

Annexes for the Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria

(First External Review Draft)

Annexes for the Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria

National Center for Environmental Assessment-RTP Division
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC

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PREFACE

Legislative Requirements

Two sections of the Clean Air Act (CAA) govern the establishment and revision of the national ambient air quality standards (NAAQS). Section 108 (U.S. Code, 2003a) directs the Administrator to identify and list “air pollutants” that “in his judgment, may reasonably be anticipated to endanger public health and welfare” and whose “presence in the ambient air results from numerous or diverse mobile or stationary sources” and to issue air quality criteria for those that are listed. Air quality criteria are intended to “accurately reflect the latest scientific knowledge useful in indicating the kind and extent of identifiable effects on public health or welfare which may be expected from the presence of [a] pollutant in ambient air.”

Section 109 (U.S. Code, 2003b) directs the Administrator to propose and promulgate “primary” and “secondary” NAAQS for pollutants listed under Section 108. Section 109(b)(1) defines a primary standard as one “the attainment and maintenance of which in the judgment of the Administrator, based on such criteria and allowing an adequate margin of safety, are requisite to protect the public health.”¹ A secondary standard, as defined in Section 109(b)(2), must “specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator, based on such criteria, is required to protect the public welfare from any known or anticipated adverse effects associated with the presence of [the] pollutant in the ambient air.”²

The requirement that primary standards include an adequate margin of safety was intended to address uncertainties associated with inconclusive scientific and technical

¹ The legislative history of Section 109 indicates that a primary standard is to be set at “the maximum permissible ambient air level ... which will protect the health of any [sensitive] group of the population” and that, for this purpose, “reference should be made to a representative sample of persons comprising the sensitive group rather than to a single person in such a group” [U.S. Senate (1970)].

² Welfare effects as defined in Section 302(h) [U.S. Code, 2005] include, but are not limited to, “effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being.”

information available at the time of standard setting. It was also intended to provide a reasonable degree of protection against hazards that research has not yet identified. See *Lead Industries Association v. EPA*, 647 F.2d 1130, 1154 (D.C. Cir. 1980), cert. denied, 449 U.S. 1042 (1980); *American Petroleum Institute v. Costle*, 665 F.2d 1176, 1186 (D.C. Cir. 1981), cert. denied, 455 U.S. 1034 (1982). Both kinds of uncertainties are components of the risk associated with pollution at levels below those at which human health effects can be said to occur with reasonable scientific certainty. Thus, in selecting primary standards that include an adequate margin of safety, the Administrator is seeking not only to prevent pollution levels that have been demonstrated to be harmful but also to prevent lower pollutant levels that may pose an unacceptable risk of harm, even if the risk is not precisely identified as to nature or degree.

In selecting a margin of safety, the U.S. Environmental Protection Agency (EPA) considers such factors as the nature and severity of the health effects involved, the size of sensitive population(s) at risk, and the kind and degree of the uncertainties that must be addressed. The selection of any particular approach to providing an adequate margin of safety is a policy choice left specifically to the Administrator's judgment. See *Lead Industries Association v. EPA*, supra, 647 F.2d at 1161-62.

In setting standards that are "requisite" to protect public health and welfare, as provided in Section 109(b), EPA's task is to establish standards that are neither more nor less stringent than necessary for these purposes. In so doing, EPA may not consider the costs of implementing the standards. See generally *Whitman v. American Trucking Associations*, 531 U.S. 457, 465-472 and 475-76 (2001).

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

**Annexes for the Integrated Science Assessment
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Authors, Contributors, and Reviewers

Authors

Dr. Tara Greaver (NO_x and SO_x Team Leader)—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jeff Arnold—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Jill S. Baron—U.S. Geological Survey, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins CO

Dr. Bernard J. Cosby, Jr.—Department of Environmental Sciences, University of Virginia, Charlottesville, VA

Ms. Rebecca Daniels—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Christine L. Goodale—Department of Ecology and Evolutionary Biology, Cornell University, Ithaca, NY

Dr. Alan T. Herlihy—Department of Fisheries & Wildlife, Oregon State University, Corvallis, OR

Dr. Jeffrey Herrick—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Alan J. Krupnick—Resources for the Future, 1616 P St NW, Washington, DC

Dr. Kathleen Fallon Lambert—Ecologic: Analysis and Communications, 39 Central Street, Suite 204, Woodstock, VT

Dr. Gregory B. Lawrence—U.S. Geological Survey Troy, NY

Dr. Todd C. McDonnell—E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR

Dr. Joseph Pinto—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Rich Scheffe—Office of Air Quality Planning and Standards (C304-02), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. Juha Siikamaki—Resources for the Future, 1616 P St NW, Washington, DC

Authors, Contributors, and Reviewers

(cont'd)

Authors

(cont'd)

Dr. Timothy J. Sullivan—E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR

Dr. Helga Van Miegroet—Department of Wildland Resources, Department of Watershed Sciences, Utah State University, Logan, UT

Dr. Paul F. Wagner—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Contributors

Dr. Russell Dickerson—Dept. of Atmospheric and Oceanic Sciences, University of Maryland, College Park, MD

Dr. Tina Fan—EOHHS/UMDNJ, Piscataway, NJ

Dr. Arlene Fiore—Geophysical Fluid Dynamics Laboratory/NOAA, Princeton, NJ

Dr. Larry Horowitz—Geophysical Fluid Dynamics Laboratory/NOAA, Princeton, NJ

Dr. William Keene—Dept. of Environmental Sciences, University of Virginia, Charlottesville, VA

Dr. Randall Martin—Dept. of Physics, Dalhousie University, Halifax, Nova Scotia

Dr. William Munger—Center for Earth and Planetary Physics, Harvard University, Cambridge, MA

Dr. Sandy Sillman—Dept. of Atmospheric and Oceanic Sciences, University of Michigan, Ann Arbor, MI

Reviewers

Dr. Lawrence Band—Department of Geography, UNC Chapel Hill, Chapel Hill, NC

Dr. Tamara Blett—Ecologist, National Park Service, PO Box 25287, Lakewood, CO

Authors, Contributors, and Reviewers

(cont'd)

Reviewers

(cont'd)

Dr. Jana Compton—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, OR

Dr. Russell Dickerson—Department of Chemistry & Chemical Physics, University of Maryland, College Park, MD

Dr. Jacqueline Geoghegan—Department of Economics, Clark University, 950 Main Street, Worcester, MA

Dr. D. Alan Hansen—Electric Power Research Institute, Palo Alto, CA

Dr. Brian Heninger—Office of Policy, Economics, and Innovation (1809T), 1200 Pennsylvania Avenue, N. W., Washington, DC

Dr. William Hogsett—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, OR

Dr. Gary Lear—Office of Air and Radiation, Office of Atmospheric Programs (6204J), Ariel Rios Building, 1200 Pennsylvania Avenue, N. W., Washington, DC

Dr. John Lehrter—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, Gulf Breeze, FL

Dr. Lingli Liu—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC

Dr. William Malm—National Park Service, CIRA/CSU 1375 Campus Delivery Fort Collins, CO

Dr. Steve McNulty—USDA Forest Service, 920 Main Campus Drive, Venture Center II, Suite 300, Raleigh, NC

Dr. James Morris—Belle W. Baruch Institute for Marine & Coastal Sciences, University of South Carolina, Columbia, SC

Dr. William Munger—School of Engineering and Applied Science Harvard University, Cambridge, MA

Dr. Knute Nadelhoffer—University of Michigan Biological Station, 9133 East State Street, Pellston, MI

Authors, Contributors, and Reviewers
(cont'd)

Reviewers
(cont'd)

Dr. Christine Negra—The Heinz Center, 900 Seventeenth Street, NW, 7th floor,
Washington, DC

Dr. Kristopher Novak—National Center for Environmental Assessment (B243-01), U.S.
Environmental Protection Agency, Research Triangle Park, NC

Dr. William Orem—U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, VA

Dr. Ellen Porter—National Park Service, NPS-ARD, PO Box 25287, Denver, CO

Dr. William Showers—Dept. of Marine, Earth and Atmospheric Sciences, North Carolina State
University, 1125 Jordan Hall, NCSU

Dr. Lisa Wainger—TN and Associates, 26197 Fawn Lane Hollywood, MD

Dr. Gail Tonnesen—University of California, 4750 West 37th Avenue, Unit 16, Denver, CO

Dr. Shaun Watmough—Dept. of Environmental and Resource Studies, Trent University, 1600
West Bank Drive, Peterborough, Ontario

Dr. Jason West—Dept. of Environmental Sciences & Engineering, University of North
Carolina, 164 Rosenau Hall, CB 7431, Chapel Hill, NC,

**U.S. Environmental Protection Agency Science Advisory Board (SAB) Staff Office Clean
Air Scientific Advisory Committee (CASAC) CASAC NO_x and SO_x Secondary NAAQS
Review Panel**

Dr. Donna Kenski, Director, Lake Michigan Air Directors Consortium, Rosemont, IL

Dr. Praveen Amar, Director, Science and Policy, NESCAUM, Boston, MA

Dr. Andrzej Bytnerowicz, Senior Scientist, Pacific Southwest Research Station, USDA Forest
Service, Riverside, CA

Ms. Lauraine Chestnut, Managing Economist, Stratus Consulting Inc., Boulder, CO

Dr. Ellis B. Cowling, Emeritus Professor, Colleges of Natural Resources and Agriculture and
Life Sciences, North Carolina State University, Raleigh, NC

Authors, Contributors, and Reviewers
(cont'd)

U.S. Environmental Protection Agency Science Advisory Board (SAB) Staff Office Clean Air Scientific Advisory Committee (CASAC) CASAC NO_x and SO_x Secondary NAAQS Review Panel

(cont'd)

Dr. Douglas Crawford-Brown, Professor and Director, Department of Environmental Sciences and Engineering, Carolina Environmental Program, University of North Carolina at Chapel Hill, Chapel Hill, NC

Dr. Charles T. Driscoll, Jr., Professor, Environmental Systems Engineering, College of Engineering and Computer Science, Syracuse University, Syracuse, NY

Dr. Paul J. Hanson, Distinguished R&D Staff Member, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

Dr. Rudolf Husar, Professor and Director, Mechanical Engineering, Engineering and Applied Science, Center for Air Pollution Impact & Trend Analysis (CAPITA), Washington University, St. Louis, MO

Dr. Dale Johnson, Professor, Department of Environmental and Resource Sciences, College of Agriculture, University of Nevada, Reno, NV

Dr. Naresh Kumar, Senior Program Manager, Environment Division, Electric Power Research Institute, Palo Alto, CA

Dr. Myron Mitchell, Distinguished Professor and Director, College of Environmental and Forestry, Council on Hydrologic Systems Science, State University of New York, Syracuse, NY

Mr. Richard L. Poirot, Environmental Analyst, Air Pollution Control Division, Department of Environmental Conservation, Vermont Agency of Natural Resources, Waterbury, VT

Dr. Armistead (Ted) Russell, Georgia Power Distinguished Professor of Environmental Engineering, Environmental Engineering Group, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA

Mr. David J. Shaw, Director, Division of Air Resources, New York State Department of Environmental Conservation, Albany, NY

Dr. Kathleen Weathers, Senior Scientist, Institute of Ecosystem Studies, Millbrook, NY

**U.S. Environmental Protection Agency Project Team
for Development of Integrated Scientific Assessment
for Oxides of Nitrogen and Sulfur**

Executive Direction

Dr. Ila Cote (Acting Director)—National Center for Environmental Assessment-RTP Division, (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Mary Ross—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Scientific Staff

Dr. Tara Greaver (NO_x and SO_x Team Leader)—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jeff Arnold—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jeffrey Herrick—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lingli Liu—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Kristopher Novak—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Paul F. Wagner—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

**U.S. Environmental Protection Agency Project Team
for Development of Integrated Scientific Assessment
for Oxides of Nitrogen and Sulfur**
(cont'd)

Technical Support Staff

Ms. Emily R. Lee—Management Analyst, National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Christine Searles—Management Analyst, National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Debra Walsh—Program Analyst, National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Richard Wilson—Clerk, National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Document Production Staff

Ms. Barbra H. Schwartz—Task Order Manager, Computer Sciences Corporation, 2803 Slater Road, Suite 220, Morrisville, NC 27560

Mr. John A. Bennett—Technical Information Specialist, Library Associates of Maryland, 11820 Parklawn Drive, Suite 400, Rockville, MD 20852

Mr. David Casson—Publication/Graphics Specialist, TekSystems, 1201 Edwards Mill Road, Suite 201, Raleigh, NC 27607

Mrs. Melissa Cesar—Publication/Graphics Specialist, Computer Sciences Corporation, 2803 Slater Road, Suite 220, Morrisville, NC 27560

Mr. Eric Ellis—Records Management Technician, InfoPro, Inc., 8200 Greensboro Drive, Suite 1450, McLean, VA 22102

Ms. Stephanie Harper—Publication/Graphics Specialist, TekSystems, 1201 Edwards Mill Road, Suite 201, Raleigh, NC 27607

Ms. Sandra L. Hughey—Technical Information Specialist, Library Associates of Maryland, 11820 Parklawn Drive, Suite 400, Rockville, MD 20852

Dr. Barbara Liljequist—Technical Editor, Computer Sciences Corporation, 2803 Slater Road, Suite 220, Morrisville, NC 27560

Ms. Molly Windsor—Graphic Artist, Computer Sciences Corporation, 2803 Slater Road, Suite 220, Morrisville, NC 27560

ANNEX ABBREVIATIONS AND ACRONYMS

ACCENT	Atmospheric Composition Change: the European Network of excellence
AIRMoN	Atmospheric Integrated Research Monitoring Network
AIRS	Atmospheric Infrared Sounder (instrument)
Al	aluminum
Al ³⁺	aluminum ion
Al _i	inorganic aluminum
Al ⁿ⁺	aluminum ion
Al _o	organic aluminum
Al(OH) ₃	aluminum hydroxide
ALSC	Adirondack Lake Survey Corporation
ALTM	Adirondack Long Term Monitoring
AMD	acid mine drainage
ANC	acid neutralizing capacity
AOD	aerosol optical depth
AQCD	Air Quality Criteria Document
AQEG	Air Quality Expert Group
AQI	Air Quality Index
AQS	Air Quality System (database)
Ar	argon
ARP	Acid Rain Program
ARS	Agricultural Research Service
As	arsenic
ASI	Acid Stress Index
asl	above sea level
ATMOS	Atmospheric Trace Molecule Spectroscopy
ATTILA	type of Lagrangian model
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
AVIRIS	Airborne Visible and Infrared Imaging Spectrometer
Ba	barium
BBW	Bear Brook Watershed
BBWM	Bear Brook Watershed, Maine
BC	black carbon
BCS	base-cation surplus
BGC	BioGeoChemical (model)
B-IBI	benthic index of biological integrity

BMPs	best management practices
BNF	bacterial nitrogen fertilization
Br	bromine
Br ⁻	bromine ion
Br ₂	molecular bromine
BrCl	bromine chloride
BrO	bromine oxide
BUV	Backscatter Ultraviolet Spectrometer
BUVD	Beneficial Use Values Database
C	carbon; concentration
¹² C	carbon-12, stable isotope of carbon
¹³ C	carbon-13, stable isotope of carbon
C _a	ambient air concentration
Ca	calcium
Ca ²⁺	calcium ion
CAA	Clean Air Act
CAAA	Amendments to the Clean Air Act
CAAAC	Clean Air Act Advisory Committee
CaCl ₂	calcium chloride
CaCO ₃	calcium carbonate
CALIPSO	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (satellite)
Ca(NO ₃) ₂	calcium nitrate
Ca(OH) ₂	calcium hydroxide
CAPMoN	Canadian Air and Precipitation Monitoring Network
CaSO ₄ ·2H ₂ O	gypsum
CASTNet	Clean Air Status and Trends Network
CB4	Carbon Bond 4 (model)
Cd	cadmium
CEC	cation exchange capacity
CENTURY	model that simulates carbon, nitrogen, phosphorus, sulfur, and water dynamics in the soil-plant system at monthly intervals over time scales of centuries and millennia
CFCs	chlorinated fluorocarbons
CG	cloud-to-ground (lightning flash)
chl <i>a</i>	chlorophyll <i>a</i>
CH ₄	methane
C ₂ H ₄	ethene
C ₂ H ₆	ethane

C_5H_8	isoprene
CH_3CHO	acetaldehyde
$CH_3C(O)$	acetyl radical
$CH_3C(O)OO$	acetyl peroxy radical
CH_2I_2	diiodomethane
CH_2O	formaldehyde
CH_3OOH	methyl hydroperoxide
CH_3-S-CH_3	dimethylsulfide, DMS
CH_3-S-H	methyl mercaptan
$(CH_3)_2SO$	dimethyl sulfoxide, DMSO
CH_3SO_3H	methanesulfonic acid
$CH_3-S-S-CH_3$	dimethyl disulfide, DMDS
C_i	interstitial air concentration
CL	critical load
Cl	chlorine
Cl^-	chlorine ion
Cl_2	molecular chlorine
CLaMS	type of Lagrangian model
CloudSat	NASA Earth observation satellite
$ClNO_2$	nitryl chloride
CMAQ	Community Multiscale Air Quality (modeling system)
CMSA	consolidated metropolitan statistical area
CO	carbon monoxide
CO_2	carbon dioxide
CO_3^-	carbonate
CONUS	continental United States
CPUE	catch per unit effort
CRREL	U.S. Army Cold Regions Research and Engineering Laboratory
CS	Consumer surplus
CS_2	carbon disulfide
CSS	coastal sage scrub (ecosystem)
CTM	chemical transport model
Cu	copper
CV	contingent valuation
CVM	contingent valuation method
Δ	difference; change
DayCent	model for daily biogeochemistry for forest, grassland, cropland, and savanna systems

DayCent-Chem	combination of DayCent-Chem and PHREEQC models
DC	dichotomous choice
DDRP	Direct Delayed Response Project
DDT	Damage Delay Time
DECOMP	decomposition model based on soil-plant system dynamics
DEP	Department of Environmental Protection
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DMDS	dimethyl disulfide, CH ₃ -S-S-CH ₃
DMS	dimethyl sulfide, CH ₃ -S-CH ₃
DMSO	dimethylsulfoxide
DNDC	Denitrification-Decomposition (model)
DO	dissolved oxygen
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
EBB	East Bear Brook
EC	elemental carbon
EEAs	Essential Ecological Attributes
ELA	Experimental Lakes Area
ELS	Eastern Lakes Survey
EMAP	Environmental Monitoring and Assessment Program
EMEFS	Eulerian Model Evaluation Field Study
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
EMF	ectomycorrhizal fungi
EOS	Earth Observation System
EPA	U.S. Environmental Protection Agency
EPT	Ephemeroptera-Plecoptera-Tricoptera (index)
ERP	Episodic Response Project
ESA	European Space Agency
EVRI	Environmental Valuation Reference Inventory
<i>F</i>	flux
F ⁻	fluorine ion
FAB	First-order Acidity Balance model
FACE	free-air CO ₂ enrichment (studies)
Fe	iron
FePO ₄	iron phosphate
FeS	iron sulfide

F-factor	fraction of the change in mineral acid anions that is neutralized by base cation release
FHM	Forest Health Monitoring
FIA	Forest Inventory and Analysis (program)
FISH	Fish in Sensitive Habitats (project)
FLEXPART	type of Lagrangian model
ForSAFE	three-component model using nitrogen, carbon cycling, and soil chemistry
FRM	Federal Reference Method
FTIR	Fourier Transform Infrared Spectroscopy
FW2	black carbon soot
F_x	flux
$\gamma\text{N}_2\text{O}_5$	reaction potential coefficient for N_2O_5
GAW	Global Atmospheric Watch (program)
GCE	Goddard Cumulus Ensemble (model)
GDP	gross domestic product
GEOS	Goddard Earth Observing System
GEOS-Chem	Goddard Earth Observing System (with global chemical transport model)
GEOS-1DAS	Goddard Earth Observing System Data Assimilation System
GFED	Global Fire Emissions Database
GHG	greenhouse gas
GOES	Geostationary Operational Environmental Satellites
GOME	Global Ozone Monitoring Experiment
g_s	stomatal conductance
GtC	global ton carbon
Gton	global ton
GWP	global warming potential
H	hydrogen; hydrogen atom
^2H	hydrogen-2, deuterium, stable isotope of hydrogen
H^+	proton, hydrogen ion; relative acidity
ha	hectare
HAPs	hazardous air pollutants
HBEF	Hubbard Brook Experimental Forest
HBES	Hubbard Brook Ecosystem Study
HBN	Hydrologic Benchmark Network
HC	hydrocarbon
HCHO	formaldehyde
HCl	hydrochloric acid

Hg	mercury
HNO ₂ , HONO	nitrous acid
HNO ₃ , HOONO	nitric acid
HNO ₄	pernitric acid
HO ₂	hydroperoxyl radical
H ₂ O ₂	hydrogen peroxide
HO ₂ NO ₂	peroxynitric acid
HOBr	hypobromous acid
HOCl	hypochlorous acid
HOX	hypohalous acid
HP	hedonic pricing
HPVM	
HSO ₃ ⁻	bisulfate ion
HSO ₄ ⁻	sulfuric acid ion
H ₂ S	hydrogen sulfide
H ₂ SO ₃	sulfurous acid
H ₂ SO ₄	sulfuric acid
HTC	
hν	photon with energy at wavelength ν
I	iodine
I ₂	molecular iodine
IA	Integrated Assessment
IADN	Integrated Atmospheric Monitoring Deposition Network
IC	intracloud (lightning flash)
ICARTT	International Consortium for Atmospheric Research on Transport and Transformation
ILWAS	Integrated Lake-Watershed Acidification Study
IPC	International Cooperative Programme
IEc	Industrial Economics
IIASA	International Institute for Applied Systems Analysis
IMPROVE	Interagency Monitoring of Protected Visual Environments
ICARTT	International Consortium for Atmospheric Research on Transport and Transformation
INO ₃	iodine nitrate
INTEX-NA	Intercontinental Chemical Transport Experiment - North America
IO	iodine oxide
IPCC	Intergovernmental Panel on Climate Change
IPCC-AR4	Intergovernmental Panel on Climate Change 4th Assessment Report
IPCC-TAR	Intergovernmental Panel on Climate Change 3rd Assessment Report

IQR	interquartile range
IR	infrared
ISA	Integrated Science Assessment
<i>J</i>	flux from a leaf
JPL	Jet Propulsion Laboratory
JRGCE	Jasper Ridge Global Climate Change Experiment
K	potassium
K ⁺	potassium ion
<i>K_a</i>	dissociation constant
<i>K_b</i>	dissociation constant
<i>K_H</i>	Henry's Law constant in M atm ⁻¹
KNO ₃	potassium nitrate
K _w	ion product of water
LAF	Lake Acidification and Fisheries
LAR	leaf-area ratio
LB	laboratory bioassay
LC _{0.01}	lethal concentration at which 0.01% of exposed animals die
LD ₃₃	lethal dose at which 33% of exposed animals die
LDH	lactic acid dehydrogenase
LIDAR	Light Detection and Ranging (remote sensing system)
LIF	laser-induced fluorescence
LIMS	Limb Infrared Monitor of the Stratosphere
LOD	limit of detection
LP	long-path
LRTAP	Long Range Transport of Air Pollution
LTER	Long-Term Ecological Research (program)
LTM	Long-Term Monitoring (project)
M	air molecule
MA	Millennium Ecosystem Assessment
MAGIC	Model of Acidification of Groundwater in Catchments (model)
MAHA	Mid-Atlantic Highlands Assessment of streams
MAQSIP	Multiscale Air Quality Simulation Platform (model)
MAT	moist acidic tundra
MAX-DOAS	multiple axis differential optical absorption spectroscopy
MBL	marine boundary layer
MDN	Mercury Deposition Network
MeHg	methylmercury
MEM	model ensemble mean

μeq	microequivalent
Mg	magnesium
Mg ²⁺	magnesium ion
MIMS	membrane inlet mass spectrometry
MM5	National Center for Atmospheric Research/Penn State Mesoscale Model, version 5
Mn	manganese
MOBILE6	Highway Vehicle Emission Factor Model
MODIS	Moderate Resolution Imaging Spectroradiometer
MOPITT	Measurement of Pollution in the Troposphere
MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
MOZART	Model for Ozone and Related Chemical Tracers
MPAN	peroxymethacrylic nitrate
MSA	metropolitan statistical area
Mt	million tons
N	nitrogen
N, n	number of observations
¹⁴ N	nitrogen-14, stable isotope of nitrogen
¹⁵ N	nitrogen-15, stable isotope of nitrogen
N ₂	molecular nitrogen; nonreactive nitrogen
NA	not available; insufficient data
Na	sodium
Na ⁺	sodium ion
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
Na ₂ MoO ₄	sodium molybdate
NAMS	National Air Monitoring Stations
NANI	Net anthropogenic nitrogen inputs
NAPAP	National Acid Precipitation Assessment Program
NASQAN	National Stream Quality Accounting Network
NARSTO	program formerly known as North American Regional Strategy for Atmospheric Ozone
NAS	National Academy of Sciences
NASA	National Aeronautics and Space Administration
Na ₂ SO ₄	sodium sulfate
NASQAN	National Stream Quality Accounting Network
NATTS	National Air Toxics Trends (network)

NAWQA	National Water Quality Assessment (program)
NCore	National Core Monitoring Network
NEE	net ecosystem exchange
NEG/ECP	New England Governors and Eastern Canadian Premiers
NEI	National Emissions Inventory
NEON	National Ecological Observatory Network
NEP	net ecosystem productivity
NFI	net factor income
NH ₃	ammonia
NH ₂	amino (chemical group)
NH ₄ ⁺	ammonium ion
NH ₄ Cl	ammonium chloride
NH ₄ NO ₃	ammonium nitrate
(NH ₄) ₂ SO ₄	ammonium sulfate
NH _x	category label for NH ₃ plus NH ₄ ⁺
NH _y	total reduced nitrogen
Ni	nickel
NILU	Norwegian Institute for Air Research
NITREX	NITROgen saturation EXperiments
nitro-PAH	nitro-polycyclic aromatic hydrocarbon
NLCD	National Land Cover Data
NMOC	nonmethane organic compound
NO	nitric oxide
NO ₂	nitrogen dioxide
NO ₂ ⁻	nitrite
NO ₃ ⁻	nitrate
N ₂ O	nitrous oxide
N ₂ O ₅	dinitrogen pentoxide
NOAA	U.S. National Oceanic and Atmospheric Administration
NOAA-ARL	U.S. National Oceanic and Atmospheric Administration Air Resources Laboratory
NOAEL	no-observed-adverse-effect level
NOEC	no-observed-effect concentration
NO _x	sum of NO and NO ₂
NO _y	sum of NO _x and NO _z ; odd nitrogen species; total oxidized nitrogen
NO _z	sum of all inorganic and organic reaction products of NO _x (HONO, HNO ₃ , HNO ₄ , organic nitrates, particulate nitrate, nitro-PAHs, etc.)
NPOESS	National Polar-orbiting Operational Environmental Satellite System
NPP	net primary production

NPS	National Park Service
N_r	reactive nitrogen
NRC	National Research Council
NS	nonsignificant
NSF	National Science Foundation
NSS	National Stream Survey
nss	non-sea salt
NSTC	National Science and Technology Council
NSWS	National Surface Water Survey
NTN	National Trends Network
NuCM	nutrient cycling model
O_2	molecular oxygen
O_3	ozone
^{16}O	oxygen-16, stable isotope of oxygen
^{18}O	oxygen-18, stable isotope of oxygen
^{19}O	oxygen-19, radioactive isotope of oxygen
OC	organic carbon
OCO	Orbiting Carbon Observatory
OCS	carbonyl sulfide
$O(^1D)$	electronically excited oxygen atom
OH	hydroxyl radical
OMI	Ozone Monitoring Instrument
$O(^3P)$	ground-state oxygen atom
P	phosphorus
P, p	probability value
P_1	1st percentile
P_5	5th percentile
P_{95}	95th percentile
P_{99}	99th percentile
PAHs	polycyclic aromatic hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PAN	peroxyacetyl nitrate
PANs	peroxyacyl nitrates
PARASOL	Polarization and Anisotropy of Reflectances for Atmospheric Sciences coupled with Observations from a Lidar (satellite)
Pb	lead
PBL	planetary boundary layer
PC	payment card

PCBs	polychlorinated biphenyl compounds
pH	relative acidity
P(HNO ₃)	production of nitric acid
PHREEQC	model for soil and water geochemical equilibrium
PIRLA	Paleocological Investigation of Recent Lake Acidification (projects)
pK _a	dissociation constant
PM	particulate matter
PM _{2.5}	particulate matter with aerodynamic diameter of ≤2.5 μm
PM ₁₀	particulate matter with aerodynamic diameter ≤10 μm
PM _{10-2.5}	particulate matter with aerodynamic diameter between 10 and 2.5 μm
PM-CAMx	Comprehensive Air Quality Model with extensions and with particulate matter chemistry
PnET	Photosynthesis and EvapoTranspiration (model)
PnET-BGC	Photosynthesis and EvapoTranspiration-BioGeoChemical (model)
PnET-CN	Photosynthesis and EvapoTranspiration model of C, water, and N balances
PnET-N-DNDC	Photosynthesis and EvapoTranspiration-Denitrification-Decomposition (model)
pNO ₃ ⁻	particulate nitrate
P(O ₃)	production of O ₃
PO ₄ ⁻ , PO ₄ ³⁻	phosphate
POPs	persistent organic pollutants
ppb	parts per billion
PPN	peroxypropionyl nitrate
ppt	parts per trillion
PRB	policy relevant background
PRE-STORM	Preliminary Regional Experiment for STORM
PROFILE	model using soil mineralogy as input
PS	producer surplus
pSO ₄ ²⁻	particulate sulfate
P(SO ₄ ²⁻)	production of sulfate
Q	flow rate; discharge
Q ₁₀	temperature coefficient
QAPP	Quality Assurance Project Plan
R	generic organic group attached to a molecule
R ²	coefficient of determination
r ²	correlation coefficient
R _a	aerodynamic resistance
R _b	boundary layer resistance

R_c	internal resistance
RADM	Regional Acid Deposition Model
RAMS	Regional Atmospheric Modeling System
RAPS	Regional Air Pollution Study
RCOO-s	strongly acidic organic anions
RC(O)OO	organic peroxy radical
RDT	Recovery Delay Time
REMAP	Regional Environmental Monitoring and Assessment Program
RH	relative humidity
RLTM	Regional Long-Term Monitoring
RMCC	Research and Monitoring Coordinating Committee
RMSE	root mean squared error
RO ₂	organic peroxy; organic peroxy
RONO ₂	organic nitrate
RO ₂ NO ₂	peroxynitrate
RP	revealed preferences
RR _x	lognormal-transformed response ratio
RuBisCO	ribulose-1,5-bisphosphate carboxylase/oxygenase
S	sulfur
³² S	sulfur-32, stable isotope of sulfur
³⁴ S	sulfur-34, stable isotope of sulfur
³⁵ S	sulfur-35, radioactive isotope of sulfur
SAA	sum of mineral acid anion concentrations
SAFE	Soil Acidification in Forest Ecosystems (model)
SAMAB	Southern Appalachian Man and the Biosphere (program)
SAMI	Southern Appalachian Mountains Initiative
SAO	Smithsonian Astrophysical Observatory
SAPRAC	Statewide Air Pollution Research Center
SBC	sum of base cation concentrations
SBUV	Solar Backscatter Ultraviolet Spectrometer
SC	safe concentration
SCAQS	Southern California Air Quality Study
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
Se	selenium; standard error
SEARCH	Southeastern Aerosol Research and Characterization Study (monitoring program)
Si	silicon
SIP	State Implementation Plan

SJAQS	San Joaquin Valley Air Quality Study
SLA	specific leaf area
SLAMS	State and Local Air Monitoring Stations
SMART	Simulation Model for Acidification's Regional Trends (model)
SMB	Simple Mass Balance (model)
SO	sulfur monoxide
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
SO ₃ ²⁻	sulfite
SO ₄ ²⁻	sulfate ion
S ₂ O	disulfur monoxide
SONEX	Subsonics Assessment Ozone and Nitrogen Oxides Experiment
SOS	Southern Oxidant Study
SOS/T	State of Science/Technology (report)
SO _x	sulfur oxides
SP	stated preferences
SPARROW	SPATIally Referenced Regressions on Watershed Attributes (model)
Sr	strontium
⁸⁶ Sr	strontium-86, stable isotope of strontium
⁸⁷ Sr	strontium-87, stable isotope of strontium
SRB	sulfate-reducing bacteria
SRP	soluble reactive phosphorus
SSWC	Steady State Water Chemistry (model)
STE	stratospheric-tropospheric exchange
STN	Speciation Trends Network
SUM06	seasonal sum of all hourly average concentrations ≥ 0.06 ppm
SVOC	semivolatile organic compound
SWAS	Shenandoah Watershed Study
τ	atmospheric lifetime
T	time; duration of exposure
TAF	Tracking and Analysis Framework (model)
T _{air}	air temperature
TAMM	Timber Assessment Market Model
TAR	Third Assessment Report
TC	total carbon; travel cost
TCM	travel cost method
TDLAS	Tunable Diode Laser Absorption Spectrometer
Tg	teragram

TIME	Temporally Integrated Monitoring of Ecosystems (program)
TN	total nitrogen
TOMS	Total Ozone Mapping Spectrometer
TOR	tropospheric ozone residual
TP	total phosphorus
TRACE-P	Transport and Chemical Evolution Over the Pacific
TSI	timber-stand improvement
TSS	total suspended solids
T _{water}	water temperature
UMD-CTM	University of Maryland Chemical Transport Model
UNECE	United Nations Economic Commission for Europe
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
UV	ultraviolet
UV-A	ultraviolet radiation of wavelengths from 320 to 400 nm
UV-B	ultraviolet radiation of wavelengths from 280 to 320 nm
V _d	deposition rate
VOC	volatile organic compound
VSD	Very Simple Dynamic (soil acidification model)
VTSSS	Virginia Trout Stream Sensitivity Study
WARMS	Waterfowl Acidification Response Modeling System
WATERSN	Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen
WBB	West Bear Brook
WEBB	Water, Energy, and Biogeochemical Budgets
WFPS	water-filled pore space
WGE	Working Group on Effects
WLS	Western Lakes Survey
WMO	World Meteorological Organization
WMP	Watershed Manipulation Project
WSA	Wadeable Stream Assessment (survey)
wt %	percent by weight
WTA	willingness-to-accept
WTP	willingness-to-pay
XNO ₃	nitrate halogen-X salt
XO	halogen-X oxide
Zn	zinc

ZnO

zinc oxide

ANNEX GLOSSARY

Acidification

The process of increasing the acidity of a system (e.g. lake, stream, and forest soil). Atmospheric deposition of acidic or acidifying compounds can acidify lakes, streams, and forest soils.

Algae

Photosynthetic, often microscopic and planktonic, organisms occurring in marine and freshwater ecosystems.

Algal bloom

A reproductive explosion of algae in a lake, river, or ocean.

Alpine

The biogeographic zone made up of slopes above the *tree line* characterized by the presence of rosette-forming *herbaceous* plants and low, shrubby, slow-growing woody plants.

ANC (Acid Neutralizing Capacity)

A key indicator of the ability of water to neutralize the acid or acidifying inputs it receives. This ability depends largely on associated biogeophysical characteristics.

Anthropogenic

Resulting from or produced by human beings.

Arid region

A land region of low rainfall, where 'low' is widely accepted to be <250 mm precipitation per year.

Atmosphere

The gaseous envelope surrounding the Earth. The dry atmosphere consists almost entirely of nitrogen and oxygen, together with trace gases including carbon dioxide and ozone.

Base cation saturation

The degree to which soil cation exchange sites are occupied with base cations (e.g. Ca^{2+} , Mg^{2+} , K^{+}) as opposed to Al^{3+} and H^{+} . Base cation saturation is a measure of soil acidification, with lower values being more acid. There is a threshold, whereby soils with base saturations under 20% (especially between 10-20%) are extremely sensitive to change.

Bioaccumulation

The phenomenon wherein toxic elements are progressively amassed in greater quantities as individuals farther up the food chain ingest matter containing those elements.

Biodiversity

The total diversity of all organisms and ecosystems at various spatial scales (from genes to entire biomes).

Buffering capacity

The ability of a body of water and its watershed to neutralize introduced acid.

Carbon sequestration

The process of increasing the carbon content of a reservoir/pool other than the atmosphere.

Catchment

An area that collects and drains rainwater.

Climate

Climate in a narrow sense is usually defined as the ‘average weather’, or more rigorously, as the statistical description in terms of the mean and variability of relevant quantities over a period of time ranging from months to thousands or millions of years. These quantities are most often surface variables such as temperature, precipitation, and wind. Climate in a wider sense is the state, including a statistical description, of the *climate system*. The classical period of time is 30 years, as defined by the World Meteorological Organization (WMO).

Critical load

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.

Denitrification

The anaerobic reduction of oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N₂O or N₂) by denitrifying bacteria.

Dry deposition

The removal of gases and particles from the atmosphere to surfaces in the absence of precipitation (e.g., rain or snow) or occult deposition.

Ecological community

A community of plants and animals characterized by a typical assemblage of species and their abundances.

Ecosystem services

Ecological processes or functions having monetary or non-monetary value to individuals or society at large. There are (i) supporting services such as productivity or biodiversity maintenance; (ii) provisioning services such as food, fibre, or fish; (iii) regulating services such as climate regulation or carbon sequestration; and (iv) cultural services such as tourism or spiritual and aesthetic appreciation.

Ecosystem

The interactive system formed from all living organisms and their abiotic (physical and chemical) environment within a given area. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, *biomes* at the continental scale, or small, well-circumscribed systems such as a small pond.

Eutrophication

The process whereby a body of water becomes over-enriched in nutrients, resulting in increased productivity (of algae or aquatic plants) and sometimes also decreased dissolved oxygen levels.

Eutrophy

Eutrophy generally refers to a state of nutrient enrichment, but it is commonly used to refer to condition of increased algal biomass and productivity, presence of nuisance algal populations, and a decrease in dissolved oxygen concentrations.

Evapotranspiration

The combined process of water evaporation from the Earth's surface and transpiration from vegetation.

Fen

The fen is a phase in the development of the natural succession from open lake, through reedbed, fen and carr, to woodland as the peat develops and its surface rises. Carr is the northern European equivalent of the swamp of the southeastern United States. It is fen overgrown with generally small trees of species.

Freshet

A great rise or overflowing of a stream caused by heavy rains or melted snow.

Greenhouse gas

Those gaseous constituents of the atmosphere, both natural and anthropogenic, that absorb and emit radiation at specific wavelengths within the spectrum of infrared radiation emitted by the Earth's surface, the atmosphere, and clouds. This property causes the greenhouse effect. Water vapour (H₂O), carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), and ozone (O₃) are the primary greenhouse gases in the Earth's atmosphere. As well as CO₂, N₂O, and CH₄, the *Kyoto Protocol* deals with the greenhouse gases sulphur hexafluoride (SF₆), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

Gross primary production

The total carbon fixed by plant through *photosynthesis*.

Heathland

A wide-open landscape dominated by low-growing woody vegetations such as heathers and heathland grasses. Heathlands generally occur on acidic, nutrient-poor, and often sandy and well-draining soils.

Hypoxic events

Events that lead to a deficiency of oxygen.

Integrated science assessment

An interdisciplinary process of combining, interpreting, and communicating knowledge from diverse scientific disciplines so that all relevant aspects of a complex societal issue can be evaluated and considered for the benefit of decision-making.

Invasive species and invasive alien species

A species aggressively expanding its range and population density into a region in which it is not native, often through outcompeting or otherwise dominating native species.

Leaching

The removal of soil elements or applied chemicals by water movement through the soil.

Lowland

In physical geography, lowland is any relatively flat area in the lower levels of regional elevation. The term can be applied to the landward portion of the upward slope from oceanic depths to continental highlands, to a region of depression in the interior of a mountainous region, to a plain of denudation, or to any region in contrast to a highland.

Net ecosystem production (NEP)

The difference between net primary production (NPP) and heterotrophic respiration (mostly decomposition of dead organic matter) of that ecosystem over the same area.

Net primary production (NPP)

The *gross primary production* minus *autotrophic respiration*, i.e., the sum of metabolic processes for plant growth and maintenance, over the same area.

Nitrification

A biological process by which ammonia is oxidized to nitrite and then to nitrate. This process is primarily accomplished by autotrophic nitrifying bacteria that obtain energy by reducing ammonium and/or nitrite to nitrate.

Nitrogen mineralization

Nitrogen mineralization is the process by which organic nitrogen is converted into plant-available inorganic forms (e.g. NH_3 or NH_4^+) by microorganisms.

Nitrogen-retention capacity

The length of time that an ecosystem can retain nitrogen by organisms (e.g., plant or microbe) and soil-organic matter. The nitrogen-retention capacity is highly affected by soil, vegetative, topographic, and land-use factors.

Nitrogen saturation

The condition when nitrogen inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem.

Occult deposition

The removal of gases and particles from the atmosphere to surfaces by fog or mist.

Ombrotrophic bog

An acidic peat-accumulating wetland that is rainwater (instead of groundwater) fed and thus particularly poor in nutrients.

pH

A measure of the relative concentration of hydrogen ions in a solution. The formula for calculating pH is: $\text{pH} = -\log_{10}[\text{H}^+]$, where $[\text{H}^+]$ represents the hydrogen ion concentration in moles per liter. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic and a pH greater than 7 is basic.

Phytoplankton

The plant forms of *plankton*. Phytoplankton are the dominant plants in the sea and are the basis of the entire marine food web. These single-celled organisms are the principal agents of photosynthetic carbon fixation in the ocean.

Primary Production

All forms of production accomplished by plants, also called primary producers. See *GPP*, *NPP*, and *NEP*.

Semi-arid regions

Regions of moderately low rainfall, which are not highly productive and are usually classified as *rangelands*. 'Moderately low' is widely accepted as between 100- and 250-mm precipitation per year.

Sensitivity

The degree to which a system is affected, either adversely or beneficially, by an effect of NO_x and/or SO_x pollution (e.g. acidification, n-nutrient enrichment, etc.). The effect may be direct (e.g., a change in growth in response to a change in the mean, range, or variability of N deposition) or indirect (e.g., changes in growth due to the direct effect of N consequently altering competitive dynamics between species and decreased biodiversity)

Streamflow

Water flow within a river channel, for example, expressed in m^3/s . A synonym for *river discharge*.

Surface runoff

The water that travels over the land surface to the nearest surface stream; *runoff* of a drainage *basin* that has not passed beneath the surface since precipitation.

Throughfall

The precipitation falling through the canopy of a forest and reaching the forest floor.

Trophic level

The position that an organism occupies in a food chain.

Tundra

A treeless, level, or gently undulating plain characteristic of the Arctic and sub-Arctic regions characterized by low temperatures and short growing seasons

Upland terrestrial ecosystem

Generally considered to be the ecosystems located at higher elevations directly above riparian zones and wetlands. Vegetation in an upland ecosystem is not in contact with groundwater or other permanent water sources.

Valuation

The economic or non-economic process of determining either the value of maintaining a given ecosystem type, state, or condition or the value of a change in an ecosystem, its components, or the services it provides.

Vulnerability

The degree to which a system is susceptible to, and unable to cope with, adverse effects of NO_x and/or SO_x air pollution. Vulnerability is a function the exposed and its *sensitivity*.

Welfare effects

Effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being, whether caused by transformation, conversion, or combination with other air pollutants (CAA 302(h)).

Wet deposition

The removal of gases and particles from the atmosphere to surfaces by rain or other precipitation.

Wetland

A transitional, regularly waterlogged area of poorly drained soils, often between an aquatic and a terrestrial *ecosystem*, fed from rain, surface water, or groundwater. Wetlands are characterized by a prevalence of vegetation adapted for life in saturated soil conditions.

Zooplankton

The animal forms of *plankton*. They consume *phytoplankton* or other zooplankton.

AX1. THE ATMOSPHERIC CHEMISTRY AND PHYSICS OF NITROGEN AND SULFUR OXIDES

AX1.1 INTRODUCTION

As noted in Chapters 1 and 2, the definition of “nitrogen oxides” (NO_x) appearing in the National Ambient Air Quality Standards (NAAQS) enabling legislation differs from the one used by atmospheric scientists and air quality control experts. The atmospheric sciences community defines NO_x as the sum of nitric oxide (NO) and nitrogen dioxide (NO_2). However, in the Federal Register Notice for the most recently published Air Quality Criteria Document (AQCD) for Oxides of Nitrogen (Federal Register, 1995), the term “nitrogen oxides” was used to “describe the sum of NO, NO_2 , and other oxides of nitrogen.” This Integrated Science Assessment (ISA) and its associated Annexes have used the legal rather than the specific scientific definition; hence the terms “oxides of nitrogen” and “nitrogen oxides” here refer to all forms of oxidized N compounds, including NO, NO_2 , and all other oxidized N-containing compounds transformed from NO and NO_2 .¹

Oxides of sulfur (SO_x) is defined here to include sulfur monoxide (SO), sulfur dioxide (SO_2) – the largest component of SO_x and the U.S. Environmental Protection Agency (EPA) Criteria Air Pollutant – sulfur trioxide (SO_3), and disulfur monoxide (S_2O). Of these, only SO_2 is present in the lower troposphere at concentrations relevant for ecological considerations.

NO and NO_2 , along with volatile organic compounds ((VOCs), the anthropogenic and biogenic hydrocarbons, aldehydes, etc.) and carbon monoxide (CO), are precursors in the formation of ozone (O_3), particulate matter (PM), and other elements of photochemical smog. Moreover, NO_2 is an oxidant, reacting to form other photochemical oxidants including organic nitrates (RONO_2) like the peroxyacyl nitrates (PANs), and can react with toxic compounds like the polycyclic aromatic hydrocarbons (PAHs) to form nitro-PAHs, some of which demonstrate greater toxicity than either reactant alone. NO_2 and SO_2 can be also be further oxidized to the

¹ This follows usage in the Clean Air Act Section 108(c): “Such criteria [for oxides of nitrogen] shall include a discussion of nitric and nitrous acids, nitrites, nitrates, nitrosamines, and other carcinogenic and potentially carcinogenic derivatives of oxides of nitrogen.” The category label used by the air pollution research and control community for the sum of all oxidized N compounds including those listed in Section 108(c) is NO_y .

1 strong mineral acids nitric acid (HNO₃) and sulfuric acid (H₂SO₄), respectively, thereby
2 contributing to the acidity of cloud, fog, and rain water and ambient particles.

3 Ammonia (NH₃) is included in this ISA both because its oxidation can be a minor source
4 of NO_x and because it is the precursor for ammonium ion (NH₄⁺), which plays a key role in
5 neutralizing acidity in ambient particles and in cloud, fog, and rain water. Excess NH₃ is also an
6 actor in nitrification of aqueous and terrestrial ecosystems, participating alone and together with
7 NO_x in the N cascade (Galloway et al., 2003). (NH₃ and NH₄⁺ are conventionally grouped
8 together under the category label NH_x.) Additionally, NH₃ is involved in the ternary nucleation
9 of new particles and reacts with gas-phase HNO₃ to form ammonium nitrate (NH₄NO₃), a major
10 constituent of ambient PM pollution in many areas of the continental United States (CONUS).

11 12 13 **AX1.2 NITROGEN OXIDES IN THE TROPOSPHERE**

14 15 **AX1.2.1 Gas-Phase Chemistry**

16 The generalized chemistry of reactive N compounds in the atmosphere is summarized in
17 Figure AX1.2-1 and described in greater detail below. NO_x is emitted by combustion sources
18 mainly as NO though with ~5 to 10% NO₂. The major combustion sources of NO_x, shown
19 schematically in Figure AX1.2-1, are motor vehicles and electrical utilities, although stationary
20 engines, off-road vehicles, and industrial facilities also emit NO_x. In addition to these emissions
21 from fossil fuel combustion, biomass burning produces NO_x. And apart from these
22 anthropogenic sources, there are also smaller natural sources, which include microbial activity in
23 soils, lightning, and wildfires.

24 NO and NO₂ are often grouped together with the category label NO_x because they are
25 emitted together and will rapidly interconvert as shown in the inner box in Figure AX1.2-1. NO₂
26 reacts with various free radicals in the gas phase and on surfaces in multiphase processes to form
27 the oxidation products shown in Figure AX1.2-1. These products include inorganic species
28 (shown on the left side of the outer box in Figure AX1.2-1) and organic species (shown on the
29 right side of the outer box in Figure AX1.2-1). The oxidized N species in the outer box are often
30 collectively termed NO_z: thus, NO_x + NO_z = NO_y. The time scale for reactions of NO_x to form
31 products shown in the outer box of Figure AX1.2-1 typically ranges from a few hours during

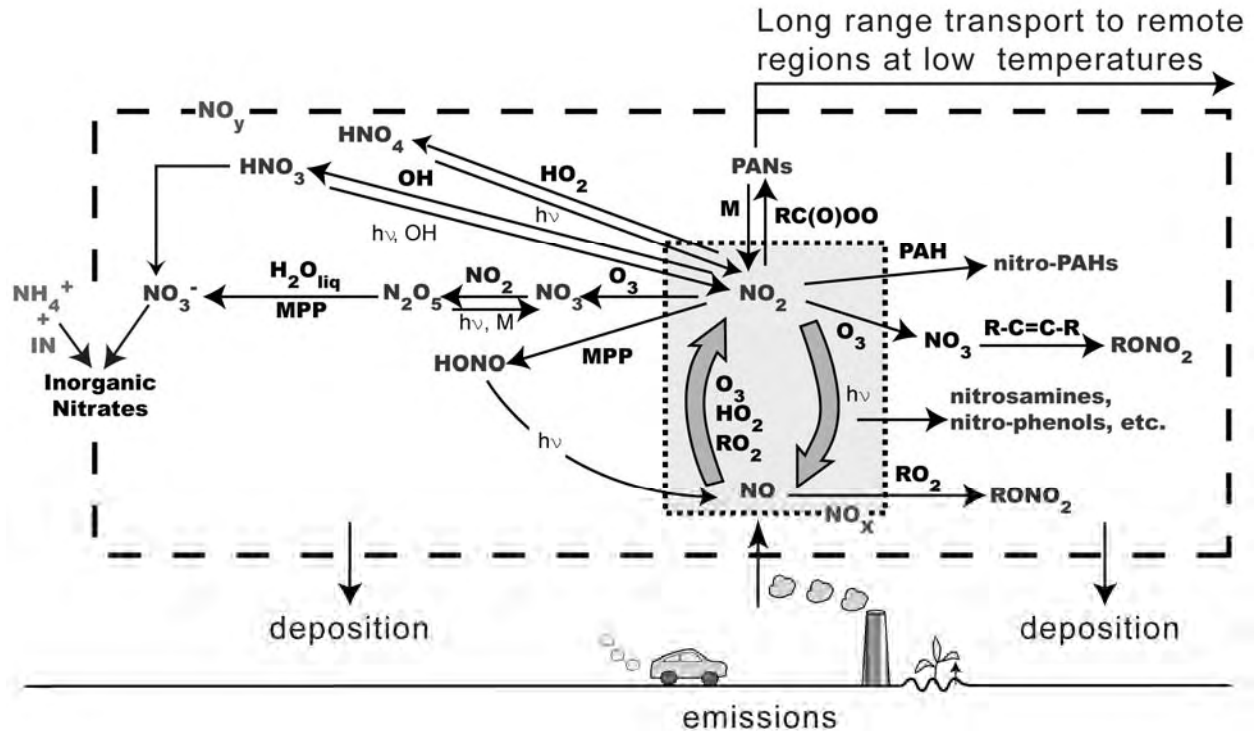


Figure AX1.2-1. Schematic diagram of the cycle of reactive, oxidized nitrogen species in the atmosphere. IN refers to inorganic particulate species (e.g., Na^+ , Ca^{++}), MPP to multiphase processes, $h\nu$ to a solar photon, and R to an organic radical. Particulate phase organic nitrates are also formed from the species on the right side of the figure.

1 summer days of greater photon flux to roughly 24 h during winter hours with less heat and
 2 sunlight.

3 As shown in Figure AX1.2-1, different sources emit NO_x at different altitudes: mobile
 4 sources nearer the earth's surface, and fixed point sources like power plants emitting from stacks
 5 10s or 100s of meters above the surface. Because prevailing winds aloft are generally stronger
 6 than those at the surface, emissions from elevated point sources can be distributed over a wider
 7 area than those emitted at the surface; and because of the time required to mix emissions down to
 8 the surface, NO_x emissions from elevated sources will tend to be transformed to the more
 9 oxidized NO_z products before they reach the surface at some distance from the source.

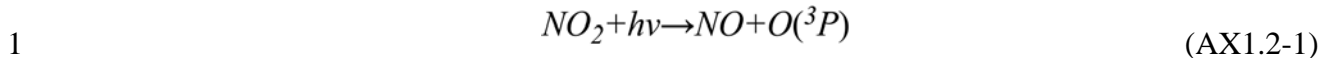
10 The concentrations ($[\]$) and atmospheric lifetimes (τ) of inorganic and organic products
 11 from reactions of NO_x vary widely in space and time. Inorganic reaction products include

1 nitrous acid (HNO_2), HNO_3 , pernitric acid (HNO_4), and particulate nitrate (pNO_3^-). While a
2 broad range of organic N compounds are emitted by combustion sources (e.g., nitrosamines and
3 nitro-PAHs), they are also formed in the atmosphere from reactions of NO and NO_2 . These
4 include PAN and isoprene nitrates, other nitro-PAHs, and the more recently identified nitrated
5 quinones. By far the largest mass fractions of NO_Z products shown in the outer box of Figure
6 AX1.2-1 are in the form of PAN and HNO_3 , although other RONO_2 , e.g., isoprene nitrates and
7 specific biogenic PANs can be important at locations nearer to biogenic sources (Horowitz et al.,
8 2007; Singh et al., 2007).

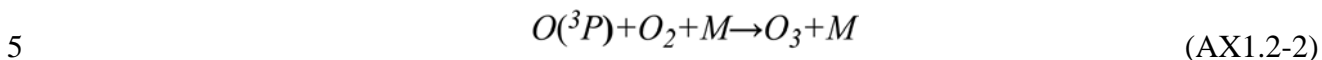
9 The role of NO_X in O_3 formation was exhaustively reviewed in Chapter 2, Section 2.2 of
10 the most recently published AQCD for O_3 (U.S. Environmental Protection Agency, 2006), and
11 has been presented in numerous texts (e.g., Seinfeld and Pandis, 1998; Jacob, 1999; Jacobson,
12 2002). The mechanisms for transporting the NO_X O_3 precursors, the factors controlling the
13 efficiency of O_3 production ($\text{P}(\text{O}_3)$) from NO_X , methods for calculating O_3 from its precursors,
14 and the methods for measuring NO_Y were all reviewed in Section 2.6 of the 2006 O_3 AQCD.
15 Here we present only the salient points from that 2006 O_3 AQCD, updated where appropriate to
16 reflect new data relevant for NO_X and its role in ecological effects.

17 Because O_3 changes are strongly nonlinear in the concentrations of its precursors VOC
18 and NO_X , O_3 is unlike other secondarily formed atmospheric species whose rates of formation
19 vary directly with their precursor emissions. At the low $[\text{NO}_X]$ usually found in environments
20 ranging from remote continental areas to rural and suburban areas downwind of urban centers,
21 the net $\text{P}(\text{O}_3)$ increases with increasing $[\text{NO}_X]$. At the high $[\text{NO}_X]$ found in downtown
22 metropolitan areas and especially near busy streets and roadways and in power plant plumes,
23 excess NO titrates O_3 , and excess hydroxyl radicals (OH) combine with NO_2 removing them
24 from the $\text{P}(\text{O}_3)$ chain. In this high $[\text{NO}_X]$ regime, NO_2 scavenges OH radicals that would
25 otherwise oxidize VOCs to produce peroxy radicals (RO_2), which would in turn oxidize NO to
26 NO_2 . In the low $[\text{NO}_X]$ regime, oxidation of VOCs generates excess free radicals; hence, $\text{P}(\text{O}_3)$
27 varies more nearly monotonically with changes in $[\text{NO}_X]$ there. Between these two regimes lies
28 a transition zone in which $\text{P}(\text{O}_3)$ and O_3 accumulation show only weak dependence on $[\text{NO}_X]$.

29 A rapid photochemical cycle in the troposphere involving photolysis of NO_2 by solar
30 UVA radiation yields NO and a ground-state oxygen atom, $\text{O}(^3\text{P})$

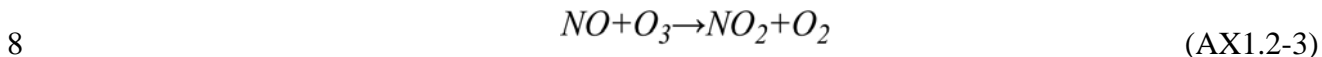


2 This ground-state oxygen atom can then combine with molecular oxygen (O₂) to form O₃, and,
3 colliding with any molecule from the surrounding air ((M) = N₂, O₂, etc.), the newly formed O₃
4 molecule loses excess energy and is stabilized

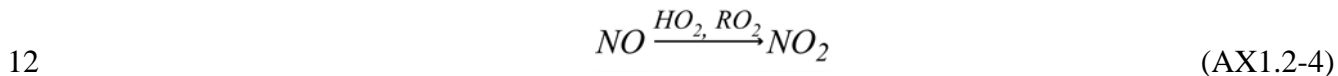


6 Reaction AX1.2-2 is the only significant reaction for forming O₃ in the troposphere.

7 NO and O₃ react to reform NO₂

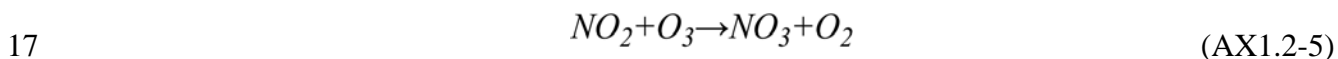


9 Reaction AX1.2-3 is responsible for O₃ decreases and NO₂ increases found near sources of NO
10 especially at night when actinic flux is 0. Oxidation of reactive VOCs leads to the formation of
11 reactive radical species permitting conversion of NO to NO₂ without O₃ as in Reaction AX1.2-4

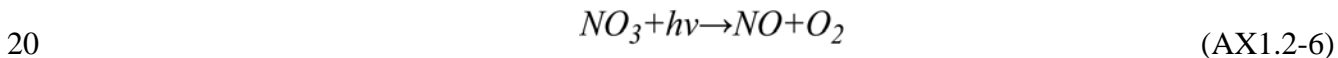


13 Ozone, therefore, can accumulate as NO₂ photolyzes as in Reaction AX1.2-1, followed
14 by Reaction AX1.2-2. Specific mechanisms for the oxidation of a number of VOCs were
15 discussed in the O₃ AQCD (U.S. Environmental Protection Agency, 2006).

16 The reaction of NO₂ with O₃ leads to the formation of NO₃⁻ radicals

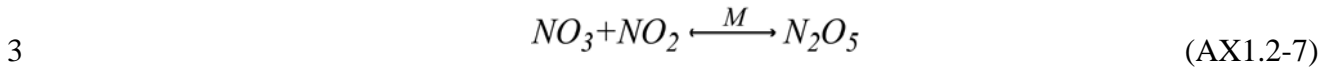


18 However, because the NO₃⁻ radical photolyzes rapidly with τ ~5 s during the photochemically
19 most active period of the day near local solar noon (Atkinson et al., 1992) by the reaction



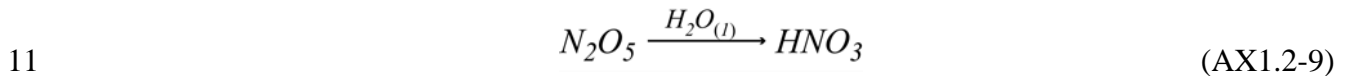
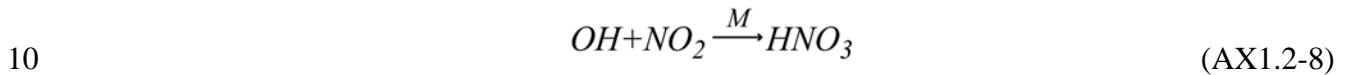
21 its concentration remains low during daylight hours. However, [NO₃⁻] can increase after sunset
22 to nighttime concentrations of <5 × 10⁷ to 1 × 10¹⁰ molecules cm⁻³ (equivalently <2 to 430 parts
23 per trillion (ppt)) over continental areas influenced by anthropogenic emissions of NO_x
24 (Atkinson et al., 1986). And during the night, when there can be no photochemically driven

1 oxidation, NO_3^- , not OH, is the system's chief oxidant. Nitrate radicals can combine with NO_2
2 to form dinitrogen pentoxide (N_2O_5)



4 and N_2O_5 both photolyzes and thermally decomposes back to NO_2 and NO_3 during the day.
5 However, $[\text{N}_2\text{O}_5]$ can accumulate during the night to parts per billion (ppb) levels in polluted
6 urban atmospheres.

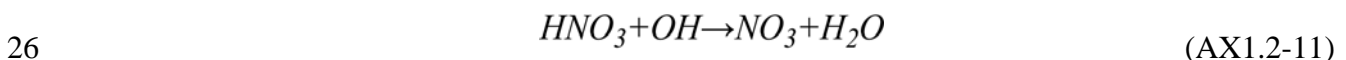
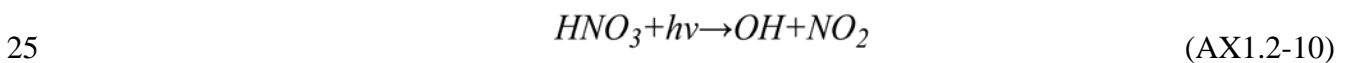
7 The tropospheric chemical removal processes for NO_x include reaction of NO_2 with the
8 OH radical mentioned above and hydrolysis of N_2O_5 in aqueous aerosol solutions, both
9 producing HNO_3



12 The gas-phase reaction of OH with NO_2 in Reaction AX1.2-8 is a major removal process for
13 NO_x in the troposphere. The timescale for conversion of NO_x to HNO_3 in the planetary
14 boundary layer (PBL) at 40 °N latitude ranges from ~4 h in July to ~16 h in January; at 25 °N
15 latitude, the timescale is 4 to 5 h; and at 50 °N latitude, from 4 to 20 h (Martin et al., 2003).
16 Reaction AX1.2-8 limits NO_x τ to a range of hours to days.

17 In addition to gas-phase HNO_3 , Golden and Smith (2000) have shown on the basis of
18 theoretical calculations that pernitrous acid (HOONO) is also produced by the reaction of NO_2
19 and OH radicals. However, this production path likely represents only a minor yield of ~15% at
20 the surface (Jet Propulsion Laboratory, 2003), and pernitrous acid will also thermally decompose
21 and can photolyze.

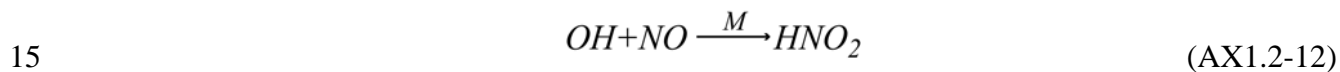
22 Gas-phase HNO_3 formed by Reaction AX1.2-8 undergoes wet and dry deposition to the
23 surface, and uptake by ambient aerosol particles. In addition, HNO_3 photolyzes and reacts with
24 OH radicals



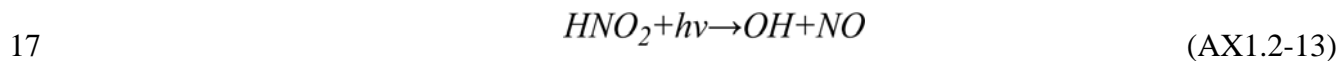
1 The HNO₃ τ with respect to these two reactions is long enough for HNO₃ to act as a reservoir
2 species for NO_x during long range transport, contributing in this way to [NO₂] after photolysis
3 returns NO₂ as in AX1.2-10, and hence to P(O₃) in areas remote from the source region of the
4 NO_x that formed the original HNO₃.

5 Geyer and Platt (2002) concluded that Reaction AX1.2-9 constituted ~10% of the
6 removal of NO_x at a site near Berlin, Germany during spring and summer. More recent work in
7 the northeastern United States indicates that this reaction proceeds at a faster rate in power plant
8 plumes than in urban plumes (Brown et al., 2006a,b; Frost et al., 2006). Furthermore,
9 uncertainty remains concerning this reaction's seasonal significance. During winter, its relative
10 importance to the total P(HNO₃) budget could be significantly greater because of the lower
11 concentration of OH radicals (from lower actinic flux) and the enhanced stability of N₂O₅ (due to
12 lower temperatures). Note, too, that Reaction AX1.2-9 is a heterogeneous reaction, which also
13 increases its uncertainty and variability.

14 Hydroxyl radicals also can react with NO to produce nitrous acid (HNO₂)

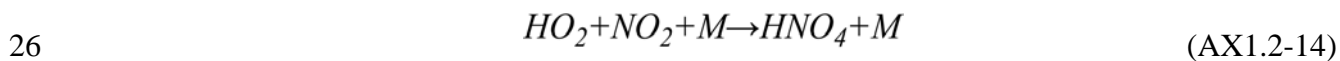


16 In daylight, HNO₂ is rapidly photolyzed back to the original reactants



18 Harris et al. (1982) suggested that photolysis of HNO₂ at sunrise could provide an important
19 early-morning source of OH radicals to drive O₃ formation. However, Reaction AX1.2-12 is a
20 negligible source of HNO₂, which is formed mainly by multiphase processes (see Annex Section
21 AX1.2-3). At night, heterogeneous reactions of NO₂ in aerosols or at the earth's surface result in
22 accumulation of HNO₂ (Lammel and Cape, 1996; Jacob, 2000; Sakamaki et al., 1983; Pitts et al.,
23 1984; Svensson et al., 1987; Jenkin et al., 1988; Lammel and Perner, 1988; Notholt et al.,
24 1992a,b).

25 Hydroperoxy (HO₂) radicals can react with NO₂ to produce HNO₄



1 which then can thermally decompose and photolyze back to its original reactants. The acids
2 formed in these gas-phase reactions are all water soluble, and thus can be incorporated into cloud
3 water droplets and into the aqueous phase of particles.

4 Although the τ of HNO_4 and N_2O_5 are on the order of only minutes-to-hours during
5 typical summer conditions, they can be much longer at lower temperatures and in the dark,
6 acting as HNO_3 does to transport NO_2 to areas remote from its original sources; however, these
7 two species are significantly less important for NO_2 transport than HNO_3 and PAN.

8 N_2O is another gas-phase oxide of nitrogen and has a τ of ~ 114 years. This long lifetime
9 results from N_2O having effectively no chemistry in the lower troposphere on urban and regional
10 scales. The chief N_2O loss pathway (with a quantum yield of ~ 1) is the photodissociation
11 process

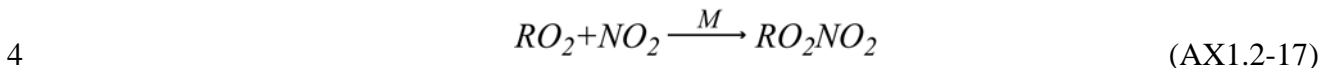
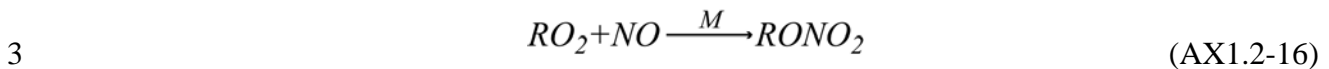


13 driven by short wavelength UV present in the stratosphere. Although there are no tropospheric
14 reactions to consider, N_2O is a greenhouse gas (GHG) with a global warming potential (GWP)
15 on the conventional 100-year time horizon of ~ 296 – i.e., N_2O is nearly 300 times more effective
16 for trapping heat in the atmosphere than carbon dioxide (CO_2) over a 100-year period (IPCC,
17 2001); its sources and role in the total budget of U.S. GHG are described with the emissions
18 sources of other nitrogen oxides in ISA Chapter 3 and Annex 2.

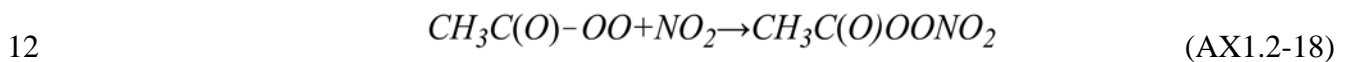
19 Because N_2O has extremely low reactivity, and hence a long τ in the troposphere, its
20 radiative forcing climate effects in the stratosphere can be both direct and indirect. By
21 comparison, the primary climate effects of NO and NO_2 are indirect and result from their role in
22 promoting $\text{P}(\text{O}_3)$ in the troposphere and, to a lesser degree, lower stratosphere, where NO_x has
23 positive radiative forcing effects. Additionally, NO_x emissions from high-altitude aircraft are
24 also likely to decrease methane (CH_4) concentrations, thereby having a negative radiative forcing
25 (IPCC, 1996). EPA does not compute GWPs for NO_x , SO_x , PM, or CO because there is no
26 agreed method to estimate the contributions from these gases that are short-lived in the
27 atmosphere, have strong spatial variability, or have only indirect effects on radiative forcing
28 (IPCC, 1996).

29 A broad range of organic N compounds can be directly emitted by combustion sources or
30 formed in the atmosphere from NO_x emissions. Oxidation of VOCs produces organic peroxy

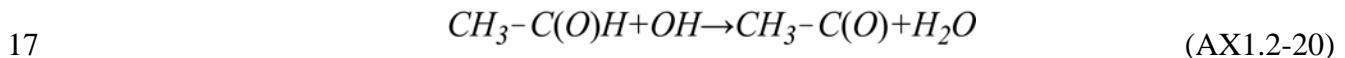
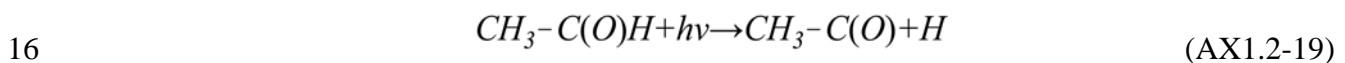
1 radicals (RO₂), as discussed in the O₃ AQCD (U.S. Environmental Protection Agency, 2006).
2 Reaction of RO₂ radicals with NO and NO₂ produces RONO₂ and peroxy nitrates (RO₂NO₂)



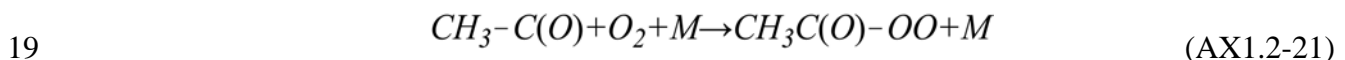
5 Reaction AX1.2-16 is a minor branch for the reaction of RO₂ with NO; the major branch
6 produces RO and NO₂, as described in the section that follows. However, the RONO₂ yield
7 increases with carbon number (Atkinson, 2000). The most important of these organic nitrates is
8 PAN, the dominant member of the broader family of peroxyacyl nitrates which includes
9 peroxypropionyl nitrate (PPN) of anthropogenic origin and peroxy methacrylic nitrate (MPAN)
10 produced from oxidation of the dominant biogenic VOC, isoprene (C₅H₈). The PANs are formed
11 by the combination reaction of acetyl peroxy radicals with NO₂



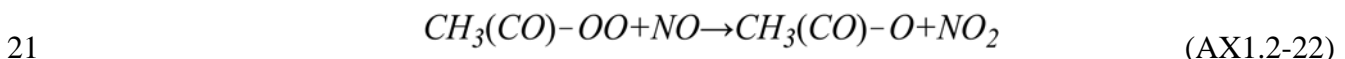
13 where the acetyl peroxy radicals are formed mainly during the oxidation of ethane (C₂H₆).
14 Acetaldehyde (CH₃CHO) is formed as an intermediate species during the oxidation of C₂H₆ and
15 can be photolyzed or react with OH radicals to yield acetyl radicals



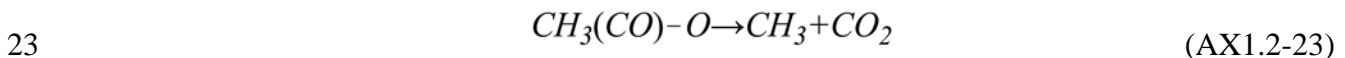
18 Acetyl radicals then react with O₂ to yield acetyl peroxy radicals



20 However, acetyl peroxy radicals will react with NO in areas of high NO concentrations



22 and the acetyl-oxy radicals will then decompose



1 Thus, formation of PAN is favored at conditions of the high ratios of NO_2 to NO most typically
2 found under low NO_x conditions. The PANs are thermally labile and will photolyze back to
3 their reactants on timescales of a few hours during warm sunlit conditions, having τ with respect
4 to thermal decomposition ranging from ~ 1 h at 298 K to ~ 2.5 days at 273 K, up to several weeks
5 at 250 K. Thus, they can provide an effective sink for NO_x at cold temperatures and high solar
6 zenith angles, allowing release of NO_2 as air masses warm, in particular by subsidence. The
7 PANs are also removed by uptake to vegetation (Sparks et al., 2003; Teklemariam and Sparks,
8 2004). To a lesser extent, HNO_3 will act in a similar way, but its high solubility and fast
9 deposition rate (V_d) mean that it is removed from the atmosphere by uptake on aqueous aerosols
10 and cloud droplets or to the surface faster than PAN.

11 Other RONO_2 may react further, depending on the functionality of the R group, but will
12 typically not return NO_2 and hence are viewed as a permanent sink for NO_x . The magnitude of
13 this sink is usually small compared to that of HNO_3 formation, but the formation of C_5H_8 nitrates
14 may be a significant sink for NO_x in the United States in summer (Liang et al., 1998).

15 The RO_2NO_2 produced by Reaction AX1.2-17 are unstable, with τ on the order of a few
16 minutes owing to thermal decomposition back to the original reactants. Thus, they, too, are
17 ineffective NO_x transport species or sinks.

18

19 **AX1.2.2 Heterogeneous-Phase Chemistry**

20 In addition to gas-phase reactions, reactions occurring on surfaces or occurring in
21 multiple phases are important for the formation of HNO_2 and pNO_3^- . These reactions can occur
22 on the surfaces of suspended particles, soil, and buildings and within aqueous media.

23 Using aircraft measurements over the northeastern United States, Brown et al. (2006)
24 found that the uptake coefficient for N_2O_5 , $\gamma\text{N}_2\text{O}_5$, on the surfaces of particles depends strongly
25 on their sulfate (SO_4^{2-}) content. They found that $\gamma\text{N}_2\text{O}_5$ was highest (0.017) in regions where the
26 aerosol [SO_4^{2-}] was highest and lower elsewhere (< 0.0016). This result contrasts with that of
27 Dentener and Crutzen (1993) who concluded that $\gamma\text{N}_2\text{O}_5$ would be independent of aerosol
28 composition, based on a value for $\gamma\text{N}_2\text{O}_5$ of 0.1, implying that the heterogeneous hydrolysis of
29 N_2O_5 would be saturated for typical ambient aerosol surface areas.

30 The importance of this reaction to tropospheric chemistry depends on the actual value of
31 $\gamma\text{N}_2\text{O}_5$. Recent laboratory studies on SO_4^{2-} and organic aerosols indicate that the $\gamma\text{N}_2\text{O}_5$ is in the

1 range of 0.01-0.05 (Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003). Tie et al.
2 (2003) found that a value of 0.04 in their global model gave the best simulation of observed
3 $[\text{NO}_x]$ over the Arctic in winter. If $\gamma\text{N}_2\text{O}_5$ is 0.01 or lower, there may be difficulty explaining the
4 loss of NO_y and formation of pNO_3^- , especially during winter. A decrease in N_2O_5 retards
5 removal of NO_x by leaving more NO_2 available for reaction, and hence increases $\text{P}(\text{O}_3)$. Based
6 on the consistency between measurements of NO_y partitioning and gas-phase models, Jacob
7 (2000) considers it unlikely that HNO_3 is recycled to NO_x in the lower troposphere in significant
8 concentrations. However, only one of the reviewed studies (Schultz et al., 2000) was conducted
9 in the marine troposphere and none was conducted in the marine boundary layer (MBL). An
10 investigation over the equatorial Pacific reported discrepancies between observations and theory
11 (Singh et al., 1996) which might be explained by HNO_3 recycling. It is important to recognize
12 that both Schultz et al. (2000) and Singh et al. (1996) involved aircraft sampling at altitudes
13 above the MBL which generally were greatly depleted in sea salt aerosols, total NO_3 (defined to
14 be $\text{HNO}_3 + \text{pNO}_3^-$), and large fractions of NO_y (see, e.g., Huebert et al., 1996). Consequently,
15 some caution is warranted when interpreting constituent ratios and NO_y budgets based on such
16 data.

17 Recent work in the Arctic has quantified significant photochemical recycling of NO_3 to
18 NO_x and attendant perturbations of OH chemistry in snow (Honrath et al., 2000; Dibb et al.,
19 2002; Domine and Shepson, 2002) which suggest the possibility that similar multiphase
20 pathways could occur in aerosols. As mentioned above, NO_3^- is photolytically reduced to NO_2^-
21 (Zafiriou and True, 1979) in acidic sea salt solutions (Anastasio et al., 1999). Further photolytic
22 reduction of NO_2^- to NO (Zafiriou and True, 1979) could provide a possible mechanism for
23 HNO_3 recycling. Early experiments reported production of NO_x during the irradiation of
24 artificial seawater concentrates containing NO_3^- (Petriconi and Papee, 1972). Based on the
25 above, HNO_3 recycling in sea salt aerosols is potentially important and warrants further
26 investigation. Other possible recycling pathways involving highly acidic aerosol solutions and
27 soot are reviewed by Jacob (2000).

28 Stemmler et al. (2006) studied the photosensitized reduction of NO_2 to HNO_2 on humic
29 acid films using radiation in the UVA through the visible spectral regions. They also found
30 evidence for reduction occurring in the dark, reactions which may occur involving surfaces
31 containing partly oxidized aromatic structures. For example, Simpson et al. (2006) found that

1 aromatic compounds constituted ~20% of organic films coating windows in downtown Toronto.
2 They calculated production rates of HNO₂ that are compatible with observations of high HNO₂
3 levels in a variety of environments. The photolysis of HNO₂ formed this way could account for
4 up to 60% of the integrated source of OH radicals in the inner planetary boundary layer. A
5 combination of high [NO₂] and surfaces of soil and buildings and other man-made structures
6 exposed to diesel exhaust would then be conducive to HNO₂ formation and, hence, to high [OH].

7 Ammann et al. (1998) reported the efficient conversion of NO₂ to HNO₂ on fresh soot
8 particles in the presence of water. They suggested that interaction between NO₂ and soot
9 particles may account for high mixing ratios of HNO₂ observed in urban environments.
10 Conversion of NO₂ to HNO₂ and subsequent photolysis and HNO₂ to NO + OH would constitute
11 a NO_x-catalyzed O₃ sink involving snow. High [HNO₂] can lead to the rapid growth in [OH]
12 shortly after sunrise, giving a “jump start” to photochemical smog formation. Prolonged
13 exposure to ambient oxidizing agents appears to deactivate this process. Broske et al. (2003)
14 studied the interaction of NO₂ on secondary organic aerosols and concluded that the uptake
15 coefficients were too low for this reaction to be an important source of HNO₂ in the troposphere.

16 Choi and Leu (1998) evaluated the interactions of HNO₃ on model black carbon soot
17 (FW2), graphite, hexane, and kerosene soot. They found that HNO₃ decomposed to NO₂ and
18 H₂O at higher HNO₃ surface coverages, i.e., P(HNO₃) > 10⁻⁴ Torr. None of the soot models
19 used were reactive at low HNO₃ coverages, at P(HNO₃) = 5 × 10⁻⁷ Torr or at temperatures below
20 220 K. They conclude that it is unlikely that aircraft soot in the upper troposphere/lower
21 stratosphere reduces HNO₃.

22 Heterogeneous production on soot at night is thought to be the mechanism by which
23 HNO₂ accumulates to provide an early morning source of HO_x (HO_x = OH + HO₂) in high NO_x
24 environments (Harrison et al., 1996; Jacob, 2000). HNO₂ has been frequently observed to
25 accumulate to levels of several ppb overnight, and this has been attributed to soot chemistry
26 (Harris et al., 1982; Calvert et al., 1994; Jacob, 2000).

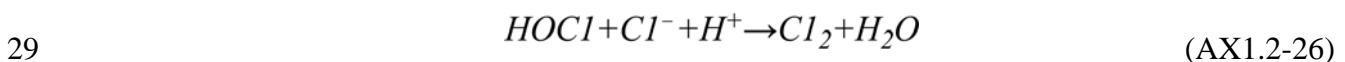
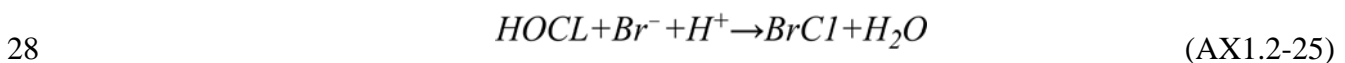
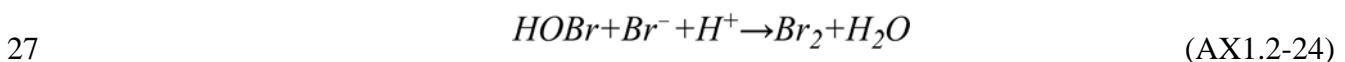
27 Longfellow et al. (1999) observed the formation of HNO₂ when CH₄, propane, hexane,
28 and kerosene soots were exposed to NO₂. They suggested that this reaction may account for
29 some part of the unexplained high [HNO₂] observed in urban areas. They commented that
30 without details about the surface area, porosity, and amount of soot available for this reaction,
31 reactive uptake values cannot be estimated reliably. Further, soot and NO₂ are produced in close

1 proximity during combustion, and large quantities of HNO₂ have been observed in aircraft
2 plumes (Longfellow et al., 1999).

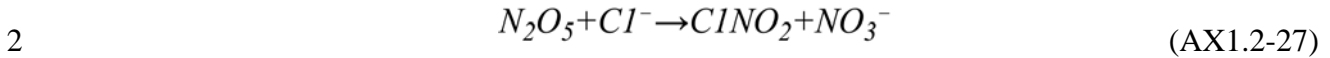
3 Saathoff et al. (2001) studied the heterogeneous loss of NO₂, HNO₃, NO₃/N₂O₅,
4 HO₂/HO₂NO₂ on soot aerosol using a large aerosol chamber. Reaction periods of up to several
5 days were monitored and results used to fit a detailed model. Saathoff et al. derived reaction
6 probabilities at 294 K and 50% relative humidity (RH) for NO₂, NO₃, HO₂, and HO₂NO₂
7 deposition to soot; for HNO₃ reduction to NO₂; and for N₂O₅ hydrolysis. When these
8 probabilities were included in photochemical box model calculations of a 4-day smog event, the
9 only noteworthy influence of soot was a 10% reduction in the second day [O₃] maximum, for a
10 soot loading of 20 μg m⁻³; i.e., roughly a factor of 10 greater than observed black carbon
11 loadings seen in urban areas of the United States, even during air pollution episodes.

12 Muñoz and Rossi (2002) conducted Knudsen cell studies of HNO₃ uptake on black and
13 grey decane soot produced in lean and rich flames, respectively. They observed HNO₂ as the
14 main species released following HNO₃ uptake on grey soot, and NO and traces of NO₂ from
15 black soot. They concluded that these update and production reactions would only have
16 relevance in special situations in urban settings where soot and HNO₃ are present in high
17 concentrations simultaneously.

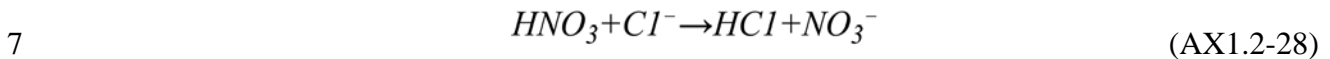
18 Data from four decades of observations on tropospheric O₃ have revealed important
19 anomalies not easily explained by the gas-phase HO_x-NO_x photochemistry described here. The
20 best-known example is the dramatic depletion of ground-level [O₃] during polar sunrise due to
21 multiphase catalytic cycles involving inorganic bromine (Br) and chloride (Cl) radicals (Barrie
22 et al., 1988; Martinez et al., 1999; Foster et al., 2001). Depletion of [O₃] in the MBL is generally
23 consistent with the model-predicted volatilization of diatomic bromide (Br₂), bromium chloride
24 (BrCl), and diatomic chloride (Cl₂) from sea salt aerosols through autocatalytic halogen
25 activation mechanisms (see, e.g., Vogt et al., 1996; von Glasow et al., 2002a) involving these
26 aqueous phase reactions



1 In polluted MBL regions at night, the heterogeneous reaction

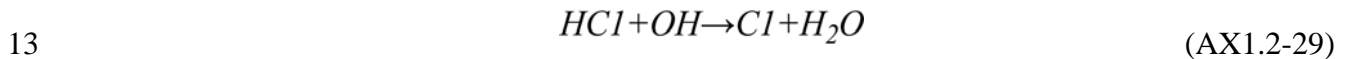


3 can also be important (Finlayson-Pitts et al., 1989; Behnke et al., 1997; Erickson et al., 1999).
4 BrCl, Cl₂, and nitryl chloride (ClNO₂) volatilize and photolyze in sunlight to produce atomic Br
5 and Cl. The acidification of sea salt aerosol via incorporation of HNO₃ (and other acids) leads to
6 the volatilization of HCl (Erickson et al., 1999)

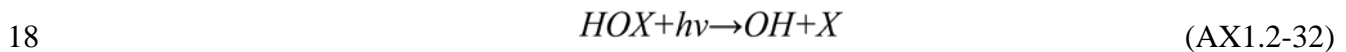
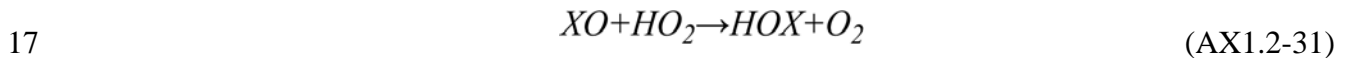
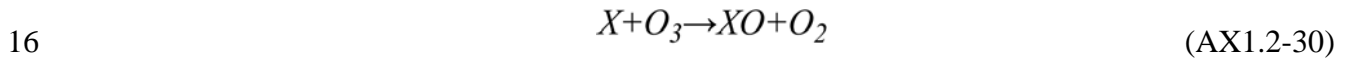


8 and the corresponding shift in phase partitioning can accelerate deposition flux to the surface of
9 total NO₃ (Russell et al., 2003; Fischer et al., 2006). However, Pryor and Sorensen (2000) have
10 shown that the dominant form of NO₃⁻ deposition is a complex function of wind speed.

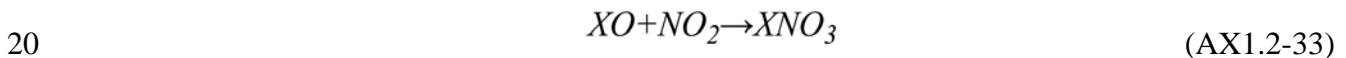
11 In polluted coastal regions where HCl from AX1.2-28 often exceeds 1 ppb, significant
12 additional atomic Cl is produced via



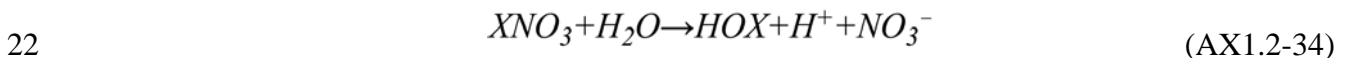
14 (Singh and Kasting, 1988; Keene et al., 2007). The Br and Cl atoms so produced then
15 catalytically destroy O₃ via



19 where (X = Br or Cl). Nitrated forms of Br and Cl can then be formed by XO attack



21 and the subsequent reaction of XNO₃ with sea salt and pSO₄²⁻ via





(where Y = Cl, Br, or I). This reaction cascade accelerates conversion of NO_X to pNO_3^- and thereby contributes directly to increased $[pNO_3^-]$ (Sander et al., 1999; Vogt et al., 1999; Pszenny et al., 2004).

The majority of XNO_3 reacts via Reaction AX1.2-35 on sea salt while Reaction AX1.2-34 is more significant for particulate SO_4^{2-} (pSO_4^{2-}). Particulate NO_3^- (pNO_3^-) from both reactions partitions with the gas-phase HNO_3 following Henry's Law. Because most aerosol size fractions in the MBL are near equilibrium with respect to HNO_3 (Erickson et al., 1999; Keene et al., 2004), both SO_4^{2-} and sea salt aerosol can sustain the catalytic removal of NO_X and re-activation of Cl and Br with no detectable change in composition. The photolytic reduction of NO_3^- in sea salt aerosol solutions then also recycles NO_X back to the gas phase (Pszenny et al., 2004).

An autocatalytic cycle involving multiphase iodine (I) chemistry also operates in the MBL (Alicke et al., 1999; Vogt et al., 1999; McFiggans et al., 2000; Ashworth et al., 2002). In this case, the primary source of I is believed to be either photolysis of diiodomethane (CH_2I_2), other I-containing gases (Carpenter et al., 1999; Carpenter, 2003), and/or perhaps diatomic iodine (I_2) (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; McFiggans, 2005) emitted by micro- and macro-flora. Sea salt and pSO_4^{2-} provide substrates for multiphase reactions that sustain the catalytic I-IO cycle. The IO radical has been measured by long-path and/or multi axis differential optical absorption spectroscopy (LP- or MAX-DOAS) at Mace Head, Ireland; Tenerife, Canary Islands; Cape Grim, Tasmania; and coastal New England, USA. Average daytime mixing ratios are on the order of 1 ppt with maxima up to 7 ppt (e.g., Allan et al., 2000; Pikelnaya et al., 2007). The reaction of IO with NO_2 followed by uptake of nitric iodine (INO_3) into aerosols in a reaction cascade analogous to that shown in Reactions AX1.2-33 through AX1.2-35 accelerates the conversion of NO_X to pNO_3^- . The reaction $IO + NO \rightarrow I + NO_2$ also influences NO_X cycling.

Most of the studies described above focused on halogen-radical chemistry and related influences on NO_X cycling in coastal and urban air. However, available evidence suggests that similar chemical transformations can proceed in other halogen-rich tropospheric air masses (see, e.g., Hebestreit et al., 1999; Stutz et al., 1999, 2002; Zingler and Platt, 2005; Wagner et al., 2001;

1 Hollwedel et al., 2004). The primary source of reactive halogens in these regions is thought to
2 be from activation along the lines of Reactions in AX1.2-23 through AX1.2-25. High
3 concentrations of BrO have also been measured in volcanic plumes (Bobrowski et al., 2003;
4 Gerlach, 2004). Although very little is known about it, the substantial emissions of inorganic
5 halogens during biomass burning (Lobert et al., 1999; Keene et al., 2006) and in association with
6 crustal dust (Keene et al., 1999; Sander et al., 2003) may also support active halogen-radical
7 chemistry and related transformations involving NO_x downwind of sources. Recent aircraft and
8 satellite observations confirm that BrO is present in the free troposphere at levels sufficient to
9 influence photochemistry significantly (see, e.g., von Glasow et al., 2004).

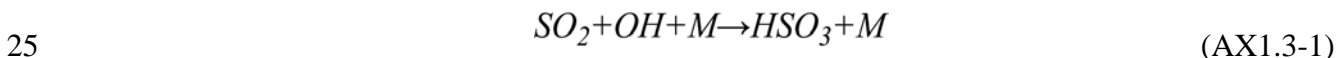
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12 **AX1.3 SULFUR OXIDES IN THE TROPOSPHERE**

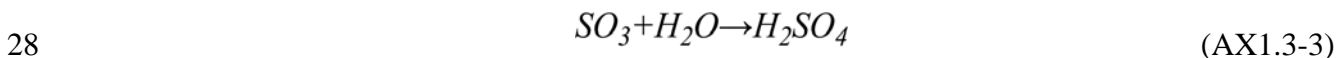
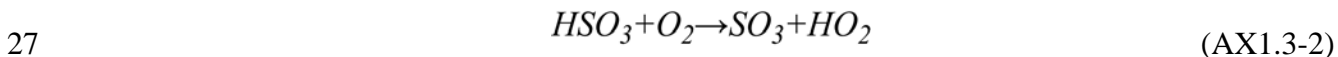
13 14 **AX1.3.1 General Sulfur Chemistry**

15 The four known monomeric sulfur oxides are SO, SO₂, SO₃, and S₂O. SO is formed by
16 photolysis of SO₂ at wavelengths <220 nm and so is found only in the middle and upper
17 stratosphere (Pinto et al., 1989). SO₃ can be emitted from the stacks of power plants and
18 industrial facilities; however, it reacts rapidly with H₂O to form H₂SO₄ in the stack or
19 immediately after release to the atmosphere. Of the four species, only SO₂ is present at
20 concentrations significant for atmospheric chemistry and ecological exposures.

21 SO₂ can be oxidized either in the gas phase through OH attack, or, owing to its high
22 solubility, in the aqueous phase in cloud water droplets; this aqueous-phase oxidation dominates
23 P(SO₄²⁻) at a ratio of ~80% (Warneck, 1999). Gas-phase oxidation of SO₂ proceeds through the
24 reaction



26 followed by



1 But because H₂SO₄ is highly soluble, it will be removed rapidly by transfer to the
2 aqueous phase of aerosol particles and cloud water droplets; see the discussion in Section AX2.4
3 below. Other pathways for SO₂ oxidation, such as reactions with HO₂ or NO₃ radicals have very
4 low rate constants (JPL, 2003) and so are insignificant on urban and regional scales.

5 SO₂ is chiefly an emitted or “primary” pollutant, though it is also produced by
6 photochemical oxidation of reduced S compounds like dimethyl sulfide (DMS; CH₃-S-CH₃),
7 hydrogen sulfide (H₂S), carbon disulfide (CS₂), carbonyl sulfide (OCS), methyl mercaptan
8 (CH₃-S-H), and dimethyl disulfide (DMDS; CH₃-S-S-CH₃). All of these compounds are largely
9 biogenic in origin and their sources are discussed in Chapter 3 and Annex 2. Excepting OCS,
10 which is lost mainly by photolysis with a τ ~6 months, these species are lost mainly through
11 attack by OH and NO₃ radicals.

12 Because tropospheric OCS is relatively long-lived, it can be transported upwards into the
13 stratosphere. Crutzen (1976) proposed that its oxidation serves as the major source of sulfate in
14 the stratospheric aerosol layer sometimes referred to the “Junge layer” (Junge et al., 1961) during
15 periods when volcanic plumes do not reach the stratosphere. By contrast, Myhre et al. (2004)
16 proposed that SO₂ transported upwards from the troposphere is the most likely source since the
17 up-flux of OCS is too small to sustain observed sulfate loadings in the Junge layer. Moreover,
18 in situ measurements of the isotopic composition of S do not match those of OCS (Leung et al.,
19 2002). Reaction with NO₃ radicals at night is the most likely major loss process for DMS and
20 CH₃-S-H.

