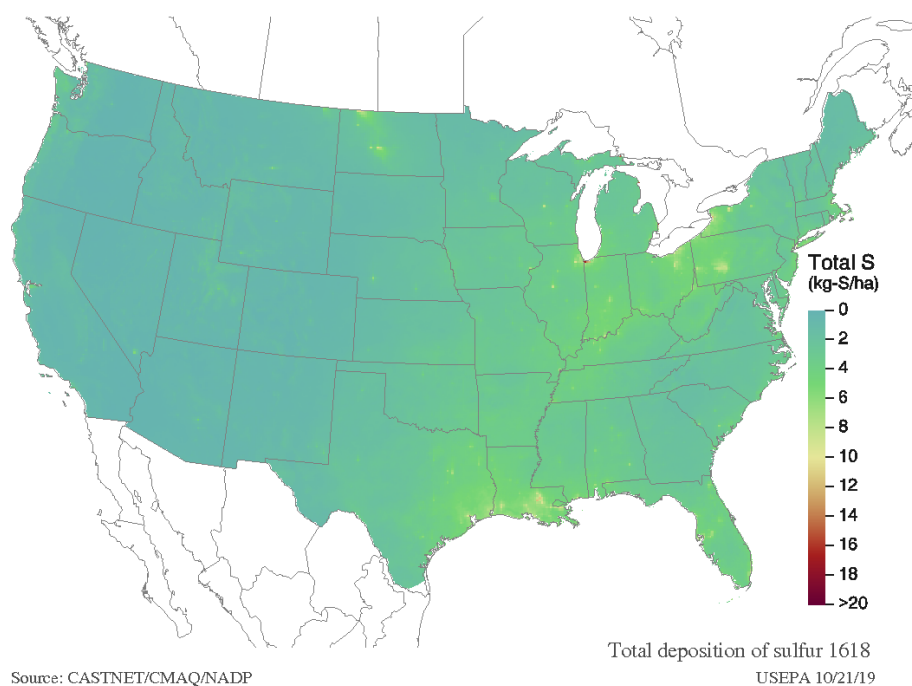
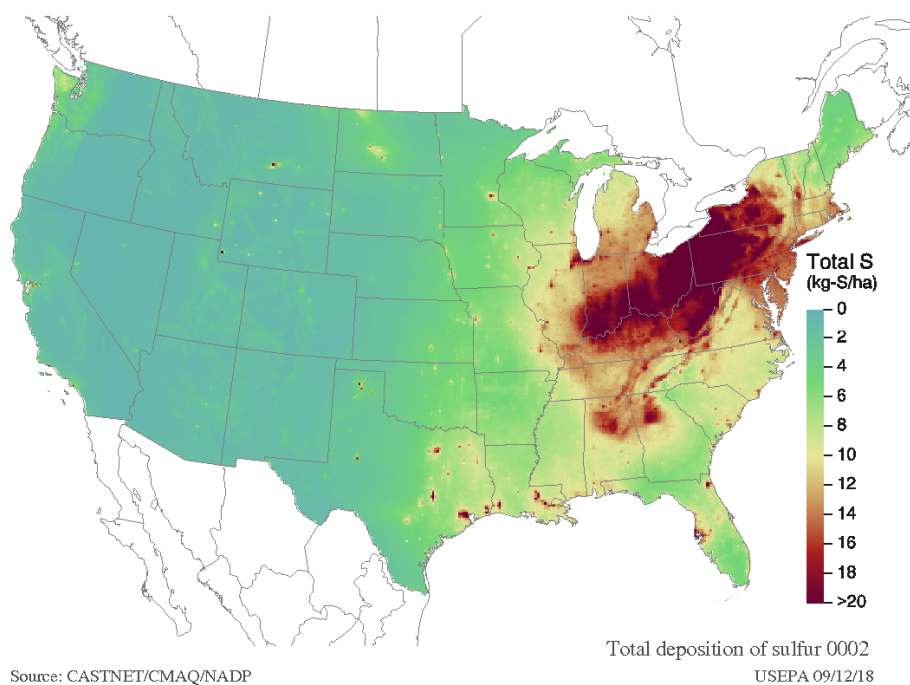
reN = reduced nitrogen.

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_2 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_x 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.

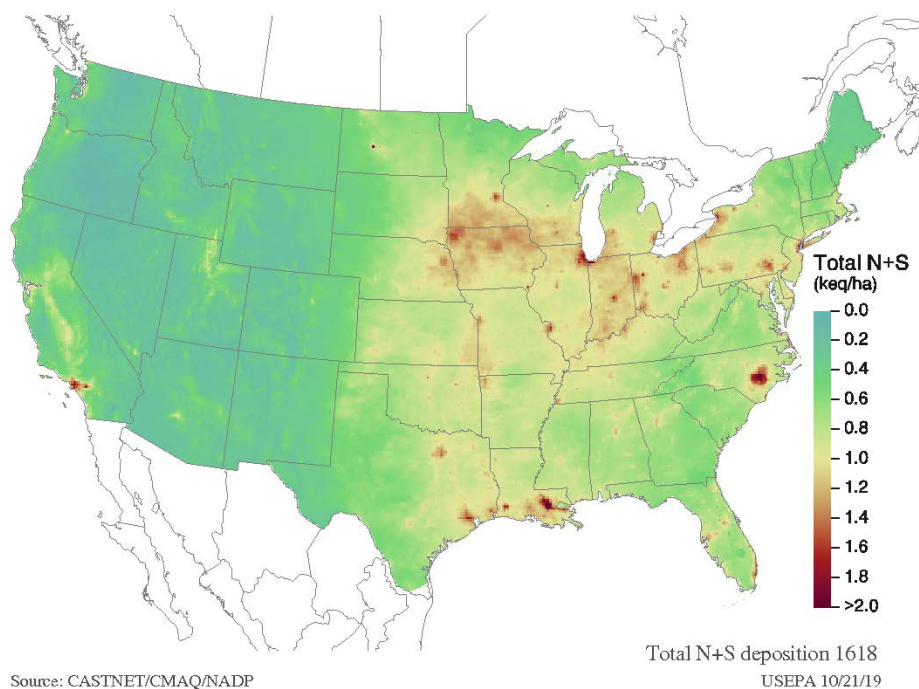
Both N and S deposition contribute to acidification of ecosystems. The pH of rainwater has increased markedly across the U.S. since 1990, coincident with decreases in the wet deposition of nitrate and SO_4^{2-} . However, there are still widespread areas affected by acidifying precipitation, mainly in the eastern U.S. (see Appendix 2.6). Total acidifying deposition (wet + dry N + S, expressed as H^+ equivalents) fluxes for 2016 to 2018 ranged from a few tenths of H^+ keq/ha/yr over much of the western U.S. to over 1.5 H^+ 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](#)).



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⁺ = 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⁺ 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 SO₂, NO₂, NO, PAN, HNO₃, 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_y and SO_x 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_y and SO_x 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_y and SO_x are high enough to injure vegetation.

NH₃ 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 NH₃ 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 NH₃ 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 NH₃ exposure. Besides being potentially phytotoxic to vegetation, NH₃ 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.

IS.4.1 Sulfur Dioxide

In the 2008 ISA, evidence was sufficient to infer a causal relationship between exposure to SO₂ and injury to vegetation. The current secondary standard for SO₂ 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_x 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 SO₂ can have acute negative effects on vegetation but does not change conclusions from the 2008 ISA regarding the causal relationship between SO₂ exposure and vegetation damage or the SO₂ 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 SO₂ and injury to vegetation.**

Increased SO₂ exposure concentrations and longer exposure times are associated with decreases in plant growth and yield. The 1982 PM-SO_x 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 SO₂ 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 SO₂ concentrations since the 1980s and that annual SO₂ 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 SO₂ emissions since the 1980s.

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, NO₂, and PAN and injury to vegetation. It is well known that in sufficient concentrations, NO, NO₂, 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, NO₂, 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, NO₂, and PAN and injury to vegetation.**

IS.4.3 Nitric Acid

In the 2008 ISA, evidence was sufficient to infer a causal relationship between exposure to HNO₃ and changes to vegetation. The 2008 ISA reported experimental exposure to HNO₃ 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. \(2009\)](#) investigated dry deposition of HNO₃ 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 HNO₃ 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 HNO₃ and changes to vegetation.**

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 N₂ 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 SO₂ 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.

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 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.

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 HNO_3 and H_2SO_4 can directly acidify soils; however, deposition of reduced forms of N (e.g., NH_X) can also cause soil acidification by releasing hydrogen ions (H^+) during the microbial oxidation of NH_4^+ to 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).

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
Process			
N saturation	X	X	New empirical evidence suggests revising the N saturation concept; specifically, it is now observed that NO_3^- leaching can occur even if the ecosystem N capacity to retain N has not yet been saturated.

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_3^- 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 Table 4-3.
NO_3^- 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 Table 4-3.
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_4^{2-} 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 Table 4-4.
SO_4^{2-} leaching		X	Atmospheric S deposition generally increases leaching of SO_4^{2-} to surface waters. The amount of deposition that causes the onset of leaching varies across the landscape. New studies on soil SO_4^{2-} leaching are summarized in Table 4-4.
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_4^{2-} and NO_3^-) 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 Table 4-5.