21 Mechanisms of the oxidation of DMS are still incompletely understood. Excess SO₄²⁻
22 in marine aerosol is related mainly to production of SO₂ from oxidation of DMS. Initial attack
23 by NO₃ and OH radicals involves H⁺ abstraction, with a smaller branch leading to OH addition
24 to the S atom, the yield from this branch varies inversely with temperature and is the major
25 pathway below 285 K (Ravishankara et al., 1997). The adduct formed may then either
26 decompose to form methane sulfonic acid (MSA), or undergo further reactions in the main
27 pathway, to yield dimethyl sulfoxide (Barnes et al., 1991). Following H atom abstraction from
28 DMS, the main reaction products include MSA and SO₂. The ratio of MSA to SO₂ is strongly
29 temperature dependent, varying from ~0.1 in tropical waters to ~0.4 in Antarctic waters
30 (Seinfeld and Pandis, 1998). Transformations among atmospheric S compounds are summarized

1 in Figure AX1.3-1, where S(IV) represents $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} ; and S(VI) represents
 2 gas-phase SO_3 and H_2SO_4 or aqueous-phase HSO_4^- and SO_4^{2-} .

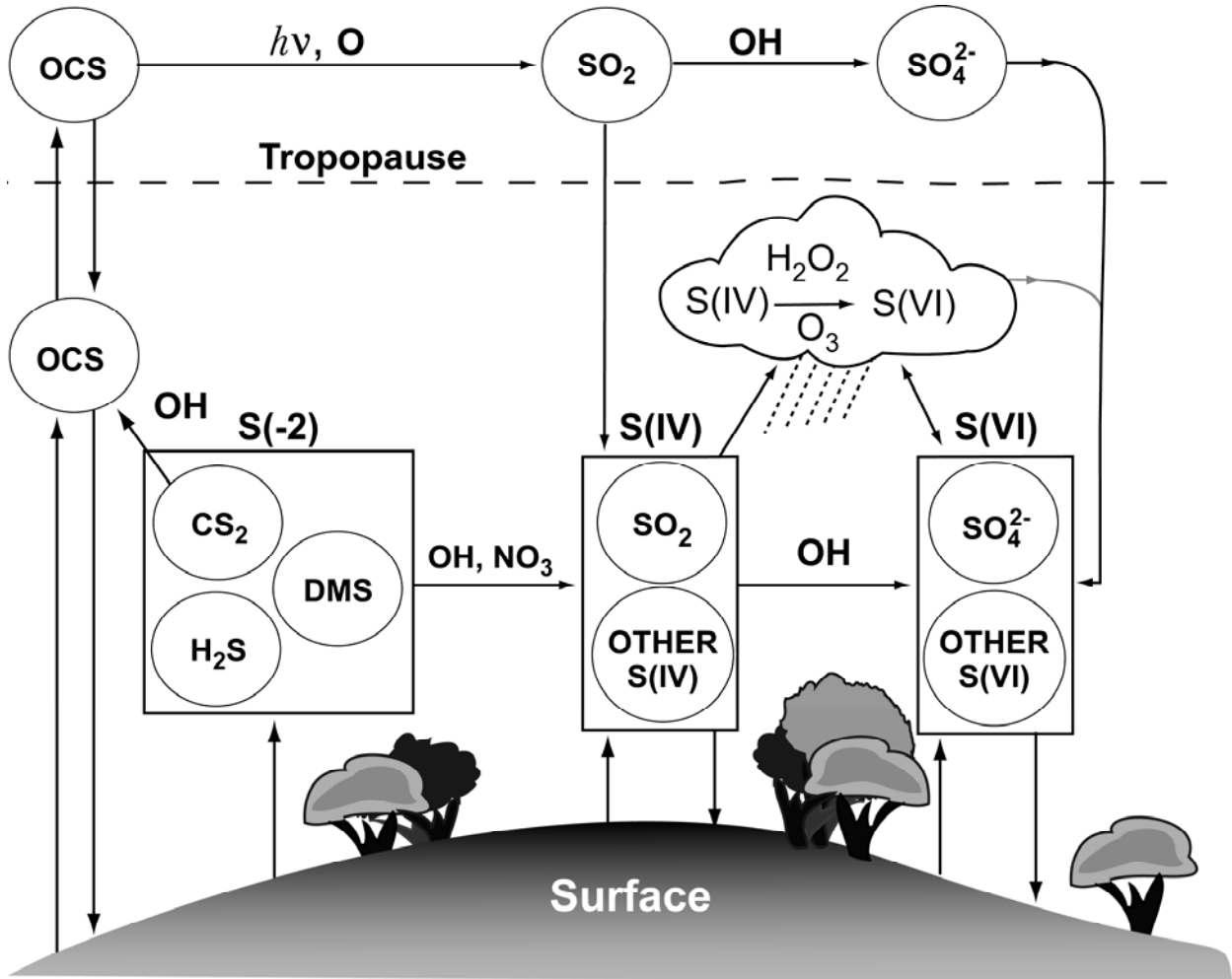


Figure AX1.3-1. Transformations of sulfur compounds in the atmosphere.

Source: Adapted from Berresheim (1995).

3 **AX1.3.2 Heterogeneous-Phase Production and Loss Processes**

4 Chemical transformations involving inorganic halogenated compounds effect changes in
 5 the multiphase cycling of sulfur oxides in ways analogous to their effects on NO_x . Oxidation of
 6 DMS by BrO produces dimethylsulfoxide (DMSO; $(\text{CH}_3)_2\text{SO}$) (Barnes et al., 1991; Toumi,
 7 1994), and oxidation by atomic Cl leads to formation of SO_2 (Keene et al., 1996). DMSO and

1 SO₂ are precursors for methanesulfonic acid (CH₃SO₃H) and H₂SO₄. In the MBL, virtually all
2 H₂SO₄ and CH₃SO₃H vapor condenses onto existing aerosols or cloud droplets, which
3 subsequently evaporate, contributing to aerosol growth and acidification. Unlike CH₃SO₃H,
4 H₂SO₄ also has the potential to produce new particles (Korhonen et al., 1999; Kulmala et al.,
5 2000); in marine air masses, these are thought to be present mainly in the free troposphere. Saiz-
6 Lopez et al. (2004) estimated that observed levels of BrO at Mace Head would oxidize (CH₃)₂S
7 ~6 times faster than OH and thereby substantially increase production rates of H₂SO₄ and other
8 condensable S species in the MBL.

9 SO₂ is also scavenged by deliquesced aerosols and oxidized to H₂SO₄ in the aqueous
10 phase along several strongly pH-dependent pathways (Chameides and Stelson, 1992; Vogt et al.,
11 1996; Keene et al., 1998). Model calculations indicate that oxidation of S(IV) by O₃ dominates
12 in fresh, alkaline sea salt aerosols, whereas oxidation by hypohalous acids (primarily HOCl)
13 dominates in moderately acidic solutions. Additional particulate non-sea salt (nss) pSO₄²⁻ is
14 generated by SO₂ oxidation in cloud droplets (Clegg and Toumi, 1998). Ion-balance calculations
15 indicate that most nss pSO₄²⁻ in short-lived sea salt size fractions (on the order of 2 to 48 h)
16 accumulates in acidic aerosol solutions and/or in acidic aerosols processed through clouds (see,
17 e.g., Keene et al., 2004).

18 The production, cycling, and associated radiative effects of S-containing aerosols in
19 marine and coastal air are regulated in part by chemical transformations involving inorganic
20 halogens; see von Glasow et al., 2002b. These transformations include: dry-deposition fluxes of
21 nss pSO₄²⁻ in marine air dominated by the sea salt size fractions (Huebert et al., 1996; Turekian,
22 2001); HCl phase partitioning that regulates sea salt pH and associated pH-dependent pathways
23 for S(IV) oxidation (Keene et al., 2002; Pszenny et al., 2004); and potentially important
24 oxidative reactions with reactive halogens for DMS and S(IV),. However, the absolute
25 magnitudes and relative importance of these S cycling processes in the MBL are poorly known.

26 Iodine chemistry has been linked to ultrafine particle bursts at Mace Head (O'Dowd
27 et al., 1999, 2002). Observed bursts coincide with the elevated concentrations of IO and are
28 characterized by particle concentrations increasing from background levels to up to
29 300,000 cm⁻³ on a time scale of seconds to minutes. This newly identified source of marine
30 aerosol would provide additional aerosol surface area for condensation of SO_x and thereby
31 presumably diminish the potential for nucleation pathways involving H₂SO₄. However, a

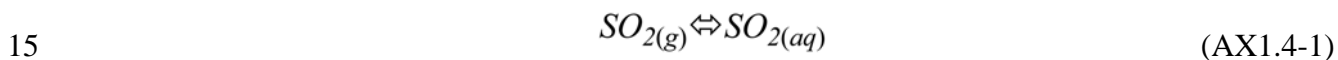
1 subsequent investigation in polluted air along the New England, USA coast found no correlation
2 between periods of nanoparticle growth and corresponding concentrations of I oxides (Russell
3 et al., 2006). Thus, the potential importance of I chemistry in aerosol nucleation and its
4 associated influence on S cycling remain highly uncertain.

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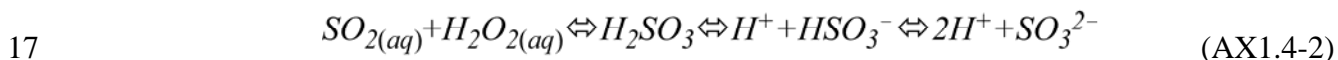
7 **AX1.4 AQUEOUS-PHASE FORMATION OF SULFATES** 8 **AND NITRATES**

9 The chief species capable of oxidizing S(IV) to S(VI) in cloud water are O₃, hydrogen
10 peroxides (H₂O₂) and organic peroxides, OH radicals, and ions of the transition metals such as
11 iron (Fe) and copper (Cu) that can catalyze oxidation by molecular oxygen (O₂).

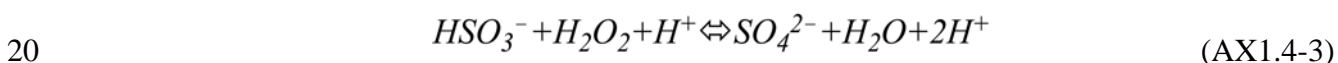
12 The basic mechanism of aqueous-phase SO₂ oxidation has long been known and is found
13 in numerous texts (see, e.g., Seinfeld and Pandis, 1998; Jacob, 2000; Jacobson, 2002):
14 dissolution of SO₂



16 followed by formation and dissociation of H₂SO₃



18 In the usual pH range of rainwater (2 to 6), the most important reaction converting S(IV) to
19 S(VI) is



21 because SO₃²⁻ is much less abundant than HSO₃⁻.

22 These major pathways for aqueous phase oxidation of S(IV) to S(VI) as a function of pH
23 are shown in Figure AX1.4-1. For pH up to ~5.3, H₂O₂ is the dominant oxidant; above 5.3, O₃
24 and Fe(III) dominant. Marine aerosols are expected to have higher pH; however, in marine
25 aerosols the Cl-catalyzed oxidation of S(IV) may be the more significant process (Zhang and
26 Millero, 1991; Hoppel and Caffrey, 2005).

27 Because NH₄⁺ is so effective in controlling acidity, where it is present it affects the rate
28 of oxidation of S(IV) to S(VI) and the rate of dissolution of SO₂ in particles and cloud droplets.

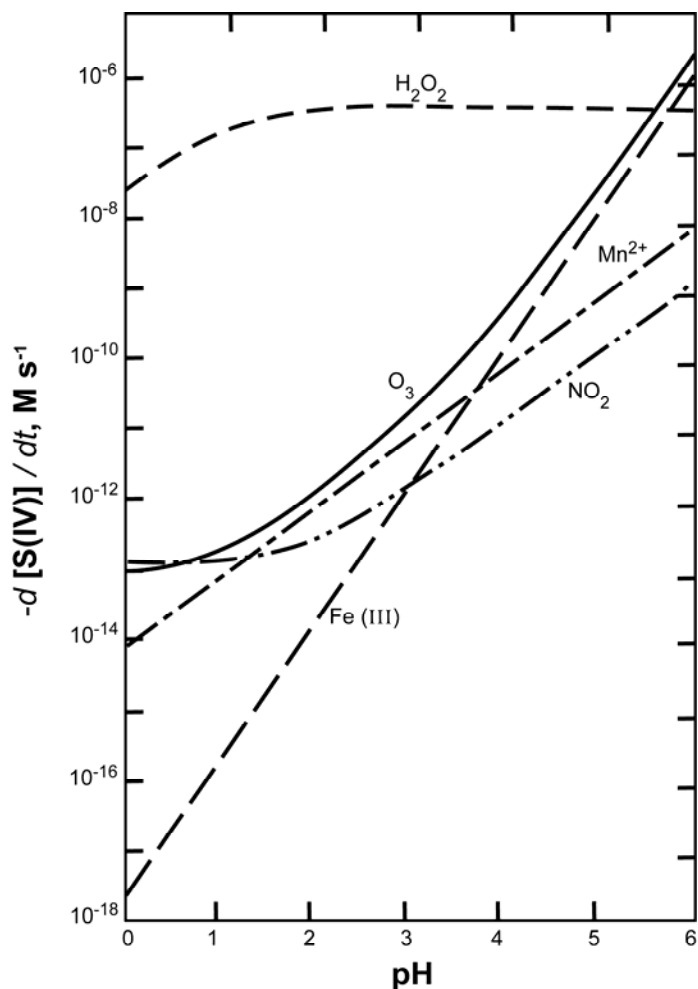


Figure AX1.4-1. Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) is shown as a function of pH. Conditions assumed are: $[\text{SO}_{2(\text{g})}] = 5 \text{ ppb}$; $[\text{NO}_{2(\text{g})}] = 1 \text{ ppb}$; $[\text{H}_2\text{O}_{2(\text{g})}] = 1 \text{ ppb}$; $[\text{O}_{3(\text{g})}] = 50 \text{ ppb}$; $[\text{Fe(III)}_{(\text{aq})}] = 0.3 \text{ }\mu\text{M}$; $[\text{Mn}^{2+}_{(\text{aq})}] = 0.3 \text{ }\mu\text{M}$.

Source: Seinfeld and Pandis (1998).

1 NO_2 can also be taken up in cloud droplets and oxidized there to NO_3^- , although because
 2 NO_2 is much less soluble than SO_2 , this pathway is of minor importance. Instead, the uptake of
 3 the highly soluble N-containing acids such as HNO_3 initiates the aqueous-phase chemistry of
 4 NO_3^- formation.

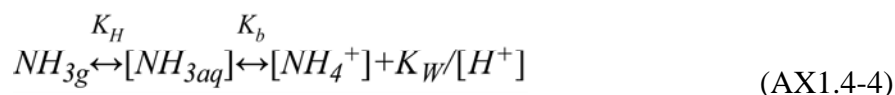
5 Warneck (1999) constructed a box model describing the oxidation chemistry of SO_2 and
 6 NO_2 including the interactions of N and S species and minor processes in sunlit cumulus clouds.
 7 (Clouds occupy about 15%, on average, of the volume of the troposphere.) The relative

1 contributions of different reactions to the oxidation of S(IV) to S(VI) and of NO₂ to NO₃⁻ are
2 shown both with and without catalytic metals in Tables AX1.4-1a and AX1.4-1b. Gas-phase
3 oxidation in clouds removes ~20% of SO₂ but ~90% of NO₂. In-cloud SO₂ is oxidized primarily
4 in the aqueous phase by H₂O₂ and, secondarily, by HNO₄. Methyl hydroperoxide (CH₃OOH)
5 also oxidizes SO₂ but in much smaller quantities because CH₃OOH is formed primarily in the
6 gas phase and its Henry's Law constant is several orders of magnitude smaller than that of H₂O₂.

7 In contrast to SO₂, NO₂ oxidation occurs mainly in the gas phase within clouds, implying
8 that gas-phase oxidation of NO₂ by OH radicals dominates.

10 **AX1.4.1 Heterogeneous Processes and NH₃**

11 The phase partitioning of NH₃ with deliquesced aerosol solutions is controlled primarily
12 by the thermodynamic properties of the system expressed as



14 where K_H and K_b are the temperature-dependent Henry's Law and dissociation constants
15 for NH₃, 62 M atm⁻¹ and 1.8 × 10⁻⁵ M, respectively; and K_w is the ion product of water,
16 1.0 × 10⁻¹⁴ M (Chameides, 1984). Reaction AX1.4-4 shows that for any [NH_x] in the system,
17 increasing aqueous concentrations of particulate H⁺ will shift the partitioning of NH₃ towards the
18 condensed phase. Consequently, under the more polluted conditions characterized by higher
19 concentrations of acidic pSO₄²⁻, the ratios of gas-phase NH₃ to pNH₄ decrease (Smith et al.,
20 2007). Thus, in marine air, where aerosol acidity varies substantially as a function of particle
21 size, NH₃ partitions preferentially to the more acidic sub-μm size fractions (e.g., Keene et al.,
22 2004; Smith et al., 2007).

23 Because the V_d of gas-phase NH₃ to the surface is substantially greater than that for the
24 sub-μm size fraction of pSO₄²⁻ with which most particulate pNH₄ is associated, dry-deposition
25 fluxes of total NH₃ are dominated by the gas-phase fraction (Russell et al., 2003; Smith et al.,
26 2007). Consequently, this partitioning with highly acidic pSO₄²⁻ effectively increases the τ of
27 total NH₃ against dry deposition loss. This shift has important consequences for NH₃ cycling
28 and potential ecological effects.

1 In coastal New England during summer, for example, air transported from rural eastern
2 Canada contains relatively low concentrations of particulate non-sea salt (nss) pSO_4^{2-} and total
3 NH_3 (Smith et al., 2007). Under these conditions, the roughly equal partitioning of total NH_3
4 between gas and particulate phases sustains dry-deposition fluxes of total NH_3 to the coastal
5 ocean with a median value of $10.7 \mu\text{mol m}^{-2} \text{day}^{-1}$. By contrast, heavily polluted air transported
6 from the industrialized midwestern United States contains nss $[\text{SO}_4^{2-}]$ and total $[\text{NH}_3]$ that are
7 approximately a factor of 3 greater than those in clean air, based on median values. In polluted
8 conditions, >85% of total NH_3 partitions to the highly acidic pSO_4^{2-} ; consequently, the median
9 dry-deposition flux of total NH_3 is 30% lower than that under the cleaner flow regime. The
10 relatively larger τ of total NH_3 against dry deposition under more polluted conditions implies
11 that, on average, total NH_3 would accumulate to higher atmospheric concentrations under these
12 conditions and hence be subject to atmospheric transport over longer distances. Consequently,
13 the importance NH_x of removal via wet deposition would also increase. Given the inherently
14 sporadic character of precipitation, we might expect by greater heterogeneity in NH_3 deposition
15 fields and in any potential responses by sensitive ecosystems downwind of major S-emission
16 regions.

17
18

19 **AX1.5 ATMOSPHERIC TRANSPORT OF NITROGEN AND** 20 **SULFUR OXIDES**

21 Major episodes of photochemical air pollution in the eastern United States and Europe
22 are associated with slow moving high-pressure systems. During the warm seasons, such weather
23 systems result in subsidence and in warm, generally cloudless conditions with light winds. This
24 produces stable conditions near the earth's surface which inhibit or reduce the extent of the
25 vertical mixing of NO_x , VOCs, and CO emitted at or near the surface. It is becoming
26 increasingly apparent that transport of photochemical air pollution and its precursor NO_x and
27 VOCs from distant sources can provide significant contributions to local events even in areas
28 where there is already substantial photochemical production. There are a number of transport
29 phenomena occurring either in the upper PBL or the free troposphere which can contribute to
30 this transport and to increased pollution at the surface. These phenomena include stratospheric-
31 tropospheric exchange (STE), deep and shallow convection, low-level jets, and the so-called
32 "conveyor belts" that serve to characterize flows around frontal systems.

1 Crutzen and Gidel (1983), Gidel (1983), and Chatfield and Crutzen (1984) hypothesized
2 that convective clouds played an important role in the rapid vertical transport of trace species and
3 first tested simple parameterizations of convective transport in atmospheric chemical models. At
4 nearly the same time, evidence was shown of venting the boundary layer by shallow, fair
5 weather cumulus clouds (e.g., Greenhut et al., 1984; Greenhut, 1986). Field experiments were
6 conducted in 1985 which resulted in verification of the hypothesis that deep convective clouds
7 are instrumental in atmospheric transport of trace constituents (Dickerson et al., 1987). Once
8 pollutants are lofted to the middle and upper troposphere, they typically have a much longer
9 chemical lifetime and, with the generally stronger winds at these altitudes, can be transported
10 large distances from their source regions. Transport of NO_x from the PBL to the upper
11 troposphere by convection generally will dilute the higher concentrations in the boundary layer
12 and will extend NO_x lifetimes from less than 24 h to several days. Photochemical reactions
13 occur during this long-range transport. Pickering et al. (1990) demonstrated that venting of
14 boundary layer NO_x by convective clouds (both shallow and deep) causes enhanced O₃
15 production in the free troposphere. The dilution of NO_x at the surface can often increase O₃
16 production efficiency (Tonnesen and Dennis, 2000). Therefore, convection aids in the
17 transformation of local pollution into a contribution to global atmospheric pollution. Downdrafts
18 within thunderstorms generally bring air with lower [NO_x] from the middle troposphere into the
19 boundary layer. Lightning produces NO which is directly injected chiefly into the middle and
20 upper troposphere; the total global production of NO by lightning remains uncertain, but is on
21 the order of 10% of the total NO budget.

22 Convective processes and small scale turbulence transport pollutants both upward and
23 downward throughout the planetary boundary layer and the free troposphere. Ozone, NO_x, CO,
24 and VOCs can be transported vertically by convection into upper part of the mixed layer on one
25 day, then transported overnight as a layer of elevated mixing ratios, perhaps by a nocturnal low
26 level jet, and then entrained into a growing convective boundary layer downwind and brought
27 back to the surface.

28 The first unequivocal observations of deep convective transport of boundary layer
29 pollutants to the upper troposphere were documented by Dickerson et al. (1987).
30 Instrumentation aboard three research aircraft measured CO, O₃, NO, NO_x, NO_y, and
31 hydrocarbons (HC) in the vicinity of an active mesoscale convective system near the

1 Oklahoma/Arkansas border during the 1985 PRE-STORM experiment. Samples taken in cloud
2 anvils approximately two hours after maturity found greatly enhanced mixing ratios inside the
3 cloud of all of the aforementioned species compared with outside it. Nitric oxide mixing ratios
4 in the anvil averaged 3-4 ppbv, with individual 3-min observations reaching 6 ppbv; boundary
5 layer NO_x was typically 1.5 ppbv or less outside the cloud. Therefore, the anvil observations
6 represent a mixture of boundary layer NO_x and NO_x contributed by lightning. Luke et al. (1992)
7 summarized the air chemistry data from all 18 flights during PRE-STORM by categorizing each
8 case according to synoptic flow patterns. Storms in the maritime tropical flow regime
9 transported large amounts of CO, O_3 , and NO_y into the upper troposphere with the
10 midtroposphere remaining relatively clean. During frontal passages a combination of stratiform
11 and convective clouds mixed pollutants more uniformly into the middle and upper levels.

12 Prather and Jacob (1997) and Jaegle et al. (1997) noted that precursors of HO_x are also
13 transported to the upper troposphere by deep convection, in addition to primary pollutants (e.g.,
14 NO_x , CO, VOCs). The HO_x precursors of most importance are water vapor, HCHO, H_2O_2 ,
15 CH_3OOH , and acetone.

16 Over remote marine areas, the effects of deep convection on trace gas distributions differ
17 from those over moderately polluted continental regions. Chemical measurements taken by the
18 NASA ER-2 aircraft during the Stratosphere-Troposphere Exchange Project (STEP) off the
19 northern coast of Australia show the influence of very deep convective events. Between 14.5
20 and 16.5 km on the February 2-3, 1987 flight, chemical profiles that included pronounced
21 maxima in CO, water vapor, and CCN, and minima of NO_y , and O_3 (Pickering et al., 1993).
22 Trajectory analysis showed that these air parcels likely were transported from convective cells
23 800-900 km upstream. Very low $[\text{NO}_y]$ and $[\text{O}_3]$ in the MBL in this remote region were
24 apparently transported upward in the convection. A similar result was noted in Central
25 Equatorial Pacific Experiment (CEPEX) (Kley et al., 1996) where a series of ozonesonde ascents
26 showed very low upper tropospheric O_3 following deep convection. It is likely that similar
27 transport of low-ozone tropical MBL air to the upper troposphere occurs in thunderstorms along
28 the east coast of Florida. Deep convection occurs frequently over the tropical Pacific. Low-
29 ozone and low- NO_x convective outflow likely will descend in the subsidence region of the
30 subtropical eastern Pacific, leading to some of the cleanest air that arrives at the west coast of the
31 United States.

1 The discussion above relates to the effects of specific convective events. Observations
2 have also been conducted by NASA aircraft in survey mode, in which the regional effects of
3 many convective events can be measured. The Subsonic Assessment Ozone and Nitrogen
4 Oxides Experiment (SONEX) field program in 1997 conducted primarily upper tropospheric
5 measurements over the North Atlantic. The regional effects of convection over North America
6 and the Western Atlantic on upper tropospheric NO_x were pronounced (Crawford et al., 2000;
7 Allen et al., 2000). A discussion of the results of model calculations of convection and its effects
8 can be found in Section 1.7.

9 10 **AX1.5.1 Effects on Photolysis Rates and Wet Scavenging**

11 Thunderstorm clouds are very optically thick and, therefore, have major effects on
12 radiative fluxes and photolysis rates. Madronich (1987) provided modeling estimates of the
13 effects of clouds of various optical depths on photolysis rates. In the upper portion of a
14 thunderstorm anvil, photolysis is likely to be enhanced by a factor of 2 or more due to multiple
15 reflections off the ice crystals. In the lower portion and beneath the cloud, photolysis is
16 substantially decreased. With enhanced photolysis rates, the NO/NO₂ ratio in the upper
17 troposphere is driven to larger values than under clear-sky conditions.

18 Thunderstorm updraft regions, which contain copious amounts of water, are regions
19 where efficient scavenging of soluble species can occur (Balkanski et al., 1993). NO is not very
20 soluble and hence wet scavenging is not a major removal process for it. However, a major NO_x
21 reservoir species, HNO₃ is highly soluble, though very few direct field measurements of the
22 amounts of specific trace gases that are scavenged in storms are available.

23 Pickering et al. (2001) used a combination of model estimates of soluble species that did
24 not include wet scavenging and observations of these species from the upper tropospheric
25 outflow region of a major line of convection observed near Fiji: >90% of the HNO₃ in the
26 outflow air appeared to have been removed by the storm, and ~50% of CH₃OOH and ~80% of
27 HCHO had been lost.

28 Because NO and NO₂ are only slightly soluble, they can be transported over longer
29 distances in the gas phase than can more soluble species which are depleted by deposition to
30 moist surfaces or taken up more readily on aqueous surfaces of particles. During transport, NO
31 and NO₂ can be transformed into the longer-lived reservoir species HNO₃ and the PANs as

1 presented above. These species can then contribute to local NO_x concentrations in remote areas
2 as it is now well established that PAN decomposition provides a major source of NO₂ in the
3 remote troposphere (Staudt et al., 2003). The decomposition of PAN in subsiding air masses
4 from Asia over the eastern Pacific could make an important contribution to both O₃ and NO_x
5 enhancement in the United States (Kotchenruther et al., 2001; Hudman et al., 2004). Further
6 details about mechanisms for transporting ozone and its precursors were described at length in
7 CD06.

8 9 10 **AX1.6 SAMPLING AND ANALYSIS FOR NO_x AND SO_x**

11 12 **AX1.6.1 NO_x Measurement Methods and Associated Issues**

13 These Annex Sections focus on current methods and promising new technologies with no
14 attempt here to cover the extensive development of these methods or of methods no longer in
15 widespread use. The descriptions here are centered on Federal Reference and Equivalent
16 Methods (FRM and FEM, respectively). More detailed discussions of the FRM, FEM, and other
17 newer methods including challenges in their field use is found in U.S. Environmental Protection
18 Agency (1993, 1996); McClenny (2000); Parrish and Fehsenfeld (2000); and Clemitshaw (2004).

19 20 **AX1.6.1.1 NO AND NO₂**

21 NO is routinely measured using the principle of gas-phase chemiluminescence induced
22 by the reaction of NO with O₃ at low pressure. However, Cardelino and Chameides (2000)
23 reported that measured NO during the afternoon was frequently at or below the operational limit
24 of detection (LOD), ~1 ppb, of the regulatory NO_x instruments even in large metropolitan
25 regions such as Washington, DC; Houston, TX; and New York, NY. The FRM for NO₂ also
26 makes use of this NO detection technique using a prerequisite step to reduce NO₂ to NO on the
27 surface of a molybdenum oxide (MoO_x) substrate heated to ~340 °C. Because the FRM monitor
28 cannot detect NO₂ directly, the [NO₂] is determined as the difference between the sample passed
29 over the heated MoO_x substrate (the nitrogen oxides total) and the sample not reduced (the NO
30 alone). However, reduction of NO₂ to NO on the MoO_x substrate is not specific to NO₂; hence,
31 chemiluminescence monitors are all subject to unknown and varying interferants in the sample

1 from other oxidized nitrogen compounds, i.e., species of NO_Z ; see the outer box elements in
2 Figure AX1.2-1.

3 Interference by NO_Z compounds has long been known (Fehsenfeld et al., 1987; Rodgers
4 and Davis, 1989; U.S. Environmental Protection Agency, 1993, 2006; Crosley, 1996;
5 Nunnermacker et al., 1998; Parrish and Fehsenfeld, 2000; McClenny et al., 2002; Dunlea et al.,
6 2007). The sensitivity of the MoO_X instrument to interference from multiple NO_Z compounds is
7 highly variable and dependent in part on instrument inlet design, the temperature of the reducing
8 substrate, and on the interactions of species with that substrate. Because of losses on inlet
9 surfaces and differences in the efficiency of reduction of NO_Z compounds on the heated MoO_X
10 substrate, NO_X as reported from these instruments can not be considered as a universal surrogate
11 for NO_Y . However, in settings close to relatively high concentration fresh emissions like those
12 in urban areas during rush hour, most of the NO_Y is present as NO_Z .

13 To the extent that all the major oxidized nitrogen species can be reduced quantitatively to
14 NO , measurements of NO_Y should be more reliable than those for NO_X , particularly at typical
15 ambient levels of NO_2 . The commercially-available NO_X monitors of the sort used in many
16 regulatory networks can be converted to measure total NO_Y simply by moving the MoO_X
17 convertor to interface directly with the sample inlet. Routinely reporting total NO_Y rather than
18 NO and reported NO_2 by subtraction as now done has the additional benefit of characterizing the
19 entire suite of oxidized nitrogen compounds to which ecosystems are exposed. Reliable
20 measurements of NO_Y and NO_2 , especially at the low concentrations observed in many areas
21 remote from sources are also crucial for evaluating the performance of the large-scale Eulerian
22 numerical chemical transport models (CTMs) of oxidant and acid production in the atmosphere.

23 There are other approaches to measuring NO_2 that do not suffer from the artifacts
24 mentioned above. For example, NO_2 can be photolytically reduced to NO , with an efficiency of
25 ~70%. At present, however, this method requires additional development to ensure its cost
26 effectiveness and reliability for extensive field deployment. The relatively low and somewhat
27 variable conversion efficiency of this technique, for example, means that increased attention to
28 frequent calibration exercises would be required for routine operation. Optical methods such as
29 those using differential optical absorption spectroscopy (DOAS) or laser induced fluorescence
30 (LIF) are also available. However, these methods are even more expensive than either the FRM
31 monitors or photolytic reduction technique and require specialized expertise to operate;

1 moreover, the DOAS is an area-integrated rather than a point-measured technique, essentially
2 decoupling this from measurements of other species at the same site.

3 LIF for NO₂ detection involves excitation of atmospheric NO₂ with laser light emitted at
4 wavelengths too long to induce photolysis. The resulting excited molecules relax in a
5 photoemissive mode and the fluorescing photons are counted. Because collisions would rapidly
6 quench the electronically excited NO₂, the reactions are conducted at low pressure. Matsumi
7 et al. (2001) describe a comparison of LIF with a photofragmentation chemiluminescence
8 instrument. The LIF system involves excitation at 440 nm with a multiple laser system. They
9 report sensitivity of 30 ppt in 10 s and good agreement between the two methods under
10 laboratory conditions at mixing ratios up to 1.0 ppb. This high-sensitivity LIF system has yet to
11 undergo long-term field tests. Cleary et al. (2002) describe field tests of a system that uses
12 continuous, supersonic expansion followed by excitation at 640 nm with a commercial cw
13 external-cavity tunable diode laser. More recently, LIF has been successfully used to detect NO₂
14 with accuracy of about 15% and detection limits well below 1 ppb. When coupled with thermal
15 dissociation, the technique also measures peroxy nitrates such as PAN, alkyl nitrates, HNO₄ and
16 HNO₃ (Cohen, 1999; Day et al., 2002; Farmer et al., 2006; Pérez et al., 2007; Thornton et al.,
17 2003). This instrument can have sampling rates >1 Hz and shows good correlation with
18 chemiluminescent techniques, but remains a research-grade device.

19 NO₂ can be detected by DOAS in an open, long-path system by measuring narrow band
20 absorption features over a background of broad band extinction (e.g., Stutz et al., 2000; Kim and
21 Kim, 2001). A DOAS system manufactured by OPSIS is a designated FEM for measuring NO₂.
22 These DOAS systems can also be configured to measure NO, HNO₂, and NO₃ radicals. Typical
23 detection limits are 0.2 to 0.3 ppbv for NO, 0.05 to 0.1 ppbv for NO₂, 0.05 to 0.1 ppbv for
24 HONO, and 0.001 to 0.002 ppbv for NO₃ at path lengths of 0.2, 5, 5, and 10 km, respectively.
25 The obvious advantage compared to fixed point measurements is that concentrations relevant to
26 a much larger area are obtained with DOAS, especially if multiple targets are used. At the same
27 time, any microenvironmental artifacts are minimized over the long path integration. A major
28 limitation in this technique had involved inadequate knowledge of absorption cross sections.
29 Harder et al. (1997) conducted an experiment in rural Colorado involving simultaneous
30 measurements of NO₂ by DOAS and by photolysis followed by chemiluminescence. They found
31 differences of as much as 110% in clean air from the west, but for NO₂ mixing ratios in excess of

1 300 ppt, the two methods agreed to better than 10%. Stutz et al. (2000) cites two
2 intercomparisons of note. NO₂ was measured by DOAS, by photolysis of NO₂ followed by
3 chemiluminescence, and by LIF in Nashville, TN during the month of July 1999 as part of the
4 Southern Oxidant Study (SOS) ([http://www.al.noaa.gov/WWWH/pubdocs/SOS/](http://www.al.noaa.gov/WWWH/pubdocs/SOS/sos99.groundsites.html)
5 [sos99.groundsites.html](http://www.al.noaa.gov/WWWH/pubdocs/SOS/sos99.groundsites.html)). On average, the three methods agreed to within 2%, with some larger
6 differences likely caused by spatial variability over the DOAS path. In another study in Europe,
7 and a multi-reflection set-up over a 15 mm path, negated the problem of spatial averaging here
8 agreement with the chemiluminescence detector following photolytic conversion was excellent
9 (slope = 1.006 ± 0.005; intercept = 0.036 ± 0.019; r = 0.99) over a concentration range from
10 about 0.2 to 20 ppbv.

11 NO can also be detected from space with DOAS-like UV spectroscopy techniques (Kim
12 et al., 2006; Ma et al., 2006). These measurements appear to track well with emissions estimates
13 and can be a useful indicator of column content as well as for identifying hot spots in sources.
14 Leigh et al. (2006) report on a DOAS method that uses the sun as a light source and compares
15 well with an in situ chemiluminescence detector in an urban environment.

16 Chemiluminescence on the surface of liquid Luminol has also been used for measurement
17 of NO₂ (Gaffney et al., 1998; Kelly et al., 1990; Marley et al., 2004; Nikitas et al., 1997; Wendel
18 et al., 1983). This technique is sensitive and linear, and more specific than hot MoO_x. Luminol
19 does not emit light when exposed to NHO₃ or alkyl nitrates, but does react with PAN. This
20 interference can be removed by chromatographic separation prior to detection and the resulting
21 measurement compares well with more specific techniques for moderate to high (≥ 1 ppb) mixing
22 ratios of NO₂.

23 Several tunable diode laser spectroscopy techniques have been used successfully for NO₂
24 detection (Eisele et al., 2003; Osthoff et al., 2006). These devices remain research grade
25 instruments, not yet practical for urban monitoring.

26

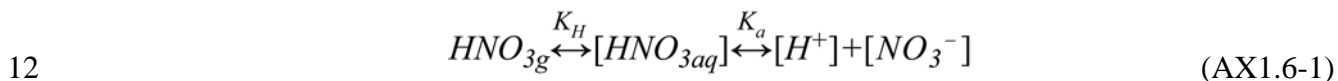
27 **AX1.6.2 Total and Speciated NO_y**

28 Gold-catalyzed CO or H₂ reduction or conversion on heated MoO_x have been used to
29 reduce total NO_y to NO before detection by chemiluminescence (Fehsenfeld et al., 1987;
30 Crosley, 1996). Both techniques offer generally reliable measurements, with response times on
31 the order of 60 s and a linear dynamic range demonstrated in field intercomparisons from

1 ~10 ppt to 10s of ppb. Under some conditions, hydrogen cyanide (HCN), NH₃, alkyl nitrates
2 (RNO₂), and acetonitrile (CH₃CN) can be converted to NO; but at normal concentrations and
3 humidity, these are minor interferants. Thermal decomposition followed by LIF has also been
4 used for NO_Y detection, as described above. In field comparisons, instruments based on these
5 two principles generally showed good agreement (Day et al., 2002) with experimental
6 uncertainty estimated to be on the order of 15 to 30%.

7
8 **AX1.6.2.1 HNO₃**

9 Accurate measurement of HNO₃ has presented a long-standing analytical challenge. In
10 this regard, it is useful to consider the major factors that control HNO₃ partitioning between the
11 gas and deliquesced-particulate phases in ambient air



13 where K_H is the Henry's Law constant in M atm⁻¹ and K_a is the acid dissociation constant in M.
14 Thus, the primary controls on HNO₃ phase partitioning are its thermodynamic properties (K_H , K_a ,
15 and associated temperature corrections), aerosol liquid water content (LWC), solution pH, and
16 kinetics. Aerosol LWC and pH are controlled by the relative mix of acids and bases in the
17 system, the hygroscopic properties of condensed compounds, and meteorological conditions,
18 chiefly RH, temperature, and pressure.

19 In the presence of chemically distinct aerosols of varying acidities (e.g., super- μm
20 predominantly sea salt and sub- μm predominantly pSO₄²⁻), HNO₃ will partition preferentially
21 with the less-acidic particles; this is consistent with observations (e.g., Huebert et al., 1996;
22 Keene and Savoie, 1998; Keene et al., 2002). The kinetics of this phase partitioning are
23 controlled by atmospheric concentrations of HNO₃ vapor and pNO₃⁻, and the size distribution
24 and τ of the particles against deposition. Sub- μm diameter aerosols typically equilibrate with the
25 gas phase in seconds to minutes while super- μm aerosols require hours to a day or more (e.g.,
26 Meng and Seinfeld, 1996; Erickson et al., 1999). Consequently, smaller aerosol size fractions
27 are typically close to thermodynamic equilibrium with respect to HNO₃ whereas larger size
28 fractions, for which τ against deposition range from hours to a few days, are often undersaturated
29 (e.g., Erickson et al., 1999; Keene and Savoie, 1998).

1 Many sampling techniques for HNO₃ employ upstream prefilters to remove particulate
2 species from sample air; these include the annular denuder, standard filterpack and mist-chamber
3 samplers. However, when chemically distinct aerosols with different pHs (e.g., sea salt and
4 pSO₄²⁻) mix together on a bulk filter, the acidity of the bulk mixture will be greater than that of
5 the less-acidic aerosols with which most of the NO₃⁻ is associated. This change in pH may cause
6 the bulk mix to be supersaturated with respect to HNO₃ leading to volatilization and, thus, to a
7 positive measurement bias in HNO₃ sampled downstream. Alternatively, when undersaturated
8 super-μm size fractions (e.g., sea salt) accumulate on a bulk filter and chemically interact over
9 time with HNO₃ in the sample air stream, scavenging may lead to a negative bias in the HNO₃
10 sampled downstream. Because the magnitude of both effects will vary as functions of the overall
11 composition and thermodynamic state of the multiphase systems, the combined influence can
12 cause net positive or net negative measurement bias in resulting data with unknown frequencies.
13 Pressure drops across particle filters can also lead to artifact volatilization and associated positive
14 bias in HNO₃ measured downstream.

15 Methods used widely for measuring HNO₃ include standard filterpacks configured with
16 nylon or alkaline-impregnated filters (e.g., Goldan et al., 1983; Bardwell et al., 1990), annular
17 denuders (EPA Method IP-9), and mist chambers (Talbot et al., 1990). Samples from these
18 instruments are typically analyzed by ion chromatography. Intercomparisons of these
19 measurement techniques (e.g., Hering et al., 1988; Tanner et al., 1989; Talbot et al., 1990) report
20 differences on the order of a factor of two or more.

21 Recently, sensitive HNO₃ measurements based on the principle of chemical ionization
22 mass spectroscopy (CIMS) have been reported (e.g., Huey et al., 1998; Mauldin et al., 1998;
23 Furutani and Akimoto, 2002; Neuman et al., 2002). The CIMS relies on selective formation of
24 ions such as SiF₅⁻·HNO₃ or HSO₄⁻·HNO₃ followed by detection via mass spectroscopy. Two
25 CIMS techniques and a filter pack technique were intercompared in Boulder, CO (Fehsenfeld
26 et al., 1998). Results indicated agreement to within 15% between the two CIMS instruments and
27 between the CIMS and filterpack methods under relatively clean conditions with HNO₃ mixing
28 ratios between 50 and 400 pptv. In more polluted air, the filterpack technique generally yielded
29 higher values than the CIMS suggesting that interactions between chemically distinct particles on
30 bulk filters is a more important source of bias in polluted continental air. Differences were also

1 greater at lower temperature when pNO_3^- corresponded to relatively greater fractions of total
2 NO_3^- .

3 A recent large field intercomparison of different techniques for HNO_3 measurement was
4 conducted in Tampa, FL in 2003 (Arnold et al., 2007) using the annular denuder + filter pack
5 time-integrated method and three semi-continuous techniques: two different implementations of
6 the $\text{NO}_Y - \text{NO}_Y^*$ denuder difference technique (Joseph and Spicer, 1978); the parallel plate wet
7 diffusion scrubber + online ion chromatography method (Boring et al., 2002); and the CIMS
8 (Huey et al., 1998). Results for 10 min aggregates computed from the various higher sampling
9 frequencies of each semi-continuous instrument showed good agreement ($R^2 > 0.7$) for afternoon
10 periods of the highest production and accumulation of HNO_3 . Further, agreement was within
11 $\pm 30\%$ even at $[\text{HNO}_3]$ less than 0.30 ppb. This study also confirmed the importance of sample
12 inlet height for HNO_3 monitoring through comparison to previous field work at this and other
13 sites when inlet heights ranged from 1.5 to 10 m, producing systematic discrepancies in
14 measured $[\text{HNO}_3]$ correlated with height of more than a factor of 2 correlated with height. The
15 correlation of this concentration discrepancy with inlet height is governed by HNO_3 's very fast
16 V_d , which is essentially at the limit of aerodynamic resistance.

17 18 **AX1.6.2.2 Other Nitrates**

19 Methods for sampling and analysis of alkyl nitrates in the atmosphere have been
20 reviewed by Parrish and Fehsenfeld (2000). PAN, PPN, and MPAN are typically measured
21 using a gas chromatograph followed by electron capture detectors (GC/ECD) (see, e.g., Gaffney
22 et al., 1998), although other techniques such as Fourier Transform InfraRed (FTIR) analysis
23 could also be used. Field measurements made using GC/ECD have reported a total uncertainty
24 of ± 5 pptv + 15% (Roberts et al., 1998).

25 In the two most extensive networks in the United States, the Interagency Monitoring of
26 Protected Visual Environments (IMPROVE) and the Speciation Trends Network (STN) – see
27 additional description of these networks in Chapter 3 and Annex 2 – pNO_3 in the $\leq 2.5 \mu\text{m}$
28 ($\text{PM}_{2.5}$) size fraction is typically collected on nylon filters downstream of annular denuders
29 coated with a basic solution to remove acidic gases such as HNO_3 , HNO_2 , and H_2SO_4 . Filter
30 extracts are then analyzed by ion chromatography (IC) for NO_3^- , SO_4^{2-} , and Cl^- . NO_2^- ions are
31 also measured by this technique but their concentrations are almost always below operation

1 LODs. However, both networks measure NO_3^- only in the $\text{PM}_{2.5}$ fraction. Because of
2 interactions with more highly acidic components on filter surfaces, there can be volatilization of
3 NO_3^- in PM_{10} samples, those particulate matter samples having an aerodynamic diameter
4 $\leq 10 \mu\text{m}$. These effects are minimized if separate aerosol size fractions are collected; i.e., by
5 separating the more acidic $\text{PM}_{2.5}$ and the more alkaline $\text{PM}_{10-2.5}$ as is done in a dichotomous
6 sampler or multistage impactor.

7

8 **AX1.6.2.3 Remote Sensing of Tropospheric NO_2 Columns**

9 The paucity of in situ NO_2 measurements motivates the inference of surface NO_2
10 concentrations from satellite measurements of tropospheric NO_2 columns. These tropospheric
11 NO_2 columns have shown a strong correlation with in situ NO_2 measurements when tested in
12 northern Italy (Ordonez et al., 2006). Table AX1.6-1 contains an overview of the three satellite
13 instruments used to retrieve tropospheric NO_2 columns from measurements of solar backscatter.

14 The retrieval involves three steps: (1) determining total NO_2 line-of-sight (slant) columns
15 by spectral fitting of solar backscatter measurements; (2) removing the stratospheric columns by
16 using data from remote regions where the tropospheric contribution to the column is small; and
17 (3) applying an air mass factor (AMF) for the scattering atmosphere to convert tropospheric slant
18 columns into vertical columns. The retrieval uncertainty is determined by items (1) and (2) over
19 remote regions where there is little tropospheric NO_2 , and by (3) over regions in regions of
20 elevated tropospheric NO_2 (Martin et al., 2002; Boersma et al., 2004). All three instruments are
21 in polar sun-synchronous orbits with global measurements in the late morning and early
22 afternoon.

23 Figure AX1.6-1 shows tropospheric NO_2 columns retrieved from the Scanning Imaging
24 Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) instrument on the
25 European ENVISAT satellite, the spatial resolution for which is seven times better than that from
26 GOME (Global Ozone Monitoring Experiment). Pronounced enhancements are evident in
27 Figure AX1.6-1 over major urban and industrial emissions. The high degree of spatial
28 heterogeneity over the southwestern United States provides empirical evidence that most of the
29 tropospheric NO_2 column is concentrated in the lower troposphere. These tropospheric NO_2
30 columns are more sensitive to NO_x in the lower troposphere than in the upper troposphere
31 (Martin et al., 2002) because of the factor of 25 decrease in the NO_2/NO ratio from the surface to

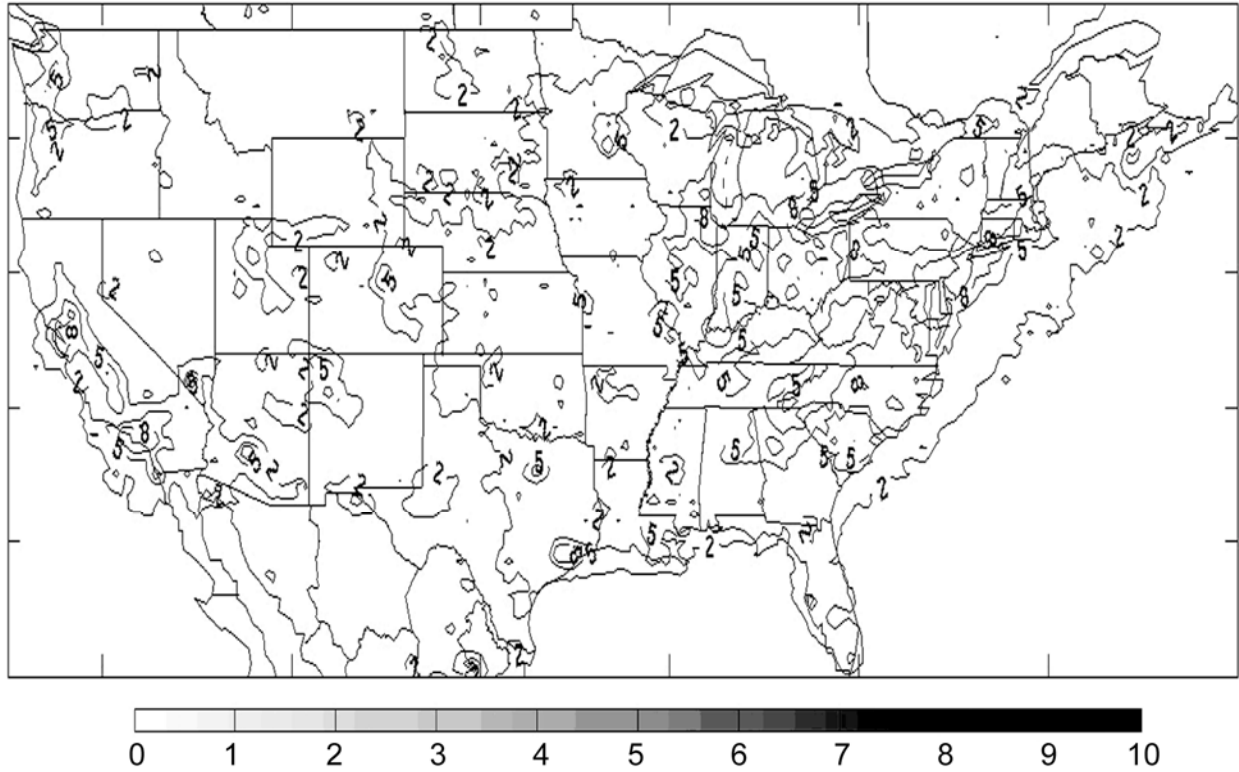


Figure AX1.6-1. Tropospheric NO₂ columns (molecules NO₂ cm⁻²) retrieved from the SCIAMACHY satellite instrument for 2004-2005.

Source: Martin et al. (2006).

1 the upper troposphere (Bradshaw et al., 1999) which is driven by the temperature dependence of
 2 the NO + O₃ reaction. Martin et al. (2004a) integrated in situ airborne measurements of NO₂ and
 3 found that during summer the lower mixed layer contains 75% of the tropospheric NO₂ column
 4 over Houston and Nashville. However, it should be noted that these measurements are also
 5 sensitive to surface albedo and aerosol loading.

6 Quantitative calculation of surface NO₂ concentrations from a tropospheric NO₂ column
 7 requires information on the relative vertical profile as described above. Comparison of vertical
 8 profiles of NO₂ in a chemical transport model (GEOS-Chem) versus in situ measurements over
 9 and downwind of North America shows a high degree of consistency (Martin et al., 2004b,
 10 2006), suggesting that chemical transport models could be used to infer the relationship between
 11 surface NO₂ concentrations and satellite observations of the tropospheric NO₂ column.
 12 However, because the satellites carrying the spectrometer are in near polar, sun-synchronous

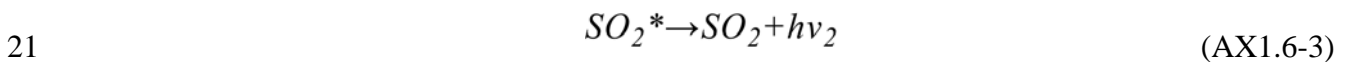
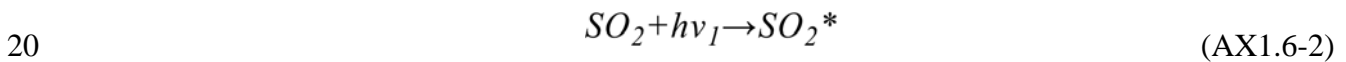
1 orbits producing measurements only once per day typically between 1000 and 1300 h local time
2 during a brief overflight, they likely miss fine time-scale features.

3

4 **AX1.6.3 SO_x Measurement Methods and Associated Issues**

5 Currently, ambient SO₂ is measured using instruments based on pulsed UV fluorescence.
6 The UV fluorescence monitoring method for atmospheric SO₂ was developed to improve upon
7 the flame photometric detection (FPD) method, which in turn had displaced the pararosaniline
8 wet chemical method. The pararosaniline method is still the EPA Federal Reference Method
9 (FRM) for atmospheric SO₂, but it is rarely used because of its complexity and slow response,
10 even in its automated forms. Both the UV fluorescence and FPD methods are designated as
11 Federal Equivalent Methods (FEMs) by EPA, but UV fluorescence has largely supplanted the
12 FPD approach because of the UV method's inherent linearity and sensitivity, and the need for
13 consumable H₂ gas for the FPD method.

14 In the UV fluorescence method, SO₂ molecules absorb UV light at one wavelength and
15 emit UV light at longer wavelengths in the process known as fluorescence through excitation of
16 the SO₂ molecule to a higher energy (singlet) electronic state. Once excited, the molecule decays
17 nonradiatively to a lower-energy electronic state from which it then decays to the original, or
18 ground, electronic state by emitting a photon of light at a longer wavelength (i.e., a lower-energy
19 photon) than the original incident photon. The process is summarized in the equations



22 where SO_2^* represents the excited state of SO₂, hv_1 , and hv_2 represent the energy of the
23 excitation and fluorescence photons, respectively, and $hv_2 < hv_1$. The intensity of the emitted
24 light is proportional to the number of SO₂ molecules in the sample gas.

25 In commercial analyzers, light from a high intensity UV lamp passes through a
26 bandwidth filter, allowing only photons with wavelengths around the SO₂ absorption peak (near
27 214 nm) to enter the optical chamber. The light passing through the source bandwidth filter is
28 collimated using a UV lens and passes through the optical chamber, where it is detected on the
29 opposite side of the chamber by the reference detector. A photomultiplier tube (PMT) is offset
30 from and placed perpendicular to the light path to detect the SO₂ fluorescence. Since the SO₂

1 fluorescence at 330 nm is different from the excitation wavelength, an optical bandwidth filter is
2 placed in front of the PMT to filter out any stray light from the UV lamp. A lens located
3 between the filter and the PMT focuses the fluorescence onto the active area of the detector and
4 optimizes the fluorescence signal. The LOD for a non-trace level SO₂ analyzer is 10 ppb (CFR,
5 2006). However, most commercial analyzers report detection limits of ~3 ppb. The EPA-
6 sponsored National Core Monitoring Network (NCORE) is intended to operate newer, trace-level
7 SO₂ instruments to increase the accuracy and precision of measurements at the much lower
8 ambient levels currently encountered in most of the United States.

9
10 **AX1.6.3.1 Sources of Positive Interference**

11 The most common source of interference to the UV fluorescence method for SO₂ is from
12 other gases that fluoresce in a similar fashion to SO₂ when exposed to UV radiation of that
13 wavelength. The most significant of these are PAHs, of which naphthalene is a prominent
14 example. Xylene is another common hydrocarbon that can cause fluorescent interference.
15 Consequently, any such aromatic hydrocarbons that are in the optical chamber can act as a
16 positive interference. To remove this source of interference, high-sensitivity SO₂ analyzers like
17 those to be used in the NCORE network have HC scrubbers to remove these compounds from the
18 sample stream before the sample air enters the optical chamber.

19 Luke (1997) reported the positive artifacts of a modified pulsed fluorescence detector
20 generated by the coexistence of nitric oxide (NO), CS₂, and a number of highly fluorescent
21 aromatic hydrocarbons such as benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, *m*-ethyltoluene,
22 ethylbenzene, and 1,2,4-trimethylbenzene. The positive artifacts could be reduced by using a
23 hydrocarbon “kicker” membrane. At a flow rate of 300 standard cc min⁻¹ and a pressure drop of
24 645 torr across the membrane, the interference from ppm levels of many aromatic hydrocarbons
25 was eliminated entirely. NO fluoresces in a spectral region close to that of SO₂. However, in
26 high-sensitivity SO₂ analyzers, the bandpass filter in front of the PMT is designed to prevent NO
27 fluorescence from being detected at the PMT. Care must be exercised when using
28 multicomponent calibration gases containing both NO and SO₂ so that the NO rejection ratio of
29 the SO₂ analyzer is sufficient to prevent NO interference.

30 The most common source of positive bias (as contrasted with positive spectral
31 interference) in high-sensitivity SO₂ monitoring is stray light reaching the optical chamber.

1 Since SO₂ can be electronically excited by a broad range of UV wavelengths, any stray light with
2 an appropriate wavelength that enters the optical chamber can excite SO₂ in the sample and
3 increase the fluorescence signal. Furthermore, stray light at the wavelength of the SO₂
4 fluorescence that enters the optical chamber may impinge on the PMT and increase the
5 fluorescence signal. Several design features are incorporated to minimize the stray light that
6 enters the chamber. These features include the use of light filters, dark surfaces, and opaque
7 tubing to prevent light from entering the chamber.

8 Nicks and Benner (2001) reported a sensitive SO₂ chemiluminescence detector based on
9 a differential measurement where response from ambient SO₂ is determined by the difference
10 between air containing SO₂ and air scrubbed of SO₂ when both air samples contain other
11 detectable sulfur species. Assuming monotonic efficiency of the sulfur scrubber, all positive
12 artifacts should also be reduced with this technique.

13 14 **AX1.6.3.2 Sources of Negative Interference**

15 Nonradiative deactivation (quenching) of excited SO₂ molecules can occur from
16 collisions with common molecules in air, including N₂, O₂, and H₂O. During collisional
17 quenching, the excited SO₂ molecule transfers energy, kinetically allowing the SO₂ molecule to
18 return to the original lower energy state without emitting a photon. Collisional quenching results
19 in a decrease in the SO₂ fluorescence and, hence, an underestimation of SO₂ concentration in the
20 air sample. Of particular concern is the variable water vapor content of air. Luke (1997)
21 reported that the response of the detector could be reduced by about 7 and 15% at water vapor
22 mixing ratios of 1 and 1.5 mole percent (RH = 35 to 50% at 20 to 25 °C and 1 atm) for a
23 modified pulsed fluorescence detector (Thermo Environmental Instruments, Model 43s).
24 Condensation of water vapor in sampling lines must be avoided, as water on the inlet surfaces
25 can absorb SO₂ from the sample air. The simplest approach to avoid condensation is to heat
26 sampling lines to a temperature above the expected dewpoint and to within a few degrees of the
27 controlled optical bench temperature. At very high [SO₂], reactions between electronically
28 excited SO₂ and ground state SO₂ might occur, forming SO₃²⁻ and SO (Calvert et al., 1978).
29 However, the possibility that this artifact might be affecting measurements at very high SO₂
30 levels has not been examined.

1 **AX1.6.3.3 Other Techniques for Measuring SO₂**

2 A more sensitive SO₂ measurement method than UV fluorescence was reported by
3 Thornton et al. (2002) using an atmospheric pressure ionization mass spectrometer. The high
4 measurement precision and instrument sensitivity were achieved by adding isotopically labeled
5 SO₂ (³⁴S¹⁶O₂) continuously to the manifold as an internal standard. Field studies showed that the
6 method precision was better than 10% and the LOD was less than 1 ppt for a sampling interval of
7 1s.

8 SO₂ can also be measured by LIF at ~220 nm (Matsumi et al., 2005). Because the laser
9 wavelength is alternately tuned to an SO₂ absorption peak at 220.6 and a bottom value at 220.2
10 nm and the difference signal at the two wavelengths is used to extract the [SO₂] value, the
11 technique eliminates with high sensitivity (5 ppt in 60 s) interference from either absorption or
12 fluorescence by other species. SO₂ can also be measured with DOAS in a way analogous to that
13 described above for NO₂.

14 Photoacoustic techniques have been employed for SO₂ detection, but generally with
15 LODs suitable only for source monitoring (Gondal, 1997; Gondal and Mastromarino, 2001).

16 A CIMS technique for SO₂ has shown sensitivity at 10 ppt or better for 1 Hz sampling
17 frequencies with an uncertainty of ~15% when a charcoal scrubber is used for zeroing and the
18 sensitivity is measured with isotopically labeled ³⁴SO₂ (Hanke et al., 2003; Huey et al., 2004;
19 Hennigan et al., 2006).

20

21 **AX1.6.4 Sampling and Analysis for SO₄²⁻, NO₃⁻, and NH₄⁺**

22 SO₄²⁻, NO₃⁻, and NH₄⁺ are commonly present in PM_{2.5}. Air is drawn through the sample
23 filter at a controlled flow rate by a pump located downstream of the sample filter. The systems
24 generally have two critical flow-rate components for the capture of fine particulate: (1) the flow
25 of air through the sampler must be at a flow rate that ensures the 2.5 μm size cut is met; and (2)
26 the flow rate must be optimized to capture the desired amount of particulate loading with respect
27 to the analytical method detection limits.

28 When using the technique described above to collect pSO₄²⁻, pNO₃⁻ and pNH₄⁺,
29 sampling artifacts can occur principally for two reasons: (1) positive sampling artifacts for all
30 three species due to chemical reactions on the filter face; and (2) negative sampling artifacts for
31 NO₃⁻ and NH₄⁺ due to decomposition and evaporation after capture on the filter.

1 **AX1.6.4.1 Denuder + Filter-based Techniques**

2 The two major PM speciation ambient air-monitoring networks in the United States, STN
3 and IMPROVE, implement the general technique sketched above with somewhat different
4 instruments and protocols. Current STN samplers include three filters: (1) Teflon for
5 equilibrated mass and elemental analysis including elemental sulfur; (2) a HNO₃-denuded Nylon
6 filter for ion analysis including NO₃⁻ and SO₄²⁻; and (3) a quartz-fiber filter for elemental and
7 organic carbon (EC and OC, respectively) analyzed using the thermal-optical reflectance (TOR)
8 method. The IMPROVE sampler, which collects two 24-h samples each week, simultaneously
9 collects one PM₁₀ sample on a Teflon filter, and three samples of PM_{2.5} on Teflon, Nylon, and
10 quartz as STN does. In each network, total mass concentrations of PM_{2.5} are determined
11 gravimetrically from the PM_{2.5} Teflon filter samples, which are also used to determine
12 concentrations of selected individual elements. The STN and IMPROVE networks represent a
13 major advance in the measurement of pNO₃, because the combination of a denuder coated with
14 either Na₂CO₃ or MgO to remove HNO₃ vapor and a nylon filter to adsorb HNO₃ vapor
15 volatilizing from the collected NH₄NO₃ particles overcomes the loss of NO₃⁻ from Teflon filters.

16 The degree of success in addressing sampling artifacts with pNH₄ in the current networks
17 is not entirely clear. Recently, new denuder+filter sampling systems have been developed to
18 measure SO₄²⁻, NO₃⁻, and NH₄⁺ with an adequate correction of NH₄⁺ sampling artifacts. One
19 denuder + filter system, the Chemcomb Model 3500 speciation sampling cartridge developed
20 by Rupprecht and Patashnick Co, Inc. could be used to collect SO₄²⁻, NO₃⁻, and NH₄⁺
21 simultaneously. The sampling system contains a single-nozzle size-selective inlet, two
22 honeycomb denuders, the aerosol filter, and two backup filters (Keck and Wittmaack, 2005).
23 The first denuder in the system is coated with 0.5% sodium carbonate and 1% glycerol and
24 collects acid gases such as HCL, SO₂, HNO₂, and HNO₃. The second denuder is coated with
25 0.5% phosphoric acid in methanol for collecting NH₃. Backup filters coated with the same
26 solutions as the denuders collect the gases behind denuded filters. A similar system based on the
27 same principle was applied by Possanzini et al. (1999). The system contains two NaCl-coated
28 annular denuders followed by other two denuders coated with NaCO₃/glycerol and citric acid,
29 respectively. This configuration was adopted to remove HNO₃ quantitatively on the first NaCl-
30 denuder. The third and forth denuder remove SO₂ and NH₃, respectively. A polyethylene
31 cyclone and a two-stage filter holder containing three filters is placed downstream of the

1 denuders. Aerosol fine particles are collected on a Teflon membrane. A backup nylon filter and
2 a subsequent citric acid impregnated filter paper collect dissociation products (HNO_3 and NH_3)
3 of NH_4NO_3 evaporated from the PM on the filter face.

4 Several methods could be used to quantify elemental S collected on filters: energy
5 dispersive X-ray fluorescence (EDXRF), synchrotron induced X-ray fluorescence, proton
6 induced X-ray emission (PIXE), total reflection X-ray fluorescence, and scanning electron
7 microscopy (SEM). EDXRF (Method IO-3.3, U.S. Environmental Protection Agency, 1997; see
8 the U.S. Environmental Protection Agency, 2004 for details) and PIXE are the most commonly
9 used methods. Since sample filters often contain very small amounts of particle deposits,
10 preference is given to methods that can accommodate small sample sizes and require little or no
11 sample preparation or operator time after the samples are placed into the analyzer. XRF meets
12 these needs and leaves the sample intact after analysis so it can be submitted for additional
13 examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF
14 typically places the filters in a vacuum which may cause volatile compounds to evaporate. As a
15 result, species such as NH_4NO_3 and certain organic compounds can be lost during the analysis.
16 The effects of this volatilization are important if the Teflon filter is to be subjected to subsequent
17 analyses of volatile species.

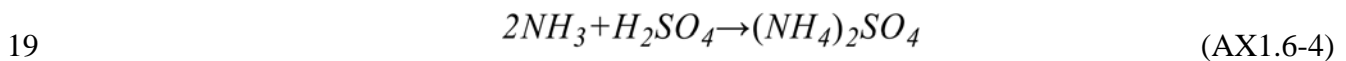
18 Polyatomic ions such as SO_4^{2-} , NO_3^- , and NH_4^+ are quantified by methods such as IC or
19 automated colorimetry for some NH_4^+ samples. All ion analysis methods require a fraction of
20 the filter to be extracted in deionized distilled water for SO_4^{2-} , and in $\text{NaCO}_3/\text{NaHCO}_3$ solution
21 for NO_3^- and then filtered to remove insoluble residues prior to analysis. The extraction volume
22 should be as small as possible to avoid over-diluting the solution and inhibiting the detection of
23 the desired constituents at levels typical of those found in ambient $\text{PM}_{2.5}$ samples. During
24 analysis, the sample extract passes through an ion-exchange column which separates the ions in
25 time for individual quantification, usually by an electroconductivity detector. The ions are
26 identified by their elution/retention times and are quantified by the conductivity peak area or
27 peak height.

28 In a side-by-side comparison of two of the major aerosol monitoring techniques (Hains
29 et al., 2007), $\text{PM}_{2.5}$ mass and major contributing species were well correlated among the different
30 methods with r-values in excess of 0.8. Agreement was good for total mass, SO_4^{2-} , OC, total
31 carbon (TC), and NH_4^+ , while NO_3^- and black carbon (BC) showed less-good fits. Based on

1 reported uncertainties, however, even daily concentrations of PM_{2.5} mass and major contributing
2 species were often significantly different at the 95% confidence level. Greater values of PM_{2.5}
3 mass and individual species were generally reported from STN methods than from the Desert
4 Research Institute Sequential Filter Samplers. These differences can only be partially accounted
5 for by known random errors. The authors concluded that the current uncertainty estimates used
6 in the STN network may underestimate the actual uncertainty.

7
8 **AXI.6.4.1.1 Positive Sampling Artifacts**

9 The reaction of SO₂ and other acid gases with basic sites on glass fiber filters or with
10 basic coarse particles on the filter leads to the formation of SO₄²⁻ or other nonvolatile salts, e.g.,
11 NO₃⁻, Cl⁻). These positive artifacts lead to the overestimates of the concentrations of PM total
12 mass and SO₄²⁻ and probably NO₃⁻ as well. These problems were largely overcome by changing
13 to quartz fiber or Teflon filters and by the separate collection of PM_{2.5}. However, the possible
14 reaction of acidic gases with basic coarse particles remains a possibility, especially with PM₁₀
15 and PM_{10-2.5} measurements. These positive artifacts could be effectively eliminated by removing
16 acidic gases in the sampling line with denuders coated with NaCl or Na₂CO₃. Positive sampling
17 artifacts also occur during measurement of pNH₄. The reaction of NH₃ with acidic particles, as
18 for example



20 either during sampling or during transportation, storage, and equilibration could lead to an
21 overestimation of pNH₄ concentrations. Techniques have been developed to overcome this
22 problem, including using a denuder coated with HF, or citric or phosphorous acid to remove NH₃
23 during sampling and to protect the collected PM from NH₃ (Suh et al., 1992, 1994; Brauer et al.,
24 1991; Koutrakis et al., 1988a,b; Keck and Wittmaack, 2006; Possanzini et al., 1999; Winberry
25 et al., 1999). Positive artifacts for pNH₄ can also develop during sample handling due to
26 contamination.

27 No chemical analysis method, no matter how accurate or precise, can adequately
28 represent atmospheric concentrations if the filters to which these methods are applied are
29 improperly handled. NH₃ is emitted directly from human sweat, breath and smoking. It can then
30 react with acidic aerosols on the filter to form (NH₄)₂SO₄, NH₄HSO₄, and NH₄NO₃ if the filter

1 was not properly handled (Sutton et al., 2000). Therefore, it is important to keep filters away
2 from NH₃ sources, such as human breath, to minimize neutralization of the acidic compounds.
3 Also, when filters are handled, preferably in a glove box, the analyst should wear gloves that are
4 antistatic and powder-free to act as an effective contamination barrier.

5
6 **AXI.6.4.1.2 Negative Sampling Artifacts**

7 Although pSO₄²⁻ is relatively stable on a Teflon filter, it is now well known that
8 volatilization losses of pNO₃ occur during sampling. For NO₃⁻, the effect on the accuracy of
9 atmospheric particulate measurements from these volatilization losses is more significant for
10 PM_{2.5} than for PM₁₀. The FRM for PM_{2.5} will likely suffer a loss of NO₃⁻ similar to that
11 experienced with other simple filter collection systems. Sampling artifacts resulting from the
12 loss of pNO₃ species represents a significant problem in areas such as southern California that
13 experience high NO₃⁻ loadings. Hering and Cass (1999) discussed errors in PM_{2.5} mass
14 measurements due to the volatilization of pNO₃. They examined data from two field
15 measurement campaigns that were conducted in southern California: (1) the Southern California
16 Air Quality Study (SCAQS) (Lawson, 1990); and (2) the 1986 California Institute of Technology
17 (CalTech) study (Solomon et al., 1992). In both these studies, side-by-side sampling of PM_{2.5}
18 was conducted with one sampler collecting particles directly onto a Teflon filter, and the second
19 using an MgO-coated denuder (Appel et al., 1981) to remove gaseous HNO₃ followed by a nylon
20 filter that absorbed the HNO₃ as it evaporated. In both studies, the PM_{2.5} mass lost from
21 NH₄NO₃ volatilization represented a significant fraction of the total PM_{2.5} mass with greater
22 losses during summer than fall: 17% versus 9% during SCAQS, and 21% versus 13% during
23 CalTech. In regard to percentage loss of NO₃⁻, as opposed to percentage loss of mass discussed
24 above, Hering and Cass (1999) found that the amount of NO₃⁻ remaining on the Teflon filter
25 samples was, on average, 28% less than that on the HNO₃-denuded Nylon filters.

26 Hering and Cass also analyzed these data by extending the evaporative model developed
27 by Zhang and McMurry (1987). Their extended model (Herring and Cass, 1999) takes into
28 account the dissociation of collected NH₄NO₃ on Teflon filters into HNO₃ and NH₃ via three
29 mechanisms: (1) the scrubbing of HNO₃ and NH₃ in the sampler inlet (John et al., 1988 showed
30 that clean PM₁₀ inlet surfaces serve as an effective denuder for HNO₃); (2) the heating of the
31 filter substrate above ambient temperature by sampling; and (3) the pressure drop across the

1 Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured
2 to be less than 0.02 atmosphere for a corresponding change in vapor pressure of 2%, so losses
3 driven by pressure drop were not considered significant. Losses from Teflon filters were found
4 to be higher during the summer than during the winter, higher during the day compared to night,
5 and were reasonably consistent with modeled predictions.

6 Finally, during the SCAQS study, particulate samples also were collected using a Berner
7 impactor and greased Tedlar substrates in size ranges from 0.05 to 10 μm in aerodynamic
8 diameter. The Berner impactor $\text{PM}_{2.5} \text{NO}_3^-$ values were much closer to those from the denuded
9 Nylon filter than those from the Teflon filter: NO_3^- from the impactor being ~2% lower than
10 that from the Nylon filter in the fall and ~7% lower in the summer. When the impactor
11 collection was compared to the Teflon filter collection for SO_4^{2-} , the results were in agreement.
12 Chang et al. (2000) discuss additional reasons for reduced loss of NO_3^- from impactors.

13 Brook and Dann (1999) observed much greater NO_3^- losses during a study in which they
14 measured pNO_3 in Windsor and Hamilton, Ontario, Canada, by three techniques: (1) a single
15 Teflon filter in a dichotomous sampler; (2) the Teflon filter in an annular denuder system (ADS);
16 and (3) total NO_3^- including both the Teflon filter and the Nylon back-up filter from the ADS.
17 The Teflon filter from the dichotomous sampler averaged only 13% of the total NO_3^- , whereas
18 the Teflon filter from the ADS averaged 46% of the total NO_3^- . The authors concluded that
19 considerable NO_3^- was lost from the dichotomous sampler filters during handling, which
20 included weighing and X-ray fluorescence (XRF) measurement in a vacuum.

21 Kim et al. (1999) also examined NO_3^- sampling artifacts by comparing denuded and non-
22 denuded quartz and Nylon filters during the PM_{10} Technical Enhancement Program (PTEP) in
23 the South Coast Air Basin of California. They observed negative NO_3^- artifacts (losses) for most
24 measurements; however, for a significant number of measurements, they observed positive NO_3^-
25 artifacts. Kim et al. (1999) pointed out that random measurement errors make it difficult to
26 measure true amounts of NO_3^- loss.

27 Diffusion denuder samplers, developed primarily to measure particle strong acidity
28 (Koutrakis et al., 1988b, 1992), also can be used to study NO_3^- volatilization. Measurements
29 were made with two versions of the Harvard-EPA Annular Denuder System (HEADS) for which
30 HNO_3 vapor was removed by a Na_2CO_3 -coated denuder and the remaining pNO_3 was reported
31 either as the sum of nonvolatile NO_3^- collected on a Teflon filter and volatilized NO_3^- collected

1 on a Na₂CO₃-coated filter downstream of the Teflon filter (full HEADS), or on a nylon filter
2 downstream of the Teflon filter (nylon HEADS). The full HEADS consistently underestimated
3 the total pNO₃ by approximately 20% compared to the Nylon HEADS.

4 Such techniques were used to measure loss of pNO₃ from Teflon filters in seven U.S.
5 cities (Babich et al., 2000). Babich et al. (2000) found significant NO₃⁻ losses in Riverside, CA;
6 Philadelphia, PA; and Boston, MA; but not in Bakersfield, CA; Chicago, IL; Dallas, TX; or
7 Phoenix, AZ, where measurements were made only during winter.

8 Tsai and Huang (1995) used a diffusion denuder to study the positive and negative
9 artifacts on glass and quartz filters. They found positive artifacts attributed to SO₂ and HNO₃
10 reaction with basic sites on glass fibers and basic particles and negative artifacts attributed to loss
11 of HNO₃ and HCl due to volatilization of NH₄NO₃ and NH₄Cl and reaction of these species with
12 acid SO₄²⁻.

13 Volatile compounds can also leave the filter after sampling but prior to filter weighing or
14 chemical analysis. Losses of NO₃, NH₄, and Cl from glass and quartz-fiber filters stored in
15 unsealed containers at ambient air temperatures for 2 to 4 weeks prior to analysis exceeded 50%
16 (Witz et al., 1990). Storing filters in sealed containers and under refrigeration will minimize
17 these losses.

18 Negative sampling artifacts due to decomposition and volatilization are also significant
19 for pNH₄. [NH₄⁺] are very sensitive to some environmental factors, such as temperature, RH,
20 acidity of aerosols, as well as to filter type (Spurny, 1999; Keck and Wittmaack, 2005). Any
21 change in these parameters during the sampling period influences the position of the equilibrium
22 between the particle and gas phase. Keck and Wittmaack (2005) observed that at temperatures
23 below 0 °C, acetate-nitrate, quartz fiber, and Teflon filters could properly collect pNH₄, NH₃,
24 and Cl⁻; but at temperatures above 0 °C, the salts were lost from quartz fiber and Teflon filters,
25 more so the higher the temperature and with no significant difference between quartz fiber and
26 Teflon filters. The salts were lost completely from denuded quartz fiber filters above ~20 °C,
27 and from non-denuded quartz fiber and Teflon filters above ~25 °C. It is anticipated that
28 current sampling techniques underestimate pNH₄ concentrations due to volatilization, but fine
29 particle mass contains many acidic compounds, and as consequence, a fraction of volatilized
30 NH₄ in the form of NH₃ can be retained on the Teflon filter by reaction with them. Therefore, it
31 is reasonable to assume that pNH₄ loss will be less than NO₃⁻ loss. Techniques have been

1 applied to pNH₄ sampling to correct its concentrations due to evaporation using a backup filter
2 coated with hydrofluoric acids, citric acid, or phosphorous acids to absorb the evaporated NH₄ as
3 NH₃; total [NH₄] then is the sum of the pNH₄ collected on the Teflon filter and [NH₃] collected
4 on the backup filter.

5

6 **AX1.6.4.2 Other Techniques**

7 An integrated collection and vaporization cell was developed by Stolzenburg and Hering
8 (2000) that provides automated 10 min resolution monitoring of fine pNO₃. In this system,
9 particles are collected by a humidified impaction process and analyzed in place by flash
10 vaporization and chemiluminescent detection of the evolved NO_x. In field tests where the
11 system was collocated with two FRM samplers, the automated NO₃ sampler results tracked those
12 from the FRM, though systematically lower. The Stolzenburg and Hering system also was
13 collocated with a HEADS and a SASS speciation sampler (MetOne Instruments). In all these
14 tests, the automated sampler was well-correlated to other samplers with slopes ranging from
15 0.95° for the FRM to 1.06 for the HEADS and correlation coefficients ranging from 0.94 to
16 0.996. During the Northern Front Range Air Quality Study in Colorado (Watson et al., 1998),
17 the automated NO₃⁻ monitor captured the 12-min variability in fine [pNO₃] with a precision of
18 ~±0.5 μg m⁻³ (Chow et al., 1998). A comparison with denuded filter measurements followed by
19 IC analysis (Chow and Watson, 1999) showed agreement to within ± 0.6 μg m⁻³ for most of the
20 measurements, but exhibited a discrepancy of a factor of 2 for elevated periods of elevated
21 [NO₃⁻]. Intercomparisons during the 1997 Southern California Ozone Study (SCOS97) in
22 Riverside, CA made over 14 days against 24-h denuder+filter sampling showed no significant
23 bias with an R² = 0.87. As currently configured, the system LOD is 0.7 μg m⁻³ and its precision
24 is 0.2 μg m⁻³.

25 Continuous methods for the quantification of aerosol S compounds first remove gaseous
26 S (chiefly SO₂, H₂S) from the sample stream by a diffusion tube denuder followed by the
27 analysis of particulate sulfur (Cobourn et al., 1978; Durham et al., 1978; Huntzicker et al., 1978;
28 Mueller and Collins, 1980; Tanner et al., 1980). Another approach is to measure total S and
29 gaseous S separately by alternately removing particles from the sample stream. Particulate S is
30 obtained as the difference between the total and gaseous S concentrations (Kittelson et al., 1978).
31 The total S content is measured by a flame photometric detector (FPD) by introducing the

1 sampling stream into a fuel-rich, hydrogen-air flame (e.g., Stevens et al., 1969; Farwell and
 2 Rasmussen, 1976) that reduces S compounds and measures the intensity of the
 3 chemiluminescence from electronically excited S molecules (S_2^*). Because the formation of S_2^*
 4 requires two S atoms, the intensity of the chemiluminescence is theoretically proportional to the
 5 square of the concentration of molecules that contain a single S atom. In practice, the exponent
 6 is between 1 and 2 and depends on the particular S compound being analyzed (Dagnall et al.,
 7 1967; Stevens et al., 1971). Calibrations are performed using both particles and gases as
 8 standards. The FPD can also be replaced by a chemiluminescent reaction with O_3 that minimizes
 9 the potential for interference and provides a faster response time (Benner and Stedman, 1989,
 10 1990). Capabilities added to the basic system include in situ thermal analysis and H_2SO_4
 11 speciation (Cobourn et al., 1978; Huntzicker et al., 1978; Tanner et al., 1980; Cobourn and
 12 Husar, 1982). Sensitivities for particulate S as low as $0.1 \mu\text{g m}^{-3}$, with time resolution ranging
 13 from 1 to 30 min, have been reported. Continuous measurements of particulate S content have
 14 also been obtained by on-line XRF analysis with resolution of 30 min or less (Jaklevic et al.,
 15 1981). During a field-intercomparison study of five different S instruments, Camp et al. (1982)
 16 reported four out of five FPD systems agreed to within $\pm 5\%$ during a 1-week sampling period.

TABLE AX1.4-1a. RELATIVE CONTRIBUTIONS OF VARIOUS REACTIONS TO THE TOTAL S(IV) OXIDATION RATE WITHIN A SUNLIT CLOUD, 10 MINUTES AFTER CLOUD FORMATION

Reaction	% of Total ^a	# of Total ^b
Gas Phase		
OH + SO ₂	3.5	3.1
Aqueous Phase		
O ₃ + HSO ₃ ⁻	0.6	0.7
O ₃ + SO ₃ ²⁻	7.0	8.2
H ₂ O ₂ + SO ₃ ⁻	78.4	82.1
CH ₃ OOH + HSO ₃ ⁻	0.1	0.1
HNO ₄ + HSO ₃ ⁻	9.0	4.4
HOONO + HSO ₃ ⁻	<0.1	<0.1
HSO ₅ ⁻ + HSO ₃ ⁻	1.2	<0.1
SO ₅ ⁻ + SO ₃ ²⁻	<0.1	<0.1
HSO ₅ ⁻ + Fe ²⁺		0.6

^a In the absence of transition metals.

^b In the presence of iron and copper ions.

Source: Adapted from Warneck (1999).

TABLE AX1.4-1b. RELATIVE CONTRIBUTIONS OF VARIOUS GAS AND AQUEOUS PHASE REACTIONS TO AQUEOUS NITRATE FORMATION WITHIN A SUNLIT CLOUD, 10 MINUTES AFTER CLOUD FORMATION

Reaction	% of Total ^a	# of Total ^b
Gas Phase		
OH + NO ₂ + M	57.7	67.4
Aqueous Phase		
N ₂ O _{5g} + H ₂ O	8.1	11.2
NO ₃ + Cl ⁻	<0.1	0.1
NO ₃ + HSO ₃ ⁻	0.7	1.0
NO ₃ + HCOO ⁻	0.6	0.8
HNO ₄ + HSO ₃ ⁻	31.9	20.5
HOONO + NO ₃ ⁻	0.8	<0.1
O ₃ + NO ₂ ⁻	<0.1	<0.1

^a In the absence of transition metals.

^b In the presence of iron and copper ions.

Source: Adapted from Warneck (1999).

TABLE AX1.6-1. SATELLITE INSTRUMENTS USED TO RETRIEVE TROPOSPHERIC NO₂ COLUMNS

Instrument	Coverage	Typical U.S. Measurement Time	Typical Resolution (km)	Return Time (days) ¹	Instrument Overview
GOME	1995-2002	10:30-11:30 AM	320 × 40	3	Burrows et al. (1999)
SCIAMACHY	2002-	10:00-11:00 AM	30 × 60	6	Bovensmann et al. (1999)
OMI	2004-	12:45-1:45 PM	13 × 24	1	Levelt et al. (2006)

¹ Return time is reported here for cloud free conditions. Note that due to precession of the satellite's orbit, return measurements are close to but not made over the same location. In practice, clouds decrease observation frequency by a factor of 2.

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1 **AX2. ECOLOGICAL EXPOSURES TO OXIDES OF**
2 **NITROGEN AND SULFUR, AND TO AMMONIA AND**
3 **AMMONIUM**

4
5
6 Estimated annual emissions of nitrogen oxides (NO_x), sulfur dioxide (SO₂; the category
7 label for all oxides of sulfur is SO_x), and ammonia (NH₃) for 2002 (U.S. Environmental
8 Protection Agency, 2006) are given in Table AX2-1. Methods for estimating these emissions,
9 quality assurance procedures, and examples of calculated emissions are given in U.S.
10 Environmental Protection Agency (1999). Recent discussions of uncertainties in current
11 emissions inventories, and strategies for improving these inventories, are found in NARSTO
12 (2005). This section provides brief summaries of information on sources and sinks of some
13 relevant NO_x and SO_x species and NH₃ and ammonium (NH₄⁺). (The category label for NH₃
14 and NH₄⁺ is NH_x.) Chemical and physical processes that transport, transform, and deposit
15 these species to ecological receptors are described here both as observed and as represented in
16 numerical chemical-transport models (CTMs). Last, estimates of the “policy-relevant
17 background” (PRB) NO_x and SO_x concentrations ([NO_x] and [SO_x], respectively) used to
18 inform policy decisions about the indicator species and levels of the National Ambient Air
19 Quality Standards (NAAQS) are presented.

20
21
22 **AX2.1 EMISSIONS OF NITROGEN OXIDES**

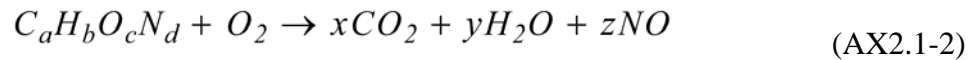
23
24 **AX2.1.1 Anthropogenic Sources of NO and NO₂**

25 Combustion chemistry at stationary sources like electrical utilities and various industries
26 accounts for roughly one-half of total anthropogenic emissions of NO_x; mobile source emissions
27 account for the rest, with on-road highway vehicles representing the major mobile source
28 component. Approximately one-half of the mobile source emissions are contributed by diesel
29 engines and one-half from gasoline-fueled vehicles and other sources.

30 Emissions of NO_x from combustion are derived from both fuel N and atmospheric N.
31 Combustion-zone temperatures > ~1300 K are required to fix atmospheric N₂



2 Below this temperature NO can be formed from fuel N by



4 Sawyer et al. (2000) have reviewed the factors associated with NO_x emissions by mobile
5 sources. Both reactions AX2.1-1 and AX2.1-2 have temperature dependencies and vary with
6 concentrations of hydroxyl radical (OH), hydroperoxy radical (HO₂) and O₂.

7 The N content in fossil fuels is highly variable, ranging from 0.05% by weight (wt %) in
8 light distillates such as diesel fuel, to 1.5 wt % in heavy fuel oils, and from 0.5 to 2.0 wt % in
9 coal (UK AQEG, 2004). The ratio of NO₂ to NO_x in present-day primary emissions ranges
10 from: 3 to 5 % from gasoline engines; 5 to 12% from heavy-duty diesel truck engines; 5 to 10%
11 from vehicles fueled by compressed natural gas; and 5 to 10% from stationary sources.
12 However, there is evidence that this ratio may be changing as the mobile source fleet begins to
13 include larger fractions of emissions-restricted diesel engines. In addition to NO_x, motor
14 vehicles also emit nitrous acid (HNO₂) with measured HNO₂ ratios to NO_x ranging from a low
15 of 0.3% in the Caldecott Tunnel, San Francisco, CA, (Kirchstetter and Harley, 1996) up to 0.5 to
16 1.0% in studies in the United Kingdom (UK AQEG, 2004). The NO₂ to NO_x ratios in emissions
17 from turbine jet engines are as high as 35% during taxi and takeoff (U.S. Environmental
18 Protection Agency, 1996). Marine transport represents an additional source of NO_x in the
19 United States, especially for coastal cities with large ports, but constitutes a larger source in the
20 EU where it is expected to represent more than 60 % of land-based NO_x sources (UK AQEG,
21 2004).

22 23 **AX2.1.2 Biogenic Sources of NO and NO₂**

24 25 **AX2.1.2.1 Soils**

26 The pathways for nitrification and denitrification include two gas-phase intermediates,
27 nitric oxide (NO) and nitrous oxide (N₂O), that can evolve from the soil microbes before
28 reaching the reaction endpoint, N₂. NO from soil metabolism is the dominant, but not exclusive,
29 source of atmospheric NO_x from the biosphere. As noted below and in Chapter 3, our
30 understanding of NO₂ exchange with vegetation suggests that there should be emissions of NO₂

1 from foliage when ambient concentrations are less than the compensation point of ~1 part per
2 billion (ppb). However, Lerdaun et al. (2000) have pointed out that present understanding of the
3 global distribution of NO_x is not consistent with the large source that would be expected in
4 remote forests if NO_2 emission were important when atmospheric concentrations were below that
5 compensation point.

6 Temperature, soil moisture, and $[\text{O}_2]$ control both the rates of reaction and, more
7 importantly, the partitioning between NO and N_2O . In flooded soils where $[\text{O}_2]$ are low, N_2O is
8 the dominant soil N gas; as soil dries, allowing more O_2 to diffuse, NO emissions increase. In
9 very dry soils, microbial activity is inhibited and emissions of both N_2O and NO decrease. N
10 metabolism in soil is strongly dependent on the substrate concentrations. Where N is limiting, it
11 is efficiently retained and little gaseous N is released. Where N is in excess of demand, gaseous
12 N emissions increase. As a consequence, soil NO emissions are highest in fertilized agriculture
13 and tropical soils (Davidson and Kinglerlee, 1997; Williams et al., 1992). N_2O is not among the
14 nitrogen oxides important for urban and regional air quality as relates to either human or
15 ecological health because its reaction potential on these scales in the troposphere is insignificant.
16 However, N_2O is also a greenhouse gas (GHG) with a significant global warming potential
17 (GWP) from its direct radiative forcing and from its role in stratospheric O_3 depletion; these are
18 described in Section AX2.1.3.

19 Emission rates of NO from cultivated soils depend mainly on fertilization levels and soil
20 temperature. Production of NO from agriculture results from both the oxidation of NH_3 emitted
21 by livestock and from soils after fertilization with NH_4^+ and NO_3^- . Estimates of these biogenic
22 N emissions are less-certain than are those for anthropogenic emissions sources. On a global
23 scale, the contribution of soil emissions to the oxidized N budget is on the order of 10%
24 (Van Aardenne et al., 2001; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998); but NO_x
25 emissions from fertilized fields are highly variable. Soil NO emissions can be estimated from
26 the fraction of the applied fertilizer N emitted as NO_x , but the flux depends strongly on land use
27 type and temperature. Estimates of globally-averaged fractional applied N lost as NO varies
28 from 0.3% (Skiba et al., 1997) to 2.5% (Yienger and Levy, 1995). The variation within biomes
29 to which fertilizer is applied, such as between shortgrass and tallgrass prairie for example,
30 introduces uncertainty of a factor of 3 (Williams et al., 1992; Yienger and Levy, 1995; Davidson
31 and Kinglerlee, 1997).

1 Local contributions to soil NO can be much greater than the global average, particularly
2 in summer and especially where corn is grown extensively. Approximately 60% of total NO_x
3 emitted by soils in the United States occurs in the central corn belt. The mass and chemical form
4 of N (whether reduced or oxidized) applied to soils, the vegetative cover, temperature, soil
5 moisture, and agricultural practices such as tillage all influence the amount of fertilizer
6 N released as NO. Williams et al. (1992) estimated that contributions to NO budgets from soils
7 in Illinois are ~26% of the emissions from industrial and commercial processes in that state. In
8 Iowa, Kansas, Minnesota, Nebraska, and South Dakota – all states with smaller human
9 populations than Illinois – soil emissions may dominate the NO budget. Nitrification of fertilizer
10 NH₃ to NO₃ in aerobic soils appears to be the dominant pathway to soil NO.

11 Emissions of NO from soils peak in summer when O₃ formation is also at a maximum.
12 The significance of agricultural emission sources of NO and NH₃ among other air pollutants was
13 described in detail in a recent National Research Council (NRC) report (NRC, 2002). That
14 report recommended immediate implementation of best management practices to control these
15 emissions, and called for additional research to quantify the magnitude of emissions and the
16 effects of agriculture on air quality. Civerolo and Dickerson (1998) report that use of the no-till
17 cultivation technique on a fertilized cornfield in Maryland reduced NO emissions by a factor
18 of 7.

19 20 **AX2.1.2.2 Biomass Burning**

21 During biomass burning, N is derived mainly from fuel N and not from atmospheric N₂
22 since temperatures required to fix atmospheric N₂ are likely to be found only in the flaming
23 crowns of the most intense boreal forest fires. N is present mainly in plants as amino (NH₂)
24 groups in amino acids. During combustion, N is released in many unidentified forms,
25 presumably as N₂, with very little remaining in the fuel ash. Emissions of NO_x are ~0.2 to 0.3%
26 relative to total biomass burned (e.g., Andreae, 1991; Radke et al., 1991). Apart from N₂, the
27 most abundant species in biomass burning plumes is NO, emissions of which account for ~10 to
28 20% relative to fuel N loadings (Lobert et al., 1991); other N-containing species such as NO₂,
29 nitriles, and NH₃ together account for a similar amount. Westerling et al. (2006) have noted that
30 the frequency and intensity of wildfires in the western U.S. have increased substantially since
31 1970, lending added importance to consideration of emissions from this sector.

1 **AX2.1.2.3 Lightning**

2 Annual global production of NO by lightning is the most uncertain source of reactive N.
3 In the last decade, literature values of the global average production rate range from 2 to 20 Tg
4 N yr⁻¹. However, most recent estimates are in the range of 3 to 8 Tg N yr⁻¹. The large and
5 persistent uncertainty stems from several factors: (1) a wide range of as much as 2 orders of
6 magnitude in NO production rates per meter of flash length; (2) uncertainty over whether cloud-
7 to-ground (CG) flashes and intracloud (IC) flashes produce substantially different [NO]; (3) the
8 global average flash rate; and (4) the ratio of the number of IC flashes to the number of CG
9 flashes. A series of midlatitude and subtropical thunderstorm events have been simulated with
10 the model of DeCaria et al. (2005), and the derived NO production per CG flash averaged
11 500 moles flash⁻¹ while average production per IC flash was 425 moles flash⁻¹ (Ott et al., 2006).
12 Estimates of the [NO] produced per flash have been made from theoretical considerations (see
13 e.g., Price et al., 1997), laboratory experiments (see e.g., Wang et al., 1998), and field
14 experiments (see e.g., Stith et al., 1999; Huntrieser et al., 2002, 2007), and through a
15 combination of cloud-resolving model simulations, observed lightning flash rates, and
16 measurements of NO in cloud anvils (see e.g., DeCaria et al., 2000, 2005; Ott et al., 2007). The
17 latter method was also used by Pickering et al. (1998), who showed that only ~5 to 20% of the
18 total NO produced by lightning in a given storm exists in the planetary boundary layer (PBL) at
19 the end of a thunderstorm event, thereby reducing its importance as an emissions source to the
20 urban and regional troposphere.

21 22 **AX2.1.3 Anthropogenic and Biogenic Sources of N₂O**

23 Nitrous oxide (N₂O) is a gas-phase oxide of N with a τ of ~114 years. This long lifetime
24 results from N₂O having effectively no chemistry in the lower troposphere on urban and regional
25 scales. Because there are no tropospheric actions or effects to consider, N₂O is not discussed
26 here as a significant oxide of nitrogen for the review of the secondary NAAQS which this Annex
27 supports. However, because N₂O is also a greenhouse gas (GHG) with a global warming
28 potential (GWP) on the conventional 100-year time horizon of ~296 – i.e., N₂O is nearly 300
29 times more effective for trapping heat in the atmosphere than CO₂ over a 100-year period (U.S.
30 Environmental Protection Agency, 2002; IPCC, 2001) – its sources and role in the total budget of
31 U.S. GHG are described here.

1 N₂O is a small contributor to the total U.S. GHG budget with only 6.5% of total GHG (on
2 a Tg CO₂ equivalents basis) in 2005 (U.S. Environmental Protection Agency, 2007). CO₂, for
3 comparison, accounted for 83.9% in the same year and CH₄ for 7.4% (U.S. Environmental
4 Protection Agency, 2007). Although atmospheric [N₂O] has increased globally by ~18% to a
5 current value of ~315 ppb owing to Western industrialization since 1750 (IPCC, 2001; Hofmann,
6 et al., 2004), there is considerable interannual variation in N₂O emissions which remains largely
7 unexplained (IPCC, 2001). N₂O emissions in the United States, for example, decreased by 2.8%
8 (or 13.4 Tg CO₂ equivalents) over the years 1990—2005 (U.S. Environmental Protection
9 Agency, 2007).

10 Because of its extremely low reactivity and hence long τ in the troposphere, the radiative
11 forcing effects from N₂O in the stratosphere are both direct and indirect. By comparison, the
12 primary climate change effects of NO and NO₂ are indirect and result from their role in
13 promoting the formation of O₃ in the troposphere and, to a lesser degree, in the lower
14 stratosphere where NO_x has positive radiative forcing effects. Additionally, NO_x emissions
15 from high-altitude aircraft are also likely to decrease [CH₄], thus having a negative radiative
16 forcing (IPCC, 1999). U.S. EPA does not compute GWPs for NO_x or SO_x or particulate matter
17 (PM) or carbon monoxide (CO) because there is no agreed method to estimate the contributions
18 from gases that are short-lived in the atmospheric, are strongly spatially variable, or have only
19 indirect effects on radiative forcing (IPCC, 1999).

20 N₂O is produced by biological processes occurring in the soil and water and by a variety
21 of anthropogenic activities in the agricultural, energy, industrial, and waste management sectors.
22 The chief anthropogenic activities producing N₂O in the United States are agricultural soil
23 management, fuel combustion in motor vehicles, manure management, production of adipic acid
24 (nylon) and nitric acid (HNO₃), wastewater treatment, and stationary fuel combustion.

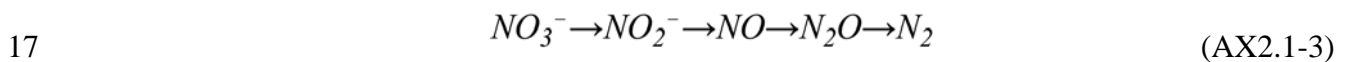
25 N₂O emissions from anthropogenic activities in the United States were 386.7 Tg CO₂
26 equivalent yr⁻¹ in the period between 1990 and 2004 (Environmental Protection Agency, 2007).
27 These emissions are the result of the fuel combustion, industrial practices, and stimulation of
28 biogenic sources through agriculture practices as listed above.

29 In 2005, N₂O emissions from mobile sources were 38.0 Tg CO₂ equivalents, or ~8% of
30 the U.S. N₂O emissions total (U.S. Environmental Protection Agency, 2007). From 1990 to
31 2005, N₂O emissions from mobile sources decreased by 13%; however, emissions increased by

1 10% in the period 1990—1998 as control technologies reduced on-road vehicle NO_x emissions
2 at the expense of increasing N₂O emissions. Since 1998, though, newer controls have led to a
3 steady decline in N₂O from mobile sources.

4 Biogenic production of N₂O stimulated through soil management accounted for >75% of
5 total U.S. N₂O emissions in 2005 (U.S. Environmental Protection Agency Inventory, 2007).
6 N₂O emissions from this source have shown no significant long-term trend because the biogenic
7 emitters are highly sensitive to the [N] applied to soils, which has been largely constant over the
8 time period (U.S. Environmental Protection Agency, 2007).

9 Biogenic N₂O emissions are predominately the result of incomplete bacterial
10 denitrification and nitrification processes that occur in soils, sediments, and water. (Figure
11 AX2.1-1 summarizes these processes.) Denitrification is a reduction process performed by
12 particular groups of heterotrophic bacteria having the ability to use nitrate (NO₃⁻) as an electron
13 acceptor during anaerobic respiration, thereby converting NO₃⁻ in soils and water to gas-phase
14 forms (Firestone and Davidson, 1989). At low [O₂], these microbial communities may use
15 NO₃⁻, nitrite (NO₂⁻), or N₂O as alternative electron acceptors to O₂, with molecular N₂ as the
16 final product in this reaction sequence (Davidson and Schimel, 1995)



18 There remains uncertainty about the conditions favoring the various products of the NO₃⁻
19 transformations. Groups of aerobic bacteria use most ammonium ion (NH₄⁺) in soils as an
20 energy source in which it is oxidized to NO₂ and then NO₃. Oxidized N products of nitrification
21 may undergo denitrification and thus feed the production of N₂O. Some bacteria are shown to be
22 nitrifiers and denitrifiers depending on the environmental conditions.

23 Emissions of NO and N₂O can be increased by agricultural practices and activities,
24 including the use of synthetic and organic fertilizers, production of N-fixing crops, cultivation of
25 soils with high organic content, and the application of livestock manure to croplands and pasture.
26 All of these practices directly add N to soils, of which a portion may then be converted to N₂O
27 on the pathway to full conversion to N₂. Indirect additions of N to soils can also result in N₂O
28 emissions from agricultural and non-agricultural systems. Indirect additions include processes
29 by which atmospheric NO_x is deposited directly to a region or N from applied fertilizer or

Denitrification: $\text{NO}_3^- \rightarrow \text{N}_2$ (gas) (N_2O intermediate product of incomplete reaction)

- General conditions that increase denitrification:
 - Low O_2
 - Flooded, anoxic soils
 - Well-drained soils with low O diffusion
 - Rainfall because O diffuses slower in wet soils
- Controls on ratios of gases are poorly understood but include
 - Soil pH
 - Relative abundance of NO_3^- and oxygen as oxidants and C as reductant
 - Acetylene may block the conversion of N_2O to N_2
 - When NO_3^- is abundant relative to C more N_2O is produced
 - Occurs in almost all types of ecosystems
 - Terrestrial
 - Freshwater
 - Coastal
 - Some oceanic ecosystems

Nitrification: oxidization of $\text{NH}_4^+ \rightarrow \text{NO}_3^-$

- Conditions that increase nitrification:
 - Higher O_2
 - C/N ratio (stimulated below ratio of 25)
 - Higher temperatures (77-86 °F)
- Causes acidity in soils

Figure AX2.1-1. Summary of biogenic denitrification and nitrification.

1 manure volatilizes into NH_3 and NO_x and then is ultimately re-deposited onto the soil in the
2 form of NH_4NO_3 , HNO_3 , and NO_x (U.S. Environmental Protection Agency, 2006).

3 Aquatic sources of N_2O may also be stimulated by environmental conditions. In some
4 ocean areas, large areas of surface water can become depleted in O_2 , allowing active
5 denitrification in open water. Oceanic N_2O can also arise from denitrification in marine
6 sediments, particularly in nutrient rich areas such as those of estuaries.

7
8

9 AX2.2 SULFUR OXIDES EMISSIONS

10 Emissions of sulfur dioxide (SO_2 ; the chief SO_x component) are due mainly to the
11 combustion of fossil fuels by electrical utilities and other industries; transportation-related
12 sources make only a very minor contribution (see Table AX2-1). As a result, most SO_2
13 emissions originate from elevated point sources. Since S is a volatile component of fuels, it is
14 almost quantitatively released during combustion and emissions can be calculated on the basis of

1 the S content of fuels to greater accuracy than for other pollutants such as NO_x or primary PM,
2 for example.

3 The major natural sources of SO₂ are volcanoes, biomass burning, and dimethylsulfide
4 (DMS) oxidation over the oceans. SO₂ constitutes a relatively minor fraction (0.005% by
5 volume) of volcanic emissions (Holland, 1978), but the ratio of hydrogen sulfide (H₂S to SO₂ is
6 highly variable in volcanic gases. Volcanic sources of SO₂ in the United States are limited to the
7 Pacific Northwest, Alaska, and Hawaii.

8 Emissions of SO₂ from burning vegetation are generally in the range of 1 to 2% of the
9 biomass burned (see e.g., Levine et al., 1999). S is bound in amino acids in vegetation and this
10 organically-bound S is released during combustion. However, unlike N, approximately one-half
11 of the S initially present in vegetation is found in the ash (Delmas, 1982). Gaseous emissions are
12 mainly in the form of SO₂ with much smaller amounts of H₂S and carbonyl sulfide (OCS). The
13 ratio of gas-phase N to S emissions is ~14, very close to the ratio in plant tissue (Andreae, 1991).
14 The ratio of reduced N and S species such as NH₃ and H₂S to their more oxidized forms, such as
15 NO and SO₂, increases from flaming to smoldering phases of combustion, as emissions of
16 reduced species are favored by lower temperatures and reduced O₂ availability.

17 Emissions of reduced S species are associated typically with marine organisms living
18 either in pelagic or coastal zones and with anaerobic bacteria in marshes and estuaries.
19 Emissions of DMS from marine plankton represent the largest single source of reduced S species
20 to the atmosphere (e.g., Berresheim et al., 1995). Other sources such as wetlands and terrestrial
21 plants and soils account for < ~5% of the DMS global flux, with most of this coming from
22 wetlands.

23 The coastal and wetland sources of DMS have a dormant period in the fall and winter
24 from plant senescence. Marshes die back in fall and winter, so DMS emissions from them are
25 lower, and reduced light levels in winter at mid-to-high latitudes reduce phytoplankton growth
26 also tending to reduce DMS emissions. Western coasts at mid-to-high latitudes have lower
27 actinic flux to drive photochemical production and oxidation of DMS. Freezing at mid and high
28 latitudes affects the release of biogenic S gases, particularly in the nutrient-rich regions around
29 Alaska. Transport of SO₂ from regions of biomass burning seems to be limited by heterogeneous
30 losses that accompany convective processes that ventilate the surface layer and the lower
31 boundary layer (Thornton et al., 1996, TRACE-P data archive).

1 However, reduced S species are also produced by several anthropogenic industrial
2 sources. For example, DMS is used in petroleum refining and in petrochemical production
3 processes to control the formation of coke and CO, and in steel mills to control dusting. It is also
4 used in a range of organic syntheses, and has a use as a food flavoring component.

7 **AX2.3 NH₃ EMISSIONS**

8 Anthropogenic emissions of NH₃ show a strikingly different pattern from those of NO_x
9 or SO₂. Three-way catalysts used in motor vehicles emit small amounts of NH₃ as a byproduct
10 during the reduction of NO_x. Stationary combustion sources make only a small contribution to
11 emissions of NH₃ because their efficient combustion favors NO_x formation, and NH₃ from
12 combustion is produced largely by inefficient, low-temperature fuel combustion. For these
13 reasons, most emissions of NH₃ arise from fertilized soils and from livestock.

14 The initial step in the oxidation of atmospheric NH₃ to NO is by reaction with OH
15 radicals. However, the τ of NH₃ from this pathway is sufficiently long (~1-2 months using
16 typical OH values of 1-2 × 10⁶ cm⁻³) so that it is a small sink compared to uptake of NH₃ by
17 cloud drops and aerosol particles and loss to dry deposition. Thus, gas-phase oxidation of NH₃
18 makes a very small contribution as a source of NO. Holland et al. (2005) estimated wet and dry
19 deposition of NH_x, based on measurements over the continental United States (CONUS), and
20 found that emissions of NH₃ in the 1999 National Emissions Inventory (NEI)
21 (<http://www.epa.gov/ttn/chief/net/1999inventory.html>) were underestimated by approximately a
22 factor of 2 or 3. Possible reasons for this error include under-representation of deposition
23 monitoring sites in populated areas and the neglect of off-shore transport in the NEI. The use of
24 fixed deposition velocities (V_d) that do not reflect local conditions at the time of measurement
25 introduces additional uncertainty into their estimates of dry deposition to which NH₃ is
26 particularly sensitive.

29 **AX2.4 EVALUATING EMISSIONS INVENTORIES**

30 Comparisons of emissions model predictions with observations have been performed in a
31 number of environments. Studies using ratios of [CO] to [NO_x] and nonmethane organic
32 compounds ([NMOC]) to [NO_x] carried out in the early 1990s in tunnels and ambient air

1 (summarized in *Air Quality Criteria for Carbon Monoxide* (U.S. Environmental Protection
2 Agency, 2000a)) indicated that emissions of CO and NMOC were systematically underestimated
3 in emissions inventories.

4 Parrish et al. (1998) and Parrish and Fehsenfeld (2000) proposed methods to derive
5 emission rates by examining measured ambient ratios among individual volatile organic
6 compounds (VOCs), NO_x, and total oxides nitrogen (NO_y). There is typically a strong
7 correlation among measured values for these species because emission sources are
8 geographically collocated, even when individual sources are different. Correlations can be
9 used to derive emissions ratios between species, including adjustments for the impact of
10 photochemical aging. Investigations of this type include correlations between CO and NO_y
11 (e.g., Parrish et al., 1991), between individual VOC species and NO_y (Goldan et al., 1995, 1997,
12 2000) and between various VOC species (Goldan et al., 1995, 1997; McKeen and Liu, 1993;
13 McKeen et al., 1996). Buhr et al. (1992) derived emission estimates from principal component
14 analysis (PCA) and other statistical methods. Many of these studies are summarized in Trainer
15 et al. (2000), Parrish et al. (1998), and Parrish and Fehsenfeld (2000). Goldstein and Schade
16 (2000) also used species correlations to identify the relative impacts of anthropogenic and
17 biogenic emissions. Chang et al. (1996, 1997) and Mendoza-Dominguez and Russell (2000,
18 2001) used the more quantitative technique of inverse modeling to derive emission rates, in
19 conjunction with results from chemistry-transport models.

20 Results from some recent emissions evaluation studies have been mixed, with some
21 studies showing agreement to within $\pm 50\%$ (U.S. Environmental Protection Agency, 2000a).
22 However, Pokharel et al. (2002) employed remotely sensed emissions from on-road vehicles and
23 fuel use data to estimate emissions in Denver. Their calculations indicated a continual decrease
24 in CO, hydrocarbons (HC), and NO emissions from mobile sources over the 6-year study period,
25 1996 through 2001. Inventories based on the ambient data were 30 to 70% lower for CO, 40%
26 higher for hydrocarbons (HC), and 40 to 80% lower for NO than those predicted by the
27 MOBILE6 on-road mobile source emissions model.

28 Improvements in many areas have resulted from the process of emissions model
29 development, evaluation, and further refinement. It should be remembered that the conclusions
30 from these reconciliation studies depend on the assumption that NO_x emissions are predicted
31 correctly by emissions factor models. Roadside remote sensing data indicate that over 50% of

1 NMHC and CO emissions are produced by less than ~10% of the vehicles (Stedman et al.,
2 1991). These “super-emitters” are typically poorly maintained vehicles. Vehicles of any age
3 engaged in off-cycle operations (e.g., rapid accelerations) emit much more than if operated in
4 normal driving modes. Bishop and Stedman (1996) found that the most important variables
5 governing CO emissions are fleet age and owner maintenance.

6 Stehr et al. (2000) reported simultaneous measurements of CO, SO₂, and NO_y at an East
7 Coast site. By taking advantage of the nature of mobile sources (they emit NO_x and CO but
8 little SO₂) and power plants (they emit NO_x and SO₂ but little CO), the authors evaluated
9 emissions estimates for the eastern United States. Results indicated that coal combustion
10 contributes 25 to 35% of the total NO_x emissions in rough agreement with emissions inventories
11 (U.S. Environmental Protection Agency, 1997).

12 Emissions inventories for North America can be evaluated by comparison to measured
13 long-term trends and or ratios of pollutants in ambient air. A decadal field study of ambient CO
14 at a rural site in the eastern United States (Hallock-Waters et al., 1999) indicates a downward
15 trend consistent with the downward trend in estimated emissions over the period 1988 to 1999
16 (U.S. Environmental Protection Agency, 1997), even when the global downward trend is taken
17 into account. Measurements at two urban areas in the United States confirmed the decrease in
18 CO emissions (Parrish et al., 2002). That study also indicated that the ratio of CO to NO_x
19 emissions decreased by approximately a factor of 3 over 12 years (such a downward trend was
20 noted in AQCD 96). Emissions estimates (U.S. Environmental Protection Agency, 1997)
21 indicate a much smaller decrease in this ratio, suggesting that NO_x emissions from mobile
22 sources may be underestimated and/or increasing. Parrish et al. (2002) concluded that O₃
23 photochemistry in U.S. urban areas may have become more NO_x-limited over the past decade.
24 (See Chapter 2 for a discussion of NO_x and its role in enhancing and limiting O₃ formation.)

25

26 **AX2.4.1 Satellite Data for Emissions Evaluations**

27 Satellite data have proved useful for optimizing estimates of emissions of NO₂ (Leue
28 et al., 2001; Martin et al., 2003; Jaegle et al., 2005). Satellite-borne instruments such as the
29 Global Ozone Monitoring Experiment (GOME) (see Martin et al., 2003 and references therein)
30 and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography

1 (SCIAMACHY) (see Bovensmann et al., 1999) retrieve tropospheric columns of NO₂ that can
2 then be combined with model-derived chemical lifetimes (τ) of NO_x to yield emissions of NO_x.

3 Top-down inference of NO_x emission inventories from the satellite observations of [NO₂]
4 columns by mass balance requires at minimum three pieces of information: (1) the retrieved
5 tropospheric [NO₂] column; (2) the ratio of tropospheric NO_x to NO₂ in the columns; and (3) the
6 NO_x τ against reaction losses to stable chemical reservoirs. (See the discussion of these
7 chemical reservoirs in Chapter 2 and Annex 1). A photochemical model has been used to
8 provide information on the latter two pieces of information. The method is most often applied to
9 land surface emissions, excluding lightning. Tropospheric NO₂ columns are largely insensitive
10 to lightning NO_x emissions since most of the lightning NO_x in the upper troposphere is present
11 as NO at the time of the satellite measurements (Ridley et al., 1996), owing to the slower
12 reactions of NO with O₃ at the altitude where lightning production is most prevalent.

13 Using satellite data Bertram et al. (2005) found clear signals in the SCIAMACHY
14 observations of short, intense NO_x pulses following springtime fertilizer application and
15 subsequent precipitation over agricultural regions of the western U.S. For the agricultural region
16 in north-central Montana, they calculated an annual SCIAMACHY top-down estimate that is
17 60% greater than a commonly-used model of soil NO_x emissions by Yienger and Levy (1995).

18 Jaeglé et al. (2005) applied additional information on the spatial distribution of emissions
19 and fire activity to partition NO_x emissions into sources from fossil fuel combustion, soils, and
20 biomass burning. Global a posteriori estimates of soil NO_x emissions are 68% larger than the a
21 priori estimates. Large increases are found for the agricultural region of the western U. S. during
22 summer, increasing total U.S. soil NO_x emissions by a factor of 2, up to 0.9 Tg N yr⁻¹.

23 Martin et al. (2006) retrieved tropospheric NO₂ columns for May 2004 to April 2005
24 from the SCIAMACHY satellite instrument to derive top-down NO_x emissions estimates via
25 inverse modeling with a global chemical transport model (GEOS-Chem). The top-down
26 emissions were combined with a priori information from a bottom-up emission inventory with
27 error weighting to achieve an improved a posteriori estimate of the global distribution of surface
28 NO_x emissions. Their a posteriori inventory improves the GEOS-Chem simulation of NO_x,
29 peroxyacetyl nitrate (PAN), and HNO₃ with respect to airborne in situ measurements over and
30 downwind of New York City. Their a posteriori inventory shows lower NO_x emissions from the
31 Ohio River valley in summer than winter, reflecting recent controls on NO_x emissions from

1 electric utilities there. Their a posteriori inventory is highly consistent ($R^2 = 0.82$, bias = 3%)
2 with the NEI 99; however, it is 68% greater than a recent inventory by Streets et al. (2003) for
3 East Asia for the year 2000.

4 5 6 **AX2.5 MONITORING NETWORKS**

7 Observational systems supporting air quality and related assessments include routine
8 regulatory networks, deposition networks, intensive field studies, remote sensing systems,
9 sondes, aircraft campaigns, satellites, and focused fixed site special purpose networks. Major
10 networks currently operating are emphasized; reference to other networks that have been
11 discontinued, or that were only intended for a specific operating period, is also provided. The
12 focus is on routinely operating North American air quality networks, with limited coverage of
13 European and international efforts relevant to North American assessments.

14 The scope of network coverage is broad and relatively shallow, reflecting intent to
15 describe the observational foundation enabling integration of spatial scales, environmental
16 media, and pollutant categories. In addition to fixed-site, surface-based air quality networks,
17 systems providing total Earth column and vertical gradient information meteorological programs
18 are included as well as operations designed to address climate forcing gases and aerosols, long
19 range transport and stratospheric ozone. Cursory descriptions of recent intensive field
20 campaigns are included to further foster integration of multiple observation platforms and air
21 quality modeling platforms.

22 23 **AX2.5.1 Routine Regulatory Air Monitoring Networks in North American**

24 Routine ambient air and deposition monitoring networks in North America provide more
25 than 3000 fixed platforms measuring numerous gaseous species and aerosol properties; see Table
26 AX2.5-1 for a listing. Many of these long-standing network systems were initialized after the
27 1970 Clean Air Act (CAA), subsequent CAA amendments, National Ambient Air Quality
28 Standards (NAAQS) reviews and National Academy of Sciences (NAS) recommendations
29 resulting in periodic step enhancements to these routine networks. Examples include CASTNET
30 and the National Atmospheric Deposition Program (NADP) addressing acidification; the
31 Photochemical Assessment Monitoring Stations (PAMS) in response to persistent O₃ pollution
32 and to monitor O₃ precursors including NO_x; and the particulate matter $\leq 2.5 \mu\text{m}$ (PM_{2.5}) network

1 to monitor aerosol- and solid-phase pollutants that can act in concert with NO_x and SO_x. Table
2 AX2.5-1 lists the networks, sponsoring agencies, site densities, dates of operation, locations, and
3 measurement parameters.

4 The relatively wide geographic distribution and persistence of exceedances of the O₃ and
5 PM NAAQS (see Figure AX2.5-1) have led to these pollutants dominating the national
6 monitoring networks. These sites remain relevant for characterizing ambient concentrations and
7 deposition of NO_x and SO_x because those species are often measured at the same locations and
8 because of the role of NO_x in the formation and destruction of O₃, and because of PM's role in
9 NO_x and SO_x deposition. Additional details about the homogeneous- and heterogeneous-phase
10 atmospheric chemistry of NO_x and SO_x are given in Chapter 2 and in Annex 1.

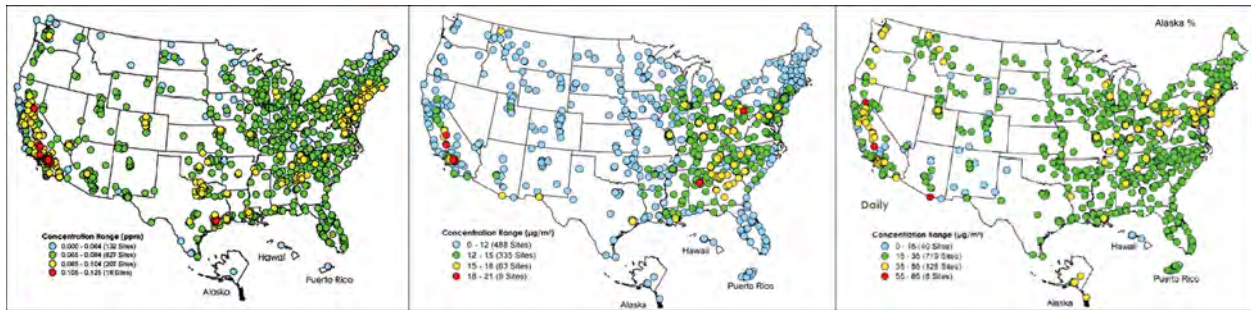


Figure AX2.5-1. 2006 air quality summaries for ozone, annual average PM_{2.5} and daily PM_{2.5}. Yellow and red sites indicate values exceeding NAAQS levels.

Source: U.S. Environmental Protection Agency (2006b).

11 Two important ambient air networks focused on environmental welfare effects were
12 established in the mid-1980s. The Interagency Agency Monitoring of Protected Visual
13 Environments (IMPROVE) network with <100 sites in National Parks and other remote
14 locations is used primarily to assess visibility impairment, but has provided a reliable long-term
15 record of PM mass and major speciation components and served as a model for the later
16 deployment of EPA's Speciation Trends Network (STN); see Figure AX2.5-2. STN has
17 provided an urban complement to characterize aerosol composition; see Figure AX2.5-3.
18 Additional, minor networks identified in Figure AX2.5-2 include those of the state and local air

Ambient Air Monitoring Stations in the United States

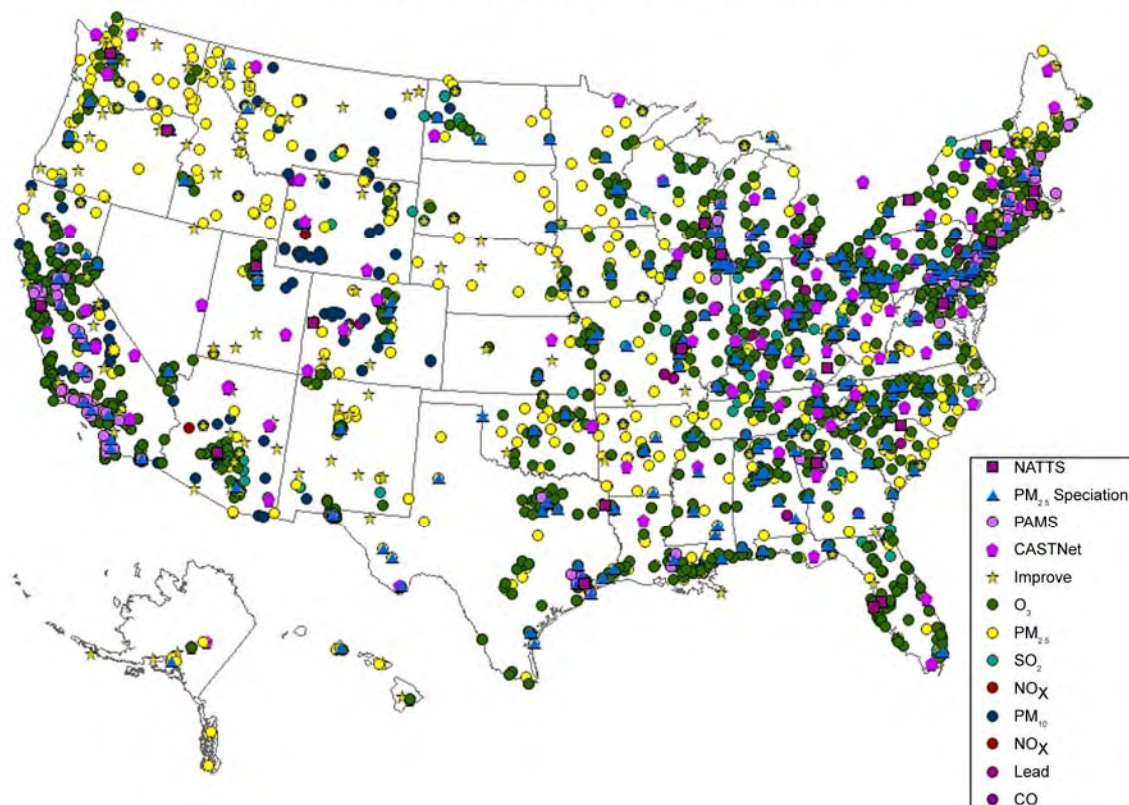


Figure AX2.5-2. Aggregate map of the majority routine U.S. monitoring stations illustrating relatively broad coverage across the continental United States with noted spatial gaps in low populated areas.

1 agencies deployed since the mid-1980s measuring a variety of aerosol-phase, solid-phase,
2 metallic, and gas-phase hazardous air pollutants (HAPs) at ~200 locations; and a modest
3 National Air Toxics Trends (NATTS) network of 23 sites.

4 CASTNET was established in the early 1990s to track changes in dry deposition of major
5 inorganic ions and gaseous precursors associated with the CAA Title 4 reductions in S and N,
6 designed to address surface water acidification in Eastern North America. Complementing
7 ongoing precipitation measurements from NADP, CASTNET (see Figure AX2.5-4) has provided
8 a valuable source of model evaluation data for many of the large regional scale applications since
9 the 1990s.

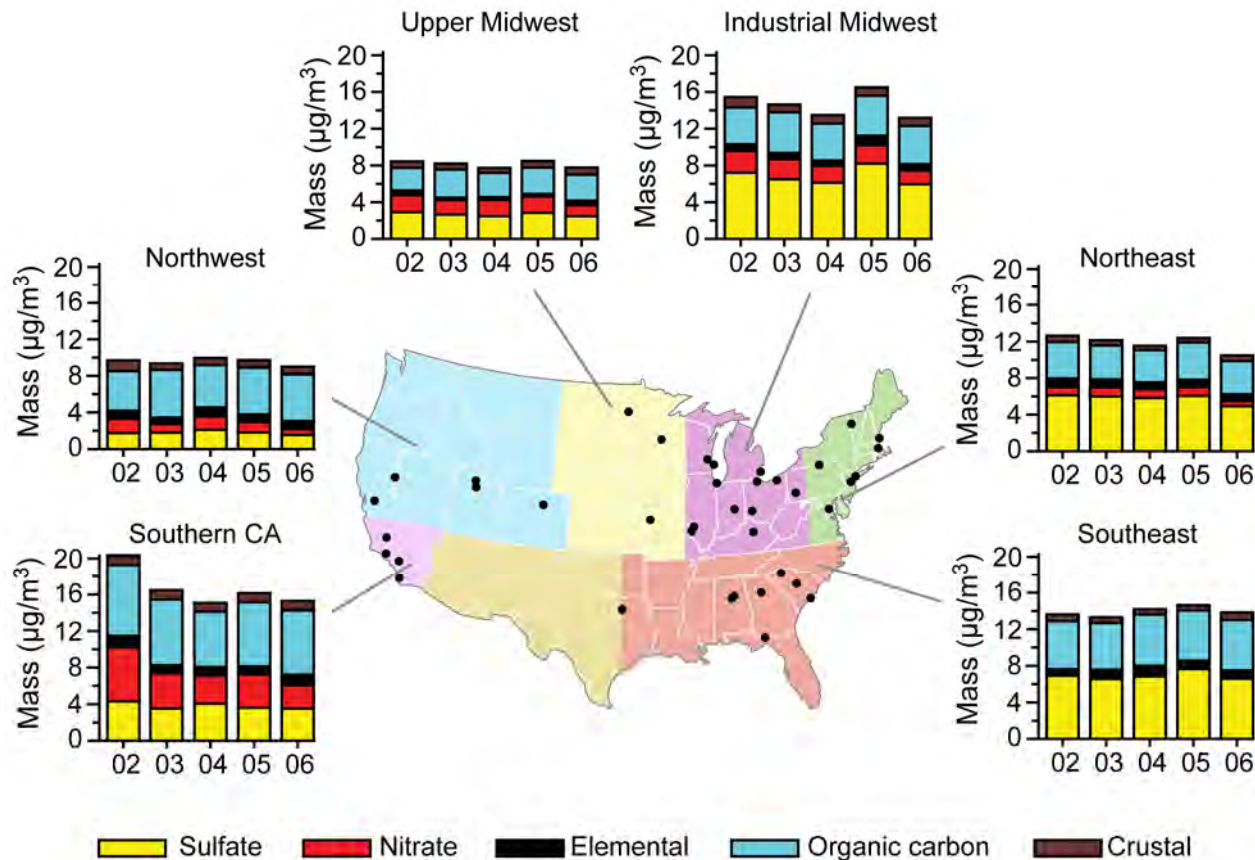


Figure AX2.5-3. Regional chemical composition of PM_{2.5} aerosols based on urban speciation sites and averaged over the entire 2006 sampling period.

Source: 2006 EPA Air Quality Trends Report (www.epa.gov/air/airtrends/index.html).

1 Deployment of the PAMS and the PM_{2.5} networks from the early 1990s through 2002
 2 markedly enhanced the spatial, temporal, and compositional attributes of gases and aerosols,
 3 partially supporting user needs beyond NAAQS compliance (e.g., public reporting and
 4 forecasting of adverse air quality; implementation efforts including air quality model evaluation,
 5 and source apportionment and pattern (spatial and temporal) analysis of precursor species).

6 State and local air agencies have measured a variety of metallic and gaseous hazardous
 7 air pollutants (HAPs) at over 200 locations since the 1980s. Typically, broad access and use of
 8 those data were compromised by a lack of centralized databases and multiple sampling and
 9 laboratory protocols enhancing data uncertainty. In response to this gap in accessible and
 10 centralized HAPs observations, the NATTS (see Figure AX2.5-3) was initiated in 2001. Current

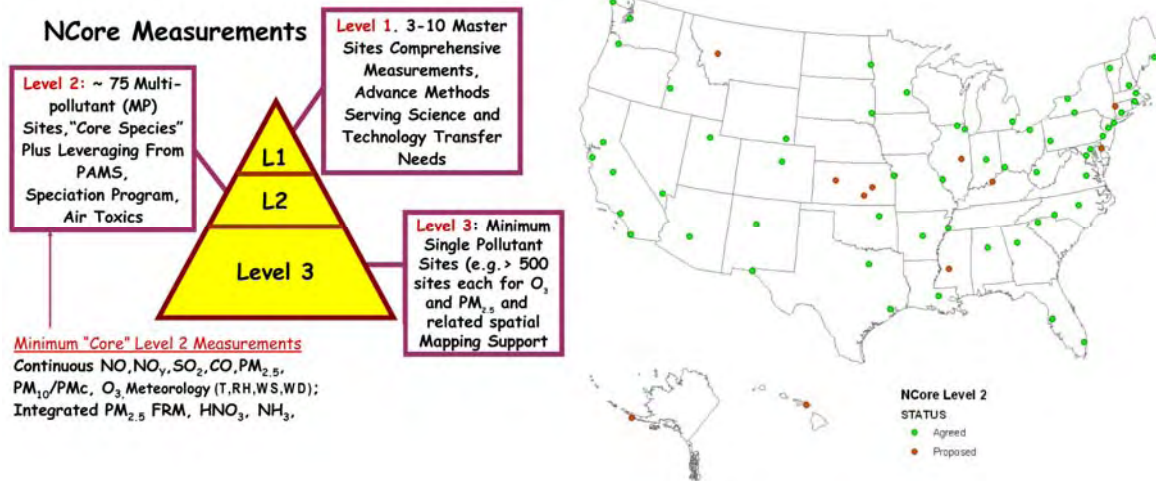


Figure AX2.5-4. Original 3-tiered NCore design (left) and proposed site locations for Level 2 multiple pollutant sites.

1 NATTS species include: acrolein, perchloroethylene, benzene, carbon tetrachloride, chloroform,
 2 trichloroethylene, 1,3-butadiene, 1,2-dichloropropane, dichloromethane, tetrachloroethylene,
 3 vinyl chloride, formaldehyde, acetaldehyde, nickel compounds, arsenic compounds, cadmium
 4 compounds, manganese compounds, beryllium, lead, hexavalent chromium, with anticipated
 5 additions of the species benzo(a)pyrene and naphthalene.

6 A new multiple pollutant-monitoring network, the National Core Monitoring Network
 7 (NCore) was incorporated in the 2006 revisions to the particulate matter standards (Federal
 8 Register, 2006). When finally implemented in 2009, NCore will provide a minimum of 75 Level
 9 2 sites (Figure AX2.5-4) in most major urban areas and important transport corridor and
 10 background locations. NCore will include a variety of trace gas, aerosol mass and speciation
 11 measurements which are intended to support multiple data user needs (e.g., air quality model
 12 evaluation, long-term epidemiological studies). In addition to establishing a multiple pollutant
 13 measurement framework, the NCore sites are intended to provide a backbone of central location
 14 sites that can be complemented by additional (existing and new) stations to address more specific
 15 spatial resolution requirements.

1 **AX2.5.2 Summaries of Routine Network Operations by Pollutant Category**

3 **AX2.5.2.1 Inorganic Gases**

4 The majority of U.S. sites measuring criteria gases (O_3 , NO_x , SO_2 , and CO) are
5 incorporated within the State and Local Air Monitoring Systems (SLAMS) networks. Most of
6 the SLAMS sites are located in populated urban locations with a variety of siting requirements
7 typically intended to site for high concentration locations resulting in an emphasis on downwind
8 (from urban center) locations for O_3 , center-city locations for NO_x , roadway intersection and
9 canyon type locations for CO , and proximity to major power generating facilities for SO_2 .
10 Derived estimates of NO_x based on standard chemiluminescence techniques continue to include
11 additional reactive N (e.g., HNO_3 and PAN) leading to positive biases in the total NO_x reported
12 during periods not dominated by fresh emissions. Most monitoring platforms include multiple
13 sensors to improve efficiency of network operations and adding interpretive value.

15 **AX2.5.2.2 Reactive Nitrogen, Nitric Acid, and Ammonia**

16 Measurements of NO_y , HNO_3 , and NH_3 serve a variety needs related to emission
17 inventory and model evaluation, inputs into observational based models which characterize the
18 responsiveness of a secondarily formed pollutant (e.g., O_3 or ammonium nitrate (NH_4NO_3)) to
19 specific precursor reductions (VOC , NO_x , or NH_3) and, with particle nitrate (pNO_3), are
20 important components of the atmospheric N budget supporting downstream watershed and
21 accountability assessments. These N species, in addition to true NO_2 (and particulate ammonium
22 (pNH_4)), are components of the total N budget and remain poorly categorized. A scarcity of
23 reliable, cost effective measurement methods instrumentation combined with minimal regulatory
24 incentive curtail advancements in nitrogen measurements. In the United States, the SEARCH
25 network is the only source of routine ambient air measurements of NO_y , NH_3 and HNO_3 .
26 Canada in partnership with CASTNET recently has deployed a network of inexpensive passive
27 ammonia samplers which have promise for characterizing broad spatial patterns, with extended
28 averaging times beyond 24 h. Most NH_3 sampling is focused on high source regions in
29 agricultural settings designed to improve emission factors for NH_3 , resulting in very limited NH_3
30 characterization of ambient environments.

1 **AX2.5.2.3 Particulate Matter Mass**

2 Nearly 1500 PM_{2.5} gravimetric sites were established before 2000 to determine
3 nonattainment status of counties throughout the United States following the 1997 promulgation
4 of the PM_{2.5} particulate matter standard. The network has evolved to add over 500 continuous
5 PM_{2.5} monitors and a reduction of 24-h gravimetric samplers below 1000 sites (see Figure
6 AX2.5-5) that support air quality forecasting and public notification of adverse air quality using
7 the Air Quality Index (AQI), a generalized indicator of exposure concern linked to the NAAQS
8 (<http://www.epa.gov/airnow/>). While this expansion of continuous PM_{2.5} sites adds spatial
9 coverage of highly temporally resolved information, the mix of instrument types compromises
10 data harmonization across sites and geographic areas with different operational characteristics.

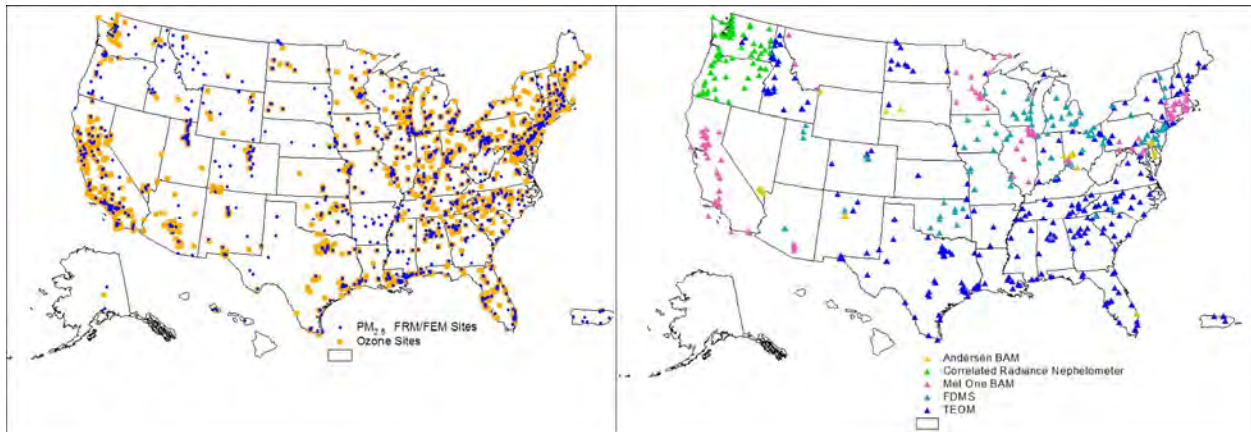


Figure AX2.5-5. Maps illustrating breadth of PM_{2.5} FRM and FEM and O₃ network (left); and PM_{2.5} continuous samplers (right). These combined networks represent the dominant use of U.S. air quality observations for NAAQS attainment designations and air quality forecast reporting.

11 In recognition of potential geographic differences, EPA has developed monitoring policy
12 (U.S. Environmental Protection Agency, 2006a) for regionally approved methods that would
13 lead to equivalency status for continuous PM_{2.5} samplers and compliance applications relative to
14 the NAAQS. Nevertheless, there will remain issues regarding data harmonization across site
15 locations as well as the use of the gravimetric mass measurement as an adequate indicator of
16 “true” aerosols when in theory, in situ continuous instruments have the potential to yield data

1 less impacted by measurement artifacts associated with volatility losses, gas adsorption, and
2 related issues associated with filter handling and equilibration. It should be noted that all filter-
3 based speciation sites (see below) also provide a gravimetric PM_{2.5} mass value relatively
4 consistent with the standard equivalent methods used for compliance.

5
6 **AX2.5.2.4 Particulate Matter Speciation**

7 IMPROVE has provided nearly a two-decade record of major components (SO₄²⁻, NO₃⁻,
8 organic and elemental carbon fractions (OC and EC, respectively), and trace metals) of PM_{2.5}
9 aerosols in pristine areas of the United States. Over 300 speciation sites were added from
10 2000—2002 in urban areas of the United States to assist assessment efforts related to the PM_{2.5}
11 standard. This coverage (see Figure AX2.5-6) across urban and rural areas has been a widely
12 used resource across disciplines (exposure/epidemiological, atmospheric science communities),
13 organizations (academia, industry, government agencies), and several spatial scales of interest
14 (long-range hemispheric transport to near source).

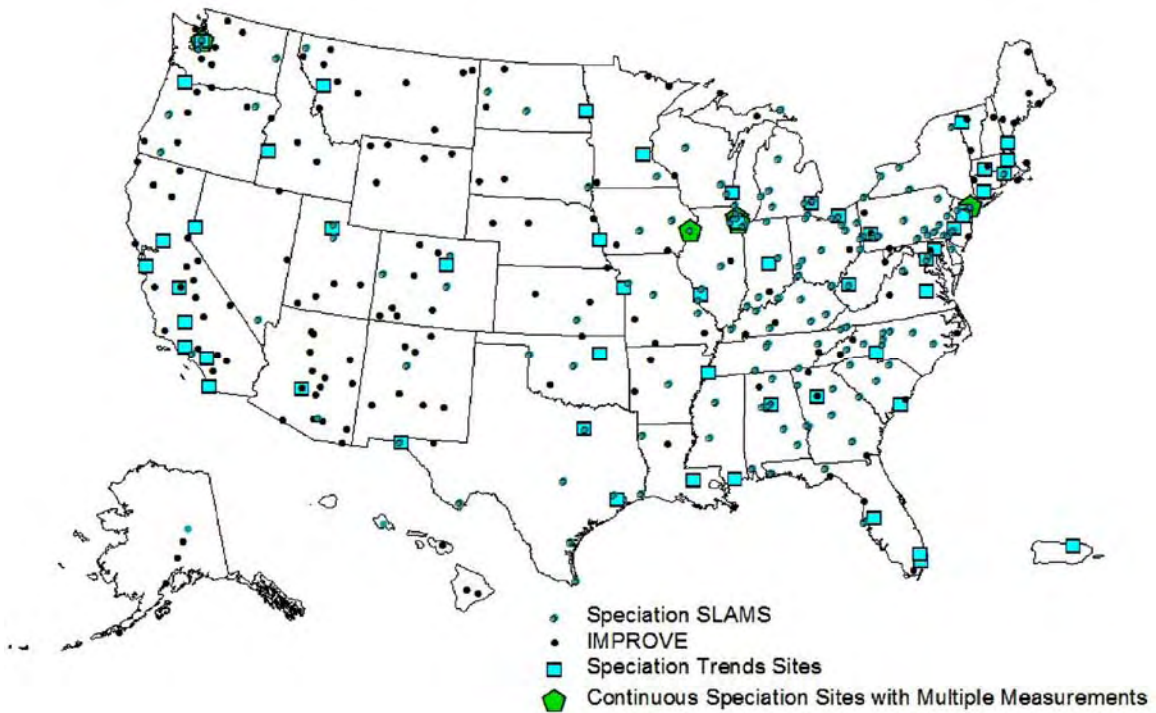


Figure AX2.5-6. Locations of chemical speciation sites delineated by program type.

1 The speciation networks typically collect a 24-h sample once every 3 or 6 days.
2 CASTNET provides weekly averaged measurements of major ions (SO_4^{2-} , NO_3^- , calcium (Ca^{2+}),
3 sodium (Na^+), potassium (K^+), NH_4^+ , and magnesium (Mg^{2+})) integrated over all aerosol sizes by
4 means of open-face filter packs. Daily, 24-h speciated samples often requested by health effects
5 researchers is limited to fewer than five sites in the United States and Canada. Similarly, a small
6 and variable number of sites, fewer than 10 most years, provide near-continuous speciation data,
7 usually limited to some combination of particulate SO_4 (pSO_4), particulate NO_3 (pNO_3), and EC
8 and OC. In addition, the 22 NATTS sites include aetholometers measuring semi-continuous
9 light absorption, often used as a surrogate for EC.

10 The EPA PM Supersites Program (Wittig and Solomon, 2006) provided highly time-
11 resolved aerosol measurements at 8 cities in the United States for a mix of time periods between
12 1999 and 2004. Depending on location and time period, a number of different instrument
13 configurations were deployed ranging from additional spatial coverage of standard speciation
14 sites to systems capturing near-continuous size-distributed chemical composition profiles.

15 16 **AX2.5.2.5 Precipitation-Based Networks**

17 Precipitation chemistry is the primary link between atmospheric and terrestrial and
18 aquatic systems. The NADP (<http://nadp.sws.uiuc.edu/>) oversees a network of more than
19 250 sites (see Figure AX2.5-7) where most of the major ions key to aquatic chemistry addressing
20 acidification and eutrophication effects are measured. The NADP includes the Mercury
21 Deposition Network (MDN) of ~90 sites and 7 Atmospheric Integrated Research Monitoring
22 Network (AIRMoN) sites providing greater temporal resolution.

23 The joint Canadian and United States Integrated Atmospheric Deposition Network
24 (IADN) (http://www.msc-smc.ec.gc.ca/iadn/index_e.html) includes a mix of master and satellite
25 stations across the Great Lakes where both precipitation and ambient air are sampled for a range
26 of toxics compounds. The IADN emphasizes many of the more persistent organic compounds
27 including polychlorinated biphenyl compounds (PCBs), pesticides, dioxins, and toxic metals
28 such as lead (Pb), cadmium (Cd), arsenic (As), and selenium (Se).

29 30 **AX2.5.3 Intensive Field Campaigns**

31 Intensive field campaigns of relatively short duration supplement routine longer term
32 monitoring networks by enhancing spatial, temporal, and compositional distribution of

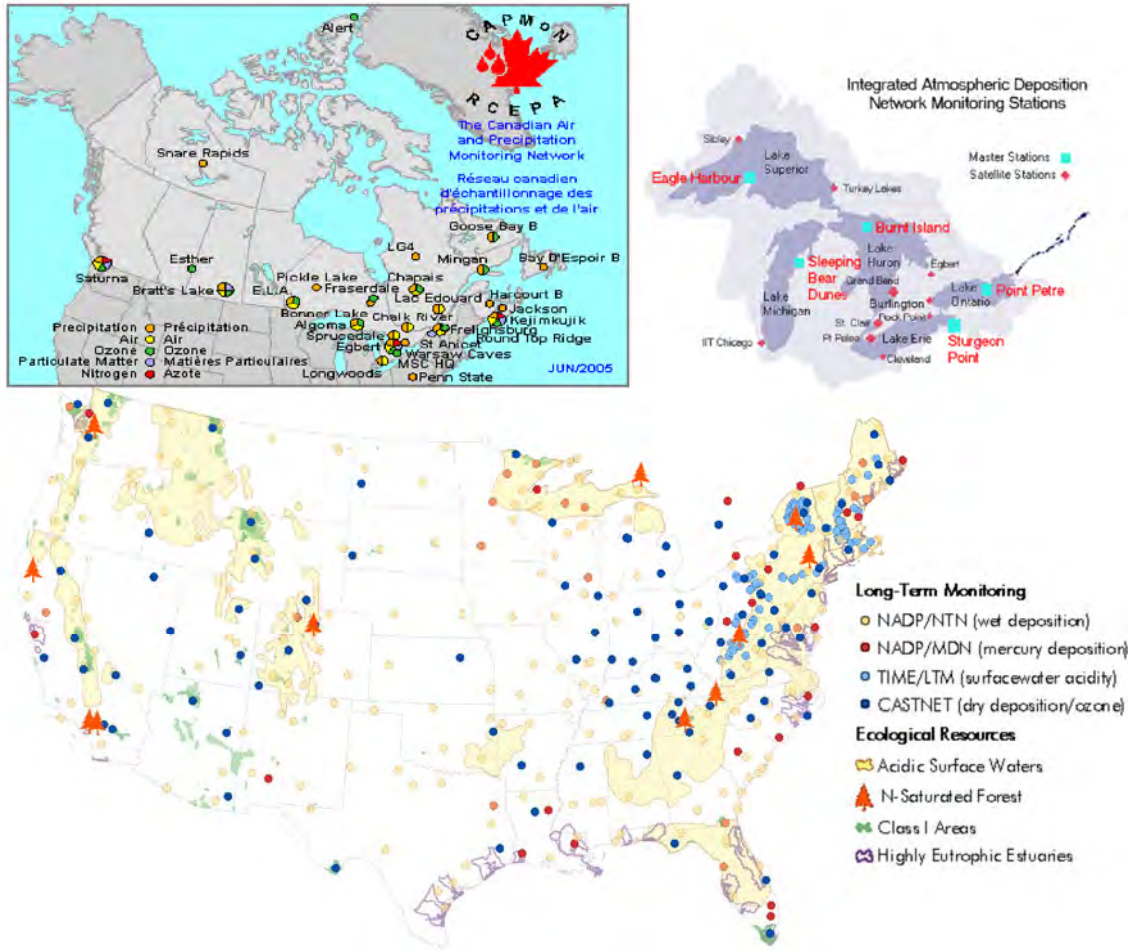


Figure AX2.5-7. Routinely operating North American precipitation and surface water networks: Upper left, Canadian Air and Precipitation Monitoring Network (CAPMON); Upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); Bottom, National Atmospheric Deposition Monitoring Program (NADP) with Time/LTM surface chemistry sites.

1 atmospheric species to better elucidate physical/chemical processes relevant to the fate, transport
 2 and removal of secondarily formed gases and aerosols. Typically, these campaigns utilize some
 3 combination of aircraft studies, high time resolved instrumentation and advanced analytical
 4 methods (in-situ and laboratory) all complementing routine ground based measurements, which
 5 usually do not address reactive gaseous species, aerosol size distributions, organic chemistry
 6 characterization and vertically stratified data.

1 There has been a long history of intensive field campaigns starting with the Regional Air
2 Pollution Study (RAPS) in the 1970s which formed the basis evaluating the early photochemical
3 gridded Eulerian airshed models used in acid deposition and O₃ assessments. Landmark
4 campaigns in the United States through the 1980s and 1990s such as the Southern California Air
5 Quality Study (SCAQS) (Lawson, 1990), the San Joaquin Valley Air Quality Study
6 (SJAQS)/Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) (Roth et al.,
7 1988) and the Southern Oxidant Study (SOS) (Cowling and Furiness, 2000) were reviewed as
8 part of the 2000 NARSTO O₃ assessment (Witting and Solomon et al., 2006). Over the last
9 decade there have been a series of field campaigns focusing on characterization of surface level
10 aerosols through the PM Supersites program (Solomon et al., 2007). While the early campaigns
11 focused on urban environments, the Eulerian Model Evaluation Field Study (EMEFS) and SOS
12 during the early 1990s shifted focus toward regional spatial scales consistent with the dominant
13 air pollution concerns (acid rain and ozone) of the time. In addition to addressing urban areas of
14 concern such as Houston, TX, and Los Angeles, CA, more recent campaigns have extended
15 spatial scales beyond regional studies to address oceanic transport and a variety of air pollution
16 issues across the Northern Hemisphere, recognizing the importance of far ranging source regions
17 and continental scale atmospheric processes. Some of these campaigns include local and
18 regional studies for the northeast and southeast United States, portions of Texas, and central and
19 southern California; intercontinental studies including those for transport across Atlantic, Pacific,
20 and Indian Ocean areas. A variety of federal and state entities have served as lead agencies for
21 these studies. Table AX2.5-2 provides a listing of studies conducted since the mid-1990s with
22 well-known campaigns as far back as the 1960s identified in footnotes.

23 A synthesis of key findings and lessons learned from major field campaigns conducted
24 over the last two decades would elevate exposure of these programs to a wider audience
25 potentially generating support to enhance and sustain atmospheric process and model evaluation
26 studies which are important complements to routine ground based and satellite observation
27 platforms. While the NARSTO database ([http://eosweb.larc.nasa.gov/PRODOCS/
28 narsto/table_narsto.html](http://eosweb.larc.nasa.gov/PRODOCS/narsto/table_narsto.html)) provides access to raw data for various field campaigns, coverage of
29 campaigns beyond North America must be acquired from other sources. The National
30 Aeronautics and Space Agency (NASA)'s Atmospheric Data Science Center
31 (<http://eosweb.larc.nasa.gov/>) also provides access to some of the more recent field campaigns.

1 These web services would benefit potential users by providing intermediate descriptions of the
2 scopes (locations, time frames, measurement systems and models) of these campaigns, including
3 key objectives and finding.

4 **AX2.5.4 Satellite-Based Air Quality Observing Systems**

6 An extensive array of satellite-based systems (see Tables AX2.5-2 and AX2.5-3) with the
7 capability of measuring atmospheric column total species has been established by United States
8 and European Satellite programs lead by NASA and the National Oceanic and Atmospheric
9 Administration (NOAA) in the United States and the European Space Agency (ESA). A suite of
10 satellites including Aqua, Aura, CALIPSO, OCO, Glory, as well as NOAA-17, NOAA-18 and
11 NPOESS, have either been launched since about the year 2000 or have other near-term proposed
12 launch dates. Collectively, the remote sensing techniques for measuring columns and/or profiles
13 of aerosols (AOD), O₃, CO, carbon dioxide (CO₂), methane (CH₄), SO₂, NO₂, chlorinated
14 fluorocarbon compounds (CFCs), other pollutants, and atmospheric parameters such as
15 temperature and H₂O content. Most of these satellites have a near-polar orbit allowing for two
16 passes per day over a given location. When taken together, a group of six satellites (Aqua, Aura,
17 CALIPSO, OCO, as well as CloudSat and PARASOL) coined the A-Train is being configured to
18 fly in a formation that crosses the equator a few minutes apart at around 1330 local time to give a
19 comprehensive picture of earth weather, climate, and atmospheric conditions.

20 Satellite imagery offers the potential to cover broad spatial areas; however, an
21 understanding of their spatial, temporal and measurement limitations is necessary to determine
22 how these systems complement ground based networks and support air quality management
23 assessments.

24 **AX2.5.4.1 Temporal Coverage and Characterization**

26 The near polar orbiting tracks of most satellites performing trace gas measurements
27 provides wide spatial coverage of reasonable horizontal (10-50 km) resolution, but delivers only
28 twice-daily snapshots of a particular species. Consequently, temporal patterns of pollutants as
29 well as a time-integrated measure of pollutant concentrations cannot be delineated explicitly
30 through satellite measurements alone. The geostationary satellite platforms such as the GOES
31 systems of NOAA do provide near-continuous coverage of physical parameters for weather
32 tracking and forecasting purposes. There are proposed campaigns within NASA and across

1 partnership Federal agencies to deploy geostationary platforms with measurement capabilities for
2 trace gases and aerosols to enhance space based characterization of tropospheric air quality
3 (Fishman et al., 2005).

4 5 **AX2.5.4.2 Spatial Coverage and Characterization**

6 Polar orbiting satellites typically provide horizontal spatial resolution between 10 and
7 100 km, depending on the angle of a particular swath segment. Spatial resolution less than
8 10 km is possible with geostationary platforms. Characterization of elevated pollutants delivered
9 by satellite systems complements of our ground based in-situ measurement networks – especially
10 considering that a considerable fraction of pollutant mass resides well above Earth’s surface.
11 With few exceptions, satellite data typically represents a total atmospheric column estimate. For
12 certain, important trace gases (e.g., NO₂, SO₂, formaldehyde) and aerosols, the majority of mass
13 resides in the boundary layer of the lower troposphere, enabling associations linking column data
14 to surface concentrations or emissions fields. For example, reasonable correlations, especially in
15 the Eastern United States, have been developed between concentrations from ground level PM_{2.5}
16 stations and aerosol optical depths (AOD) from NASA’s Moderate Resolution Imaging
17 Spectroradiometer (MODIS) aboard the Aqua and Terra satellites (Engel-Cox et al., 2004); see
18 the example in Figure AX2.5-8. The Infusing Satellite Data into Environmental Applications
19 (IDEA; <http://idea.ssec.wisc.edu/>) site provides daily displays and interpretations of MODIS and
20 surface air quality data. The Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation
21 (CALIPSO) satellite (discussed below) provides some ability to resolve aerosol vertical
22 gradients.

23 In contrast to aerosols, most O₃ mass resides in the stratosphere. Various techniques have
24 been developed to extract the stratospheric signal to yield a tropospheric ozone residual (TOR),
25 based on known homogeneities in the stratosphere and the use of chemical transport models and
26 multiple measurements. Early approaches (Fishman, 1978) before and during the Total Ozone
27 Mapping Spectrometer (TOMS) studies combined limb (angled view to characterize
28 stratosphere) and nadir (downward view, characterizing total column) techniques to derive
29 tropospheric ozone residuals. The 2004 launch of NASA’s Aura mission with multiple ozone
30 sensors is starting to produce more refined tropospheric ozone maps; see e.g., Figure AX2.5-9.
31 However, delineating boundary layer ozone from free tropospheric reservoirs continues to pose
32 significant interpretation challenges.

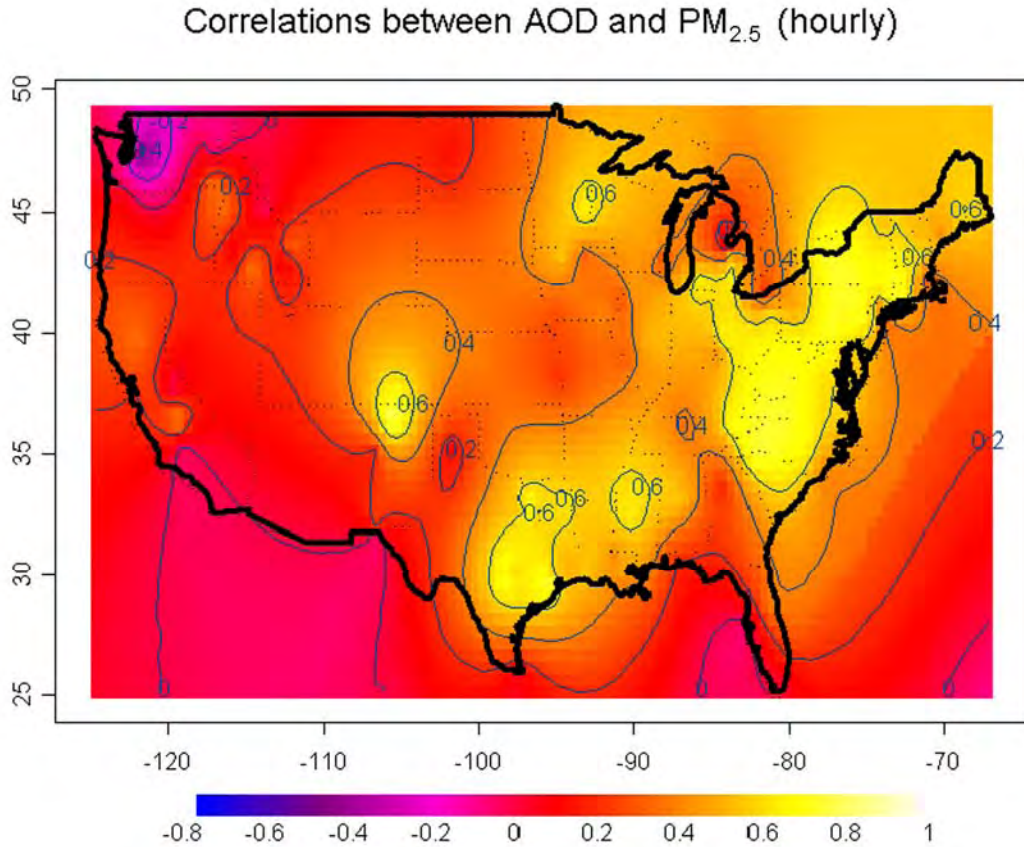


Figure AX2.5-8. Correlation surfaces between MODIS AOD and hourly PM_{2.5} surface sites from April-September 2002.

Source: Engel-Cox et al. (2004).

1 ***Measurement Issues***

2 Most satellite air quality observations are based on spectroscopic techniques typically
 3 using reflected solar radiation as a broad source of UV through IR electromagnetic radiation
 4 (LIDAR aboard CALIPSO does utilize an active laser as the radiation source). While the science
 5 of satellite based measurements of trace gases and aerosols is relatively mature, interferences
 6 related to surface reflections, cloud attenuation and overlapping spectra of nearby species require
 7 adequate filtering and accounting for in processing remote signals. For example, aerosol events
 8 episodes associated with clouds often are screened out in developing in applications involving
 9 AOD characterizations through MODIS. Correlations between AOD and surface aerosols

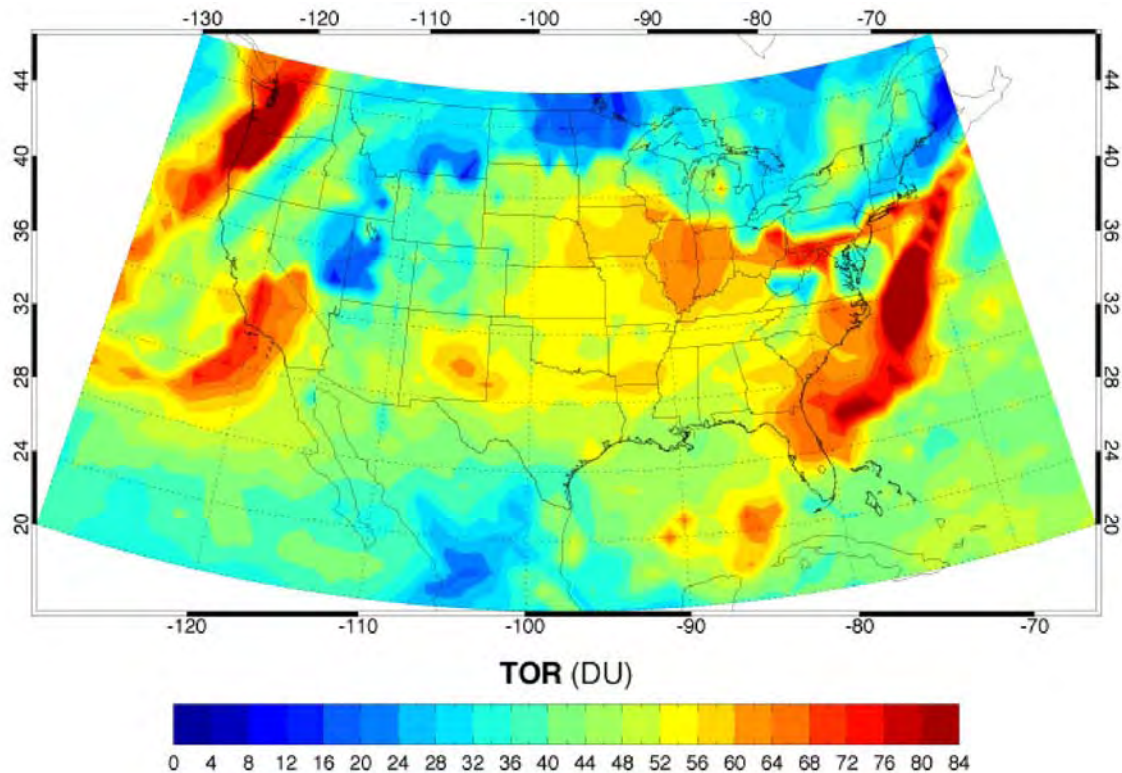


Figure AX2.5-9. Daily averaged tropospheric ozone column levels derived from NASA's OMI Dobson Units for June 22, 2005.

Source: J. Szykman, Environmental Protection Agency and J. Fishman, NASA.

- 1 generally are better in the eastern United States relative to the West because due to excessive
- 2 surface light scattering from relatively barren land surfaces.
- 3 Use of satellite data in air quality management assessments. Satellite data, particularly
- 4 fire and smoke plume observations and GOES meteorological data, support various air quality
- 5 forecasting efforts servicing public health advisories. Forecasting is driven by characterizing the
- 6 environment in current and immediate-future time frames, on the order of 1 to 3 days. Air
- 7 quality assessments require greater confidence in a systems response behavior to longer term,
- 8 and usually much greater, changes in emissions, land use and meteorology; which requires
- 9 greater confidence in formulation of numerous physical and chemical processes. Despite these
- 10 differences, research and application products originally catalyzed by forecasting objectives
- 11 generally overlap well with retrospective air quality assessment needs, the focus of this
- 12 discussion.

1 Satellite products complement existing observational platforms and support the air
2 quality assessment process through:

- 3 1. direct observational evidence of regional and long-range intercontinental
4 transport,
- 5 2. emission inventory improvements through inverse modeling,
- 6 3. evaluation of Air Quality Models,
- 7 4. tracking emissions trends (accountability), and
- 8 5. complementing surface networks through filling of spatial gaps.

9
10 As air quality assessments evolve toward including more pollutant categories, an
11 attendant need to characterize a variety of spatial (and temporal) scales parallels places demands
12 on developing more compositionally rich characterizations of air pollutants. Satellite
13 technologies combined with partnerships with Federal agencies such as NASA and NOAA are
14 assisting the air quality community by providing data that covers broad spatial regimes in areas
15 lacking ground based monitors and, more importantly, a vertical compliment to our horizontal
16 surface based networks. Although breathing zone monitoring is a rich data source, most
17 pollutant mass resides beyond the representative reach of surface stations. During well mixed
18 conditions with stable pressure systems during the afternoon, pollutant levels aloft often correlate
19 well with surface conditions offering potential for “gap filling” in the surface based networks.
20 Perhaps of greater utility is the use of satellite data to evaluate air quality models used to
21 estimate air quality consequences of future emissions and climate scenarios. Satellite
22 observations can be applied as a constraints on modeled total column mass or emission fields.

23 Satellites support hemispherical and global scale air quality assessments, which are
24 projected to be of increasing importance to North American air quality as both the relative
25 contribution of transported air pollution and air quality-climate interactions increases over the
26 next few decades. The pattern of gradual lowering of air quality standards as shown in Figure
27 AX2.5-10 also raises the importance of transported air pollution. The 2006 revision of the daily
28 $PM_{2.5}$ NAAQS from 65 to 35 $\mu g m^{-3}$ will increase the relative contribution of trans-oceanic dust
29 transport to violations. Direct observational evidence of long distance transport clearly can be
30 viewed with satellite imagery as shown in Figure AX2.5-11. Satellites often provide the only

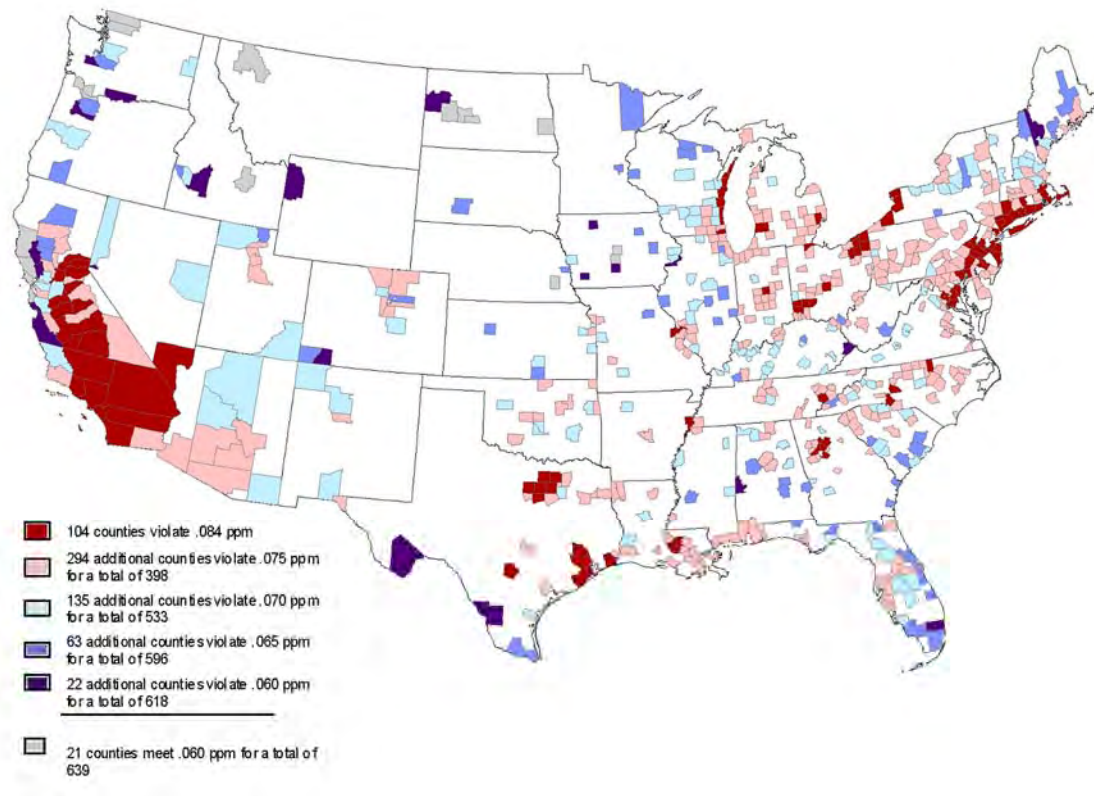


Figure AX2.5-10. Escalating range of counties violating various levels of the ozone NAAQS, based on 2003-2005 observations.

1 observation base for evaluating global scale air quality models in regions lacking adequate
 2 measurement and emissions inventory resources.

3 Launched in 2004, NASA’s Aura satellite mission ([http://www.nasa.gov/mission_pages/](http://www.nasa.gov/mission_pages/aura/spacecraft/index.html)
 4 [aura/spacecraft/index.html](http://www.nasa.gov/mission_pages/aura/spacecraft/index.html)) deploys sensors potentially capable of measuring all criteria gases,
 5 CH₄, CH₂O, nitric aciHNO₃d, N₂O, H₂O vapor, OH and HO₂ radicals and AOD – a multiple
 6 pollutant space based complement to the NCore multiple pollutant ground based network and
 7 intensive field campaigns. NASA’s Orbiting Carbon Observatory (OCO), scheduled to be
 8 launched in 2008, will be dedicated to tracking carbon dioxide levels which currently are
 9 captured on the Aqua based Atmospheric Infrared Sounder (AIRS) instrument. The Aqua, Terra,
 10 Aura and OCO all are part of NASA’s Earth Observation System (EOS). Tropospheric column
 11 level ozone for the contiguous United States derived from the Ozone Monitoring Instrument

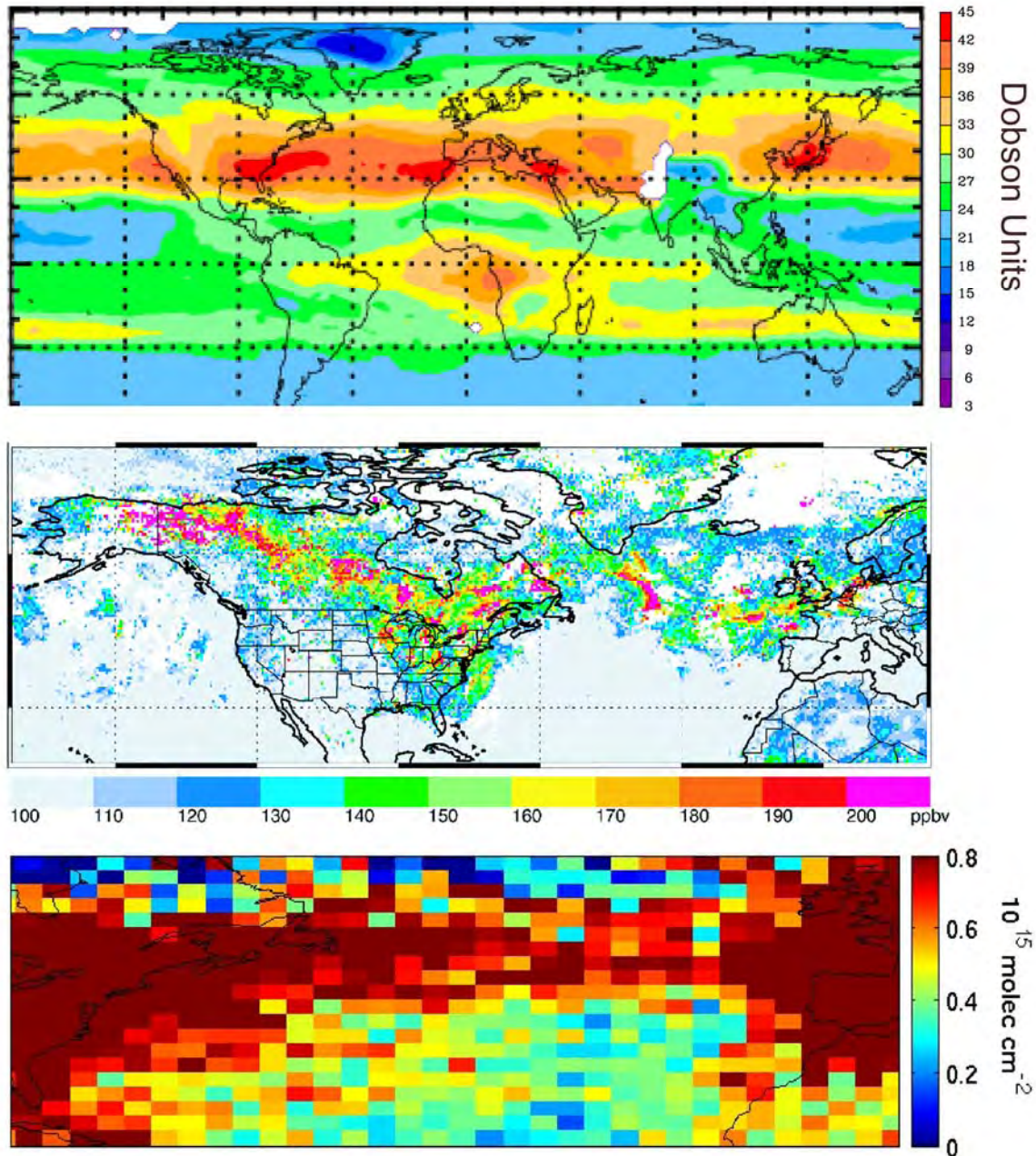


Figure AX2.5-11. Panels capturing trans-Atlantic transport: summer 1997 tropospheric ozone from GOME (top), CO column totals from MOPITT for July 2004 (middle), Tropospheric NO₂ from SCIAMACHY for summer 2004 (bottom).

Source: Top: Liu et al. (2006), Middle: Pfister et al (2006), Bottom: Martin et al. (2006).

1 (OMI, Figure AX2.5-9) provides broad horizontal spatial coverage consistent with global
2 (~100 km) and regional scale (~30 km) Chemical Transport Models (CTM). When used in
3 combination with CTMs, satellite column estimates can be used as an observation-driven top-
4 down check and modification through inverse modeling of emission inventories. Satellite data
5 for CO, NO₂, and HCHO as shown in Figure AX2.5-12, as an indicator for biogenic isoprene,
6 have been used for improving emission inventories (Fu et al., 2007; Martin et al., 2003, 2006).
7 As longer-term records are developed, satellite imagery offers another means of checking
8 progress of major emission strategy plans as well as illustrating emissions growth in developing
9 parts (East Asia) of the world as shown in Figures AX2.5-13 and Figures AX2.5-14.

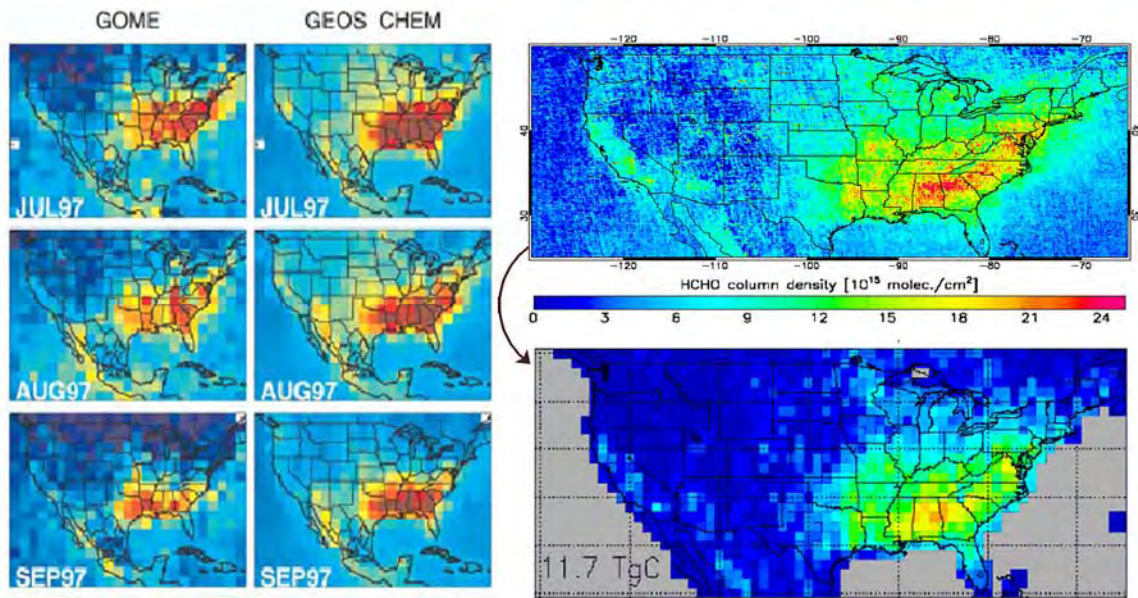


Figure AX2.5-12. Comparisons between GEOSchem global model and GOME derived formaldehyde fields (left); Summer 2006 OMI column HCHO and translation to isoprene emission estimates (right).

Source: Abbot et al. (2003) and Palmer et al. (2006).

10 An August 2006 incursion of African dust transported across the Atlantic Ocean
11 demonstrates the use of Satellite imagery capturing long-range transport events. NASA's Cloud-
12 Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) mission launched in
13 April 2006 provides both column total and vertically resolved aerosol estimates using an active

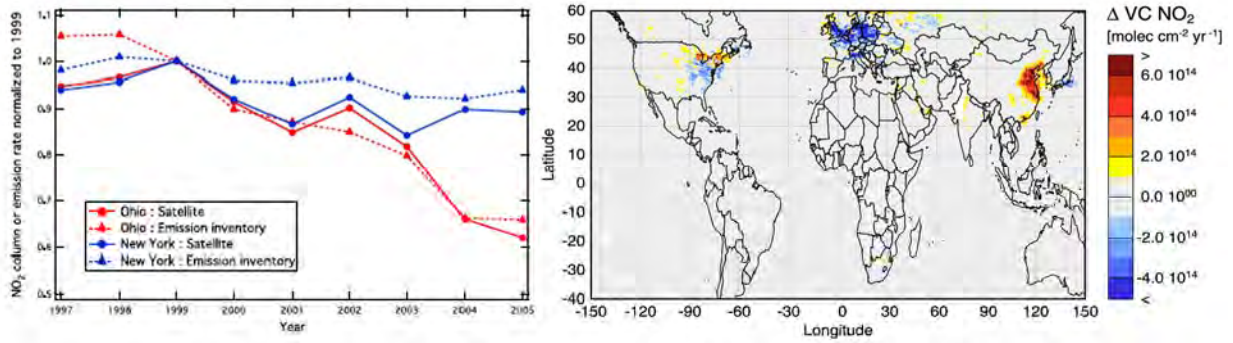


Figure AX2.5-13. Superimposed eastern United States emission and combined GOME and SCIAMACHY NO₂ 1997-2002 trends (left); GOME NO₂ trends from 1995 – 2002 (right). Clear evidence of reductions in midwest United States and European NO_x emissions, and increased NO_x generated in eastern Asia.

Source: Kim et al. (2006) and Richter et al. (2005).

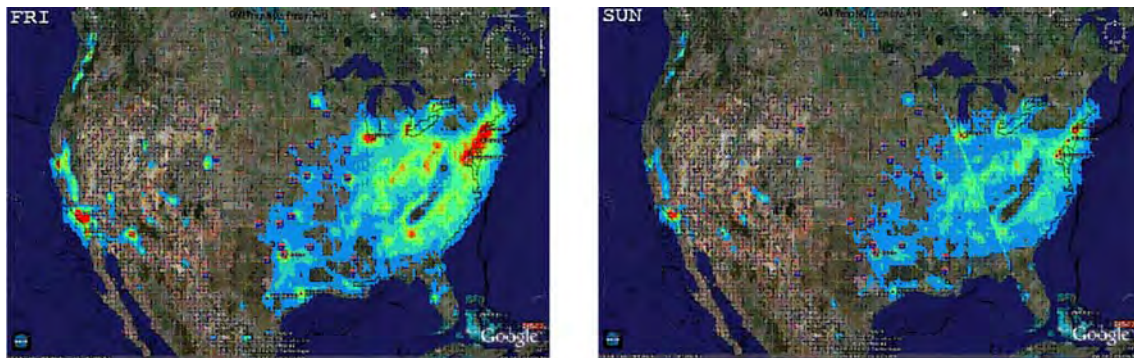


Figure AX2.5-14. 2004 OMI NO₂ column images aggregated for all Fridays (left) and Sundays (right) indicating weekend/weekday patterns associated with reduced Sunday emissions.

Source: Husar (2005; <http://capiton.wustl.edu/CAPITA/>).

- 1 light source (LIDAR) to quantify light scattering. Resolving vertical gradients provides
- 2 enhanced support for diagnosing CTM behavior and allows for screening of plumes reaching the
- 3 surface in developing correlations between surface and satellite observations. CALIPSO builds
- 4 on the ongoing success of the MODIS instrument aboard NASA’s Terra (EOS AM) and Aqua
- 5 (EOS PM) satellites which has provided AOD for use in:

- 1 • Supporting development of wildfire and prescribed burning emission inventories
2 (The 2005 NEI will include emissions from fires utilizing MODIS),
- 3 • Evaluating ability of air quality models such as CMAQ to characterize total
4 column aerosol loadings, and
- 5 • Complimenting ground based PM_{2.5} monitors by filling in spatial gaps and adding
6 intelligence to conceptualize our understanding of aerosol episodes (see
7 <http://idea.ssec.wisc.edu/>).

8 9 **AX2.5.5 European Air Monitoring Networks**

10 Extensive air monitoring networks have also been implemented in Europe. In addition to
11 the SVOC programs discussed above, many European-based programs are served by centralized
12 organization structures linked to international efforts such as Convention on Long Range
13 Transport of Air Pollution (LRTAP) (<http://www.unece.org/env/lrtap/>) and the underlying
14 technical assessment body, the Co-operative Programme for Monitoring and Evaluation of the
15 Long-range Transmission of Air Pollutants in Europe (EMEP). The Global Atmospheric Watch
16 (GAW) program (http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html) under the
17 World Meteorological Organization (WMO) provides quality assurance guidelines and data
18 access to an important body of air quality measurements relevant to assessing intercontinental
19 pollution transport and climate forcing phenomena. The Norwegian Institute for Air Research
20 (NILU) (http://www.nilu.no/index.cfm?ac=topics&folder_id=4572&lan_id=3), maintains a
21 database for much of the European based networks. These programs are noted not only as
22 resources for large spatial scale environmental assessments, but also as examples of coordination
23 and data harmonization that could be extended or replicated for North American purposes. The
24 MOZAIC aircraft atmospheric chemistry vertical profile measurements illustrate the close
25 linkage between European observation systems and air quality modeling and process formulation
26 studies. European-based efforts in deposition monitoring relevant to sensitive ecosystems
27 preceded efforts in North America and continue to lead the International community in
28 coordinated efforts in sustaining science based measurement programs.

29 Table AX2.5-5 includes combined contributions from all countries ranging from a few
30 sites to tens of sites per country. Measurements for a variety of air pollutants are addressed

1 including O₃, heavy metals, persistent organic pollutants (POPs), PM, VOCs, and deposition
2 from acidifying and eutrophying compounds.

3 4 5 **AX2.6 AMBIENT CONCENTRATIONS**

6 7 **AX2.6.1 NO_x and NO_y**

8 Figure AX2.6-1 shows ambient [NO₂] measured at all monitoring sites located within
9 Metropolitan Statistical Areas (MSAs) in the United States from 2003 through 2005. As can be
10 seen from Figure AX2.6-1, mean [NO₂] are ~15 ppb for averaging periods ranging from a day to
11 a year, with an interquartile range (IQR) of 10 to 15 ppb. However, the average daily maximum
12 hourly NO₂ concentrations are ~30 ppb. These values are about twice as high as the 24 h
13 averages. The highest maximum hourly concentrations (~200 ppb) are more than a factor of ten
14 higher than the mean hourly or 24-h concentrations.

15 Recall from the discussion in Chapter 2 that the FRM for NO₂ is subject to positive
16 interference by other oxidized nitrogen compounds (NO_Z) and that the degree of interference can
17 be substantial. In particular, Dunlea et al. (2007) found an average of about 22% of ambient NO₂
18 (~9 to 50 ppb) measured in Mexico City was due to interference from NO_Z compounds.
19 Comparable levels of NO₂ are found in many locations in the United States. The Dunlea et al.
20 (2007) results were based on comparison between the chemiluminescent instrument with other
21 optical techniques. Peak interference of up to 50% was found during afternoon hours and was
22 associated with O₃ and NO_Z compounds such as HNO₃ and the alkyl and multifunctional alkyl
23 nitrates.

24 Data for concentrations of NO_Z constituent species in urban areas in the United States are
25 sparse. The most comprehensive set of data for any NO_Z species was obtained for HNO₃ as part
26 of the Children's Health Study for which gas-phase HNO₃ was measured at 12 sites in Southern
27 California from 1994 through 2001 (Alcorn and Lurmann, 2004). Levels ranged from <1 ppb to
28 >10 ppb in general, the highest [HNO₃] and the highest ratio of [HNO₃] / [NO₂] were found
29 downwind of central Los Angeles in the San Bernadino Valley during summer, as one would
30 expect for this more-oxidized N product.

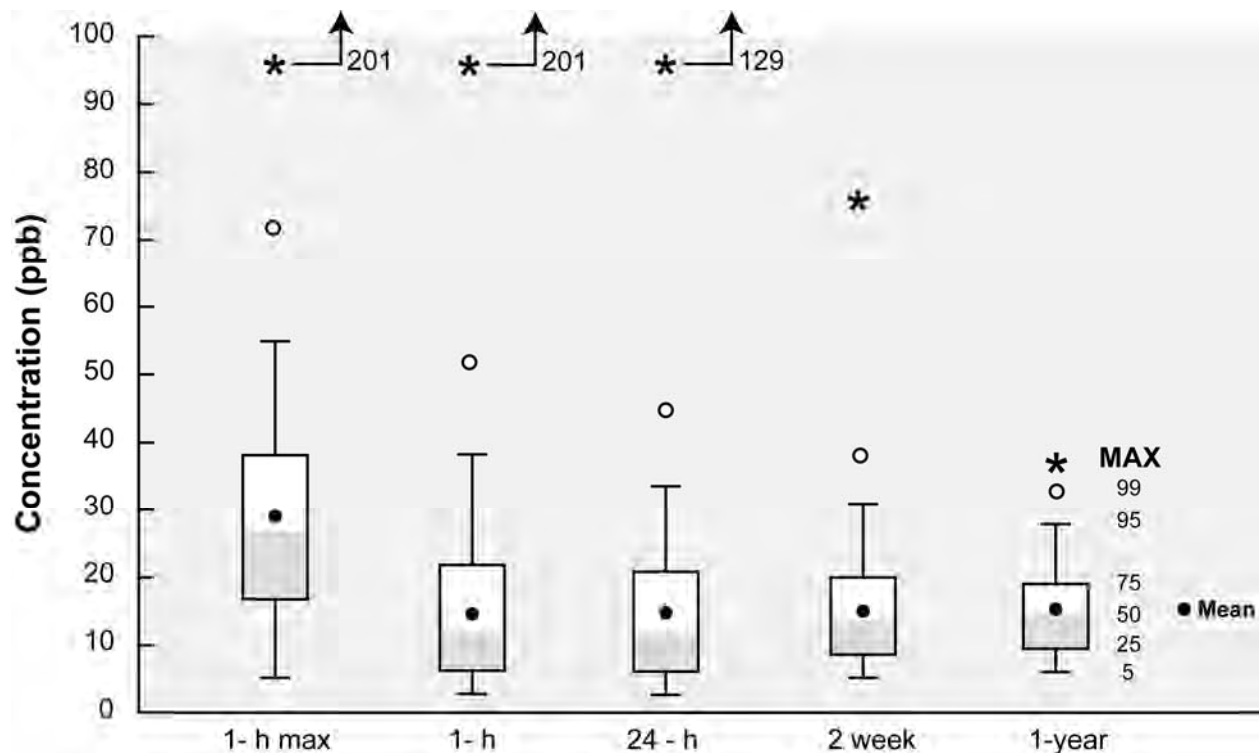


Figure AX2.6-1. Ambient concentrations of NO₂ measured at all monitoring sites located within Metropolitan Statistical Areas in the United States from 2003 through 2005.

1 Measurements of HNO₂ in urban areas are very limited; however, data from Stutz et al.,
 2 (2004) and Wang and Lu, (2006) indicate that [HNO₂] are <1 ppb even under heavily polluted
 3 conditions (with the highest levels found during the night and just after dawn and lowest values
 4 found in the afternoon). Several field studies such as Hayden et al. (2003) in rural Quebec,
 5 Williams et al. (1987) near Boulder, CO, and Singh et al. (2007) in aircraft flights over eastern
 6 North America have also found much higher levels of NO_z compounds than NO_x in relatively
 7 unpolluted rural air.

8 Calculations with EPA's Community Multiscale Air Quality (CMAQ) modeling system
 9 for the Mid-Atlantic region in a domain from Virginia to southern New Jersey showed that the
 10 highest [HNO₃] and [RONO₂] occur during mid-afternoon, consistent with their formation by
 11 photochemical processes also producing O₃. Model simulations of an O₃ episode in July 2002
 12 made for the Maryland State O₃ Implementation Plan (SIP) showed episode averages of the ratio

1 of the further-oxidized N species like HNO₃ to NO₂ ranging from 0.26 to 3.6 in rural Virginia,
2 with the highest ratios in rural areas and lowest ratios in urban centers nearer the sources of fresh
3 NO_x emissions.

4 5 **AX2.6.1.1 Small-Scale Concentration Variability in the Vertical**

6 Inlets to instruments for monitoring gas phase criteria pollutants can be located from 3 to
7 15 m above ground level (CFR 58, Appendix E, 2002). Depending on the pollutant, either there
8 can be positive, negative, or no vertical gradient from the surface to the monitor inlet. Positive
9 gradients (i.e., concentrations increase with height) result when pollutants are formed over large
10 areas by atmospheric photochemical reactions (i.e., secondary pollutants such as O₃) and
11 destroyed by deposition to the surface or by reaction with pollutants emitted near the surface.
12 Pollutants that are emitted by sources at or just above ground level show negative vertical
13 gradients. Pollutants with area sources (widely dispersed surface sources) and that have minimal
14 deposition velocities show little or no vertical gradient. Restrepo et al. (2004) compared data for
15 criteria pollutants collected at fixed monitoring sites at 15 m above the surface on a school
16 rooftop to those measured by a van whose inlet was 4 m above the surface at monitoring sites in
17 the South Bronx during two sampling periods in November and December 2001. They found
18 that CO, SO₂, and NO₂ showed negative vertical gradients, whereas O₃ showed a positive
19 vertical gradient and PM_{2.5} showed no significant vertical gradient. [NO₂] obtained at 4 m (mean
20 ~74 ppb) were about a factor of 2.5 higher than at 15 m (mean ~30 ppb). Because tail pipe
21 emissions occur at lower heights, [NO₂] could have been much higher nearer to the surface and
22 the underestimation of [NO₂] by monitoring at 15 m even larger. Restrepo et al. (2004) noted
23 that the use of the NO₂ data obtained by the stationary monitors underestimates human exposures
24 to NO₂ in the South Bronx.