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	<p>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 (Appendix 5 and Appendix 8). Inorganic Al is minimally soluble at pH 6.0, but solubility increases steeply at pH below 5.5.</p> <p>New studies on Al in soils are summarized in Table 4-6.</p>
Nitrification	X	X	<p>Nitrification releases 2 mol hydrogen ion (H⁺) per mol NH₄⁺ converted to NO₃⁻, acidifying soils. As soil inorganic N accumulates, net nitrification rates often increase, and NO₃⁻ can leach from the ecosystem.</p> <p>New N gradient and meta-analysis studies confirm N addition increases nitrification. New studies on nitrification are summarized in Table 4-6.</p>
Denitrification	X		<p>Denitrification is the microbial reduction of NO₃⁻ to NO₂⁻, NO, the greenhouse gas N₂O, and N₂, 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 Table 4-6.</p>
DOC leaching	X	X	<p>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 Table 4-10.</p>
Decomposition	X	X	<p>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.</p> <p>New studies are summarized in Table 4-8.</p>
Indicator			
Soil [N]	X	X	<p>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.</p>
Soil C:N ratio	X	X	<p>Decreasing soil C:N linked to changes in decomposition and increases in nitrification and NO₃⁻ leaching.</p> <p><20–25 causes increased nitrification and elevated risk of NO₃⁻ leaching in the U.S. and <25–30 for increased NO₃⁻ leaching in Europe.</p>

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 Appendix 5).
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 Appendix 5).
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; Al³⁺ = aluminum(III); Bc = base cations; C = carbon; Ca = calcium; DOC = dissolved organic carbon; H⁺ = hydrogen ion; ha = hectare; K = potassium; kg = kilogram; Mg = magnesium; N = nitrogen; N₂ = molecular (atmospheric) nitrogen; N₂O = nitrous oxide; Na = sodium; NE = northeastern; NH₄⁺ = ammonium; NO = nitric oxide; NO₂⁻ = nitrite; NO₃⁻ = nitrate; S = sulfur; SE = southeastern; SO₄²⁻ = 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 NO_y + NH_x + organic N) that occurred over the previous century was largely due to three main causes: (1) widespread cultivation of crops that promote conversion of N₂ gas to organic N through biological N fixation, (2) fossil fuel combustion converting atmospheric N₂ and fossil N to NO_x, and (3) the Haber-Bosch process, which converts nonreactive N₂ 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 NO₃⁻ 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 NH_4^+ to 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 NO_3^- created by nitrification may be leached, biologically immobilized, or denitrified. Denitrification is the microbial reduction of NO_3^- to NO_2^- , NO, the greenhouse gas N_2O , and 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, NO_3^- addition showed the strongest stimulation of N_2O 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%), N_2O emissions (+134%), and denitrification (+84%).

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 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 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 km² by 1975 before declining; whereas, for NO₃⁻ leaching, the area exceeding the minimum CL peaked at roughly 3.4 million km² around 1995.

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.**

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.

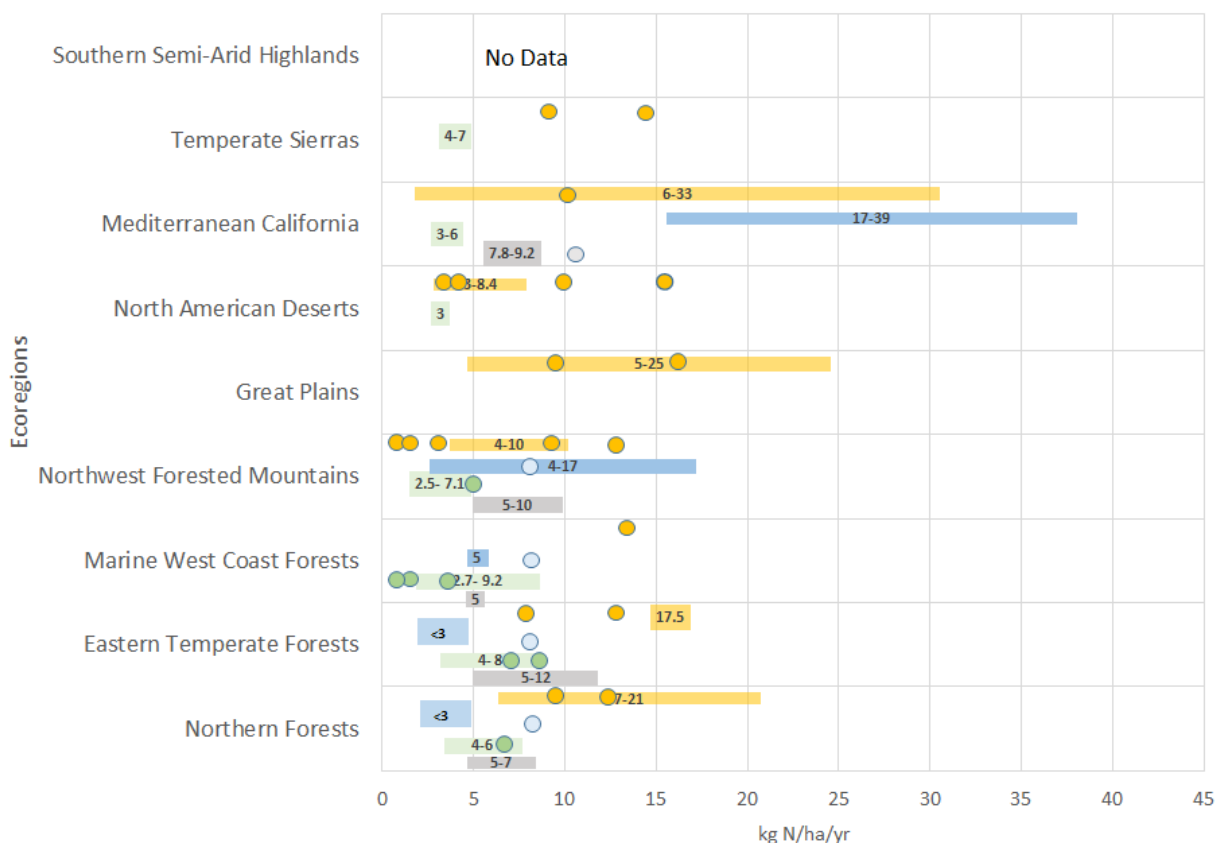
IS.5.2.2 National-Scale Sensitivity and Critical Loads

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 km², respectively, before declining marginally by 2006. The minimum forest tree health CL was exceeded in 2.41 million km² 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).

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^+ 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.

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.

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.**

IS.5.3.3 National-Scale Sensitivity and Critical Loads

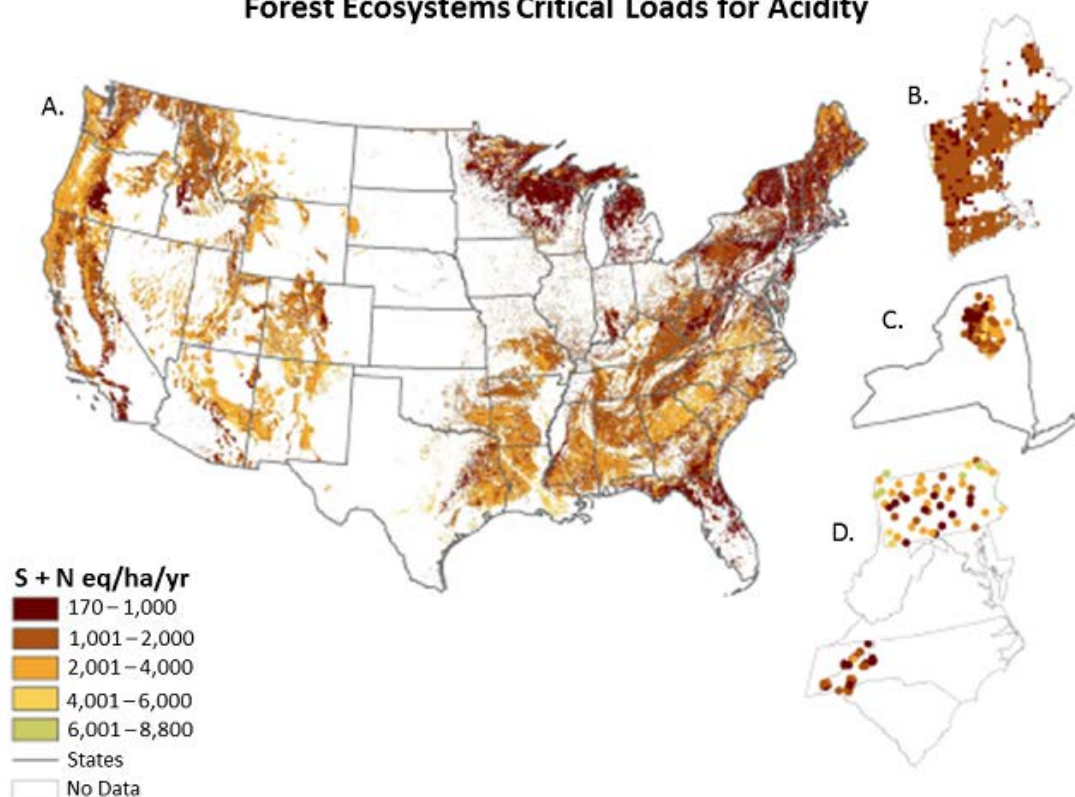
The sensitivity of soils to acidifying deposition is discussed in detail in Appendix 4. In general, surficial geology is the principal factor governing the sensitivity of terrestrial ecosystems soil to acidification from S and N deposition. Other factors that contribute to the sensitivity of soils to 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⁺ 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).

Forest Ecosystems Critical Loads for Acidity



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

(A) [McNulty et al. \(2007\)](#); CLs are mapped at 1-km² grids (center map). For uncertainty, see [Li and McNulty \(2007\)](#). (B) [Duarte et al. \(2013\)](#); CLs are mapped at 4-km² grids. (C and D) [Phelan et al. \(2014\)](#); CLs are mapped for each sampling site (Pennsylvania). [McDonnell et al. \(2014\)](#); [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.

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, 2016e, 2009b](#)), streams ([U.S. EPA, 2016f](#)), wetlands ([U.S. EPA, 2016g](#)), and coastal waters ([U.S. EPA, 2016d](#)). 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).

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 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 SO_4^{2-} , 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.**

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 NO₃⁻ 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 NO₃⁻ 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 SO₄²⁻ to surface waters (Appendix 4). The 2008 ISA found that S deposition alters soil and drainage water chemistry through sustained leaching of SO₄²⁻, associated changes in soil chemistry, and accumulation of S in the soil through adsorption and biological assimilation. Declines in lake SO₄²⁻ 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 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
Process			
NO ₃ ⁻ leaching into water bodies	X	X	Leaching from terrestrial ecosystems is an important source of NO ₃ ⁻ in freshwater ecosystems. See NO ₃ ⁻ leaching in Table IS-2 .