25 26 **AX2.6.2 Sinks**

27 Several reactive N are species are deposited to vegetation, among them, HNO₃, NO₂,
28 PAN, and other organic nitrates.

29 **AX2.6.2.1 HNO₃**

30 Field observations based on concentration gradients of HNO₃ and using eddy covariance
31 techniques demonstrate rapid deposition that approaches the aerodynamic limit (as constrained

1 by atmospheric turbulence) in the Wesely (1989) formulation based on analogy to resistance.
2 Surface resistance to HNO₃ uptake by vegetation is negligible. Deposition rates are independent
3 of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the
4 leaf cuticle as well as leaf surfaces. The HNO₃ V_d typically exceeds 1 cm s⁻¹ and exhibits a diel
5 pattern controlled by turbulence characteristics of midday maxima and lower values at night in
6 the more-stable boundary layer.

7
8 **AX2.6.2.2 NO₂**

9 NO₂ interaction with vegetation is more complex than that for HNO₃ in part because very
10 fast measurements of NO₂ flux are confounded by the rapid interconversion of NO, NO₂, and O₃
11 (Gao et al., 1991). Application of ¹⁵N-labeled NO₂ demonstrates that NO₂ is absorbed and
12 metabolized by foliage (Siegwolf et al., 2001; Möcker et al., 1998; Segschneider et al., 1995;
13 Weber et al., 1995). Exposure to NO₂ induces activation of nitrate reductase (Weber et al., 1995,
14 1998), a necessary enzyme for assimilating oxidized N. Understanding of NO₂ interactions with
15 foliage is largely based on leaf cuvette and growth chamber studies which expose foliage or
16 whole plants to controlled [NO₂] and measure the fraction of NO₂ removed from the chamber air.
17 A key finding is that the fit of NO₂ flux to [NO₂], has a non-0 intercept, implying a compensation
18 point or internal concentration. In studies at very low [NO₂], emission from foliage is observed
19 (Teklemariam and Sparks, 2006). Evidence for a compensation point is not solely based on the
20 fitted intercept. The NO₂ uptake rate to foliage is clearly related to stomatal conductance.
21 Internal resistance is variable, and may be associated with concentrations of reactive species such
22 as ascorbate in the plant tissue that react with NO₂ (Teklemariam and Sparks, 2006). Foliar NO₂
23 emissions show some dependence on N content (Teklemariam and Sparks, 2006). Internal NO₂
24 appears to derive from plant N metabolism.

25 Two approaches to modeling NO₂ uptake by vegetation are the resistance-in-series
26 analogy which considers flux (*F*) as the product of concentration (*C*) and V_d, related to the sum
27 of aerodynamic, boundary layer, and internal resistances (*R_a*, *R_b*, and *R_c*, respectively); positive
28 fluxes are from atmosphere to foliage. These terms are related as shown in equations AX2.6-1
29 and AX2.6-2

30
$$F=CV_d \quad \text{(AX2.6-1)}$$

1
$$V_d = (R_a + R_b + R_c)^{-1} \quad (\text{AX2.6-2})$$

2 The terms R_a and R_b are controlled by turbulence in the mixed layer; R_c is dependent on
3 characteristics of the foliage and soil and may be viewed as a combination of resistance internal
4 to the foliage and external on the cuticle, soils, and bark. This approach is very similar to the
5 method most often used to predict deposition with regional air quality models (Wesely, 1989).
6 Typically, the NO_2 V_d is less than that for O_3 due to the surface's generally higher resistance to
7 NO_2 uptake, consistent with NO_2 's lower reactivity.

8 Alternatively, NO_2 exchange with foliage can be modeled from a physiological
9 standpoint where the flux from the leaf (J) is related to the stomatal conductance (g_s) and a
10 concentration gradient between the ambient air and interstitial air in the leaf ($C_a - C_i$). This
11 approach best describes results for exchange with individual foliage elements, and is expressed
12 per unit leaf or needle area. While this approach provides linkage to leaf physiology, it is not
13 straightforward to scale up from the leaf to the ecosystem

14
$$J = g_s(C_a - C_i) \quad (\text{AX2.6-3})$$

15 This model implicitly associates the compensation point with a finite internal
16 concentration. Typically observed compensation points are ~1 ppb; values of internal $[\text{NO}_2]$ are
17 consistent with metabolic pathways that include NO_x . In this formulation, the uptake will be
18 linear with $[\text{NO}_2]$, which is typically measured in foliar chamber studies.

19 Several studies have shown the UV dependence of NO_2 emissions, which implies some
20 photo-induced surface reactions to release NO_2 . Rather than model this as a UV-dependent
21 internal concentration, it would be more realistic to add an additional term to account for
22 emission that is dependent on light levels and other surface characteristics

23
$$J = g_s(C_a - C_i) = J_s(UV) \quad (\text{AX2.6-4})$$

24 The mechanisms for surface emission are discussed below. Measurement of NO_2 flux is
25 confounded by the rapid interconversion of NO , NO_2 , and O_3 (Gao et al., 1991).

1 **AX2.6.2.3 PAN**

2 PAN is phytotoxic and absorbed at the leaf. Observations based on inference from
3 concentration gradients and rates of loss at night (Shepson et al., 1992; Schrimpf et al., 1996) and
4 from leaf chamber studies (Teklemariam and Sparks, 2004) have indicated that uptake of PAN is
5 slower than that of O₃; however, recent work in coniferous canopies with direct eddy covariance
6 PAN flux measurements indicated a V_d more similar to that of O₃. Uptake of PAN is under
7 stomatal control, has non-0 deposition at night, and is influenced by leaf wetness (Turnipseed
8 et al., 2006). On the other hand, flux measurements determined by gradient methods over a grass
9 surface showed a V_d closer to 0.1 cm s⁻¹, with uncertainty on the order of a factor of 10 (Doskey
10 et al., 2004). Whether the discrepancies are methodological or indicate intrinsic differences
11 between different vegetation is unknown. Uptake of PAN is smaller than its thermal
12 decomposition in all cases.

13 14 **AX2.6.2.4 Other RONO₂**

15 The biosphere also interacts with NO_x through HC emissions and their subsequent
16 reactions to form multi-functional RONO₂. Formation of the hydroxyalkyl nitrates occurs after
17 OH attack on VOCs. In one sense, this mechanism is simply an alternate pathway for OH to
18 react with NO_x to form a rapidly depositing species. If VOC were not present, OH would be
19 available to react with NO₂ when it is present to form HNO₃.

20 Isoprene nitrates are an important class of RONO₂. Isoprene reacts with OH to form a
21 radical that adds NO₂ to form the hydroxyalkyl nitrate. The combination of hydroxyl and nitrate
22 functional group makes these compounds especially soluble with low vapor pressures, so they
23 likely deposit rapidly (Shepson et al., 1996; Treves et al., 2000). Many other unsaturated HCs
24 react by analogous routes. Observations at Harvard Forest show a substantial fraction of the total
25 of all gas-phase forms of oxidized N (category label is NO_y) not accounted for by NO, NO₂ and
26 PAN, which is attributed to the RONO₂ (Horii et al., 2006; Munger et al., 1998). Furthermore,
27 the total NO_y flux exceeds the sum of HNO₃, NO_x, and PAN, which implies that the RONO₂ are
28 a substantial fraction of the total N deposition. Other observations showing evidence of
29 hydroxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

30 Formation of the hydroxyalkyl nitrates occurs after VOC + OH reaction. In some sense,
31 this mechanism is just an alternate pathway for OH to react with NO_x to form a rapidly

1 depositing species. If VOC were not present, OH would be available to react with NO₂ when it
2 is present instead to form HNO₃.

3
4 **AX2.6.2.5 HNO₂**

5 HNO₂ formation on vegetative surfaces at night has long been observed based on
6 measurements of positive gradients (Harrison and Kitto, 1994). Surface reactions of NO₂
7 enhanced by moisture were proposed to explain these results. Production was evident at sites
8 with high ambient NO₂; at low concentration, uptake of HNO₂ exceeded the source.
9 Daytime observations of HNO₂ when rapid photolysis is expected to deplete ambient
10 concentrations to very low levels implies a substantial source of photo-induced HNO₂ formation
11 at a variety of forested sites where measurements have been made. Estimated source strengths
12 are 200 to 1800 parts per trillion (ppt) h⁻¹ in the surface layer (Zhou et al., 2002a, 2003), which
13 is ~20 times faster than all nighttime sources.

14 HNO₂ sources could be important to OH/HO₂ budgets as HNO₂ is rapidly photolyzed by
15 sunlight to OH and NO. Additional evidence of light-dependent reactions to produce HNO₂
16 comes from discovery of a HNO₂ artifact in pyrex sample inlet lines exposed to ambient light.
17 Either covering the inlet or washing it eliminated the HNO₂ formation (Zhou et al., 2002b).
18 Similar reactions might serve to explain observations of UV-dependent production of NO_x in
19 empty foliar cuvettes that had been exposed to ambient air (Hari et al., 2003; Raivonen et al.,
20 2003).

21 Production of HNO₂ in the dark is currently believed to occur via a heterogeneous
22 reaction involving NO₂ on wet surfaces (Jenkin et al., 1988; Pitts et al., 1984; He et al., 2006;
23 Sakamaki et al., 1983), and it is proposed that the mechanism has first-order dependence in both
24 NO₂ and H₂O (Kleffmann et al., 1998; Svensson et al., 1987) despite the stoichiometry.
25 However, the molecular pathway of the mechanism is still under debate. Jenkin et al. (1988)
26 postulated a H₂O•NO₂ water complex reacting with gas phase NO₂ to produce HNO₂, which is
27 inconsistent with the formation of an N₂O₄ intermediate leading to HNO₂ as proposed by
28 Finlayson-Pitts et al. (2003). Another uncertainty is whether the reaction forming HNO₂ is
29 dependent on water vapor (Svensson et al., 1987; Stutz et al., 2004) or water adsorbed on
30 surfaces (Kleffmann et al., 1998). Furthermore, the composition of the surface and the available
31 amount of surface or surface-to-volume ratio can significantly influence the HNO₂ production

1 rates (Kaiser and Wu, 1977; Kleffmann et al., 1998; Svensson et al., 1987), which may explain
2 the difference in the rates observed between laboratory and atmospheric measurements.

3 There is no consensus on a chemical mechanism for photo-induced HONO production.
4 Photolysis of HNO₃ or NO₃⁻ absorbed on ice or in surface water films has been proposed
5 (Honrath et al., 2002; Ramazan et al., 2004; Zhou et al., 2001, 2003). Alternative pathways
6 include NO₂ interaction with organic surfaces such as humic substances (George et al., 2005;
7 Stemmler et al., 2006). Note that either NO₃⁻ photolysis or heterogeneous reaction of NO₂ are
8 routes for recycling deposited nitrogen oxides back to the atmosphere in an active form. Nitrate
9 photolysis would return nitrogen that heretofore was considered irreversibly deposited, surface
10 reactions between NO₂ and water films or organic molecules would decrease the effectiveness of
11 observed NO₂ deposition if the HONO were re-emitted.

12 13 **AX2.6.3 Sulfur Oxides**

14 SO₂ data collected from the SLAMS and National Air Monitoring Stations (NAMS)
15 networks show that the decline in SO₂ emissions from electric generating utilities has improved
16 air quality. There has not been a single monitored exceedance of the SO₂ annual ambient air
17 quality standard in the United States since 2000, according to the U.S. Environmental Protection
18 Agency Acid Rain Program (ARP) 2005 Progress Report (U.S. Environmental Protection
19 Agency, 2006b). EPA's trends data (www.epa.gov/airtrends) reveal that the national composite
20 average SO₂ annual mean ambient concentration decreased by 48% from 1990 to 2005, with the
21 largest single-year reduction coming in 1994-1995, the ARP's first operating year (U.S.
22 Environmental Protection Agency, 2006b). Figure AX2.6-2 depicts data for SO₂ emissions in
23 the continental United States (CONUS) in these years that reflect this reduction with individual
24 state-level totals.

25 These emissions data trends are consistent with the trends in the observed ambient
26 concentrations from the Clean Air Status and Trends Network (CASTNet). Following
27 implementation of the Phase I controls on ARP sources between 1995 and 2000, significant
28 reductions in [SO₂] and ambient [SO₄²⁻] were observed at CASTNet sites throughout the eastern
29 United States. The mean annual [SO₂] and [SO₄²⁻] from CASTNet's long-term monitoring sites
30 can be compared using two 3-year periods (1989 through 1991 and 2003 through 2005) in
31 Figures AX2.6-3a and AX2.6-3b for SO₂, and Figures AX2.6-4a and AX2.6-4b for SO₄²⁻.

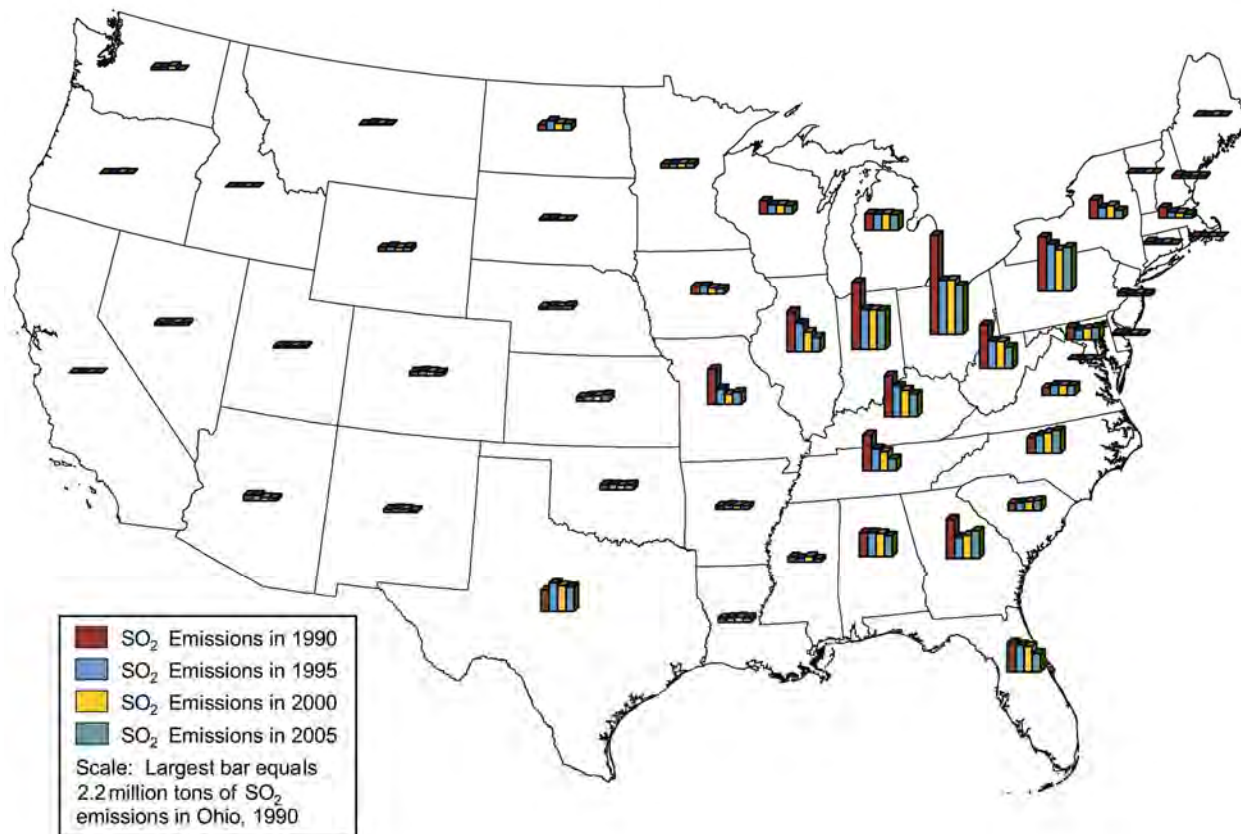


Figure AX2.6-2. State-level SO₂ emissions, 1990-2005.

Source: Environmental Protection Agency Clean Air Markets Division (www.epa.gov/airmarkets/index.html).

1 From 1989 through 1991, that is, in the years prior to implementation of the ARP Phase I,
 2 the highest ambient mean [SO₂] and [SO₄²⁻] were observed in western Pennsylvania and along
 3 the Ohio River Valley: >20 µg m⁻³ (~8 ppb) SO₂ and >15 µg m⁻³ SO₄²⁻. As with SO₂, in the
 4 years since the ARP controls were enacted, both the magnitude of SO₄²⁻ concentrations and their
 5 areal extent have been significantly reduced, with the largest decreases again coming along the
 6 Ohio River Valley.

7 Figure AX2.6-5 depicts for the CONUS the magnitude and spatial distribution of SO₂
 8 emissions in 2006 from sources in the ARP. This depiction shows clearly the continuing
 9 overrepresentation of SO₂ sources in the United States east of the Mississippi River as compared
 10 to west of it, a trend even stronger in the central Ohio River Valley and which was evident in the

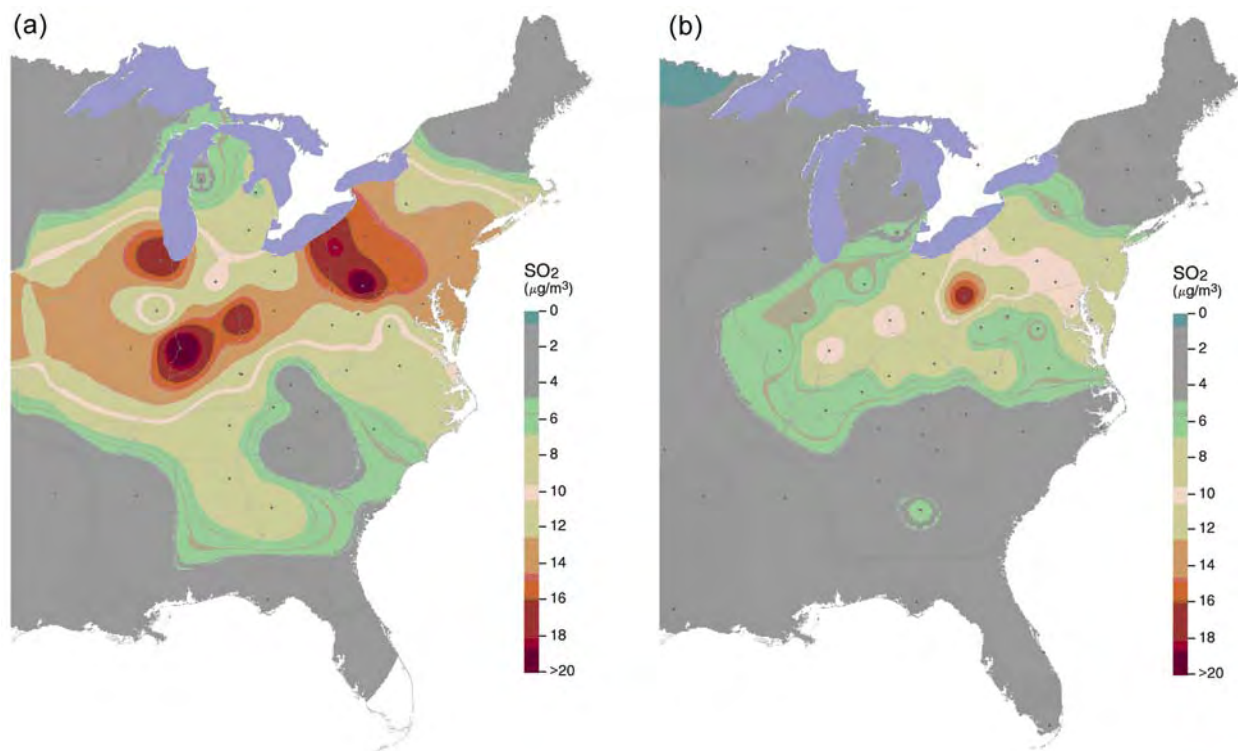


Figure AX2.6-3a,b. Annual mean ambient SO₂ concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

* Dots on all maps represent monitoring sites. Lack of shading for southern Florida indicates lack of monitoring coverage.

Source: Environmental Protection Agency, CASTNet (www.epa.gov/castnet/).

1 smoothed concentration plots in Figures AX2.6-3a and AX2.6-3b. As shown in Table AX2.6-1,
 2 regional distributions of [SO₂] and [SO₄²⁻] averaged for the 3 years 2003 through 2005 reflect
 3 this geospatial emissions source difference as well.

4

5 **AX2.6.4 Spatial and Temporal Variability of Ambient [SO₂]**

6 [SO₂] have been falling throughout all regions of the United States as demonstrated by
 7 the CASTNet data reviewed above. In and around most individual Consolidated Metropolitan
 8 Statistical Areas (CMSAs), the trends are also toward lower SO₂ levels. Table AX2.6-2 shows
 9 that many annual and even 1-h mean concentrations for the years 2003 through 2005 were
 10 consistently at or below the operating LOD of ~3 ppb for the standard SO₂ monitor deployed in
 11 the regulatory networks, while the aggregate mean value over all 3 years and all sites in and

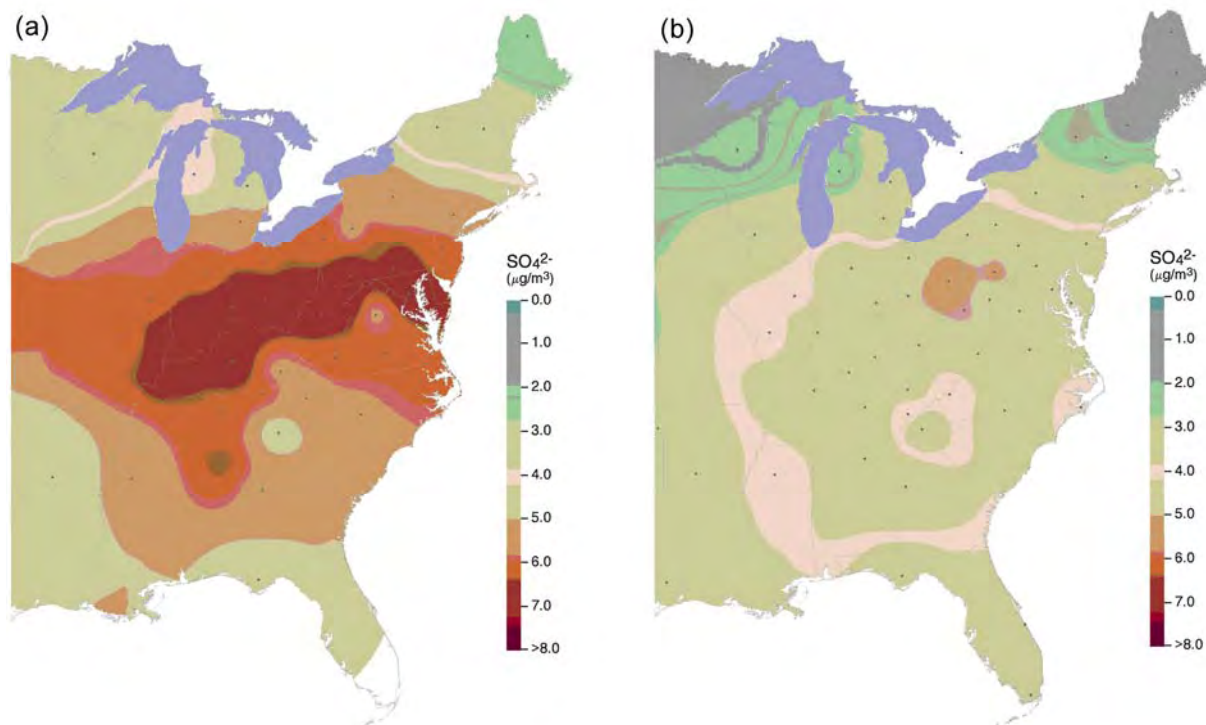


Figure AX2.6-4a,b. Annual mean ambient SO_4^{2-} Concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

* Dots on all maps represent monitoring sites. Lack of shading for southern Florida indicates lack of monitoring coverage.

Source: Environmental Protection Agency, CASTNet (www.epa.gov/castnet/).

- 1 around the CMSAs was just above the LOD at ~ 4 ppb, and is identical to the 1 h and 24 h means.
- 2 Hence, it appears reasonable to aggregate up in time from available 1 h samples to daily and
- 3 even annual exposure estimates.
- 4 Figure AX2.6-6 shows the composite diurnal variation in hourly SO_2 concentrations in
- 5 boxplot form from all monitors reporting SO_2 data into the Air Quality System (AQS) database.
- 6 The AQS contains measurements of air pollutant concentrations in the 50 states, plus the District
- 7 of Columbia, Puerto Rico, and the Virgin Islands for the six criteria air pollutants (SO_2 , NO_2 ,
- 8 PM, CO, Pb, O_3) and hazardous air pollutants. The same data were used to construct Table
- 9 AX2.6-2 and to configure Figure AX2.6-6. As can be seen from Figure AX2.6-6, concentrations
- 10 beneath the 95th percentile level are indistinguishable from each other, but are typically in the

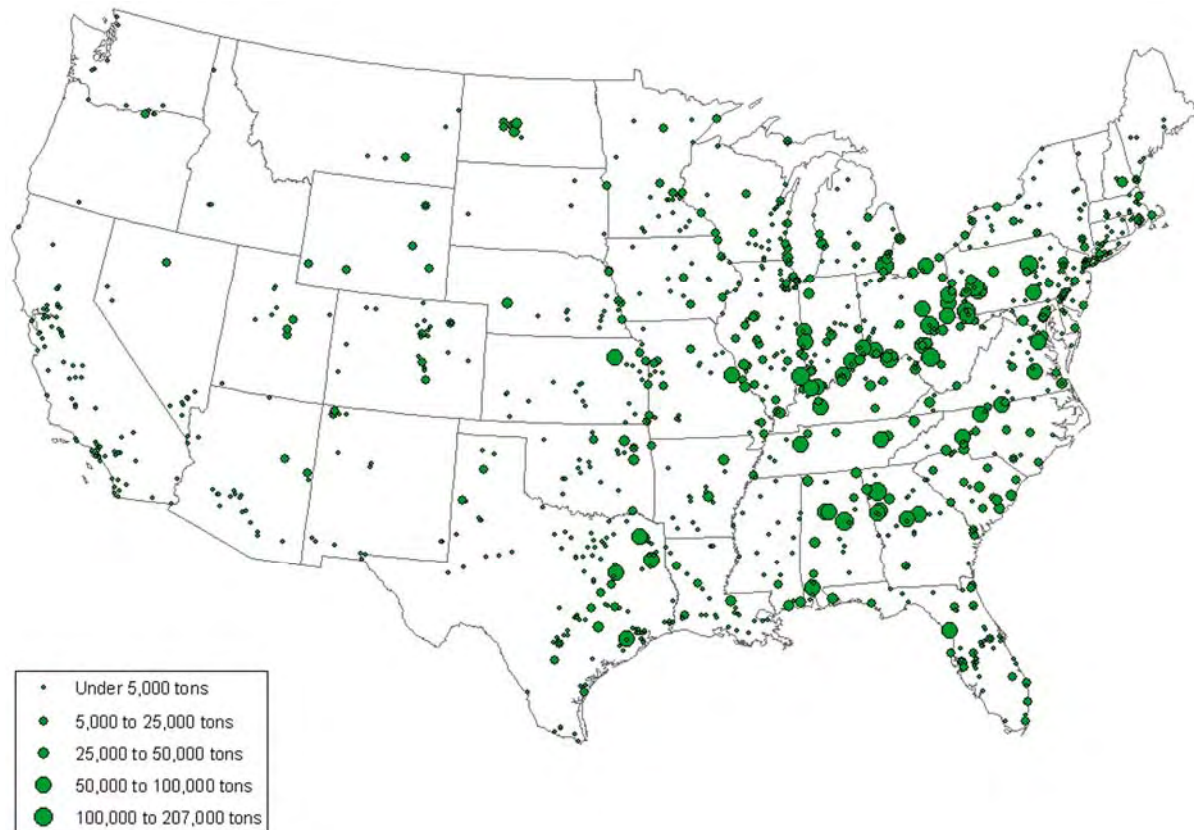


Figure AX2.6-5. Annual SO₂ Emissions in 2006 for Acid Rain Program Cooperating Facilities.

Source: Environmental Protection Agency, Clean Air Markets Division (www.epa.gov/airmarkets/index.html).

1 range of only a few ppb. However, the peaks in the distribution at any hour of the day can be a
 2 factor of 10 or more higher than values in the bulk of the concentration distribution. Overall,
 3 there is some indication that the highest values are reached either at midday or during the middle
 4 of the night. Daytime peaks could result from down mixing of air aloft due to convective
 5 activity, as SO₂ is emitted mainly by elevated sources. Nighttime peaks are more likely due to
 6 trapping of local emissions beneath a shallow nocturnal boundary layer.

7 To be sure, the maximum 1 h concentration observed at some sites in and around some
 8 CMSAs did still exceed the mean by a large margin, with maximum 1-h values in Table AX2.6-2
 9 of >600 ppb. However, the 50th percentile maximum value outside CMSAs, 5 ppb, was only
 10 slightly greater than the 1 h, 24 h, and annual mean values of 4 ppb. The 50th percentile

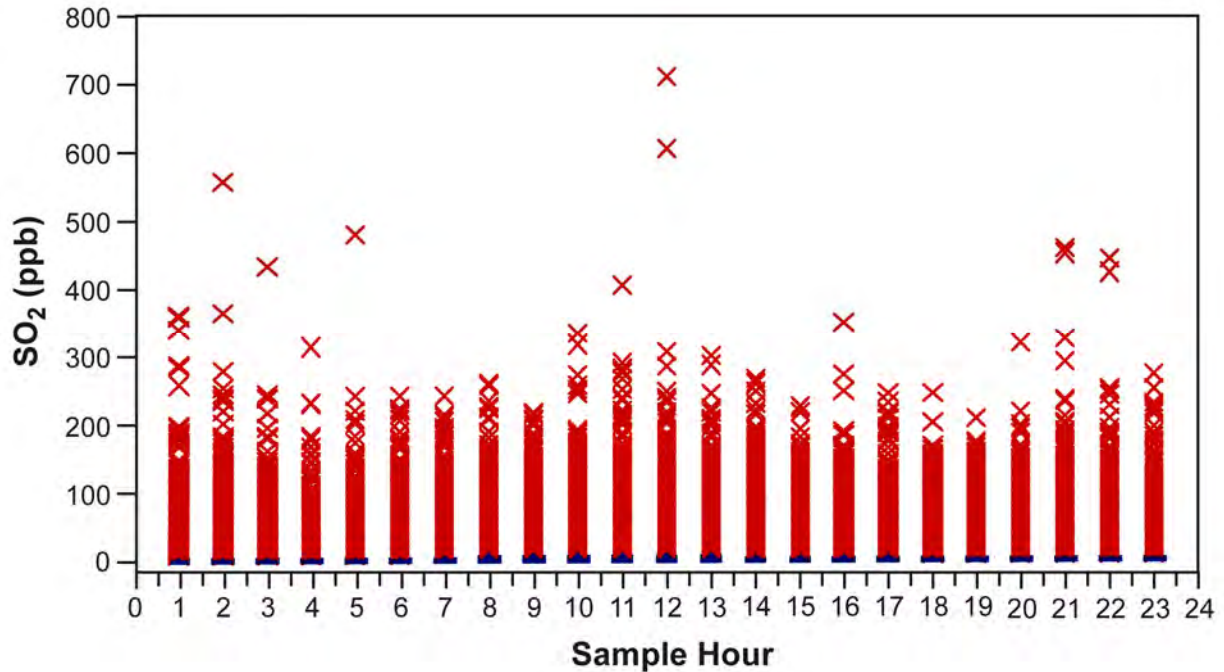


Figure AX2.6-6. Boxplot of hourly SO₂ concentrations across all cities in focus.

1 maximum value inside CMSAs, 7 ppb, was 75% greater than these longer-term averages,
 2 reflecting heterogeneity in source strength and location. In addition, even with 1 h maximum
 3 values of >600 ppb, the maximum annualized mean value for all CMSAs was still <16 ppb, and,
 4 hence, below the current annual primary SO₂ NAAQS.

5
6

7 **AX2.7 FAST HOMOGENEOUS REACTIONS**

8 Inferences from observations at Blodgett Forest suggest that radicals from O₃ + VOC
 9 react with NO_x in the canopy to produce HNO₃ and RONO₂ among other species. This
 10 mechanism would contribute to canopy retention of soil NO emission in forests with high VOC
 11 possibly more effectively than the NO to NO₂ conversion and foliar uptake of NO₂ that has been
 12 proposed to reduce the amount of soil NO that escapes to the supra-canopy atmosphere (Jacob
 13 and Bakwin, 1991).

1 **AX2.8 NITROGEN AND SULFUR DEPOSITION ACROSS THE** 2 **LANDSCAPE**

3 Emissions of SO_x and NO_x have decreased substantially in the last 35 years (see Table
4 AX2.8-1). From 1970 until 2005, NO_x emissions are down from 26.9 million tons per year
5 (Mt yr⁻¹) to 19 Mt yr⁻¹ and SO₂ emissions are down from 31.2 to 15 Mt yr⁻¹. These decreases in
6 emissions have led to correlative decreases in N and S atmospheric deposition across the
7 landscape.

8 Deposition maps were developed by CASTNET to show the composition of total
9 deposition for N and S (see Figures AX2.8-1 through AX2.8-4). The maps are labeled with
10 estimated total deposition at each site, and a pie chart showing the relative proportion of wet and
11 dry deposition or the chemical components of the deposition. Wet deposition is estimated from
12 the interpolated concentration as measured by the National Atmospheric Deposition
13 Program/National Trends Network (NADP/NTN) multiplied by the measured rainfall at the site.
14 Dry deposition is estimated from the measured ambient air concentrations of the chemical
15 multiplied by the obtained from an inferential model of linked resistances. (See the CASTNET
16 QAPP for more information on methods). It is important to recognize that NH₃ is not included in
17 these total N estimates because it is not currently measured in these regulatory networks, even
18 though it is a major component of total N in some areas.

19 Data in this section are presented to show deposition across the landscape; finer-scale
20 data and maps of sensitive and vulnerable regions and ecosystems are presented in other
21 sections. Data presented in the maps and charts represent 3 yr averages. For example, “89-91”
22 is the average total deposition of 1989, 1990, and 1991 for a given site. Only sites having valid
23 total deposition for at least two of the three years are shown and in some instances, sites only met
24 this criterion for one of the two reporting periods. Because of differences like these, direct site-
25 by-site comparisons are not possible everywhere. However, the maps here do provide useful
26 information on trends in deposition and the spatial extent of N and S deposition.

27 28 **AX2.8.1 Nitrogen**

29 For the years 2004-2006, mean N deposition was greatest in the Ohio River basin,
30 specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg ha⁻¹ yr⁻¹,
31 respectively. N deposition is lower in other parts of the East, including the Southeast and in

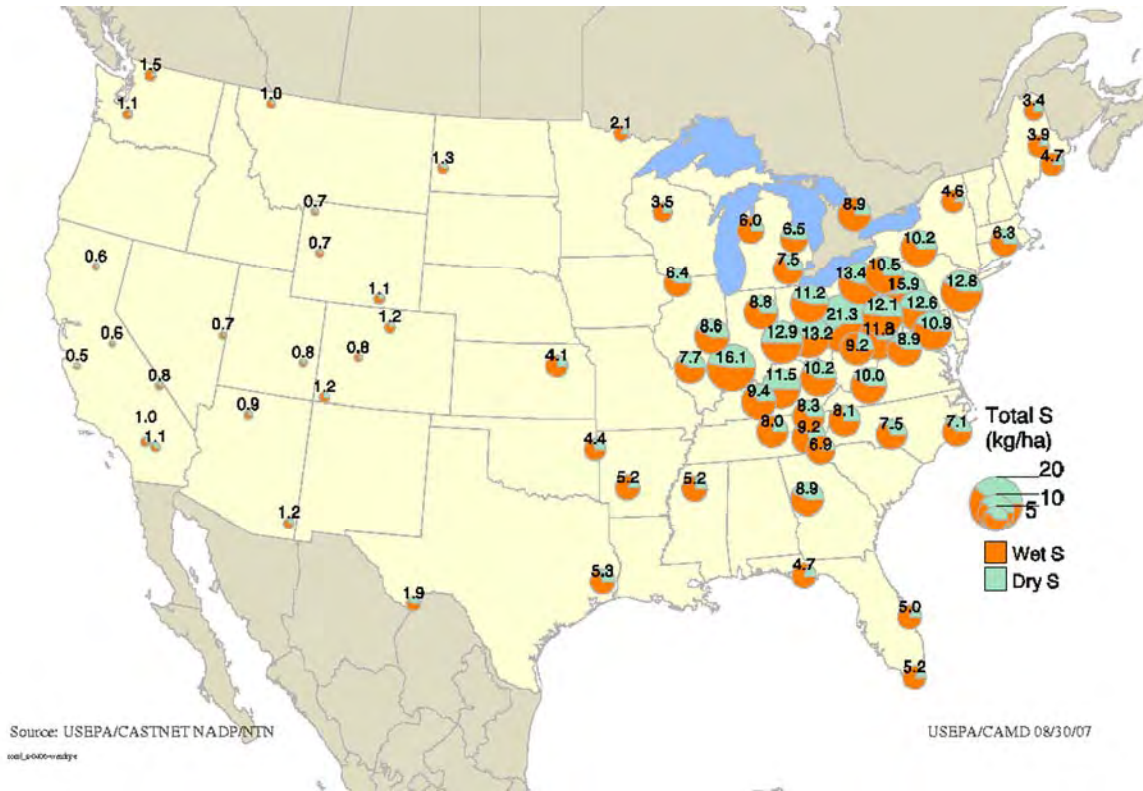


Figure AX2.8-1. Total average yearly wet and dry sulfur deposition for 2004—2006 (top) and 1989—1991 (bottom).

1 northern New England. In the central United States, Kansas and Oklahoma reported the highest
 2 deposition (7.0 and $6.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Like S, N deposition is generally much lower in the
 3 western United States, and is highest in urban areas in southern California and Denver (4.8 and
 4 $3.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$). It should be noted, however, that large portions of the United States west of
 5 the Mississippi River are poorly covered by the current deposition monitoring networks as these
 6 maps make clear. Hence, the actual degree of heterogeneity in the West is largely unknown.

7 Because NO_x emissions decreased by $\sim 25\%$ between 1990 and 2005, recent N deposition
 8 is lower compared with average deposition for the years 1989 to 1991. For 1989 to 1991, several
 9 recording stations in the Ohio River basin reported average annual deposition rates in excess of
 10 $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Data are lacking, however, for much of the central and western United States
 11 and little can be said for changes between the two reporting periods in these areas for the reasons

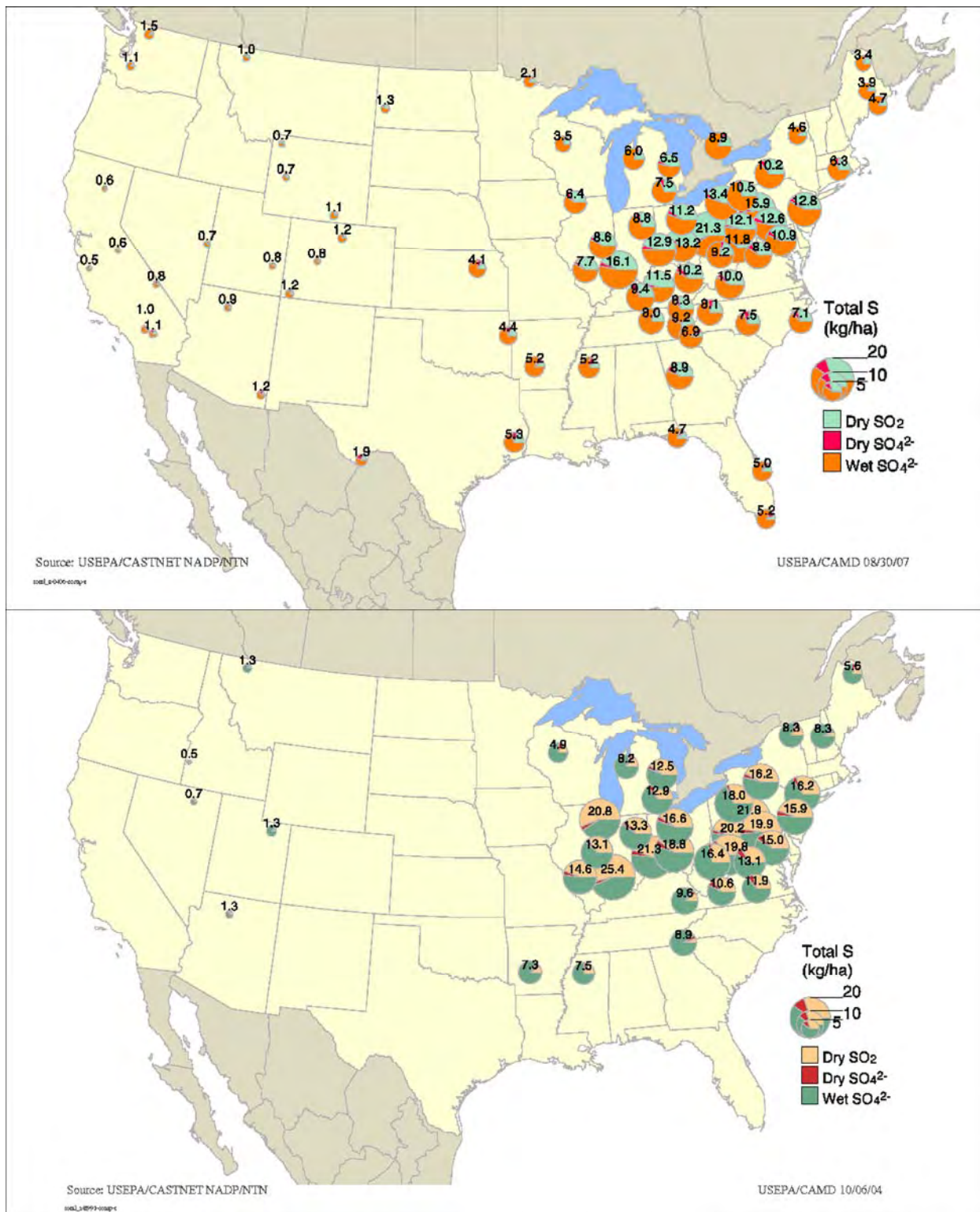


Figure AX2.8-2. Total average yearly sulfur deposition by species for 2004—2006 (top) and 1989—1991 (bottom).

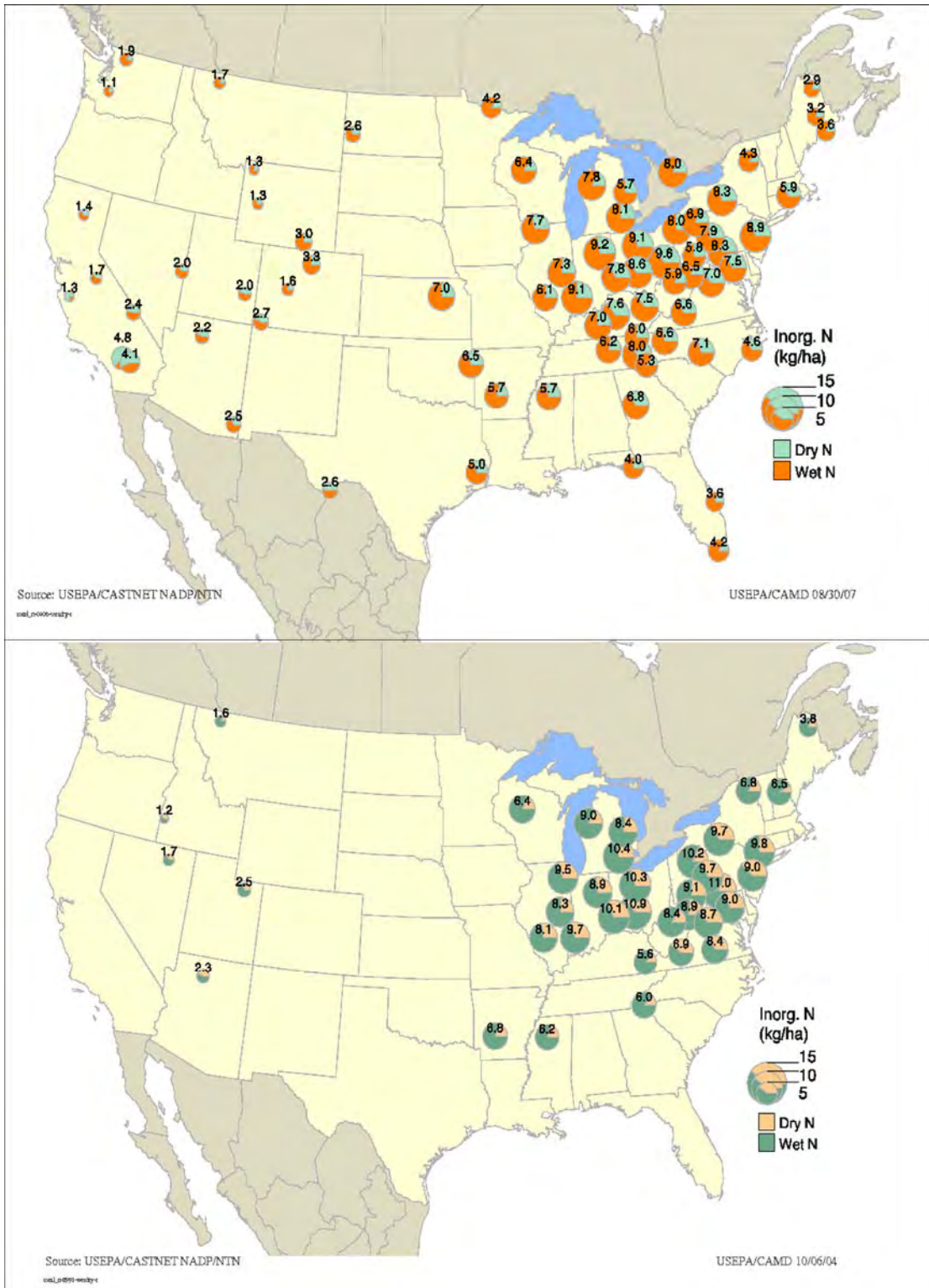


Figure AX2.8-3. Total average yearly wet and dry inorganic nitrogen deposition for 2004—2006 (top) and 1989—1991 (bottom).

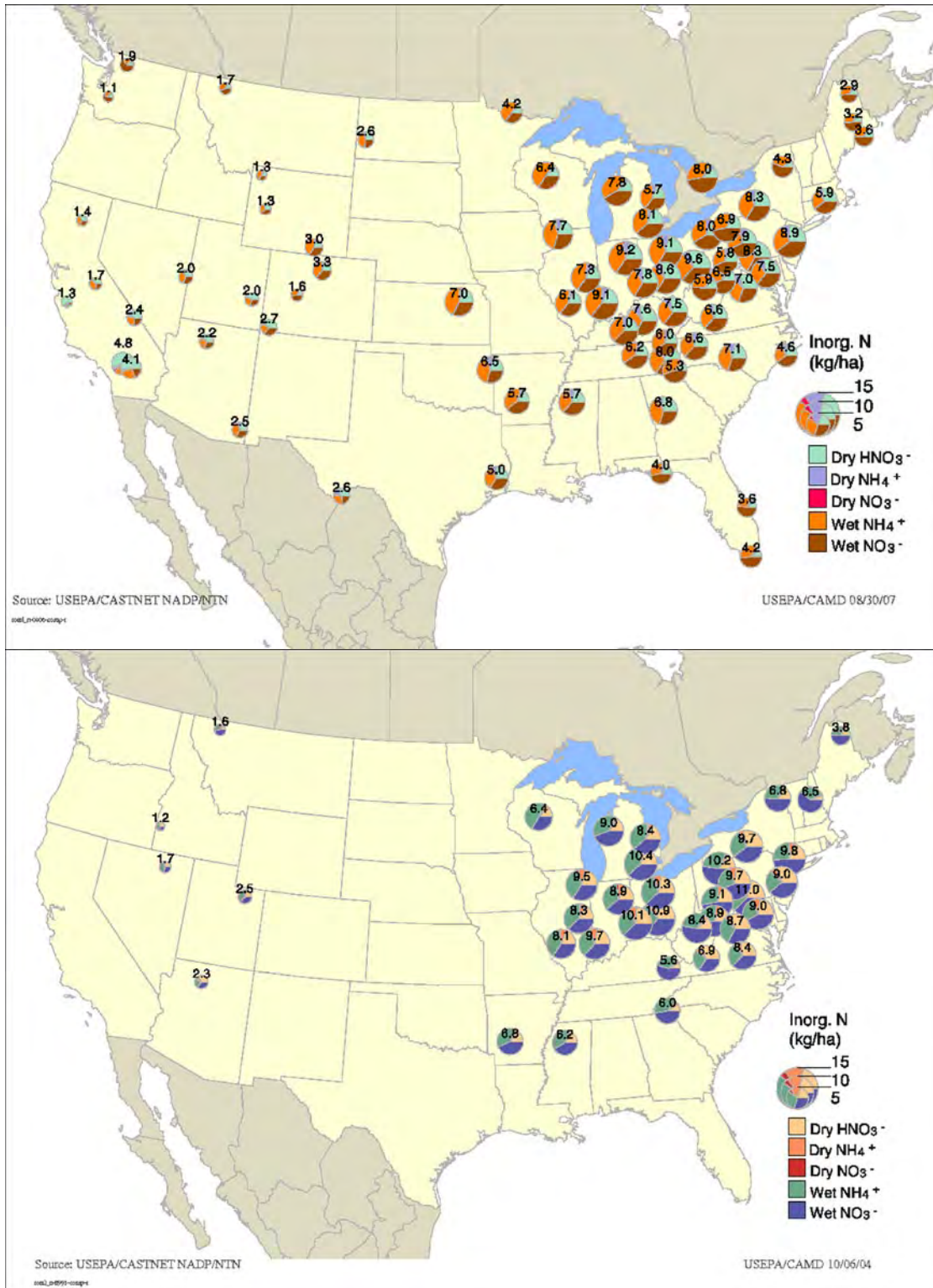


Figure AX2.8-4. Total average yearly inorganic nitrogen deposition by species for 2004—2006 (top) and 1989—1991 (bottom).

1 given above. The greatest mass of N deposition primarily occurred as wet NO_3^- and NH_4^+ ,
2 followed in importance by dry HNO_3 , dry NH_4^+ , and dry NO_3^- . Although most deposition for
3 both reporting periods occurred as wet deposition, there were some exceptions, including parts of
4 California where N deposition was primarily dry.

5 6 **AX2.8.2 Sulfur**

7 For the most recent 3-year reporting period available (2004 to 2006), mean S deposition
8 was greatest in the eastern United States east of the Mississippi River, with the highest
9 deposition of $21.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in the Ohio River basin. Most recording stations throughout the
10 Ohio River basin report 3-year total S deposition averages $>10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and many other
11 stations in the East report deposition $>5 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Data are sparse for the central and west
12 United States, but, where available, indicate lower values than in most of the East, ranging from
13 4.1 to $5.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Total S deposition in the United States west of the 100th meridian is
14 lower, with all recording stations reporting $<2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and many reporting $<1.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

15 Station-by-station comparisons between averaging periods are difficult because some
16 stations do not have sufficient data to report a mean for the sampling period. There are,
17 however, clear regional decreases in S deposition across the country. S deposition for
18 1989—1991 (the earliest 3 year reporting period available) is almost uniformly greater than for
19 the most recent three-year average (2004—2006). Deposition since 1989-1991 has declined
20 throughout the Ohio River basin (from a previous high of $25.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$), New England, and
21 the Mid-Atlantic, consistent with the ~48% decrease in SO_2 emissions nationwide between 1990
22 and 2005 (Table AX2.8-1). Very little coverage for the western and central United States was
23 available for the 1989—2001 reporting period, but sites with data show a similar decrease. For
24 both the 1989—1991 and 2004—2006 reporting periods, S was primarily deposited as wet SO_4^{2-}
25 followed by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry
26 SO_4^{2-} .

27 28 29 **AX2.9 EXAMPLE NO_2 AND HNO_3 FLUX DATA FROM HARVARD** 30 **FOREST**

1 Harvard Forest is a rural site in central Massachusetts, where ambient NO_x , NO_y , and
2 other pollutant concentrations and fluxes of total NO_y have been measured since 1990 (Munger
3 et al., 1996).

4 An intensive study in 2000 utilized a Tunable Diode Laser Absorption Spectrometer
5 (TDLAS) to measure NO_2 and HNO_3 . TDLAS has an inherently fast response, and for species
6 such as NO_2 and HNO_3 with well-characterized spectra it provides an absolute and specific
7 measurement. Absolute concentrations of HNO_3 were measured, and the flux inferred based on
8 the dry deposition inferential method that uses momentum flux measurements to compute a
9 deposition velocity and derives an inferred flux (Wesely and Hicks, 1977; Hicks et al., 1987).
10 Direct eddy covariance calculations for HNO_3 were not possible because the atmospheric
11 variations were attenuated by interaction with the inlet walls despite very short residence time
12 and use of fluorinated silane coatings to make the inlet walls more hydrophobic. Nitrogen Oxide
13 response was adequate to allow both concentration and eddy covariance flux determination.
14 Simultaneously, NO and NO_y eddy covariance fluxes were determined with two separate O_3
15 chemiluminescence detectors, one equipped with a H_2 -gold catalyst at the inlet to convert all
16 reactive nitrogen compounds to NO . Additionally, the measurements include concentration
17 gradients for NO , NO_2 , and O_3 over several annual cycles to examine their vertical profiles in the
18 forest canopy.

19 Overall, the results show typical NO_2 concentrations of 1 ppb under clean-air conditions
20 and mean concentrations up to 3 ppb at night and 1 ppb during daytime for polluted conditions.
21 Net positive fluxes (emission) of NO_2 were evident in the daytime and negative fluxes
22 (deposition) were observed at night (Figure AX2.9-1). Nitric oxide fluxes were negative during
23 the daytime and near zero at night.

24 In part, the opposite NO and NO_2 fluxes are simply consequences of variable NO/NO_2
25 distributions responding to vertical gradients in light intensity and O_3 concentration, which
26 resulted in no net flux of NO_x (Gao et al., 1993). In the Harvard Forest situation, the NO
27 and NO_2 measurements were not at the same height above the canopy, and the resulting
28 differences derive at least in part from the gradient in flux magnitude between the two inlets
29 (Figure AX2.9-2). At night, when NO concentrations are near 0 due to titration by ambient O_3
30 there is not a flux of NO to offset NO_2 fluxes. Nighttime data consistently show NO_2 deposition

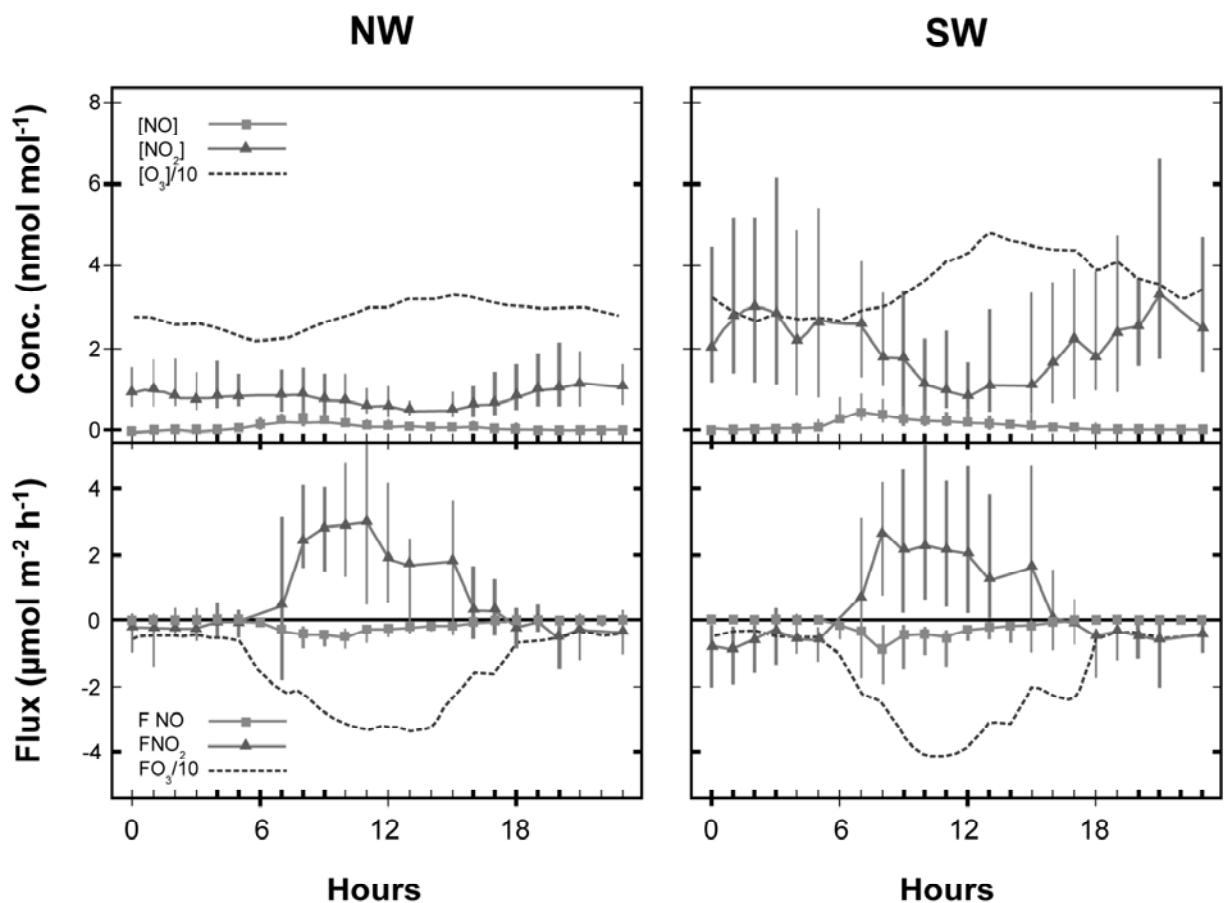


Figure AX2.9-1. Diel cycles of median concentrations (upper panels) and fluxes (lower panels) for the Northwest clean sector, left panels) and Southwest (polluted sector, right panels) wind sectors at Harvard Forest, April–November, 2000, for NO, NO₂, and O₃/10. NO and O₃ were sampled at a height of 29 m, and NO₂ at 22 m. Vertical bars indicate 25th and 27th quartiles for NO and NO₂ measurements. NO₂ concentration and nighttime deposition are enhanced under southwesterly conditions, as are O₃ and the morning NO maximum.

Source: Horii et al. (2004).

1 (Figure AX2.9-3), which increases with increasing NO₂ concentrations. Concentrations above
 2 10 ppb were rare at this site, but the few high NO₂ observations suggest a nonlinear dependence
 3 on concentration. The data fit a model with V_d of -0.08 plus an enhancement term that was
 4 second order in NO₂ concentration. The second order term implies that NO₂ deposition rates to
 5 vegetation in polluted urban sites would be considerably larger than what was observed at this
 6 rural site.

Simple Model

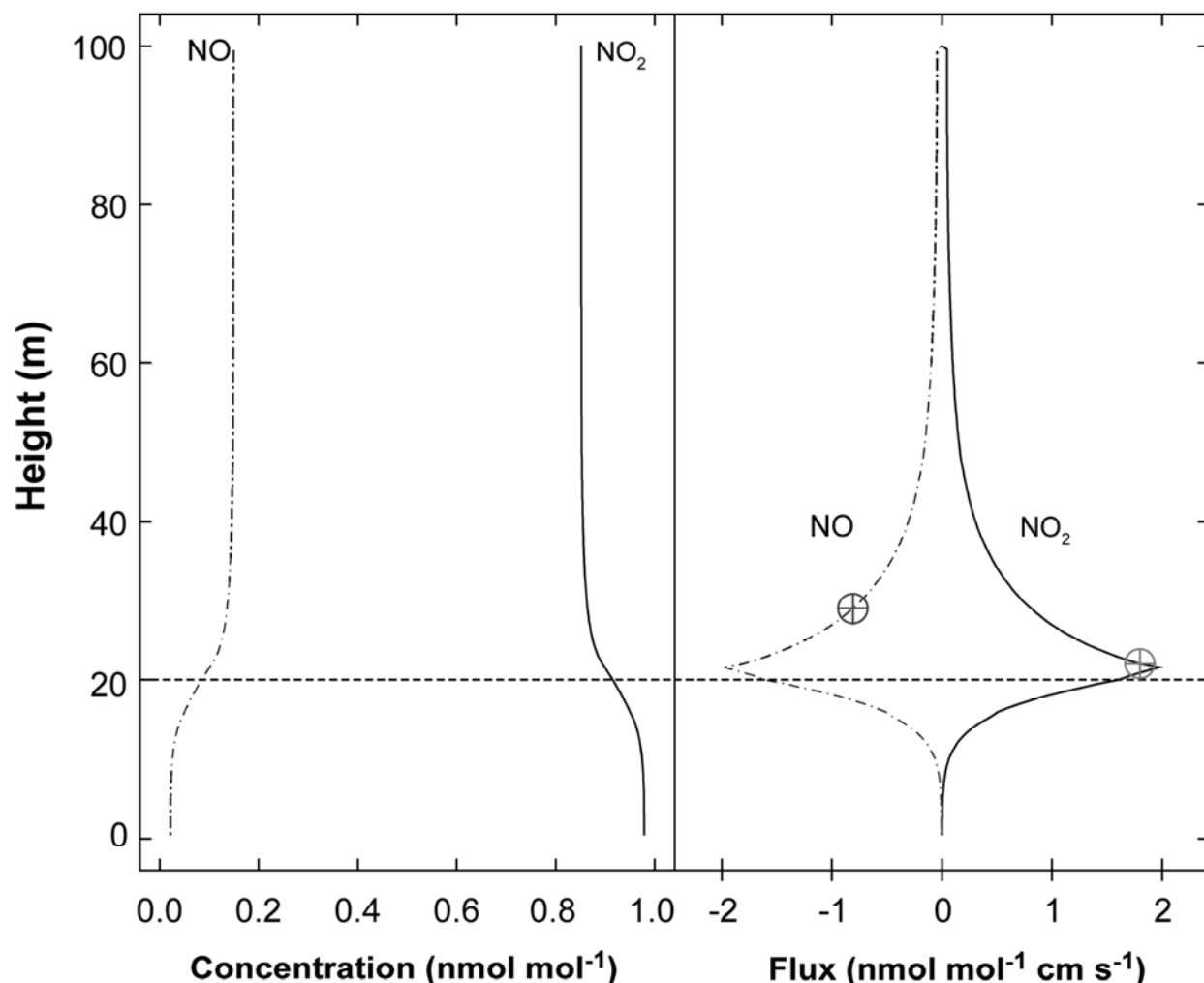


Figure AX2.9-2. Simple NO_x photochemical canopy model outputs. Left panel, concentrations of NO (dashed) and NO₂ (solid); right, fluxes of NO (dashed) and NO₂ (solid). Symbols indicate measurement heights for NO (29m) and NO₂ (22m) at Harvard Forest. The model solves the continuity equation for NO concentration at 200 levels, $d/dz(-Kc(dNO/dz)) = PNO - LNO$, where $PNO = [NO]/t1$, $LNO = [NO]/t2$, and zero net deposition or emission of NO_x is allowed. NO_x (NO + NO₂) is normalized to 1ppb. $t1 = 70s$ in this example. Due to the measurement height difference, observed upward NO₂ flux due to photochemical cycling alone should be substantially larger than observed downward NO flux attributable to the same process.

Source: Horii (2002).

$$F_{\text{NO}_2}(\text{night}) = F_0 + V_0 [\text{NO}_2] + a [\text{NO}_2]^2$$

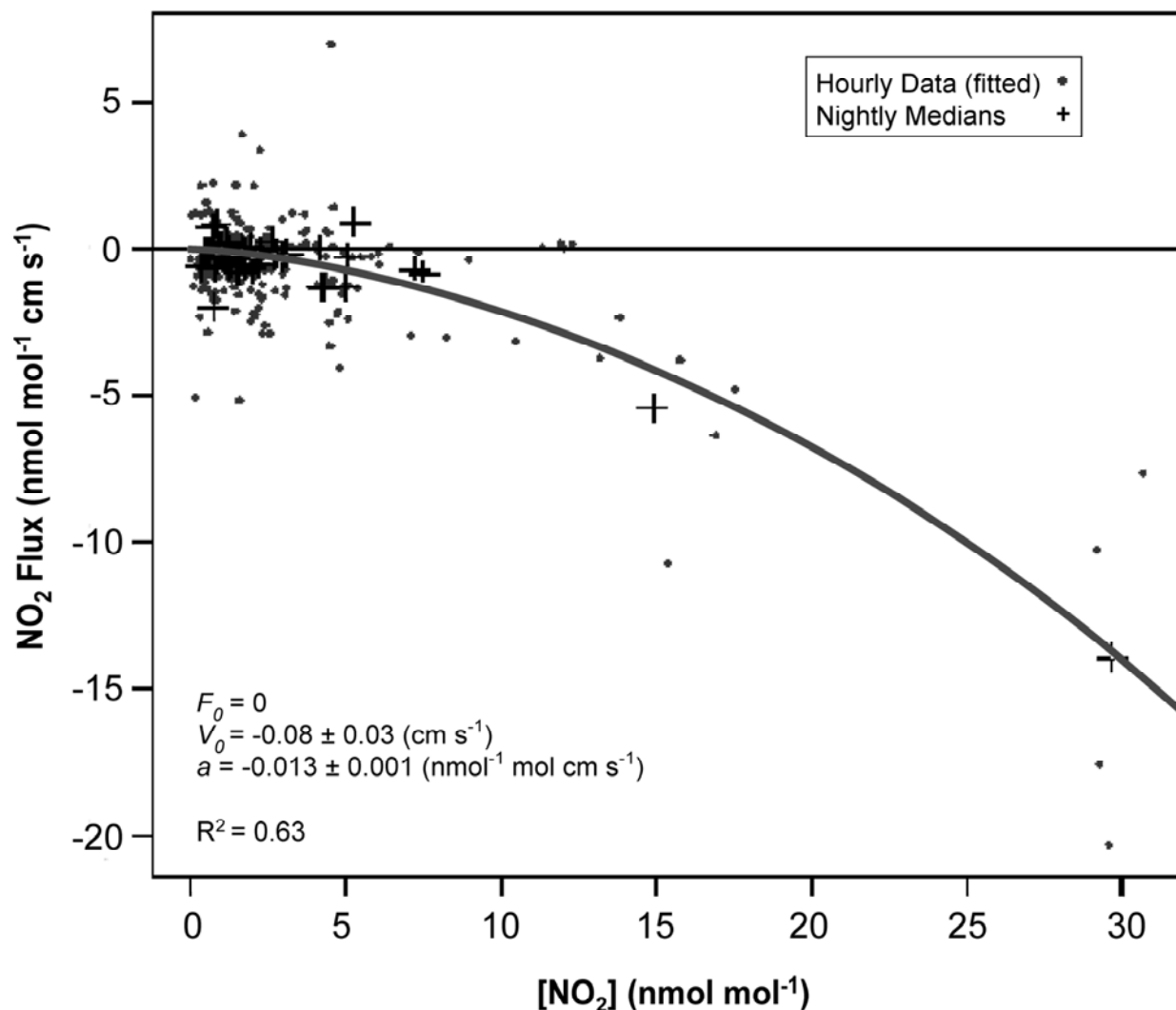


Figure AX2.9-3. Hourly (dots) and median nightly (pluses) NO_2 flux vs. concentration, with results of least squares fit on the hourly data (curve). The flux is expressed in units of concentration times velocity ($\text{nmol mol}^{-1} \text{ cm s}^{-1}$) in order to simplify the interpretation of the coefficients in the least squares fit. Pressure and temperature corrections have been taken into account in the conversion from density to mixing ratio.

Source: Horii et al. (2004).

1 After accounting for the time of the NO-NO₂ null cycle during the measurement
2 sampling period, the net NO_x flux can be derived. Overall, there was a net deposition of NO_x
3 during the night and essentially zero flux in the day, with large variability in the magnitude and
4 sign of individual flux observations. For the periods with [NO₂] > 2 ppb, deposition was always
5 observed. These canopy-scale field observations are consistent with a finite compensation point
6 for NO₂ in the canopy that offsets foliar uptake or even reverses it when concentrations are
7 especially low. At concentrations above the compensation point, NO_x is absorbed by the
8 canopy. Examination of concentration profiles corroborates the flux measurements (Figure
9 AX2.9-4). During daytime for low-NO_x conditions, there is a local maximum in the
10 concentration profile near the top of the canopy where O₃ has a local minimum, which is
11 consistent with foliar emission or light-dependent production of NO_x in the upper canopy.
12 Depletion is evident for both NO_x and O₃ near the forest floor. Air reaching the ground has
13 passed through the canopy where uptake is efficient and the vertical exchange rates near the
14 ground are slow. At night, the profiles generally decrease with decreasing height above the
15 ground, showing only uptake. At higher concentrations, the daytime NO_x concentrations are
16 nearly constant through the canopy; no emission is evident from the sunlit leaves.

17 Figure AX2.9-5 compares observed fluxes of all the observed species. The measured
18 NO_x and estimated PAN fluxes are small relative to the observed total NO_y flux. In clean air,
19 HNO₃ accounts for nearly all the NO_y flux and the sum of all measured species is about equal to
20 the NO_y concentration. However, in polluted conditions, unmeasured species are up to 25% of
21 the NO_y, and HNO₃ fluxes cannot account for all the total NO_y flux observed. Likely, these
22 unmeasured NO_y species are hydroxyalkyl nitrates and similar compounds and are rapidly
23 deposited. Although NO₂ uptake may be important to the plant, because it is an input directly to
24 the interior of foliage that can be used immediately in plant metabolism, it is evidently not a
25 significant part of overall nitrogen deposition to rural sites. The deposition of HNO₃ and
26 multifunctional organic nitrates are the largest elements of the nitrogen dry deposition budget.
27 Two key areas of remaining uncertainty are the production of HNO₂ over vegetation and the role
28 of very reactive biogenic VOCs. HNO₂ is important because its photolysis is a source of OH
29 radicals, and its formation may represent an unrecognized mechanism to regenerate
30 photochemically active NO_x from NO₃ that had been considered terminally removed from the
31 atmosphere.

NO_x PROFILES

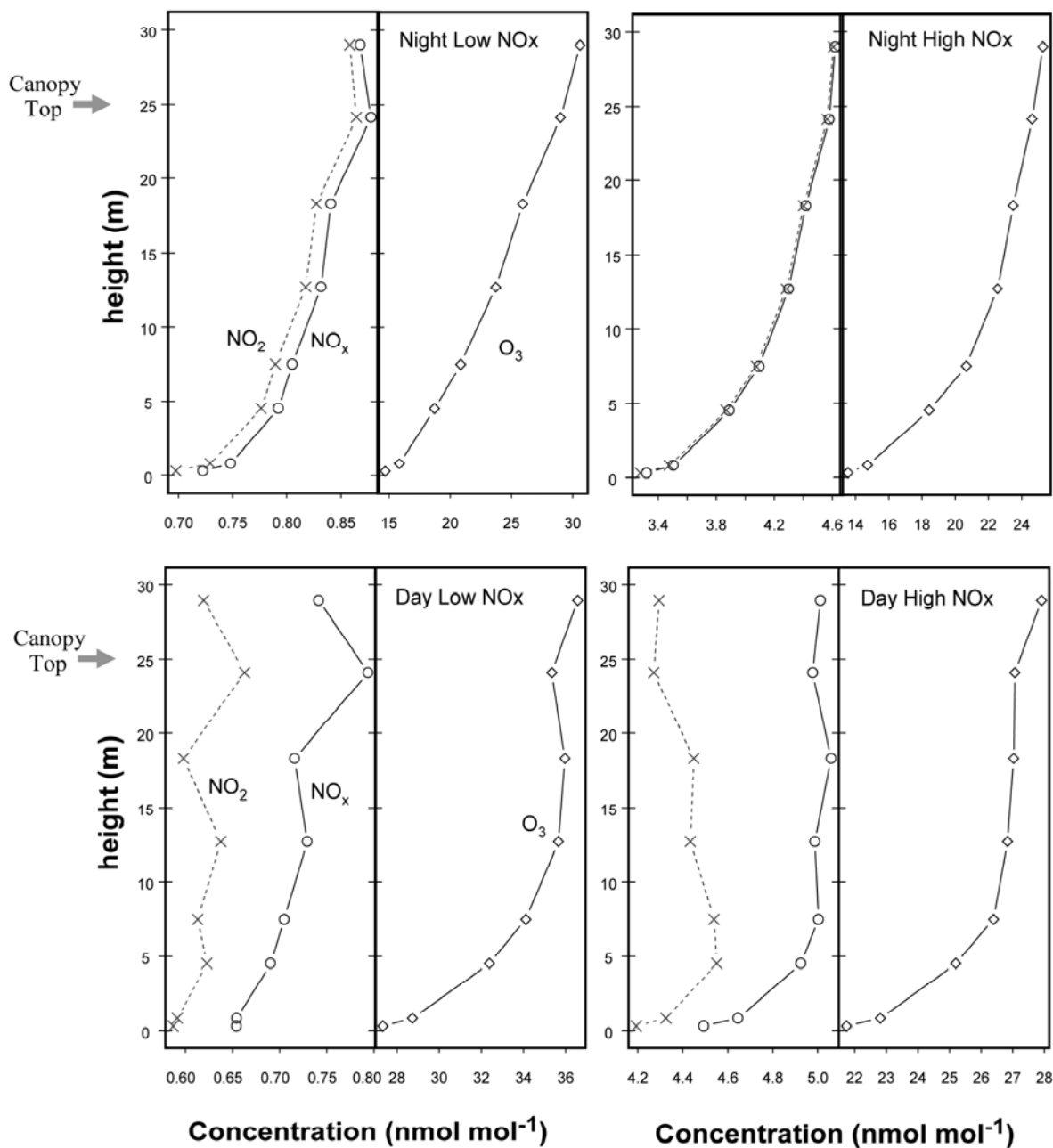


Figure AX2.9-4. Averaged profiles at Harvard Forest give some evidence of some NO₂ input near the canopy top from light-mediated ambient reactions, or emission from open stomates.

Source: Horii et al. (2004).

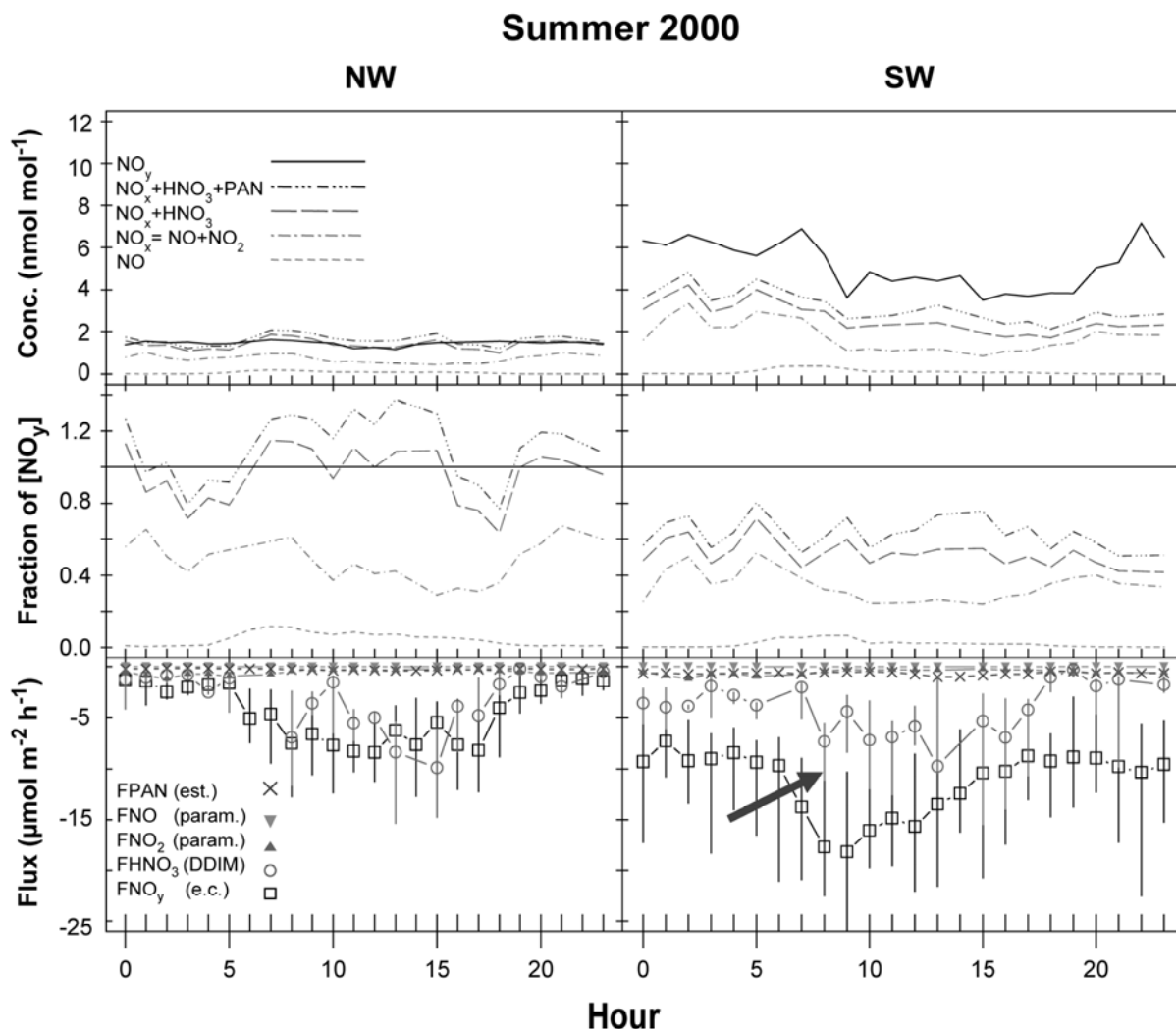


Figure AX2.9-5. Summer (June-August) 2000 median concentrations (upper panels), fractions of NO_Y (middle panels), and fluxes (lower panels) of NO_Y and component species separated by wind direction (Northwest on the left and Southwest on the right). Vertical lines in the flux panels show 25th and 75th quartiles of $F(\text{NO}_Y)$ and $F(\text{HNO}_3)$; negative fluxes represent deposition; $F(\text{NO}_X)$ is derived from eddy covariance $F(\text{NO})$ and $F(\text{NO}_2)$ measurements (corrected for photochemical cycling), $F(\text{HNO}_3)$ is inferred, and $F(\text{NO}_Y)$ was measured by eddy covariance. The sum of NO_X , HNO_3 , and PAN accounts for all of the NO_Y concentration and flux for Northwesterly (unpolluted background) flows, whereas up to 50% of NO_Y and $F(\text{NO}_Y)$ under Southwesterly flows are in the form of reactive nitrogen species whose fluxes are not measured or estimated here.

Source: Horii et al. (2006).

1 **AX2.10 METHODS USED TO CALCULATE CONCENTRATIONS OF**
2 **NITROGEN OXIDES AND THEIR CHEMICAL**
3 **INTERACTIONS IN THE ATMOSPHERE**

4 Atmospheric chemical transport models (CTMs) are the major tools used to calculate the
5 relations among O₃, other oxidants and their precursors, the transport and transformation of air
6 toxics, the production of secondary organic aerosols, the evolution of the particle size
7 distribution, and the production and deposition of pollutants affecting ecosystems. CTMs are
8 driven by emissions inventories for primary species such as the precursors for O₃ and PM and by
9 meteorological fields produced by other numerical prediction models. Meteorological quantities
10 such as winds and temperatures are taken from operational analyses, reanalyses, or circulation
11 models. In most cases, these are off-line analyses, i.e., they are not modified by radiatively
12 active species such as O₃ and particles generated by the model.

13 Emissions of precursor compounds can be divided into anthropogenic and natural source
14 categories, and natural sources can be further divided into biotic (vegetation, microbes, animals)
15 and abiotic (biomass burning, lightning) categories as presented above. However, the distinction
16 between natural sources and anthropogenic sources is often difficult to make, as human activities
17 affect directly or indirectly emissions from what would have been considered natural sources
18 during the preindustrial era. Thus, emissions from plants and animals used in agriculture have
19 been referred to as anthropogenic or natural in different applications. Wildfire emissions may be
20 considered to be natural, except that forest management practices may have led to the buildup of
21 fuels on the forest floor, thereby altering the frequency and severity of forest fires.

22
23 **AX2.10.1 CTMs**

24 Atmospheric CTMs have been developed for application over a wide range of spatial
25 scales ranging from neighborhood to global. Regional-scale CTMs are used to: (1) obtain better
26 understanding of the processes controlling the formation, transport, and destruction of gas- and
27 particle-phase criteria and hazardous air pollutants; and (2) understand the relations between
28 concentrations of secondary pollutant products and concentrations of their precursors such as
29 NO_x and VOCs and the factors leading to acid deposition and possible damage to ecosystems;
30 and (3) understand relations among the concentration patterns of various pollutants that may
31 exert adverse effects.

1 Global-scale CTMs are used to address issues associated with climate change and
2 stratospheric O₃ depletion, and to provide boundary conditions for the regional-scale models.
3 The CTMs include simplified mathematical descriptions of atmospheric transport, the transfer of
4 solar radiation through the atmosphere, chemical reactions, and removal to the surface by
5 turbulent motions and precipitation for pollutants emitted into the model domain. The upper
6 boundaries of the CTMs extend anywhere from the top of the mixed layer to the mesopause at
7 ~80 km in order to obtain more realistic boundary conditions for problems involving
8 stratospheric dynamics.

9 There are two major formulations of CTMs in current use. In the first approach,
10 grid-based, or Eulerian, air quality models, the domain to be modeled is subdivided into a
11 three-dimensional array of grid cells. Spatial derivatives in the species continuity equations are
12 cast in finite-difference or, less often, in finite-element form, and a system of equations for the
13 concentrations of all the chemical species in the model are solved numerically in each grid.
14 Time-dependent continuity or mass conservation equations are solved for each species including
15 terms for transport, chemical production and destruction, and emissions and deposition (if
16 relevant) in each cell. Chemical processes are simulated with ordinary differential equations,
17 and transport processes are simulated with partial differential equations.

18 A second approach, less common than the Eulerian grid, is the hybrid Lagrangian-
19 Eulerian model, in which certain aspects of atmospheric chemistry and transport are treated with
20 a Lagrangian approach and others with the Eulerian methods described above; see e.g., Stein
21 et al., 2000. The Eulerian approach is more general in that it includes processes that mix air
22 parcels and allows integrations to be carried out for long periods during which individual air
23 parcels lose their identity. There are, however, techniques for including the effects of mixing in
24 Lagrangian models such as FLEXPART (e.g., Zanis et al., 2003), ATTILA (Reithmeier and
25 Sausen, 2002), and CLaMS (McKenna et al., 2002).

26 27 **AX2.10.1.1 Regional-Scale CTMs**

28 Major modeling efforts within the U.S. Environmental Protection Agency center on the
29 Community Multiscale Air Quality modeling system (CMAQ) (Byun and Ching, 1999; Byun
30 and Schere, 2006). A number of other modeling platforms using Lagrangian and Eulerian
31 frameworks have been reviewed in the 96 AQCD for O₃ (U.S. Environmental Protection
32 Agency, 1997), and in Russell and Dennis (2000). The capabilities of a number of CTMs

1 designed to study local- and regional-scale air pollution problems are summarized by Russell
2 and Dennis (2000). Evaluations of the performance of CMAQ are given in Arnold et al. (2003),
3 Eder and Yu (2005), Appel et al. (2005), and Fuentes and Raftery (2005). The domain of
4 CMAQ can extend from several hundred km to the hemispherical scale. In addition, both of
5 these classes of models allow the resolution of the calculations over specified areas to vary.
6 CMAQ is most often driven by the MM5 mesoscale meteorological model (Seaman, 2000),
7 though it may be driven by other meteorological models (e.g., RAMS). Simulations of O₃
8 episodes over regional domains have been performed with a horizontal resolution as low as 1
9 km, and smaller calculations over limited domains have been accomplished at even finer scales.
10 However, simulations at such high resolutions require better parameterizations of
11 meteorological processes such as boundary layer fluxes, deep convection and clouds (Seaman,
12 2000), and finer-scale emissions. Finer spatial resolution is necessary to resolve features such
13 as urban heat island circulations; sea, bay, and land breezes; mountain and valley breezes, and
14 the nocturnal low-level jet.

15 The most common approach to setting up the horizontal domain is to nest a finer grid
16 within a larger domain of coarser resolution. However, there are other strategies such as the
17 stretched grid (e.g., Fox-Rabinovitz et al., 2002) and the adaptive grid. In a stretched grid, the
18 grid's resolution continuously varies throughout the domain, thereby eliminating any potential
19 problems with the sudden change from one resolution to another at the boundary. Caution
20 should be exercised in using such a formulation, because certain parameterizations that are valid
21 on a relatively coarse grid scale (such as convection) may not be valid on finer scales. Adaptive
22 grids are not fixed at the start of the simulation, but instead adapt to the needs of the simulation
23 as it evolves (e.g., Hansen et al., 1994). They have the advantage that they can resolve processes
24 at relevant spatial scales. However, they can be very slow if the situation to be modeled is
25 complex. Additionally, if adaptive grids are used for separate meteorological, emissions, and
26 photochemical models, there is no reason a priori why the resolution of each grid should match,
27 and the gains realized from increased resolution in one model will be wasted in the transition to
28 another model. The use of finer horizontal resolution in CTMs will necessitate finer-scale
29 inventories of land use and better knowledge of the exact paths of roads, locations of factories,
30 and, in general, better methods for locating sources and estimating their emissions.

1 The vertical resolution of these CTMs is variable, and usually configured to have higher
2 resolution near the surface and decreasing aloft. Because the height of the boundary layer is of
3 critical importance in simulations of air quality, improved resolution of the boundary layer height
4 would likely improve air quality simulations. Additionally, current CTMs do not adequately
5 resolve fine scale features such as the nocturnal low-level jet in part because little is known about
6 the nighttime boundary layer.

7 CTMs require time-dependent, 4-dimensional wind fields for the period of simulation.
8 The winds may be either generated by a model using initial fields alone or with four-dimensional
9 data assimilation to improve the model's performance, fields (i.e., model equations can be
10 updated periodically or "nudged", to bring results into agreement with observations. Modeling
11 efforts typically focus on simulations of several days' duration, the typical time scale for
12 individual O₃ episodes, but there have been several attempts at modeling longer periods. For
13 example, Kasibhatla and Chameides (2000) simulated a four-month period from May to
14 September of 1995 using MAQSIP. The current trend in modeling applications is towards
15 annual simulations. This trend is driven in part by the need to better understand observations of
16 periods of high wintertime PM (e.g., Blanchard et al., 2002) and the need to simulate O₃ episodes
17 occurring outside of summer.

18 Chemical kinetics mechanisms (a set of chemical reactions) representing the important
19 reactions occurring in the atmosphere are used in CTMs to estimate the rates of chemical
20 formation and destruction of each pollutant simulated as a function of time. Unfortunately,
21 chemical mechanisms that explicitly treat the reactions of each individual reactive species are too
22 computationally demanding to be incorporated into CTMs. For example, a master chemical
23 mechanism includes approximately 10,500 reactions involving 3603 chemical species (Derwent
24 et al., 2001). Instead, "lumped" mechanisms, that group compounds of similar chemistry
25 together, are used. The chemical mechanisms used in existing photochemical O₃ models contain
26 significant uncertainties that may limit the accuracy of their predictions; the accuracy of each of
27 these mechanisms is also limited by missing chemistry. Because of different approaches to the
28 lumping of organic compounds into surrogate groups, chemical mechanisms can produce
29 somewhat different results under similar conditions. The CB-IV chemical mechanism (Gery
30 et al., 1989), the RADM II mechanism (Stockwell et al., 1990), the SAPRC (e.g., Wang
31 et al., 2000a,b; Carter, 1990), and the RACM mechanisms can be used in CMAQ. Jimenez

1 et al. (2003) provide brief descriptions of the features of the main mechanisms in use and they
2 compared concentrations of several key species predicted by seven chemical mechanisms in a
3 box model simulation over 24 h. The average deviation from the average of all mechanism
4 predictions for O₃ and NO over the daylight period was <20%, and was 10% for NO₂ for all
5 mechanisms. However, much larger deviations were found for HNO₃, PAN, HO₂, H₂O₂, ethene
6 (C₂H₄), and isoprene (C₅H₈). An analysis for OH radicals was not presented. The large
7 deviations shown for most species imply differences between the calculated lifetimes of
8 atmospheric species and the assignment of model simulations to either NO_x-limited or radical
9 quantity limited regimes between mechanisms. Gross and Stockwell (2003) found small
10 differences between mechanisms for clean conditions, with differences becoming more
11 significant for polluted conditions, especially for NO₂ and organic peroxy radicals. They caution
12 modelers to consider carefully the mechanisms they are using. Faraji et al. (2005) found
13 differences of 40% in peak 1 h [O₃] in the Houston-Galveston-Brazoria area between simulations
14 using SAPRAC and CB4. They attributed differences in predicted [O₃] to differences in the
15 mechanisms of oxidation of aromatic hydrocarbons.

16 CMAQ and other CTMs (e.g., PM-CAMx) incorporate processes and interactions of
17 aerosol-phase chemistry (Mebust et al., 2003). There have also been several attempts to study
18 the feedbacks of chemistry on atmospheric dynamics using meteorological models, like MM5
19 (e.g., Grell et al., 2000; Liu et al., 2001a; Lu et al., 1997; Park et al., 2001). This coupling is
20 necessary to simulate accurately feedbacks such as may be caused by the heavy aerosol loading
21 found in forest fire plumes (Lu et al., 1997; Park et al., 2001), or in heavily polluted areas.
22 Photolysis rates in CMAQ can now be calculated interactively with model produced O₃, NO₂,
23 and aerosol fields (Binkowski et al., 2007).

24 Spatial and temporal characterizations of anthropogenic and biogenic precursor emissions
25 must be specified as inputs to a CTM. Emissions inventories have been compiled on grids of
26 varying resolution for many hydrocarbons, aldehydes, ketones, CO, NH₃, and NO_x. Emissions
27 inventories for many species require the application of some algorithm for calculating the
28 dependence of emissions on physical variables such as temperature and to convert the
29 inventories into formatted emission files required by a CTM. For example, preprocessing of
30 emissions data for CMAQ is done by the SMOKE (Spare-Matrix Operator Kernel Emissions)
31 system. For many species, information concerning the temporal variability of emissions is

1 lacking, so long-term (e.g., annual or O₃-season) averages are used in short-term, episodic
2 simulations. Annual emissions estimates are often modified by the emissions model to produce
3 emissions more characteristic of the time of day and season. Significant errors in emissions can
4 occur if inappropriate time dependence or a default profile is used. Additional complexity arises
5 in model calculations because different chemical mechanisms are based on different species, and
6 inventories constructed for use with another mechanism must be adjusted to reflect these
7 differences. This problem also complicates comparisons of the outputs of these models because
8 one chemical mechanism may produce some species not present in another mechanism yet
9 neither may agree with the measurements.

10 In addition to wet deposition, dry deposition (the removal of chemical species from the
11 atmosphere by interaction with ground-level surfaces) is an important removal process for
12 pollutants on both urban and regional scales and must be included in CTMs. The general
13 approach used in most models is the resistance in series method, in which dry deposition is
14 parameterized with a V_d , which is represented as $V_d = (r_a + r_b + r_c)^{-1}$ where r_a , r_b , and r_c
15 represent the resistance due to atmospheric turbulence, transport in the fluid sublayer very near
16 the elements of surface such as leaves or soil, and the resistance to uptake of the surface itself.
17 This approach works for a range of substances, although it is inappropriate for species with
18 substantial emissions from the surface or for species whose deposition to the surface depends on
19 its concentration at the surface itself. The approach is also modified somewhat for aerosols: the
20 terms r_b and r_c are replaced with a surface V_d to account for gravitational settling. In their
21 review, Wesely and Hicks (2000) point out several shortcomings of current knowledge of dry
22 deposition. Among those shortcomings are difficulties in representing dry deposition over
23 varying terrain where horizontal advection plays a significant role in determining the magnitude
24 of r_a and difficulties in adequately determining a V_d for extremely stable conditions such as those
25 occurring at night (e.g., Mahrt, 1998). Under the best of conditions, when a model is exercised
26 over a relatively small area where dry deposition measurements have been made, models still
27 commonly show uncertainties at least as large as $\pm 30\%$ (e.g., Massman et al., 1994; Brook et al.,
28 1996; Padro, 1996). Wesely and Hicks (2000) state that an important result of these comparisons
29 is that the current level of sophistication of most dry deposition models is relatively low, and that
30 deposition estimates therefore must rely heavily on empirical data. Still larger uncertainties exist

1 when the surface features in the built environment are not well known or when the surface
2 comprises a patchwork of different surface types, as is common in the eastern United States.

3 The initial conditions, i.e., the concentration fields of all species computed by a model,
4 and the boundary conditions, i.e., the concentrations of species along the horizontal and upper
5 boundaries of the model domain throughout the simulation must be specified at the beginning of
6 the simulation. It would be best to specify initial and boundary conditions according to
7 observations. However, data for vertical profiles of most species of interest are sparse. The
8 results of model simulations over larger, preferably global, domains can also be used. As may be
9 expected, the influence of boundary conditions depends on the lifetime of the species under
10 consideration and the time scales for transport from the boundaries to the interior of the model
11 domain (Liu et al., 2001b).

12 Each of the model components described above has associated uncertainty, and the
13 relative importance of these uncertainties varies with the modeling application. The largest
14 errors in photochemical modeling are still thought to arise from the meteorological and
15 emissions inputs to the model (Russell and Dennis, 2000). Within the model itself, horizontal
16 advection algorithms are still thought to be significant source of uncertainty (e.g., Chock and
17 Winkler, 1994), though more recently, those errors are thought to have been reduced (e.g.,
18 Odman and Ingram, 1996). There are also indications that problems with mass conservation
19 continue to be present in photochemical and meteorological models (e.g., Odman and Russell,
20 1999); these can result in significant simulation errors. The effects of errors in initial conditions
21 can be minimized by including several days “spin-up” time in a simulation to allow the model to
22 be driven by emitted species before the simulation of the period of interest begins.