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
SO ₄ ²⁻ leaching into water bodies		X	Leaching from terrestrial ecosystems is an important source of SO ₄ ²⁻ in freshwater ecosystems. See SO ₄ ²⁻ leaching in Table IS-2 .
Nitrification	X	X	Nitrification is an acidifying process, releasing 2 mol hydrogen ion (H ⁺) per mol NH ₄ ⁺ converted to NO ₃ ⁻ . As the N cycle becomes enriched through cumulative N addition, net nitrification rates often increase, and NO ₃ ⁻ concentrations increase.
Denitrification	X		Denitrification is the microbial process that transforms NO ₃ ⁻ by anaerobically reducing it to NO ₂ ⁻ , NO, N ₂ O, and N ₂ .
DOC leaching into water bodies	X	X	DOC contributes to acidity of freshwater ecosystems. See DOC leaching in Table IS-2 .
Indicator			
Surface water [NO ₃ ⁻]	X	X	Increased N deposition (to surface waters or to terrestrial watershed; see Table IS-2) increases the water NO ₃ ⁻ concentration. High concentrations of NO ₃ ⁻ in lakes and streams, indicative of terrestrial ecosystem N saturation, have been found at a variety of locations throughout the U.S. (U.S. EPA, 2006b ; Stoddard, 1994). Comparison of preindustrial estimates to modern measurements suggested elevated concentrations in water bodies as a result of N deposition (Fenn et al., 2011).
Surface water DIN	X		Increased N deposition increases DIN in most freshwater aquatic environments, largely as NO ₃ ⁻ .
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 ₄ ²⁻]		X	Increased S deposition (to surface waters or to terrestrial watershed, see Table IS-2) increases the water SO ₄ ²⁻ concentration. Comparison of preindustrial estimates to modern measurements suggested elevated concentrations in water bodies are a result of S 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 SO ₄ ²⁻ and NO ₃ ⁻ concentrations. Many base cations (especially Ca ²⁺) are important nutrients for aquatic biota.

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 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 µeq/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 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 µmol/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 µmol/L.

Al = aluminum; ANC = acid-neutralizing capacity; Ca = calcium; CO₂ = carbon dioxide; DIN = dissolved inorganic nitrogen; DOC = dissolved organic carbon; H⁺ = hydrogen ion; ha = hectare; kg = kilogram; L = liter; µeq = microequivalents; µmol = micromole; N = nitrogen; N₂ = molecular (atmospheric) nitrogen; N₂O = nitrous oxide; NE = northeast; NH₄⁺ = ammonium; NO = nitric oxide; NO₂ = nitrogen oxide; NO₃⁻ = nitrate; P = phosphorus; S = sulfur; SO₄²⁻ = 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. \(2001\)](#) characterized chronically acidic lakes and streams as having ANC of <0 µeq/L throughout the year, while episodic acidification occurs when ANC falls below 0 µeq/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, SO₄²⁻ concentration, NO₃⁻ 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, 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, 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, 2008](#); [Driscoll et al., 2001](#)). 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, 2008](#)), 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 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 SO_4^{2-} in surface waters before the period of peak S emissions in the early 1970s. After the peak, 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 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 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 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 \(2008\); 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 NO_3^- in surface waters. The concentration of 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).

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.

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](#).

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.**

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_3^- 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.

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 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 NO_3^- concentrations increase in response to increasing N deposition; [Baron et al. \(2011\)](#)]. 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 NO_3^- concentrations occur was estimated by [Pardo et al. \(2011b\)](#). 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 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.

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.

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⁺ 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

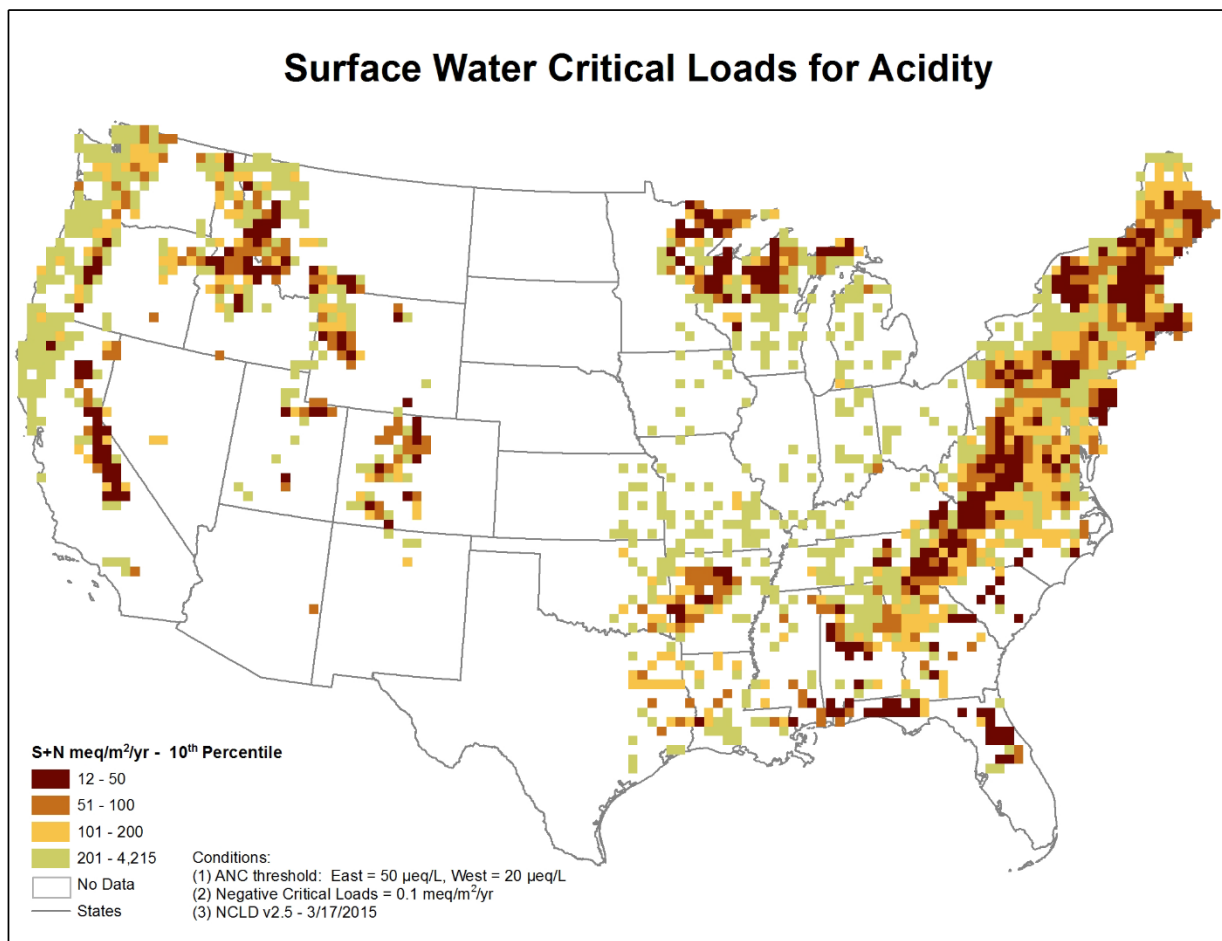
The effects of low pH and ANC and of high inorganic Al concentrations have been well characterized in fish for many decades (Appendix 8.3.6). The 2008 ISA reported that acidification impairs gill function and can cause respiratory and circulatory failure in fish. Sensitivity to pH and inorganic Al varies 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. \(1990\)](#) 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.

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-km² 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., 2012](#)). Future decreases in SO_4^{2-} deposition are suggested to be more effective in that region in increasing Adirondack lake water ANC than equivalent decreases in 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.

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](#)).

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 NO_3^- reduction to 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 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 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.**

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 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 NH_3 oxidation was accomplished only by Proteobacteria in marine environments. New research has discovered that some archaea can also oxidize 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 O_2 in the water. Decreasing DO can create hypoxic (<2 mg/L of dissolved 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 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, 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.

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.

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](#).

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).

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 O₂ 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 NH₃⁺/NH₄⁺ 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 NH₄⁺, while diatoms generally thrive in the presence of oxidized forms of N such as NO₃⁻ (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 NH₄⁺ than with NO₃⁻. 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).

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).

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 CO₂, 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).

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).

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 km² [8,776 mi²; [U.S. EPA \(2017b\)](#)]. 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 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 ≥ 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.

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.

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 NO_3^- and NH_4^+ leaching, DON leaching, N mineralization, denitrification rates, and N_2O 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 N_2O 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 N₂O, 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, CO₂ emissions, and CH₄ 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.

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.**

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).

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).

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.

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_x 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 SO₄²⁻ 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 SO₄²⁻ deposition. Recent research supports these relationships between S deposition and ecological endpoints and provides the basis for SO_x deposition levels, water column SO₄²⁻ concentrations, and water column sulfide concentrations protective of plants and animals.

IS.9.1 Biogeochemistry

SO_x 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 SO₄²⁻ concentration, as it is for acidifying effects. The 2008 ISA reported that chemical reduction of SO₄²⁻ was an important indicator of SO_x effects on water chemistry because the process generates ANC. There are no new studies on ANC generation through SO₄²⁻ reduction, although microbial SO₄²⁻ 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 SO₄²⁻ reduction, the products of microbial SO₄²⁻ transformation may be more reliable indicators of S enrichment effects

than surface water 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 SO_4^{2-} concentrations and water or sediment MeHg concentrations (see Appendix 12.3.5). Another product of SO_4^{2-} reduction, sulfide (measured as surface water or sediment pore water 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 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 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.

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.

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 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 SO_4^{2-} toxicity. The product of microbial 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 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).