23 While the effects of poorly specified boundary conditions propagate through the model’s
24 domain, the effects of these errors remain undetermined. Because many meteorological
25 processes occur on spatial scales, which are smaller than the model grid spacing (either
26 horizontally or vertically) and thus are not calculated explicitly, parameterizations of these
27 processes must be used and these introduce additional uncertainty.

28 Uncertainty also arises in modeling the chemistry of O₃ formation because it is highly
29 nonlinear with respect to [NO_x]. Thus, the volume of the grid cell into which emissions are
30 injected is important because the nature of O₃ chemistry (i.e., O₃ production or titration) depends
31 in a complicated way on the concentrations of the precursors and the OH radical as noted earlier.

1 The use of ever-finer grid spacing allows regions of O₃ titration to be more clearly separated
2 from regions of O₃ production. The use of grid spacing fine enough to resolve the chemistry in
3 individual power-plant plumes is too demanding of computer resources for this to be attempted
4 in most simulations. Instead, parameterizations of the effects of sub-grid-scale processes such as
5 these must be developed; otherwise, serious errors can result if emissions are allowed to mix
6 through an excessively large grid volume before the chemistry step in a model calculation is
7 performed. In light of the significant differences between atmospheric chemistry taking place
8 inside and outside of a power plant plume (e.g., Ryerson et al., 1998 and Sillman, 2000),
9 inclusion of a separate, meteorological module for treating large, tight plumes is necessary.
10 Because the photochemistry of O₃ and many other atmospheric species is nonlinear, emissions
11 correctly modeled in a tight plume may be incorrectly modeled in a more dilute plume.
12 Fortunately, it appears that the chemical mechanism used to follow a plume's development need
13 not be as detailed as that used to simulate the rest of the domain, as the inorganic reactions are
14 the most important in the plume see (e.g., Kumar and Russell, 1996). The need to include
15 explicitly plume-in-grid chemistry only down to the level of the smallest grid disappears if one
16 uses the adaptive grid approach mentioned previously, though such grids are more
17 computationally intensive. The differences in simulations are significant because they can lead
18 to significant differences in the calculated sensitivity of O₃ to its precursors (e.g., Sillman et al.,
19 1995).

20 Because the chemical production and loss terms in the continuity equations for individual
21 species are coupled, the chemical calculations must be performed iteratively until calculated
22 concentrations converge to within some preset criterion. The number of iterations and the
23 convergence criteria chosen also can introduce error.

24 25 **AX2.10.1.2 Global-Scale CTMs**

26 The importance of global transport of O₃ and O₃ precursors and their contribution to
27 regional O₃ levels in the United States is slowly becoming apparent. There are presently on the
28 order of 20 three-dimensional global models that have been developed by various groups to
29 address problems in tropospheric chemistry. These models resolve synoptic meteorology, O₃
30 NO_x-CO-hydrocarbon photochemistry, have parameterizations for wet and dry deposition, and
31 parameterize sub-grid scale vertical mixing processes such as convection. Global models have
32 proven useful for testing and advancing scientific understanding beyond what is possible with

1 observations alone. For example, they can calculate quantities of interest that cannot be
2 measured directly, such as the export of pollution from one continent to the global atmosphere or
3 the response of the atmosphere to future perturbations to anthropogenic emissions.

4 Global simulations are typically conducted at a horizontal resolution of about 200 km².
5 Simulations of the effects of transport from long-range transport link multiple horizontal
6 resolutions from the global to the local scale. Finer resolution will only improve scientific
7 understanding to the extent that the governing processes are more accurately described at that
8 scale. Consequently, there is a critical need for observations at the appropriate scales to evaluate
9 the scientific understanding represented by the models.

10 During the recent IPCC-AR4 tropospheric chemistry study coordinated by the European
11 Union project Atmospheric Composition Change: the European Network of excellence
12 (ACCENT), 26 atmospheric CTMs were used to estimate the impacts of three emissions
13 scenarios on global atmospheric composition, climate, and air quality in 2030 (Dentener et al.,
14 2006a). All models were required to use anthropogenic emissions developed at IIASA (Dentener
15 et al., 2005) and GFED version 1 biomass burning emissions (Van der Werf et al., 2003) as
16 described in Stevenson et al. (2006). The base simulations from these models were evaluated
17 against a suite of present-day observations. Most relevant to this assessment report are the
18 evaluations with ozone and NO₂, and for nitrogen and sulfur deposition (Stevenson et al., 2006;
19 Van Noije et al., 2006; Dentener et al., 2006a), which are summarized briefly below.

20 An analysis of the standard deviation of zonal mean and tropospheric column O₃ reveals
21 large inter-model variability in the tropopause region and throughout the polar troposphere,
22 likely reflecting differences in model tropopause levels and the associated stratospheric injection
23 of O₃ to the troposphere (Stevenson et al., 2006). O₃ distributions in the tropics also exhibit large
24 standard deviations (~30%), particularly as compared to the mid-latitudes (~20%), indicating
25 larger uncertainties in the processes that influence ozone in the tropics: deep tropical convection,
26 lightning NO_x, isoprene emissions and chemistry, and biomass burning emissions (Stevenson
27 et al., 2006).

28 Stevenson et al. (2006) found that the model ensemble mean (MEM) typically captures
29 the observed seasonal cycles to within one standard deviation. The largest discrepancies
30 between the MEM and observations include: (1) an underestimate of the amplitude of the
31 seasonal cycle at 30°-90°N with a 10 ppb overestimate of winter ozone, possibly due to the lack

1 of a seasonal cycle in anthropogenic emissions or to shortcomings in the stratospheric influx of
2 O₃; and (2) an overestimate of O₃ throughout the northern tropics. However, the MEM was
3 found to capture the observed seasonal cycles in the Southern Hemisphere, suggesting that the
4 models adequately represent biomass burning and natural emissions.

5 The mean present-day global O₃ budget across the current generation of CTMs differs
6 substantially from that reported in the IPCC TAR, with a 50% increase in the mean chemical
7 production (to 5100 Tg O₃ yr⁻¹), a 30% increase in the chemical and deposition loss terms (to
8 4650 and 1000 Tg O₃ yr⁻¹, respectively) and a 30% decrease in the mean stratospheric input flux
9 (to 550 Tg O₃ yr⁻¹) (Stevenson et al., 2006). The larger chemical terms as compared to the IPCC
10 TAR are attributed mainly to higher NO_x (as well as an equatorward shift in distribution) and
11 isoprene emissions, although more detailed NMHC schemes and/or improved representations of
12 photolysis, convection, and stratospheric-tropospheric exchange may also contribute (Stevenson
13 et al., 2006).

14 A subset of 17 of the 26 models used in the Stevenson et al. (2006) study was used to
15 compare with three retrievals of NO₂ columns from the GOME instrument (Van Noije et al.,
16 2006) for the year 2000. The higher resolution models reproduce the observed patterns better,
17 and the correlation among simulated and retrieved columns improved for all models when
18 simulated values are smoothed to a 5° × 5° grid, implying that the models do not accurately
19 reproduce the small-scale features of NO₂ (Van Noije et al., 2006). Van Noije et al. (2006)
20 suggested that variability in simulated NO₂ columns may reflect a model differences in OH
21 distributions and the resulting NO_x lifetimes, as well as differences in vertical mixing which
22 strongly affect partitioning between NO and NO₂. Overall, the models tend to underestimate
23 concentrations in the retrievals in industrial regions (including the eastern United States) and
24 overestimate them in biomass burning regions (Van Noije et al., 2006).

25 Over the eastern United States, and industrial regions more generally, the spread in
26 absolute column abundances is generally larger among the retrievals than among the models,
27 with the discrepancy among the retrievals particularly pronounced in winter (Van Noije et al.,
28 2006), suggesting that the models are biased low, or that the European retrievals may be biased
29 high as the Dalhousie/SAO retrieval is closer to the model estimates. The lack of seasonal
30 variability in fossil fuel combustion emissions may contribute to a wintertime model
31 underestimate (Van Noije et al., 2006) that is manifested most strongly over Asia. In biomass

1 burning regions, the models generally reproduce the timing of the seasonal cycle of the
2 retrievals, but tend to overestimate the seasonal cycle amplitude, partly due to lower values in the
3 wet season, which may reflect an underestimate in wet season soil NO emissions (Van Noije
4 et al., 2006; Jaegle et al., 2004, 2005).

5

6 **AX2.10.2 Computed Deposition with CTMs**

7 Both wet and dry deposition are highly parameterized in global CTMs. While all current
8 models implement resistance schemes for dry deposition, the generated V_d generated from
9 different models can vary highly across terrains (Stevenson et al., 2006). The accuracy of wet
10 deposition in global CTMs is tied to spatial and temporal distribution of model precipitation and
11 the treatment of chemical scavenging. Dentener et al. (2006b) compared wet deposition across
12 23 models with available measurements around the globe. Figures AX2.10-1 and AX2.10-2
13 below extract the results of a comparison of the 23-model mean versus observations from
14 Dentener et al. (2006b) over the eastern United States for nitrate and sulfate deposition,
15 respectively. The mean model results are strongly correlated with the observations ($r > 0.8$), and
16 usually capture the magnitude of wet deposition to within a factor of 2 over the eastern United
17 States (Dentener et al., 2006b). Dentener et al. (2006b) conclude that 60-70% of the
18 participating models capture the measurements to within 50% in regions with quality controlled
19 observations. This study then identified world regions receiving $>1000 \text{ mg N m}^{-2} \text{ yr}^{-1}$ (the
20 “critical load”) and found that 20% of the natural vegetation (non-agricultural) in the United
21 States is exposed to nitrogen deposition in excess of the critical load threshold (Dentener et al.,
22 2006b).

23 Convective transport in global chemistry and transport models is treated as a sub-grid-
24 scale process that is parameterized typically using cloud mass flux information from a general
25 circulation model or global data assimilation system. While GCMs can provide data only for a
26 “typical” year, data assimilation systems can provide “real” day-by-day meteorological
27 conditions, such that CTM output can be compared directly with observations of trace gases.
28 The NASA Goddard Earth Observing System Data Assimilation System (GEOS-1 DAS and
29 successor systems) (Schubert et al., 1993; Bloom et al., 1996, 2005) provides archived global
30 data sets for the period 1980 to present, at $2^\circ \times 2.5^\circ$ or better resolution with 20 layers or more in

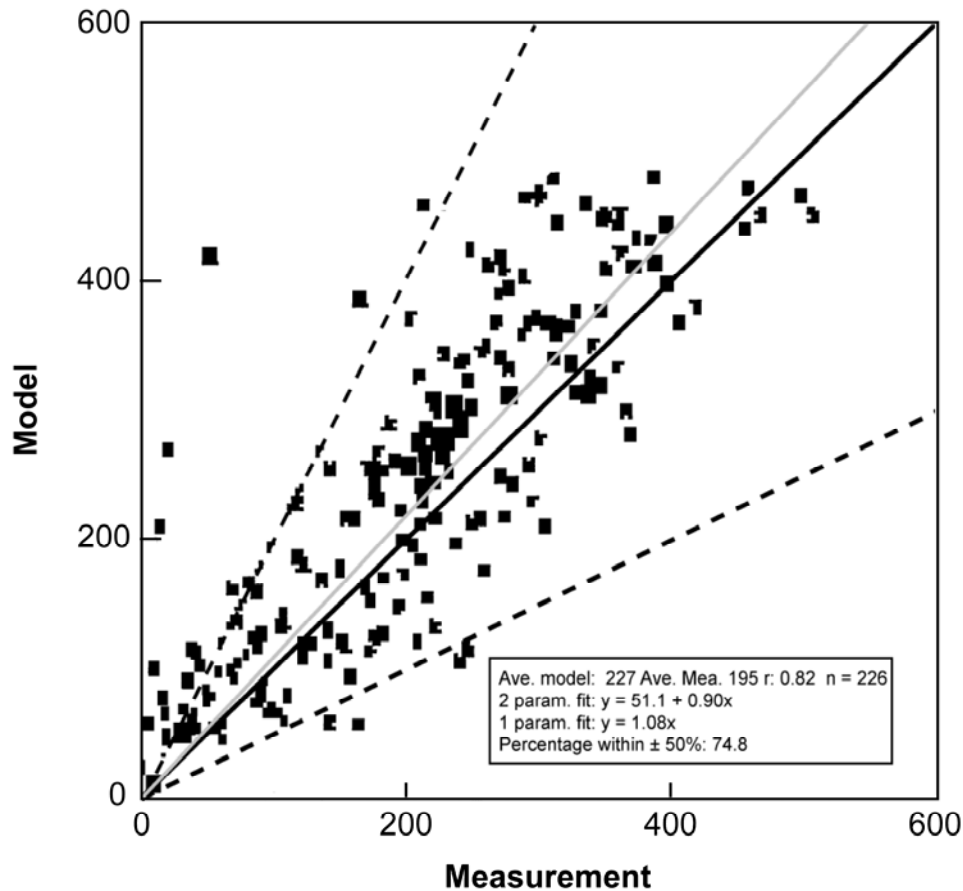


Figure AX2.10-1. Scatter plot of total nitrate (HNO_3 plus aerosol nitrate) wet deposition ($\text{mg(N)m}^{-2}\text{yr}^{-1}$) of the mean model versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through 0.

Source: Dentener et al. (2006b).

- 1 the vertical. Deep convection is parameterized with the Relaxed Arakawa Schubert scheme
- 2 (Moorthi and Suarez, 1992) in GEOS-1 and GEOS-3 and with the Zhang and McFarlane (1995)
- 3 scheme in GEOS-4. Pickering et al. (1995) showed that the cloud mass fluxes from GEOS-1
- 4 DAS are reasonable for the 10-11 June 1985 PRE-STORM squall line based on comparisons
- 5 with the GCE model (cloud-resolving model) simulations of the same storm. In addition, the
- 6 GEOS-1 DAS cloud mass fluxes compared favorably with the regional estimates of convective

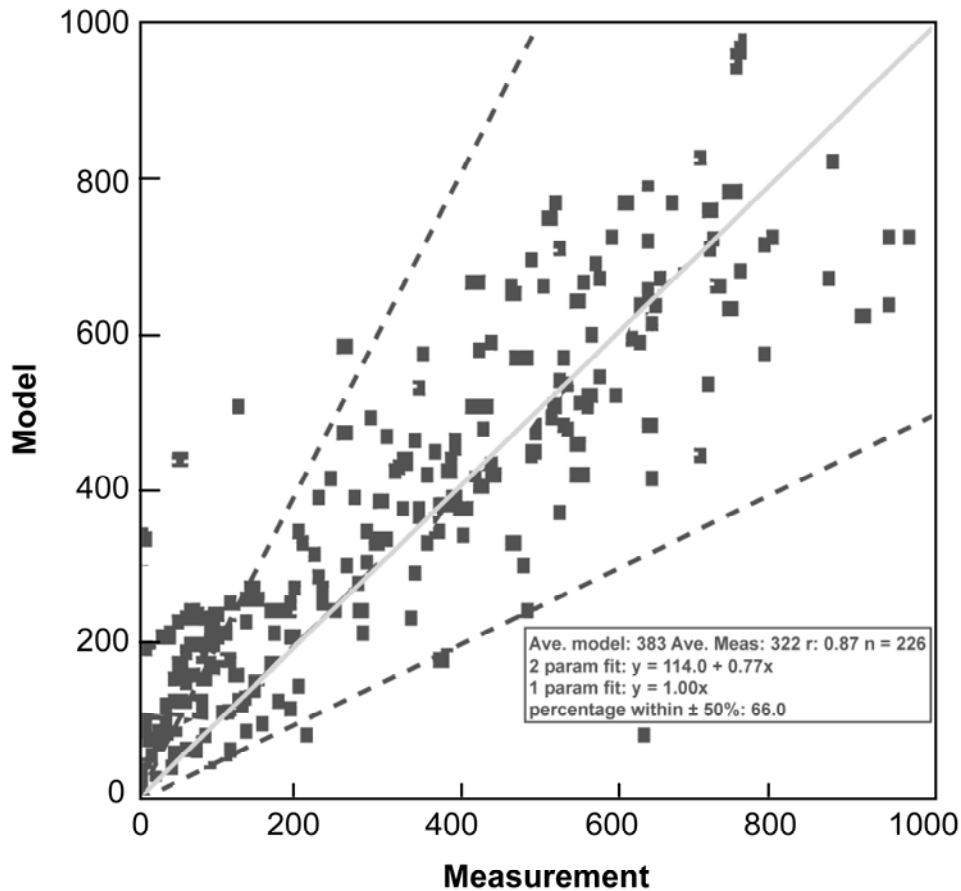


Figure AX2.10-2. Same as Figure AX2.10-1 but for sulfate wet deposition ($\text{mg(S)m}^{-2}\text{yr}^{-1}$).

Source: Dentener et al. (2006b).

1 transport for the central United States presented by Thompson et al. (1994). However, Allen
 2 et al. (1997) have shown that the GEOS-1 DAS overestimates the amount and frequency of
 3 convection in the tropics and underestimates the convective activity over midlatitude marine
 4 storm tracks.

5 Global models with parameterized convection and lightning have been run to examine the
 6 roles of these processes over North America. Lightning contributed 23% of upper tropospheric
 7 NO_Y over the SONEX region according to the UMD-CTM modeling analysis of Allen et al.
 8 (2000). During the summer of 2004 the NASA Intercontinental Chemical Transport
 9 Experiment - North America (INTEX-NA) was conducted primarily over the eastern two-thirds
 10 of the United States, as a part of the International Consortium for Atmospheric Research on

1 Transport and Transformation (ICARTT). Deep convection was prevalent over this region
2 during the experimental period. Cooper et al. (2006) used a particle dispersion model simulation
3 for NO_x to show that 69-84% of the upper tropospheric O_3 enhancement over the region in
4 Summer 2004 was due to lightning NO_x . The remainder of the enhancement was due to
5 convective transport of O_3 from the boundary layer or other sources of NO_x . Hudman et al.
6 (2007) used a GEOS-Chem model simulation to show that lightning was the dominant source of
7 upper tropospheric NO_x over this region during this period. Approximately 15% of North
8 American boundary layer NO_x emissions were shown to have been vented to the free
9 troposphere over this region based on both the observations and the model.

10 Such methods were used by Pickering et al. (1992b) to examine transport of urban
11 plumes by deep convection. Transport of an Oklahoma City plume by the 10-11 June 1985
12 PRE-STORM squall line was simulated with the 2-D GCE model. This major squall line passed
13 over the Oklahoma City metropolitan area, as well as more rural areas to the north. Chemical
14 observations ahead of the squall line were conducted by the PRE-STORM aircraft. In this event,
15 forward trajectories from the boundary layer at the leading edge of the storm showed that almost
16 75% of the low-level inflow was transported to altitudes exceeding 8 km. Over 35% of the air
17 parcels reached altitudes over 12 km. Tracer transport calculations were performed for CO,
18 NO_x , O_3 , and HC. Rural boundary-layer NO_x was only 0.9 ppb, whereas the urban plume
19 contained ~3 ppb. In the rural case, mixing ratios of 0.6 ppb were transported up to 11 km.
20 Cleaner air descended at the rear of the storm lowering NO_x at the surface from 0.9 to 0.5 ppb.
21 In the urban plume, mixing ratios in the updraft core reached 1 ppb between 14 and 15 km. At
22 the surface, the main downdraft lowered $[\text{NO}_x]$ from 3 to 0.7 ppb.

23 Regional chemical transport models have been used for applications such as simulations
24 of photochemical O_3 production, acid deposition, and fine PM. Walcek et al. (1990) included a
25 parameterization of cloud-scale aqueous chemistry, scavenging, and vertical mixing in the
26 chemistry model of Chang et al. (1987). The vertical distribution of cloud microphysical
27 properties and the amount of sub-cloud-layer air lifted to each cloud layer are determined using a
28 simple entrainment hypothesis (Walcek and Taylor, 1986). Vertically integrated O_3 formation
29 rates over the northeast United States were enhanced by ~50% when the in-cloud vertical
30 motions were included in the model.

1 Wang et al. (1996) simulated the 10-11 June 1985 PRE-STORM squall line with the
2 NCAR/Penn State Mesoscale Model (MM5) (Grell et al., 1994; Dudhia, 1993). Convection was
3 parameterized as a sub-grid-scale process in MM5 using the Kain and Fritsch (1993) scheme.
4 Mass fluxes and detrainment profiles from the convective parameterization were used along with
5 the 3-D wind fields in CO tracer transport calculations for this convective event.

6 7 **AX2.10.3 CTM Evaluation**

8 The comparison of model predictions with ambient measurements represents a crucial
9 task for establishing the accuracy of photochemical models and evaluating their ability to serve
10 as the basis for making effective control strategy decisions. The evaluation of a model's
11 performance, or its adequacy to perform the tasks for which it was designed can only be
12 conducted within the context of measurement errors and artifacts. Not only are there analytical
13 problems, but there are also problems in assessing the representativeness of monitors at ground
14 level for comparison with model values which represent typically an average over the volume of
15 a grid box.

16 Evaluations of CMAQ are given in Arnold et al. (2003) and Fuentes and Raftery (2005).
17 Discrepancies between model predictions and observations can be used to point out gaps in
18 current understanding of atmospheric chemistry and to spur improvements in parameterizations
19 of atmospheric chemical and physical processes. Model evaluation does not merely involve a
20 straightforward comparison between model predictions and the concentration field of the
21 pollutant of interest. Such comparisons may not be meaningful because it is difficult to
22 determine if agreement between model predictions and observations truly represents an accurate
23 treatment of physical and chemical processes in the CTM or the effects of compensating errors in
24 complex model routines. Ideally, each of the model components (emissions inventories,
25 chemical mechanism, meteorological driver) should be evaluated individually. However, this is
26 rarely done in practice.

27 Global-scale CTMs have generally been evaluated by comparison with measurements for
28 a wide array of species, rather than just for O₃ (e.g., Wang et al., 1998; Emmons et al., 2000; Bey
29 et al., 2001; Hess, 2001; Fiore et al., 2002). These have included evaluation of major primary
30 species (NO_x, CO, and selected VOCs) and an array of secondary species (HNO₃, PAN, H₂O₂)
31 that are often formed concurrently with O₃. Models for urban and regional O₃ have also been

1 evaluated against a broader ensemble of measurements in a few cases, often associated with
2 measurement intensives (e.g., Jacobson et al., 1996; Lu et al., 1997; Sillman et al., 1998). The
3 results of a comparison between observed and computed concentrations from Jacobson et al.
4 (1996) for the Los Angeles Basin are shown in Figures AX2.10-3a,b.

5 The highest concentrations of primary species usually occur in close proximity to
6 emission sources (typically in urban centers) and at times when dispersion rates are low. The
7 diurnal cycle includes high concentrations at night, with maxima during the morning rush hour,
8 and low concentrations during the afternoon (Figure AX2.10-3a). The afternoon minima are
9 driven by the much greater rate of vertical mixing at that time. Primary species also show a
10 seasonal maximum during winter, and are often high during fog episodes in winter when vertical
11 mixing, is suppressed. By contrast, secondary species such as O₃ are typically highest during the
12 afternoon (the time of greatest photochemical activity), on sunny days and during summer.
13 During these conditions, concentrations of primary species may be relatively low. Strong
14 correlations between primary and secondary species are generally observed only in downwind
15 rural areas where all anthropogenic species are simultaneously elevated. The difference in the
16 diurnal cycles of primary species (CO, NO_x, and ethane) and secondary species (O₃, PAN, and
17 HCHO) is evident in Figure AX2.10-3b.

18 Models for urban and regional chemistry have been evaluated less extensively than
19 global-scale models in part because the urban/regional context presents a number of difficult
20 challenges. Global-scale models typically represent continental-scale events and can be
21 evaluated effectively against a sparse network of measurements. By contrast, urban/regional
22 models are critically dependent on the accuracy of local emission inventories and event-specific
23 meteorology, and must be evaluated separately for each urban area that is represented. The
24 evaluation of urban- and regional-scale models is also limited by the availability of data.
25 Measured [NO_x] and speciated [VOC] are widely available through the EPA PAMs network, but
26 questions have been raised about the accuracy of those measurements and the data have not yet
27 been analyzed thoroughly. Evaluation of urban/regional models versus measurements has
28 generally relied on results from a limited number of field studies in the United States. Short-
29 term, research-grade measurements for species relevant to O₃ formation, including VOCs, NO_x,

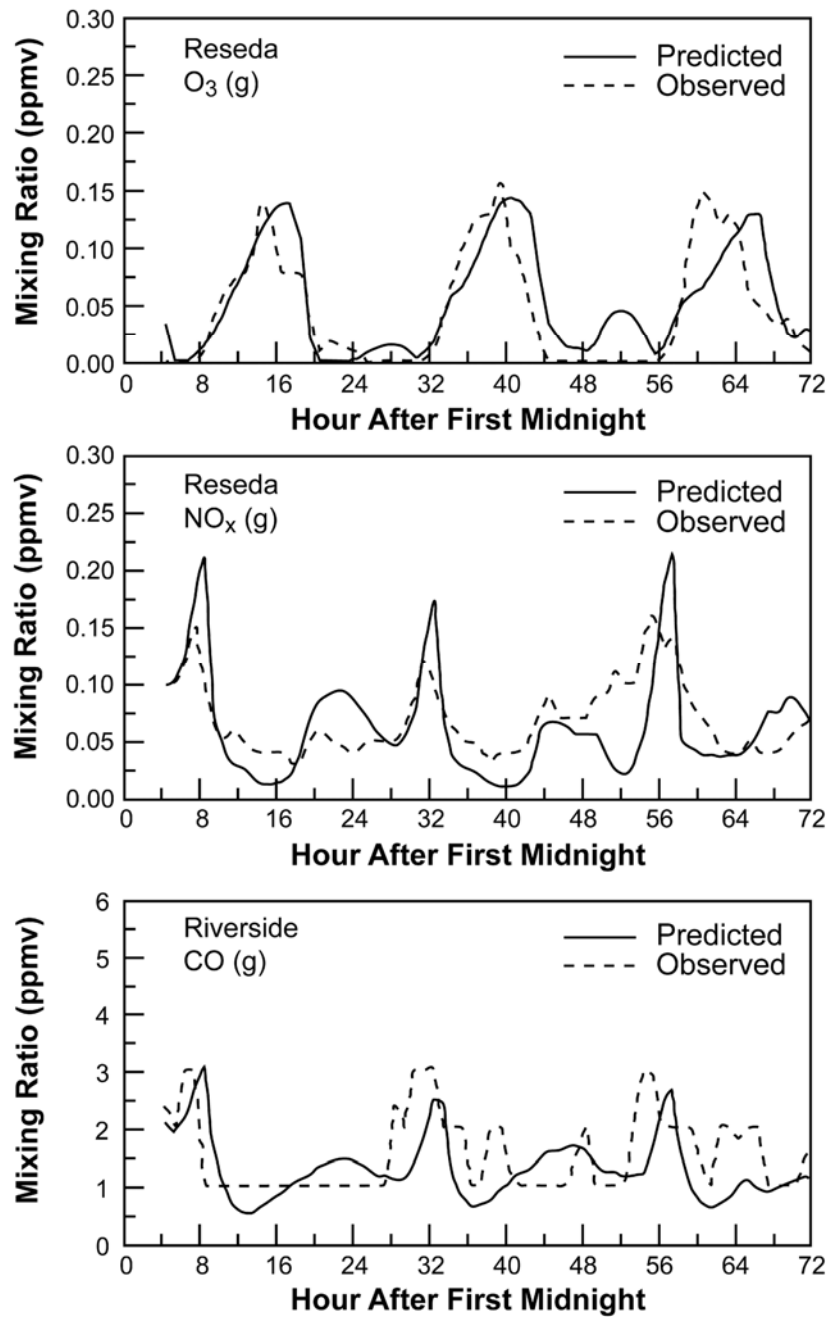


Figure AX2.10-3a. Time series for measured gas-phase species in comparison with results from a photochemical model. The dashed lines represent measurements, and solid lines represent model predictions (in parts per million, ppm) for August 26–28, 1988 at sites in southern California. The horizontal axis represents hours past midnight, August 25. Results represent O₃ and NO_x at Reseda, and CO at Riverside.

Source: Jacobson et al. (1996).

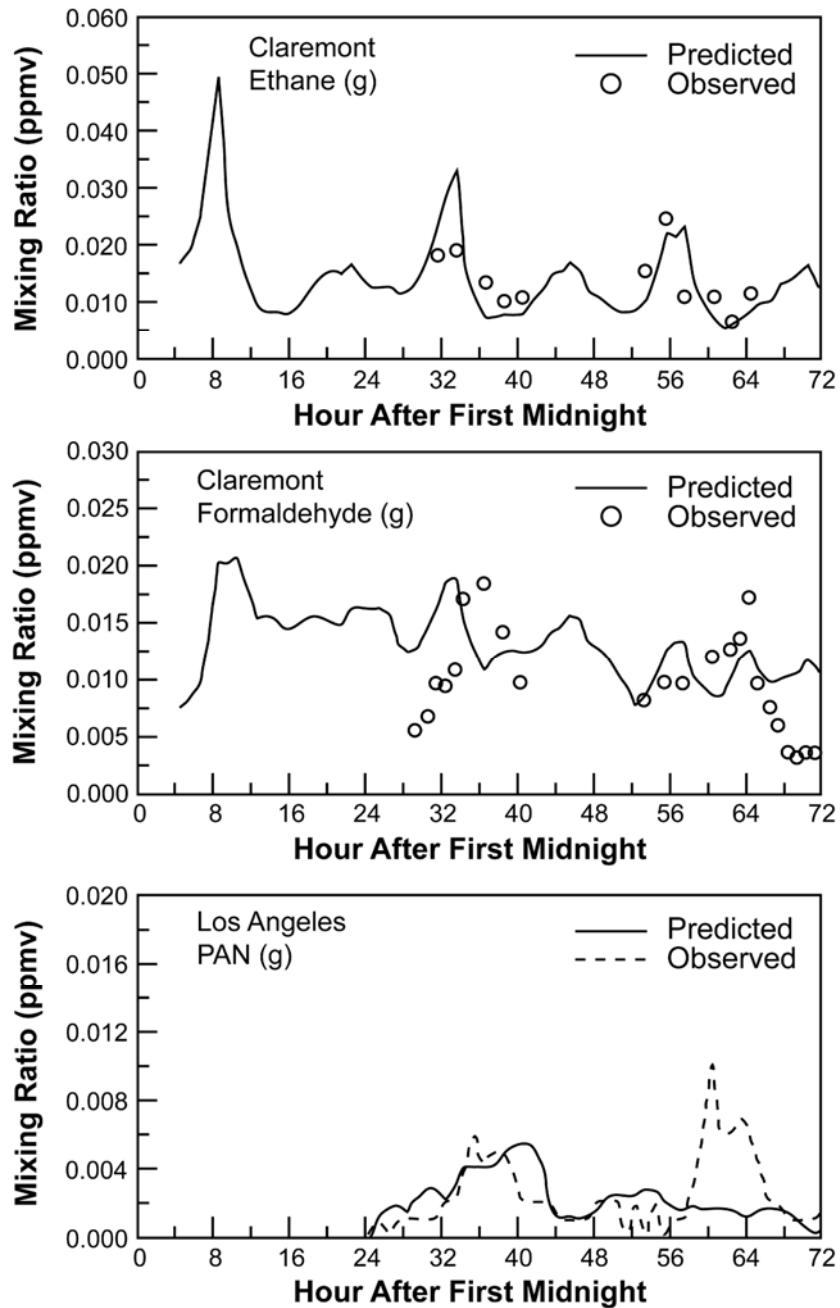


Figure AX2.10-3b. Time series for measured gas-phase species in comparison with results from a photochemical model. The circles represent measurements, and solid lines represent model predictions (in parts per million, ppm) for August 26–28, 1988 at sites in southern California. The horizontal axis represents hours past midnight, August 25. Results represent ethane and formaldehyde at Claremont, and PAN at Los Angeles.

Source: Jacobson et al. (1996).

1 PAN, HNO₃, and H₂O₂ are also available at selected rural and remote sites; see e.g., Daum et al.,
2 1990, 1996; Martin et al., 1997; Young et al., 1997; Thompson et al., 2000; Hoell et al., 1997,
3 1999; Fehsenfeld et al., 1996; Emmons et al., 2000; Hess, 2001; Carroll et al., 2001. The
4 equivalent measurements are available for some polluted rural sites in the eastern United States,
5 but only at a few urban locations; see, e.g., Meagher et al., 1998; Hübler et al., 1998; Kleinman
6 et al., 2000, 2001; Fast et al., 2002. Extensive measurements have also been made in Vancouver
7 (Steyn et al., 1997) and in several European cities; see, e.g., Staffelbach et al., 1997; Prévôt et al.,
8 1997, Dommen et al., 1999; Geyer et al., 2001; Thielman et al., 2001; Martilli et al., 2002;
9 Vautard et al., 2002.

10
11

12 **AX2.11 COMPUTING ATMOSPHERIC DEPOSITION TO SPECIFIC** 13 **LOCATIONS**

14 Inputs of “new” N, i.e., non-recycled, exogenous N mostly anthropogenic in origin, are
15 often key factors controlling primary productivity in N-sensitive estuarine and coastal waters
16 (Paerl et al., 2000). Increasing trends in urbanization, agricultural intensity, and industrial
17 expansion have led to increases in N deposited from the atmosphere on the order of a factor of
18 10 in the previous 100 years (Swackhamer et al., 2004). Direct fluxes of atmospheric N to ocean
19 and gulf waters along the northeast and southeast United States are now roughly equal to or
20 exceed the load of new N from riverine inputs at 11, 5.6, and 5.6 kg N ha⁻¹ for the northeast
21 Atlantic coast of the United States, the southeast Atlantic coast of the United States, and the
22 U.S. eastern Gulf of Mexico, respectively (Paerl et al., 2002).

23 This N deposition takes different forms physically and chemically. Physically,
24 deposition can be direct, with the loads resulting from air pollutants depositing directly to the
25 surface of a body of water, usually a large body of water like an estuary or lake. In addition,
26 there is an indirect deposition component derived from deposition of N or S air pollutants to the
27 rest of the watershed, both land and water, of which some fraction is transported through runoff,
28 rivers, streams, and groundwater to the waterbody of concern.

29 Direct and indirect deposition to watersheds depend on air pollutant concentrations in the
30 airshed above the watershed. The shape and extent of the airshed is quite different from that of
31 the watershed. In a watershed, everything that falls in its area, by definition, flows into a single
32 body of water. An airshed, by contrast, is a theoretical concept that defines the source area

1 containing the emissions contributing a given level, often 75%, to the deposition in a particular
2 watershed or to a given waterbody. Hence, airsheds are modeled domains containing the sources
3 estimated to contribute a given level of deposition from each pollutant of concern. The principal
4 NO_x airsheds and corresponding watersheds for several regions in the eastern United States are
5 shown in Figure AX2.11-1.

6 N inputs have been studied in several east and Gulf Coast estuaries owing to concerns
7 about eutrophication there. N from atmospheric deposition in these locations is estimated to be
8 10 to 40% of the total input of N to many of these estuaries, and could be higher for some.
9 Estimates of total N loadings to estuaries or to other large-scale elements in the landscape are
10 then computed using measurements of wet and dry N deposition where these are available and
11 interpolated with or without a set of air quality model predictions such as the Extended Regional
12 Acid Deposition Model (Ext-RADM) (Mathur and Dennis, 2000; Dennis, 1997; Dennis
13 et al., 1990).

14 Table AX2.11-1 lists several waterbodies for which atmospheric N inputs have been
15 computed and ratioed to total N loads. The contribution from the atmosphere ranges from a low
16 of 2-8% for the Guadalupe Estuary in south Texas to highs of ~38% in the New York Bight and
17 the Albemarle-Pamlico Sound in North Carolina.

18 Chemically, N deposited from the atmosphere directly or indirectly can be present as an
19 oxide – NO_x, NO, NO₂, NO₃, etc, (see the descriptions in Chapter 2) – or in reduced form as
20 NH₃ and NH₄ or as dissolved or particulate organic N; see the listing in Table AX2.11-2 for a
21 division of these and an approximate ranking of source strengths.

22 NO and NO₂, chiefly from fossil fuel combustion, dominates the total N pollution in the
23 United States at ~50 to 75% of the total; see the descriptions of this chemistry in Chapter 2 and
24 of sources just above here.

25 Confined animal feeding operations and other intensified agricultural production methods
26 have resulted in greatly increased volumes of animal wastes, of which 30 to 70% may be emitted
27 as NH₃ (Whitall and Paerl, 2001). The increase in reduced N deposition in the United States
28 measured as increased NH₄⁺ deposition correlates well with the local and regional increases in
29 this agricultural intensity (Whitall and Paerl, 2001). Moreover, the increases in NH₄⁺ deposition
30 in the United States track the effects in Europe where animal operations have dominated
31 agricultural production for much of the previous 100 years and where NH₄⁺ is the dominant form

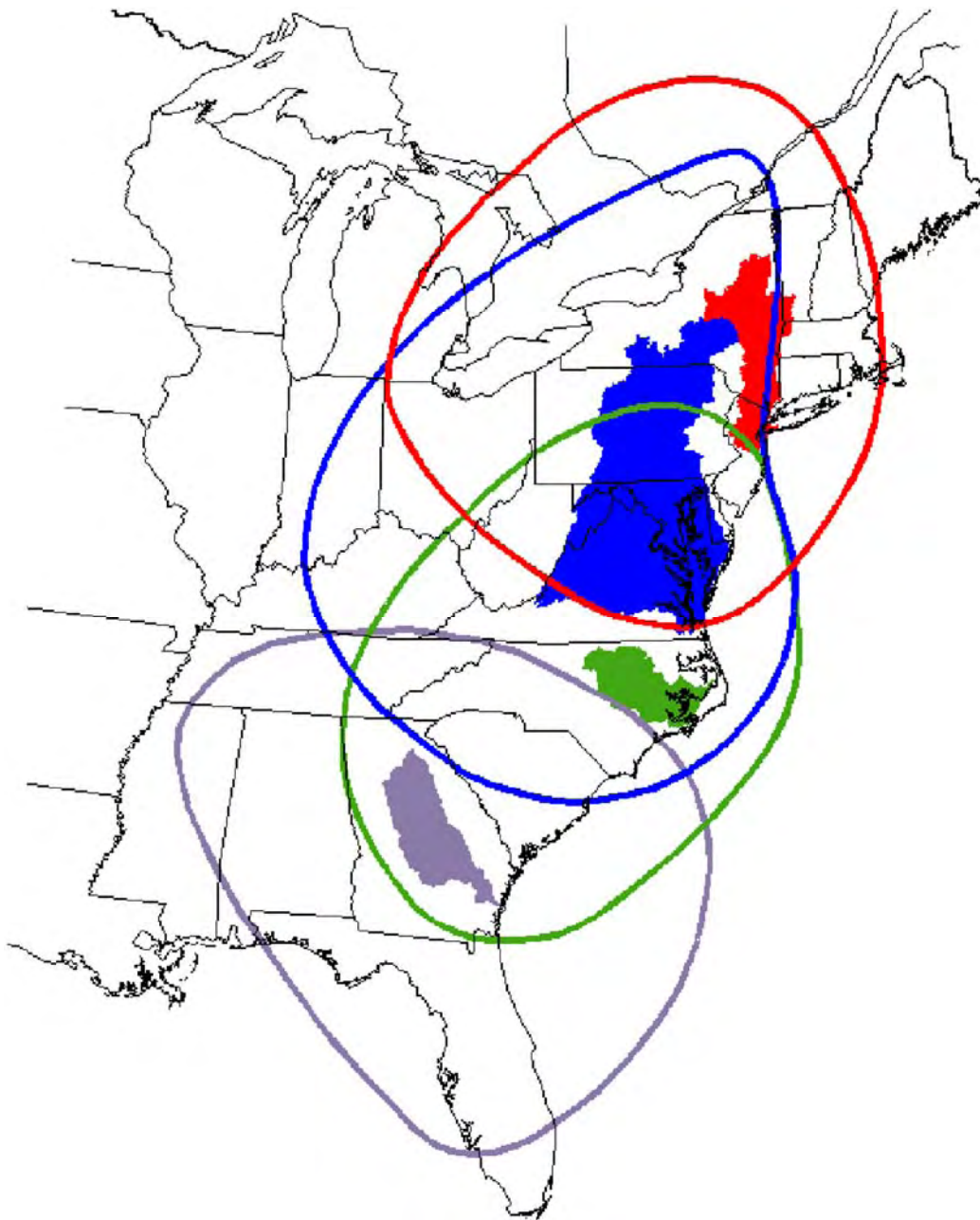


Figure AX2.11-1. Principal airsheds and watersheds for oxides of nitrogen for these estuaries: Hudson/Raritan Bay; Chesapeake Bay; Pamlico Sound; and Altamaha Sound (listed from North to South). Airshed extents developed by R. Dennis, NOAA-ARL.

1 of N deposited from the atmosphere (Holland et al., 1999). Tables AX2.11-3 and AX2.11-4 list
 2 several important watersheds and their respective oxidized (Table AX2.11-3) and reduced (Table

1 AX2.11-4) airsheds. Airsheds for oxidized N tend to be larger than those for reduced N owing to
2 differences in the transport and deposition of NO_x and NH_x described briefly above and in more
3 detail in Chapter 2 and in Annex 1.

4 Considerable uncertainty attaches to estimates of the third form of atmospherically
5 derived N, organic N, in part because convenient methods for measurement and analysis are not
6 widely available; see Table AX2.11-2. Intensive studies at individual sites have shown,
7 however, that for the North Carolina coast, for example, 30% of rain water N and deposition
8 consisted of organic N, 20-30% of which was then available to primary producers on time scales
9 of hours to days (Peierls and Paerl, 1997).

10 11 12 **AX2.12 POLICY RELEVANT BACKGROUND CONCENTRATIONS** 13 **OF NITROGEN AND SULFUR OXIDES**

14 Background concentrations of NO_x and SO_x used for purposes of informing decisions
15 about NAAQS are referred to as PRB concentrations. PRB concentrations are those
16 concentrations that would occur in the United States in the absence of anthropogenic emissions
17 in continental North America (defined here as the United States, Canada, and Mexico). PRB
18 concentrations include contributions from natural sources everywhere in the world and from
19 anthropogenic sources outside these three countries. Biogenic emissions from agricultural
20 activities are not considered in the formation of PRB concentrations.

21 Background levels so defined facilitate separation of pollution levels that can be
22 controlled by U.S. regulations (or through international agreements with neighboring countries)
23 from levels that are generally uncontrollable by the United States. The U.S. Environmental
24 Protection Agency's human health and environmental risk assessments generally estimate risks
25 for levels in excess of these PRB concentrations.

26 Contributions to PRB concentrations include natural emissions of NO₂, SO₂, and
27 photochemical reactions involving natural emissions of reduced N and S compounds, as well as
28 their long-range transport from outside North America. Natural sources of NO₂ and its
29 precursors include biogenic emissions, wildfires, lightning, and the stratosphere. Natural sources
30 of reduced N compounds, mainly NH₃, include biogenic emissions and wildfires. Natural
31 sources of reduced S species include anaerobic microbial activity in wetlands and volcanic
32 activity. Volcanos and biomass burning are the major natural source of SO₂. Biogenic

1 emissions from agricultural activities are not considered in the formation of PRB concentrations.
2 Discussions of the sources and estimates of emissions are given in Section AX2.6.2.

3 The MOZART-2 global model of tropospheric chemistry (Horowitz et al., 2003) is used
4 to diagnose the PRB contribution to N and S oxides concentrations, as well as to total (wet plus
5 dry) deposition. The model setup for the present-day simulation has been published in a series of
6 papers from a recent model intercomparison (Dentener et al., 2006a,b; Shindell et al., 2006;
7 Stevenson et al., 2006; Van Noije et al., 2006). MOZART-2 is driven by National Center for
8 Environmental Prediction meteorological fields and IIASA 2000 emissions at a resolution of
9 $1.9^\circ \times 1.9^\circ$ with 28 sigma levels in the vertical, and it includes gas- and aerosol phase chemistry.
10 Results shown in Figures AX2.12-1 to AX2.12-5 are for the meteorological year 2001. Note that
11 color images are available on the web. An additional PRB simulation was conducted in which
12 continental North American anthropogenic emissions were set to zero.

13 First, the role of PRB in contributing to $[\text{NO}_2]$ and $[\text{SO}_2]$ in surface air is considered.
14 Figure AX2.12-1 shows the annual mean $[\text{NO}_2]$ in surface air in the base case simulation (top
15 panel) and from the PRB simulation (middle panel), along with the percentage contribution of
16 the background to the total base case $[\text{NO}_2]$ (bottom panel). Maximum concentrations in the
17 base case simulation occur along the Ohio River Valley and in the Los Angeles basin just as they
18 do in reported measurements; see the section on emissions and concentrations above. While
19 present-day concentrations are often >5 ppb, PRB is <300 ppt over most of the CONUS and
20 <100 ppt in the eastern United States. The distribution of PRB (middle panel of Figure
21 AX2.12-1) largely reflects the distribution of soil NO emissions, with some local enhancements
22 due to biomass burning such as is seen in western Montana. In the northeastern United States,
23 where present-day $[\text{NO}_2]$ are highest, PRB contributes $<1\%$ to the total concentrations.

24 The spatial pattern of present-day SO_2 concentrations over the United States is similar to
25 that of NO_2 , with highest concentrations (>5 ppb) along the Ohio River valley (upper panel
26 Figure AX2.12-2). Background SO_2 concentrations are orders of magnitude smaller, below
27 10 ppt over much of the United States (middle panel of Figure AX2.12-2). Maximum PRB
28 concentrations of SO_2 are 30 ppt. In the Northwest where there are geothermal sources of SO_2 ,
29 the contribution of PRB to total SO_2 is 70 to 80%. However, with the exception of the West
30 Coast where volcanic SO_2 emissions enhance PRB concentrations, the PRB contributes $<1\%$ to
31 present-day SO_2 concentrations in surface air (bottom panel Figure AX2.12-2).

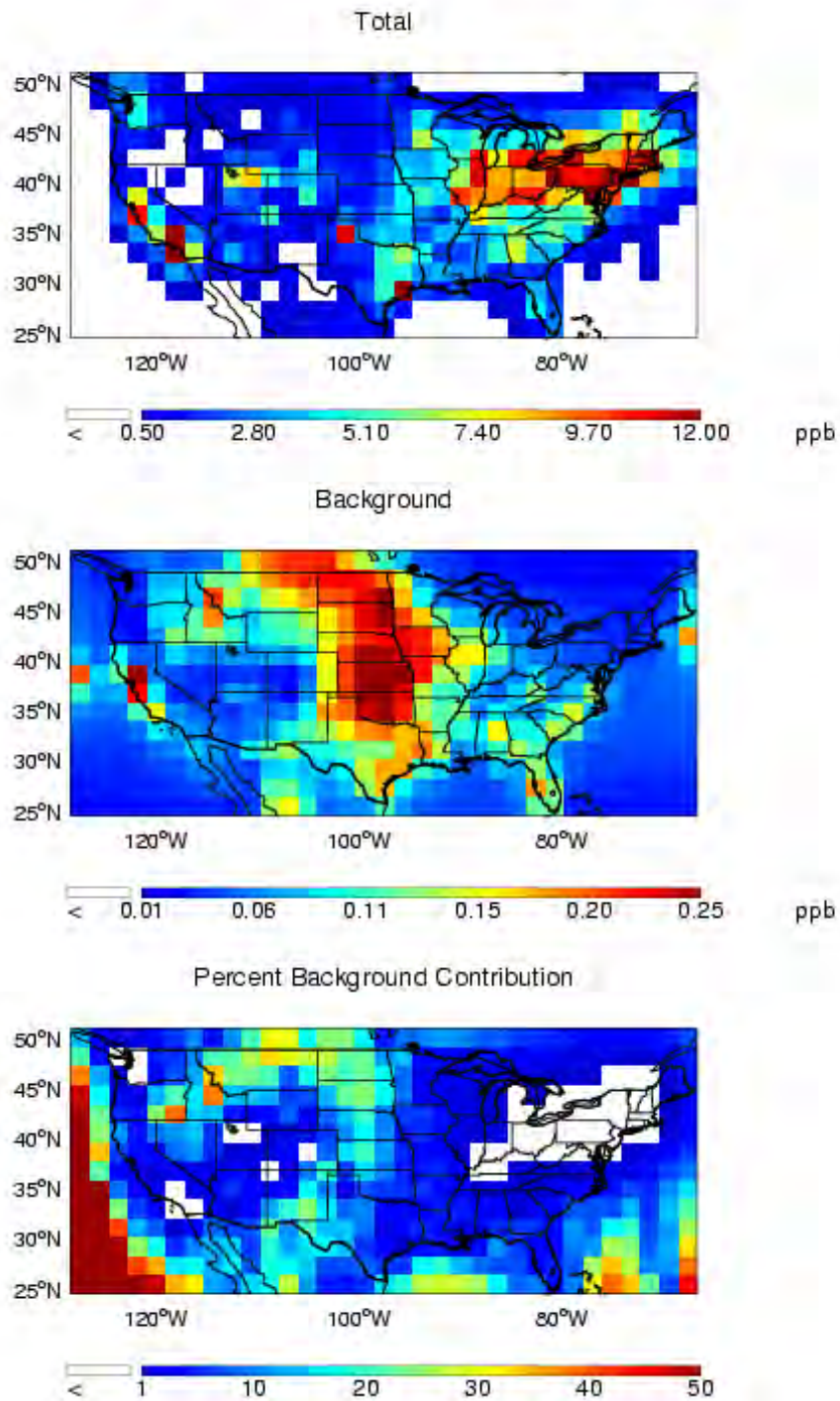


Figure AX2.12-1. Annual mean concentrations of NO₂ (ppb) in surface air over the United States in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations. Please see text for details.

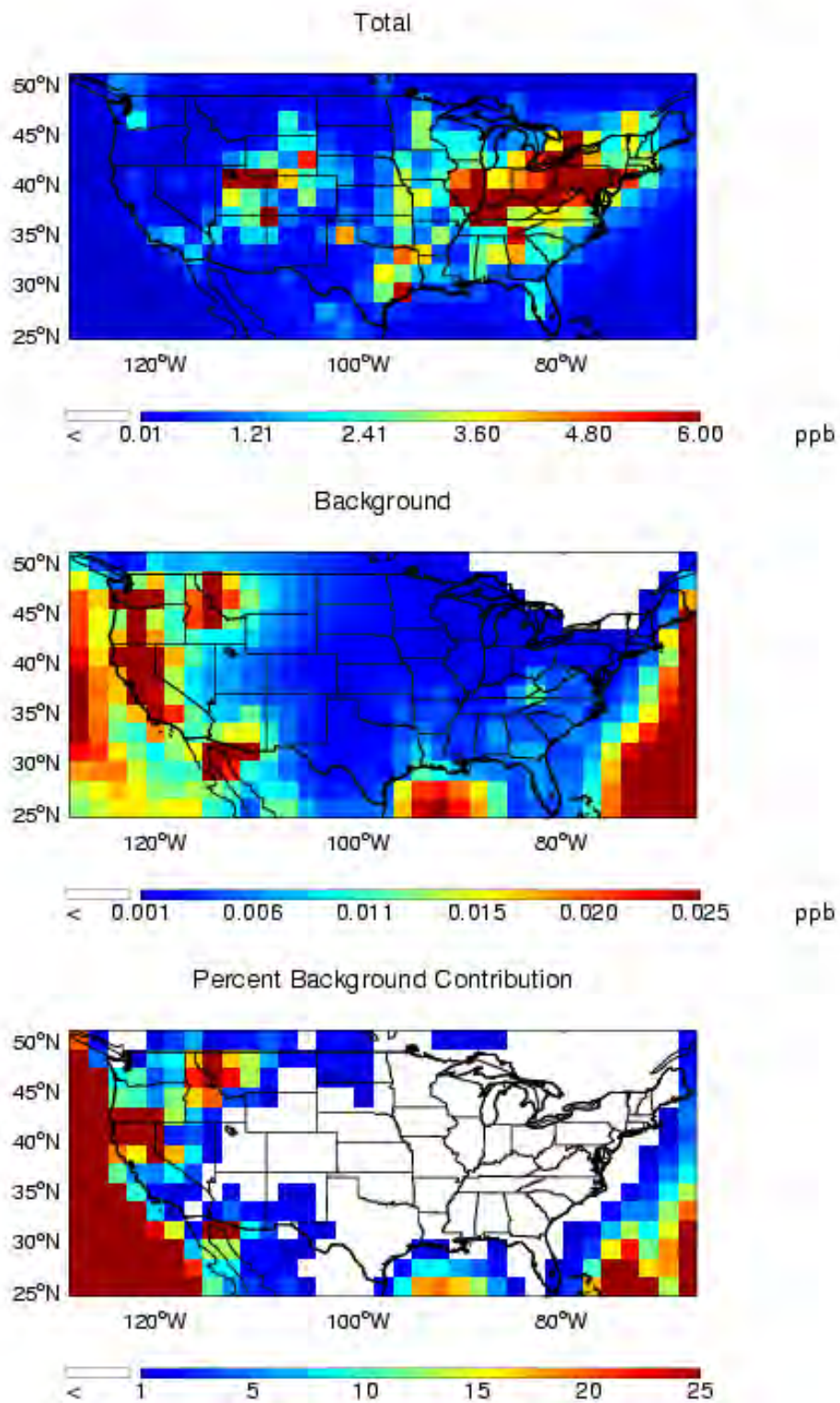


Figure AX2.12-2. Same as Figure AX2.12-1 but for SO₂ concentrations.

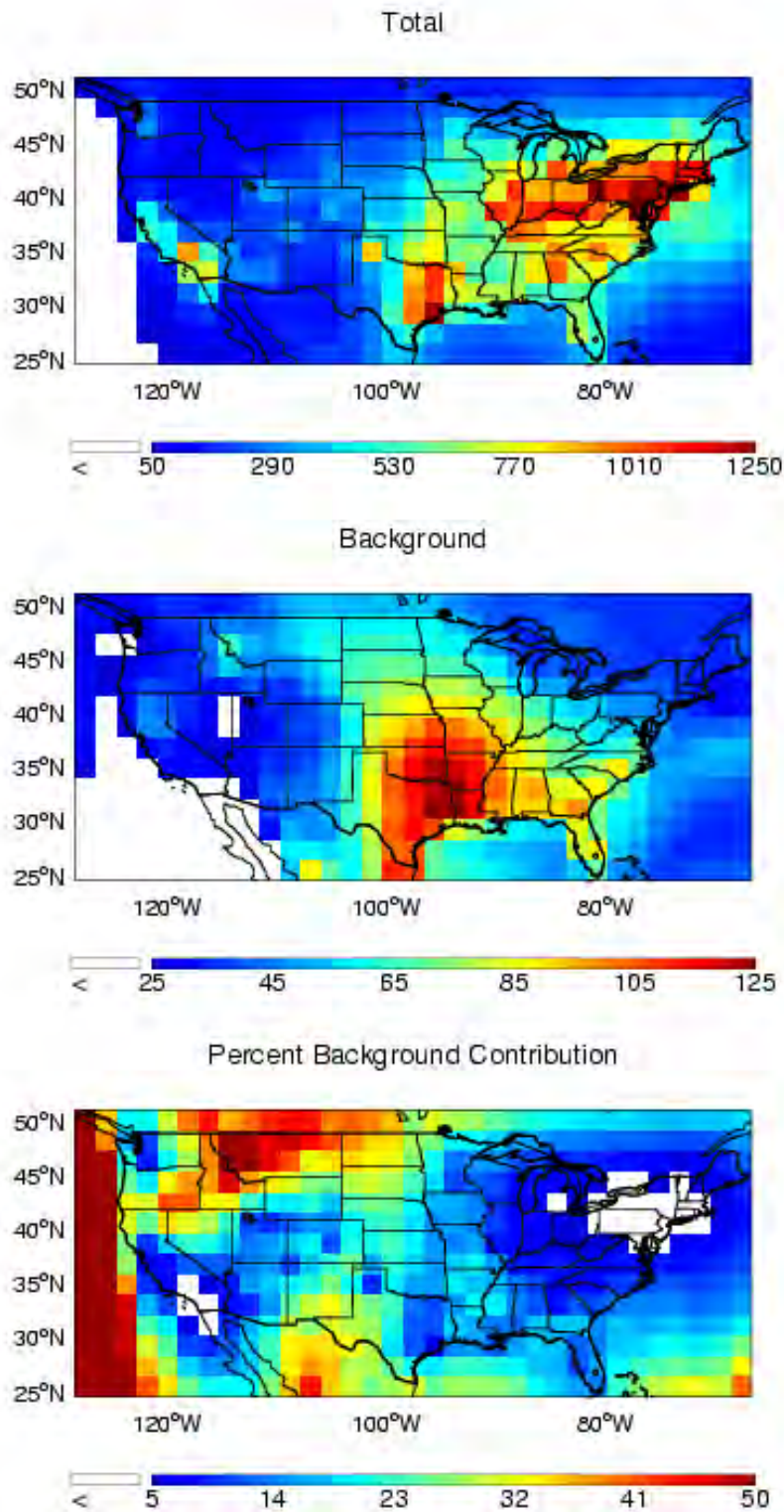


Figure AX2.12-3. Same as for Figure AX2.12-1 but for wet and dry deposition of HNO₃, NH₄NO₃, NO_x, HO₂NO₂, and organic nitrates (mg N m⁻²y⁻¹).

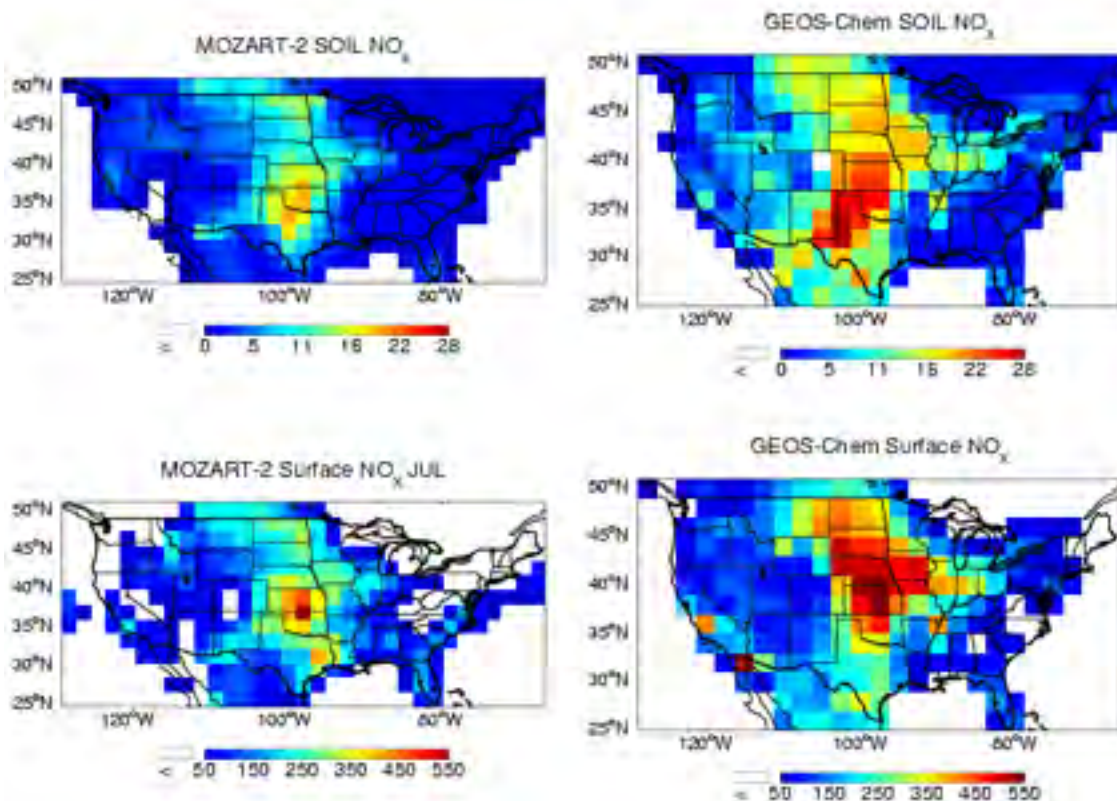


Figure AX2.12-4. Same as Figure AX2.12-1 but for SO_x deposition (SO₂ + SO₄) (mg S m⁻²y⁻¹).

1 The spatial pattern of NO_y (defined here as HNO₃, NH₄NO₃, NO_x, HO₂NO₂, and organic
 2 nitrates) wet and dry deposition is shown in Figure AX2.12-3. Figure AX2.12-3 (upper panel)
 3 shows that highest values are found in the eastern United States in and downwind of the Ohio
 4 River Valley. The pattern of N deposition in the PRB simulation (Figure AX2.12-3, middle
 5 panel), however, shows maximum deposition centered over Texas and in the Gulf Coast region,
 6 reflecting a combination of N emissions from lightning in the Gulf region, biomass burning in
 7 the Southeast, and from microbial activity in soils (maximum in central Texas and Oklahoma).
 8 The bottom panel of Figure AX2.12-3 shows that the PRB contribution to N deposition is less
 9 than 20% over the eastern United States, and typically <50% in the western United States where
 10 NO_y deposition is low (25-50 mg N m⁻² yr⁻¹).

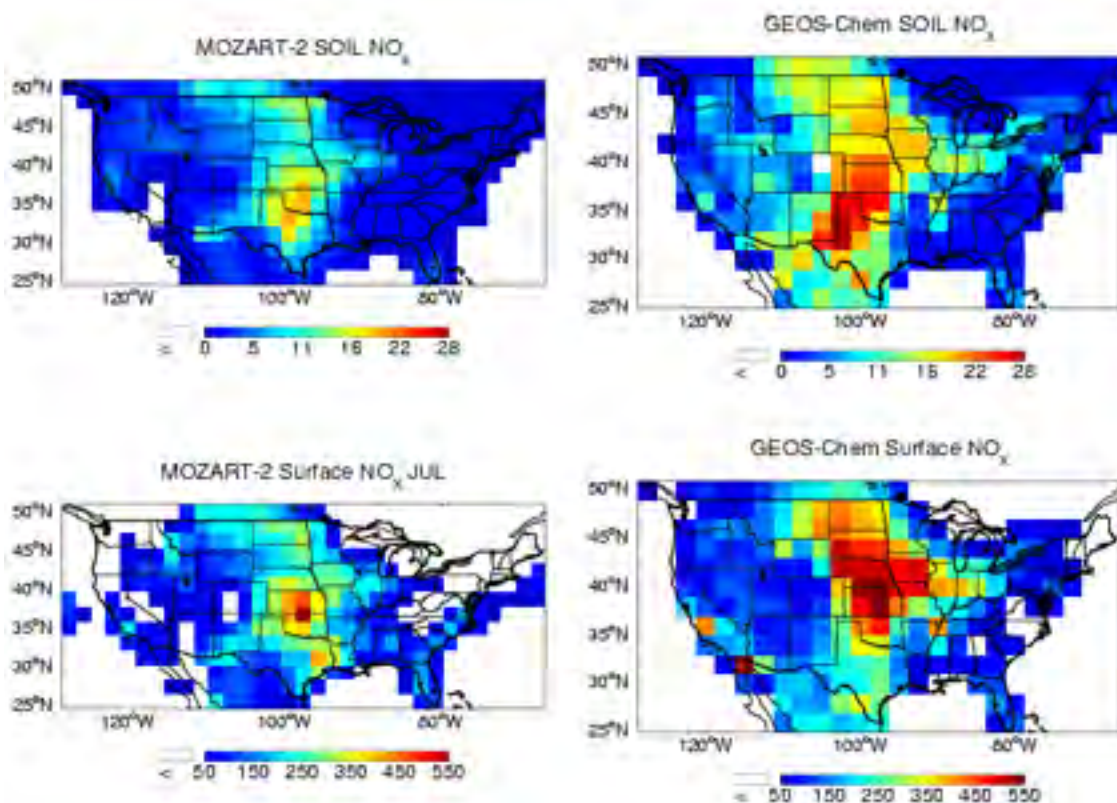


Figure AX2.12-5. July mean soil NO emissions (upper panels; 1×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$) and surface PRB NO_x concentrations (lower panels; ppt) over the United States from MOZART-2 (left) and GEOS-Chem (right) model simulations in which anthropogenic O₃ precursor emissions were set to zero in North America.

1 Present-day SO_x deposition is largest in the Ohio River Valley, likely due to coal-burning
 2 power plants in that region, while background deposition is typically at least an order of
 3 magnitude smaller (Figure AX2.12-4). Over the eastern United States, the background
 4 contribution to SO_x deposition is <10%, and it is even smaller (<1%) where present-day SO_x
 5 deposition is highest. The contribution of PRB to pSO₄ deposition is highest in the western
 6 United States (>20%) because of geothermal sources of SO₂ and oxidation of dimethyl sulfide in
 7 the surface of the eastern Pacific.

8 Thus far, the discussion has focused on results from the MOZART-2 tropospheric
 9 chemistry model. In Figure AX2.12-5, results from MOZART-2 are compared with those from

1 another tropospheric chemistry model, GEOS-Chem (Bey et al., 2001), which was previously
2 used to diagnose PRB O₃ (Fiore et al., 2003; U.S. Environmental Protection Agency, 2006a). In
3 both models, the surface PRB NO_x concentrations tend to mirror the distribution of soil NO
4 emissions, which are highest in the Midwest. The higher soil NO emissions in GEOS-Chem (by
5 nearly a factor of 2) as compared to MOZART-2 reflect different assumptions regarding the
6 contribution to soil NO emissions largely through fertilizer, since GEOS-Chem total soil NO
7 emissions are actually higher than MOZART-2 (0.07 versus 0.11 Tg N) over the United States in
8 July. Even with the larger PRB soil NO emissions, surface NO_x concentrations in GEOS-Chem
9 are typically <500 ppt.

10 It is also instructive to consider measurements of SO₂ at relatively remote monitoring
11 sites, i.e., site located in sparsely populated areas not subject to obvious local sources of pollution.
12 Berresheim et al. (1993) used a type of atmospheric pressure ionization mass spectrometer
13 (APIMS) at Cheeka Peak, WA (48.30 N 124.62 W, 480 m asl), in April 1991 during a field study
14 for DMS oxidation products: [SO₂] ranged between 20 and 40 ppt. Thornton et al. (2002) have
15 also used an APIMS with an isotopically labeled internal standard to determine background
16 [SO₂] and found 25 to 40 ppt in northwestern Nebraska in October 1999 at 150 m above ground
17 using the NCAR C-130 aircraft platform (Thornton, unpublished data). These data are
18 comparable to remote central south Pacific convective boundary layer [SO₂] (Thornton et al.,
19 1999).

20 Volcanic sources of SO₂ in the United States are limited to the Pacific Northwest, Alaska,
21 and Hawaii. Since 1980 the Mt. St. Helens volcano in Washington Cascade Range (46.20 N,
22 122.18 W, summit 2549 m asl) has been a variable source of SO₂. Its major effects came in the
23 explosive eruptions of 1980, which primarily affected the northern part of the mountainous west
24 of the United States. The Augustine volcano near the mouth of the Cook Inlet in southwestern
25 Alaska (59.363 N, 153.43 W, summit 1252 m asl) has had SO₂ emissions of varying extents
26 since its last major eruptions in 1986. Volcanoes in the Kamchatka peninsula of the eastern
27 region of Siberian Russia do not especially affect surface concentrations in northwestern North
28 America. The most serious effects in the United States from volcanic SO₂ occurs on the island
29 of Hawaii. Nearly continuous venting of SO₂ from Mauna Loa and Kilauea produce SO₂ in such
30 large amounts that >100 km downwind of the island, [SO₂] can be >30 ppb (Thornton and
31 Bandy, 1993). Depending on wind direction, the Kona region of the Hawaiian west coast has

1 had significant effects from SO₂ and pSO₄ for the past decade. Indeed, [SO₂] in Volcanoes
2 National Park, HI were in excess of the 3-h and the 24-h NAAQS in the 2004 to 2005 reporting
3 period.

4 In summary, the PRB contribution to NO_x and SO_x over the CONUS is very small,
5 except for SO₂ in areas with volcanic activity.

TABLE AX2-1. EMISSIONS OF NITROGEN OXIDES, AMMONIA, AND SULFUR DIOXIDE IN THE UNITED STATES IN 2002

2002 Emissions (Tg/yr)	NO _x ¹	NH ₃	SO ₂
Source Category			
TOTAL ALL SOURCES	23.19	4.08	16.87
FUEL COMBUSTION TOTAL	9.11	0.02	14.47
FUEL COMB. ELEC. UTIL	5.16	<0.01	11.31
Coal	4.50	<0.01	10.70
Bituminous	2.90		8.04
Subbituminous	1.42		2.14
anthracite & lignite	0.18		0.51
Other	<0.01		
Oil	0.14	<0.01	0.38
Residual	0.13		0.36
Distillate	0.01		0.01
Gas	0.30	<0.01	0.01
Natural	0.29		
Process	0.01		
Other	0.05	<0.01	0.21
Internal Combustion	0.17	<0.01	0.01
FUEL COMBUSTION INDUSTRIAL	3.15	<0.01	2.53
Coal	0.49	<0.01	1.26
Bituminous	0.25		0.70
Subbituminous	0.07		0.10
Anthracite & Lignite	0.04		0.13
Other	0.13		0.33
Oil	0.19	<0.01	0.59
Residual	0.09		0.40
Distillate	0.09		0.16
Other	0.01		0.02
Gas	1.16	<0.01	0.52
Natural	0.92		
Process	0.24		
Other	<0.01		
Other	0.16	<0.01	0.15
wood/bark waste	0.11		
liquid waste	0.01		
Other	0.04		
Internal Combustion	1.15	<0.01	0.01
FUEL COMB. OTHER	0.80	<0.01	0.63
Commercial/Institutional Coal	0.04	<0.01	0.16
Commercial/Institutional Oil	0.08	<0.01	0.28
Commercial/Institutional Gas	0.25	<0.01	0.02
Misc. Fuel Comb. (Except Residential)	0.03	<0.01	0.01
Residential Wood	0.03		<0.01

**TABLE AX2-1 (cont'd). EMISSIONS OF NITROGEN OXIDES, AMMONIA, AND
SULFUR DIOXIDE IN THE UNITED STATES IN 2002**

2002 Emissions (Tg/yr)	NO_x¹	NH₃	SO₂
Residential Other	0.36		0.16
distillate oil	0.06		0.15
bituminous/subbituminous	0.26		<0.01
Other	0.04		<0.01
INDUSTRIAL PROCESS TOTAL	1.10	0.21	1.54
CHEMICAL & ALLIED PRODUCT MFG	0.12	0.02	0.36
Organic Chemical Mfg	0.02	<0.01	0.01
Inorganic Chemical Mfg	0.01	<0.01	0.18
Sulfur compounds			0.17
Other			0.02
Polymer & Resin Mfg	<0.01	<0.01	<0.01
Agricultural Chemical Mfg	0.05	0.02	0.05
ammonium nitrate/urea mfg.		<0.01	
Other		0.02	
Paint, Varnish, Lacquer, Enamel Mfg	0.00		0.00
Pharmaceutical Mfg	0.00		0.00
Other Chemical Mfg	0.03	<0.01	0.12
METALS PROCESSING	0.09	<0.01	0.30
Non-Ferrous Metals Processing	0.01	<0.01	0.17
Copper			0.04
Lead			0.07
Zinc			0.01
Other			<0.01
Ferrous Metals Processing	0.07	<0.01	0.11
Metals Processing	0.01	<0.01	0.02
PETROLEUM & RELATED INDUSTRIES	0.16	<0.01	0.38
Oil & Gas Production	0.07	<0.01	0.11
natural gas			0.11
Other			0.01
Petroleum Refineries & Related Industries	0.05	<0.01	0.26
fluid catalytic cracking units		<0.01	0.16
Other		<0.01	0.07
Asphalt Manufacturing	0.04		0.01
OTHER INDUSTRIAL PROCESSES	0.54	0.05	0.46
Agriculture, Food, & Kindred Products	0.01	<0.01	0.01
Textiles, Leather, & Apparel Products	<0.01	<0.01	<0.01
Wood, Pulp & Paper, & Publishing Products	0.09	<0.01	0.10

**TABLE AX2-1 (cont'd). EMISSIONS OF NITROGEN OXIDES, AMMONIA, AND
SULFUR DIOXIDE IN THE UNITED STATES IN 2002**

2002 Emissions (Tg/yr)	NO_x¹	NH₃	SO₂
Rubber & Miscellaneous Plastic Products	<0.01	<0.01	<0.01
Mineral Products	0.42	<0.01	0.33
cement mfg	0.24		0.19
glass mfg	0.01		
Other	0.10		0.09
Machinery Products	<0.01	<0.01	<0.01
Electronic Equipment	<0.01	<0.01	<0.01
Transportation Equipment	<0.01		<0.01
Miscellaneous Industrial Processes	0.01	0.05	0.02
SOLVENT UTILIZATION	0.01	<0.01	<0.01
Degreasing	<0.01	<0.01	<0.01
Graphic Arts	<0.01	<0.01	<0.01
Dry Cleaning	<0.01	<0.01	<0.01
Surface Coating	<0.01	<0.01	<0.01
Other Industrial	<0.01	<0.01	<0.01
Nonindustrial	<0.01		
Solvent Utilization NEC	<0.01		
STORAGE & TRANSPORT	<0.01	<0.01	0.01
Bulk Terminals & Plants	<0.01	<0.01	<0.01
Petroleum & Petroleum Product Storage	<0.01	<0.01	<0.01
Petroleum & Petroleum Product Transport	<0.01	<0.01	<0.01
Service Stations: Stage II	<0.01		<0.01
Organic Chemical Storage	<0.01	<0.01	<0.01
Organic Chemical Transport	0.01		<0.01
Inorganic Chemical Storage	<0.01	<0.01	<0.01
Inorganic Chemical Transport	<0.01		<0.01
Bulk Materials Storage	0.01	<0.01	<0.01
WASTE DISPOSAL & RECYCLING	0.17	0.14	0.03
Incineration	0.06	<0.01	0.02
Industrial			
Other			<0.01
Open Burning	0.10	<0.01	<0.01
Industrial			<0.01
Land clearing debris			
Other			<0.01
Public Operating Treatment Works	<0.01	0.14	<0.01
Industrial Waste Water	<0.01	<0.01	<0.01
Treatment, Storage, and Disposal Facility	<0.01	<0.01	<0.01
Landfills	<0.01	<0.01	<0.01
Industrial			<0.01

**TABLE AX2-1 (cont'd). EMISSIONS OF NITROGEN OXIDES, AMMONIA, AND
SULFUR DIOXIDE IN THE UNITED STATES IN 2002**

2002 Emissions (Tg/yr)	NO_x¹	NH₃	SO₂
Other			<0.01
Other	<0.01	<0.01	<0.01
TRANSPORTATION TOTAL	12.58	0.32	0.76
HIGHWAY VEHICLES	8.09	0.32	0.30
Light-Duty Gas Vehicles & Motorcycles	2.38	0.20	0.10
light-duty gas vehicles	2.36		0.10
Motorcycles	0.02		0.00
Light-Duty Gas Trucks	1.54	0.10	0.07
light-duty gas trucks 1	1.07		0.05
light-duty gas trucks 2	0.47		0.02
Heavy-Duty Gas Vehicles	0.44	<0.01	0.01
Diesels	3.73	<0.01	0.12
heavy-duty diesel vehicles	3.71		
light-duty diesel trucks	0.01		
light-duty diesel vehicles	0.01		
OFF-HIGHWAY	4.49	<0.01	0.46
Non-Road Gasoline	0.23	<0.01	0.01
Recreational	0.01		
Construction	0.01		
Industrial	0.01		
lawn & garden	0.10		
Farm	0.01		
light commercial	0.04		
Logging	<0.01		
airport service	<0.01		
railway maintenance	<0.01		
recreational marine vessels	0.05		
Non-Road Diesel	1.76	<0.01	0.22
Recreational	0.00		
Construction	0.84		
Industrial	0.15		
lawn & garden	0.05		
Farm	0.57		
light commercial	0.08		
Logging	0.02		
airport service	0.01		
railway maintenance	<0.01		
recreational marine vessels	0.03		
Aircraft	0.09		0.01
Marine Vessels	1.11		0.18
Diesel	1.11		
residual oil			
Other			

**TABLE AX2-1 (cont'd). EMISSIONS OF NITROGEN OXIDES, AMMONIA, AND
SULFUR DIOXIDE IN THE UNITED STATES IN 2002**

2002 Emissions (Tg/yr)	NO_x¹	NH₃	SO₂
Railroads	0.98		0.05
Other	0.32	<0.01	0.00
liquefied petroleum gas	0.29		
compressed natural gas	0.04		
MISCELLANEOUS	0.39	3.53	0.10
Agriculture & Forestry	<0.01	3.45	<0.01
agricultural crops		<0.01	
agricultural livestock		2.66	
Other Combustion		0.08	0.10
Health Services			
Cooling Towers			
Fugitive Dust			
Other			
Natural Sources	3.10	0.03	

¹ Emissions are expressed in terms of NO₂.

² Emissions based on Guenther et al. (2000).

Source: U.S. Environmental Protection Agency (2006a).

TABLE AX2.5-1. MAJOR ROUTINE OPERATING AIR MONITORING NETWORKS⁵

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
State/Local/Federal Networks					
NCore ¹ —National Core Monitoring Network	EPA	75	2008	O ₃ , NO/NO ₂ /NO _Y , SO ₂ , CO, PM _{2.5} /PM _{10-2.5} ² , PM _{2.5} speciation, NH ₃ , HNO ₃ , surface meteorology ³	http://www.epa.gov/ttn/amtic/monstratdoc.htm
SLAMS ¹ —State and Local Ambient Monitoring Stations	EPA	~3000	1978	O ₃ , NO _X /NO ₂ , SO ₂ , PM _{2.5} /PM ₁₀ , CO, Pb	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
STN—PM _{2.5} Speciation Trends Network	EPA	300	1999	PM _{2.5} , PM _{2.5} speciation, major ions, metals	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.html
PAMS—Photochemical Assessment Monitoring Network	EPA	75	1994	O ₃ , NO _X /NO _Y , CO, speciated VOCs, carbonyls, surface meteorology and upper air	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
IMPROVE—Interagency Monitoring of Protected Visual Environments	NPS	110 plus 67 protocol sites	1988	PM _{2.5} /PM ₁₀ , major ions, metals, light extinction, scattering coefficient	http://vista.cira.colostate.edu/IMPROVE/
CASTNe—Clean Air Status and Trends Network	EPA	80+	1987	O ₃ , SO ₂ , major ions, calculated dry deposition, wet deposition, total deposition for S/N, surface meteorology	http://www.epa.gov/castnet/
GPMP—Gaseous Pollutant Monitoring Network	NPS	33	1987	O ₃ , NO _X /NO/NO ₂ , SO ₂ , CO, surface meteorology, (plus enhanced monitoring of CO, NO, NO _X , NO _Y , and SO ₂ plus canister samples for VOC at three sites)	http://www2.nature.nps.gov/air/Monitoring/network.cfm#data
POMS—Portable Ozone Monitoring Stations	NPS	14	2002	O ₃ , surface meteorology, with CASTNet-protocol filter pack (optional) sulfate, nitrate, ammonium, nitric acid, sulfur dioxide	http://www2.nature.nps.gov/air/studies/portO3.cfm
Passive Ozone Sampler Monitoring Program	NPS	43	1995	O ₃ dose (weekly)	http://www2.nature.nps.gov/air/Studies/Passives.cfm

TABLE AX2.5-1 (cont'd). MAJOR ROUTINE OPERATING AIR MONITORING NETWORKS⁵

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
State/Local/Federal Networks (cont'd)					
NADP/NTN—National Atmospheric Deposition Program / National Trends Network	USGS	200+	1978	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/
NADP/MDN—National Atmospheric Deposition Program / Mercury Deposition Network	None	90+	1996	Mercury from precipitation chemistry	http://nadp.sws.uiuc.edu/mdn/
AIRMoN—National Atmospheric Deposition Program / Atmospheric Integrated Research Monitoring Network	NOAA	8	1984	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/AIRMoN/
IADN—Integrated Atmospheric Deposition Network	EPA	20	1990	PAHs, PCBs, and organochlorine compounds are measured in air and precipitation samples	http://www.epa.gov/glnpo/monitoring/air
NAPS—National Air Pollution Surveillance Network	Canada	152+	1969	SO ₂ , CO, O ₃ , NO, NO ₂ , NO _x , VOCs, SVOCs, PM ₁₀ , PM _{2.5} , TSP, metals	http://www.etcentre.org/NAPS/
CAPMoN—Canadian Air and Precipitation Monitoring Network	Canada	29	2002	O ₃ , NO, NO ₂ , NO _y , PAN, NH ₃ , PM _{2.5} , PM ₁₀ and coarse fraction mass, PM _{2.5} speciation, major ions for particles and trace gases, precipitation chemistry for major ions	http://www.msc.ec.gc.ca/capmon/index_e.cfm
Mexican Metropolitan Air Quality Network	Mexico	93	???	O ₃ , NO _x , CO, SO ₂ , PM ₁₀ , TSP	See CEC, 19977

TABLE AX2.5-1 (cont'd). MAJOR ROUTINE OPERATING AIR MONITORING NETWORKS⁵

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
Air Toxics Monitoring Networks					
NATTS—National Air Toxics Trends Station	EPA	23	2005	VOCs, Carbonyls, PM ₁₀ metals ⁴ , Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
State/Local Air Toxics Monitoring	EPA	250+	1987	VOCs, Carbonyls, PM ₁₀ metals ⁴ , Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
NDAMN—National Dioxin Air Monitoring Network	EPA	34	1998- 2005	CDDs, CDFs, dioxin-like PCBs	http://cfpub2.epa.gov/ncea/cfm/recordisplay.cfm?deid=22423
Tribal Monitoring Networks					
Tribal Monitoring ⁶	EPA	120+	1995	O ₃ , NO _X /NO ₂ , SO ₂ , PM _{2.5} /PM ₁₀ , CO, Pb	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
Industry/Research Networks					
New Source Permit Monitoring	None	variable	variable	O ₃ , NO _X /NO ₂ , SO ₂ , PM _{2.5} /PM ₁₀ , CO Pb	Contact specific industrial facilities
HRM Network—Houston Regional Monitoring Network	None	9	1980	O ₃ , NO _X , PM _{2.5} /PM ₁₀ , CO, SO ₂ , Pb, VOCs, surface meteorology	http://hrm.radian.com/houston/how/index.htm
ARIES / SEARCH—Aerosol Research Inhalation Epidemiology Study / Southeastern Aerosol Research and Characterization Study experiment	None	8	1992	O ₃ , NO/NO ₂ /NO _Y , SO ₂ , CO, PM _{2.5} /PM ₁₀ , PM _{2.5} speciation, major ions, NH ₃ , HNO ₃ , scattering coefficient, surface meteorology	http://www.atmospheric-research.com/studies/SEARCH/index.html
SOS - SERON—Southern Oxidant Study - Southeastern Regional Oxidant Networks	EPA	~40	1990	O ₃ , NO, NO _Y , VOCs, CO, surface meteorology	http://www.ncsu.edu/sos/pubs/sos3/State_of_SOS_3.pdf

TABLE AX2.5-1 (cont'd). MAJOR ROUTINE OPERATING AIR MONITORING NETWORKS

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
National/Global Radiation Networks					
RadNet—formerly Environmental Radiation Ambient Monitoring System (ERAMS)	EPA	200+	1973	Radionuclides and radiation	http://www.epa.gov/enviro/html/erams/
SASP—Surface Air Sampling Program	DHS	41	1963	⁸⁹ Sr, ⁹⁰ Sr, naturally occurring radionuclides, ⁷ Be, ²¹⁰ Pb	http://www.eml.doe.gov/databases/sasp/
NEWNET—Neighborhood Environmental Watch Network	DOE	26	1993	Ionizing gamma radiation, surface meteorology	http://newnet.lanl.gov/stations.asp
CTBT—Comprehensive Nuclear Test Ban Treaty	DOE	80	1996	Radionuclides and noble gases	http://www.clw.org/archive/coalition/briefv3n14.htm
Other Networks					
UV Index—EPA Sunwise Program	EPA	~50 U.S. cities	2002	Calculated UV radiation index	http://www.epa.gov/sunwise/uvindex.html
UV Net—Ultraviolet Monitoring Program	EPA	21	2002	Ultraviolet solar radiation (UV-B and UV-A bands)	http://www.epa.gov/uvnet/access.html
UV-B Monitoring and Research Program	USDA	35	1992	UV-B radiation	http://uvb.nrel.colostate.edu/UVB/jsp/uvb_climate_network.jsp
SURFRAD—Surface Radiation Budget Network	NOAA	7	1993	Solar and infrared radiation, direct and diffuse solar radiation, photosynthetically active radiation, UVB, spectral solar, meteorological parameters	http://www.srrb.noaa.gov/surfrad/index.html
PRIMENet—Park Research & Intensive Monitoring of Ecosystems NETWORK	NPS	14	1997	Ozone, wet and dry deposition, visibility, surface meteorology, and ultraviolet radiation	http://www.forestry.umt.edu/research/MFCES/programs/primenet/
BioWatch	No details				

TABLE AX2.5-2. AIR MONITORING NETWORKS/CAMPAIGNS FOR NON-ROUTINE SPECIAL INTENSIVE STUDIES

Lead Agency¹	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data	Notes
Texas	17	2006	O ₃ , NO _x , NO _y , SO ₂ , haze, visibility, CO, VOC, solar radiation, surface meteorology, upper air	http://www.utexas.edu/research/ceer/texaqsII/PDF/12-12-04_Projected_SurfaceSites_tbl.pdf	Researchers from universities, state and federal agencies, private industry, and local governments are joining forces to conduct a major field study to address air quality issues in the eastern half of Texas. The study, planned for a period extending from Apr 2005 through Oct 2006, will examine regional ozone formation, transport of ozone and ozone precursors, meteorological and chemical modeling, issues related to ozone formation by highly reactive emissions, and particulate matter formation. It is anticipated that the information from the study will be the scientific basis used for developing State Implementation Plans (SIPs) for ozone (with concentrations averaged over 8 h), regional haze, and, if necessary, for fine particulate matter (particulate matter less than 2.5 microns in diameter, PM _{2.5})
NOAA	1 ship, 2 aircraft	2006	O ₃ , NO, NO ₂ , NO _y , VOCs, CO ₂ , CO, SO ₂ , HNO ₃ , NH ₃ , other reactive pollutants, aerosols, meteorological parameters and upper air	http://esrl.noaa.gov/csd/2006/	For TexAQS 2006, the NOAA air quality component will investigate, through airborne and sea-based measurements, the sources, and processes that are responsible for photochemical pollution and regional haze during the summertime in Texas. The focus of the study will be the transport of ozone and ozone precursors within the state and the impact of the long-range transport of ozone or its precursors.

TABLE AX2.5-2 (cont'd). AIR MONITORING NETWORKS/CAMPAIGNS FOR NON-ROUTINE SPECIAL INTENSIVE STUDIES

Lead Agency ¹	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data	Notes
NOAA	3 aircraft	2006	O ₃ , NO, NO ₂ , NO _y , VOCs, CO ₂ , CO, SO ₂ , HNO ₃ , NH ₃ , other reactive pollutants, aerosols, meteorological parameters, altitude -- NOAA aircraft	http://cloud1.arc.nasa.gov/intex-b/	The export of air pollutants from urban to regional and global environments is a major concern because of wide-ranging potential consequences for human health, cultivated and natural ecosystems, visibility degradation, weather modification, changes in radiative forcing, and tropospheric oxidizing capacity. During the spring of 2006 a highly integrated atmospheric field experiment was performed over and around North America. The Megacity Initiative: Local and Global Research Observations (MILAGRO), http://www.eol.ucar.edu/projects/milagro/ , resulted through a highly coordinated collaboration between NSF (through MIRAGE-Mex), DOE (through MAX-Mex), NASA (through INTEX-B) and a variety of research institution in the U.S. and Mexico and involved ground and air borne activities centered on Mexico City, Mexico during March 2006. MILAGRO goals were greatly facilitated and enhanced by a number of concurrent and coordinated national and international field campaigns and global satellite observations. After MILAGRO, NASA continued investi

¹EPA-- Environmental Protection Agency; NASA -- National Aeronautics and Space Administration; NOAA -- National Oceanic and Atmospheric Administration; NPS -- National Park Service
NSF -- National Science Foundation; UCSD -- University of California San Diego (Scripts Institution of Oceanography)

²This study is part of the Central California Air Quality Studies (CCAQS) which comprise the California Regional Particulate Air Quality Study (CRPAQS) and the Central California Ozone Study (CCOS). CCAQS is a multi-year effort of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. Prior studies in California included: Southern California Ozone Study (SCOS97) -- 1997; Integrated Monitoring Study (IMS95) -- 1995; San Joaquin Valley Air Quality Study (SJAQS) -- 1990; SARMAP Ozone Study -- 1990; Southern California Air Quality Study (SCAQS) -- 1987.

³Historically, there have been many other field studies in the 1960s - 1990s that are not reflected in this table that involve both fixed monitoring sites and aircraft; well known examples include Regional Air Pollution Study (RAPS), Large Power Plant Effluent Study (LAPPES), Northeast Corridor Regional Modeling Program (NECRMP), Northeast Regional Oxidant Study (NEROS), Persistent Elevated Pollutant Episode (PEPE), and Lake Michigan Ozone Study (LMOS).

TABLE AX2.5-3. SATELLITE-BASED AIR QUALITY OBSERVING SYSTEMS^{1,4}

Instrument	Satellite Platform ³	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
OLS (Operational Linescan System)	DMSP satellites	DOD	1962?	Identify fires and smoke plume	Polar Imagery only	http://www.af.mil/factsheets/factsheet.asp?fsID=94
BUV (Backscatter Ultraviolet Spectrometer)	Nimbus 4	NASA	1970-1980	O ₃ , CO ₂ , SO ₂	Sun synchronous	http://nssdc.gsfc.nasa.gov/database/MasterCatalog?sc=1970-025A
SBUV (Solar Backscatter Ultraviolet Spectrometer)	Nimbus 7	NASA	1978-1993	O ₃ , SO ₂	Polar	http://jwocky.gsfc.nasa.gov/n7toms/nimbus7tech.html
TOMS (Total Ozone Mapping Spectrometer)	Nimbus 7 Meteor 3 Earth-Probe	NASA	1978-1993 1991-1994 1996	O ₃ , SO ₂ , Aerosols	Polar ~100 km	http://toms.gsfc.nasa.gov/fltmodel/spacecr.html
LIMS (Limb Infrared Monitor of the Stratosphere)	Nimbus 7	NASA	1978-1979	O ₃ , HNO ₃ , NO ₂ ,	Polar	http://lims.gats-inc.com/about_lim.html
ATMOS (Atmospheric Trace Molecule Spectroscopy)	Spacelab 3 ATLAS -- 1,2,3	NASA	1985, 1992, 1993, 1994	O ₃ , CFC13, CF2Cl2, ClONO2, HCl, HF, CO, CH ₄ , HCN, HNO ₃ , NO, NO ₂ , N ₂ O, N ₂ O ₅ , Aerosols		http://remus.jpl.nasa.gov/atmos/sl3.html
CLAES (Cryogenic Limb Array Etalon Spectrometer)	UARS	NASA	1991-1993	O ₃ , CFC13, CF2Cl2 ClONO2, CH ₄ , HNO ₃ , NO, NO ₂ , N ₂ O, N ₂ O ₅ , Aerosols		http://umpgal.gsfc.nasa.gov/
HALOE (Halogen Occultation Experiment)	UARS	NASA	1991-2005	O ₃ , HCl, HF, CH ₄ , NO, NO ₂ , Aerosols		http://umpgal.gsfc.nasa.gov/

TABLE AX2.5-3 (cont'd). SATELLITE-BASED AIR QUALITY OBSERVING SYSTEMS^{1,4}

Instrument	Satellite Platform³	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
ISAMS (Improved Stratospheric and Mesospheric Sounder)	UARS	NASA	1991-1992	O ₃ , CO, CH ₄ , NO ₂ , N ₂ O, N ₂ O ₅ Aerosols		http://umpgal.gsfc.nasa.gov/
MLS (Microwave Limb Sounder)	UARS	NASA	1991-1999	O ₃ , ClO, CH ₃ CN, HNO ₃ , SO ₂		http://umpgal.gsfc.nasa.gov/
GOES Imager (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Fire products for WF_ABBA (imagery) and GASP (aerosol optical depth)	Geostationary	http://www.nesdis.noaa.gov/
GOES Sounder (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Total column O ₃	Geostationary	http://cimss.ssec.wisc.edu/goes/goesmain.html#sndrinfo
AVHRR (Advanced Very High Resolution Radiometer)	NOAA-15 NOAA-16 NOAA-17 ²	NOAA	1998	Aerosol optical depth, particle size information and vegetation/drought index products related to air quality through fires	Polar 4 km	http://noaasis.noaa.gov/NOAASIS/ml/avhrr.html
SBUV/2 (Solar Backscattered Ultraviolet Radiometer Model 2)	NOAA-16 NOAA-17 ²	NOAA	2000	Total and profile O ₃ from surface to top of atmosphere in ~5 km thick Umkehr layers	Polar	http://www2.ncdc.noaa.gov/docs/podug/html/c4/sec4-4.htm
MOPITT (Measurement of Pollution in the Troposphere)	EOS Terra	NASA	1999	CO, CH ₄	Polar 22 × 22 km ²	http://www.eos.ucar.edu/mopitt/

TABLE AX2.5-3 (cont'd). SATELLITE-BASED AIR QUALITY OBSERVING SYSTEMS^{1,4}

Instrument	Satellite Platform ³	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
MISR (Multi-angle Imaging SpectroRadiometer)	EOS Terra	NASA	1999	Aerosol properties and plume height information near the vicinity of fires	Polar ~1 km	http://www-misr.jpl.nasa.gov/mission/introduction/welcome.html
MODIS (Moderate Resolution Imaging Spectroradiometer)	EOS Terra EOS Aqua	NASA	1999 2002	O ₃ , aerosol optical depth, particle size information, fine particle fraction, and forest fires	Polar 1 km	http://modarch.gsfc.nasa.gov/index.php
AIRS (Atmospheric Infrared Sounder)	EOS Aqua	NASA	2002	Total column ozone, surface temperature, temperature and moisture vertical profiles, (plus under development are CO and CO ₂ total column, O ₃ vertical distribution, and CH ₄ distribution)	Polar 50 km	http://www-airs.jpl.nasa.gov/
HIRDLS (High Resolution Dynamics Limb Sounder)	EOS Aura	NASA	2004	O ₃ , CFC1 ₃ , CF ₂ Cl ₂ , ClONO ₂ , CH ₄ , HNO ₃ , NO ₂ , N ₂ O, N ₂ O ₅ ,	Aerosols	Polar http://aura.gsfc.nasa.gov/index.html
MLS (Microwave Limb Sounder)	EOS Aura	NASA	2004	O ₃ , BrO, ClO, HOCl, HCl, CO, HCN, CH ₃ CN, HNO ₃ , N ₂ O, OH, HO ₂ , SO ₂	Polar	http://aura.gsfc.nasa.gov/index.html
OMI (Ozone Monitoring Instrument)	EOS Aura	NASA	2004	O ₃ , BrO, OClO, HCHO, NO ₂ , SO ₂ and aerosol	Polar	12 × 24 km ² http://aura.gsfc.nasa.gov/index.html

TABLE AX2.5-3 (cont'd). SATELLITE-BASED AIR QUALITY OBSERVING SYSTEMS^{1,4}

Instrument	Satellite Platform³	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
TES (Total Emission Spectrometer)	EOS Aura	NASA	2004	O ₃ , NO _y , CO, SO ₂ , CH ₄	Polar 26 × 42 km	http://aura.gsfc.nasa.gov/index.html
CALIPSO (Cloud-Aerosol Lidar & Infrared Pathfinder Satellite Observations)	CALIPSO	NASA	2005	Aerosol optical depth, backscatter, extinction	Polar 0.3 × 0.3 km ²	http://www-calipso.larc.nasa.gov/about/
OMPS	Ozone Mapping and Profiling Suite NPOESS - Preparatory Project	NOAA	2006	Total column and vertical profile ozone data	Polar	http://www.ipnoaa.gov/Projects/npp.html
VIIRS (Visible Infrared Imaging Radiometer Suite)	NPOESS - Preparatory Project	NOAA	2006	Aerosol optical depth	Polar	http://www.ipnoaa.gov/Projects/npp.html
Orbiting Carbon Observatory	OCO	NASA	2008	CO ₂	Polar	http://oco.jpl.nasa.gov/
APS & TIM (Aerosol Polarimetry Sensor & Total Irradiance Monitor)	Glory	NASA	2008	Black carbon soot, other aerosols, total solar irradiance, cloud images Sun-synchronous, circular	Low Earth Orbit	http://glory.gsfc.nasa.gov/

¹Non-U.S. satellite systems are not included in table at this time.