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 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 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 SO_4^{2-} , because many strains of SRPs possess the recently identified gene pair *hgcAB*, and pair their metabolism of C with both dissimilatory 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 SO_4^{2-} concentrations within U.S. water bodies. Multiple lines of evidence support a relationship between SO_4^{2-} surface water concentrations and MeHg concentration or production in various freshwater systems. Linear relationships between 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 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 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 SO_x deposition stimulates mercury methylation in North American ecosystems. Current research suggests that mercury methylation generally peaks between 10 and 100 mg 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.

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 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 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).

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_x 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 SO₄²⁻ 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_x, Hg, or PM deposition (see Appendix 12.6).

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 Ca^{2+} , Mg^{2+} , and 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 μm) 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).

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.

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 (NO_3^- , 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, SO_4^{2-} , or 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_i 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 \(2008\)](#); 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.

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 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 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.

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 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).

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 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.

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_x, SO_x, 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., 2017](#)). 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., 2017](#)). 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.

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_x, SO_x, 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, 2017a](#)).

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_x, NO_y, and NH_x. 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.

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). SO₂ and NO_x emission uncertainties for electricity-generating units, the major source of SO₂ and an important source of NO_x, are in the 10–15% range because emissions are usually continuously monitored (Appendix 2.2.3). NO_x emission uncertainties for mobile sources, the largest source of NO_x, arise from differences in engine type, size, age, and maintenance, as well as fuel composition and emission control equipment. Overestimation of NO_x emissions from mobile sources was proposed as an explanation for modeled NO_x concentration bias in several studies. However, mixed results have been observed across several studies when modeled concentrations were compared with measurements. Estimates of NO_x 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_x 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_x emissions than others (Appendix 2.2.3).

In contrast, total NH_3 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_3 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_3 emissions (Appendix 2.2.3). Activity rates, including those for mobile source emissions, are also difficult to quantify, contributing to uncertainty in NH_3 emission estimates (Appendix 2.2.3).

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_2 monitoring network, the NCore network for multipollutant concentration monitoring including NO_y , 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_4^{2-} , 5–13% for NO_3^- , and 2–6% for NH_3 in 2016 (Appendix 2.4.5). Additional uncertainty is associated with estimating dry deposition from NTN concentration data. Uncertainties of 30% for SO_2 and 40% for HNO_3 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_4^{2-} and NO_3^- and less than 20% for NH_3 . 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_3 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_2 monitoring from the national SO_2 monitoring network include a precision of 2.0% (Appendix 2.4.4). Data quality objectives for NO_y 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_2 (Appendix 2.4.2) and 10–45% for SO_2 (Appendix 2.4.4) have been reported for cloud-free conditions.

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_x , but partitioning resulted in overpredicting SO_2 and underpredicting SO_4^{2-} . In a recent CMAQ evaluation, SO_2 concentrations were overestimated by 39 to 47%, and SO_4^{2-} 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_3^- 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_3^- , SO_4^{2-} , and ≤ 15 to 60% for NH_3 (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_x (including both bidirectional gas exchange and canopy reactions), bidirectional exchange of NH₃ with biota and soils, and processes determining transference ratios that relate average concentration to deposition (Appendix 2.5).

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.

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](#)).

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. \(2014\)](#)]. 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 (± 5 to ± 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](#)).

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 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 \(2008\)](#) summarized CL research and monitoring needs identified by [U.S. EPA \(2006a\)](#) at the time of the previous (2009) U.S. EPA Risk and Exposure Assessment.

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, 2011](#)). 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 NO_x from lightning processes, and improving the amount of samples of CL estimates at several ecoregions ([U.S. EPA, 2011](#)).

IS.15 References

- Alexander, RB; Smith, RA; Schwarz, GE; Boyer, EW; Nolan, JV; Brakebill, JW. (2008). Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environ Sci Technol* 42: 822-830.
<http://dx.doi.org/10.1021/es0716103>
- Baker, JP; Bernard, DP; Christensen, SW; Sale, MJ; Freda, J; Heltcher, K; Marmorek, D; Rowe, L; Scanlon, P; Suter, G; Warren-Hicks, WJ; Welbourn, PM. (1990). Biological effects of changes in surface water acid-base chemistry. (NAPAP Report 13). Washington, DC: National Acid Precipitation Assessment Program.
<https://ntrl.ntis.gov/NTRL/dashboard/searchResults.xhtml?searchQuery=PB92100494>
- Baldigo, BP; Lawrence, GB; Bode, RW; Simonin, HA; Roy, KM; Smith, AJ. (2009). Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA. *Ecol Indic* 9: 226-239.
<http://dx.doi.org/10.1016/j.ecolind.2008.04.004>
- Balvanera, P; Pfisterer, AB; Buchmann, N; He, JS; Nakashizuka, T; Raffaelli, D; Schmid, B. (2006). Quantifying the evidence for biodiversity effects on ecosystem functioning and services. *Ecol Lett* 9: 1146-1156. <http://dx.doi.org/10.1111/j.1461-0248.2006.00963.x>
- Barnthouse, LW; Munns, RM, Jr; Sorensen, MT. (2008). Population-level ecological risk assessment. Pensacola, FL: Taylor & Francis.
<http://www.crcpress.com/product/isbn/9781420053326>
- Baron, JS; Driscoll, CT; Stoddard, JL; Richer, EE. (2011). Empirical critical loads of atmospheric nitrogen deposition for nutrient enrichment and acidification of sensitive US lakes. *Bioscience* 61: 602-613. <http://dx.doi.org/10.1525/bio.2011.61.8.6>
- Bartell, SM. (2007). Ecosystem effects modeling. In GW SuterII (Ed.), *Ecological risk assessment* (2nd ed., pp. 413-432). Boca Raton, FL: CRC Press.
- Bell, MD; Phelan, J; Blett, TF; Landers, D; Nahlik, AM; Van Houtven, G; Davis, C; Clark, CM; Hewitt, J. (2017). A framework to quantify the strength of ecological links between an environmental stressor and final ecosystem services. *Ecosphere* 8.
<http://dx.doi.org/10.1002/ecs2.1806>
- Bonten, LTC; Reinds, GJ; Groenenberg, JE; de Vries, W; Posch, M; Evans, CD; Belyazid, S; Braun, S; Moldan, F; Sverdrup, HU; Kurz, D. (2015). Dynamic geochemical models to assess deposition impacts and target loads of acidity for soils and surface waters. In W de Vries; JP Hettelingh; M Posch (Eds.), *Critical loads and dynamic risk assessments: Nitrogen, acidity and metals in terrestrial and aquatic ecosystems* (pp. 225-251). Bilthoven, The Netherlands: Springer Netherlands. http://dx.doi.org/10.1007/978-94-017-9508-1_8
- Bowman, WD; Nemergut, DR; McKnight, DM; Miller, MP; Williams, MW. (2014). A slide down a slippery slope - Alpine ecosystem responses to nitrogen deposition. *Plant Ecol Divers* 8: 727-738. <http://dx.doi.org/10.1080/17550874.2014.984786>

- Boyd, J; Banzhaf, S. (2007). What are ecosystem services? The need for standardized environmental accounting units. *Ecol Econ* 63: 616-626.
- Bricker, S; Longstaff, B; Dennison, W; Jones, A; Boicourt, K; Wicks, C; Woerner, J. (2007). Effects of nutrient enrichment in the nation's estuaries: A decade of change: National estuarine eutrophication update. Silver Spring, MD: National Centers for Coastal Ocean Science. <https://repository.library.noaa.gov/view/noaa/17779>
- CAA (Clean Air Act). (1990). Clean Air Act, as amended by Pub. L. No. 101-549, section 108: Air quality criteria and control techniques, 42 USC 7408. <http://www.law.cornell.edu/uscode/text/42/7408>
- Caires, AM; Chandra, S; Hayford, BL; Wittmann, ME. (2013). Four decades of change: Dramatic loss of zoobenthos in an oligotrophic lake exhibiting gradual eutrophication. *Freshw Sci* 32: 692-705. <http://dx.doi.org/10.1899/12-064.1>
- Cardinale, BJ; Duffy, JE; Gonzalez, A; Hooper, DU; Perrings, C; Venail, P; Narwani, A; Mace, GM; Tilman, D; Wardle, DA; Kinzig, AP; Daily, GC; Loreau, M; Grace, JB; Larigauderie, A; Srivastava, DS; Naeem, S. (2012). Biodiversity loss and its impact on humanity [Review]. *Nature* 486: 59-67. <http://dx.doi.org/10.1038/nature11148>
- Cardinale, BJ; Matulich, KL; Hooper, DU; Byrnes, JE; Duffy, E; Gamfeldt, L; Balvanera, P; O'Connor, MI; Gonzalez, A. (2011). The functional role of producer diversity in ecosystems. *Am J Bot* 98: 572-592. <http://dx.doi.org/10.3732/ajb.1000364>
- Charles, DF; Christie, S. (1991). Acidic deposition and aquatic ecosystems: Regional case studies. In DF Charles; S Christie (Eds.). New York, NY: Springer-Verlag. <http://dx.doi.org/10.1007/978-1-4613-9038-1>
- Clark, CM; Bell, MD; Boyd, JW; Compton, JE; Davidson, EA; Davis, C; Fenn, ME; Geiser, L; Jones, L; Blett, TF. (2017). Nitrogen-induced terrestrial eutrophication: Cascading effects and impacts on ecosystem services. *Ecosphere* 8: e01877. <http://dx.doi.org/10.1002/ecs2.1877>
- Clark, CM; Phelan, J; Doraiswamy, P; Buckley, J; Cajka, JC; Dennis, RL; Lynch, J; Nolte, CG; Spero, TL. (2018). Atmospheric deposition and exceedances of critical loads from 1800-2025 for the conterminous United States. *Ecol Appl* 28: 978-1002. <http://dx.doi.org/10.1002/eap.1703>
- Clarke, JF; Edgerton, ES; Martin, BE. (1997). Dry deposition calculations for the clean air status and trends network. *Atmos Environ* 31: 3667-3678. [http://dx.doi.org/10.1016/S1352-2310\(97\)00141-6](http://dx.doi.org/10.1016/S1352-2310(97)00141-6)
- Collins, M; Knutti, R; Arblaster, J; Dufresne, JL; Fichet, T; Friedlingstein, P; Gao, X; Gutowski, WJ, Jr; Johns, T; Krinner, G; Shongwe, M; Tebaldi, C; Weaver, AJ; Wehner, M. (2013). Long-term climate change: Projections, commitments and irreversibility. In TF Stocker; D Qin; GK Plattner; MMB Tignor; SK Allen; J Boschung; A Nauels; Y Xia; V Bex; PM Midgley (Eds.), *Climate change 2013: The physical science basis Contribution of working group I to the fifth assessment report of the Intergovernmental Panel on Climate Change* (pp. 1029-1136). Cambridge, UK: Cambridge University Press. <http://www.ipcc.ch/report/ar5/wg1/>

- Costanza, R; De Groot, R; Braat, L; Kubiszewski, I; Fioramonti, L; Sutton, P; Farber, S; Grasso, M. (2017). Twenty years of ecosystem services: How far have we come and how far do we still need to go? *Ecosyst Serv* 28: 1-16.
<http://dx.doi.org/10.1016/j.ecoser.2017.09.008>
- Csavina, J; Roberti, JA; Taylor, JR; Loescher, HW. (2017). Traceable measurements and calibration: a primer on uncertainty analysis. *Ecosphere* 8.
<http://dx.doi.org/10.1002/ecs2.1683>
- Curry, JA; Webster, PJ. (2011). Climate science and the uncertainty monster. *Bull Am Meteorol Soc* 92: 1667-1682. <http://dx.doi.org/10.1175/2011BAMS3139.1>
- Dias, T; Clemente, A; Martins-Loução, MA; Sheppard, L; Bobbink, R; Cruz, C. (2014). Ammonium as a driving force of plant diversity and ecosystem functioning: observations based on 5 years' manipulation of N dose and form in a Mediterranean ecosystem. *PLoS ONE* 9: e92517. <http://dx.doi.org/10.1371/journal.pone.0092517>
- Doak, DF; Bigger, D; Harding, EK; Marvier, MA; O'Malley, RE; Thomson, D. (1998). The statistical inevitability of stability-diversity relationships in community ecology. *Am Nat* 151: 264-276. <http://dx.doi.org/10.1086/286117>
- Doney, SC. (2010). The growing human footprint on coastal and open-ocean biogeochemistry [Review]. *Science* 328: 1512-1516. <http://dx.doi.org/10.1126/science.1185198>
- Driscoll, CT; Lawrence, GB; Bulger, AJ; Butler, TJ; Cronan, CS; Eagar, C; Lambert, KF; Likens, GE; Stoddard, JL; Weathers, KC. (2001). Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. *Bioscience* 51: 180-198. [http://dx.doi.org/10.1641/0006-3568\(2001\)051\[0180:ADITNU\]2.0.CO;2](http://dx.doi.org/10.1641/0006-3568(2001)051[0180:ADITNU]2.0.CO;2)
- Duarte, N; Pardo, LH; Robin-Abbott, MJ. (2013). Susceptibility of forests in the northeastern USA to nitrogen and sulfur deposition: Critical load exceedance and forest health. *Water Air Soil Pollut* 224: 1355. <http://dx.doi.org/10.1007/s11270-012-1355-6>
- Duffy, JE; Cardinale, BJ; France, KE; McIntyre, PB; Thebault, E; Loreau, M. (2007). The functional role of biodiversity in ecosystems: Incorporating trophic complexity. *Ecol Lett* 10: 522-538.
- Fakhraei, H; Driscoll, CT; Renfro, JR; Kulp, MA; Blett, TF; Brewer, PF; Schwartz, JS. (2016). Critical loads and exceedances for nitrogen and sulfur atmospheric deposition in Great Smoky Mountains National Park, United States. *Ecosphere* 7: 1-28.
<http://dx.doi.org/10.1002/ecs2.1466>
- Fakhraei, H; Driscoll, CT; Selvendiran, P; DePinto, JV; Bloomfield, J; Quinn, S; Rowell, HC. (2014). Development of a total maximum daily load (TMDL) for acid-impaired lakes in the Adirondack region of New York. *Atmos Environ* 95: 277-287.
<http://dx.doi.org/10.1016/j.atmosenv.2014.06.039>
- Fakhraei, HK; Driscoll, CT; Kulp, MA; Renfro, JR; Blett, TF; Brewer, PF; Schwartz, JS. (2017a). Sensitivity and uncertainty analysis of PnET-BGC to inform the development of Total Maximum Daily Loads (TMDLs) of acidity in the Great Smoky Mountains National Park. *Environ Modell Softw* 95: 156-167. <http://dx.doi.org/10.1016/j.envsoft.2017.06.013>

- [Fakhraei, HK; Driscoll, CT; Kulp, MA; Renfro, JR; Blett, TF; Brewer, PF; Schwartz, JS.](#) (2017b). Sensitivity and uncertainty analysis of PnET-BGC to inform the development of Total Maximum Daily Loads (TMDLs) of acidity in the Great Smoky Mountains National Park: Supplementary materials [Supplemental Data]. Environ Modell Softw 95.
- [Fenn, ME; Allen, EB; Weiss, SB; Jovan, S; Geiser, LH; Tonnesen, GS; Johnson, RF; Rao, LE; Gimeno, BS; Yuan, F; Meixner, T; Bytnerowicz, A.](#) (2010). Nitrogen critical loads and management alternatives for N-impacted ecosystems in California [Review]. J Environ Manage 91: 2404-2423. <http://dx.doi.org/10.1016/j.jenvman.2010.07.034>
- [Fenn, ME; Driscoll, CT; Zhou, Q; Rao, LE; Meixner, T; Allen, EB; Yuan, F; Sullivan, TJ.](#) (2015). Use of Combined Biogeochemical Model Approaches and Empirical Data to Assess Critical Loads of Nitrogen. In Environmental Pollution Series. http://dx.doi.org/10.1007/978-94-017-9508-1_10
- [Fenn, ME; Jovan, S; Yuan, F; Geiser, L; Meixner, T; Gimeno, BS.](#) (2008). Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. Environ Pollut 155: 492-511. <http://dx.doi.org/10.1016/j.envpol.2008.03.019>
- [Fenn, ME; Lambert, KF; Blett, TF; Burns, DA; Pardo, LH; Lovett, GM; Haeuber, RA; Evers, DC; Driscoll, CT; Jefferies, DS.](#) (2011). Setting limits: Using air pollution thresholds to protect and restore U.S. ecosystems. (Issues in Ecology No. 14). Washington, DC: Ecological Society of America. <https://www.esa.org/esa/wp-content/uploads/2013/03/issuesinecology14.pdf>
- [Frost, TM; Fischer, JM; Klug, JL; Arnott, SE; Montz, PK.](#) (2006). Trajectories of zooplankton recovery in the Little Rock Lake whole-lake acidification experiment. Ecol Appl 16: 353-367. <http://dx.doi.org/10.1890/04-1800>
- [Futter, MN; Klaminder, J; Lucas, RW; Laudon, H; Köhler, SJ.](#) (2012). Uncertainty in silicate mineral weathering rate estimates: Source partitioning and policy implications. Environ Res Lett 7: 1-8. <http://dx.doi.org/10.1088/1748-9326/7/2/024025>
- [Galloway, JN; Aber, JD; Erisman, JW; Seitzinger, SP; Howarth, RW; Cowling, EB; Cosby, BJ.](#) (2003). The nitrogen cascade. Bioscience 53: 341-356.
- [Galloway, JN; Cowling, EB.](#) (2002). Reactive nitrogen and the world: 200 years of change [Review]. Ambio 31: 64-71. [http://dx.doi.org/10.1639/0044-7447\(2002\)031\[0064:RNATWY\]2.0.CO;2](http://dx.doi.org/10.1639/0044-7447(2002)031[0064:RNATWY]2.0.CO;2)
- [Galloway, JN; Schlesinger, WH; Clark, CM; Grimm, NB; Jackson, RB; Law, BE; Thornton, PE; Townsend, AR; Martin, R.](#) (2014). Ch. 15: Biogeochemical cycles. In JM Melillo; TC Richmond; GW Yohe (Eds.), Climate change impacts in the United States: The third National Climate Assessment (pp. 350-368). Washington, DC: U.S. Global Change Research Program. <http://dx.doi.org/10.7930/J0X63JT0>
- [Gamfeldt, L; Lefcheck, JS; Byrnes, JEK; Cardinale, BJ; Duffy, JE; Griffin, JN.](#) (2015). Marine biodiversity and ecosystem functioning: what's known and what's next? Oikos 124: 252-265. <http://dx.doi.org/10.1111/oik.01549>