²As of 3/15/06 the operational satellite platforms may need to include NOAA-18.

³CALIPSO -- Cloud-Aerosol Lidar & Infrared Pathfinder Satellite Observations

DMSP-- Defense Meteorological Satellite Program

EOS -- Earth Observing System

GOES -- Geostationary Operational Environmental Satellites

NOAA -- National Oceanic and Atmospheric Administration

NPOESS -- National Polar-orbiting Operational Environmental Satellite System

OCO -- Orbiting Carbon Observatory

UARS -- Upper Atmosphere Research Satellite

⁴See the following table for additional information on NASA satellites, instrument systems, pollutants measured, and data availability:

TABLE AX2.5-4 (cont'd). KEY ATMOSPHERIC CHEMISTRY AND DYNAMICS DATA SETS AT THE NASA GODDARD DAAC

Missions	Nimbus 4	Nimbus 7	Nimbus 7 Meteor 3 ADEOS 1 Earth- Probe	Nimbus 7	Spacelab 3, ATLAS 1, 2, 3	UARS				ERS-2	Terra Aqua	Aqua	Aura			
Instruments	BUV	SBUV	TOMS	LIMS	ATMOS	CLAES	HALOE	SAMS	MLS	GOME	MODIS	AIRS	OMI	HIRDLS	MLS	TES*
Data Period	Apr '70- May '77	Nov '78- May '93	Nov '78- Present	Oct '78- May '79	'85, '92, '93, '94	Oct '91- May '93	Oct '91- Present	Sep '91- Jul '92	Sep '91- Jul '99	April '95- Present	Mar '00- Present	Sep '02- Present	Jul '04- Present	Jul '04- Present	Jul '04- Present	Jul '04- Present
Spectral Region	255- 380 nm	255- 340 nm	309-360 312-380 nm	6.2- 15 μ m	2.98-15 μ m	3.5-12.7 μ m	2.43-10.25 μ m	4.6- 16.6 μ m	63, 183, 205 GHz	240- 790 nm	0.4-14 μ m	0.4-1.1, 3.74- 5.4 μ m	270- 500 nm	6.12- 17.76 μ m	118, 190, 240, 640 GHz, 2.5 THz	3.2- 15.4 μ m
Bands	13	13	6	6	16	9	8	8	3	3072	36	2382	1560	22	5	12
H ₂ O/ Humidity				•	•	•	•	•	•	•	•	•		•	•	•
SO ₂	•	•	•						•	•			•		•	
Aerosols			•		•	•	•	•			•		•	•		
Cloud	•	•	•								•	•	•	•		
Temperature				•		•	•	•	•		•	•		•	•	•
Geopotential Height				•					•			•		•	•	
Reflectance	•	•	•								•	•	•			

Please note that the table above does not contain parameters from all sensors and products. Also available from the GES DAAC are many more Atmospheric and Earth Sciences data products from AIRS, AMSU-A, HSB, MODIS, SeaWiFS, OCTS, CZCS, TRMM (PR, TMI, VIRS), TOVS Pathfinder, Data Assimilation Model (GEOS-1, GEOS-DAS, CPC/ACDB), UARS (HRDI, WINDII, SOLSTICE, SUSIM, PEM), SORCE, several Field Campaigns, and Interdisciplinary data sets consisting of 70 geophysical Earth Sciences parameters. TOMS & SBUV reprocessed data (version-8) are now available on DVD-ROM. The MLS and OMI-Aura products & Visualization tools are now available from GES DISC.



Source: Aura instrument 'TES' is archived at the NASA Langley Atmospheric Sciences Data Center (<http://eosweb.larc.nasa.gov/>) <http://disc.gsfc.nasa.gov/>.

TABLE AX2.5-5. INTERNATIONAL AND EUROPEAN AIR MONITORING PROGRAMS

Network	Lead Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
EMEP – Co-operative Programmed for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (encompasses networks for ~37 European countries and organizations)	UNECE	270	1977	Acidifying / Eutrophying Compounds (precipitation): SO ₄ , NO ₃ , NH ₄ , trace elements, pH, acidity (air): SO ₂ , NO ₂ , HNO ₃ , NH ₃ , PM ₁₀ , PM _{2.5} , major ions O ₃ Heavy Metals precipitation, major ions, PM _{2.5} , PM ₁₀ , Hg, wet deposition POPs precipitation, air, deposition Particulate Matter PM _{2.5} , PM ₁₀ , EC, OC, TC, BC VOC Hydrocarbons, Carbonyls	http://www.nilu.no/projects/ccc/emepdata.html
EUROTRAC—The European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents over Europe	International Executive Committee (European Countries)	???	1986	EUROTRAC programs performed analyses utilizing data from existing or specially designed monitoring networks in order to: 1. elucidate the chemistry and transport of ozone and other photo-oxidants in the troposphere, e.g., TOR—30 O ₃ stations and ALPTRAC—15 snow-monitoring sites 2. identify processes leading to the formation of acidity in the atmosphere, particularly those involving aerosols and clouds. 3. understand uptake and release of atmospheric trace substances by the biosphere.	http://www.gsf.de/eurotrac/index_what_is.html

TABLE AX2.5-5 (cont'd). INTERNATIONAL AND EUROPEAN AIR MONITORING PROGRAMS

Network	Lead Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
EUROTRAC-2 -- The EUREKA project on the transport and chemical transformation of trace constituents in the troposphere over Europe; second phase. Subprojects: – AEROSOL – BIATEX-2 – CAPMAN – CMD – EXPORT-E2 – GENEMIS – GLOREAM – LOOP – MEPOP – PROCLOUD – SATURN – TOR-2 – TRAP45 – TROPOSAT	International Scientific Secretariat (European Countries and EU)	???	1996	EUROTRAC-2 programs performed analyses utilizing data from existing monitoring networks in order to: support the further development of abatement strategies within Europe by providing an improved scientific basis for the quantification of source-receptor relationships for photo-oxidants and acidifying substances.	http://www.gsf.de/eurotrac/index_what_is.html

TABLE AX2.6-1. REGIONAL DISTRIBUTION OF SO₂ AND SO₄²⁻ AMBIENT CONCENTRATIONS, AVERAGED FOR 2003-2005

Region	Concentration	
	SO ₂ (ppb)	SO ₄ ²⁻ (µg m ⁻³)
Mid-Atlantic	3.3	4.5
Midwest	2.3	3.8
Northeast	1.2	2.5
Southeast	1.3	4.1

TABLE AX2.6-2. DISTRIBUTIONS OF TEMPORAL AVERAGING INSIDE AND OUTSIDE CMSAS

Averaging Time Monitor Locations	n	Mean	Percentiles								
			1	5	10	25	30	50	70	75	90
1-h Maximum Concentration											
Inside CMSAs	332405	13	1	1	1	3	4	7	13	16	30
Outside CMSAs	53417	13	1	1	1	1	2	5	10	13	31
1-h Avg Concentration											
Inside CMSAs	7408145	4	1	1	1	1	1	2	4	5	10
Outside CMSAs	1197179	4	1	1	1	1	1	2	3	3	7
24-h Avg Concentration											
Inside CMSAs	327918	4	1	1	1	1	2	3	5	6	10
Outside CMSAs	52871	4	1	1	1	1	1	2	3	4	8
Annual Avg Concentration											
Inside CMSAs	898	4	1	1	1	1	2	4	5	6	8
Outside CMSAs	143	4	1	1	1	1	2	3	4	5	8
Aggregate 3-yr Avg Concentration, 2003-2005											
Inside CMSAs	283	4	1	1	1	2	3	3	5	5	8
Outside CMSAs	42	4	1	1	1	2	2	3	4	5	8

*Values are ppb

**CMSA = Consolidated Metropolitan Statistical Area

TABLE AX2.8-1. DATA SHOWING GENERAL DECREASE IN EMISSIONS OF SEVERAL CRITERIA POLLUTANTS FROM 1970 TO 2005

	Millions of Tons Per Year							
	1970	1975	1980	1985 ¹	1990	1995	2000 ¹	2005 ²
Nitrogen Oxides (NO _x) ³	26.9	26.4	27.1	25.8	25.2	24.7	22.3	19
Particulate Matter (PM) ⁴	12.2 ¹	7.0	6.2	3.6	3.2	3.1	2.3	2
PM ₁₀	NA	NA	NA	NA	2.3	2.2	1.8	2
PM _{2.5} ⁵								
Sulfur Dioxide (SO ₂)	31.2	28.0	25.9	23.3	23.1	18.6	16.3	15

¹In 1985 and 1996 EPA refined its methods for estimating emissions. Between 1970 and 1975, EPA revised its methods for estimating particulate matter emissions.

²The estimates for 2005 are preliminary.

³NO_x estimates prior to 1990 include emissions from fires. Fires would represent a small percentage of the NO_x emissions.

⁴PM estimates do not include condensable PM, or the majority of PM_{2.5} that is formed in the atmosphere from 'precursor' gases such as SO₂ and NO_x.

⁵EPA has not estimated PM_{2.5} emissions prior to 1990.

Source: http://www.epa.gov/airtrends/2006/emissions_summary_2005.html.

TABLE AX2.11-1. ATMOSPHERIC NITROGEN LOADS RELATIVE TO TOTAL NITROGEN LOADS IN SELECTED GREAT WATERS*

Waterbody	Total Nitrogen Load (million kg/yr)	Atmospheric Nitrogen Load (million kg/yr)	Percent Load from the Atmosphere
Albemarle-Pamlico Sounds	23	9	38
Chesapeake Bay	170	36	21
Delaware Bay	54	8	15
Long Island Sound	60	12	20
Narragansett Bay	5	0.6	12
New York Bight	164	62	38
Based on ADN loads from the watershed only (excluding direct nitrogen deposition to the bay surface):			
Waquoit Bay, MA	0.022	0.0065	29
Based on ADN directly to the waterbody (excluding ADN loads from the watershed):			
Delaware Inland Bays	1.3	0.28	21
Flanders Bay, NY	0.36	0.027	7
Guadalupe Estuary, TX	4.2-15.9	0.31	2-8
Massachusetts Bays	22-30	1.6-6	5-27
Narragansett Bay	9	0.4	4
Newport River Coastal Waters, NC	0.27-0.85	0.095-0.68	>35
Potomac River, MD	35.5	1.9	5
Sarasota Bay, FL	0.6	0.16	26
Tampa Bay, FL	3.8	1.1	28

ADN = atmospheric deposition of nitrogen

Source: *Table from Deposition of Air Pollutants to the Great Waters-3rd Report to Congress (U.S. Environmental Protection Agency, 2000b).

**TABLE AX2.11-2. NATURAL AND ANTHROPOGENIC SOURCES OF
ATMOSPHERIC NITROGEN COMPOUNDS (THE MAJOR CHEMICAL FORMS
OF ATMOSPHERIC NITROGEN COMPOUNDS ARE THE REDUCED, OXIDIZED,
AND ORGANIC FORMS)**

Chemical Form	Sources (in approximate order of importance)
Reduced Nitrogen Ammonia/Ammonium (NH ₃ , NH ₄ ⁺)	Agricultural Livestock waste (volatilized NH ₃) Chemical fertilizers (volatilized NH ₃) Biomass burning Dust from deforestation and land clearing Urban and Rural (non-agricultural) Wastewater treatment (volatilized NH ₃) Fossil fuel combustion (from automobile catalytic converters) Natural Biomass burning (forest and grass fire) Decomposition of organic matter Dust and aerosols Volcanism
Oxidized Nitrogen Nitrogen Oxides (NO, NO ₂ , NO ₃)	Urban and Rural (non-agricultural) Fossil fuel combustion Mobile & stationary engines Powerplants and industrial Natural Biomass burning Lightning Photolysis of N ₂ O (air, land, water) Dust and aerosols generated by storms Microbially mediated volatilization
Organic Nitrogen (Dissolved and Particulate)	Agricultural Dust and volatilization of wastes ?? Urban and Rural (non-agricultural) Dust or aerosols ?? Natural Atmospheric photochemical and lighting Biological production in oceans ??

?? = possible, but little known about sources

Source: Swackhamer et al. (2004).

TABLE AX2.11-3. CHARACTERISTICS OF OXIDIZED-NITROGEN AIRSHEDS

Watershed	Size (km ²)	Size Factor Over Watershed Area	% Ox-N Deposition Explained	Airshed NO _x Emissions	
				as % of E. North America	Efficiency of Deposition % dep. per % emiss.
Casco Bay	624,000	244	47	10	4.7
Great Bay	547,000	214	60	13	4.6
Narragansett Bay	595,200	138	73	18	4.1
Long Island Sound	905,600	22	70	23	3.0
Hudson/Raritan Bay	912,000	22	62	25	2.5
Barnegat Bay	505,600	361	67	16	4.2
Delaware Bay	729,600	22	75	26	2.9
Delaware Inland Bays	326,400	584	52	12	4.3
Chesapeake Bay	1,081,600	6.5	76	34	2.2
Pamlico Sound	665,600	25	63	18	3.5
Winyah Bay	886,400	19	69	24	2.9
Charleston Harbor	806,400	20	56	18	3.1
St. Helena Sound	588,800	48	59	11	5.4
Altamaha	678,400	18	68	13	5.2
Tampa Bay	256,000	45	76	5	15.2
Apalachee Bay	441,600	31	50	9	5.6
Apalachicola Bay	812,800	16	69	17	4.1
Mobile Bay	992,000	8.7	68	17	4.0
Lake Pontchartrain	659,200	17	63	11	5.7
Barataria-Terrebonne	409,600	55	63	8	7.9

Source: <http://www.epa.gov/AMD/Multimedia/characteristicsTable.html>; table generated by Robin Dennis, NOAA/USEPA.

**TABLE AX2.11-4. CHARACTERISTICS OF PRINCIPAL AIRSHEDS FOR
REDUCED-NITROGEN DEPOSITION**

Watershed	Principal Red-N Airshed Area (km²)	Red-N Area as % of OX-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH₃ Emission as % of E. North American Emissions
Chesapeake Bay	668,000	64%	55%	11%
Pamlico Sound	406,000	61%	60%	6.8%
Apalachee Bay	310,000	70%	45-50% est.	4.3%

Source: <http://www.epa.gov/AMD/Multimedia/reducedTable.html>; table generated by Robin Dennis, NOAA-ARL/USEPA-NERL.

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AX3. ECOSYSTEM MONITORING AND MODELS

AX3.1 INTRODUCTION

A tremendous amount of research has been conducted in the United States, and elsewhere, over the past three decades on the ways in which atmospheric deposition of sulfur (S) and nitrogen (N) affect the health, condition, and vitality of aquatic, transitional, and terrestrial ecosystems. Much of this work has focused on developing a better understanding of acidification and nutrient enrichment processes. Some of this work has been highly quantitative, allowing researchers to determine key process rates in multiple ecosystem compartments. Nevertheless, quantification of overall ecosystem response requires a higher level of process rate aggregation. It is important to develop quantitative understanding of the extent of past ecosystem effects in response to atmospheric S and N deposition, the extent to which conditions will worsen or recover under continued or reduced deposition levels, and the sustained loads of deposition that would be required to prevent further ecosystem damage and to allow damaged ecosystems to recover. This kind of quantitative understanding cannot evolve directly out of process-based research. It requires development of mathematical models that encode process knowledge and link it in such a way as to produce quantitative estimates of change in resource conditions over time in response to changes in the major forcing functions, including atmospheric deposition, climate, and landscape disturbance. As described in this annex, many such models have been developed and used to estimate past and future changes in ecosystem condition. Such models cannot be validated, *per se*, because environmental systems are never closed and because important processes yield conflicting, often opposing, results. Therefore, a model can produce the right answer for the wrong reason (Oreskes et al., 1994). Similarly, a particular process may not be important at a particular site where a model is tested, but assume much greater importance elsewhere. For these reasons, it is critical that environmental models be tested and confirmed at multiple locations that exhibit differing conditions and pollutant loads before they are used as the foundation for public policy (Sullivan, 2000).

Some of the best data with which to test and confirm environmental models are derived from long-term monitoring sites. These are locations where one or more attributes of a natural ecosystem compartment (i.e., surface water, soil, plants) is periodically sampled and analyzed

1 over a long period of time. Such data are often especially valuable for sites which experience
2 rather large changes in one of the forcing functions (often atmospheric deposition). This enables
3 evaluation of the extent to which the model accurately captures the dynamics of ecosystem
4 response(s) that occur. Because many environmental attributes undergo rather substantial intra-
5 and inter-annual variability in response to climatic variation and other changes, a long period of
6 record is required before a monitoring data set can be used for evaluation of ecosystem response
7 or for model confirmation.

8 Long-term monitoring data provide not only data with which to test model projections,
9 but also a reality check on scientific understanding of damage and recovery processes. If
10 observed (monitored) changes are not in agreement with process understanding, it is possible or
11 perhaps likely that one or more key processes is not well-understood or well-formulated in the
12 model.

13 This annex summarizes the primary long-term monitoring sites and programs in the
14 United States, and the principal mathematical models used to simulate environmental responses
15 to atmospheric S and N deposition. Quantitative data derived from the model projections and
16 from trends analyses of the monitoring data provide an important part of the foundation for
17 evaluating the past, current, and future effects of S and N deposition, and expected recovery as
18 emissions levels decrease in the future.

19 20 21 **AX3.2 ECOSYSTEM MONITORING**

22 The effects of acidic and N nutrient deposition on ecosystems require long-term study.
23 Changes in ecosystems often occur gradually, and sustained monitoring of key variables
24 provides the principal record of change over time. Monitoring data are also useful for
25 establishing a baseline of resource conditions and determining if short-term events were unusual
26 or extreme (Lovett et al., 2007). There are limited monitoring programs and data to document
27 ecosystem responses to changes in atmospheric deposition in the past. It is often difficult to
28 sustain funding for ecosystem monitoring, perhaps because results are produced slowly and
29 because results are seldom viewed as novel. Nevertheless, monitoring data provide some of the
30 best means for evaluating the completeness of the scientific knowledge base and for testing how
31 robust our projections of future conditions might be. This section describes some of the more

1 important and useful monitoring programs for evaluating the effects of N and S deposition on
2 ecosystems in the United States.

3 There are long-term monitoring sites scattered throughout the United States where
4 samples are periodically collected and analyzed to determine the condition of aquatic,
5 transitional, or terrestrial ecosystem elements. Some have been in operation for only a short
6 period of time; others have continued for decades. None extend back far enough to have
7 documented resource conditions prior to the advent of high levels of atmospheric S and N
8 deposition. Some of the monitoring sites exist as an individual entity, or small collection of
9 sites, often established primarily for research purposes. Despite the research focus, many of
10 these long-term research sites include collection of monitoring data. Other long-term monitoring
11 sites exist as part of large regional programs with a specific focus on long-term monitoring. The
12 most significant individual monitoring sites and networks are discussed below.

13 Lovett et al. (2007) reviewed the characteristics of successful environmental monitoring
14 programs, and argued that monitoring is a fundamental part of environmental science and policy.
15 Their analysis underscored the fact that environmental monitoring costs little relative to the value
16 of the resources that it protects and the policy that it informs. Monitoring data also have
17 substantial added value because they can be used for multiple purposes, including various
18 research objectives.

19 Ecosystems also require long-term study because most changes occur slowly. When
20 more rapid change does occur, for example in response to an extreme event, a long-term record
21 is needed to put the effects of the extreme event into proper context.

22

23 **AX3.2.1 Major U.S. Environmental Protection Agency Monitoring** 24 **Programs**

25

26 **AX3.2.1.1 Environmental Monitoring and Assessment Program**

27 The EPA Environmental Monitoring and Assessment Program (EMAP) began regional
28 surveys of the nation's surface waters in 1991 with a survey of Northeastern U.S. lakes. Since
29 then, EMAP and Regional-EMAP (REMAP) surveys have been conducted on lakes and streams
30 throughout the country. The objective of these EMAP surveys is to characterize ecological
31 condition across populations of surface waters. EMAP surveys are probability surveys where
32 sites are picked using a spatially balanced systematic randomized sample so that the results can

1 be used to make estimates of regional extent of condition (e.g., number of lakes, length of
2 stream). EMAP sampling typically consists of measures of aquatic biota (fish,
3 macroinvertebrates, zooplankton, and periphyton), water chemistry, and physical habitat.

4 Of particular interest with respect to acidic deposition effects were two EMAP surveys
5 conducted in the 1990s, the Northeastern Lake Survey and the Mid-Atlantic Highlands
6 Assessment of streams (MAHA). The Northeastern Lake Survey was conducted in summer from
7 1991 to 1994 and consisted of 345 randomly selected lakes in the states of New York, New
8 Jersey, Vermont, New Hampshire, Maine, Rhode Island, Connecticut, and Massachusetts
9 (Whittier et al., 2002). To make more precise estimates of the effects of acidic deposition, the
10 sampling grid was intensified to increase the sample site density in the Adirondacks and New
11 England Uplands areas known to be susceptible to acidic deposition. The MAHA study was
12 conducted on 503 stream sites from 1993 to 1995 in the states of West Virginia, Virginia,
13 Pennsylvania, Maryland, Delaware, and the Catskill Mountain region of New York (Herlihy
14 et al., 2000). Sampling was done during spring baseflow. Sample sites were restricted to first
15 through third order streams as depicted on the USGS 1:100,000 digital maps used in site
16 selection. To make more precise estimates of the effects of acidic deposition, the sampling grid
17 was intensified to increase the sample site density in the Blue Ridge, Appalachian Plateau, and
18 Ridge section of the Valley and Ridge ecoregions. Results from both of these surveys were used
19 to develop and select the sampling sites for the Temporally Integrated Monitoring of Ecosystems
20 (TIME) program, which is described below.

21 22 **AX3.2.1.2 Temporally Integrated Monitoring of Ecosystems (TIME) and Long-Term** 23 **Monitoring (LTM) Programs**

24 There are two surface water chemistry monitoring programs, administered by EPA, that
25 are especially important to inform the assessment of aquatic ecosystem responses to changes in
26 atmospheric deposition. These are the TIME program (Stoddard et al., 2003) and the Long-term
27 Monitoring (LTM) program (Ford et al., 1993; Stoddard et al., 1998a). These efforts focus on
28 portions of the United States most affected by the acidifying influence of S and N deposition,
29 including lakes in the Adirondack Mountains of New York and in New England, and streams in
30 the Northern Appalachian Plateau and Blue Ridge in Virginia and West Virginia. Both projects
31 are operated cooperatively with numerous collaborators in state agencies, academic institutions
32 and other federal agencies. The TIME and LTM projects have slightly different objectives and

1 structures, which are outlined below. Stoddard et al. (2003) conducted a thorough trends
2 analysis of the TIME and LTM data.

3
4 **AX3.2.1.2.1 TIME Project**

5 At the core of the TIME project is the concept of probability sampling, whereby each
6 sampling site is chosen statistically from a pre-defined target population. Collectively, the
7 monitoring data collected at the sites are representative of the target population of lakes or
8 streams in each study region (Figure AX3.2-1). The target populations in these regions include
9 lakes and streams likely to be responsive to changes in acidic deposition, defined in terms of acid
10 neutralizing capacity (ANC), which represents an estimate of the ability of water to buffer acid.
11 It can be either calculated (calculated ANC = sum of base cations – sum of mineral acid anions,
12 where all concentrations are in $\mu\text{eq/L}$) or titrated in the laboratory (Gran ANC). Measurement of
13 Gran ANC uses the Gran technique to find the inflection point in an acid-base titration of a water
14 sample (Gran, 1952). In the Northeast, the TIME target population consists of lakes with a Gran
15 ANC less than 100 $\mu\text{eq/L}$. In the Mid-Atlantic, the target population is upland streams with
16 Gran ANC less than 100 $\mu\text{eq/L}$. In both regions, the sample sites selected for future monitoring
17 were selected from the EMAP survey sites in the region (section AX3.2.1.1) that met the TIME
18 target population definition.

19 Each lake or stream is sampled annually (in summer for lakes; in spring for streams), and
20 results are extrapolated with known confidence to the target population(s) as a whole using the
21 EMAP site population expansion factors or weights (Larsen and Urquhart, 1993; Larsen et al.,
22 1994; Stoddard et al., 1996; Urquhart et al., 1998). TIME sites were selected using the methods
23 developed by the EMAP (Paulsen et al., 1991; Herlihy et al., 2000). The TIME project began
24 sampling northeastern lakes in 1991. Data from 43 Adirondack lakes can be extrapolated to the
25 target population of low ANC lakes in that region. There are about 1,000 low-ANC Adirondack
26 lakes, out of a total population of 1830 lakes with surface area greater than 1 ha. Data from 30
27 lakes (representing about 1,500 low-ANC lakes, out of a total population of 6,800) form the basis
28 for TIME monitoring in New England. Probability monitoring of Mid-Atlantic streams began in
29 1993. Stoddard et al. (2003) analyzed data from 30 low-ANC streams in the Northern
30 Appalachian Plateau (representing about 24,000 km of low-ANC stream length out of a total
31 stream length of 42,000 km).

Acid-Sensitive Regions of the Eastern United States
Temporally Integrated Monitoring of Ecosystem (TIME) Sites

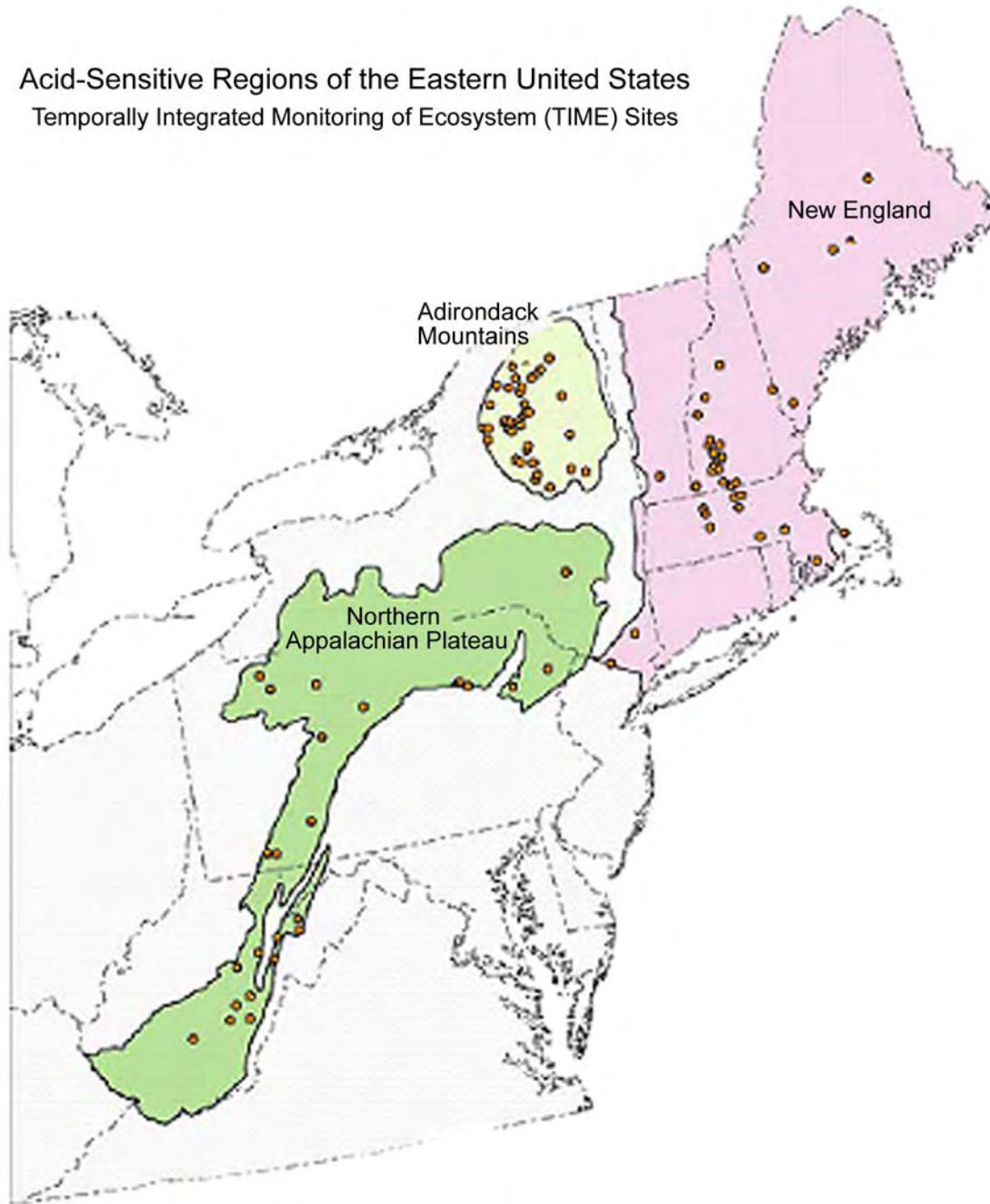


Figure AX3.2-1. Location of acid-sensitive regions of the northern and eastern U.S. for which statistical survey data are available in the 1990s, and locations of individual TIME sites used in trend analysis.

Source: Stoddard et al. (2003).

1 The initial 1993-1995 EMAP-MAHA sample in the Mid-Atlantic was not dense enough
2 to obtain enough sites in the TIME target population in the Blue Ridge and Valley and Ridge
3 ecoregions. In 1998, another denser random sample was conducted in these ecoregions to
4 identify more TIME sites. After pooling TIME target sites taken from both MAHA and the 1998
5 survey, there are now 21 TIME sites in the Blue Ridge and Ridge and Valley that can be used for
6 trend detection in this aggregate ecoregion in the Mid-Atlantic in addition to the Northern
7 Appalachian Plateau ecoregion.

8 9 **AX3.2.1.2.2 *Long-Term Monitoring Project***

10 As a complement to the statistical lake and stream sampling in TIME, the LTM project
11 samples a subset of generally acid-sensitive lakes and streams that have long-term data, many
12 dating back to the early 1980s (Figure AX3.2-2). These sites are sampled 3 to 15 times per year.
13 This information is used to characterize how some of the most sensitive of aquatic systems in
14 each region are responding to changing deposition, as well as giving information on seasonal
15 variation in water chemistry. In most regions, a small number of higher-ANC (e.g., Gran ANC
16 greater than 100 $\mu\text{eq/L}$) sites are also sampled, and help separate temporal changes due to acidic
17 deposition from those attributable to other disturbances (e.g., climate, land use change). Because
18 of the availability of long-term records (more than two decades) at many LTM sites, their trends
19 can also be placed in a better historical context than those of the TIME sites, where data are only
20 available starting in the 1990s.

21 Monitored water chemistry variables include pH, ANC, major anions and cations,
22 monomeric aluminum (Al), silicon (Si), specific conductance, dissolved organic carbon (DOC),
23 and dissolved inorganic carbon (DIC). The field protocols, laboratory methods, and quality
24 assurance procedures are specific to each team of investigators. This information is contained in
25 the cited publications of each research group. The EMAP and TIME protocols and quality
26 assurance methods are generally consistent with those of the LTM cooperators. Details of LTM
27 data from each region are given below.

28 New England lakes: The LTM project collects quarterly data from lakes in Maine
29 (sampled by the University of Maine; Kahl et al., 1991; Kahl et al., 1993) and Vermont (data
30 collected by the Vermont Department of Environmental Conservation; Stoddard and Kellogg,
31 1993; Stoddard et al., 1998b). Data from 24 New England lakes were available for the trend
32 analysis reported by Stoddard et al. (2003) for the time period 1990 to 2000. In addition to

Acid-Sensitive Regions of the Northern and Eastern United States
Long-Term Monitoring (LTM) Sites

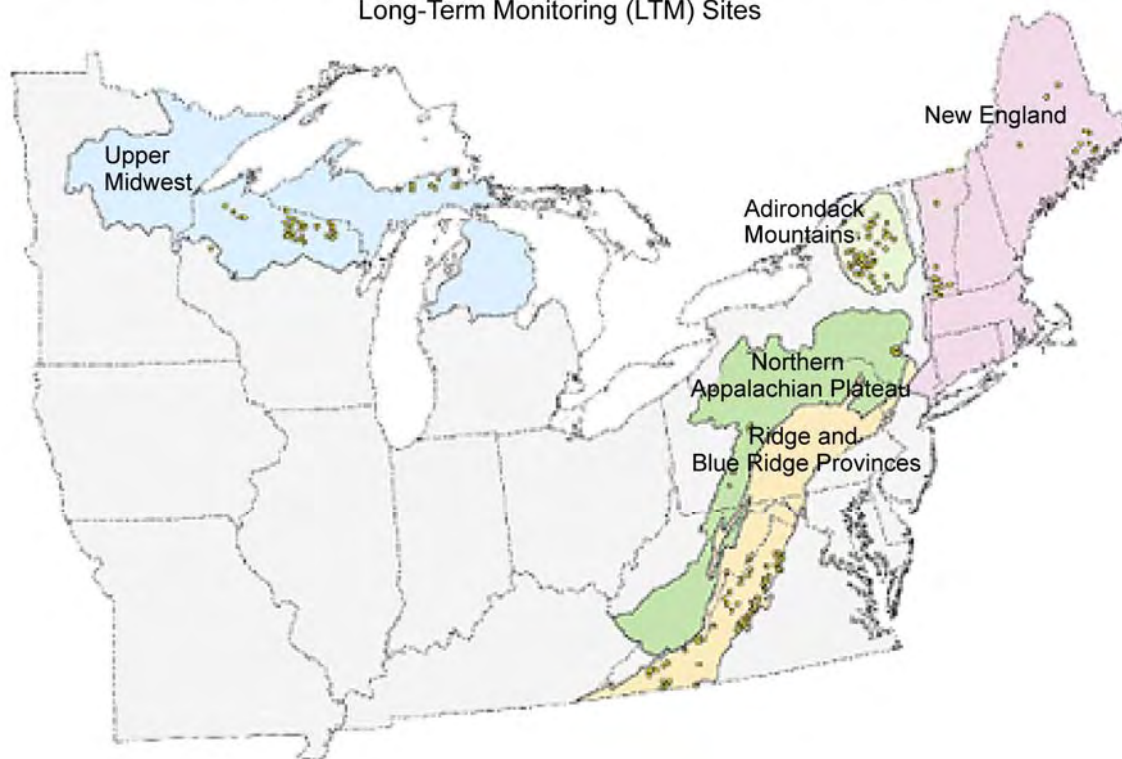


Figure AX3.2-2. Location LTM sites used in the 2003 Surface Water report.

Source: Stoddard et al. (2003).

1 quarterly samples, a subset of these lakes have outlet samples collected on a weekly basis during
2 the snowmelt season; these data are used to characterize variation in spring chemistry. The
3 majority of New England LTM lakes have mean Gran ANC values ranging from -20 to
4 100 $\mu\text{eq/L}$; two higher ANC lakes (Gran ANC between 100 and 200 $\mu\text{eq/L}$) are also monitored.
5 Adirondack lakes: The trend analysis of Stoddard et al. (2003) included data from 48
6 Adirondack lakes, sampled monthly by the Adirondack Lake Survey Corporation (Driscoll and
7 Van Dreason, 1993; Driscoll et al., 1995); a subset of these lakes are sampled weekly during
8 spring snowmelt to help characterize spring season variability. Sixteen of the lakes have been
9 monitored since the early 1980s; the others were added to the program in the 1990s. The
10 Adirondack LTM dataset includes both seepage and drainage lakes, most with Gran ANC values

1 in the range –50 to 100 µeq/L; three lakes with Gran ANC between 100 µeq/L and 200 µeq/L are
2 also monitored.

3 Appalachian Plateau streams: Stream sampling in the Northern Appalachian Plateau is
4 conducted about 15 times per year, with the samples spread evenly between baseflow (e.g.,
5 summer and fall) and high flow (e.g., spring) seasons. Data from four streams in the Catskill
6 Mountains (collected by the U.S. Geological Survey; Murdoch and Stoddard, 1993), and five
7 streams in Pennsylvania (collected by Pennsylvania State University; DeWalle and Swistock,
8 1994) were analyzed by Stoddard et al. (2003). All of the Northern Appalachian LTM streams
9 have mean Gran ANC values in the range –25 to 50 µeq/L.

10 Upper Midwest lakes: Forty lakes in the Upper Midwest were originally included in the
11 LTM project, but funding in this region was terminated in 1995. The Wisconsin Department of
12 Natural Resources (funded by the Wisconsin Acid Deposition Research Council, the Wisconsin
13 Utilities Association, the Electric Power Research Institute and the Wisconsin Department of
14 Natural Resources) has continued limited sampling of a subset of these lakes, as well as carrying
15 out additional sampling of an independent subset of seepage lakes in the state. The data reported
16 by Stoddard et al. (2003) included 16 lakes (both drainage and seepage) sampled quarterly
17 (Webster et al., 1993), and 22 seepage lakes sampled annually in the 1990s. All of the Upper
18 Midwest LTM lakes exhibit mean Gran ANC values from –30 to 80 µeq/L.

19 Ridge/Blue Ridge streams: Data from the Ridge and Blue Ridge provinces consist of a
20 large number of streams sampled quarterly throughout the 1990s as part of the Virginia Trout
21 Stream Sensitivity Study (Webb et al., 1989), and a small number of streams sampled more
22 intensively (as in the Northern Appalachian Plateau). A total of 69 streams, all located in the
23 Ridge section of the Ridge and Valley province, or within the Blue Ridge province, and all
24 within the state of Virginia, had sufficient data for the trend analyses by Stoddard et al. (2003).
25 The data are collected cooperatively with the University of Virginia and the National Park
26 Service. Mean Gran ANC values for the Ridge and Blue Ridge data range from –15 to
27 200 µeq/L, with 7 of the 69 sites exhibiting mean Gran ANC greater than 100 µeq/L.

28

29 **AX3.2.2 Forest Inventory and Analysis Program of USDA Forest Service**

30 The USDA Forest Service’s Forest Inventory and Analysis (FIA) program authority is
31 mandated under the Forest and Rangeland Renewable Resources Research Act of 1978

1 (PL 95-307). Earlier, the program was known as the Forest Survey and has been run
2 continuously since the 1930s. The FIA Program collects, analyzes, and reports information on
3 the status and trends of America's forests: how much forest exists, where it exists, who owns it,
4 and how it is changing, as well as how the trees and other forest vegetation are growing and how
5 much has died or has been removed in recent years. (See <http://www.fia.fs.fed.us> for more
6 information).

7 Currently, FIA plots are divided into three phases. Phase 1 establishes approximately
8 three million samples via remote sensing (aerial photographs, digital orthoquads, and satellite
9 imagery). These samples are used to classify land as forest or nonforest. As defined by the U.S.
10 Forest Service, forest land is any land ≥ 1 acre in size that is at least 10% stocked by forest trees
11 of any size. Phase 2 establishes a subset of the Phase 1 plots for ground sampling, approximately
12 one field sample site for every 6,000 acres for a total of about 125,000 plots. The forest
13 characteristics measured include forest type, site attributes, tree species, tree size, and overall
14 tree condition. Phase 3 plots are the Forest Health Monitoring (FHM) plots, and are a subset of
15 Phase 2 plots. Phase 2 and Phase 3 plots are remeasured every 5 years. Each year, different
16 plots are sampled within defined regions, so that statistical trends for the overall region can be
17 developed on an annual basis.

18 Phase 2 measurements consist primarily of basic vegetation measurements and general
19 site description. From these measurements information is obtained on tree diameter, tree length,
20 tree quality for use as lumber, tree damage, stocking and seedling and sapling counts.

21 Approximately one of every 16 Phase 2 plots is measured for forest health attributes in
22 addition to Phase 2 attribute measurements. These plots are known as Phase 3 plots. There is
23 approximately one Phase 3 plot for every 96,000 acres, for a total of roughly 7,800 plots.
24 Measurements for Phase 3 plots include tree crown conditions, lichen community composition,
25 understory vegetation, down woody debris, and soil attributes. Ozone injury to vegetation is also
26 monitored at some Phase 3 plots. Comprehensive reviews of the FIA sampling strategy may be
27 found in Brand et al. (2000) and McRoberts et al. (2004). Goodale et al. (2002) used FIA data to
28 generate estimates of carbon sequestration in forest ecosystems in the United States in 1990 and
29 1991. The home page for the National FIA program can be found at: <http://fia.fs.fed.us/>.

1 **AX3.2.2.1 Lichens**

2 Lichens are organisms consisting of both fungi and algae. Lichens are very responsive to
3 environmental stressors in forests, including changes in forest structure, air quality, and climate.
4 Many studies have documented the close relationship between lichen communities and air
5 pollution, especially SO₂ and acidifying or fertilizing N- and S-based pollutants. The
6 composition of an epiphytic lichen community is one of the best biological indicators of air
7 pollution in forests, because epiphytic lichens rely totally on atmospheric sources of nutrition.

8 In several studies (e.g., Muir and McCune, 1988), lichens have given much clearer
9 responses to N and S pollutants (in terms of diversity, total abundance, and community
10 composition) than either leaf symptoms or tree growth, and have been one of the few
11 components of terrestrial ecosystems to show a clear relationship to gradients of acidic
12 deposition in the eastern United States.

13 Although trees may respond to moderate, chronic levels of air pollution deposition, all of
14 the other influences on tree growth, such as variation in soils, make the responses of trees to
15 pollutants difficult to measure in the field. Epiphytic lichens may be used to assess potential air
16 quality impacts on forest ecosystem health and productivity that are difficult to measure directly.
17 Long-term observation of lichen community change provides early indication of improving or
18 deteriorating air quality. Epiphytic lichens also have important biological roles in many forests,
19 including nitrogen fixation, food for animals (deer, caribou, voles, and flying squirrels), and
20 nesting material for small mammals and birds. Typically, 10 to 50 lichen species per FIA plot.

21 Lichen community information contributes to the investigation of several key forest
22 ecosystem concerns: the contamination of natural resources, biodiversity, and
23 productivity/sustainability. Lichen community data are collected by personnel that receive FIA
24 training on field procedures at the beginning of each field season. They are trained to observe
25 the presence or absence of lichen species, to estimate the abundance of each species, and to
26 collect lichen specimens for identification by a specialist, a lichenologist. Identifications by the
27 lichenologist are part of quality assurance and quality control procedures. Errors are further
28 minimized by audits of the field. The method has two parts that are performed simultaneously.
29 (1) In each standard 0.38 ha FIA plot (see [http://www.fia.fs.fed.us/library/field-guides-methods-
30 proc/docs/2006/p3_3-0_sec10_10_2005.pdf](http://www.fia.fs.fed.us/library/field-guides-methods-proc/docs/2006/p3_3-0_sec10_10_2005.pdf) for plot design and field methods) the field crew
31 searches for macrolichens on woody plants and collects samples of each lichen believed to be a

1 distinct species. Tree and shrub bases below 0.5 m are excluded from sampling. Lichens on
2 fallen branches and other lichen litter may be included. Given the large plot area, fallen branches
3 typically provide an excellent sample of the canopy lichens. The collection represents the
4 species diversity of macrolichens in the plot as fully as possible, with a maximum time limit of
5 2 hours. (2) The field crew estimates the abundance of each species using a four-step scale:
6 1 = rare (<3 individuals in plot); 2 = uncommon (4-10 individuals in plot); 3 = common (>10
7 individuals in plot but less than half of the boles and branches have that species present); and
8 4 = abundant (more than half of boles and branches in the plot have the subject species present).
9 As plots are finished, specimens are sent to specialists for identification. Note that the field crew
10 need not accurately assign species names to the lichens, but must be able to distinguish among
11 species, and be able to estimate abundances accurately.

12 Two procedures are used for constructing plot-level indices: (1) Species richness: A
13 component of diversity, species richness is the total number of epiphytic macrolichen species
14 found in the lichen plot. (2) Community gradients: The dominant gradients across the region are
15 determined using accepted statistical methods. Relationships of these gradients to forest
16 structure, climate and air quality are then analyzed. Scores for air quality and climate are
17 calculated for each plot and are used to answer questions about air quality and forest
18 productivity/sustainability and biodiversity. Data and more information FIA lichen surveys can
19 be found at: <http://fia.fs.fed.us/lichen/>.

20 The lichen community indicator was developed in the Southeast in 1990-93 by Bruce
21 McCune and Jonathan Dey, funded jointly by EPA and the USDA Forest Service (EMAP
22 Program). Forest Health Monitoring (FHM) pilot projects were run in 1994-96 in a variety of
23 eastern states and Colorado, Oregon, Washington and California in the west. The lichen
24 community indicator was included in regular permanent plot surveys starting in 1997 (FHM
25 1997-1999, FIA after 1999). Regional gradient models have been developed for the southeast
26 (1994), the northeast (1997), and Colorado (1998), and are being developed for the Midatlantic
27 States (1999-2000) the Pacific Northwest (2001), and California (2003). Lichen communities
28 are now a Phase 3 indicator in the Forest Inventory and Analysis Program (FIA).

29 30 **AX3.2.2.2 Soil Quality**

31 Another type of forest health data that the FIA program collects on their Phase 3 plots is
32 Soil Quality. The FIA program began consistent sampling related to the Soil Quality Indicator in

1 2001. The Soil Quality Indicator collects information through field measurements on Forest
2 Inventory and Analysis (FIA) sample plots and laboratory analyses. Soil condition indicators
3 such as erosion, compaction, and soil chemistry are monitored over time and used to demonstrate
4 trends. Details of the Soil Quality measurements of FIA can be found here: [http://nrs.fs.fed.us/
5 fia/topics/soils/](http://nrs.fs.fed.us/fia/topics/soils/).

6 FIA field personnel collect soil data during the Phase 3 field season, which begins in
7 early June and ends in September. Soil samples are sent to the laboratory immediately after
8 collection where they are stabilized by air drying. Laboratory analyses are conducted throughout
9 the fall and winter following the field season. On-plot measurements include soil compaction
10 and bare soil observations. Soil compaction, the percentage of the soil surface exhibiting
11 evidence of soil compaction as well as the type of compaction, is measured by ocular estimation.
12 The relative amount of bare soil is also estimated. Field measurements related to erosion and
13 compaction estimates are made on all four subplots on the Phase 3 field plot. Soil samples are
14 collected on FIA sample plots along soil sampling lines adjacent to subplots 2, 3, and 4. Soils
15 are collected if the soil sampling location is in a forested condition. A total of five samples are
16 collected on each plot (three forest floor, two mineral soil). The entire forest floor layer is
17 sampled from a known area after measuring the thickness of the litter and duff layers at the
18 north, south, east, and west edges of a 12-inch diameter sampling frame. Only organic material
19 that is < one-fourth-inch diameter is collected; rocks and larger woody materials are discarded
20 prior to collection.

21 Once the forest floor has been removed, mineral and organic soils are sampled
22 volumetrically by collecting cores from two depths: 0 to 4 inches and 4 to 8 inches. The texture
23 of each layer is estimated in the field and characterized as organic, loamy, clayey, sandy, or
24 coarse sandy. Following soil sampling, the depth to any restrictive horizon within the top 20
25 inches is estimated using a soil probe. Soil samples are mailed to the regional laboratory for
26 physical and chemical analysis.

27 In the lab, mineral soil samples collected from FIA plots are analyzed for a suite of
28 physical and chemical properties including:

- 29 • Bulk density, water content, and coarse fragment (>2-mm) content
- 30 • pH (water and 0.01 M CaCl₂)
- 31 • Total carbon

- 1 • Total inorganic carbon (carbonates) (pH > 7.5 soils only)
- 2 • Total nitrogen
- 3 • Exchangeable cations (Na, K, Mg, Ca, Al, Mn)
- 4 • Extractable sulfur and trace metals (Sr, Ba, Mn, Ni, Cu, Zn, Cd, Pb)
- 5 • Extractable phosphorus (Bray 1 method for pH < 6 soils, Olsen method for pH > 6
- 6 soils)

7 Forest floor and litter samples are analyzed for:

- 8 • Bulk density and water content
- 9 • Total carbon
- 10 • Total nitrogen

11 Soil chemical and physical properties can be highly variable in the field and are
12 expensive to analyze. As a result, interpretation of soil chemical data is confounded by spatial
13 variability within the plot. In addition, depending upon the soil type, both the number of samples
14 and the methods used in collecting these samples may vary between plots, complicating
15 compilation and estimation procedures. Finally, soil samples reflect conditions only in the forest
16 floor and upper 20 cm of the soil. In many systems, the upper portion of the soil profile is likely
17 to be more responsive to disturbance, providing a useful index for monitoring changes in soil
18 properties over time.

19

20 **AX3.2.3 Major U.S. Geological Survey Monitoring Programs**

21

22 **AX3.2.3.1 National Water Quality Assessment (NAWQA) Program**

23 The NAWQA Program was created in 1991 by the USGS to assess the nation's water
24 quality in 51 study units defined primarily by major drainage divides. These study units
25 comprise approximately 50% of the conterminous United States. The major objectives of the
26 program are to determine (1) the condition of the nation's streams, rivers, and ground water, (2)
27 whether these conditions are changing over time, and (3) how these conditions are affected by
28 natural features and human activities.

29 The major priority of the NAWQA Program since its inception has been on watersheds
30 that have experienced impacts from agriculture and various forms of development. The location
31 of sites, sampling frequency, and types of measurements taken, all reflect this priority. Each

1 study unit runs on a 9-year cycle, with approximately one-third of the study units beginning the
2 cycle every 3 years. Each 9-year cycle is comprised of 3 years of intensive data collection and
3 6 years of low-level assessment. Three types of sampling sites are established within each study
4 unit: integrator sites, indicator sites, and synoptic sites. Integrator sites are located on major
5 rivers at points that drain much or all of the study unit. Indicator sites drain large fractions of the
6 study unit that are representative of a particular landscape or land use type. Some indicator sites
7 are also located to evaluate point sources of water pollution, and some are located downstream of
8 undisturbed drainages to provide reference, or background conditions. Reference indicator sites
9 are generally located too low in the drainage basin for assessment of surface water acidification.
10 Sites associated with synoptic studies are chosen for the purpose of improving spatial resolution
11 of data collection within the study unit. The strategies for site selection, sampling, and analysis
12 for synoptic sites are issue-specific and keyed to hydrologic conditions, times, and places of
13 specific interest for the targeted water quality issue.

14 During the 3-year intensive sampling period, integrator and indicator sites are sampled
15 multiple times, both on a periodic frequency and in association with high flows. The sampling
16 approach for synoptic studies varies depending on the issue of interest, but is usually done within
17 the second or third year of the intensive sampling period. During the six years of the low-level
18 assessment, sampling usually involves base-flow sampling of high priority integrator sites, and
19 possibly some sampling of indicator sites.

20 Water quality measurements vary among study units, but usually include pathogens,
21 nutrients (including N and S), trace elements, pesticides, industrial organics, suspended
22 sediment, salinity, temperature, acidity, and dissolved oxygen.

23 NAWQA studies have resulted in over 1000 reports on an extensive list of water quality
24 issues, including freshwater and marine eutrophication associated with nitrogen pollution. None
25 deal with acidification, however. Program details and access to publications can be obtained at
26 <http://water.usgs.gov/nawqa/>.

27

28 **AX3.2.3.2 Hydrologic Benchmark Network**

29 The Hydrologic Benchmark Network (HBN) was started in 1963 by the USGS and
30 gradually grew to include 57 river gauging stations and 1 lake-stage station in 39 states by 1990.
31 Most of the stations have been established at the outlet of watersheds that were virtually free of
32 human activities, located in places such as in national parks and forests, wilderness areas, or

1 nature preserves. Streamflow was initially monitored continuously at each station, and samples
2 were collected every month for water-quality analyses that included concentrations of nutrients
3 and all major ions. The frequency of water sampling at HBN stations was decreased to quarterly
4 in 1986 because of budgetary restrictions. Sampling was discontinued in October 1997, except
5 for a small study in the eastern United States that focused on the initial response of rivers to
6 decreases in industrial emissions mandated by the Clean Air Act Amendments of 1990
7 (http://www.epa.gov/oar/oaq_caa.html/).

8 All HBN watersheds were evaluated in 2002 to determine whether upstream development
9 had made them unsuitable as reference watersheds. The 36 sites that best met the network
10 criteria were selected for continued streamflow monitoring, and water sampling was reinitiated at
11 15 of those 36 sites. In 2003, 15 of the original HBN stations were equipped with refrigerated,
12 automated samplers and telemetry systems that allow program coordinators to monitor stream
13 conditions and adjust sampling frequency and capture unique stream conditions or special
14 sampling needs. The automated sampling system is designed to collect samples through a wide
15 range of flow conditions and to transmit data by satellite. About 25 water samples are collected
16 annually at each HBN water quality station and refrigerated on site until retrieved by field
17 personnel who visit the sites regularly. The most recent trends analysis was done by Clow and
18 Mast (1999) to evaluate long-term trends in stream chemistry with respect to the Clean Air Act.
19 The program is further described in a fact sheet that can be found at:
20 <http://ny.water.usgs.gov/pubs/fs/fs20053135/>.

21 22 **AX3.2.3.3 U.S. Geological Survey New York City Water Quality Network**

23 The New York District of the U.S. Geological Survey operates a water quality network
24 throughout the water supply watershed for New York City, in the Catskill Mountain region. The
25 purpose of the network is to provide stream flow and water quality data at key locations within
26 the watershed. There are currently 34 sites throughout the network at which stream flow data are
27 collected, and at thirteen of those sites stream water quality data are also collected. The water
28 quality network is composed of paired “nodes” consisting of one or more “upper nodes” that
29 provide water quality of undeveloped, forested watersheds, and “lower nodes” that provide
30 downstream water quality data that may reflect some level of development within the watershed.

31 Water quality sampling for this program began at the 13 sites in 1998-99. Water samples
32 are collected biweekly and during high flow for approximately 6 storms per year. All water

1 samples are analyzed for concentrations of nutrients and major ions. Because streams in this
2 area are also affected by acidic deposition, acid-neutralizing capacity and 3 forms of Al are also
3 measured. Further details on the program are available at: [http://ny.cf.er.usgs.gov/
4 nyc/unoono.cfm](http://ny.cf.er.usgs.gov/nyc/unoono.cfm).

5

6 **AX3.2.3.4 Catskill Long-Term Monitoring Sites**

7 Within the Catskill Mountain region of New York state, stream samples are collected and
8 stream flow is measured at three locations within the Neversink River basin, and at one site on
9 Rondout Creek. Water samples are collected biweekly and during most storms. These sites are
10 currently part of the EPA LTM program, but also are affiliated with other programs. Sampling at
11 two of the four sites began in the mid 1980s, whereas sampling at the remaining two sites began
12 in 1991. The primary purpose of these sites is to monitor effects of acidic deposition on stream
13 chemistry. The full suite of analytes needed to assess acidic deposition effects are measured on
14 these water samples.

15

16 **AX3.2.3.5 Buck Creek, Inlet, New York**

17 Stream flow and water chemistry are monitored at three locations within Buck Creek
18 watershed, in the western Adirondack Region of New York. Samples are collected biweekly and
19 during most storms at each location. Sampling began in 1998 at two sites and 2001 at the third
20 site. The full suite of analytes needed to assess acidic deposition effects is measured on these
21 water samples. Measurements of ANC and pH were also collected at one site weekly for the
22 period of 1991 to 2001 (Lawrence et al., 2004). Recent data from Buck Creek are presented in
23 Lawrence et al. (2007). Buck Creek is the only stream within the acidified region of the
24 Adirondacks where base flow and storm samples are collected in conjunction with flow
25 monitoring.

26

27 **AX3.2.4 National Science Foundation Long-Term Ecological Research 28 Network**

29 The Long-Term Ecological Research (LTER) program constitutes a loose network of 26
30 sites (Table AX3.2-1), funded by the National Science Foundation (NSF). There is increasing
31 concern over such globally significant problems as loss of biodiversity, climate change,
32 destruction of forests, depletion of stratospheric ozone, regional air and water pollution, and soil

1 erosion. The research conducted at the various LTER sites has examined and continues to
2 examine aspects of these problems and provides scientific information which has been invaluable
3 in the formation of public policy. Site locations and research activities are summarized in Table
4 AX3.2-1. A few of the sites that have been used most extensively for evaluation of long-term
5 effects of nitrogen and sulfur deposition are discussed in greater detail below.

6 7 **AX3.2.4.1 Hubbard Brook Experimental Forest**

8 The Hubbard Brook Ecosystem Study (HBES) at Hubbard Brook Experimental Forest
9 (HBEF) is the longest-running precipitation and stream chemistry (1963 to present) monitoring
10 program in the United States (see <http://www.hubbardbrook.org>). HBEF was established in
11 1955 as a major center for hydrologic research in New England. The site is located within the
12 boundaries of the White Mountain National Forest in central New Hampshire. The 3138-ha,
13 bowl-shaped valley has hilly terrain, ranging from 222 to 1015 m elevation. The HBES
14 originated in 1960 with the intention of applying the small watershed approach to the study of
15 element fluxes and cycles. The goal of the study is to develop a better understanding of
16 ecological patterns and processes that characterize the northern forest in eastern North America,
17 and its response to both natural and human disturbances. In 1987, HBEF joined the NSF's
18 LTER network (<http://www.lternet.edu>). Hubbard Brook is renowned for its long-term record of
19 measurements, landscape-scale experiments of whole watersheds, and the involvement of
20 scientists from diverse disciplines and institutions.

21 The HBEF is entirely forested, mainly with deciduous northern hardwoods: sugar maple
22 (*Acer saccharum*), beech (*Fagus grandifolia*), and yellow birch (*Betula allegheniensis*), and
23 some white ash (*Fraxinus americana*) on the lower and middle slopes. Other less abundant
24 species include mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), and
25 trembling aspen (*Populus tremuloides*). Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*),
26 and white birch (*Betula papyrifera* var. *cordifolia*) are abundant at higher elevations and on rock
27 outcrops. Hemlock (*Tsuga canadensis*) is found along the main Hubbard Brook. Pin cherry
28 (*Prunus pensylvanica*), a shade intolerant species, dominates all sites for the first decade
29 following a major forest disturbance. Logging operations ending around 1915-1917 removed
30 large portions of the conifers and better quality, accessible hardwoods. The present second-
31 growth forest is even-aged and composed of about 80 to 90% hardwoods and 10 to 20% conifers.

1 The HBEF is an oblong basin about 8 km long by 5 km wide. Hubbard Brook is the
2 single major stream draining the basin. Numerous smaller tributary streams of varying size drain
3 into Hubbard Brook including Watershed 6 (WS-6), which is the biogeochemical reference
4 watershed.

5 One of the strengths of the HBES is the long-term monitoring program. Table AX3.2-2
6 lists the major parameters included in the HBES long-term monitoring study. The monitoring
7 data illustrate that short-term observations can be misleading and that decades of monitoring may
8 be required to detect real changes in complex ecosystems. The long-term record at the HBEF
9 provides: (1) insight into ecosystem function; (2) empirical data for testing models and
10 generating hypotheses; (3) a record of extreme or unusual events; and (4) information that is
11 relevant to regional national and global environmental issues.

12 Some of the monitoring is done on experimentally manipulated watersheds. There are
13 nine gaged watersheds at the HBEF, four of which have been treated experimentally. A tenth
14 ungauged watershed was also treated. Table AX3.2-3 includes summary data on the various
15 watersheds. Datasets for long-term monitoring can be found at [http://www.hubbardbrook.org/
16 data/dataset_search.php](http://www.hubbardbrook.org/data/dataset_search.php). The datasets most often used to examine ecosystem response to
17 ambient deposition of N and S are from WS-6 and Mirror Lake, since they have not been
18 experimentally manipulated. Watershed 6 is the biogeochemical reference catchment at HBEF
19 where monitoring began in June 1963. Measured stream chemistry parameters include major
20 anions and cations, pH, silica, dissolved organic and inorganic carbon, specific conductance,
21 dissolved oxygen, ANC, and PO₄. Stream chemistry data can be accessed at
22 [http://www.hubbardbrook.org/ data/dataset.php?id=8](http://www.hubbardbrook.org/data/dataset.php?id=8). The normal sampling interval for WS-6 is
23 weekly, with more frequent samples taken at times of increased discharge.

24 Monitoring of streamflow and water chemistry has shown that the study watersheds have
25 similar characteristics. Within each watershed there are a variety of soils, vegetation,
26 microtopographical features, and micro-climate. Nevertheless, the composition of these
27 variables seems to be similar from watershed-to-watershed. Thus, the effects of experimental
28 manipulations of watersheds can be adequately evaluated by comparison with neighboring
29 unmanipulated watersheds.

30 The most conspicuous streamflow characteristic is the seasonal shift from large volume
31 of flow in spring to very low flow in late summer and early autumn. These yearly highs and

1 lows reflect seasonal spring snowmelt that often occurs over a few days or weeks and the slow
2 progressive decrease in flow from the transpirational draft in summer, respectively. The
3 numerous streams in the HBEF range from small ephemeral channels that often dry up during
4 summer to a large perennial 5th-order stream (Hubbard Brook).

5 Mirror Lake is a 15-ha oligotrophic clearwater lake adjacent to HBEF. The lake
6 normally mixes in spring and fall, and is ice-covered from about December 1st to April 15th
7 each year. Part of the drainage to the lake originates in the Experimental Forest. The lake water
8 is dilute, slightly acidic, and quite clear, with low productivity and low concentrations of
9 nutrients in the water. Numerous studies have been conducted on Mirror Lake since the mid-
10 1960s, including extensive physical, chemical, biological, and paleoecological research (cf.
11 Likens, 1985). Data are available since 1967 for lakewater concentrations at discrete depths for
12 base cations, pH, and dissolved oxygen. Ammonium, major anions, phosphate, and dissolved
13 silica have been measured routinely since 1970, although some data are available prior to these
14 dates for each solute. Other standard monitoring data include temperature and specific
15 conductance at each depth. Prior to 1990, not all records had complete solute arrays. Since
16 1990, DIC and ANC have also been measured on a routine basis, although some prior data do
17 exist for those parameters. The usual sampling interval for Mirror Lake is four to six times each
18 year, especially at times of maximum and minimum thermal stratification. Data for Mirror Lake
19 and inlet and outlet streams can be found at: [http://www.hubbardbrook.org/data/
20 dataset_search.php](http://www.hubbardbrook.org/data/dataset_search.php).

21 The soils, vegetation, and climate at the HBEF are characteristic of the northern
22 hardwood forest complex, which spans much of the north-central and northeastern United States
23 and southeastern Canada. Streamflow and stream chemistry reflect the landscape characteristics
24 of the drainage area. Consequently, results from the relatively small watersheds at the HBEF are
25 to a first approximation representative of a much larger regional area. During the scientific
26 debate that occurred prior to passage of the Clean Air Act Amendments of 1990, the trends in
27 sulfate (SO_4^{2-}) concentrations in streamwater and precipitation at HBEF were very influential in
28 convincing scientists and policy makers that decreasing S emissions would yield large decreases
29 in the concentration of SO_4^{2-} in precipitation and streamwater in the northeastern United States
30 (Lovett et al., 2007). Monitoring data collected since 1963 (Figure AX3.2-3) played a major role
31 in development of the watershed-ecosystem concept and methods for analyzing and

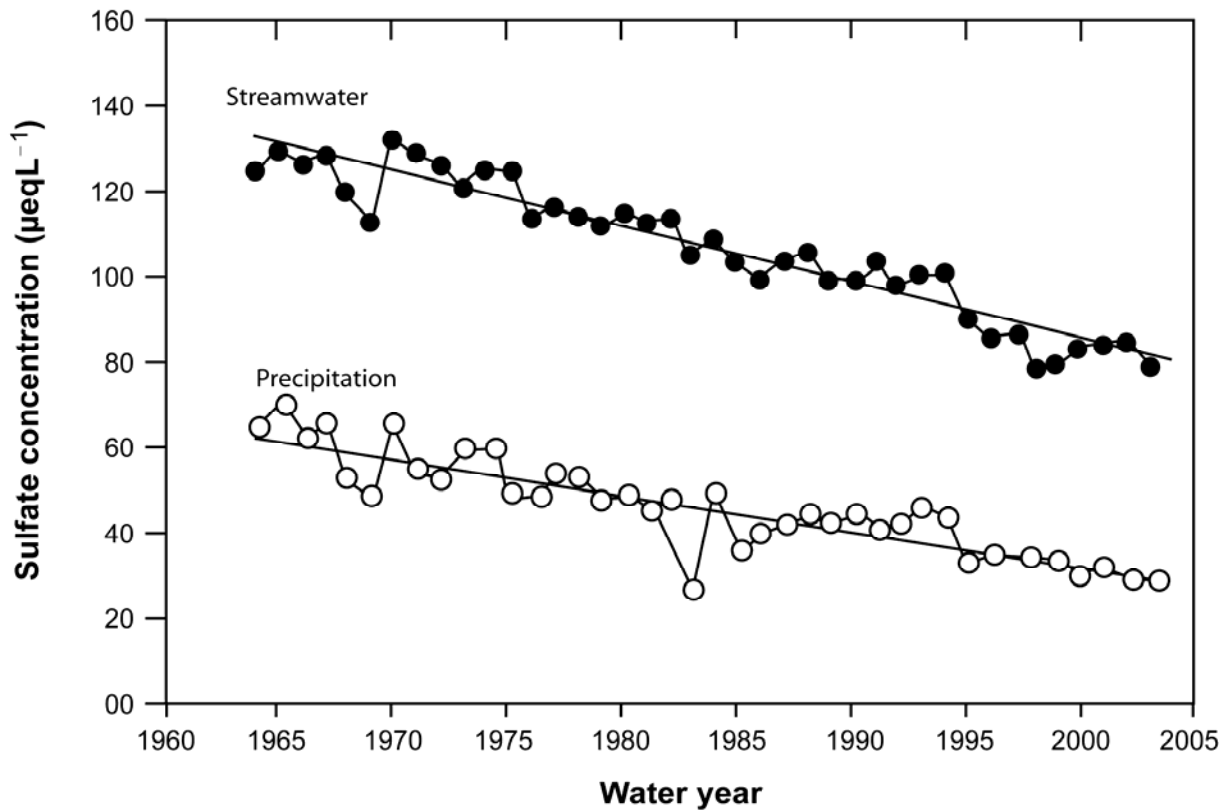


Figure AX3.2-3. Long-term record of SO₄²⁻ concentration in streamwater and precipitation at Watershed 6 of HBEF.

Source: Lovett et al. (2007); updated from Likens et al. (2002).

1 understanding watershed biogeochemical cycles (Bormann and Likens, 1967; Likens et al., 1978;
 2 Likens and Bormann, 1995; Lovett et al., 2007).

3 An extensive effort has been made to bring together some of the results of research that
 4 had been done at Hubbard Brook over the last several decades. Over the duration of the HBES
 5 there have been six books and more than 1,000 papers published. In addition, more than 500
 6 abstracts were published and more than 100 graduate theses completed. A complete list of titles
 7 is available at http://www.hubbardbrook.org/pubs/pub_search.php. To date, four synthesis
 8 volumes have been completed (Likens et al., 1977; Bormann and Likens, 1979; Likens, 1985,
 9 1992).

1 **AX3.2.4.2 Coweeta**

2 The Coweeta LTER research program (<http://coweeta.ecology.uga.edu/>) in North
3 Carolina is based in the eastern deciduous forest of the Blue Ridge Physiographic Province of the
4 southern Appalachian Mountains. The program entails long-term cooperation between the
5 University of Georgia and the USDA Forest Service Coweeta Hydrologic Laboratory. The
6 research program centers on the effects of disturbance and environmental gradients on
7 biogeochemical cycling, and the underlying watershed ecosystem processes that regulate and
8 respond to those cycles. Coweeta represents one of the longest continuous environmental studies
9 of any North American landscape.

10 The research at Coweeta focuses largely on how water, soil, and forest resources respond
11 to management practices, natural disturbances, and the atmospheric environment. It also aims to
12 identify practices that mitigate impacts on these watershed resources. Current topics of emphasis
13 include (1) analyses of long-term changes in hydrology, nutrient cycling, and productivity in
14 response to management practices and natural disturbances; (2) assessment of prescribed burning
15 effects on the forest environment; (3) interdisciplinary implementation of ecosystem
16 management on the national forests; (4) effects of climatic change on productivity; (5) impacts of
17 atmospheric deposition on forest processes and ecosystems; (6) cumulative effects of land use
18 practices on water quality; (7) physiological studies of forest carbon balance and competition;
19 and (8) biodiversity.

20 Investigators at the Coweeta Hydrologic Laboratory have recorded nitrogen dynamics of
21 streams and precipitation in mature mixed hardwood-covered watersheds since 1972. Research
22 has been conducted on responses to management practices such as clearcutting, selective cutting,
23 conversion of native hardwood to coniferous forest, and old-field succession. Reference
24 watersheds were characterized as in a transition phase between stage 0 and stage 1 of watershed
25 N saturation. Evidence for stage 3 of N saturation, where the watershed is a net source of N
26 rather than a N sink, was found for the most disturbed watershed at Coweeta.

27 The Coweeta Basin comprises 2185 hectares within the Blue Ridge geologic province in
28 North Carolina. The laboratory has been dedicated to forest hydrology research since its
29 establishment in 1933. Elevations range from 679 to 1592 m. More than 50 km of streams drain
30 the area.

1 Coweeta is the first major mountain range contacted by air masses moving over the
2 industrialized Piedmont region to the south. Analyses of precipitation chemistry have shown the
3 influence of both local and regional activities on nutrient inputs to forest ecosystems.

4 Since Coweeta was established, 32 weirs have been installed on streams. Seventeen of
5 these weirs are currently operational. Stream gauging was initiated on most watersheds between
6 1934 and 1938, and stream chemistry measurements date back to 1968.

7 Research has been conducted on eight mixed hardwood control areas and 13 catchments
8 where forest management prescriptions have been applied. Past treatments have included
9 varying intensities of cutting, ranging from light selection through clear-cutting; conversion of
10 hardwoods to grass and subsequent succession to hardwoods; multiple-use management;
11 mountain farming; and the application of herbicides and fertilizers.

12 Research and monitoring data from Coweeta has been extensively analyzed and reported
13 in the scientific literature. Example recent publications include Swank and Vose (1997),
14 Grossman et al. (1998), Schofield et al. (2001), and Scott and Helfman (2001).

15 Long-term changes in soils have been identified in reference and managed watersheds
16 over two decades (Knoepp and Swank, 1994). For example, changes in exchangeable soil cation
17 content varied with aspect: concentrations decreased on a north-facing slope but were stable on
18 a south-facing slope. The demonstrated impacts of forest management practices have varied
19 considerably. Soils in a white pine plantation showed stable C levels, but cations declined.

20 Commercial sawlog harvest resulted in large increases in soil C and cation
21 concentrations, which remained elevated for 17 years. Whole-tree harvest resulted in decreased
22 soil C for the next 14 years. Clearly soil response to harvest varies with type of harvest and site.
23 Long-term studies like these have proven useful in guiding ecosystem management projects in
24 the southern Appalachians (Meyer and Swank, 1996).

25 26 **AX3.2.4.3 Walker Branch**

27 Walker Branch Watershed is located on the U.S. Department of Energy's Oak Ridge
28 Reservation in Tennessee. The 97.5 ha Walker Branch watershed has been the site of long-term,
29 intensive environmental studies since the late-1960s (see <http://walkerbranch.ornl.gov/>).

30 The forest soils are acidic, very cherty, infertile, and permeable. They are formed over
31 dolomitic bedrock, but retain little evidence of their carbonate parent material. The forest

1 vegetation is primarily oak-hickory with scattered pine on the ridges and mesophytic hardwoods
2 in the valleys.

3 Initially, the research and monitoring of Walker Branch centered primarily on the
4 geologic and hydrologic processes that control the amounts and chemistry of water moving
5 through the watershed. Past projects have included:

- 6 • watershed hydrology and forest nutrient dynamics,
- 7 • forest micrometeorology,
- 8 • atmospheric deposition,
- 9 • International Biological Program Eastern Deciduous Forest Biome Project,
- 10 • trace element cycling and stream nutrient spiraling, and
- 11 • effects of acidic deposition on canopy processes and soil chemistry.

12 These projects have all contributed to a more complete understanding of how forest
13 watersheds function and have provided insights into the solution of energy-related problems
14 associated with air pollution, contaminant transport, and forest nutrient dynamics. Available
15 long-term data at this site include:

- 16 • Daily climate data
- 17 • Monthly climate data
- 18 • Precipitation
- 19 • Atmospheric deposition
- 20 • Stream discharge and annual runoff
- 21 • Stream chemistry
- 22 • Vegetation

23 24 **AX3.2.5 Water, Energy, and Biogeochemical Budgets (WEBB) Program**

25 The Water, Energy, and Biogeochemical Budgets (WEBB) Program was started in 1991
26 at 5 small watersheds in the United States to examine water, energy, and biogeochemical fluxes
27 and to determine the effects of atmospheric deposition, climatic variables, and human influences
28 on watershed processes. The 5 sites are at Loch Vale, Colorado; Luquillo Experimental Forest,
29 Puerto Rico; Panola Mountain, Georgia; Sleepers River, Vermont; and Trout Lake, Wisconsin.
30 These sites are supported, in part, by other programs in the USGS, other Federal and State
31 Agencies, and Universities. Two of these sites, Loch Vale and Sleepers River, have been used

1 extensively to evaluate the effects of atmospheric sulfur and nitrogen deposition, and are
2 described here. Each of those sites is also part of the LTER network.

3
4 **AX3.2.5.1 Sleepers River**

5 The Sleepers River Research Watershed in northeastern Vermont was established by the
6 Agricultural Research Service (ARS) of the U.S. Department of Agriculture in 1959 and is now
7 operated jointly by the U.S. Geological Survey (USGS) and the U.S. Army Cold Regions
8 Research and Engineering Laboratory (CRREL), with collaboration from several other Federal
9 agencies and universities (see <http://nh.water.usgs.gov/projects/sleepers/index.htm>). The USGS
10 uses hydrologic measurements and chemical and isotopic tracing techniques to determine how
11 water moves from the hillslope to the stream, and what processes cause chemical changes,
12 including the neutralization of acid rain. Research results provide insights on how pollutants
13 move through ecosystems, and how ecosystems may respond to climatic change.

14 The watershed is covered by 1 to 4 m of glacial till, a compacted fine silty material that
15 formed underneath glacial ice as it moved overland. The till was formed primarily from local
16 bedrock, which is a calcareous granulite/quartz-mica phyllite. About 60 to 80 cm of soil has
17 developed in the till. Weathering of calcite in the till and bedrock causes highly buffered
18 streamflow, compared to most streams in New England, and a nutrient-rich biological
19 environment. Sleepers River is, therefore, an end member in regional biogeochemical cycling
20 studies (Hornbeck et al., 1997).

21 The Sleepers River area has reverted from a predominately cleared, agricultural
22 landscape to a mostly forested one. A Northern Hardwood forest, dominated by sugar maple,
23 white ash, yellow birch, and beech, with lesser amounts of red spruce and balsam fir, now covers
24 two-thirds of the area; the remaining open land is primarily pasture and hayfields. Dairy farming
25 and logging are the primary human enterprises in the watershed. The average annual
26 temperature is 6 °C and the average annual precipitation is 1.1 m, 20% to 30% of which falls as
27 snow.

28 Sleepers River has one of the longest historical hydrologic and climatologic data bases
29 for a cold-region area in the United States, featuring measurements of precipitation and
30 streamflow since 1959, snow depth and corresponding water content since 1960, soil frost depth
31 since 1984 (Shanley and Chamblers, 1999), and ground-water levels since 1991. These and

1 other measurements constitute a valuable resource for hydrologic modeling and for the
2 evaluation of climatic changes. Sampling site locations are shown in Figure AX3.2-4.

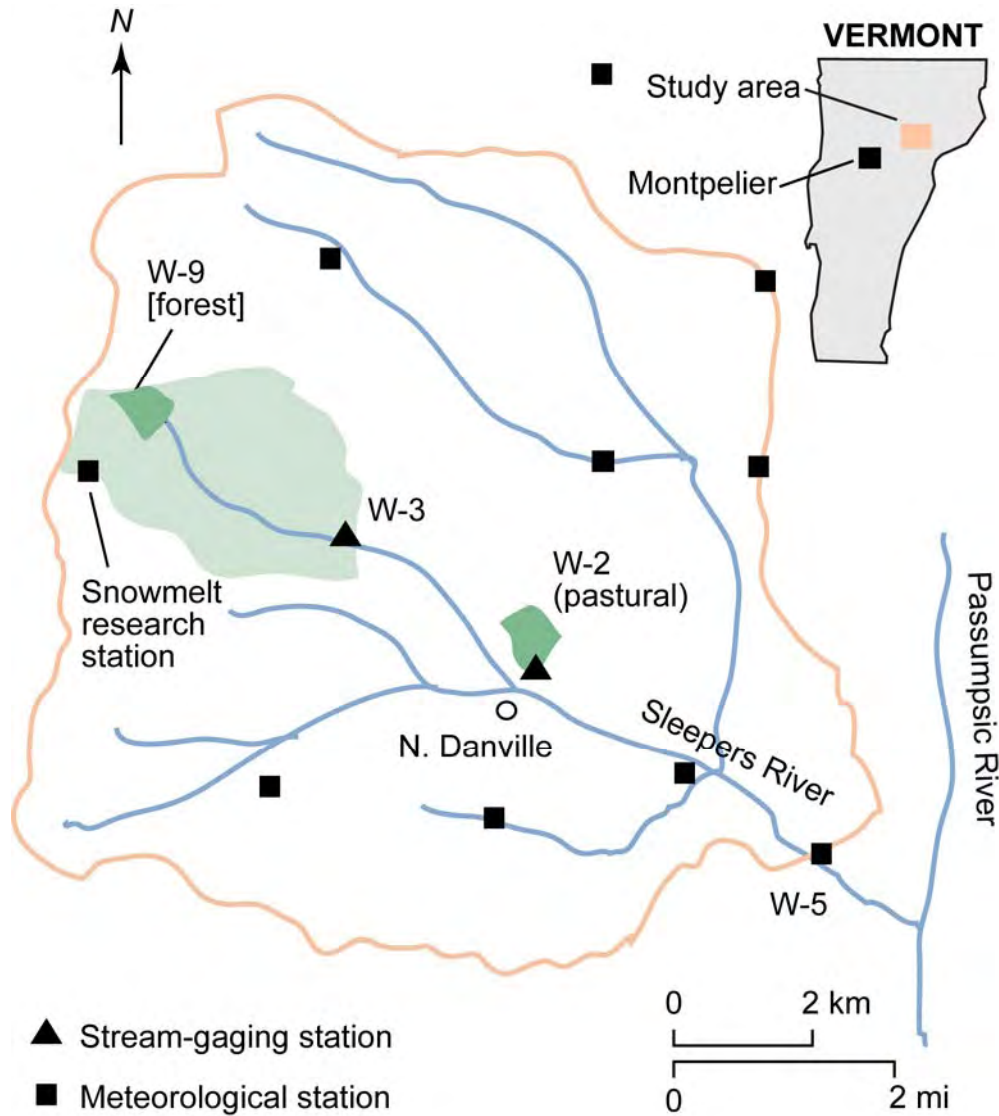


Figure AX3.2-4. Location of sampling stations in Sleepers River watershed, Vermont.

3 Recent research findings include the following:
4 • Precipitation is acidic, but streamflow is well-buffered from calcite weathering in till
5 and bedrock.

- 1 • Infiltrating snowmelt causes ground water to rise into the permeable soil zone, where
2 it moves rapidly downslope.
- 3 • Naturally occurring isotopic and chemical tracers indicate that “old” water dominates
4 streamflow, and that water acquires solutes from weathering and biogeochemical
5 processes along both deep and shallow flowpaths.
- 6 • Nitrate (NO_3^-) in streamflow is supplied primarily by mineralization and nitrification
7 in the soil, rather than directly by the nitrogen content of precipitation.

8 The fate of NO_3^- in the forest ecosystem is being investigated by analysis of both the N
9 and O isotopes of the NO_3^- ion. The isotopic composition of NO_3^- in streamflow matches that
10 of NO_3^- produced by mineralization and nitrification in the soil, indicating that streamflow NO_3^-
11 is derived from the soil and not from the rain or snowmelt that causes the high flow (Kendall
12 et al., 1995). This finding suggests that most incoming atmospheric nitrogen is incorporated at
13 least temporarily in the soil where it is utilized by the biota.

14 15 **AX3.2.5.2 Loch Vale**

16 The Loch Vale Watershed is a 661-ha alpine/subalpine basin located in the south-central
17 Rocky Mountains, about 100 km northwest of Denver, Colorado. The basin is in a roadless area
18 in Rocky Mountain National Park and is accessed by a 5-km hike or ski from the trailhead near
19 Bear Lake. The western boundary of the basin is the Continental Divide; streams drain to the
20 northeast. Basin elevations range from 4192 m (13,153 ft) at Taylor Peak to 3110 m (10,200 ft)
21 at the outlet. There are two main subbasins in Loch Vale: Andrews Creek drains the northern
22 subbasin, and Icy Brook drains the southern subbasin. These two creeks join above The Loch,
23 which is the lowest of three lakes in the basin. Stream gauges are operated on Andrews Creek,
24 Icy Brook, and at The Loch outlet. Water chemistry monitoring occurs at The Loch and on both
25 inlet streams (see <http://nh.water.usgs.gov/projects/sleepers/index.htm>).

26 Large glaciers that covered much of Rocky Mountain National Park during the late
27 Pleistocene sculpted the basin into characteristic glacial landforms, including steep U-shaped
28 valleys, cirques, and arêtes. When the glaciers retreated about 12,500 years ago, they deposited
29 till of varying thickness, which is confined mostly to the forested, lower part of the basin.
30 Smaller, more recent glacial advances left younger till, talus, and rock deposits in the upper parts
31 of the basin. The younger glacial and periglacial deposits are largely unvegetated.

1 Available water chemistry data include major ions, nutrients, dissolved inorganic carbon
2 (DIC), dissolved organic carbon (DOC), and, for selected samples, a range of isotopes including
3 $^2\text{H}/\text{H}$, $^{18}\text{O}/^{16}\text{O}$, $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ in nitrate ion, ^{35}S , $^{34}\text{S}/^{32}\text{S}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^{13}C , ^{12}C). Monitoring of
4 precipitation and hydrology include the following elements:

- 5 • Precipitation: quantity- 3 sites continuous; chemistry, 1 site, biweekly.
- 6 • Stream discharge, 2 sites (Andrews Creek-Loch Vale, Icy Brook-Loch Vale)
- 7 • Stream chemistry, (Andrews Creek, Icy Brook-Loch Vale)
- 8 • Spring discharge, conductance, and temperature, 3 sites continuous.
- 9 • Spring water chemistry, 3 sites biweekly, 20-30 sites once during low-flow season.
- 10 • Soil lysimeters, 5 sites, biweekly to monthly during summer and fall.
- 11 • Snowpack amount and chemistry (depth, snow-water equivalent) basin-wide survey
12 at maximum accumulation, index sites biweekly to monthly.
- 13 • Selected microenvironment runoff, e.g., rock outcrop, talus fields, weekly to monthly.
- 14 • Meteorology: 3 sites (wind speed, wind direction, air temperature, incoming and
15 outgoing radiation, relative humidity), continuous.
- 16 • Gas flux (CO_2 and CH_4) in wetland, forest, and talus soils, weekly to monthly; CO_2
17 concentrations in surface waters at 10-15 sites several times annually.
- 18 • Snowmelt lysimeter discharge and chemistry, monitored for three years, currently
19 inactive.

20 Atmospheric deposition of nitrogen to Loch Vale is high compared to most other sites in
21 the Rockies, although considerably lower than most impacted sites in eastern North America and
22 Europe. The alpine/subalpine ecosystem at Loch Vale exhibits symptoms of advanced
23 watershed nitrogen saturation, indicating sensitivity to nitrogen deposition. Talus landscapes
24 contribute substantially to nitrogen export in streamflow, and soil microbial processes are
25 important in cycling nitrogen, even in areas such as talus that have little soil development.
26 Research at this site indicates that nitrogen export is a function of both deposition and internal
27 nitrogen-cycling processes that are affected by variability in climate.

1 **AX3.2.6 Other Studies**

3 **AX3.2.6.1 Bear Brook**

4 The Bear Brook Watershed (BBW) is located in eastern Maine (44°52'15" Latitude,
5 68°06'25" Longitude), approximately 60 km from the Atlantic coastline. The BBW is a paired
6 watershed study funded by EPA since 1987 as part of The Watershed Manipulation Project
7 (WMP) within the National Acid Precipitation Assessment Program (NAPAP) (see
8 <http://hydromodel.com/bbwm.htm>; <http://www.umaine.edu/DrSoils/bbwm/bbwm.html>). As a
9 long-term research watershed, the BBW includes bench-scale, micro-site, plot, and whole
10 watershed investigations. The major purposes of the BBW project were to:

- 11 1. Identify and quantify the major processes that control surface water acidity, with a
12 major emphasis on (1) the role of excess sulfate and nitrate provided via
13 atmospheric deposition and experimental application, and (2) the rate of cation
14 supply from chemical weathering and cation desorption;
- 15 2. Assess the quantitative and qualitative responses at the watershed level to different
16 (both increased and decreased) levels of acidic deposition;
- 17 3. Evaluate the ability of existing models of water acidification to predict short- and
18 long-term chemical variations in surface water chemistry and to predict watershed
19 soil responses to increased and decreased loading of strong acids.

20 The watershed includes two first order streams: East Bear Brook (EBB) and West Bear
21 Brook (WBB). On each stream, a catchment outlet was selected and gauged so that both streams
22 have about the same catchment area (EBB = 10.7 ha and WBB = 10.2 ha). Since streams are
23 close and face the same slope direction, the watersheds are geographically similar and are
24 appropriate for a paired watershed study. Streamflow has been monitored with a standard
25 V-notch weir. Flow data are sampled at 5-min intervals. Both watersheds have a maximum
26 discharge of about 0.01 m³/ha/sec or 0.15 m³/s. Annual water yield relative to incoming
27 precipitation for WBB ranges from 68 to 77% and EBB ranges from 62-68%.

28 Stream channels in each watershed are well defined. Each stream bed is approximately
29 1 m wide at the weir and water flows over exposed bedrock in places. Elsewhere, the
30 streambeds are comprised of boulders and gravel. Both streams have undergone intermittent dry

1 periods during summer over the course of the study. One V-notch weir was constructed on each
2 of the streams during winter 1987-1988. Mean discharge in each stream is about 0.13 cfs.

3 Sampling frequency at the weirs was every three weeks during the winter of 1986-1987
4 and at least weekly thereafter. On the basis of sampling conducted prior to beginning the
5 manipulation experiment (1987-1989), the streams had the following characteristics: ANC,
6 -5 to 90 $\mu\text{eq/L}$; air-equilibrated pH, 4.7 to 7.2; specific conductance of approximately
7 26 $\mu\text{S/cm}$; and DOC of 1 to 4 mg C/l.

8 Soils in the Bear Brook watersheds are primarily Spodosols. The average depth of the
9 overburden in the watersheds is 0.5 m, with a range of 0 to 5.2 m. Soil pH (0.01M CaCl_2) values
10 ranged from 2.9 in the O horizon, to 3.9 in the B horizon, to 4.4 in the C horizon. The bedrock is
11 primarily metamorphosed and folded polytropic graded beds and quartzites, with granitic dikes. The
12 surficial material is till.

13 The forest is comprised primarily of deciduous species with areas of conifers. Tree
14 species include American beech (*Fagus grandifolia*), birch (*Betula* sp.), maple (*Acer* sp.), red
15 spruce (*Picea rubens*), balsam fir (*Abies balsamea*), white pine (*Pinus strobus*), and hemlock
16 (*Tsuga canadensis*). Coniferous stands, which occupy approximately 17% of the total watershed
17 area, occur more commonly in the upper, steeper portions of the watersheds.

18 Although the Bear Brook project was intended as an experimental manipulation of West
19 Bear Brook, there is also great value in the long-term monitoring data collected at East Bear
20 Brook, the non-manipulated reference watershed. This two-decade long monitoring record
21 provides information on the response of an acid-sensitive low-order stream in Maine to changes
22 that have occurred in atmospheric deposition since 1986.

23 Results of the Bear Brook project have been widely published (cf. Kahl et al., 1993;
24 Norton et al., 1994; 1999a,b).

25 26 **AX3.2.6.2 Virginia Trout Stream Sensitivity Study and Shenandoah National Park's** 27 **Surface Water Acidification Study**

28 The SWAS-VTSSS program is a monitoring and research network focused on low-order,
29 high-gradient streams associated with public lands in western Virginia (see
30 <http://swas.evsc.virginia.edu/>). The objectives of the program are to increase understanding of
31 factors that govern biogeochemical conditions and stressor-response relationships in forested
32 mountain watersheds of the central Appalachian region. Success in addressing these scientific

1 and problem-oriented objectives has been achieved through development of a data collection
2 network that accounts for spatial gradients, as well as temporal variation, in the chemical
3 composition of the region's relatively undisturbed headwater streams.

4 The program is notable for the length of the continuous data record that has been
5 obtained, including the longest-running record (28 years) of stream water composition and
6 discharge in the National Park System. The SWAS component of the program, which now
7 includes 14 streams in Shenandoah National Park, was initiated in 1979. The VTSSS
8 component, which now includes 51 streams in National Forests and other conservation lands,
9 was initiated in 1987. The distribution of SWAS-VTSSS study sites in relation to public lands is
10 shown in Figure AX3.2-5.

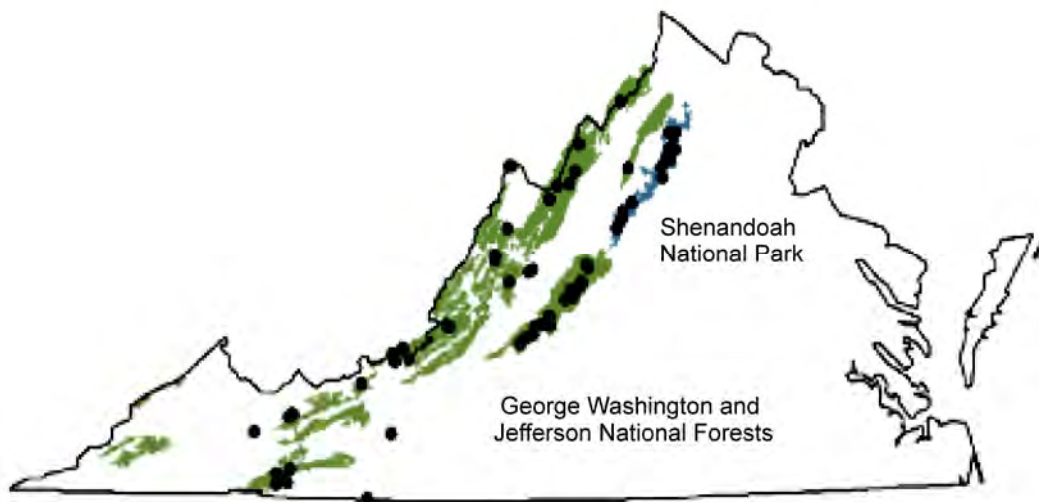


Figure AX3.2-5. SWAS-VTSS Program Study Sites. The length of the stream water chemical composition record for SWAS-VTSSS study watersheds is 20 to 28 years. SWAS sites are located in Shenandoah National Park (shaded blue). VTSSS sites are mainly located in Virginia's National Forests (shaded green).

11 The SWAS-VTSSS program has been maintained as a cooperative effort involving the
12 Department of Environmental Sciences at the University of Virginia, the National Park Service,
13 the U.S. Environmental Protection Agency, the USDA Forest Service, the U.S. Geological

1 Survey, the Virginia Department of Game and Inland Fisheries, and Trout Unlimited. The
2 monitoring sites account for ecological variation among the region's forested mountain
3 watersheds with a data-collection strategy that represents: (1) spatial variation through the
4 distribution of hydrochemical monitoring within a lithologic classification system; and (2)
5 temporal variation through long-term data collection at fixed locations sampled at different
6 frequencies.

7 The lithologic classification system includes 6 classes based on the physical and chemical
8 properties of bedrock formations in the region. Acid neutralizing capacity (ANC) and
9 concentrations of related acid-base constituents in stream waters, as well as other biotic and
10 abiotic properties of watersheds, differ among the lithologic classes.

11 The SWAS-VTSSS data collection framework is most-well developed in the Blue Ridge
12 Mountains Province within Shenandoah National Park, where stream water composition data are
13 collected seasonally at 14 sites, weekly at 6 sites, and every four hours during episodic high-flow
14 conditions at 3 sites with continuous discharge gauging. Stream water composition data are
15 collected on a seasonal basis at an additional 51 sites located outside of the Park, in both the Blue
16 Ridge Mountains and Ridge and Valley Provinces.