- [Gamfeldt, L; Snäll, T; Bagchi, R; Jonsson, M; Gustafsson, L; Kjellander, P; Ruiz-Jaen, MC; Fröberg, M; Stendahl, J; Philipson, CD; Mikusiński, G; Andersson, E; Westerlund, B; Andrén, H; Moberg, F; Moen, J; Bengtsson, J.](#) (2013). Higher levels of multiple ecosystem services are found in forests with more tree species. *Nat Commun* 4: 1340. <http://dx.doi.org/10.1038/ncomms2328>
- [Geiser, LH; Jovan, SE; Glavich, DA; Porter, MK.](#) (2010). Lichen-based critical loads for atmospheric nitrogen deposition in Western Oregon and Washington Forests, USA. *Environ Pollut* 158: 2412-2421. <http://dx.doi.org/10.1016/j.envpol.2010.04.001>
- [Grantz, DA; Garner, JHB; Johnson, DW.](#) (2003). Ecological effects of particulate matter. *Environ Int* 29: 213-239. [http://dx.doi.org/10.1016/S0160-4120\(02\)00181-2](http://dx.doi.org/10.1016/S0160-4120(02)00181-2)
- [Greaver, TL; Clark, CM; Compton, JE; Vallano, D; Talhelm, AF; Weaver, CP; Band, LE; Baron, JS; Davidson, EA; Tague, CL; Felker-Quinn, E; Lynch, JA; Herrick, JD; Liu, L; Goodale, CL; Novak, KJ; Haeuber, RA.](#) (2016). Key ecological responses to nitrogen are altered by climate change. *Nat Clim Chang* 6: 836-843. <http://dx.doi.org/10.1038/NCLIMATE3088>
- [Greaver, TL; Liu, L; Bobbink, R.](#) (2011). Wetlands. In *Assessment of nitrogen deposition effects and empirical critical loads of nitrogen for ecoregions of the United States* (General Technical Report NRS-80) (pp. 193-208). Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station. <http://www.nrs.fs.fed.us/pubs/gtr/gtr-nrs-80chapters/17-greaver.pdf>
- [Groffman, PM; Kareiva, P; Carter, S; Grimm, NB; Lawler, J; Mack, M; Matzek, V; Tallis, H.](#) (2014). Ch. 8: Ecosystems, biodiversity, and ecosystem service. In JM Melillo; TC Richmond; GW Yohe (Eds.), *Climate change impacts in the United States: The third National Climate Assessment* (pp. 195-219). Washington, DC: U.S. Global Change Research Program. <http://dx.doi.org/10.7930/J0TD9V7H>
- [Hernández, DL; Vallano, DM; Zavaleta, ES; Tzankova, Z; Pasari, JR; Weiss, S; Selmants, PC; Morozumi, C.](#) (2016). Nitrogen pollution is linked to US listed species declines. *Bioscience* 66: 213-222. <http://dx.doi.org/10.1093/biosci/biw003>
- [Hesthagen, T; Fiske, P; Skjelkvale, BL.](#) (2008). Critical limits for acid neutralizing capacity of brown trout (*Salmo trutta*) in Norwegian lakes differing in organic carbon concentrations. *Aquatic Ecology* 42: 307-316. <http://dx.doi.org/10.1007/s10452-008-9191-x>
- [Hooper, DU; Adair, EC; Cardinale, BJ; Byrnes, JEK; Hungate, BA; Matulich, KL; Gonzalez, A; Duffy, JE; Gamfeldt, L; O'Connor, MI.](#) (2012). A global synthesis reveals biodiversity loss as a major driver of ecosystem change. *Nature* 486: 105-U129. <http://dx.doi.org/10.1038/nature11118>
- [Horn, KJ; Thomas, RQ; Clark, CM; Pardo, LH; Fenn, ME; Lawrence, GB; Perakis, SS; Smithwick, EAH; Baldwin, D; Braun, S; Nordin, A; Perry, CH; Phelan, JN; Schaberg, PG; St. Clair, SB; Warby, R; Watmough, S.](#) (2018). Growth and survival relationships of 71 tree species with nitrogen and sulfur deposition across the conterminous. *PLoS ONE* 13: Article #e0205296. <http://dx.doi.org/10.1371/journal.pone.0205296>

- Howarth, RW. (2008a). Coastal nitrogen pollution: A review of sources and trends globally and regionally. *Harmful Algae* 8: 14-20. <http://dx.doi.org/10.1016/j.hal.2008.08.015>
- Howarth, RW. (2008b). Estimating atmospheric nitrogen deposition in the Northeastern United States: Relevance to Narragansett Bay. In A Desbonnet; BA Cost-Pierce (Eds.), *Science for ecosystem-based management: Narragansett Bay in the 21st century* (pp. 47-65). New York: Springer New York. http://dx.doi.org/10.1007/978-0-387-35299-2_3
- IPCC (Intergovernmental Panel on Climate Change). (2007). *Climate change 2007: Impacts, adaptation and vulnerability*. Cambridge, UK: Cambridge University Press. https://www.ipcc.ch/publications_and_data/publications_ipcc_fourth_assessment_report_wg2_report_impacts_adaptation_and_vulnerability.htm
- Irvine, IC; Greaver, T; Phelan, J; Sabo, RD; Van Houtven, G. (2017). Terrestrial acidification and ecosystem services: effects of acid rain on bunnies, baseball, and Christmas trees. *Ecosphere* 8. <http://dx.doi.org/10.1002/ecs2.1857>
- Isbell, F; Calcagno, V; Hector, A; Connolly, J; Harpole, WS; Reich, PB; Scherer-Lorenzen, M; Schmid, B; Tilman, D; van Ruijven, J; Weigelt, A; Wilsey, BJ; Zavaleta, ES; Loreau, M. (2011). High plant diversity is needed to maintain ecosystem services. *Nature* 477: 199-202. <http://dx.doi.org/10.1038/nature10282>
- Isbell, F; Craven, D; Connolly, J; Loreau, M; Schmid, B; Beierkuhnlein, C; Bezemer, TM; Bonin, C; Bruehlheide, H; de Luca, E; Ebeling, A; Griffin, JN; Guo, Q; Hautier, Y; Hector, A; Jentsch, A; Kreyling, J; Lanta, V; Manning, P; Meyer, ST; Mori, AS; Naeem, S; Niklaus, PA; Polley, HW; Reich, PB; Roscher, C; Seabloom, EW; Smith, MD; Thakur, MP; Tilman, D; Tracy, BF; van Der Putten, WH; van Ruijven, J; Weigelt, A; Weisser, WW; Wilsey, B; Eisenhauer, N. (2015). Biodiversity increases the resistance of ecosystem productivity to climate extremes. *Nature* 526: 574-U263. <http://dx.doi.org/10.1038/nature15374>
- Johnson, PT; Ostfeld, RS; Keesing, F. (2015). Frontiers in research on biodiversity and disease [Review]. *Ecol Lett* 18: 1119-1133. <http://dx.doi.org/10.1111/ele.12479>
- Johnson, PTJ; Townsend, AR; Cleveland, CC; Glibert, PM; Howarth, RW; McKenzie, VJ; Rejmankova, E; Ward, MH. (2010). Linking environmental nutrient enrichment and disease emergence in humans and wildlife. *Ecol Appl* 20: 16-29. <http://dx.doi.org/10.1890/08-0633.1>
- Kleijn, D; Bekker, RM; Bobbink, R; De Graaf, MCC; Roelofs, JGM. (2008). In search for key biogeochemical factors affecting plant species persistence in heathland and acidic grasslands: a comparison of common and rare species. *J Appl Ecol* 45: 680-687. <http://dx.doi.org/10.1111/j.1365-2664.2007.01444.x>
- Lacoul, P; Freedman, B; Clair, T. (2011). Effects of acidification on aquatic biota in Atlantic Canada. *Environ Rev* 19: 429-460. <http://dx.doi.org/10.1139/a11-016>
- Latimer, JS; Rego, SA. (2010). Empirical relationship between eelgrass extent and predicted watershed-derived nitrogen loading for shallow New England estuaries. *Estuar Coast Shelf Sci* 90: 231-240. <http://dx.doi.org/10.1016/j.ecss.2010.09.004>

- Lawrence, GB; Dukett, JE; Houck, N; Snyder, P; Capone, S. (2013). Increases in dissolved organic carbon accelerate loss of toxic Al in Adirondack lakes recovering from acidification. *Environ Sci Technol* 47: 7095-7100. <http://dx.doi.org/10.1021/es4004763>
- Li, H; McNulty, SG. (2007). Uncertainty analysis on simple mass balance model to calculate critical loads for soil acidity. *Environ Pollut* 149: 315-326. <http://dx.doi.org/10.1016/j.envpol.2007.05.014>
- Maestre, FT; Quero, JL; Gotelli, NJ; Escudero, A; Ochoa, V; Delgado-Baquerizo, M; García-Gómez, M; Bowker, MA; Soliveres, S; Escolar, C; García-Palacios, P; Berdugo, M; Valencia, E; Gozalo, B; Gallardo, A; Aguilera, L; Arredondo, T; Blones, J; Boeken, B; Bran, D; Conceição, AA; Cabrera, O; Chaieb, M; Derak, M; Eldridge, DJ; Espinosa, CI; Florentino, A; Gaitán, J; Gatica, MG; Ghiloufi, W; Gómez-González, S; Gutiérrez, JR; Hernández, RM; Huang, X; Huber-Sannwald, E; Jankju, M; Miriti, M; Monerri, J; Mau, RL; Morici, E; Naseri, K; Ospina, A; Polo, V; Prina, A; Pucheta, E; Ramírez-Collantes, DA; Romão, R; Tighe, M; Torres-Díaz, C; Val, J; Veiga, JP; Wang, D; Zaady, E. (2012). Plant species richness and ecosystem multifunctionality in global drylands. *Science* 335: 214-218. <http://dx.doi.org/10.1126/science.1215442>
- Malley, DF; Chang, PSS. (1994). Assessing the health of a zooplankton community in a small Precambrian Shield lake during recovery from experimental acidification. *J Aquat Ecosys Health* 3: 273-286. <http://dx.doi.org/10.1007/BF00115286>
- McCann, KS. (2000). The diversity-stability debate. *Nature* 405: 228-233. <http://dx.doi.org/10.1038/35012234>
- McCrackin, ML; Harrison, JA; Compton, JE. (2013). A comparison of NEWS and SPARROW models to understand sources of nitrogen delivered to US coastal areas. *Biogeochemistry* 114: 281-297. <http://dx.doi.org/10.1007/s10533-012-9809-x>
- Mcdonnell, TC; Belyazid, S; Sullivan, TJ; Bell, M; Clark, C; Blett, T; Evans, T; Cass, W; Hyduke, A; Sverdrup, H. (2018a). Vegetation dynamics associated with changes in atmospheric nitrogen deposition and climate in hardwood forests of Shenandoah and Great Smoky Mountains National Parks, USA. *Environ Pollut* 237: 662-674. <http://dx.doi.org/10.1016/j.envpol.2018.01.112>
- Mcdonnell, TC; Reinds, GJ; Sullivan, TJ; Clark, CM; Bonten, LTC; Mol-Dijkstra, JP; Wamelink, GWW; Dovciak, M. (2018b). Feasibility of coupled empirical and dynamic modeling to assess climate change and air pollution impacts on temperate forest vegetation of the eastern United States. *Environ Pollut* 234: 902-914. <http://dx.doi.org/10.1016/j.envpol.2017.12.002>
- McDonnell, TC; Sullivan, TJ; Hessburg, PF; Reynolds, KM; Povak, NA; Cosby, BJ; Jackson, W; Salter, RB. (2014). Steady-state sulfur critical loads and exceedances for protection of aquatic ecosystems in the U.S. Southern Appalachian Mountains. *J Environ Manage* 146: 407-419. <http://dx.doi.org/10.1016/j.jenvman.2014.07.019>
- McNulty, SG; Cohen, EC; Myers, JAM; Sullivan, TJ; Li, H. (2007). Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. *Environ Pollut* 149: 281-292. <http://dx.doi.org/10.1016/j.envpol.2007.05.025>
- Naeem, S; Li, SB. (1997). Biodiversity enhances ecosystem reliability. *Nature* 390: 507-509.

- Nanus, L; McMurray, JA; Clow, DW; Saros, JE; Blett, T; Gurdak, JJ. (2017). Spatial variation of atmospheric nitrogen deposition and critical loads for aquatic ecosystems in the Greater Yellowstone Area. *Environ Pollut* 223: 644-656. <http://dx.doi.org/10.1016/j.envpol.2017.01.077>
- NAPAP (National Acid Precipitation Assessment Program). (2011). National acid precipitation assessment program report to congress 2011: An integrated assessment. Washington, DC: U.S. Environmental Protection Agency, Clean Air Markets Division. <http://ny.water.usgs.gov/projects/NAPAP/>
- Nilsson, J; Grennfelt, P. (1988). Critical loads for sulphur and nitrogen: Report from a workshop held at Skokloster, Sweden, 19-24 March 1988. Skokloster, Sweden: Nordic Council of Ministers: Copenhagen.
- NRC (National Research Council). (2000). Clean coastal waters: Understanding and reducing the effects of nutrient pollution. In *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*. Washington, DC: The National Academies Press. <http://dx.doi.org/10.17226/9812>
- O'Dea, CB; Anderson, S; Sullivan, T; Landers, D; Casey, CF. (2017). Impacts to ecosystem services from aquatic acidification: using FECS-CS to understand the impacts of air pollution. *Ecosphere* 8. <http://dx.doi.org/10.1002/ecs2.1807>
- Padgett, PE; Parry, SD; Bytnerowicz, A; Heath, RL. (2009). Image analysis of epicuticular damage to foliage caused by dry deposition of the air pollutant nitric acid. *J Environ Monit* 11: 63-74. <http://dx.doi.org/10.1039/b804875d>
- Pardo, LH; Fenn, ME; Goodale, CL; Geiser, LH; Driscoll, CT; Allen, EB; Baron, JS; Bobbink, R; Bowman, WD; Clark, CM; Emmett, B; Gilliam, FS; Greaver, TL; Hall, SJ; Lilleskov, EA; Liu, L; Lynch, JA; Nadelhoffer, KJ; Perakis, SS; Robin-Abbott, MJ; Stoddard, JL; Weathers, KC; Dennis, RL. (2011a). Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecol Appl* 21: 3049-3082. <http://dx.doi.org/10.1890/10-2341.1>
- Pardo, LH; Robin-Abbott, MJ; Driscoll, CT. (2011b). Assessment of nitrogen deposition effects and empirical critical loads of nitrogen for ecoregions of the United States. In *Assessment of nitrogen deposition effects and empirical critical loads of Nitrogen for ecoregions of the United States*. (NRS-80). Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station. <http://www.nrs.fs.fed.us/pubs/38109>
- Petratis, PS; Latham, RE. (1999). The importance of scale in testing the origins of alternative community states. *Ecology* 80: 429-442. [http://dx.doi.org/10.1890/0012-9658\(1999\)080\[0429:TIOSIT\]2.0.CO;2](http://dx.doi.org/10.1890/0012-9658(1999)080[0429:TIOSIT]2.0.CO;2)
- Phelan, J; Belyazid, S; Jones, P; Cajka, J; Buckley, J; Clark, C. (2016). Assessing the effects of climate change and air pollution on soil properties and plant diversity in sugar maple-beech-yellow birch hardwood forests in the northeastern United States: Model simulations from 1900 to 2100. *Water Air Soil Pollut* 227: 84. <http://dx.doi.org/10.1007/s11270-016-2762-x>

- [Phelan, J; Belyazid, S; Kurz, D; Guthrie, S; Cajka, J; Sverdrup, H; Waite, R.](#) (2014). Estimation of soil base cation weathering rates with the PROFILE model to determine critical loads of acidity for forested ecosystems in Pennsylvania, USA: Pilot application of a potential national methodology. *Water Air Soil Pollut* 225: 2109-2128. <http://dx.doi.org/10.1007/s11270-014-2109-4>
- [Pinder, RW; Davidson, EA; Goodale, CL; Greaver, TL; Herrick, JD; Liu, L.](#) (2012). Climate change impacts of US reactive nitrogen. *Proc Natl Acad Sci USA* 109: 7671-7675. <http://dx.doi.org/10.1073/pnas.1114243109>
- [Povak, NA; Hessburg, PF; McDonnell, TC; Reynolds, KM; Sullivan, TJ; Salter, RB; Cosby, BJ.](#) (2014). Machine learning and linear regression models to predict catchment- level base cation weathering rates across the southern Appalachian Mountain region, USA. *Water Resour Res* 50: 2798-2814. <http://dx.doi.org/10.1002/2013WR014203>
- [Reich, PB; Tilman, D; Isbell, F; Mueller, K; Hobbie, SE; Flynn, DF; Eisenhauer, N.](#) (2012). Impacts of biodiversity loss escalate through time as redundancy fades. *Science* 336: 589-592. <http://dx.doi.org/10.1126/science.1217909>
- [Reinds, G; de Vries, W.](#) (2010). Uncertainties in critical loads and target loads of sulphur and nitrogen for European forests: Analysis and quantification. *Sci Total Environ* 408: 1960-1970. <http://dx.doi.org/10.1016/j.scitotenv.2009.12.001>
- [Rhodes, C; Bingham, A; Heard, AM; Hewitt, J; Lynch, J; Waite, R; Bell, MD.](#) (2017). Diatoms to human uses: linking nitrogen deposition, aquatic eutrophication, and ecosystem services : Supplementary materials. *Ecosphere* 8.
- [Rockstrom, J; Steffen, W; Noone, K; Persson, A; Chapin, FS, III; Lambin, EF; Lenton, TM; Scheffer, M; Folke, C; Schellnhuber, HJ; Nykvist, B; de Wit, CA; Hughes, T; van Der Leeuw, S; Rodhe, H; Sorlin, S; Snyder, PK; Costanza, R; Svedin, U; Falkenmark, M; Karlberg, L; Corell, RW; Fabry, VJ; Hansen, J; Walker, B; Liverman, D; Richardson, K; Crutzen, P; Foley, JA.](#) (2009). A safe operating space for humanity. *Nature* 461: 472-475. <http://dx.doi.org/10.1038/461472a>
- [Root, HT; Geiser, LH; Jovan, S; Neitlich, P.](#) (2015). Epiphytic macrolichen indication of air quality and climate in interior forested mountains of the Pacific Northwest, USA. *Ecol Indic* 53: 95-105. <http://dx.doi.org/10.1016/j.ecolind.2015.01.029>
- [Scheffe, RD; Lynch, JA; Reff, A; Kelly, JT; Hubbell, B; Greaver, TL; Smith, JT.](#) (2014). The aquatic acidification index: A new regulatory metric linking atmospheric and biogeochemical models to assess potential aquatic ecosystem recovery. *Water Air Soil Pollut* 225: 1838. <http://dx.doi.org/10.1007/s11270-013-1838-0>
- [Schwede, DB; Dennis, RL; Bitz, M.](#) (2009). The watershed deposition tool: A tool for incorporating atmospheric deposition in water-quality analyses(1). *J Am Water Resour Assoc* 45: 973-985. <http://dx.doi.org/10.1111/j.1752-1688.2009.00340.x>
- [Schwede, DB; Lear, GG.](#) (2014). A novel hybrid approach for estimating total deposition in the United States - Supplemental information [Supplemental Data]. *Atmos Environ* 92: 207-220. <http://dx.doi.org/10.1016/j.atmosenv.2014.04.008>