17 Stream water samples collected through the SWAS and VTSSS programs are analyzed
18 for ANC, pH, and the major anions (sulfate, nitrate, and chloride) and cations (calcium,
19 magnesium, potassium, and sodium) by methods appropriate for low-ionic strength natural
20 waters. Both the SWAS and VTSSS sample streams were selected based on geographic
21 distribution, representation of the major bedrock types underlying the mountain ridges in the
22 region, and minimization of recent watershed disturbance. All but a few of the sample streams
23 currently support reproducing populations of native brook trout. All of the sample streams
24 supported brook trout populations historically.

25 Sustained data collection in a network constructed of intensively studied sites nested
26 within a geographically extensive set of less intensively studied sites has allowed detection and
27 interpretation of change that has occurred in a context of multiple time scales and stressors.
28 Responses to multi-year changes in acidic deposition have been reflected in long-term trends in
29 quarterly concentrations of sulfate, ANC, and other acid-base constituents of streams in the
30 network. Expectations for southeastern watersheds with soils that retain sulfur, for example,
31 have been confirmed by the lack of regional improvement in stream water quality following

1 reductions in acidic deposition mandated by the Clean Air Act. The acid-base chemistry of
2 streams in the network also varies seasonally and on shorter time scales. Weekly and higher-
3 frequency automated stream water sampling during periods of high runoff have supported the
4 study of episodically more-acidic conditions, including the study of fish sensitivity with in-
5 stream bioassays and development of models to predict severity and recurrence intervals.

6 By accounting for significant spatial gradients and temporal patterns in the region, the
7 SWAS-VTSSS hydrochemical data collection program provides a basis for both observing and
8 interpreting watershed-scale change, as well as an informed foundation for process-oriented
9 research. Monitoring data and research findings obtained through the SWAS-VTSSS program
10 have contributed to increased scientific understanding, as well as to policy formulation and
11 implementation.

12 The mathematical model, MAGIC (Model of Acidification of Groundwater in
13 Catchments), was first calibrated using data obtained for White Oak Run, a SWAS-VTSSS study
14 stream in Shenandoah National Park. MAGIC is the most widely used acid-base chemistry
15 model in the United States and Europe and the principal model used by the National Acid
16 Precipitation Assessment Program in the 1980s to estimate future damage to lakes and streams in
17 the eastern United States. The MAGIC model has since been applied in a number of regional
18 assessments that relied extensively on stream water and soils data obtained through the SWAS-
19 VTSSS program. Among these are:

- 20 • The Southern Appalachian Mountain Initiative, a multi-state effort to evaluate
21 alternative approaches to solving regional air-pollution problems. MAGIC
22 projections indicated that even ambitious emission control strategies would not result
23 in near-term recovery of the region's most acidified surface waters – a consequence
24 of base-cation depletion in soils exposed to decades of acidic deposition.
- 25 • The Shenandoah Assessment, an assessment of acidification effects on aquatic
26 systems in Shenandoah National Park. MAGIC reconstructions indicated that Park
27 streams associated with base-poor bedrock lost about 70 $\mu\text{eq L}^{-1}$ between 1900 and
28 1990. MAGIC projections indicated that some streams may recover given
29 prospective reductions in acidic deposition, but others will not.

30 Data and findings provided through the SWAS-VTSSS program have also proven
31 relevant to the evaluation and implementation of national air pollution control policies. The

1 SWAS-VTSSS program provides data for the EPA's long-term monitoring of surface water
2 response to legislated reductions in sulfur emissions. Whereas sulfate concentrations in surface
3 water declined during the 1990–2000 period for four northeastern regions with sensitive surface
4 waters, the SWAS-VTSSS study region, in contrast, experienced increasing stream-water sulfate
5 concentrations and continuing acidification.

6 Recent publications that were based on analyses of SWAS-VTSSS data include Cosby
7 et al. (1991), Stoddard et al. (2003), Sullivan et al. (2003, 2004), and Webb et al. (2004).

8 9 **AX3.2.6.3 Fernow**

10 The Fernow Experimental Forest, established in 1934, is located just south of the city of
11 Parsons in the most mountainous region of West Virginia. It is surrounded by the Monongahela
12 National Forest, which comprises about 900,000 acres of rugged, hilly terrain. Most research at
13 Fernow is focused on improvement of forest management (see [http://www.fs.fed.us/ne/
14 parsons/fehome.htm](http://www.fs.fed.us/ne/parsons/fehome.htm)).

15 Scientists at Fernow are developing information and techniques for sustainably managing
16 hardwood forests in the central Appalachians. The mixed hardwood forest covers about 78% of
17 West Virginia and supplies important timber products, provides recreational opportunities, and
18 supports a diverse assemblage of wildlife and plant species.

19 The Fernow Experimental Forest was heavily logged between 1905 and 1911. The forest
20 now contains about 1900 ha of second- and third-growth Appalachian hardwood stands, which
21 are representative of average to better than average sites found on approximately 4 million ha of
22 the forest type in West Virginia and surrounding states. At the lowest elevations, the original
23 forests consisted mainly of hardwoods, with eastern hemlock (*Tsuga canadensis* [L.] Carr.)
24 along stream bottoms and on north slopes. Forests at the higher elevations were dominated by
25 red spruce (*Picea rubens* Sarg.) and hemlock. Small patches of pure spruce occurred on the tops
26 of the mountains.

27 Elevations in the Fernow range from 533 to 1112 m, with slopes of 10% to 60%. A rock
28 layer composed of fractured hard sandstone and shale underlies most of the Fernow. A majority
29 of the soils are of the Calvin and Dekalb series, which originated from these rocky materials
30 (loamy-skeletal mixed mesic Typic Dystrochrepts). On the southeastern part of the forest,
31 Greenbrier limestone outcrops to produce a midslope zone of limestone soil of the Belmont
32 series (fine-loamy mixed mesic Typic Hapludalfs). Almost all Fernow soils, including the

1 sandstone, shale, and limestone soils, are well-drained, medium textured loams and silt loams.
2 Average soil depth is about 1 m, and average soil pH is about 4.5.

3 A rainy, cool climate is typical on the Experimental Forest. Precipitation, which averages
4 about 145 cm per year, is evenly distributed throughout the year. Mean annual temperature is
5 about 9 °C, and the length of the growing season is approximately 145 days.

6 The forest types and conditions today reflect the site qualities and past history of the area.
7 Oaks (*Quercus* spp.) are most common and are found on all sites along with American beech
8 (*Fagus grandifolia* Ehrh.) and sweet birch (*Betula lenta* L.). Excellent sites in coves and on
9 north slopes support primarily northern red oak (*Quercus rubra* L.), sugar maple (*Acer*
10 *saccharum* Marsh.), yellow-poplar (*Liriodendron tulipifera* L.), black cherry (*Prunus serotina*
11 Ehrh.), white ash (*Fraxinus americana* L.), basswood (*Tilia americana* L.), cucumbertree
12 (*Magnolia acuminata* L.), and beech. Fair sites on south and east slopes usually support oak
13 stands composed of red oak, white oak (*Quercus alba* L.), chestnut oak (*Quercus prinus* L.), and
14 scarlet oak (*Quercus coccinea* Muenchh.). Other fair site species include red maple (*Acer*
15 *rubrum* L.), sweet birch, black gum (*Nyssa sylvatica* Marsh.), sassafras (*Sassafras albidum*
16 Nutt.), and sourwood (*Oxydendrum arboreum* [L.] DC.). Good sites commonly support a
17 mixture of excellent and fair site species. Black locust (*Robinia pseudoacacia* L.), sweet birch,
18 and Fraser magnolia (*Magnolia fraseri* Walt.) are consistent but generally minor components of
19 the forest on all sites. American chestnut was a major forest component until it was eliminated
20 by the chestnut blight.

21 The Fernow Experimental Forest encompasses practically the entire Elk Lick Run
22 drainage, which is about 5.8 km long and 3.5 km across at the widest point. Elk Lick Run has
23 seven major tributaries including Big Spring, which drains a headwater limestone formation.
24 Headwater areas on two of these tributaries have been gauged to show how forest management
25 influences streamflow.

26 Research on the Fernow Experimental Forest by the Timber and Watershed Project
27 scientists is done in cooperation with the Monongahela National Forest, West Virginia
28 University, Marshall University, Pennsylvania State University, Virginia Tech, and the West
29 Virginia Division of Natural Resources.

30 Scientific studies on the Fernow have followed two lines of research, with considerable
31 overlap. Silvicultural research, focused mostly on mixed hardwood stands, addresses questions

1 relating to regenerating, growing, tending, and harvesting trees and stands. Watershed research
2 has addressed some of the more basic questions about water use by forests and forest hydrology,
3 as well as critical issues affecting roads, best management practices, and forest management
4 effects on water and soil resources. The Fernow also has been in the forefront of research on
5 acidic deposition and nitrogen saturation. A whole-watershed acidification study has been
6 conducted since 1989. Recently, research on threatened and endangered species has assumed a
7 more prominent role, due to the presence of Indiana bat and running buffalo clover on the
8 Fernow.

9 10 **AX3.2.6.4 NEON**

11 The National Ecological Observatory Network (NEON) is a continental-scale research
12 platform that is primarily focused on discovering and understanding the impacts of climate
13 change, land-use change, and invasive species on ecology. It will also generate data that will be
14 useful for assessing effects of NO_x and SO_x deposition on ecosystems. NEON has not yet been
15 implemented; it is described here because it represents an ambitious monitoring program that is
16 expected to be very useful in the near future. NEON will gather long-term data on ecological
17 responses of the biosphere to changes in land use and climate, and on feedbacks with the
18 geosphere, hydrosphere, and atmosphere. NEON is proposed as a national observatory,
19 consisting of distributed sensor networks and experiments, linked by advanced cyber
20 infrastructure to record and archive ecological data for at least 30 years. Using standardized
21 protocols and an open data policy, NEON is intended to gather essential data for developing
22 scientific understanding and theory required to manage the nation's ecological challenges. The
23 program description is found at www.neoninc.org/.

24 25 26 **AX3.3 MODELING**

27 28 **AX3.3.1 Principal Ecosystem Models Used in the United States**

29 It is particularly difficult to study endpoints at the larger levels of biological organization
30 (e.g., at the population, community, biogeochemical, and ecosystem-level) with monitoring
31 studies. Geographic areas are larger, and timeframes are longer, rendering it difficult to obtain
32 data in sufficient quantity to detect impacts unless they are exceptionally severe. Therefore, the

1 most common approach to study endpoints at these scales is to develop and apply a model.
2 Models may be calibrated using data from monitoring, survey, or laboratory or field experiments
3 and are useful tools in predicting larger-scale, longer-term impacts. However, verifying the
4 predictions and assessing the overall validity of the model can be challenging.

5 Some of the most frequently used ecosystem models designed to quantify effects of
6 atmospheric N and S deposition are discussed below. It is important to note that the ecosystem
7 models are parameterized for specific areas and may not be readily applicable to other locations
8 without significant re-parameterization.

9 There are four principal models that are currently being used in the United States to
10 assess the effects of S and N deposition on terrestrial and freshwater aquatic ecosystems:
11 MAGIC, NuCM, PnET/BGC, and DayCent-Chem. Two models, SPARROW and WATERSN,
12 are commonly used to evaluate nitrogen loading to large river systems and to estuaries. These
13 six models are briefly reviewed in the following sections. Each review begins with a summary
14 of the provenance and conceptual basis of the model and contains references to some of the
15 published applications. This is followed by a more detailed description of the processes included
16 in the model, the inputs required, and the output variables simulated by the model.

17 The ranges of process complexity, temporal resolution and spatial discretization
18 represented in these models are considerable. These ranges make comparative summaries of
19 inputs, outputs, and processes across the models problematic. The models are all currently in use
20 because they are, in a sense, complementary to each other, with each providing an approach or
21 satisfying requirements unique to their own structure and intended applications. As a result,
22 there is no good way to develop satisfying comparative equivalences among the components of
23 the various structures. It is also beyond the scope of this document to present the level of detail
24 necessary to run any of the models. The descriptions below must of necessity be brief.
25 References to appropriate texts designed to provide more detail are given for each model.

26 Following the discussion of the four models most frequently used in the United States,
27 there are brief descriptions of the most important models of S and N deposition effects that are
28 being used in Europe and elsewhere.

29
30 **AX3.3.1.1 MAGIC**

31 The MAGIC (Model of Acidification of Groundwater in Catchments) (Cosby et al.,
32 1985a,b,c) model is a mathematical model of soil and surface water acidification in response to

1 atmospheric deposition based on process-level information about acidification. MAGIC has
2 been applied extensively in North America and Europe to both individual sites and regional
3 networks of sites, and has also been used in Asia, Africa and South America. The utility of
4 MAGIC for simulating a variety of water and soil acidification responses at the laboratory, plot,
5 hillslope, and catchment scales has been tested using long-term monitoring and experimental
6 manipulation data.

7 MAGIC has been widely used in policy and assessment activities in the United States and
8 in several countries in Europe (e.g., Cosby et al., 1985c, 1990, 1995, 1996; Whitehead et al.,
9 1988, 1997; Hornberger et al., 1989; Jenkins et al., 1990; Wright et al., 1990, 1994, 1998; Beier
10 et al., 1995; Moldan et al., 1998; Sullivan and Cosby, 1998; Ferrier et al., 2001; Clair et al.,
11 2004; Sullivan et al., 2006).

12 13 *MAGIC Model Structure*

14 MAGIC is a lumped-parameter model of intermediate complexity, developed to predict
15 the long-term effects of acidic deposition on surface water chemistry (see Figure AX3.3-1). The
16 model simulates soil solution chemistry and surface water chemistry to predict the monthly and
17 annual average concentrations of the major ions in these waters. MAGIC consists of: (1) a
18 section in which the concentrations of major ions are assumed to be governed by simultaneous
19 reactions involving sulfate adsorption, cation exchange, dissolution-precipitation- speciation of
20 aluminum, and dissolution-speciation of inorganic carbon; and (2) a mass balance section in
21 which the flux of major ions to and from the soil is assumed to be controlled by atmospheric
22 inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of
23 MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and
24 from this pool change over time owing to changes in atmospheric deposition, the chemical
25 equilibria between soil and soil solution shift to give changes in surface water chemistry. The
26 degree and rate of change of surface water acidity thus depend both on flux factors and the
27 inherent characteristics of the affected soils.

28 Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with
29 selectivity coefficients for each base cation and aluminum. Sulfate adsorption is represented by
30 a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by
31 equilibrium with a solid phase of aluminum trihydroxide. Aluminum speciation is calculated by
32 considering hydrolysis reactions as well as complexation with sulfate, fluoride and dissolved

Major Pools and Fluxes

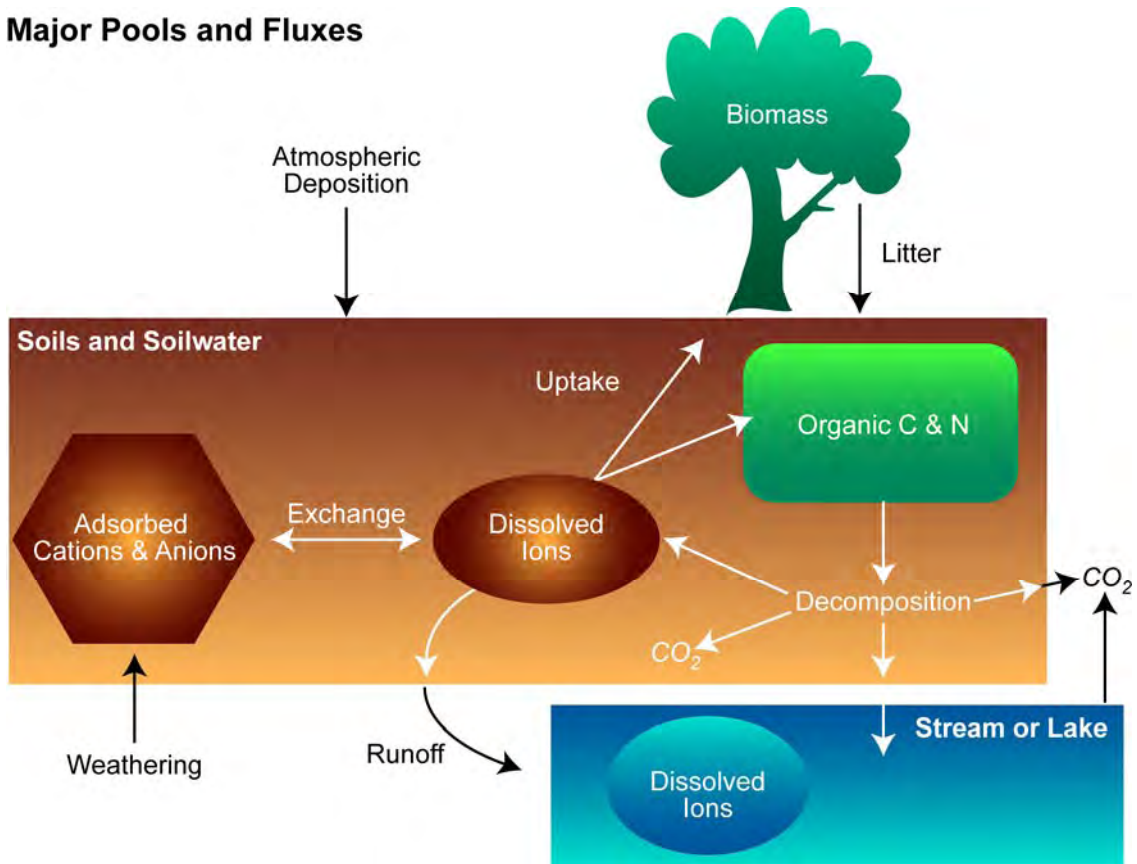


Figure AX3.3-1. Conceptual structure of the MAGIC model showing major pools and fluxes included in simulation of effects of S and N deposition.

1 organic compounds. Effects of carbon dioxide on pH and on the speciation of inorganic carbon
 2 are computed from equilibrium equations. Organic acids are represented in the model as tri-
 3 protic analogues. Weathering rates are assumed to be constant. Two alternate mechanisms are
 4 offered for simulation of nitrate and ammonium in soils and water: either (1) first order
 5 equations representing net uptake and retention; or (2) a set of equations and compartments
 6 describing process-based nitrogen dynamics controlled by carbon and nitrogen pools and fluxes
 7 in the compartments.

8 Atmospheric deposition fluxes for the base cations and strong acid anions are required as
 9 inputs to the model. These inputs are generally assumed to be uniform over the catchment.
 10 Atmospheric fluxes are calculated from concentrations of the ions in precipitation and the
 11 rainfall volume into the catchment. The atmospheric fluxes of the ions must be corrected for dry

1 deposition of gas, particulates and aerosols and for inputs in cloud/fog water. The volume
2 discharge for the catchment must also be provided to the model. In general, the model is
3 implemented using average hydrologic conditions and meteorological conditions in annual or
4 seasonal simulations, i.e., mean annual or mean monthly deposition, precipitation and lake
5 discharge are used to drive the model. Values for soil and surface water temperature, partial
6 pressure of carbon dioxide and organic acid concentrations must also be provided at the
7 appropriate temporal resolution.

8 The MAGIC model can be implemented as a one- or two-soil representation of a
9 catchment with or without wetlands. Atmospheric deposition enters the soil compartment(s) and
10 the equilibrium equations are used to calculate soil water chemistry. The water is then routed to
11 the stream compartment, and the appropriate equilibrium equations are reapplied to calculate
12 runoff chemistry. Input-output mass balance equations are provided for base cations and strong
13 acid anions, and charge balance is required for all ions in each compartment (for complete details
14 of the model see Cosby et al., 1985a,b,c, 2001).

15 For most applications, model outputs for 15 stream water variables are used. These
16 variables consist of the concentrations of 10 ions (H; Ca; Mg; Na; K; NH₄; SO₄; NO₃; Cl; and
17 total inorganic Al), the stream discharge (Q), stream pH, sum of base cation concentrations
18 (SBC = Ca + Mg + Na + K + NH₄), sum of mineral acid anion concentrations (SAA = Cl + SO₄
19 + NO₃) and the charge balance acid neutralizing capacity (ANC = SBC - SAA). These variables
20 are expressed in units of m/yr (or m/mo) for Q, μmol/L for inorganic Al, and μeq/L for all other
21 variables. In addition, model output for 7 soil and soilwater variables are frequently used, the
22 total base saturation and individual cation saturations for Ca, Mg, Na, and K, the soilwater pH
23 and the Ca/Al ratio in soil water.

24 The aggregated nature of the model requires that it be calibrated to observed data from a
25 system before it can be used to examine potential system response. Calibrations are based on
26 volume weighted mean annual or seasonal fluxes for a given period of observation. The length
27 of the period of observation used for calibration is not arbitrary. Model output will be more
28 reliable if the annual flux estimates used in calibration are based on a number of years rather than
29 just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment
30 runoff. Averaging over a number of years reduces the likelihood that an “outlier” year (very dry,
31 etc.) is used to specify the primary data on which model forecasts are based. On the other hand,

1 averaging over too long a period may remove important trends in the data that need to be
2 simulated by the model.

3 The calibration procedure requires that stream water quality, soil chemical and physical
4 characteristics, and atmospheric deposition data be available for each catchment. The water
5 quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg,
6 Na, and K) and acid anions (Cl, SO₄, and NO₃) and the pH. The soil data used in the model
7 include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable
8 bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be
9 estimates of total deposition, not just wet deposition. In some instances, direct measurements of
10 either atmospheric deposition or soil properties may not be available for a given site with stream
11 water data. In these cases, the required data can often be estimated by: (a) assigning soil
12 properties based on some landscape classification of the catchment; and (b) assigning deposition
13 using model extrapolations from some national or regional atmospheric deposition monitoring
14 network.

15 Soil data for model calibration are usually derived as aeri ally averaged values of soil
16 parameters within a catchment. If soils data for a given location are vertically stratified, the soils
17 data for the individual soil horizons at that sampling site can be aggregated based on horizon,
18 depth, and bulk density to obtain single vertically aggregated values for the site, or the stratified
19 data can be used directly in the model.

20 Calibration of the model (and estimation of historical changes at the modeled sites)
21 requires a temporal sequence of historical anthropogenic deposition. Current understanding of
22 ecosystem responses to acidic deposition suggests that future ecosystem responses can be
23 strongly conditioned by historical acid loadings. Thus, as part of the model calibration process,
24 the model should be constrained by some measure of historical deposition to the site. However,
25 such long-term, continuous historical deposition data may not exist. The usual approach is to use
26 historical emissions data as a surrogate for deposition. The emissions for each year in the
27 historical period can be normalized to emissions in a reference year (a year for which observed
28 deposition data are available). Using this scaled sequence of emissions, historical deposition can
29 be estimated by multiplying the total deposition estimated for each site in reference year by the
30 emissions scale factor for any year in the past to obtain deposition for that year.

1 **AX3.3.1.2 NuCM**

2 The current NuCM model is based on the original ILWAS (Integrated Lake Watershed
3 Acidification Study) model of the 1980s (cf. Chen et al., 1984; Goldstein et al., 1984; Gherini
4 et al., 1985). NuCM was developed as an extension to the ILWAS model by investigators in the
5 Integrated Forest Study (see Johnson and Lindberg, 1992), and the model code was written by
6 Tetra-Tech, Inc. (Liu et al., 1991). NuCM was developed to explore potential effects of
7 atmospheric deposition, fertilization and harvesting in forest ecosystems. Because NuCM was
8 designed primarily for simulating the effects of atmospheric deposition on nutrient cycling
9 processes, its construction emphasizes soil and soil solution chemistry (Liu et al., 1991). As a
10 stand-level model, NuCM incorporates all major nutrient cycling processes (uptake,
11 translocation, leaching, weathering, organic matter decay, and accumulation). Vegetation is
12 divided into leaf, bole and root compartments for under- and overstory vegetation. NuCM
13 simulates the cycling of N, P, K, Ca, Mg, Na, and S based on expected optimal growth rates
14 (input by the user and reduced in the event of nutrient limitation), user-defined litterfall,
15 weathering, N and S mineralization rates, soil minerals composition, initial litter, soil organic
16 matter pools, and C/N ratios.

17 The model has been calibrated for different vegetation types, including a loblolly pine
18 (*Pinus taeda* L.) stand at Duke University (Johnson et al., 1995), a mixed deciduous stand at
19 Walker Branch (Johnson et al., 1993) and a red spruce (*Picea rubens* Sarg.) stand in the Great
20 Smoky Mountains (Johnson et al., 1996). The NuCM model was used as part of the Southern
21 Appalachian Mountain Assessment (Sullivan et al., 2002).

22
23 *NuCM Model Structure*

24 In NuCM, the ecosystem is represented as a series of vegetation and soil components.
25 The overstory consists of one generic conifer and one generic deciduous species of specified
26 biomass and nutrient concentration (foliage, branch, bole, roots). For mixed species stands,
27 average values for biomass and nutrient concentration by component must be used. NuCM also
28 includes an understory, which can be divided into canopy, bole, and roots. Maximum potential
29 vegetative growth in the model is defined by the user and is constrained in the model by the
30 availability of nutrients and moisture. The forest floor is simulated from litterfall inputs and
31 litter decay. Litterfall mass inputs are defined by the user, and litter decay is represented as a
32 four stage process where: (1) coarse litter decays to fine litter; (2) fine litter decays to humus and

1 cations; (3) humus decays to organic acids, NH_4^+ , SO_4^{2-} , H^+ , and CO_2 ; and (4) organic acids
2 decay to NH_4^+ , SO_4^{2-} , H^+ , and CO_2 . Each stage is represented as a first-order equation.

3 The soil includes multiple layers (up to 10), and each layer can have different physical
4 and chemical characteristics. The user defines bulk density, cation exchange capacity,
5 exchangeable cations, adsorbed phosphate and sulfate, and four soil minerals and their
6 composition. These inputs define the initial soil exchangeable/adsorbed pools and total pools.
7 Initial total soil N pools are simulated from litterfall and decay, as described above, and user-
8 defined C/N ratios. Vegetation, litter, and soil pools change over a simulation in response to
9 growth, litterfall and decomposition, and nutrient fluxes via deposition, leaching and weathering.

10 The processes that govern interactions among these pools include translocation, uptake,
11 foliar exudation and leaching, organic matter decay, nitrification, anion adsorption, cation
12 exchange and mineral weathering. Translocation, defined as the removal of nutrients from
13 foliage prior to litterfall, is user-specified. Maximum uptake is calculated from biomass and
14 nutrient concentrations; actual uptake is equal to this maximum value when sufficient nutrients
15 are available and reduced when nutrients become limiting. Reduced uptake first allows reduced
16 nutrient concentrations in plant tissues, then causes a reduction in growth. Foliar exudation and
17 leaching rates are simulated as proportional to foliar concentrations using user-defined
18 coefficients.

19 Mineral weathering reactions are described in the model using rate expressions with
20 dependencies on the mass of mineral present and solution-phase hydrogen-ion concentration
21 taken to a fractional power. Cation exchange is represented by the Gapon equation. The model
22 simulates a tri-protic organic acid with a fixed charge density. Nitrification is represented in the
23 form of a Michaelis–Menton rate expression. Phosphate adsorption is represented by a linear
24 isotherm, and SO_4^{2-} adsorption is represented by a Langmuir adsorption isotherm.

25 Climate inputs to the NuCM model are through input meteorological files (typically 1 to
26 5 years long), which are repeated in order to generate long-term simulations. The meteorological
27 files contain daily values for precipitation quantity, maximum and minimum air temperature,
28 cloud cover, dewpoint, atmospheric pressure, and wind speed. Monthly soil temperature data are
29 also required.

30 Precipitation is routed through the canopy and soil layers and evapotranspiration, deep
31 seepage, and lateral flow are simulated. The movement of water through the system is simulated

1 using the continuity equation, Darcy's equation for permeable media flow, and Manning's
2 equation for free surface flow. Percolation occurs between layers as a function of layer
3 permeability's and differences in moisture content. Nutrient pools associated with soil solution,
4 the ion exchange complex, minerals, and soil organic matter are all tracked explicitly by NuCM.

5 Wet deposition is calculated from precipitation amounts and user-input air quality files
6 which define precipitation concentrations on a monthly basis. Dry deposition is calculated from
7 air concentrations in the air quality files combined with user-defined deposition velocities and
8 simulated leaf areas. Leaching is calculated from soilwater percolation and simulated soil
9 solution concentrations using the soil chemical and biological algorithms defined above for each
10 soil horizon.

11 The only processes in the NuCM model that are explicitly temperature-dependent are
12 evaporation, occurrence of precipitation as rainfall versus snowfall, snowpack melting, litter
13 decay, and nitrification. Temperature affects processes such as cation exchange, mineral
14 weathering, and uptake only indirectly. Precipitation effects are manifested strictly through the
15 hydrologic simulations; none of the nutrient processes are dependent explicitly upon moisture.

16 17 **AX3.3.1.3 PnET-BGC**

18 PnET/BGC is an integrated dynamic biogeochemical model that simulates chemical
19 transformations of vegetation, soil and drainage water. The PnET-BGC model was formulated
20 by linking two submodels (vegetation and biogeochemical) to allow for the simultaneous
21 simulation of major element cycles in forest and interconnected aquatic ecosystems. The
22 vegetation submodel is based on PnET-CN (Aber and Federer, 1992; Aber and Driscoll, 1997;
23 Aber et al., 1997), a simple generalized model of monthly carbon, water, and nitrogen balances
24 that provides estimates of net primary productivity, N uptake, and water balances. The
25 biogeochemical submodel BGC (Gbondo-Tugbawa et al., 2001), expands PnET to include
26 vegetation and organic matter interactions of other elements (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Si , S , P , Al^{3+} ,
27 Cl^- , and F^-), abiotic soil processes, solution speciation, and surface water process.

28 PnET-BGC was initially developed for and applied to the northern hardwood forest
29 ecosystem. The model has been tested using vegetation, soil and water chemistry data from the
30 Hubbard Brook Experiment Forest (HBEF) (Gbondo-Tugbawa et al., 2001). The model has
31 subsequently been applied to intensively studied watersheds in the Adirondack and Catskill

1 regions of New York and applied regionally to the Adirondacks (Chen and Driscoll, 2005b) and
2 northern New England (Chen and Driscoll, 2005a,c). PnET-BGC has also been used to evaluate
3 the effects of current and future atmospheric deposition scenarios (Gbondo-Tugbawa and
4 Driscoll, 2002; Sullivan et al., 2006).

5
6 *PnET-BGC Model Structure*

7 PnET/BGC simulates major biogeochemical processes, such as forest canopy element
8 transformations, hydrology, soil organic matter dynamics, nitrogen cycling, geochemical
9 weathering, and chemical equilibrium reactions in solid and solution phases, and allows for
10 simulations of land disturbance (see Figure AX3.3-2). The model uses mass transfer
11 relationships to describe weathering, canopy interactions and surface water processes. Chemical
12 equilibrium relationships describe anion adsorption, cation exchange and soil solution and
13 surface water speciation. Soil solution equilibrium reactions are described using the tableau
14 approach (Morel and Hering, 1993). A more detailed description of the model can be found in
15 Gbondo-Tugbawa et al. (2001).

16 The model operates on a monthly time step and is applied at the stand to small-watershed
17 scale. The process of photosynthesis, growth and productivity, litter production and decay,
18 mineralization of organic matter, immobilization, and nitrification in PnET have been described
19 in Aber and Federer (1992) and Aber et al. (1997). The BGC submodel uses the Gaines–Thomas
20 formulation (White and Zelazny, 1986) to describe cation exchange reactions within the soil.
21 The exchangeable cations considered in the model include Ca^{2+} , Mg^{2+} , Na^+ , H^+ , Al^{3+} , K^+ , and
22 NH_4^+ . A pH-dependent adsorption isotherm is used to describe the sulfate adsorption process.
23 The speciation of monomeric aluminum is calculated in the model, including both organic and
24 inorganic forms. Organic acids are described using a triprotic analogue (Driscoll et al., 1994)
25 and the total amount of organic acids is estimated as a certain fraction (based on the charge
26 density) of DOC. The model simulates ANC in surface waters as an analogue to ANC measured
27 by Gran plot analysis, by considering the contributions of DIC, organic anions and Al complexes
28 (Driscoll et al., 1994).

29 The PnET/BGC model requires inputs of climate, wet and dry deposition chemistry, and
30 weathering data. Climate inputs consist of minimum and maximum air temperature, solar
31 radiation, and precipitation. The model uses a constant dry-to-wet deposition ratio by default,
32 but a variable ratio can also be applied (Chen and Driscoll, 2004). The model inputs utilize

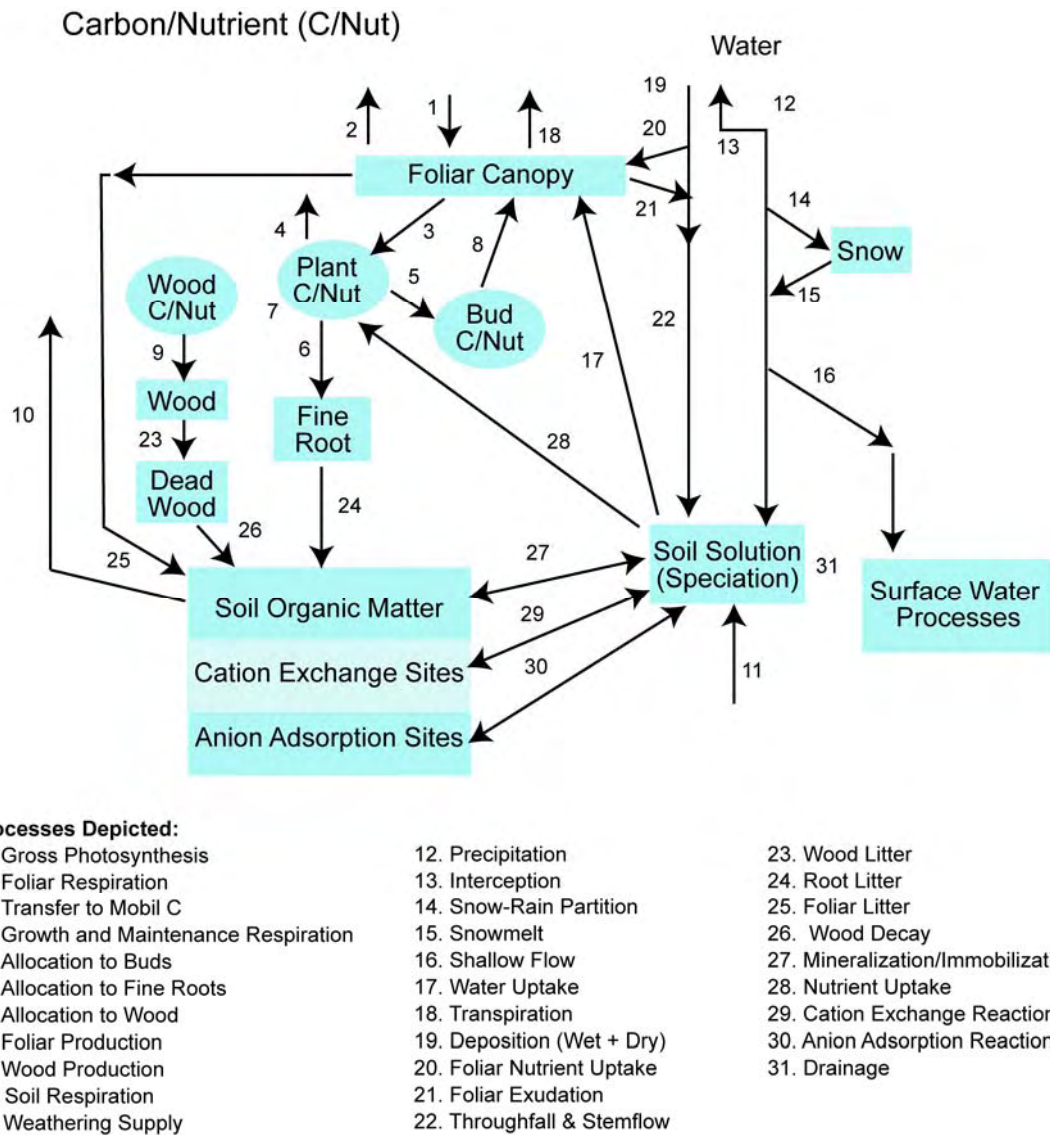


Figure AX3.3-2. Structure of the PnET-BGC model illustrating the compartments and flow paths of carbon and nutrients (C/Nut) within the model.

Source: Gbondo-Tugbawa et al. (2001).

1 canopy enhancement factors to depict the increased dry deposition observed in coniferous and
 2 mixed forest stands compared to hardwood forests. Deposition and weathering fluxes for all
 3 major elements are required as model inputs. Weathering rates are assumed to remain constant
 4 over time.

1 Calibration of PnET-BGC is based on empirical relationships and observations. The
2 model uses historical reconstructions of climate, atmospheric deposition, and land disturbance in
3 order to construct hindcasts of the response of forests to past acidic deposition. The model can
4 also be used to predict the response of acid-sensitive forest ecosystems to future changes in
5 acidic deposition, for example in response to controls on atmospheric emissions. A detailed
6 description of the model, including a detailed uncertainty analysis of parameter values, is
7 available in Gbondo-Tugbawa et al. (2001).

8 9 **AX3.3.1.4 DayCent-Chem**

10 DayCent-Chem links two widely accepted and tested models, one of daily
11 biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent (Parton et al.,
12 1998), and the other of soil and water geochemical equilibrium, PHREEQC (Parkhurst and
13 Appelo, 1999). The linked DayCent/PHREEQC model was created to capture the
14 biogeochemical responses to atmospheric deposition and to explicitly consider those
15 biogeochemical influences on soil and surface water chemistry. The linked model expands on
16 DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions
17 of many other chemical species in surface water.

18 Hartman et al. (2007) used DayCent-Chem to investigate how wet and dry deposition
19 affect biological assimilation, soil organic matter composition, ANC and pH of surface waters,
20 and also Al mobilization, soil base cation depletion, and base cation flux. Model results were
21 tested against a long-term data set available from Andrews Creek in Loch Vale Watershed,
22 Rocky Mountain National Park, Colorado.

23 24 *DayCent-Chem Model Structure*

25 DayCent is the daily time-step versions of CENTURY, a non-spatial, lumped parameter
26 model that simulates C, N, P, S, and water dynamics in the soil-plant system at a monthly
27 timestep over time scales of centuries and millennia (Parton et al., 1994). CENTURY can
28 represent a grassland, crop, forest, or savanna system with parameters that describe the site-
29 specific plant community and soil properties. DayCent, the daily timestep version of
30 CENTURY, adds layered soil temperature, a trace gas submodel, a more detailed soil hydrology
31 submodel, and explicitly represents inorganic N as either NO_3^- or NH_4^+ (Parton et al., 1998;
32 Kelly et al., 2000; Del Grosso et al., 2001). DayCent 5 is an object-oriented model written in the

1 C++ programming language that implements a layered soil structure and algorithms to manage
2 soil layers. The model is initialized with an organic soil depth and up to 10 soil layers, where
3 each layer has a specified thickness, texture, bulk density, field capacity, wilting point, and
4 saturated hydraulic conductivity.

5 PHREEQC is a model based on equilibrium chemistry of aqueous solutions interacting
6 with minerals, gases, exchangers, and sorption surfaces. The model is written in the C
7 programming language and has an extensible chemical database. Version 2.7 of PHREEQC is
8 used in the linked DayCent-Chem model to compute aqueous speciation, ion-exchange
9 equilibria, fixed-pressure gas-phase equilibria, dissolution and precipitation of mineral phases to
10 achieve equilibrium, and irreversible aqueous mineral phase reactions. The aqueous model uses
11 ion-association and Debye Huckel expressions. Ion-exchange reactions are modeled with the
12 Gaines-Thomas convention and equilibrium constants are derived from Appelo and Postma
13 (1993).

14 The DayCent-Chem model inputs are climate drivers consisting of daily precipitation,
15 and minimum and maximum air temperatures. The model also requires daily atmospheric wet
16 deposition concentrations for precipitation species Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NH_4^+ , NO_3^- , SO_4^{2-} ,
17 and H^+ and daily dry deposition amounts or dry/wet ratios for all precipitation species. Initial
18 conditions for model simulations include: (1) initial snowpack water content and chemical
19 composition; (2) initial soil solution concentrations; and (3) initial exchangeable cations in each
20 soil layer. Potential annual denudation rates for each mineral phase that could be dissolved in
21 the soil, groundwater, or stream solutions must also be provided.

22 DayCent-Chem implements a geochemical submodel of layered pools and properties that
23 provides information exchange, such as of water fluxes and solute concentrations, between the
24 coupled models, and calculates daily geochemical outputs. The geochemical submodel defines
25 soil layers and a groundwater pool that correspond to those in Day-Cent 5's original soil class.
26 Surface water concentrations are computed in a two-step process where solutes are first
27 transported, and then PHREEQC undertakes solution reactions. At each timestep, the model
28 updates exchangeable base cation pools and soil solutions in each soil layer, along with
29 groundwater and stream solutions.

30 DayCent 5 output includes daily evapotranspiration; soilwater content; outflow; inorganic
31 and organic C, N, P, and S stream fluxes; C, N, P, and S contents in soil and plant pools; net

1 primary production (NPP); nutrient uptake; trace gas flux; and heterotrophic respiration. In
2 addition to standard DayCent 5 outputs, at each daily timestep the model writes the solution
3 chemistry for soil layers, groundwater, and stream.

4 5 **AX3.3.1.5 SPARROW**

6 SPATIally Referenced Regressions on Watersheds (SPARROW) is a hybrid
7 statistical/deterministic model used to estimate pollutant sources and contaminant transport in
8 surface waters. SPARROW can be used to estimate pollutant loading to downstream receiving
9 waters for a number of water quality constituents. The model as constructed for evaluating N
10 export to estuaries will be presented here.

11 SPARROW was first described by Smith et al. (1997) as a water quality model designed
12 to reduce problems with interpreting watershed data as a result of sparse sampling, network bias,
13 and basin heterogeneity. SPARROW combines regression techniques and process information
14 regarding contaminant transport and retention in watershed and riverine systems. Literature
15 values for watershed retention rates are used; in-stream retention of N is estimated by a first-
16 order decay function (Smith et al., 1997).

17 Others have developed similar regression models relating in-stream water quality
18 measurements to watershed nutrient sources and basin attributes (Howarth et al., 1996; Jaworski
19 et al., 1997; Mueller et al., 1997). These simple correlative models assume that contaminate
20 sources and sinks are homogenously distributed and do not make a distinction between
21 watershed and in-stream loss processes. SPARROW is distinct from these methods by
22 incorporating spatial representation of basin attributes in the model. Model correlations between
23 basin attributes and water quality measurements are strengthened by incorporating these spatial
24 references (Smith et al., 1997; Alexander et al., 2001). Spatially referenced basin attributes
25 include land use, point and non-point N sources, temperature, soil permeability, and stream
26 density, among others. Figure AX3.3-3 (Preston and Brakebill, 1999) shows the mathematical
27 form of the SPARROW model.

28 Smith et al. (1997) provided an example of SPARROW model development for
29 application to the conterminous United States. Their exploratory model included five N sources
30 and eight land surface characteristics as potential factors that deliver N from land to water. In-
31 stream decay coefficients for three stream size classes were also tested for significance (Table
32 AX3.3-1) (Smith et al., 1997).

$$L_i = \sum_{n=1}^N \sum_{j \in J(i)} \beta_n S_{n,j} e^{(-\alpha' Z_j)} e^{(-\delta' Z_{i,j})}$$

where

L_i = load in reach i ;

n, N = source index where N is the total number of considered sources;

$J(i)$ = the set of all reaches upstream and including reach i , except those containing or upstream of monitoring stations upstream of reach i ;

β_n = estimated source parameter;

$S_{n,j}$ = contaminant mass from source n in drainage to reach j ;

α = estimated vector of land-to-water delivery parameters;

Z_j = land-surface characteristics associated with drainage to reach j ;

δ = estimated vector of instream-loss parameters; and

$T_{i,j}$ = channel transport characteristics.

Figure AX3.3-3. Mathematical form of the SPARROW model.

Source: Preston and Brakebill (1999).

1 The final model resulted in the inclusion of each of the five N sources and three
 2 (temperature, soil permeability, and stream density) of the eight land to water delivery factors.
 3 Parameter selection was primarily based on statistical significance. Further discussion regarding
 4 the exclusion of precipitation and irrigated land, both of which were determined to be significant,
 5 can be found in Smith et al. (1997). Parameter estimates are evaluated for robustness through the
 6 use of bootstrap analysis.

7 The bootstrap procedure involves randomly selecting, with replacement, M monitored
 8 loads and associated predictor variables from among the observations in the data set (M is the
 9 number of monitored reaches in the reach network). Where a sampled observation has an
 10 upstream monitored load as one of its predictors, the monitored value is used, regardless of
 11 whether the upstream station appears in the bootstrap sample. Coefficient values are estimated
 12 from the bootstrap sample. The bootstrap process is repeated 200 times, resulting in 200
 13 estimates of each coefficient. From these estimates, the mean coefficient value (called the

1 bootstrap estimate), minimum confidence interval, and probability that the estimated coefficient
2 has the wrong sign are determined (Smith et al., 1997).

3 Spatial referencing in the model occurs in two ways: (1) land surface polygons are
4 mapped in conjunction with nonpoint contaminant sources and the land-water delivery variables
5 (temperature, soil permeability, stream density, etc.) and (2) the stream reach network is mapped
6 along with point sources, channel transport characteristics, and measured transport rates. The
7 positive impacts of this spatial referencing can be quantified by eliminating the channel decay
8 coefficients from the model and creating a new model with only the contaminant sources and
9 land-water delivery variables in the original model (Smith et al., 1997). Removing this spatial
10 reference provided by the reach network results in a model with significantly higher mean
11 squared error and lower predictive capacity (Table AX3.3-2) (Smith et al., 1997).

12 SPARROW has also been applied to spatially identify N sources at the scale of the
13 Chesapeake Bay watershed (Preston and Brakebill, 1999). A similar set of N sources, land-to-
14 water delivery parameters, and in-stream loss rates to those used in Smith et al. (1997) were
15 considered for this model (Preston and Brakebill, 1999). Only estimates for parameters that were
16 used in the final model are given in Table AX3.3-3.

17 The final model included five N sources, one land-to-water deliver parameter (soil
18 permeability), and four in-stream loss rates (including reservoir retention). Comparisons
19 between predicted and observed N loading provided an r^2 value of 0.961 (Preston and Brakebill,
20 1999). Because the data that are used in SPARROW are spatially referenced, model results can
21 be mapped. Figure AX3.3-3 (Preston and Brakebill, 1999) shows the delivered yield of total N
22 (lbs/acre/yr), after accounting for in-stream losses, across the Chesapeake Bay watershed.
23 Regions of the watershed estimated to be responsible for relatively high N loading can be clearly
24 identified though this spatial representation.

25 The relative source contributions of N loading to the Bay can be compared graphically.
26 The ability to quantify and spatially locate N sources in this manner is useful for prioritizing land
27 management activities.

28 29 **AX3.3.1.6 WATERSN**

30 The Watershed Assessment Tool for Evaluating Reduction Strategies for Nitrogen
31 (WATERSN) model is a steady-state numerical N budgeting model that estimates the amount of
32 N exported to rivers and estuaries from forest, agricultural, and urban land uses. The model is

1 intended to provide an understanding of the relative contribution of N export from these land
 2 uses to estuaries, and to evaluate N export reduction strategies that are specific to each land
 3 type (Driscoll et al., 2007). Figure AX3.3-4 shows a conceptual diagram of the N budgeting
 4 system used in WATERSN.

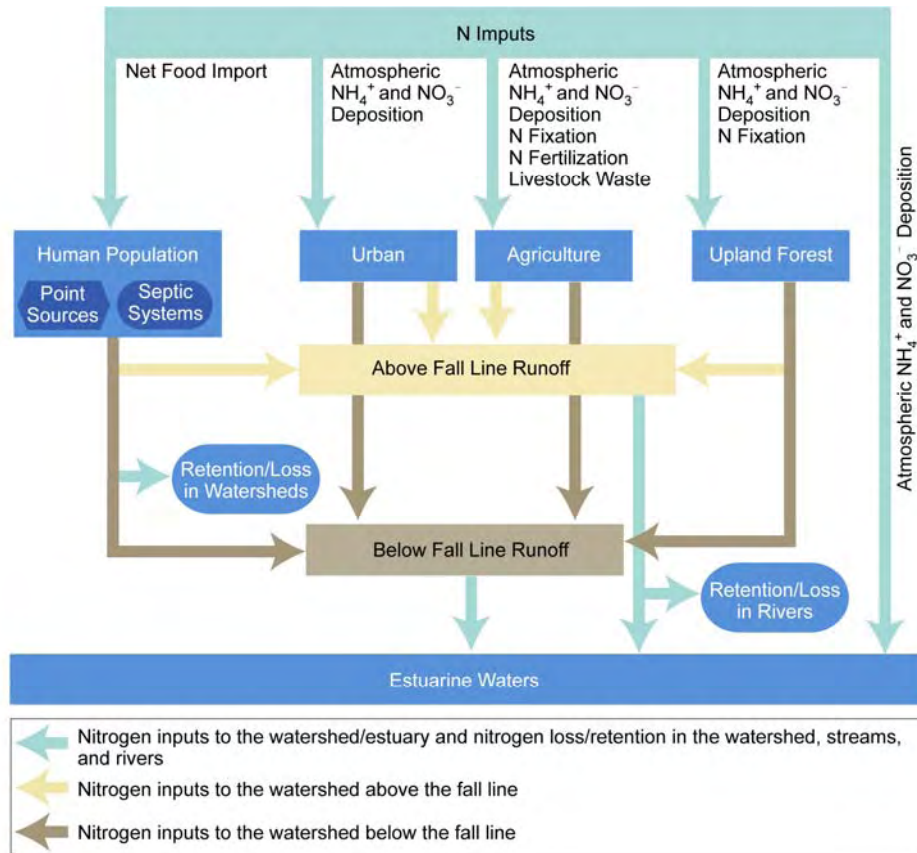


Figure AX3.3-4. Schematic diagram of the WATERSN approach to estimate the contribution made by different nitrogen sources to the total nitrogen inputs an estuary.

Source: Castro et al. (2003).

5 A detailed description of the original model calculations is provided in Castro et al.
 6 (2001). Subsequent model applications (Castro and Driscoll, 2002; Castro et al., 2003; Driscoll
 7 et al., 2003; Whitall et al., 2004) have developed modifications to the approach originally
 8 described in Castro et al. (2001).

1 WATERSN uses calculations described in Jordan and Weller (1996) to estimate N inputs
2 to the watershed/estuary system. Estimated anthropogenic sources of N inputs to the modeled
3 watershed/estuary system include: (1) crop and lawn fertilizer application, (2) biotic N fixation
4 by leguminous crops and pastures, (3) atmospheric deposition of wet and dry inorganic N (NH_4^+ ,
5 NO_3^-), (4) net N import of food for human consumption, and (5) net N import of feed for
6 livestock (Castro and Driscoll, 2002).

7
8 *Agricultural Areas*

9 N available for water-borne export to estuaries from agricultural lands is determined as
10 the difference between N inputs and outputs (Castro et al., 2001). Modeled N inputs to
11 agricultural lands consist of wet and dry atmospheric NH_4^+ and NO_3^- deposition, N fertilization,
12 biotic N fixation, and livestock waste (Castro and Driscoll, 2002). Wet and dry deposition are
13 derived from NADP and CASTNET data. Average annual wet deposition rates of NH_4^+ and
14 NO_3^- are taken from NADP sites in or near the study watersheds. Dry deposition of NH_4^+ and
15 NO_3^- is calculated as an average of all CASTNET sites nearest to the study watersheds.
16 WATERSN assumes that dry deposition of both NH_4^+ and NO_3^- to the estuary surface is 25%
17 less than dry deposition to the watershed (Castro and Driscoll, 2002). Meyers et al. (2000)
18 described the uncertainty of estimates of wet and dry deposition and considered it to be no less
19 than a factor of 2. Estimates of N fertilization are taken from agricultural census data.
20 WATERSN assumes that all fertilizer sold in a county is applied in that county. This is
21 considered to be the most certain N input to the model ($\pm 25\%$) (Castro and Driscoll, 2002).
22 WATERSN estimates both non-symbiotic and symbiotic N fixation for crops, pastures, hay
23 fields and upland forests. Non-symbiotic rates were taken from literature values for crops,
24 orchards, upland forests, and non-wooded pastures (Woodmansee, 1978; Stevenson, 1982;
25 Hendrickson, 1990). Symbiotic rates of N fixation are based on type of legume, crop N harvest,
26 N in unharvested portions of crops, soil N availability, and fertilization rate. These estimates are
27 less certain than for N fertilization, but are noted as being a relatively minor N source in most of
28 the study watersheds. Livestock waste was calculated as the difference between livestock
29 consumption of N in feed and production of N in meat, milk, and eggs for human consumption
30 (Jordan and Weller, 1996).

1 Nitrogen outputs from agricultural land include crop harvest, pasture grazing,
2 volatilization of NH_3 and denitrification. Data regarding crop harvest are obtained from
3 agricultural census. Nitrogen removed through crop harvest is estimated by multiplying the crop
4 harvest by the percent N in each crop. Estimates for grazing are based on sheep, cattle, and
5 horse populations (USDA online database in Castro and Driscoll, 2002), their dietary N
6 requirements, and proportion of dietary N obtained from grazing (Jordan and Weller, 1996).
7 Ammonia volatilization is assumed to be 10% of the N input from fertilizer and atmospheric
8 deposition, and 20% of livestock manure inputs (Schlesinger and Hartley, 1992). Denitrification
9 rates were originally estimated as 10 to 30% of the N inputs from fertilizer and atmospheric
10 deposition and 20% of livestock N waste. Subsequent applications of WATERSN (Castro et al.,
11 2003) modified denitrification rates from agricultural lands to vary with the mean watershed
12 temperature and are based on a denitrification activity Q_{10} value of 2 (Stanford et al., 1975; Maag
13 et al., 1997). A Q_{10} value of 2 suggests that the denitrification rate used by the model will
14 change by a factor of 2 for every 10 degree change in temperature based on a direct relationship
15 between temperature and denitrification.

16 17 *Urban Areas*

18 Nitrogen inputs to urban areas include atmospheric and non-atmospheric sources. The
19 total atmospheric N deposition input to urban areas is taken as the total (wet + dry) inorganic
20 (NO_3^- and NH_4^+) N deposition rate to the watershed multiplied by the total urban area in the
21 watershed. Non-atmospheric sources include point sources (primarily waste water treatment
22 plants) and non-point sources (septic systems and pervious/impervious surface runoff) of N in
23 urban areas (Castro and Driscoll, 2002).

24 Nitrogen outputs from urban areas include waste water treatment plant effluent, septic
25 system leachate, and total N runoff from pervious and impervious lands. Measured total N data
26 are used to calculate N export for wastewater treatment plants that have available data. A strong
27 regression relationship between measured total N discharged from wastewater treatment plants
28 and human populations that use wastewater treatment facilities is used to estimate total N
29 discharges from wastewater treatment plants that do not have total N monitoring data available.
30 Septic system output is determined by multiplying watershed specific human per capita N
31 excretion rates by the human population of the watershed. WATERSN assumes that 75% of

1 this N is exported to the estuary (Castro and Driscoll, 2002). The soil water assessment tool
2 (SWAT) is used to estimate non-point source non-atmospheric total N runoff from pervious and
3 impervious urban lands. SWAT is a distributed parameter, continuous time model applicable at
4 the watershed scale. Required inputs to SWAT include climatic variables, soil properties,
5 elevation, vegetation information, and land use. SWAT is designed to predict land use and land
6 management impacts on water, sediment, and agricultural yields in large watersheds (Castro and
7 Driscoll, 2002). The model assumes that 75% of atmospheric N inputs to urban areas is exported
8 to the estuary (Fisher and Oppenheimer, 1991). Alternatively, this N export term can be
9 modified.

10 *Upland Forests*

12 Nitrogen inputs to forests are assumed to be in the form of atmospheric deposition and
13 non-symbiotic N fixation. Outputs from forests are estimated with a non-linear regression
14 relationship between wet deposition of inorganic N and stream water export of dissolved
15 inorganic nitrogen (DIN) developed using results from a multitude of forest watershed studies.
16 Exported dissolved organic nitrogen (DON) was assumed to be equal to 50% of the inorganic N
17 export (Castro and Driscoll, 2002).

18 *Watershed and In-Stream Nitrogen Retention*

20 Model validation efforts using measured N fluxes from the USGS National Stream
21 Quality Accounting Network (NASQAN) have shown that WATERSN tends to overestimate N
22 export from watersheds to estuaries (Castro and Driscoll, 2002). These differences are not
23 unexpected since WATERSN does not account for watershed and in-stream N sinks. Attempts
24 have been made to improve flux estimates by accounting for watershed and in-stream N retention
25 (Castro et al., 2001, 2003; Castro and Driscoll, 2002). A summary of the N retention rates
26 applied to WATERSN in these studies is given in Table AX3.3-4.

27 Castro and Driscoll (2002) assumed that 30% of the total N that entered rivers above the
28 fall line was lost during transport to the fall line and that inputs that enter the river below the fall
29 line were not attenuated because of the relatively short travel times to the estuary. This 30% in-
30 stream N retention value represents the median retention value obtained in previous studies of
31 northeastern United States rivers (Castro et al., 2001), and falls within the range of retention
32 values estimated by Howarth et al. (1996) and Alexander et al. (2000). Castro and Driscoll

1 (2002) also incorporated watershed N retention fractions specific to individual land uses. They
2 assumed that 60% of the excess N from agricultural land and septic systems was lost (retained
3 within the watershed) due to watershed processes. Support for this value of N retention was
4 given by several reports of riparian N removal rates from agricultural land, ranging from about
5 50 to 90% (Lowrance et al., 1983; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985;
6 Jordan et al., 1993). After incorporating these assumptions, predicted fluxes closely matched
7 ($r^2 = 0.909$) measured fluxes.

8 Driscoll et al. (2003) applied WATERSN to investigate anthropogenic N loading to
9 estuaries in the northeastern United States. The objectives of the study were to apply
10 WATERSN to (1) quantify the inputs of reactive N to the region (Figure AX3.3-5), (2) discuss
11 the ecological effects of regional elevated anthropogenic reactive N inputs, and (3) evaluate
12 management options aimed at mitigating the effects of these elevated anthropogenic N inputs.
13 Modeled N reduction scenarios included reductions in atmospheric N emissions, increased N
14 removal efficiencies of wastewater treatment plants, offshore pumping of wastewater, reductions
15 in agricultural N runoff to surface waters, and an integrated management scenario consisting of a
16 combination of N reductions from multiple sources. Other studies have applied WATERSN to
17 address similar issues related to N loading to estuaries in other regions of the United States.
18 (Castro et al., 2003; Whitall et al., 2004; Whitall and Bricker, 2006).

19

20 **AX3.3.2 Additional Effects Models Used Widely in Europe**

21 The models of the effects of S and N deposition described below have been used
22 primarily in Europe. These descriptions are derived in part from the UNECE Convention of
23 Long-Range Transboundary Air Pollution Modelling and Mapping manual (Posch et al., 2003).

24

25 **AX3.3.2.1 The Very Simple Dynamic Model**

26 The Very Simple Dynamic (VSD) soil acidification model is frequently used in Europe to
27 simulate acidification effects in soils when observed data are sparse. It only includes weathering,
28 cation exchange, N immobilization processes, and a mass balance for cations, sulfur and
29 nitrogen. It resembles the model presented by Reuss (1980) which, however, did not consider
30 nitrogen processes. In the VSD model, the various ecosystem processes have been limited to a
31 few key processes. Processes that are not taken into account include (1) canopy interactions, (2)
32 nutrient cycling processes, (3) N fixation and NH_4 adsorption, (4) sulfate transformations

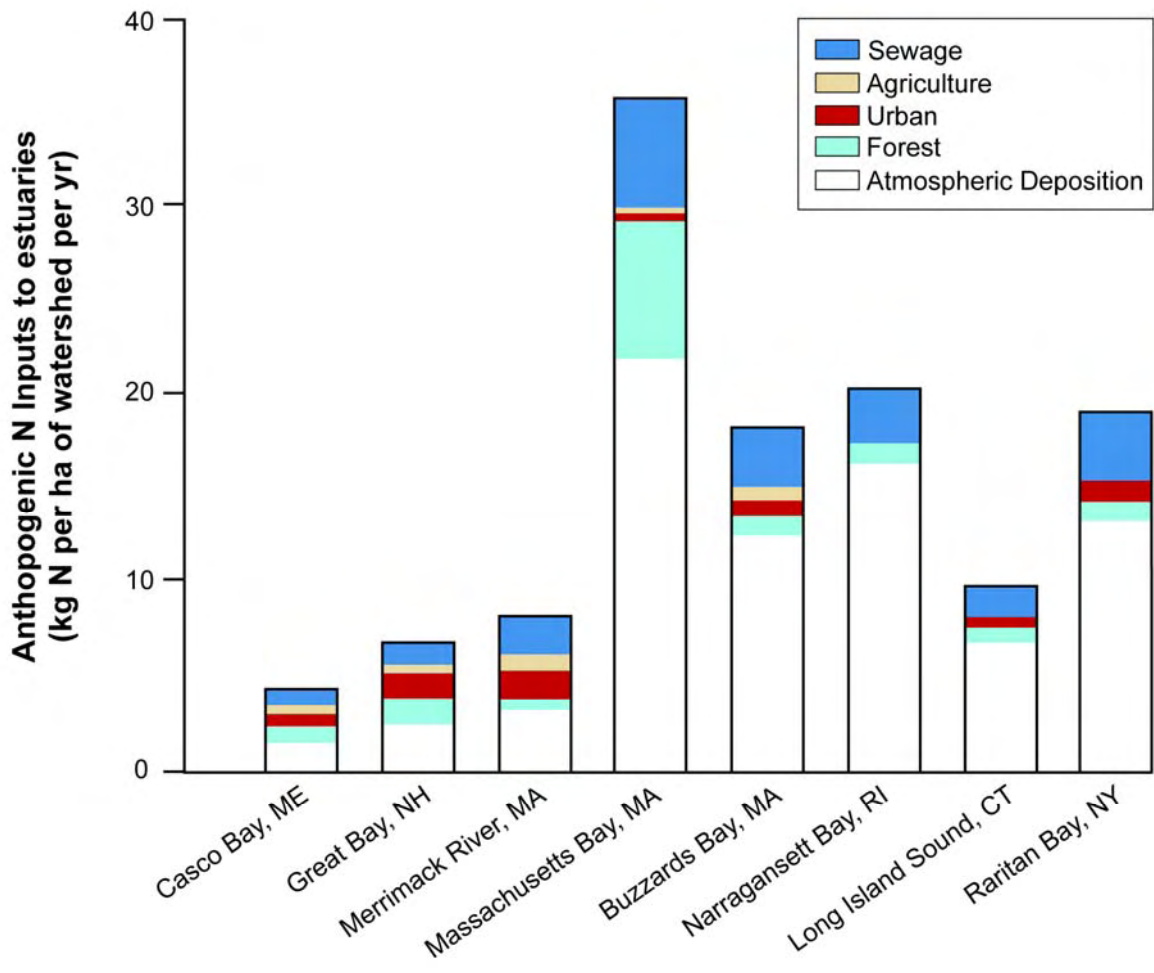


Figure AX3.3-5. WATERSN model estimates of anthropogenic N inputs to the estuaries of the northeastern United States, in kilograms per hectare per year.

Source: Driscoll et al. (2003).

1 (adsorption, uptake, immobilization, and reduction), (5) formation and protonation of organic
 2 anions, and (6) complexation of Al.

3 The VSD model consists of a set of mass balance equations, describing the soil input-
 4 output relationships, and a set of equations describing the rate-limited and equilibrium soil

1 processes. The soil solution chemistry in VSD depends solely on the net element input from the
2 atmosphere (deposition minus net uptake minus net immobilization) and the geochemical
3 interaction in the soil (CO₂ equilibria, weathering of carbonates and silicates, and cation
4 exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g.,
5 uptake and silicate weathering) or by equilibrium reactions (e.g., cation exchange). It models the
6 exchange of Al, H, and Ca + Mg + K with Gaines-Thomas or Gapon equations.

7 Solute transport in VSD is described by assuming complete mixing of the element input
8 within one homogeneous soil compartment with a constant density and a fixed depth. Since
9 VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration
10 of the soil water leaving this layer (mostly the rootzone). The annual water flux percolating from
11 this layer is taken as being equal to the annual precipitation excess. The time step of the model is
12 one year, and therefore seasonal variations are not considered. A detailed description of the
13 VSD model can be found in Posch and Reinds (2003).

14 15 **AX3.3.2.2 SMART**

16 The Simulation Model for Acidification's Regional Trends (SMART) model is similar to
17 the VSD model, but somewhat extended. It is described in De Vries et al. (1989) and Posch
18 et al. (1993). As with the VSD model, the SMART model consists of a set of mass balance
19 equations, describing soil input-output relationships, and a set of equations describing the rate-
20 limited and equilibrium soil processes. It includes most of the assumptions and simplifications
21 given for the VSD model; and justifications for them can be found in De Vries et al. (1989).

22 SMART models the exchange of Al, H, and divalent base cations using Gaines Thomas
23 equations. Additionally, SO₄²⁻ adsorption is modeled using a Langmuir equation (as in MAGIC)
24 and organic acids can be described as mono-, di-, or tri-protic. Furthermore, it does include a
25 balance for carbonate and Al, thus allowing application to a range of site conditions, from
26 calcareous soils to completely acidified soils that do not have an Al buffer left. Recently, a
27 description of the complexation of aluminum with organic acids has been included. The
28 SMART model has been developed with regional applications in mind, and an early example of
29 an application to Europe can be found in De Vries et al. (1994).

1 **AX3.3.2.3 SAFE**

2 The Soil Acidification in Forest Ecosystems (SAFE) model has been developed at the
3 University of Lund (Warfvinge et al., 1993) and a recent description of the model can be found
4 in Alveteg and Sverdrup (2002). The main differences between the SMART and MAGIC
5 models are: (a) weathering of base cations is not a model input, but it is modeled with the
6 PROFILE (sub-)model, using soil mineralogy as input (Warfvinge and Sverdrup, 1992); (b)
7 SAFE is oriented to soil profiles in which water is assumed to move vertically through several
8 soil layers (usually 4); (c) Cation exchange between Al, H, and (divalent) base cations is
9 modeled with Gapon exchange reactions, and the exchange between soil matrix and the soil
10 solution is diffusion-limited.

11 The standard version of SAFE does not include SO_4^{2-} adsorption although a version, in
12 which SO_4^{2-} adsorption is dependent on SO_4^{2-} concentration and pH has recently been
13 developed (Martinson et al., 2003). The SAFE model has been applied to many sites and more
14 recently also regional applications have been carried out for Sweden (Alveteg and Sverdrup,
15 2002) and Switzerland (Kurz et al., 1998).

16

17 **AX3.3.3 Other Models**

18 There are scores of models that can be useful in the context of developing a better
19 understanding of the ecological effects of atmospheric S and N deposition. In the preceding
20 sections, we have attempted to summarize a relatively small number of models that are most
21 commonly used for this purpose in the United States and Europe, in particular those that
22 contribute to substantive conclusions presented in the ISA. There are many other models that are
23 not covered in the discussion presented in this annex. Several are highlighted in Table AX3.3-5.

TABLE AX3.2-1. LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
H.J. Andrews Experimental Forest (AND) 44.2, -122.2	Path 46 Row 29; Lat/Long: 44°14'N / 122°11'W	Oregon State University; USDA Forest Service Pacific Northwest Research Station	Temperate coniferous forest. Douglas-fir/western hemlock/ western red cedar; true fir and mountain hemlock; streams	Successional changes in ecosystems; forest-stream interactions; population dynamics of forest stands; patterns and rates of decomposition; disturbance regimes in forest landscapes
Arctic Tundra (ARC) 68.6, -149.6	Path 73, Row 12; Lat/Long: 68°38'N / 149°34'W	The Ecosystem Center, Marine Biological Laboratory; Universities of Alaska, Massachusetts, Minnesota, Cincinnati, and Kansas; Clarkson University	Arctic tundra, lakes, streams. Tussock tundra; heath tundra; riverine willows; oligotrophic lakes; headwater streams	Research topics: Movement of nutrients from land to stream to lake; changes due to anthropogenic influences; controls of ecological processes by nutrients and by predation
Baltimore Ecosystem Study (BES) 39.1, -76.3	Path 15, Row 33; Lat/Long 38°54' 04' (N), 76°52' 04' (W)	Institute of Ecosystem Studies; USDA Forest Service, Johns Hopkins University; University of Maryland; Baltimore County and College Park; University of North Carolina; Parks and People Foundation; US Geological Survey; Yale University	Eastern deciduous forest/ Suburban Agriculture fringe, urban parks, residential and commercial patches, riparian and stream habitats	Patch dynamics of built, social, biological, and hydrological components of the metropolitan area; feedback's between social, economic, and ecological components of an urban ecosystem; effect of infrastructure and development on fluxes of nutrients, energy, and water in upland, stream, and coastal regions of metropolitan Baltimore

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Bonanza Creek Experimental Forest (BNZ) 64.8, -148.0	Path 69, Row 15; Lat/Long: 64°45'N / 148°00'W	University of Alaska; Institute of Northern Forestry, USDA Forest Service, Pacific Northwest Research Station	Taiga. Areas of boreal forest including permafrost- free uplands and permafrost-dominated north slopes and lowlands; floodplain seres	Successional processes associated with wildfire and floodplains; facilitative and competitive interactions among plant species throughout succession; plant- mediated changes in resource and energy availability for decomposers; herbivorous control of plant species composition; hydrologic regime and stream ecology
Cedar Creek Natural History Area (CDR) 45.4, -93.2	Path 27, Row 28; Lat/Long: 45°24'N / 93°12'W	University of Minnesota	Eastern deciduous forest and tallgrass prairie. Old fields; oak savanna and forest, conifer bog; lakes; pine forest; wetland marsh and carr	Successional dynamics; primary productivity and disturbance patterns; nutrient budgets and cycles; climatic variation and the wetland/upland boundary; plant- herbivore dynamics

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Central Arizona - Phoenix (CAP) 33.5, -11.2	Path 36, Row 37 and Path 36, Row 36° - These have been used by CAP although Path 37, Row 37 is centered more closely in the City of Phoenix	Arizona State University (Main and West)	Sonoran Desert scrub. Urban parks, residential, interior remnant desert patches, commercial and industrial patches, urban fringe, regulated river and floodplain (dry), effluent-dominated river	Interactions of ecological and socio-economic systems in an urban environment; influence of land use change on ecological patterns and processes; movement of nutrients through highly manipulated, urban flowpaths; interactions of introduced and native species in urban environment; millennium- and century-scale geomorphic change in landforms and interaction with engineered landscapes
Coweeta Hydrologic Laboratory (CWT) 35.0, -83.5	Path 18, Row 36; Lat/Long: 35°00'N / 83°30'W	University of Georgia; USDA Forest Service, Southeastern Forest Experiment Station	Eastern deciduous forest. Hardwood forests and white pine plantations	Long-term dynamics of forest ecosystems including forest disturbance and stress along an environmental gradient; stream ecosystems along an environmental gradient; and the riparian zone as a regulator of terrestrial-aquatic linkages

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Harvard Forest (HFR) 42.5, -72.2	Path 13, Row 30; Lat/Long: 42°32'N / 72°10'W	Harvard University; Universities of New Hampshire and Massachusetts; The Ecosystem Center, Marine Biological Laboratory	Eastern deciduous forest. Hardwood-white-pine- hemlock forest; spruce swamp forest; conifer plantations	Long-term climate change, disturbance history and vegetation dynamics; comparison of community, population, and plant architectural responses to human and natural disturbance; forest- atmosphere trace gas fluxes; organic matter accumulation, decomposition and mineralization; element cycling, fine root dynamics and forest microbiology
Hubbard Brook Experimental Forest (HBR) 43.9, -71.8	Path 13, Row 29; Lat/Long: 43°56'N / 71°45'W	Yale, Cornell, and Syracuse Universities; Institute of Ecosystem Studies; USDA Forest Service, Northeastern Forest Experiment Station	Eastern deciduous forest. Northern hardwood forests in various developmental stages, spruce-fir forests; streams and lakes	Vegetation structure and production; dynamics of detritus in terrestrial and aquatic ecosystems; atmosphere-terrestrial-aquatic ecosystem linkages; heterotroph population dynamics; effects of human activities on ecosystems

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Jornada Experimental Range (JRN) 32.5, -106.8	Path 33, Row 37; Lat/Long: 32°30'N / 106°45'W	New Mexico State University; USDA ARS Jornada Experimental Range; Duke University, NC; NOAA, Research Triangle Park, NC; University of New Mexico; Dartmouth College, NH; Oregon Graduate Center; Texas Technological University; SUNY Buffalo, NY; University of Keele, UK; Kings College, London, UK; EPA-EMAP, Las Vegas, NV	Hot desert. Playa, piedmont, and swale; bajada, basin, mountain and swale shrubland; mesquite dunes	Desertification; factors affecting primary production; animal-induced soil disturbances; direct and indirect consumer effects; vertebrate and invertebrate population dynamics; grazing effects on ecosystem structure and function; biodiversity and ecosystem function; small mammal effects on soil and vegetation heterogeneity; soil microbial processes; surface hydrology; trace gas emissions from soils; eolian processes
W.K. Kellogg Biological Station (KBS) 42.4, -85.4	Path 21, Row 31; Lat/Long: 85°24'W / 42°24'N	Michigan State University, Michigan Agricultural Experiment Station	Row-crop agriculture. Conventional and organic-based corn-soybean-wheat cultivation; perennial biomass cultivation; native successional communities	Ecological interactions underlying the productivity and environmental impact of production-level cropping systems; patterns, causes, and consequences of microbial, plant, and insect diversity in agricultural landscapes; gene transfer, community dynamics, biogeochemical fluxes

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Konza Prairie Research Natural Area(KNZ) 39.1, -94.6	Path 28, Row 33; Lat/Long: 39°05'N / 96°35'W	Kansas State University	Tallgrass prairie. Tallgrass prairie; gallery forest; prairie stream	Effects of fire, grazing and climatic variability on ecological patterns and processes in tallgrass prairie ecosystems, use of remotely sensed data and geographic information systems to evaluate grassland structure and dynamics
Luquillo Experimental Forest (LUQ) 18.3, -65.8	Path 4, Row 47 and 48; Lat/Long: 18°18'N / 65°47'W	Center for Energy and Environment Research, University of Puerto Rico; Institute of Tropical Forestry, USDA Forest Service, Southern Experiment Station	Tropical rainforest. Tabonuco forest; palo Colorado forest; palm brake; dwarf forest and montane streams	Patterns of and ecosystem response to different patterns of disturbance; land-stream interactions; effect of management on ecosystem properties; integration of ecosystem models and geographic information systems
McMurdo Dry Valleys - Antarctica (MCM) -78.0, +165.0	Path 56, Row 116	Desert Research Institute, Reno, Nevada; U.S. Geological Survey, Boulder, Colorado	Polar desert oases	Microbial ecosystem dynamics in arid soils, ephemeral streams, and closed basin lakes; resource and environmental controls on terrestrial, stream and lake ecosystems; material transport between aquatic and terrestrial ecosystems; ecosystem response to greater hydrologic flux driven by warming climate
Niwot Ridge/Green Lakes Valley (NWT) 40.1, -105.6	Path 34, Row 32; Lat/Long: 40°03'N / 105°37'W	Institute of Arctic and Alpine Research, University of Colorado	Alpine tundra; Fellfield; meadow; herbaceous and shrub tundras; cliffs and talus; glacial lakes; streams and wetlands	Patterns and controls of nutrient cycling; trace gas dynamics, plant primary productivity and species composition; geomorphology, and paleoecology

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
North Temperate Lakes (NTL) 46.0, -89.7 and 43.1, 89.4	Path 25, Row 28 and Path 24, Row 30 Lat/Long: 46°00'N / 89°40'W and 89°24' / 43°06'	Center for Limnology, University of Wisconsin-Madison, Wisconsin	Northern temperate lakes in glacial landscapes in urban, agricultural and forested watersheds. Oligotrophic, dystrophic and eutrophic lakes; temporary forest ponds; warm and cold streams; sphagnum-leatherleaf bog; conifer swamp; mixed deciduous and coniferous forests	Physical, chemical and biological limnology; hydrology and geochemistry; climate forcing; producer and consumer ecology; ecology of invasions; ecosystem variability; lakescape and landscape ecology
Palmer Station (PAL) Antarctica -64.7, -64.0	Path 219 , Row 105; Lat/Long: 64°40'S / 64°W	University of California, Santa Barbara; Old Dominion University	Polar marine. Coastal and open ocean pelagic communities; seabird nesting areas	Oceanic-ice circulation and models; sea-ice dynamics; biological/physical interactions; effect of sea ice on primary production, consumer populations and apex predators; bio-optical models of primary production; spatial distribution and recruitment in consumer populations; seabird population dynamics and reproductive ecology
Plum Island Sound (PIE) 42.67, -70.99	Path 12, Row 30; Lat/Long: 42°40' / 70°59' Site has the following X and Y bounds in decimal coordinates: X min = -71.22 X max = -70.75 Y min = 42.50 Y max = 42.83. The total area is approximately 37 km x 37 km or 1369 km ²	The Ecosystems Center, Marine Biological Laboratory; Universities of South Carolina and New Hampshire; Massachusetts Audubon; Wells, Maine, NERRS	Coastal estuary	Linkages between land and coastal waters involving organic carbon and organic nitrogen inputs to estuarine ecosystems from watersheds with various land covers and uses

TABLE AX3.2-1 (cont'd). LTER SITE LOCATIONS AND BASIC SITE DESCRIPTION INFORMATION

Site*	Landsat WRS	Institutional Affiliations	Principal Biome/Main Communities	Research Topics
Sevilleta National Wildlife Refuge (SEV) 34.3, -106.8	Path 33, Row 36; To acquire entire site area, Path 32, Row 36, Path 32, Row 37 and Path 33, Row 37 are also needed. Lat/ Long: 34°19' / 106°62'W	University of New Mexico; U.S. Fish and Wildlife Service	Multiple--intersection of subalpine mixed-conifer forest/meadow, riparian cottonwood forest, dry mountainland, grassland, cold desert, hot desert. Conifer savanna; creosote bush; desert grassland; mesquite and sand dunes; Great Basin shrub and shortgrass steppes; tallgrass swales; riparian communities	Landscape and organism population dynamics in a biome tension zone; semiarid watershed ecology; climate change; biospheric/atmospheric interactions; paleobotany/archaeology; microbial role in gas flux; and control of landscape heterogeneity; scale effects on spatial and temporal variability
Shortgrass Steppe (SGS) 40.8, -104.8	Path 33, Row 32; Lat/Long: 40°49'N / 104°46'W	Colorado State University; USDA Forest Service; USDA Agricultural Research Service	Floodplain; shrubland; saltmeadow	Soil water; above- and belowground net primary production; plant population and community dynamics; effects of livestock grazing; soil organic matter accumulation and losses, soil nutrient dynamics; and ecosystem recovery from cultivation
Virginia Coast Reserve (VCR) 37.5, -74.8	Path 14, Row 34; Lat/Long: 37°30'N / 75°40'W	University of Virginia	Coastal barrier islands. Sandy intertidal; open beach; shrubthicket; mature pine forest; salt marsh; estuary	Holocene barrier island geology; salt marsh ecology, geology, and hydrology; ecology/evolution of insular vertebrates; primary/secondary succession; life-form modeling of succession

**TABLE AX3.2-2. CURRENT LONG-TERM MONITORING DATA SETS
DEVELOPED THROUGH THE HUBBARD BROOK ECOSYSTEM STUDY**

Physical/Hydrologic Monitoring

Instantaneous streamflow (9 stations)
 Daily precipitation (24 stations)
 Class A weather station data
 Weekly snow depth on snow courses
 Daily soil temperature and moisture

Solution Chemistry

Weekly bulk precipitation (6-10 stations)
 Monthly soil solution WS5, WS6
 Weekly stream at weirs of WS19
 Monthly stream within WS5, WS6

Air Chemistry

(SO₂, HNO₃, particulates, ozone)

Organisms

Bird populations
 Phytophagous insect populations
 WS2, WS4, WS5, WS6
 Vegetation biomass, chemistry

Mirror Lake

Instantaneous streamflow (3 inlets, outlet)
 Daily precipitation (2 stations)
 Weekly chemistry (3 inlets, outlet)
 Bi-monthly limnology (temp, chemistry, plankton)

Soils

Forest floor mass, chemistry (WS6, WS5; 5-yr intervals)
 Chemical and physical properties from soil pits (WS5)
 Chemical and physical properties from soil bags

TABLE AX3.2-3. STUDY WATERSHEDS AT HBEF

WS	Area (ha)	Slope (°)	Aspect	Elevation (m)	Gauge Type	Initial Yr
1	11.8	18.6	S22°E	488-747	V-notch weir	1956
2	15.6	18.5	S31°E	503-716	V-notch weir	1957
3	42.4	12.1	S23°W	527-732	V-notch weir	1957
4	36.1	15.6	S40°E	442-747	V-notch weir	1960
5	21.9	15.4	S24°E	488-762	V-notch weir, San Dimas flume	1962
6	13.2	15.8	S32°E	549-792	V-notch weir, San Dimas flume	1963
7	77.4	12.4	N16°W	619-899	V-notch weir, San Dimas flume	1965
8	59.4	14.0	N12°W	610-905	V-notch weir, San Dimas flume	1968
9	68.4		NE	685-910	V-notch weir	1995
10	12.1		SE	470-595	None	1970

TABLE AX3.3-1. RESULTS OF PARAMETRIC AND BOOTSTRAP REGRESSIONS OF TOTAL NITROGEN AT 414 NASQAN STATIONS ON BASIN ATTRIBUTES

Model Parameters	Coefficient Units ^a	Exploratory Model		Final Model					
		Parametric Coefficient	P	Parametric Coefficient	Parametric P	Bootstrap Coefficient	Lower 90% CI ^b	Upper 90% CI ^b	Bootstrap P
Nitrogen source β									
Point sources	dimensionless	0.4112	0.0004	0.3464	0.0049	0.4401	0.0864	0.8173	<0.005
Fertilizer application	dimensionless	2.798	0.0154	1.278	0.0022	1.433	0.6149	2.373	<0.005
Livestock waste production	dimensionless	1.340	0.1553	0.9723	0.0629	1.058	0.0859	1.919	0.005
Atmospheric deposition	dimensionless	3.334	0.2513	6.465	0.0033	6.555	3.270	9.323	<0.005
Nonagricultural land	kg/ha/yr	38.49	0.0154	14.67	0.0005	16.65	7.130	29.89	<0.005
Land to water delivery α									
Temperature	$^{\circ}\text{F}^{-1}$	0.0228	0.0001	0.0196	0.0001	0.0198	0.0117	0.0259	<0.005
Slope ^c	%	0.2034	0.2187						
Soil permeability	h/cm	0.0295	0.0022	0.0442	0.0001	0.0447	0.0334	0.0572	<0.005
Stream density ^c	km^{-1}	0.0205	0.0124	0.0215	0.0095	0.0243	-0.0003	0.0450	0.025
Wetland ^d	dimensionless	0.7177	0.2962						
Irrigated land ^e	dimensionless	1.101	0.0001						
Precipitation ^f	cm	38.52	0.0057						
Irrigated water use ^g	cm	0.0772	0.3117						
In-stream decay ^h δ									
δ_1 ($Q < 28.3 \text{ m}^3/\text{s}$)	d^{-1}	0.2917	0.0001	0.3758	0.0001	0.3842	0.2981	0.4768	<0.005
δ_2 ($28.3 \text{ m}^3/\text{s} < Q < 283 \text{ m}^3/\text{s}$)	d^{-1}	0.1099	0.0001	0.1233	0.0001	0.1227	0.0621	0.1710	<0.005
δ_3 ($Q > 283 \text{ m}^3/\text{s}$)	d^{-1}	0.0352	0.1794	0.0406	0.1321	0.0408	0.0176	0.0685	0.015
R^2		0.8822		0.8743					
Mean square error		0.4310		0.4543					
Number of observations		414		414					

^aDependent variable (nitrogen transport) in kilograms per yr

^bMinimum bootstrap confidence intervals (CI)

^cVariable enters the model in reciprocal form

^dRatio of wetland area to total land area

^eRatio of irrigated land area to total cropland area

^fProduct of reciprocal precipitation and one minus the ratio of irrigated land area to total cropland area

^gRatio of irrigated land area to irrigated water use

^hDecay coefficients fit separately for stream reaches with mean streamflow (Q) corresponding to indicated intervals. The streamflow interval breakpoints of 28.3 and 282 m^3/s correspond to 1000 and 10,000 ft^3/s , respectively

Source: Smith et al. (1997).

TABLE AX3.3-2. EFFECT OF SPATIAL REFERENCING ON MEASURES OF REGRESSION MODEL PERFORMANCE FOR PREDICTING TOTAL NITROGEN FLUX USING THE SPARROW MODEL

Model Components	Mean Square Error	R ²
Includes full spatial referencing (SPARROW) ^a	0.4544	0.8743
Excludes in-stream decay and reservoir retention	0.9659 ^b	0.7307

^aIncludes final model terms as specified in Table AX3.3-1

^bIn a likelihood ratio test, the sum of squares of error of the spatially restricted model is significantly ($p < 0.001$) larger than that of the fully spatially referenced model (SPARROW)

TABLE AX3.3-3. PARAMETER ESTIMATES, PROBABILITY LEVELS, AND REGRESSION RESULTS FOR THE CHESAPEAKE BAY TOTAL NITROGEN SPARROW MODEL

Explanatory Variables	Parameter Estimates	Probability Level
Nitrogen sources	β	
Point Sources	1.496	<0.005
Urban area (acres)	7.008	0.010
Fertilizer application (lb/yr)	0.2790	<0.005
Livestock waste production (lb/yr)	0.3361	<0.005
Atmospheric deposition (lb/yr)	1.024	<0.005
Land-to-water delivery	α	
Temperature (°F)	–	–
Precipitation (in)	–	–
Avg slope (%)	–	–
Soil permeability (in/h)	0.0754	0.095
Stream density (l/mi)	–	–
Wetland (%)	–	–
Instream loss (days) ^a	δ	
T1 ($Q \leq 200 \text{ ft}^3/\text{s}$)	0.7595	<0.005
T2 ($200 \text{ ft}^3/\text{s} < Q \leq 1,000 \text{ ft}^3/\text{s}$)	0.3021	<0.005
T3 ($Q > 1,000 \text{ ft}^3/\text{s}$)	0.0669	<0.005
Tu (reservoir retention)	0.4145	<0.005
R-squared	0.961	
Mean square error	0.1669	
Number of observations	79	

^aT, travel time

Q, stream discharge

lb/yr, pounds per yr

°F, degrees Fahrenheit

in/h, inches per hour

mi, mile;

in, inches

%, percent

ft³/s, cubic feet per second

–, value not statistically significant

Source: Preston and Brakebill (1999).

TABLE AX3.3-4. SUMMARY OF N RETENTION RATES USED IN RECENT WATERSN STUDIES

Study	Retention Type	% N Retention
Castro et al. (2001)	In Stream*	30%
	Agriculture	50%
Castro and Driscoll (2002)	In Stream*	30%
	Agriculture	60%
Castro et al. (2003)	Agriculture	40%
	Septic System	40%
	In Stream	Adjusted until predicted N flux matched observed fluxes

*In-stream N retention was only applied to lengths of river located above the “fall line”. Below fall line N inputs to streams were assumed to not be attenuated due to the relatively short travel time to the estuary. The “fall line” is defined as the boundary between the Piedmont and Coastal Plain physiographic provinces in the eastern United States.

Source: Castro and Driscoll (2002).

TABLE 3.3-5. SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
QUAL2K		A	S	1	QUAL2K is one dimensional river and stream water quality model. QUAL2K assumes: that the channel is well-mixed vertically and laterally; steady state hydraulics; diurnal water-quality kinetics. QUAL2K addresses point and non-point loads, BOD/DO, non-living particulate organic matter (detritus); denitrification; sediment-water interactions; bottom algae; pH (both alkalinity and total inorganic carbon).
WASP7	Water Quality Analysis Simulation Program	A	S	2	WASP is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3 dimensional systems, and a variety of pollutant types. The time varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the model. WASP also can be linked with hydrodynamic and sediment transport models that can provide flows, depths velocities, temperature, salinity and sediment fluxes.
CE-QUAL-RIV1; CE-QUAL-R1; CE-QUAL-W2; CE-QUAL-ICM	Water quality models (river, reservoir, and estuary/coastal) supported by USACE	A	N	3	CE-QUAL-R1 is a one-dimensional, vertical reservoir model and CE-QUAL-W2 is a two-dimensional (vertical and longitudinal), laterally averaged, hydrodynamic and water quality model. These two models are widely used by the Corps of Engineers, other federal and state agencies, the private sector, and agencies in other countries. CE-QUAL-RIV1 was developed for highly unsteady flow conditions, such as storm water flows and streams below peaking hydropower dams. CE-QUAL-ICM run in a 2D mode. This approach has been used for large, shallow waterways, harbors, and embayments.
RCA	Row Column AESOP	A	N	4	RCA evaluates the fate and transport of conventional and toxic pollutants in surface waterbodies in one, two, or three dimensions. RCA has been linked to various hydrodynamic models. Subroutines have been developed to model coliforms, pathogens, BOD/DO, simple and advanced eutrophication, wetland systems, and toxic contaminants. A sediment nutrient flux subroutine permits the coupling of the water column and sediment bed.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
WARMS	Waterfowl Acidification Response Modeling System	A	N	McNicol et al. (1995), McNicol (2002)	WARMS includes an acidification model linked to fish and waterfowl models. WARMS uses pH, area, dissolved organic carbon, total phosphorus, and presence of fish to estimate preacidification, present and eventual steady-state values for pH, fish presence and waterfowl breeding parameters under proposed SO ₂ emission scenarios.
GT-MEL	Georgia Tech hydrologic model and the Multiple Element Limitation model	I	N	5	GT-MEL is a spatially distributed, process-based ecohydrology model that links a land surface hydrology model with a terrestrial biogeochemistry model. GT-MEL differs from other available ecohydrology models in its simplicity, flexibility, and theoretical foundation. The coupled GT-MEL simulates the cycling and transport of water and nutrients (C, N and P) within hillslopes and watersheds. The model runs on a daily time step and can be applied to user-defined landscape units that may vary in shape and size (m ² to km ²). Thus, GT-MEL can provide detailed spatial and temporal information on nutrient acquisition and turnover in plants and soils, and terrestrial flow pathways and discharge of water and nutrients to surface waters. The same set of model equations applies to any terrestrial ecosystem – agricultural crops, forests, grasslands, wetlands, tundra, etc. GT-MEL simulates the effects of multiple interacting stressors, including changes in land use, land cover, climate, atmospheric CO ₂ and nitrogen deposition.
ILWAS	Integrated Lake-Watershed Acidification Study	I	N	Gherini et al. (1985)	ILWAS was developed to predict changes in surface water acidity given changes in the acidity of precipitation and dry deposition. The model routes precipitation through the forest canopy, soil horizons, streams and lakes using mass balance concepts and equations which relate flow to hydraulic gradients. The physical-chemical processes which change the acid-base characteristics of the water are simulated by rate (kinetic) and equilibrium expressions and include mass transfers between gas, liquid and solid phases.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
THMB/IBIS		I	N	6, 7	THMB is a mechanistic simulation model of large river systems that has been used recently in combination with a dynamic terrestrial ecosystem model IBIS to quantify nitrate flux in the Mississippi River Basin. The coupled models simulate time-varying flow and storage of water and N in rivers, wetlands, and reservoirs, based on major source inputs, subsurface drainage and N leaching, topography, and precipitation and evaporation. Evaluations of the model in the Mississippi basin indicated that the model accurately simulated inter-annual variability in the water and N budget from 1960 to 1994.
BIOME-BGC	Biome-BGC is a multi-biome generalization of FOREST-BGC	T	N	8	Biome-BGC is a computer program that estimates fluxes and storage of energy, water, carbon, and nitrogen for the vegetation and soil components of terrestrial ecosystems. The primary model purpose is to study global and regional interactions between climate, disturbance, and biogeochemical cycles.
DNDC	Denitrification-decomposition model	T	N	9	DNDC was initially developed to quantifying nitrous oxide (N ₂ O) emissions from agricultural soils in the United States. The capability of the model to simulate soil biogeochemistry also allows DNDC to model emissions from other ecosystems through linkages with vegetation models; the model can be applied from field site to regional scales. The core of DNDC is a soil biogeochemistry model.
EPIC	Agricultural dynamic simulation model	T	N	11	EPIC is a widely used dynamic simulation model that describes the influence of agricultural management on crop productivity and erosion. The model has been used in studies of climate change, agricultural management and policy, and water-quality. EPIC simulates N cycling processes in soils-including mineralization, nitrification, immobilization, ammonia volatilization and denitrification, runoff and subsurface leaching based on physical principles and parameter values derived from extensive model testing and specific field validation.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems	T	N	12	GLEAMS was developed from both EPIC and CREAMS and employs a more explicit description of soil water content. In GLEAMS, the concentration of nitrate-N removed via denitrification is a function of the factors describing the soil water content, the soil temperature, and the organic C content. Under this formulation, denitrification only occurs if the soil water content is greater than a parameter related to the soil water content at field capacity and saturation. The fraction of soil nitrate- N lost to denitrification increases quickly as soil water content increases beyond the field capacity. The EPIC and GLEAMS method of simulating denitrification neglects denitrification that may occur in anaerobic micro-zones when the soil is not at field capacity or saturation.
Hole-in-the-pipe	Hole-in-the-pipe	T	N	Davidson et al. (2000)	The Hole-in-Pipe model relates the emissions of nitrous oxides to common soil processes. It regulates soil emissions of NO and N ₂ O at two levels: 1st, the rate of nitrogen cycling through ecosystems, which is symbolized by the amount of nitrogen flowing through the pipes, affects total emissions of NO and N ₂ O; 2nd, soil water content and perhaps other factors affect the ratio of N ₂ O:NO emissions, symbolized by the relative sizes of the holes through which nitric oxide and nitrous oxide "leak". Soil water content is so important because it controls the transport of oxygen into soil and the transport of NO, N ₂ O, and N ₂ out of soil.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
MERLIN	Model of Ecosystem Retention and Loss of Inorganic Nitrogen	T	N	Cosby et al. (1997), Kjonaas and Wright (1998)	MERLIN is a catchment-scale mass-balance model of linked carbon and nitrogen cycling in ecosystems for simulating leaching losses of inorganic nitrogen. It considers linked biotic and abiotic processes affecting the cycling and storage of nitrogen. The model is aggregated in space and time and contains compartments intended to be observable and/or interpretable at the plot or catchment scale. The structure of the model includes the inorganic soil, a plant compartment, and two soil organic compartments. Fluxes in and out of the ecosystem and between compartments are regulated by atmospheric deposition, hydrological discharge, plant uptake, litter production, wood production, microbial immobilization, mineralization, nitrification, and denitrification. Nitrogen fluxes are controlled by carbon productivity, the C:N ratios of organic compartments and inorganic nitrogen in soil solution. Inputs include time series, constants, rates, source terms, and soil characteristics (Cosby et al., 1997).
NLM	Waquoit Bay Nitrogen Loading Model	T	N	RTI International (2001)	The Waquoit Bay Nitrogen Loading model estimates inputs from different nitrogen sources to defined land use categories and then estimates losses of nitrogen in various compartments of the watershed ecosystem, including the groundwater. This empirical nitrogen loading model produces long-term avg output. It is not currently endorsed by a federal agency but has been published in peer-reviewed journals. Most applications of the model have focused on the Cape Cod area of Massachusetts. The empirical data for this model are specific to that area and the model simulates nitrogen transport exclusively in the subsurface (i.e., overland transport is not considered).