- Simkin, SM; Allen, EB; Bowman, WD; Clark, CM; Belnap, J; Brooks, ML; Cade, BS; Collins, SL; Geiser, LH; Gilliam, FS; Jovan, SE; Pardo, LH; Schulz, BK; Stevens, CJ; Suding, KN; Throop, HL; Waller, DM. (2016). Conditional vulnerability of plant diversity to atmospheric nitrogen deposition across the United States. *Proc Natl Acad Sci USA* 113: 4086-4091. <http://dx.doi.org/10.1073/pnas.1515241113>
- Stoddard, JL. (1994). Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. In LA Baker (Ed.), *Environmental Chemistry of Lakes and Reservoirs* (Advances in chemistry series no. 237 ed., pp. 223-284). Washington, DC: American Chemical Society. <http://dx.doi.org/10.1021/ba-1994-0237.ch008>
- Sullivan, TJ; Cosby, BJ; Driscoll, CT; McDonnell, TC; Herlihy, AT. (2011a). Target loads of atmospheric sulfur deposition protect terrestrial resources in the Adirondack Mountains, New York against biological impacts caused by soil acidification. *Journal of Environmental Studies and Sciences* 1: 301-314. <http://dx.doi.org/10.1007/s13412-011-0062-8>
- Sullivan, TJ; Cosby, BJ; Driscoll, CT; McDonnell, TC; Herlihy, AT; Burns, DA. (2012). Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York. *Water Resour Res* 48: W01547. <http://dx.doi.org/10.1029/2011wr011171>
- Sullivan, TJ; Cosby, BJ; Jackson, WA. (2011b). Target loads of atmospheric sulfur deposition for the protection and recovery of acid-sensitive streams in the Southern Blue Ridge Province. *J Environ Manage* 92: 2953-2960. <http://dx.doi.org/10.1016/j.jenvman.2011.07.014>
- Suter, GW; Norton, SB; Fairbrother, A. (2005). Individuals versus organisms versus populations in the definition of ecological assessment endpoints. *Integr Environ Assess Manag* 1: 397-400. <http://dx.doi.org/10.1002/ieam.5630010409>
- Tilman, D. (2000). Causes, consequences and ethics of biodiversity. *Nature* 405: 208-211. <http://dx.doi.org/10.1038/35012217>
- Tilman, D; Downing, JA. (1994). Biodiversity and stability in grasslands. *Nature* 367: 363-365. <http://dx.doi.org/10.1038/367363a0>
- Tilman, D; Lehman, CL; Bristow, CE. (1998). Diversity-stability relationships: Statistical inevitability or ecological consequence? *Am Nat* 151: 277-282.
- Tilman, D; Reich, PB; Isbell, F. (2012). Biodiversity impacts ecosystem productivity as much as resources, disturbance, or herbivory. *Proc Natl Acad Sci USA* 109: 10394-10397. <http://dx.doi.org/10.1073/pnas.1208240109>
- Tominaga, K; Aherne, J; Watmough, SA; Alveteg, M; Cosby, BJ; Driscoll, CT; Posch, M. (2009). Voyage without constellation: Evaluating the performance of three uncalibrated process-oriented models. 40: 261-272. <http://dx.doi.org/10.2166/nh.2009.085>
- Turney, CSM; Palmer, J; Maslin, MA; Hogg, A; Fogwill, CJ; Southon, J; Fenwick, P; Helle, G; Wilmshurst, JM; McGlone, M; Bronk Ramsey, C; Thomas, Z; Lipson, M; Beaven, B; Jones, RT; Andrews, O; Hua, Q. (2018). Global peak in atmospheric radiocarbon provides a potential definition for the onset of the anthropocene epoch in 1965. *Sci Rep* 8: 3293. <http://dx.doi.org/10.1038/s41598-018-20970-5>

- [U.S. EPA](#) (U.S. Environmental Protection Agency). (1993). Air quality criteria for oxides of nitrogen (final, 1993) [EPA Report]. (EPA/600/8-91/049aF-cF). Washington, DC: U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office.
<http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=40179>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (1998). Guidelines for ecological risk assessment [EPA Report]. (EPA/630/R-95/002F). Washington, DC: U.S. Environmental Protection Agency, Risk Assessment Forum. <https://www.epa.gov/risk/guidelines-ecological-risk-assessment>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2004). Air quality criteria for particulate matter [EPA Report]. (EPA/600/P-99/002aF-bF). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment- RTP Office.
<http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=87903>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2006a). Multi-agency critical loads workshop: sulfur & nitrogen deposition effects on freshwater and terrestrial ecosystems Final report [EPA Report]. (EPA 68-W-03-02). Washington, DC.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2006b). Wadeable streams assessment: A collaborative survey of the nation's streams [EPA Report]. (EPA 841-B-06-002). Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development, Office of Water. <http://www.epa.gov/owow/streamsurvey>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2008). Integrated science assessment for oxides of nitrogen and sulfur: Ecological criteria [EPA Report]. (EPA/600/R-08/082F). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment- RTP Division.
<http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=201485>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2009a). Integrated science assessment for particulate matter [EPA Report]. (EPA/600/R-08/139F). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment- RTP Division.
<http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=216546>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2009b). National lakes assessment: A collaborative survey of the nations lakes. (EPA/841/R-09/001). Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development, Office of Water. https://www.epa.gov/sites/production/files/2013-11/documents/nla_newlowres_fullrpt.pdf
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2009c). Risk and exposure assessment for review of the secondary National Ambient Air Quality Standards for oxides of nitrogen and oxides of sulfur [EPA Report]. (EPA/452/R-09/008A). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Health and Environmental Impacts Division.
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2011). Policy assessment for the review of the secondary national ambient air quality standards for oxides of nitrogen and oxides of sulfur [EPA Report]. (EPA-452/R-11-004a). Washington, DC.
<http://www3.epa.gov/ttn/naaqs/standards/no2so2sec/data/20110114pamain.pdf>

- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2013). Integrated science assessment for lead [EPA Report]. (EPA/600/R-10/075F). Research Triangle Park, NC: U.S. Environmental Protection Agency, National Center for Environmental Assessment. <http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=255721>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2015). Preamble to the integrated science assessments [EPA Report]. (EPA/600/R-15/067). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, RTP Division. <https://cfpub.epa.gov/ncea/isa/recorddisplay.cfm?deid=310244>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016a). Integrated review plan for the national ambient air quality standards for particulate matter [EPA Report]. (EPA-452/R-16-005). Research Triangle Park, NC. <https://yosemite.epa.gov/sab/sabproduct.nsf/0/eb862b233fbd0cde85257dda004fcb8c!OpenDocument&TableRow=2.0>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016b). Integrated science assessment (ISA) for sulfur oxides health criteria (Second external review draft) [EPA Report]. (EPA/600/R-16/351). Washington, DC. <https://cfpub.epa.gov/ncea/isa/recorddisplay.cfm?deid=326450>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016c). Integrated science assessment for oxides of nitrogen-health criteria (final report) [EPA Report]. (EPA/600/R-15/068). Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment. http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=526855
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016d). National coastal condition assessment 2010. (EPA 841-R-15-006). Washington, DC: U.S. Environmental Protection Agency, Office of Water, Office of Research and Development. <https://www.epa.gov/national-aquatic-resource-surveys/ncca>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016e). National lakes assessment 2012: A collaborative survey of lakes in the United States [EPA Report]. (EPA 841-R-16-113). Washington, D.C. <https://nationallakesassessment.epa.gov/>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016f). National rivers and streams assessment 2008-2009: A collaborative survey. (EPA/841/R-16/007). Washington, DC: U.S. Environmental Protection Agency, Office of Water, Office of Research and Development. <https://www.epa.gov/national-aquatic-resource-surveys/national-rivers-and-streams-assessment-2008-2009-report>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2016g). National wetland condition assessment 2011: A collaborative survey of the nation's wetlands (pp. 1-105). (EPA-843-R-15-005). Washington, DC. <https://www.epa.gov/national-aquatic-resource-surveys/national-wetland-condition-assessment-2011-report>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2017a). Integrated review plan for the secondary national ambient air quality standards for ecological effects of oxides of nitrogen, oxides of sulfur and particulate matter [EPA Report]. (EPA-452/R-17-002). Research Triangle Park, NC.

- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2017b). Northern Gulf of Mexico hypoxic zone [Website]. Washington, DC. Retrieved from <https://www.epa.gov/ms-hf/northern-gulf-mexico-hypoxic-zone>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2019). U.S. EPA Integrated Science Assessment for particulate matter [EPA Report]. (EPA/600/R-19/188). <https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=347534>
- [U.S. EPA](#) (U.S. Environmental Protection Agency). (2020). 2017 National Emissions Inventory complete release: technical support document. <https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-technical-support-document-tsd>
- [Walker, WE; Harremoes, P; Rotmans, J; Van Der Sluijs, JP; Van Asselt, MBA; Janssen, P; Kraye Von Krauss, MP.](#) (2003). Defining uncertainty: a conceptual basis for uncertainty management in model-based decision support. Integrated Assessment 4: 5-17. <http://dx.doi.org/10.1076/iaij.4.1.5.16466>
- [Whitfield, CJ; Phelan, JN; Buckley, J; Clark, CM; Guthrie, S; Lynch, JA.](#) (2018). Estimating base cation weathering rates in the USA: challenges of uncertain soil mineralogy and specific surface area with applications of the profile model. Water Air Soil Pollut 229: 61. <http://dx.doi.org/10.1007/s11270-018-3691-7>
- [Williams, JJ; Chung, SH; Johansen, AM; Lamb, BK; Vaughan, JK; Beutel, M.](#) (2017a). Evaluation of atmospheric nitrogen deposition model performance in the context of US critical load assessments. Atmos Environ 150: 244-255. <http://dx.doi.org/10.1016/j.atmosenv.2016.11.051>
- [Williams, JJ; Lynch, JA; Saros, JE; Labou, SG.](#) (2017b). Critical loads of atmospheric N deposition for phytoplankton nutrient limitation shifts in western U.S. mountain lakes. Ecosphere 8: e01955. <http://dx.doi.org/10.1002/ecs2.1955>
- [Williams, MR; Filoso, S; Longstaff, BJ; Dennison, WC.](#) (2010). Long-term trends of water quality and biotic metrics in Chesapeake Bay: 1986 to 2008. Estuaries Coasts 33: 1279-1299. <http://dx.doi.org/10.1007/s12237-010-9333-y>
- [Worm, B; Barbier, EB; Beaumont, N; Duffy, JE; Folke, C; Halpern, BS; Jackson, JBC; Lotze, HK; Micheli, F; Palumbi, SR; Sala, E; Selkoe, KA; Stachowicz, JJ; Watson, R.](#) (2006). Impacts of biodiversity loss on ocean ecosystem services. Science 314: 787-790. <http://dx.doi.org/10.1126/science.1132294>
- [Zavaleta, ES; Pasari, JR; Hulvey, KB; Tilman, GD.](#) (2010). Sustaining multiple ecosystem functions in grassland communities requires higher biodiversity. Proc Natl Acad Sci USA 107: 1443-1446. <http://dx.doi.org/10.1073/pnas.0906829107>
- [Zhang, Y; Chen, HYH; Reich, PB.](#) (2012). Forest productivity increases with evenness, species richness and trait variation: a global meta-analysis. J Ecol 100: 742-749. <http://dx.doi.org/10.1111/j.1365-2745.2011.01944.x>