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
Simple Mass Balance Method/Steady State Mass Balance	"Mass balance approach"	T	N	Bhattacharya et al. (2004), Likens et al. (1996), Rodriguez and Macias (2006)	<p>Examples of two mass balance approaches are:</p> <p>Simple Mass Balance: This model is based on a balance of inputs and outputs of nitrogen according to the equation:</p> $N_{\text{dep}} + N_{\text{fix}} = N_i + N_u + N_{\text{ad}} + N_{\text{de}} + N_{\text{fire}} + N_{\text{eros}} + N_{\text{vol}} + N_{\text{le}}$ <p>where the subscripts denote: dep (deposition); fix (fixation); i (immobilization); u (uptake); ad (adsorption); de (denitrification); fire (N loss during combustion); eros (erosion); vol (volatilization); le (leaching).</p> <p>Steady State Mass Balance: This method is the most commonly used method for analysis of critical loads of acid deposition. Its basic principle is based on identifying the long-term avg sources of acidity and alkalinity in order to determine the maximum acid input that will balance the system at a biogeochemical safe-limit. Several assumptions have been made in the steady state calculations. First, it is assumed that ion exchange is at steady state and there is no net change in base saturation or no net transfer of acid neutralizing capacity (ANC) from soil solution to the ion exchange matrix. It is assumed that for nitrogen there is no net denitrification, adsorption or desorption and the nitrogen cycle is at steady state. Sulfate is also assumed to be at steady state: no sulfide oxidation, sulfate uptake, sulfate permanent fixation or sulfate reduction are significant. Simple hydrology is assumed where there is straight infiltration through the soil profile.</p>

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
HSPF/LSPC	Hydrological Simulation Program - FORTRAN	T*	S	12, 13	HSPF simulates watershed hydrology and water quality for conventional and toxic pollutants. HSPF incorporates watershed-scale ARM and NPS models into a basin-scale analysis framework that includes fate and transport in stream channels. It is a comprehensive model of watershed hydrology and water quality that allows the integrated simulation of land and soil contaminant runoff processes with In-stream hydraulic and sediment-chemical interactions. LSPC is a simplified version of HSPF. Although LSPC was designed to provide a less data intensive alternative to HSPF for modeling very large scale watersheds, it can also be used to model smaller, more detailed watersheds. The primary disadvantage of this simplified version of HSPF is that the developers eliminated the atmospheric deposition routines found in HSPF. For each model run, it automatically generates comprehensive text-file output by subwatershed for all land-layers, reaches, and simulated modules, which can be expressed on hourly or daily intervals. Output from LSPC has been linked to other model applications such as EFDC, WASP, and CE-QUAL-W2.
PLOAD	Pollutant Loading Model	T*	S	14	PLOAD is part of EPA's BASINS (Better Assessment Science Integrating Point and Nonpoint Sources) program and estimates nonpoint pollution sources on an annual basis. PLOAD can be combined with geographic information system (GIS)-based data coverages to rapidly estimate nitrogen loading to the bay using pass-through rates based on land uses from EPA guidance documents, literature, or other studies. This model is not precipitation driven nor does it include nitrogen speciation; however, the model does capture differences in nitrogen transport for different land uses in the watersheds.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
SWAT	Soil and Water Assessment Tool	T*	S	van Griensven and Bauwens (2001), 15	SWAT is a public domain river basin scale model actively developed and primarily supported by the USDA (and included within EPA's BASINS framework), that quantifies the impact of land management practices in large, complex watersheds. SWAT is a physically based model that applies to all land uses and to include stormwater runoff in its calculations. The model simulates ammonia, nitrate, and organic nitrogen throughout the waterbodies and vegetation in the modeled system. At this time SWAT only accepts the nitrate concentration in the rain as the nitrogen atmospheric component.
WARMF	Watershed Analysis Risk Management Framework	T*	S	16	WARMF includes a GIS-based watershed model that calculates daily runoff, shallow ground water flow, hydrology and water quality of a river basin. A river basin is divided into a network of land catchments (including canopy and soil layers), stream segments, and lake layers for hydrologic and water quality simulations. Inputs include meteorology, air quality, point source, reservoir release, and flow diversion data. WARMF also includes two watershed approach modules for Consensus building and TMDL calculation.
DRAINMOD		T*	N	17	DRAINMOD quantifies N losses and transport from agricultural lands with shallow water tables where artificial drainage systems are used. Watershed-scale versions of DRAINMOD have been developed and evaluated based on data collected on a NC coastal plain. DRAINMOD is based on water balances in the soil and at the soil surface. It uses functional methods to quantify infiltration, subsurface drainage, surface drainage, evapotranspiration, seepage, freezing, thawing, snowmelt, and seepage. The model predicts the water table depth and soil water contents above the water table, drainage rates and the other hydrologic components on an hourly and daily basis for long periods of hydrologic record. Hydrologic predictions of the model have been tested and found to be reliable for a wide range of soil, crop, and climatological conditions.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
INCA		T*	N	Wade et al. (2005)	INCA is a water and N mass balance simulation model; it estimates the integrated effects of point and diffuse N sources on stream nitrate and ammonium concentrations and loads and also estimates the N loads related to processes in the plant/soil system. It has been most commonly applied to watersheds within the UK, but more recently has been modified for use in other European watersheds. INCA quantifies plant uptake of nitrate and ammonium, nitrification, denitrification, and mineralization and immobilization within each land-use type and subcatchment. Biogeochemical reactions are limited to the soil zone from which water and N are leached to deeper groundwater.
LWWM	Linked Watershed/Waterbody Model	T*	N	18	The original release of the LWWM coupled the RUNOFF Block of the EPA's SWMM model (Version 4.21) with the EPA's Water Quality Analysis Program (WASP5). All components of the LWWM were accessed via a user-friendly operating shell. The LWWM included a GIS interface based on Arc/INFO to automate the reduction of spatial data within a watershed (i.e., land use and soils) for input into the RUNOFF Block of SWMM. The LWWM included pre-processors for inputting data into the RUNOFF Block of SWMM, WASP5 (Eutro and Toxi), and two hydrodynamic models associated with WASP5 (RIVMOD and DYNHYD5), as well as a graphical post-processor for the review of output from all model components. The post-processor was also the means by which nonpoint source loading files from RUNOFF were mapped to WASP segments.
ReNuMa	Regional Nutrient Management Model	T*	N	19	ReNuMa is based on the Generalized Watershed Loading Function (GWLf) model that has been used widely for purposes such as TMDL development. ReNuMa improves on GWLf by incorporating Net Anthropogenic Nitrogen Inputs (NANI) accounting system. The model now considers atmospheric deposition, fertilizer application, septic system effluents, nitrogen fixation, and denitrification.

TABLE 3.3-5 (cont'd). SOME EXAMPLES OF MODELS THAT COULD CONTRIBUTE TO DEVELOPMENT OF A BETTER UNDERSTANDING OF THE ECOLOGICAL EFFORTS OF ATMOSPHERIC S AND N DEPOSITION, BUT THAT ARE NOT EXPLICITLY ADDRESSED IN THIS ANNEX

Model	Name	Type ¹	Support ²	Reference/ Website ³	Notes
RHESS		T*	N	Boyer et al. (2006)	RHESS has been used to explore N dynamics at the watershed scale. RHESSys simulates the coupled effects of C, N, and hydrological processes by coupling biogeochemical dynamics from the BIOME_BGC and the NGAS model used in DAYCENT. Streamflow is based on the implementation of variable source-area concepts based on topography, quantifying routing of water through the landscape from patch to patch using either a lumped topographic approach adapted from TOPMODEL or a distributed approach adapted from the DHSVM model

¹Type: A = aquatic; I = integrated aquatic/terrestrial; T = terrestrial; T* = watershed

²Support: S = currently supported by EPA; N = currently not supported by EPA

³Websites:

- 1: River and Stream Water Quality Model (QUAL2K); <http://www.epa.gov/athens/wwqtsc/html/qual2k.html>
- 2: U.S.EPA's WASP Website; <http://epawasp.com/>
- 3: U.S. Army Core of Engineers Environmental Laboratory - Water Quality Models; <http://el.ercd.usace.army.mil/products.cfm?Topic=model&Type=watqual>
- 4: Hydroqual: Row Column AESOP (RCA) Modeling Code Description and Technical Capabilities; http://www.hydroqual.com/pdf/RCA_Desc_doc.pdf
- 5: Woods Hole Marine Lab, Ecosystems Center MEL home page <http://ecosystems.mbl.edu/Research/Models/mel/welcome.html>
- 6: IBIS (Integrated Biosphere Simulator); <http://water.usgs.gov/software/hspf.html>
- 7: THMB (Terrestrial Hydrology Model with Biogeochemistry) - formerly HYDRA; <http://www.sage.wisc.edu/download/HYDRA/hydra.html>
- 8: Biome-BGC: Terrestrial Ecosystem Process Model, Version 4.1.1; http://www.daac.ornl.gov/MODELS/guides/biome-bgc_guide.html
- 9: Denitrification Modeling Workshop: Model Summary; <http://marine.rutgers.edu/BGC/RCNsite/WS1/WS1models/DNDC-2.pdf>
- 10: EPIC Fact Sheet; <http://www.brc.tamus.edu/epic/epfact2004.htm>
- 11: GLEAMS Y2K Update Website; http://www.tifon.uga.edu/sewrl/Gleams/gleams_y2k_update.htm
- 12: U.S. EPA's HSPF Website; <http://www.epa.gov/ceampubl/swater/hspf/>
- 13: USGS's Water Resources Applications Software: HSPF Website; <http://water.usgs.gov/software/hspf.htm>
- 14: U.S. EPA's Better Assessment Science Integrating Point & Nonpoint Sources (BASINS) Website; <http://www.epa.gov/waterscience/basins/>
- 15: Soil & Water Assessment Tool <http://www.brc.tamus.edu/swat/>
- 16: US EPA's Watershed Analysis Risk Management Framework (WARMF) Website; <http://www.epa.gov/athens/wwqtsc/html/warmf.html>
- 17: DRAINMOD Download Website; http://www.bae.ncsu.edu/soil_water/drainmod/
- 18: Linked Watershed Waterbody Model at the Southwest Florida Water Management District; <http://www.swfwmd.state.fl.us/software/lwmm.htm>
- 19: Regional Nutrient Management (ReNuMa) at Cornell University College of Agriculture and Life Sciences; <http://www.eeb.cornell.edu/biogeonanc/usda/renuma.htm>

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AX4. ACIDIFICATION EFFECTS FROM SULFUR AND NITROGEN

AX4.1 EFFECTS ON BIOGEOCHEMICAL PROCESSES ALONG ACIDIFICATION PATHWAYS

AX4.1.1 Atmospheric Deposition and Canopy Interaction

Airborne NO_x and SO_x particles, gasses, precursors, and transformation products are removed from the atmosphere by wet, dry, and occult deposition. This atmospheric cleansing process lowers the long-term buildup of these pollutants in the air and therefore moderates the potential for direct human health effects caused by their inhalation. However, deposition also transfers atmospheric pollutants to other environmental media where they can alter the structure, function, diversity, and sustainability of complex terrestrial, transitional, and aquatic ecosystems.

AX4.1.1.1 Wet Inputs

Wet deposition of major ions is relatively well-characterized throughout the United States, largely because of the extensive networks of monitoring stations, especially the National Acid Deposition Program/National Trends Network (NADP/NTN; see description in Section AX2.5.1). Wet deposition of sulfur (S) and nitrogen (N) varies by about two orders of magnitude from the least polluted to most polluted sites. Interpolated values for a recent 5-year period of record (1998 to 2002), averaged to cancel out intra- and interannual variations, is shown in Figure AX4.1-1. Highest values of both S and N wet deposition are generally found in the eastern United States, especially in a band from the southern Appalachian Mountains to New York and New England.

Biogeochemical acidification processes are generally mediated by water. Precipitation and snowmelt combine with moisture transferred to the terrestrial ecosystem by fog or cloud cover and transport atmospherically deposited substances to the soil, where many of the interactions occur.

AX4.1.1.2 Dry Inputs

Dry deposition inputs of S, N, and base cations are not well characterized, and cannot be directly measured. In general, dry deposition is highest in close proximity to pollution sources.

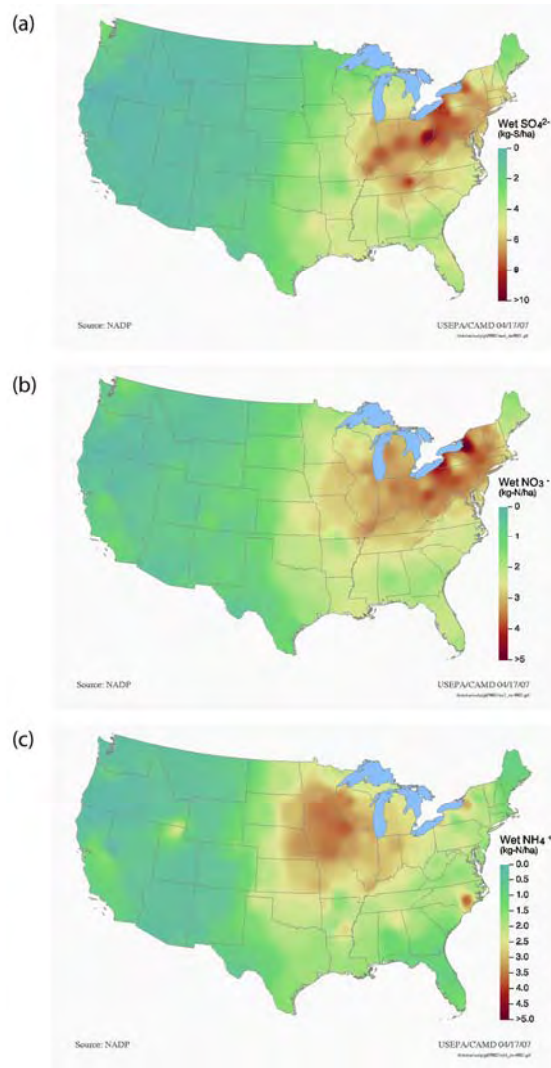


Figure AX4.1-1. Map of annual average wet deposition, over the period 1998 to 2002, based on interpolated values for the NADP/NTN monitoring network. Deposition is depicted for (a) sulfur, (b) oxidized nitrogen, and (c) reduced nitrogen, in units of kilograms of sulfur or nitrogen per hectare per year.

- 1 Estimated dry deposition rates are usually somewhat lower than wet deposition at the same
- 2 location (Figure AX4.1-2). There are exceptions to this pattern, however, such as in and near the
- 3 Los Angeles Basin where the rate of dry deposition of N is among the highest in the United
- 4 States, and wet deposition is very low due to the arid climate.

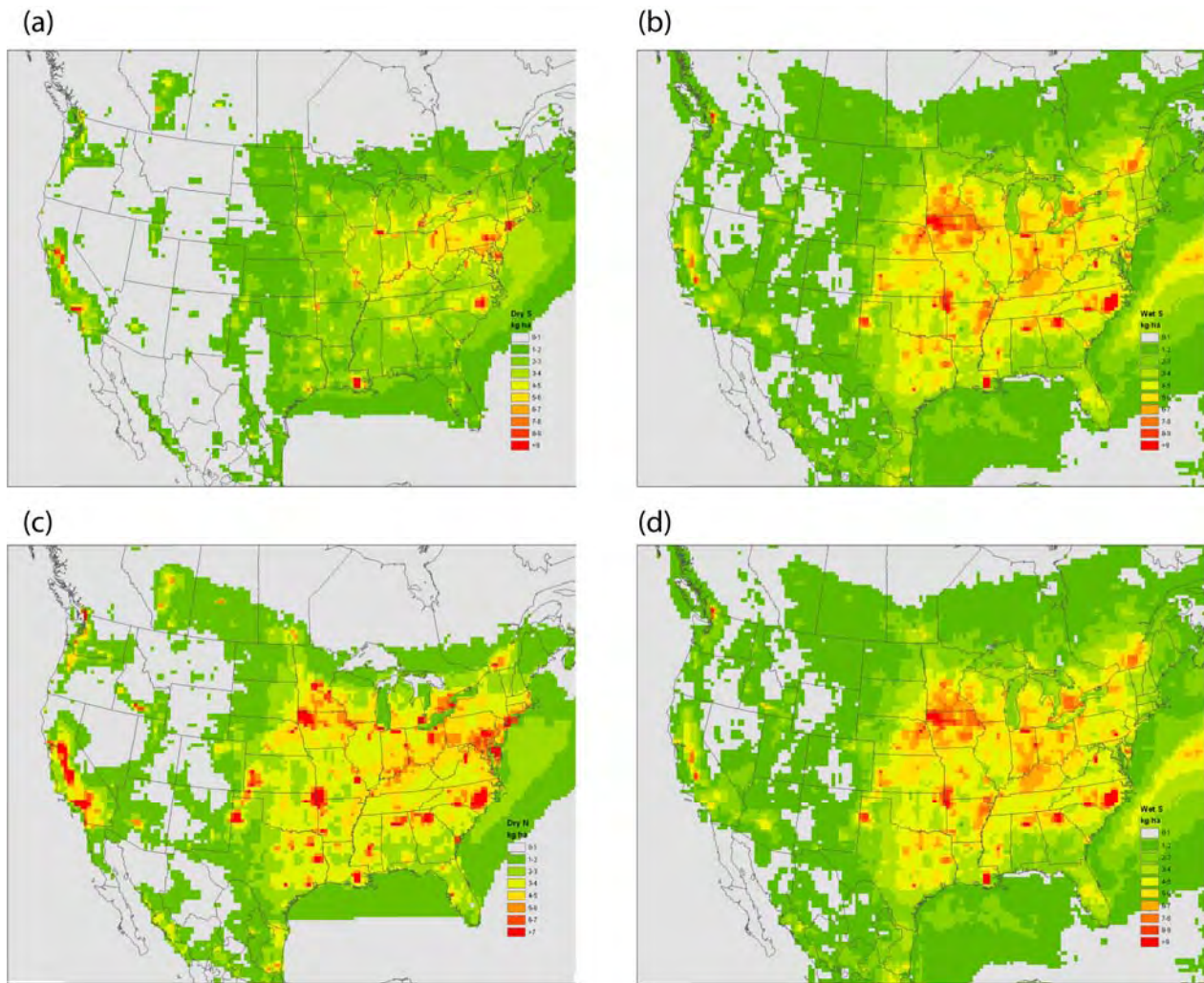


Figure AX4.1-2. CMAQ model estimates of wet and dry deposition data for the year 2001. Deposition is depicted for (a) dry sulfur, (b) wet sulfur, (c) dry nitrogen, and (d) wet nitrogen, in units of kilograms of sulfur or nitrogen per hectare per year.

1 Dry deposition varies substantially with differences in vegetative canopy. For example,
 2 dry deposition rates are much higher to coniferous vegetation, as compared with deciduous,
 3 broad-leaf vegetative surfaces.

4 Estimates of total wet plus dry deposition for the eastern United States have been
 5 generated with the Community Multiscale Air Quality (CMAQ) model (Figure AX4.1-3).

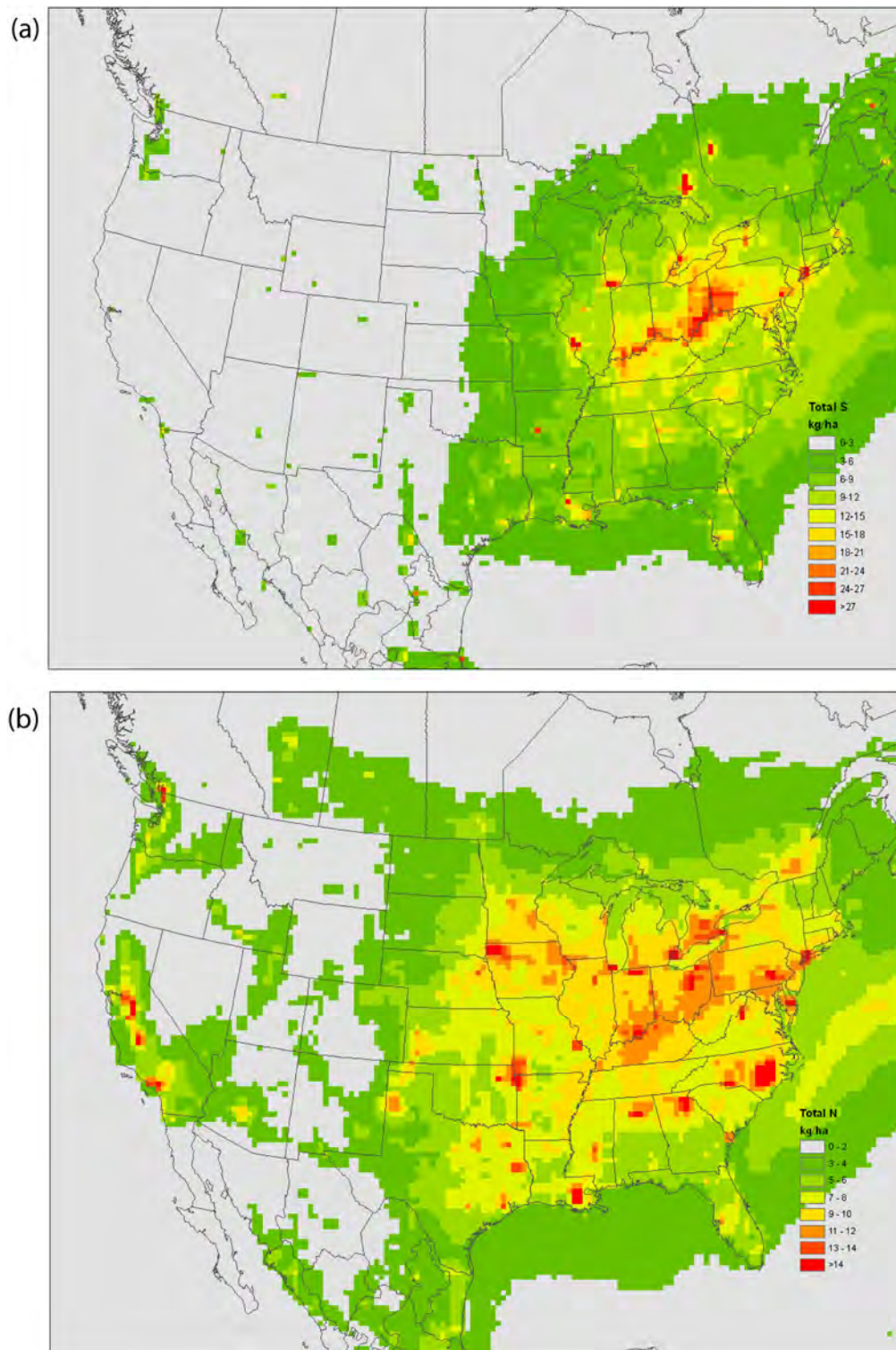


Figure AX4.1-3. CMAQ model estimates of total wet plus dry deposition for the eastern United States in 2001. Deposition is depicted for (a) sulfur and (b) nitrogen, in units of kilograms of sulfur or nitrogen per hectare per year.

1 **AX4.1.1.3 Occult Inputs**

2 Occult deposition tends to be high only at coastal (fog-influenced) and high-elevation
3 (cloud-influenced) locations. Cloud deposition, although seldom measured, is believed to
4 become appreciable at elevations above about 1,000 m in the eastern United States. At some
5 high-elevation locations, cloud deposition can equal or exceed wet plus dry deposition.

6
7 **AX4.1.1.4 Canopy Enhancement and Uptake**

8 Inputs of N and S in wet, dry, and occult deposition first interact with the vegetative
9 canopy. This interaction can occur a few centimeters above the ground in some alpine or
10 grassland ecosystems to over 100 m above the ground in some forest canopies. In the canopy,
11 deposited pollutants (especially N) can be taken up by the plants or by organisms that live within
12 the canopy or on the leaf surface. Most of the deposited S moves as throughfall to the soil where
13 it can be temporarily, or permanently, adsorbed on the soil. Sulfur that is not adsorbed on the
14 soil moves readily into drainage water.

15 Earlier reviews (i.e., Hosker and Lindberg, 1982; Taylor et al., 1988) summarized
16 information on the deposition of N to vegetation surfaces and interactions between pollutant
17 deposition and canopy and leaf surfaces. Deposited N that is not taken up within the canopy
18 then falls to the ground as throughfall, where plants, bacteria, and fungi compete for it. This
19 competition for deposited N has long been known to play an important role in determining the
20 extent to which N deposition will stimulate plant growth and the degree to which added N is
21 retained within the ecosystem (U.S. Environmental Protection Agency, 1993). The available
22 surface area of vegetation, onto which N gasses readily diffuse, has a significant effect on the dry
23 deposition of N (Heil and Bruggink, 1987). Coniferous forests tend to increase deposition rates
24 (both dry and wet) relative to deciduous forests, and landscape features such as elevation, aspect,
25 and forest edge can play an important role in creating high levels of variability in deposition rates
26 in complex terrain (Weathers et al., 2000).

27
28 **AX4.1.2 Interactions with Soil**

29 Although some vegetative uptake of deposited N occurs in the canopy, the cumulative
30 depositional inputs (wet, dry, occult) from the atmosphere to the terrestrial environment are
31 largely transferred from the vegetative surfaces of the plant community to the soil. Much of this
32 transfer is accomplished by water movement, as throughfall. Within the soil, a host of

1 biogeochemical processes occur. These processes control the extent to which atmospheric
2 deposition affects ecosystem structure and function.

3 Sulfur deposition moves through watershed soils and into surface waters in anionic form,
4 as sulfate (SO_4^{2-}). Sulfate is the most important anion contributed by acidic deposition in most,
5 but not all, parts of the United States. In some regions (notably the glaciated Northeast, Upper
6 Midwest, and West), much of the deposited S moves readily through soils into streams and lakes.
7 Thus, SO_4^{2-} has been classified as a mobile anion. However, SO_4^{2-} is less mobile in some areas,
8 most notably the unglaciated southeastern United States. The extent of SO_4^{2-} mobility is an
9 important factor governing the degree to which S deposition contributes to soil and water
10 acidification, base cation depletion, and aluminum (Al) mobilization, each of which can harm
11 biological components of sensitive ecosystems.

12 Atmospheric inputs of both S and N can cause acidification of soil, soil water, and fresh
13 drainage water (lakes and streams). In most regions of the United States that have experienced
14 acidification effects from air pollution, those effects have mainly been due to S deposition.
15 There are also, however, some regions, especially in the western United States, where resources
16 are more threatened by N inputs than by S inputs. This is at least partially due to the very low
17 levels of S deposition received at many western locations. There are also regions (portions of the
18 Northeast, West Virginia, and high elevations in North Carolina and Tennessee) where both
19 atmospheric S and N contribute substantially to the observed acidification.

20 Air pollution is not the sole cause of soil acidity. High rates of soil acidification occur in
21 low-deposition regions of the western United States because of internal soil processes, including
22 tree N uptake and nitrification associated with extensive N fixation, for example on sites
23 occupied by red alder trees (*Alnus rubra*) (Johnson et al., 1991b). Acidic deposition is not a
24 necessary condition for having acidic soils, as evidenced by the common occurrence of acidic
25 soils in unpolluted forests of the northwestern United States and Alaska (Johnson et al., 1991b).

26 27 **AX4.1.2.1 Sulfur Retention and Release**

28 Because the levels of S deposition have been substantially reduced in response to
29 emissions control legislation, the acidity associated with atmospherically deposited S is now
30 approximately equal to or less than that associated with N in most of the eastern half of the
31 United States, but S continues to be the greater agent of soil and water acidification in most

1 regions impacted by acidic deposition. The role of SO_4^{2-} as the major acidifier is reflected in
2 concentrations of SO_4^{2-} (expressed as $\mu\text{eq/L}$) that greatly exceed concentrations of nitrate (NO_3^-)
3 in most surface waters, during most of the year (Stoddard et al., 2003). When S moves from
4 soils to surface waters in the form of SO_4^{2-} , an equivalent amount of cations, or countercharge, is
5 also transported. If the countercharge is provided by cations other than H^+ and Al^{3+} , the base
6 saturation of the soil is reduced, as the acidity of the soil water is neutralized (Van Breemen
7 et al., 1983). Continued SO_4^{2-} leaching can deplete the base supply of the soil, thereby
8 impairing the soil's ability to neutralize further acidic deposition and preventing acidification of
9 soil water, and by connection, surface water. Loss of soil base saturation is a cumulative effect
10 that increases the sensitivity of the watershed to further acidic deposition. Watersheds that were
11 capable of fully neutralizing a particular level of acidic deposition two to three decades ago may
12 no longer be capable of fully neutralizing that level today because of the cumulative effect of
13 acidic deposition on soil base saturation (Lawrence and Huntington, 1999).

14 Cumulative effects of S deposition can also result from the adsorption of SO_4^{2-} to soil
15 particles, a process that removes SO_4^{2-} from soil solution, and therefore prevents leaching of
16 cations and further acidification of soil. However, this potentially reversible process results in an
17 accumulation of S in the soil, which can contribute to soil acidification if, and when, that SO_4^{2-}
18 is eventually released back into solution. The degree to which SO_4^{2-} adsorbs on soil is
19 dependent on soil characteristics. Soils in the United States that most effectively adsorb SO_4^{2-}
20 occur south of the maximum extent of glaciation that occurred during the most recent ice age
21 (Rochelle and Church, 1987; Rochelle et al., 1987). Sulfate adsorption is strongly pH dependent,
22 and a decrease in soil pH resulting from acidic deposition can enhance the ability of soil to
23 adsorb SO_4^{2-} (Fuller et al., 1987).

24 Considerable effort in the 1980s went into the computation of S budgets for watersheds
25 and forest plots, to evaluate S retention and release. These budgets were subject to
26 complications from fluxes that could not be measured directly, such as dry deposition and
27 weathering, but generally indicated net S retention at sites south of the line of glaciation—a
28 result attributed to net adsorption of SO_4^{2-} (Rochelle et al., 1987; Cappellato et al., 1998).
29 Through the 1990s little or no decrease in SO_4^{2-} concentrations occurred in streams below the
30 glaciation line, despite regional decreases in atmospheric deposition of S (Webb et al., 2004).
31 This lack of response has been generally attributed to the net release of adsorbed SO_4^{2-} , resulting

1 from a shift in equilibrium between the adsorbed and solution phases under conditions of
2 decreased atmospheric inputs of SO_4^{2-} . This interpretation is supported by a decrease in
3 concentrations of adsorbed SO_4^{2-} from 1982 to 1990 in a Piedmont soil in South Carolina that
4 received decreasing levels of S deposition during this period (Markewitz et al., 1998). This same
5 soil also experienced an increase in adsorbed SO_4^{2-} from 1962 to 1972 (Markewitz et al., 1998).
6 The only published S budget more recent than 1992 for an unglaciated site in the United States
7 (Castro and Morgan, 2000) also suggests a net release of SO_4^{2-} . This upland Maryland
8 watershed released 1.6 times more SO_4^{2-} than measured in throughfall in 1996-97. Additional
9 information was obtained in the German study of Martinson et al. (2005) in which a “clean-roof”
10 was used to exclude acidic deposition since 1989. Data collection enabled calibration of a model
11 that predicted elevated concentrations of desorbed SO_4^{2-} in soil water for at least several
12 decades. Although decreased levels of deposition are most likely resulting in net SO_4^{2-}
13 desorption, limited research is available on sulfate desorption over time periods relevant to the
14 time scale of decreased levels of S deposition (Johnson and Mitchell, 1998).

15 Numerous S budgets were also compiled in the 1980’s for glaciated sites, and results
16 generally indicated that inputs approximately equaled outputs on an annual basis (Rochelle et al.,
17 1987). Little or no S retention at glaciated sites was attributed to relatively low SO_4^{2-} -adsorption
18 capacity in soils. Balanced S budgets implied that decreases in atmospheric deposition of S
19 would lead directly to decreases in SO_4^{2-} leaching, and the strong correlation between decreases
20 in atmospheric deposition and decreases in SO_4^{2-} concentrations in surface waters is widely
21 recognized as an indication of this direct linkage (Stoddard et al., 2003). However, considerable
22 evidence also indicates that S inputs in glaciated ecosystems do not behave conservatively, but
23 instead are cycled through microbial and plant biomass (David et al., 1987; Alewell and Gehre,
24 1999; Likens et al., 2002). As a result, large quantities of S are stored in organic forms within
25 the soil. David et al. (1987) found that annual S deposition (wet plus dry) at a site in the central
26 Adirondack region of New York was about 1% of the organic S pool in the soil. Houle et al.
27 (2001) estimated that annual S deposition at 11 sites in North America ranged from 1% to 13%
28 of the organic S pool in soil.

29 Courchesne et al. (2005) measured a downward trend in water-soluble SO_4 from 1993 to
30 2002 in glaciated soils in Quebec, and attributed this response to net desorption of SO_4^{2-} rather
31 than release of organically associated S. However, during this period, deposition of SO_4^{2-} was

1 essentially unchanged. They attributed this discrepancy to a delay in the release of adsorbed
2 SO_4^{2-} in response to a decrease in S deposition over the previous decade. These authors did not
3 provide a mechanism to explain how desorption can continue under conditions of constant SO_4^{2-}
4 inputs, however. On the basis of the abundant evidence of biological S cycling, it seems more
5 likely that the delay observed by Courchesne et al. (2005) is the result of biological controls over
6 the release of S.

7 Much of the organic S stored in soil is in carbon-bonded forms that are relatively
8 unreactive, but can be mineralized to SO_4^{2-} in oxic conditions, typically found in moderately
9 well-drained to well-drained soils (Johnson and Mitchell, 1998). Furthermore, strong
10 correlations have been shown between levels of atmospheric deposition of S and concentrations
11 of S in soil (Driscoll et al., 2001; Novák et al., 2001). Long-term increases in concentrations of
12 total S in soils that are at least partially attributable to increases in organic S have also been
13 documented (Knights et al., 2000; Lapenis et al., 2004). The study of Houle et al. (2001) did not
14 find a relation between these factors, however. A Swedish “clean-roof” study also provides
15 some insights into the role of organic S in possibly delaying recovery (Morth et al., 2005). After
16 9 years of pre-industrial levels of S deposition, the amount of S in runoff still exceeded inputs by
17 30%. Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

18 In summary, research on effects of atmospheric S deposition on soils has indicated
19 pronounced changes in soils from sustained SO_4^{2-} leaching and accumulation of S through
20 physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S
21 from soils at a number of sites is a likely response to decreased atmospheric inputs. The gradual
22 loss of previously accumulated S is resulting in continued SO_4^{2-} leaching and soil acidification.
23 Uncertainties in estimates of ecosystem fluxes such as weathering and dry deposition, and
24 complications in discerning the effects of desorption from mineralization make it difficult to
25 predict when S outputs will no longer exceed inputs. Current research based on experimental
26 reduction of S inputs suggests that this process will occur on a decadal time scale (Martinson
27 et al., 2005, Morth et al., 2005). The long-term role of carbon-bonded S adds further uncertainty
28 because enhancement of S mineralization by a warming climate could also affect S retention and
29 release (Knights et al., 2000; Driscoll et al., 2001).

1 **AX4.1.2.2 Base Cation Depletion**

2 Neutralization of acidity involves the release of base cations from the soil into soil water,
3 through weathering, cation exchange, and mineralization (Van Breemen et al., 1983). If the
4 acidity is associated with anions that are mobile within the soil environment, the cations will be
5 leached out of the soil into ground waters or surface waters. Loss of base cations from soil is a
6 natural process, but the limited mobility of anions associated with naturally derived acidity
7 (organic acids and carbonic acid) controls the rate of base cation leaching under conditions of
8 low atmospheric deposition of S and N. Because inputs of sulfuric and nitric acid in acidic
9 deposition provide anions that are more mobile in the soil environment than anions of naturally
10 derived acids, these mineral acid anions accelerate natural rates of base cation leaching (Cronan
11 et al., 1978). This explains the finding of Lawrence et al. (1999b) that pronounced differences in
12 base-cation leaching rates occur in upper B-horizon soil along an elevational gradient in acidic
13 deposition levels.

14 Soil acidification can lead to deficiency of plant nutrients. Calcium (Ca^{2+}) is essential for
15 many aspects of plant physiology, including root development, wood formation, cell membrane
16 integrity, and cell wall structure. Acidic deposition increases leaching losses of Ca^{2+} and other
17 base cations and also increases Al concentrations in soil solution. Mobilized Al can bind to fine
18 root tips, further limiting Ca^{2+} , and magnesium (Mg^{2+}) uptake (Shortle and Smith, 1988; Shortle
19 et al., 1997).

20 Base cations are common in rocks and soils, but largely in forms that are unavailable to
21 plants. There is a pool of bioavailable base cations (termed exchangeable base cations) that are
22 adsorbed to negatively charged surfaces of soil particles. They can enter solution by exchanging
23 with other dissolved cations including acidic cations such as H^+ or Al^{3+} . Base cations in this
24 pool are gradually leached from the soil in drainage water, but are constantly resupplied through
25 weathering. Weathering slowly breaks down rocks and minerals, releasing base cations to the
26 pool of adsorbed base cations in the soil. The balance between base cation supply and base
27 cation loss determines whether the pool of available base cations is increasing or decreasing in
28 size. Net forest growth can also potentially lower exchangeable base cation concentrations
29 through uptake of nutrient cations (Ca, Mg, and K), but these cations remain in the terrestrial
30 ecosystem and can become available in the future through mineralization or canopy leaching. It
31 has long been known that leaching of base cations by acidic deposition might deplete the soil of

1 exchangeable bases faster than they are resupplied (Cowling and Dochinger, 1980). However,
2 base cation depletion of soils had not been demonstrated at the time of the last SO_x Air Quality
3 Criteria Document (AQCD) (U.S. Environmental Protection Agency, 1982).

4 Data that clearly showed soil base cation depletion in the United States did not become
5 available until the 1990s, although decreases in exchangeable Ca²⁺ concentrations between the
6 periods 1947 to 1950 and 1987 to 1988 had been identified in European soils through repeated
7 sampling (Billett et al., 1990; Falkengren-Grerup and Eriksson, 1990). In the only repeated
8 sampling in the United States in which the original soil sample pre-dated acidic deposition,
9 Johnson et al. (1994b) documented a decrease in exchangeable Ca²⁺ concentrations in both the O
10 (combined Oa and Oe horizons) and B horizons from 1930 to 1984. Richter et al. (1994) also
11 observed Ca²⁺ depletion in the B horizon from 1960 to 1990, in repeated sampling of Piedmont
12 soil in South Carolina. The studies of Johnson et al. (1994b) and Richter et al. (1994)
13 acknowledged the potential role of acidic deposition in causing the loss of Ca²⁺, but focused on
14 net forest growth as the primary cause.

15 Through reanalysis of archived soils, Lawrence et al. (1995) measured decreases in
16 concentrations of exchangeable Ca²⁺ and acid-extractable Ca²⁺ in Oa horizons of spruce stands
17 from 1969-70 to 1987-92 and presented relationships in soil chemistry that were not consistent
18 with changes expected from vegetation uptake effects, but that could be explained by acidic
19 deposition. Drohan and Sharpe (1997) also observed a decrease in Ca²⁺ concentrations in Oa and
20 A horizons at 11 sites across Pennsylvania that were sampled in 1957 or 1959 and again in 1993,
21 although effects of vegetation and acidic deposition were not distinguished.

22 The most thorough soil re-sampling study in the United States was conducted by Bailey
23 et al. (2005) in northwestern Pennsylvania. Between 1967 and 1997, pronounced decreases,
24 attributed largely to acidic deposition, were measured in exchangeable Ca²⁺ and Mg²⁺
25 concentrations in Oa/A horizons and throughout the B horizon. Courchesne et al. (2005) found
26 higher concentrations of exchangeable Ca²⁺ in the O horizon (combined Oe and Oa horizons) in
27 2002 than in 1994 at one of three sampling areas within a 5.1 ha watershed, but no significant
28 differences at the other two locations. No significant differences were found for exchangeable
29 Mg²⁺ at the three locations in the O horizon. In the upper 10 cm of the B horizon, no significant
30 differences were found in exchangeable Ca²⁺, but at two of three locations, exchangeable Mg²⁺
31 concentrations were lower in 2002 than in 1994. The 8-year interval between sampling in this

1 study is the shortest time in which changes in exchangeable base cations have been reported for
2 North American soils.

3 In a regionally designed assessment of changes in soil-exchange chemistry, Sullivan et al.
4 (2006a) found that base saturation and exchangeable Ca^{2+} concentrations in the Adirondack
5 region of New York had decreased in the upper 10 cm of the B horizon between the mid 1980s
6 and 2003, in watersheds of lakes with ANC less than 200 $\mu\text{eq/L}$. Soil chemistry in 36 lake
7 watersheds in the mid 1980s was compared to soil chemistry in 32 lake watersheds in 2003.
8 Although this study did not involve repeated sampling of the same sites, the comparison could be
9 made on a regional basis because the sampling locations were selected randomly in both the mid
10 1980s and in 2003, and a large and similar number of sites were included in both samplings.

11 In a widely cited article, Likens et al. (1996) used a watershed mass balance approach to
12 estimate changes in ecosystem Ca^{2+} pools at HBEF and found a sustained decrease in
13 exchangeable Ca^{2+} concentrations from 1963 to 1993. The maximum depletion rate occurred in
14 1972, at the estimated peak in acidic deposition levels. The dependence on Ca:Na ratios to
15 estimate Ca^{2+} weathering fluxes in this analysis adds uncertainty to the magnitude of changes
16 reported for the exchangeable Ca^{2+} pool (Bailey et al., 2003). Two additional mass balance
17 studies used Sr isotopes to evaluate changes in soil Ca^{2+} pools and fluxes. The study of Bailey
18 et al. (1996) estimated substantial depletion rates in a watershed in the White Mountains of New
19 Hampshire. Miller et al. (1993) estimated that inputs from weathering and atmospheric
20 deposition approximately equaled leaching losses at a site in the Adirondack Mountains in New
21 York. The different findings in these two studies are related to differences in the mineralogical
22 composition of the respective soils. However, the Miller et al. (1993) study also estimated that
23 50 to 60% of the Ca^{2+} in vegetation and the forest floor was derived from the atmosphere, despite
24 the fact that the weathering flux was estimated to be three times the rate of atmospheric inputs.
25 This result suggests that Ca^{2+} supply from weathering in the lower profile is not reaching the
26 upper soil where most root activity occurs, and that Ca^{2+} depletion has occurred in the upper soil.

27 The study of Yanai et al. (1999) investigated changes in Ca^{2+} and Mg^{2+} concentrations
28 and content in northeastern hardwood stands over time intervals ranging from 10 to 21 years.
29 The general conclusion of this study was that little or no change in O horizon (Oi, Oe, and Oa
30 horizons) exchange chemistry occurred. However, a decrease in exchangeable Ca^{2+}
31 concentrations in the Oa horizon was observed in this study at the HBEF from 1978 to 1997,

1 although no change was observed in this soil in exchangeable Mg^{2+} concentrations, or Ca^{2+} or
2 Mg^{2+} content in the Oa horizon. Results of this study were complicated by high spatial
3 variability and differences in field sampling techniques between the original collection and the
4 resampling (Yanai et al., 1999). Yanai et al. (2005) also found little difference over 15 years in
5 exchangeable and extractable Ca^{2+} and Mg^{2+} concentrations in Oa horizons at 6 sites, and in O
6 horizons (combined Oe and Oa horizons) at 13 sites, in hardwood stands in New Hampshire. In
7 this study, it was also estimated that a difference greater than 50% would be needed to be
8 statistically detected due to a large degree of spatial variability. Although most repeated
9 sampling studies did identify decreases in exchangeable base cations in the Oa or O horizon, the
10 results of Yanai et al. (2005) indicated that this change may not occur at all sites and may be
11 difficult to detect in some soils due to inconsistencies in identifying horizon separations during
12 sampling.

13 Through direct and inferred evidence of Ca^{2+} depletion, and additional research on soil
14 processes, a detailed understanding of the mechanisms of Ca^{2+} depletion has developed over the
15 past two decades. Ulrich (1983) explained Ca^{2+} depletion as a three-stage process in which
16 buffering of acidity in the mineral soil is first accomplished by weathering of carbonates and
17 other mineral forms that weather relatively rapidly. Once these mineral forms are depleted,
18 buffering is accomplished largely by cation exchange, in which H^+ is substituted for base cations
19 and concentrations of exchangeable base cations decrease. Once the buffering capacity provided
20 by cation exchange is depleted, acid neutralization is accomplished by weathering of crystalline
21 minerals that contain large amounts of silicon (Si) and Al and relatively small amounts of base
22 cations. At this stage, Al is mobilized within the soil and exchangeable Al concentrations
23 increase. The shift in acid buffering from base cation exchange to alumino-silicate weathering
24 and exchangeable Al was documented in Russian soils sampled three times over 75 years
25 (Lawrence et al., 2005).

26 The effect of decreasing concentrations of exchangeable base cations on cation leaching
27 in mineral soil was shown in simulation modeling by Reuss (1983). Below a base saturation of
28 20%, leaching of Ca^{2+} decreases substantially and becomes less sensitive to variations in acid
29 inputs as base saturation decreases further. This relationship was later shown experimentally by
30 Lawrence et al. (1999a). Samples from the upper B-horizon in nearly all of the Adirondack lake
31 watersheds sampled by Sullivan et al. (2006a) had base saturation values less than 20%, as did

1 soils at 11 sites in New York, Vermont, New Hampshire, and Maine in a regional study of
2 mature spruce-fir forests (David and Lawrence, 1996). Exchangeable Ca^{2+} concentrations
3 (expressed as a percentage of cation exchange capacity [CEC]) in the regional spruce-fir study
4 were weakly correlated with an estimate of the relative weathering potential of parent material in
5 the upper 10 cm of the B horizon ($r^2 = 0.44$). However, these factors were strongly correlated in
6 the Oa horizon ($r^2 = 0.92$) (Lawrence et al., 1997). Because mineral weathering in the B horizon
7 is the primary source of soil Ca^{2+} , a strong relationship between weathering potential and
8 exchangeable Ca^{2+} concentrations would be expected in this horizon. The weak correlation
9 suggests that concentrations of Ca^{2+} had decreased into the Al-buffering range sometime in the
10 past. The parent material signature in the Oa horizon was likely maintained through vegetative
11 recycling—uptake of Ca^{2+} from the O and B horizons, followed by transport back into the
12 O horizon in litterfall.

13 In summary, evidence from repeated sampling and studies of soil processes indicate that
14 decreases in exchangeable base cation concentrations in both Oa and B horizons are common
15 and widespread in the eastern United States. Factors such as logging and net forest growth are
16 likely to have contributed to this decrease in varying degrees, but acidic deposition has played a
17 major role (Lawrence et al., 1987; Huntington, 2000). The magnitudes and rates at which Ca^{2+}
18 depletion has occurred are less clear.

19 These base cation depletion issues relate directly to the chemical recovery potential of
20 acidified soils and surface waters. Replenishment of exchangeable base cation concentrations
21 on soils will require that inputs from weathering and atmospheric deposition exceed losses from
22 leaching and vegetative uptake. Inputs of Ca^{2+} from atmospheric deposition decreased sharply
23 in the east through the 1980s (Hedin et al., 1994), and have remained relatively stable since
24 that time (<http://nadp.sws.uiuc.edu/>). Atmospheric deposition of SO_4^{2-} currently remains
25 several factors higher than that of Ca^{2+} even at sites where SO_4^{2-} levels are relatively low
26 (<http://nadp.sws.uiuc.edu/>), so chemical recovery at current acidic deposition levels will require
27 inputs of base cations from weathering that are considerably greater than inputs from the
28 atmosphere.

29 Because of the importance of weathering to the base-cation status of soils, a great deal of
30 effort has been made to estimate *in situ* weathering flux with a variety of methods (Miller et al.,
31 1993; Likens et al., 1996; Bailey et al., 2003). The complexity and variability of factors that

1 affect weathering flux rates, such as soil mineralogy, particle surfaces, soil organic matter,
2 moisture flux, and a host of other factors that are difficult to quantify, add large uncertainties
3 to weathering flux estimates. Weathering rates estimated in geochemical models are generally
4 assumed to be constant overtime, but lower weathering rates were observed in a soil sampled
5 in 1987 than in the same soil sampled and archived in 1949-50 (Zulla and Billett, 1994). Further
6 complexity in weathering flux rates results from the possible role of mycorrhizae in penetrating
7 silicate minerals to extract base cations while remaining isolated from the soil solution
8 (Van Breemen et al., 2000; Blum et al., 2002). Lastly, as yet unidentified sources of base cations
9 may exist in forest soils. Bailey et al. (2003) found that elevated rates of Ca^{2+} loss from forest
10 harvesting continued for 30 years after disturbance, but the source of the additional Ca^{2+} being
11 lost could not be identified. Until estimates of *in situ* weathering fluxes are better constrained
12 and more data become available from repeated soil sampling, predictions of recovery of
13 exchangeable base cation concentrations will be highly uncertain.

14

15 **AX4.1.2.3 Aluminum Mobilization**

16 Through the natural process of podzolization, dissolved organic acids derived from
17 partially decomposed organic matter in the O horizon move into the mineral soil where they
18 weather soil particles and release Al into solution. As soil solution moves deeper into the profile,
19 acidity is neutralized and Al is deposited as a secondary mineral or more likely as an organic Al
20 (Al_o) complex (DeConinck, 1980). The limited mobility of organic anions results in retention of
21 most Al within the mineral soil (often in the Bh horizon). Complexation with dissolved organic
22 matter can increase the mobility of Al within the soil and lead to transport of organic Al into
23 surface waters from shallow soils that are high in organic matter (Lawrence et al., 1986).

24 Through the introduction of mineral acidity associated with anions that are more mobile
25 than those from organic matter, acidic deposition mobilizes Al that had previously been
26 deposited in the upper mineral soil. This occurs when release of base cations is insufficient to
27 neutralize the inputs of acid. In contrast to Al mobilized by organic acids, this process mobilizes
28 Al in inorganic forms, and in doing so, increases exchangeable Al concentrations within the
29 B horizon (Driscoll et al., 1985; Lawrence et al., 1995) and results in transport of inorganic Al
30 into surface waters (Driscoll et al., 1985). Increased concentrations of exchangeable Al in the
31 mineral soil have been identified through repeated sampling in the United States and Europe
32 over periods ranging from 17 years to 41 years in studies by Billet et al. (1990), Falkengren-

1 Grerup and Eriksson (1990), Bailey et al. (2005), and Lawrence et al. (2005). In areas of Europe
2 with excessively high acidic deposition levels, evidence of Al depletion in the mineral soil has
3 also been found (Mulder et al., 1989; Lapenis et al., 2004), but Al depletion has not been
4 documented in the United States.

5 Aluminum can be directly toxic to plants, but in natural systems, is more likely to impair
6 growth by restricting uptake of Ca^{2+} through accumulation in root tissues (Thornton et al., 1987;
7 Vogt et al., 1987a,b; McLaughlin and Wimmer, 1999). The study of Shortle and Smith (1988)
8 was the first to attribute the decline of red spruce (*Picea ruben*) in northern New England to an
9 imbalance of Al^{3+} and Ca^{2+} in fine root development.

10 Based on results of soil surveys in red spruce forests throughout the northeastern United
11 States that had been acidified to varying degrees, Lawrence et al. (1995) found that Al
12 dissolution in the mineral soil caused by SO_4^{2-} and NO_3^- supplied by acidic deposition can
13 decrease the availability of Ca^{2+} in the overlying forest floor. Once mobilized, Al can move
14 upward into the forest floor through capillary water movement, a rise in the soil water level
15 during saturated conditions, and uptake by roots in the mineral soil followed by litterfall.
16 Because Al^{3+} has a higher affinity for negatively charged soil surfaces than Ca^{2+} , introduction of
17 Al into the forest floor where root-uptake of nutrients is greatest displaces Ca^{2+} from the cation
18 exchange complex. Therefore, Ca^{2+} is more easily leached into drainage water (Lawrence et al.,
19 1995; Lawrence and Huntington, 1999).

20 Increases in exchangeable Al concentrations in the O horizon have been documented over
21 periods from 17 to 30 years (Lawrence et al., 1995; Drohan and Sharpe, 1997; Bailey et al.,
22 2005), although the study of Yanai et al. (2005) did not find consistent changes in Oa horizons
23 over 15 years.

24 Numerous papers have evaluated solubility controls on Al in both the mineral soil and the
25 O horizon. These papers have commonly related Al solubility to gibbsite ($\text{Al}(\text{OH})_3$) or a
26 gibbsite-like mineral to determine if inorganic Al concentrations could be predicted from
27 gibbsite solubility constants and pH (e.g., Johnson et al., 1981; David and Driscoll, 1984; Cronan
28 and Goldstein, 1989; Lawrence and David, 1977). These efforts have shown that inorganic Al
29 concentrations are often undersaturated with respect to gibbsite and do not support Al-
30 trihydroxide as the primary control in natural systems. Gibbsite solubility should therefore be

1 considered a useful point of reference in evaluating Al-solubility rather a mineral form that is an
2 important control of Al solubility in natural systems.

3 Through the 1990s, evidence accumulated to indicate that secondary Al in the mineral
4 soil is in a form associated with organic matter, and in some soils, imogolite (Dahlgren and
5 Walker, 1993; Mulder and Stein, 1994; Berggren and Mulder, 1995; Simonsson and Berggren,
6 1998; Skyllberg, 1999). Organic matter also plays a major role in controlling Al solubility in
7 O horizons. This interaction has been described by Cronan et al. (1986) in O horizons through
8 the bound Al ratio, which reflects the equivalents of adsorbed Al per mol of carboxyl groups
9 (Cronan et al., 1986). Tipping et al. (1995) described Al solubility on organic and mineral soil
10 horizons through equilibrium humic ion binding. Each of these approaches has had success in
11 describing dissolved Al concentrations in organic soils as a function of pH through formulations
12 that rely on concentrations of solid-phase organic bound Al. Further work has shown these
13 relationships to be specific to the particular horizon, and the pool sizes of Al and humic
14 substances (Lofts et al., 2001). However, inputs of acidity may alter concentrations of solid-
15 phase organic bound Al (Lawrence and David, 1977). Changes in atmospheric deposition levels
16 may therefore shift these relationships over time as soils further acidify or recover.

17 In summary, the natural downward movement and deposition of Al within the upper soil
18 profile is altered by acidic deposition if the release of base cations is insufficient to buffer inputs
19 of acid. Rather than be deposited as an alumino-organic complex, Al mobilized by acidic
20 deposition tends to stay in solution in an inorganic form that can be transported to surface waters.
21 Depletion of exchangeable base cations precedes the mobilization of inorganic Al. Therefore, as
22 base cation concentrations decrease, exchangeable Al concentrations increase. Increases in
23 concentrations of exchangeable Al have been documented at several locations in base-cation
24 depleted soils in the United States and Europe. In soils with base saturation values less than
25 20%, the ratio of exchangeable Ca to Al is typically less than 1 in upper mineral soils (Lawrence
26 et al., 2005). Soil chemical recovery will require a decrease in exchangeable Al concentrations
27 and Al saturation, but it is unclear what level of Ca weathering flux, and for what length of time,
28 would be required to decrease soil exchangeable Al concentrations. Furthermore, it is currently
29 unclear whether exchangeable Al concentrations are continuing to increase, remaining stable, or
30 decreasing. Current levels of base cations in soil solution suggest that decreases in exchangeable
31 Al are currently not occurring. Predictions of future trends in exchangeable Al concentrations

1 remain highly uncertain because of our partial understanding of mechanisms through which
2 mineral matter and organic matter interact to control dissolved Al concentrations. Possible
3 changes in the dynamics of soil organic matter that could be expected from climate change add
4 further uncertainty to future trends in exchangeable Al concentrations in soils.

5 6 **AX4.1.2.4 Soil Acidification**

7 Soil acidification in the context of acidic deposition can refer to a decrease in soil pH, a
8 decrease in soil percent base saturation, an increase in Al mobilization, or a combination of these
9 changes. Soil acidification occurs in response to inputs of sulfuric and nitric acid, which can be
10 neutralized by weathering or base cation exchange. If atmospheric inputs of sulfuric and nitric
11 acid pass through the soil in solution without neutralization, the soil is not acidified.

12 Neutralization of drainage water is accomplished at the expense of soil base cations. To evaluate
13 soil acidification, the soil must be considered in terms of the surface organic layer (the primary
14 rooting zone), of which the Oa horizon (or in some studies the O horizon, which combines the
15 Oe and Oa horizons) is an important component, and the B horizon, which lies below the Oa
16 horizon and is primarily comprised of mineral matter.

17 The H⁺ deposited from the atmosphere can have a direct effect on soil pH. However, net
18 uptake of nutrient cations by vegetation can also generate acidity within the soil, and a
19 considerable amount of natural organic acidity is produced in the Oa horizon through the partial
20 decomposition of organic matter and net uptake of nutrient cations. This process can decrease
21 the pH of soil water in the Oa horizon well below the lowest pH values measured in acidic
22 deposition (Krug et al., 1985; Lawrence et al., 1995). Soils under coniferous vegetation are most
23 acidified by organic acids, and are unlikely to have experienced a lowering of pH in the Oa
24 horizon as a result of acidic deposition (Johnson and Fernandez, 1992; Lawrence et al., 1995).
25 Soils influenced primarily by hardwood species tend to be less acidic naturally, and are therefore
26 more susceptible to decreased pH in the Oa horizon from acidic deposition. Johnson et al.
27 (1994a,b) found a statistically significant decrease in soil pH from 1930 to 1984 in soils of the
28 Adirondack region of New York that had an initial pH of 4.0 to 5.5, but no decrease in pH in
29 soils with an initial pH less than 4.0. This decrease in Oa horizon pH was attributed to a
30 combination of acidic deposition and changing vegetation dynamics. Bailey et al. (2005) also
31 found a statistically significant decrease in pH that averaged 0.9 units in combined Oa/A
32 horizons in western Pennsylvania from 1967 to 1997. This study attributed the observed soil

1 acidification primarily to acidic deposition (Bailey et al., 2005). A second study in hardwood
2 stands and mixed stands in Pennsylvania also found lower soil pH in O/A horizons in either the
3 1957 to 1961 period or 1979, as compared with 1993 (Drohan and Sharpe, 1997).

4 In the B horizon of soils north of the maximum extent of glaciation, CEC is largely
5 derived from organic matter, whereas in older southern soils the surface charge of highly
6 weathered clay minerals is the primary source of CEC. The CEC derived from organic matter is
7 pH-dependent. Decreases in pH result in a decreases in CEC. In both cases, the CEC of the B
8 horizon is much lower than in organic-rich surface horizons (Oa or A horizons). Less acidity
9 from organic matter and a limited capacity for buffering due to low CEC makes the B horizon
10 more susceptible to a lowering of pH from acidic deposition, and decreases in pH lower the
11 CEC, further reducing the acid-buffering capacity from cation exchange. Two studies in the
12 United States have provided measurements to assess changes in soil pH in the B horizon from
13 acidic deposition. Bailey et al. (2005) found lower pH values in the upper B horizon in
14 northwestern Pennsylvania soils in 1967 than in 1997, at 50 cm depth ($p < 0.001$) and at 100 cm
15 depth ($p < 0.001$), which were largely attributable to acidic deposition. Markewitz et al. (1998)
16 also found pronounced decreases in soil pH down to 60 cm in highly weathered Piedmont soils
17 from 1962 to 1990. The latter study was conducted in a former cotton field in which loblolly
18 pines were planted in 1956-57. Forest regrowth undoubtedly played a large role in the soil pH
19 changes that were measured, but atmospheric deposition was estimated to account for 38% of the
20 H^+ inputs during the 28 years that elapsed between measurements.

21 Other studies in Europe have found similar decreases in soil pH of the B horizon that
22 could be attributed, at least in part, to acidic deposition. These include the study of Lawrence
23 et al. (2005) in northwestern Russia, which documented decreases in soil pH in the B horizon
24 down to 90 cm, from 1926 to 1964, and further decreases from 1964 to 2001. Acidic deposition
25 was identified as the probable primary cause of decreasing pH in this study. The study of
26 Lawrence et al. (2005) also observed a decrease in CEC in this soil, as did a previous study of
27 Russian soils (Lapenis et al., 2004). The decrease in pH was likely to have contributed to the
28 decreased CEC of these soils, but a more important factor may have been a decrease in organic
29 carbon concentrations that was also measured. To our knowledge, data to assess possible
30 changes in CEC in soils in the United States has not become available, but change in CEC has
31 implications for recovery potential of soils from acidic deposition effects (Sullivan et al., 2006b).

1 Increased CEC driven by increases in pH could foster soil recovery by increasing the opportunity
2 for adsorption of base cations, as soil solution becomes less acidic. Decreases in soil organic
3 matter driven by climate and/or vegetation changes, such as those seen in Russian soils, would
4 result in a decrease in acid-buffering capacity through cation-exchange. There are currently no
5 data in the United States that indicate increases in soil pH associated with recent declines in
6 acidic deposition levels. These data limitations make future projections of recovery of soil pH
7 highly uncertain.

8

9 **AX4.1.2.5 Nitrogen Saturation**

10 Atmospheric N deposition does not necessarily cause adverse environmental effects. In
11 many areas, the most significant conspicuous effect is an increase in forest productivity (Kauppi
12 et al., 1992). However, in some areas, especially at high elevation sites, terrestrial ecosystems
13 have become N-saturated and high levels of deposition cause increased NO_3^- -leaching losses in
14 drainage waters (Aber et al., 1989; Stoddard, 1994; Stoddard et al., 1998). The term N-saturated
15 has been defined in a variety of ways, all reflecting a condition whereby the input of N (mainly
16 as NO_3^- and ammonium [NH_4^+]) to the ecosystem exceeds the requirements of terrestrial biota,
17 and a substantial fraction of the incoming N leaches out of the ecosystem in groundwater and
18 surface water. This enhanced NO_3^- leaching can displace and deplete Ca^{2+} and other base
19 cations in forest soils and can cause acidification of drainage waters.

20 Forest growth in the United States has traditionally been viewed as being limited by the
21 availability of N (Aber et al., 1989). Most forests take up the additional N provided by
22 atmospheric deposition with few or no signs of N-saturation. However, evidence grew through
23 the 1990s to indicate that decades of atmospheric deposition of N had increased the availability
24 of NO_3^- and NH_4^+ in some terrestrial ecosystems to levels that were no longer growth limiting to
25 forest vegetation. This condition of excess N results in net nitrification and associated NO_3^-
26 leaching in drainage water. As with SO_4^{2-} leaching, NO_3^- leaching removes base cations from
27 the soil. Leaching associated with NO_3^- is less than that associated with SO_4^{2-} in most
28 ecosystems in the United States that are affected by acidic deposition, but concentrations of
29 NO_3^- in some streams are high enough to suggest a substantial role for NO_3^- in cation leaching,
30 particularly during periods of high soil-water flux during the non-growing season (Aber et al.,
31 2003).

1 Severe symptoms of N saturation, have been observed in high-elevation, nonaggrading
2 spruce-fir ecosystems in the Appalachian Mountains, as well as in the eastern hardwood
3 watersheds at Fernow Experimental Forest near Parsons, WV and throughout the northeastern
4 United States. Mixed conifer forests and chaparral watersheds with high smog exposure in the
5 Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^-
6 concentrations documented within wildlands in North America (Bytnerowicz and Fenn, 1996;
7 Fenn et al., 1998).

8 Some examples of N-saturated forests in North America, including estimated inputs and
9 outputs, are shown in Table AX4.1-1 (Fenn et al., 1998). The Harvard Forest hardwood stand in
10 western Massachusetts absorbed $> 900 \text{ kg N/ha}$ without significant NO_3^- leaching during an
11 8-year N amendment study (Table AX4.1-1) (Fenn et al., 1998). In contrast, NO_3^- leaching
12 losses were high at the Harvard Forest pine sites. In the 8-year experimental study, NO_3^-
13 leaching was observed in the pine stand after the first year (1989) in the high-N application plots,
14 and further increases were observed in 1995 and 1996. The hardwood stand did not show
15 significant increases in NO_3^- leaching until 1996. The differences in response of the pine and
16 hardwood stands indicate that the mosaic of community types across the landscape must be
17 considered when evaluating landscape-scale responses to N deposition (Magill et al., 2000).

18 Utilization of N in the terrestrial ecosystem is accomplished through complex interactions
19 between plants and microbes that are not fully understood (Schimel and Bennett, 2004). Long-
20 term N retention is largely accomplished by incorporation of N into soil organic matter through
21 biological assimilation (Aber et al., 1998), and to a lesser extent by abiotic processes that are
22 not well understood (Dail et al., 2001). The forms in which N is assimilated by plants and
23 microbes are determined by availability, as described in Schimel and Bennett (2004). In the
24 most N-limited ecosystems, competition between plants and microbes is high and N is
25 assimilated primarily in depolymerized organic forms, resulting in low mineralization rates
26 and minimal buildup of inorganic N in the soil. Increased availability of N increases the
27 mineralization rate, which enhances competition between plants and microbes for available NH_4^+
28 produced by mineralization. Further increase in the availability of N (for example by high levels
29 of atmospheric N deposition) lessens competition for NH_4^+ between plants and microbes and
30 leads to increased production of NO_3^- by autotrophic nitrifying bacteria. Some of this NO_3^- can
31 be taken up by plants and microbes, but because much of the N demand is satisfied by NH_4^+

1 under these conditions, NO_3^- tends to be mobile within the soil, enabling it to leach to drainage
2 water. Based on the definitions of Aber et al. (1989, 1998) and Stoddard (1994), the first stage
3 of N saturation is reached when competition between plants and microbes for NH_4^+ has
4 decreased to the point that net nitrification occurs.

5 Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream
6 waters (Webb et al., 1995), eutrophy estuaries and marine waters (Fisher and Oppenheimer,
7 1991), and deplete soils of nutrient base cations, especially Ca^{2+} and Mg^{2+} (Likens et al., 1998).
8 Considerable evidence is available to link N deposition to acidification of soils. Much of this
9 evidence comes from the northeastern United States, where increased accumulation of N in soil
10 is suggested by a strong positive correlation between atmospheric deposition levels and total
11 N concentration in the Oa horizon, at sites in New York, Vermont, New Hampshire, and Maine
12 (Driscoll et al., 2001b). Further evidence that atmospheric deposition has increased availability
13 of N in soil is shown by a strong negative correlation between atmospheric deposition levels and
14 the C:N ratio of the Oa horizon in this region (Aber et al., 2003). If the C:N ratio falls below
15 about 25, nitrification is stimulated, resulting in elevated NO_3^- in surface waters (Aber et al.,
16 2003). Similar results were found in Europe, where a C:N ratio of 24 was identified as the
17 critical level below which nitrification occurred (Emmett et al., 1998).

18 Analyses have been conducted in the northeastern United States and Europe to examine
19 the relationships between N deposition and NO_3^- leaching to surface waters. The relationship
20 between measured wet deposition of N and streamwater output of NO_3^- was evaluated by
21 Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by
22 Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than
23 approximately 5.6 kg N/ha/yr. Stoddard (1994) presented a geographical analysis of patterns of
24 watershed loss of N throughout the northeastern United States. He identified approximately
25 100 surface water sites in the region with sufficiently intensive data to determine their N status.
26 Sites were coded according to their presumed stage of N retention, and sites ranged from Stage 0
27 (background condition) through Stage 2 (chronic effects). The geographic pattern in watershed
28 N retention depicted by Stoddard (1994) followed the geographic pattern of N deposition. Sites
29 in the Adirondack and Catskill Mountains in New York, where N deposition was about 11 to
30 13 kg N/ha/yr, were typically identified as Stage 1 (episodic effects) or Stage 2. Sites in Maine,
31 where N deposition was about half as high, were nearly all Stage 0. Sites in New Hampshire and

1 Vermont, which received intermediate levels of N deposition, were identified as primarily Stage
2 0, with some Stage 1 sites. Based on this analysis, a reasonable threshold of N deposition for
3 transforming a northeastern site from the “natural” Stage 0 condition to Stage 1 would
4 correspond to the deposition levels found throughout New Hampshire and Vermont,
5 approximately 8 kg N/ha/yr. This agreed with Driscoll et al.’s (1989) interpretation, which
6 would probably correspond to total N inputs near 8 to 10 kg N/ha/yr. This is probably the
7 approximate level at which episodic aquatic effects of N deposition would become apparent in
8 many watersheds of the eastern United States.

9 Analysis of data from surveys of N outputs from 65 forested plots and catchments
10 throughout Europe were conducted by Dise and Wright (1995) and Tietema and Beier (1995).
11 Below the throughfall inputs of about 10 kg N/ha/yr, there was very little N leaching at any of
12 the study sites. At throughfall inputs greater than 25 kg N/ha/yr, the study catchments
13 consistently leached high concentrations of inorganic N. At intermediate deposition values
14 (10 to 25 kg N/ha/yr), Dise and Wright (1995) observed a broad range of watershed responses.
15 Nitrogen output was most highly correlated with N input ($r^2 = 0.69$), but also significantly
16 correlated with S input, soil pH, percent slope, bedrock type, and latitude. A combination of
17 N input (positive correlation) and soil pH (negative correlation) explained 87% of the variation
18 in N output at the study sites (Dise and Wright, 1995).

19 The threshold level of atmospheric deposition that causes release of NO_3^- to surface
20 waters was identified by Aber et al. (2003) as approximately 7 kg N/ha/yr for the northeastern
21 United States. In watersheds receiving N deposition above this level, concentrations of NO_3^- in
22 surface waters were positively correlated with atmospheric deposition, whereas most watersheds
23 with deposition less than 7 kg/ha/yr had little or no NO_3^- (undetectable at most sites) in their
24 surface waters (Aber et al., 2003). The threshold value of 7 kg/ha/yr was based on atmospheric
25 deposition levels for the base of forested watersheds. When scaled to included higher deposition
26 levels expected at upper elevations this value was estimated to equal about 10 kg/ha/yr, similar to
27 the European estimate of Dise et al. (1998).

28 The common deposition threshold for release of NO_3^- to surface waters in forested
29 watersheds found in the northeastern United States and Europe represents an important advance
30 in relating N inputs to ecosystem effects, but a considerable amount of variability in ecosystem
31 response has also been demonstrated. Lovett et al. (2000b) found that 39 watersheds in the

1 Catskill region of New York State retained from 49% to 90% of atmospheric N inputs. Castro
2 and Morgan (2000) showed that NO_3^- export from watersheds in eastern North America can
3 range from nearly 0 to over 400 eq/ha/yr in watersheds that receive similar levels of inorganic
4 N in wet deposition in the range of 400 to 500 eq/ha/yr.

5 Experimental additions of N to plots and watersheds have also demonstrated variations in
6 terrestrial retention of N. Additions of N (approximately twice ambient deposition) to hardwood
7 watersheds in Maine (25 kg N/ha/yr) and West Virginia (35.5 kg N/ha/yr), which were releasing
8 NO_3^- to surface waters prior to the additions, resulted in substantial increases in NO_3^-
9 concentrations in soil water and stream water within the first treatment year (Kahl et al., 1993a;
10 Peterjohn et al., 1996). Additions of 25 kg N/ha/yr to spruce plots in Vermont (ambient bulk
11 deposition 5.4 kg N/ha/yr), in which net nitrification did not occur prior to treatment, triggered
12 net nitrification in the second year of treatment, whereas nitrification was not triggered until the
13 third year in plots receiving 19.8 kg N/ha/yr (McNulty et al., 1996). Similar results to these were
14 seen in two studies from Colorado. Additions of 25 kg N/ha/yr to old-growth spruce plots in
15 Loch Vale watershed (ambient bulk deposition ~4-5 kg N/ha/yr) doubled N mineralization rates
16 and stimulated nitrification, while the addition of the same amount to plots receiving ambient
17 bulk deposition of ~2.0 kg N/ha/yr in Fraser Experimental Forest elicited no microbial response
18 but significantly increased foliar and organic soil horizon N (Rueth et al., 2003). A comparison
19 study of old-growth spruce plots across a depositional gradient in Colorado found mineralization
20 rates to be higher where N deposition ranged from 3 to 5 kg N/ha/yr than where N deposition
21 ranged from 1 to 2 kg N/ha/yr, with measurable nitrification rates at sites with the highest
22 deposition amounts (Rueth and Baron, 2002). In marked contrast to these results, concentrations
23 of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest,
24 which received additions of 150 kg N/ha/yr (Magill et al., 2004). Concentrations of (NO_3^- +
25 NH_4^+) in hardwood plots receiving 50 kg N/ha/yr were not yet detectable in the 15th year of
26 treatments. The same treatments were applied to red pine (*Pinus resinosa*) plots, which
27 exhibited elevated concentrations of (NO_3^- + NH_4^+) in soil water after 1 year of 150 kg N/ha/yr
28 doses, and after 5 years of 50 kg N/ha/yr doses.

29 In general, deciduous forest stands in the eastern United States have not progressed
30 toward N-saturation as rapidly or as far as spruce-fir stands. Deciduous forests may have a
31 greater capacity for N retention than coniferous forests. In addition, deciduous forests tend to be

1 located at lower elevation and receive lower atmospheric inputs of N. Many deciduous forests
2 have higher rates of N uptake and greater N requirement than spruce-fir forests. Decreased
3 growth and increased mortality have more commonly been observed in high-elevation coniferous
4 stands than in lower elevation hardwood forests, and these differences have been partially
5 attributed to excess inputs of N (Aber et al., 1998). Indeed, many of the lower elevation
6 deciduous stands are N-deficient and are therefore likely to benefit (i.e., grow faster), at least up
7 to a point, with increased inputs of N.

8 There are examples of N saturation in lower-elevation eastern forests, especially in West
9 Virginia. For example, progressive increases in streamwater NO_3^- and Ca^{2+} concentrations were
10 measured at the Fernow Experimental Forest in the 1970s and 1980s (Edwards and Helvey,
11 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000). This watershed has received higher N
12 deposition (average throughfall input of 22 kg/ha/yr of N in the 1980s) than is typical for low-
13 elevation areas of the eastern United States, however (Eagar et al., 1996), and this may help to
14 explain the observed N saturation.

15 Varying responses to N additions reflect differences in N status of the treatment sites.
16 These variations have most often been attributed to disturbance history, dating back a century or
17 more (Goodale and Aber, 2001). Sites which have undergone disturbances that cause loss of soil
18 N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and
19 experimental inputs of N. Nitrogen retention capability often decreases with stand age, which
20 suggests that older forests are more susceptible than younger forests to becoming N-saturated
21 (Hedin et al., 1995). Aber et al. (1998) surmised that land use history may be more important
22 than cumulative atmospheric deposition of N in determining the N status of a forest ecosystem.

23 Although considerable progress has been made in understanding the factors that control
24 N retention, efforts to quantify net N retention through known processes have not been fully
25 successful. Assimilation of N by mycorrhizae followed by exudation as dissolved organic matter
26 was proposed by Aber et al. (1998) as a possible explanation for unaccounted conversion of
27 inorganic N into soil organic matter. However, Frey et al. (2004) found that elevated N inputs
28 reduced active mycorrhizal biomass, fungal diversity and fungal:bacterial biomass ratios. These
29 results suggested a decreased role for mycorrhizae in fixation of N under elevated N inputs.

30 Abiotic transformation of inorganic N into soil organic matter has also been proposed as
31 a possible mechanism to explain high rates of N retention in soil, and some evidence has been

1 presented to support this possibility. Dail et al. (2001) observed retention of $^{15}\text{NO}_3^-$ and $^{15}\text{NO}_2$
2 in sterile soil, but the method of sterilization may have increased dissolved organic carbon
3 (DOC) concentrations and artificially increased the opportunity for formation of soluble organic
4 N compounds. Davidson et al. (2003) developed the ferrous wheel hypothesis to explain
5 incorporation of inorganic N into organic matter. The hypothesized mechanism involves
6 conversion of NO_3^- to NO_2^- through oxidation of Fe^{2+} . Testing of this hypothesis *in situ* was not
7 found in the literature, but the small amount of Fe^{2+} that typically occurs in the forest floor,
8 where presumably much of the conversion to organic N occurs, may limit the importance of this
9 pathway. Fitzhugh et al. (2003) showed that NO_2^- produced in the first step of nitrification may
10 be directly converted to soluble organic N rather than becoming fully oxidized to NO_3^- .
11 However, concentrations of introduced $^{15}\text{NO}_2$ in this experiment were several orders of
12 magnitude higher than that normally seen in forest soils. Therefore, the evidence at this time for
13 abiotic retention of N is not fully convincing, and the importance of this process requires further
14 research.

15 In addition to our limited understanding of N retention mechanisms, there is no direct
16 information on ecosystem recovery from N saturation in the United States. This may be at least
17 partly because atmospheric deposition of N has been relatively stable in the eastern United States
18 over the past two to three decades. An important source of information on N recovery responses
19 has been provided by the European NITREX study, which reduced ambient N deposition for
20 5 years with roofs constructed over experimental plots in Germany and The Netherlands. At the
21 German site, deposition was reduced from approximately 38 kg N/ha/yr to levels that varied
22 from 10 to 20 kg N/ha/yr. At the Dutch site, deposition was reduced from 45 kg N/ha/yr to
23 levels that varied from 1 to 10 kg N/ha/yr. At both of these sites, deposition levels before the
24 experiment were approximately three to four times greater than the highest deposition levels
25 commonly found in the eastern United States, whereas after the reduction, levels at the Dutch
26 site fell within the range of deposition in the eastern United States over the past two decades, and
27 values at the German site were somewhat higher than this range (Ollinger et al., 1993; Emmett
28 et al., 1998). The decrease in ambient N inputs resulted in a marked decrease in N outputs at
29 each site within 2 to 3 years. The responses at the two sites were somewhat different, however.
30 At the Dutch site, outputs of N exceeded inputs both before and after experimental reduction of
31 inputs. At the German site, inputs exceeded outputs before and after reduction of inputs, but

1 outputs were more similar to inputs after the reduction. At both sites, outputs after the reduction
2 in deposition remained two to three times higher than outputs commonly measured in the eastern
3 United States.

4 Thus, atmospheric deposition of N has increased N availability in soils, which has led to
5 increased nitrification and associated acidification of soil and soil water. The N retention
6 capacity of soils is strongly dependant on land-use history, however, so the relationships between
7 N deposition and ecosystem N status and percent of terrestrial retention are variable. In general,
8 however, atmospheric deposition of 10 kg N/ha/yr or higher is required for appreciable amounts
9 of NO_3^- to leach to surface waters in the eastern United States and northern Europe. Future
10 projections of chemical recovery from N-driven acidification are uncertain because (1) retention
11 mechanisms are not fully understood, and (2) there are only limited data on recovery responses.
12 European experiments that reduced inputs of N found decreased outputs of N within 2 to 3 years,
13 which indicates a relatively rapid response to decreased deposition levels. However, these
14 studies are difficult to directly apply to the United States because deposition levels were much
15 higher at the European sites prior to the experiment, and the 5-year duration of the experiments
16 only demonstrated recovery to levels of N saturation that are higher than the more heavily
17 impacted sites in the eastern United States.

18 High concentrations of lake or streamwater NO_3^- , indicative of ecosystem saturation,
19 have been found at a variety of locations throughout the United States, including the San
20 Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the
21 Front Range of Colorado (Baron et al., 1994; Williams et al., 1996a,b), the Allegheny Mountains
22 of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and
23 Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al.,
24 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994). All of these regions,
25 except Colorado, received relatively high (more than about 10 kg N/ha/yr) atmospheric
26 deposition of oxidized N throughout the 1980s and 1990s. In contrast, the Front Range of
27 Colorado receives less than about 4 or 5 kg N/ha/yr of total (wet plus dry) deposition (Sullivan
28 et al., 2005), less than half of the total N deposition received at these other locations. The cause
29 of N-saturation at high-elevation western watersheds that receive low to moderate levels of
30 atmospheric deposition has been a subject of debate. High concentrations of NO_3^- in surface
31 waters in the western United States are not widespread. Nitrate concentrations during the fall

1 sampling season were low in most western lakes sampled in the Western Lakes Survey (WLS).
2 Only 24 sampled lakes were found to have NO_3^- concentrations greater than $10 \mu\text{eq/L}$. Of those,
3 19 lakes were situated at high elevation, most above 3,000 m. Cold temperatures in such lakes
4 undoubtedly play an important role in maintaining high NO_3^- concentrations by limiting
5 biological uptake processes. The high NO_3^- concentrations are likely to affect acid-base
6 chemistry only where ANC is low. Eight lakes showed high NO_3^- ($>10 \mu\text{eq/L}$) and low ANC
7 ($<50 \mu\text{eq/L}$), all of which occurred at elevations higher than 3,100 m. Four were located in
8 Colorado, two in Wyoming, and one each in California and Utah. In all cases, pH was above 6.5
9 and ANC was greater than or equal to $15 \mu\text{eq/L}$. Such lakes are sensitive to episodic pulses of
10 NO_3^- acidity; such pulses have been reported from Colorado Front Range lakes (Williams and
11 Tonnessen, 2000). Episodic acidification of western lakes could be important biologically.

12 In the Uinta Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of
13 the lakes included within the WLS had $\text{NO}_3^- > 10 \mu\text{eq/L}$. This suggests that N deposition in
14 these areas may have exceeded the capability of these systems to assimilate N. It is unknown if
15 these concentrations of NO_3^- represent effects from anthropogenic sources or if this constituted a
16 natural condition associated with inhibited NO_3^- assimilation in cold alpine environments.

17 Williams et al. (1996a,b) contended that N-saturation is occurring throughout high-
18 elevation catchments of the Colorado Front Range. Many lakes in the Colorado Front Range
19 have chronic NO_3^- concentrations greater than $10 \mu\text{eq/L}$ and concentrations during snowmelt are
20 frequently much higher, due at least in part to leaching from tundra, exposed bedrock, and talus
21 areas. Although biological N demand may be high in subalpine forests, uptake is limited in
22 alpine areas by large N inputs from snowmelt, steep watershed gradients, rapid water flushing,
23 extensive areas having little or no soil development, and limitations on the growth of
24 phytoplankton in some alpine lakes by factors other than N (e.g., phosphorus [P], temperature)
25 (Baron et al., 1994).

26 27 **AX4.1.3 Interactions With Soil Water**

28 Acidification from S and N deposition can have several important chemical and
29 biological effects. In particular, there are changes in the acid-base status of surface and soil
30 water which can cause short-term or long-term toxicity to aquatic or terrestrial biota. An
31 environmental stressor that changes the natural processes that occur in the soil can adversely

1 affect plant species composition and water storage and discharge in forested ecosystems.
2 Deposition of S and N from the atmosphere can change nutrient (e.g., Ca^{2+} , Mg^{2+} , K^+ , N)
3 availability, rates of organic matter decomposition, mobilization of metals (including Al) to soil
4 solution, and microbial activities in the soil. Acidic deposition usually increases the
5 concentration of SO_4^{2-} and NO_3^- in drainage water. These anions are charge-balanced by
6 cations derived from the soil cation exchange complex or released through mineral weathering.
7 The cations can include base cations such as Ca^{2+} and Mg^{2+} and acid cations such as H^+ and Al^{n+} .
8 When the concentration of H^+ and/or Al^{n+} in drainage water increases, toxic conditions may
9 result.

10 Watershed processes control the extent of ANC generation and its contribution from soils
11 to drainage waters as acidified water moves through the soil profile. These processes regulate
12 the extent to which drainage waters will be acidified in response to acidic deposition. Especially
13 important is the concentration of acid anions (including SO_4^{2-} , NO_3^- , and organic acid anions) in
14 soil solution. Organic acid anions, produced in upper soil horizons by decomposition processes,
15 normally precipitate out of solution as drainage water percolates through lower mineral soil
16 horizons. Drainage waters at greater depth generally have relatively high ANC. The addition of
17 the strong acid anions NO_3^- and NO_3^- from atmospheric deposition allows soil acidification and
18 anion leaching processes to occur at greater depths, thereby allowing water rich in SO_4^{2-} and/or
19 NO_3^- to emerge from mineral soil into drainage waters. If these anions are charge-balanced by
20 H^+ and/or Al^{n+} cations, the water will have low pH and could be toxic to aquatic biota.

21 Hydrology is an important controlling factor for atmospheric deposition effects in
22 virtually all environments (Turner et al., 1991). The depth and composition of soils, talus, and
23 colluvium and watershed slope influence the residence time of water within the watershed, the
24 extent to which snowmelt and rainfall runoff interact with soils and geologic materials which can
25 neutralize deposited acids, and the extent of NO_3^- uptake by lichens, microbes, plants and other
26 biota. Therefore, hydrological conditions and water flow paths are critical in regulating both
27 NO_3^- leaching and acid neutralization within the watershed.

28 Chemical hydrograph separation techniques have been used to trace the movement of
29 water through watersheds (Caine, 1989). Old water which was stored from the previous year
30 often contributes most of the stream flow early in the snowmelt process. New water from fresh

1 snowmelt may contribute the majority of the streamflow after the seasonal snowmelt peak flows
2 have been achieved.

3
4 **AX4.1.3.1 Sulfate Leaching**

5 The leaching of atmospherically deposited SO_4^{2-} from soils to soil waters, and eventually
6 to surface waters, is the dominant mechanism controlling soil acidification, Al toxicity to plants
7 and aquatic organisms, base cation depletion from soils, and surface water acidification.
8 Virtually all aspects of ecosystem acidification are controlled mostly by SO_4^{2-} mobility in most
9 affected ecosystems in the United States. Nitrate mobility is important in some locations, but in
10 most affected areas the dominant mobile strong acid anion is SO_4^{2-} .

11 In regions affected by acidic deposition, the total concentration of mineral acid anions in
12 surface waters (mainly SO_4^{2-}) has changed from historical conditions. In response to these
13 changes in SO_4^{2-} concentration, the concentrations of other ions in surface water must also have
14 changed to maintain electroneutrality. The leaching of SO_4^{2-} does not directly cause
15 environmental effects. Rather, it is the changes in these other ions that are responsible for
16 environmental effects of drainage water acidification. As concentration increased, other anions
17 (mainly bicarbonate) must have decreased and/or cations (e.g., base cations, hydrogen ion, or Al)
18 must have increased to maintain charge balance.

19
20 **AX4.1.3.2 Nitrate Leaching**

21 Nitrate leaching losses from soils to drainage waters are governed by a complex suite of
22 ecosystem processes in addition to N inputs from atmospheric deposition. In particular,
23 mineralization and nitrification processes play important roles in regulating the quantity of, and
24 temporal variability in, the concentration of NO_3^- in soil solution, and consequently leaching
25 losses from the rooting zone (Reuss and Johnson, 1985; Joslin et al., 1987; Johnson et al.,
26 1991b,c). Thus, NO_3^- leaching is mostly under biological control and typically shows
27 pronounced seasonal variability (Van Miegroet et al., 1993). Peak concentrations of NO_3^- in soil
28 solution appear to be largely responsible for the potentially toxic peaks in Al concentration that
29 sometimes occur in soil solution, although SO_4^{2-} may also play a role by serving to elevate
30 chronic Al concentrations (Eagar et al., 1996).

31 High leaching of NO_3^- in soil water and streamwater draining high-elevation spruce-fir
32 forests has been documented in numerous studies in the Southern Appalachian Mountain region

1 (cf. Joslin et al., 1992; Van Miegroet et al., 1992a,b; Joslin and Wolfe, 1994; Nodvin et al.,
2 1995). This high NO_3^- leaching has been attributed to a combination of high N deposition, low
3 N uptake by forest vegetation, and inherently high N release from soils. Forest age is another
4 major factor-affecting uptake, with mature forests requiring minimal N for new growth and,
5 hence, often exhibiting higher NO_3^- leaching than younger, faster growing stands (Goodale and
6 Aber, 2001). Old-growth red spruce stands in the Southern Appalachians have been
7 demonstrated to have significantly slower growth rates than stands younger than 120 years
8 (Smith and Nicholas, 1999). The latter feature is associated with low C:N ratios in mineral soil,
9 high N mineralization potential and high nitrification (Joslin et al., 1992; Eagar et al., 1996).

10 In most terrestrial ecosystems in the United States, N is strongly retained and there is
11 limited mobility of NO_3^- . Exceptions to this pattern tend to occur in spatially limited regions
12 that receive high levels of total N deposition (higher than about 10 to 20 kg N/ha/yr) and in
13 alpine and subalpine environments that have little soil or vegetative development over substantial
14 portions of the watersheds.

15

16 **AX4.1.3.3 Base Cation Leaching**

17 Leaching of SO_4^{2-} and NO_3^- must be balanced by leaching of an equivalent amount of
18 cation charge. When strong acid anion leaching is charge-balanced by base cation leaching, soils
19 can be acidified. However, this base cation leaching prevents or retards acidification of soil
20 water and surface water. Therefore, there are both positive and negative outcomes associated
21 with base cation leaching. In base-poor soils, exchangeable Ca^{2+} , Mg^{2+} , or K^+ can be depleted
22 by SO_4^{2-} and NO_3^- leaching to the point that nutrient deficiencies develop in vegetation. If base
23 cation leaching is not sufficient to neutralize the mineral acidity associated with SO_4^{2-} and NO_3^- ,
24 then drainage waters will experience decreased pH, increased Al_i concentrations, and perhaps
25 become toxic to aquatic biota.

26 Acidification results obtained using different approaches can be quantitatively compared
27 by computing the surface water response as a fraction of the change in SO_4^{2-} concentration or
28 change in $\text{SO}_4^{2-} + \text{NO}_3^-$ concentration. This is most frequently done using the F-factor
29 (Henriksen, 1984), which is defined as the fraction of the change in mineral acid anions that is
30 neutralized by base cation release. When surface water acidifies in response to acidic deposition,
31 changes in ANC and/or Al_i concentration comprise an appreciable percentage of the overall

1 surface water response to increased $[\text{SO}_4^{2-} + \text{NO}_3^-]$ and therefore the F-factor is considerably
2 less than 1.0 (Sullivan, 1990). If, however, most of the $[\text{SO}_4^{2-} + \text{NO}_3^-]$ increase causes a
3 corresponding increase in base cation concentrations, the F-factor will approach 1.0.

4 5 **AX4.1.3.4 Aluminum Leaching**

6 Aluminum is naturally abundant in soils and has a pH-dependent solubility in water. Al
7 is essentially insoluble at pH above about 6.0. Solubility increases dramatically at pH values
8 below about 5.5. In addition, solubility is enhanced by the formation of soluble organic
9 complexes (Schnitzer and Skinner, 1963; Lind and Hem, 1975). One of the most important
10 geochemical effects of acidic deposition is increased mobilization of Al from soils to streams and
11 lakes (Cronan and Schofield, 1979; Mason and Seip, 1985). Aluminum concentrations in
12 drainage waters having pH below about 5.0 are often an order of magnitude higher than in
13 circumneutral waters.

14 Processes that control the mobilization, speciation, and toxicity of Al in areas affected by
15 acidic deposition have been intensively studied since preparation of the last AQCD for SO_x in
16 1982. Nevertheless, these processes are still not well understood, and our ability to predict the
17 Al component of the acidification response remains limited (Sullivan and Cosby, 1998).

18 Aluminum is toxic to tree roots, although much higher concentrations of Al in soil
19 solution are required to elicit a toxic response as compared with the toxicity of Al to fish in
20 surface water. High concentrations of Al in soil solution can reduce plant growth, thereby
21 restricting the ability of plants to take up water and nutrients, particularly Ca^{2+} (Parker et al.,
22 1989). Interference with Ca^{2+} uptake by Al is a greater problem for forest growth than the
23 effects of direct toxicity (Shortle and Smith, 1988). Calcium is an ameliorant for Al toxicity to
24 roots, as well as to fish. Magnesium, and to a lesser extent sodium (Na^+) and K^+ , have also been
25 associated with reduced Al toxicity. Neither the molecular basis for Al toxicity to plant roots nor
26 the basis for the reduction in toxicity caused by base cations is well understood.

27 Potential effects of Al mobilization to surface and soil waters include alterations in
28 nutrient cycling (Dickson, 1978; Eriksson, 1981), pH buffering effects (Driscoll and Bisogni,
29 1984), toxicity to aquatic biota (Driscoll et al., 1980; Schofield and Trojnar, 1980; Baker and
30 Schofield, 1982), and toxicity to terrestrial vegetation (Ulrich et al., 1980).

1 **AX4.1.4 Interactions with Transitional Ecosystems**

2 The sections of this report that discuss effects of atmospheric S and N deposition on
3 transitional ecosystems are primarily concerned with various types of wetlands. Wetlands are
4 often referred to as marshes, swamps, bogs, fens, wet meadows, wet heathlands, potholes,
5 sloughs, floodplains, mires, and lagoons (Mitsch and Gosselink, 2000). A widely accepted
6 wetland definition is given by Cowardin et al. (1979):

7 Wetlands are lands transitional between terrestrial and aquatic systems where
8 the water table is usually at or near the surface or the land is covered by shallow
9 water. Wetlands must have one or more of the following three attributes: (1) at
10 least periodically, the land supports predominantly hydrophytes; (2) the
11 substrate is predominantly undrained hydric soil; and (3) the substrate is nonsoil
12 and is saturated with water or covered by shallow water at some time during the
13 growing season of each year.

14 In this report, peatlands are defined as specific types of wetlands that accumulate partially
15 decayed plant matter (peat) and include bogs and fens (Mitsch and Gosselink, 2000). Riparian
16 zones and ponds are also categorized as transitional ecosystems in this report.

17
18 **AX4.1.4.1 Sulfur Storage and Release in Transitional Ecosystems**

19 Although S is generally mobile in upland soils in most parts of the United States,
20 wetlands act as both sources and sinks of atmospherically deposited S. Wetlands retain and
21 release S in response to variations in hydrology, which in turn affect oxidation and the reduction
22 process in wetland soils. Ito et al. (2005) evaluated the influence of land cover types on SO_4^{2-}
23 fluxes in Adirondack lake watersheds. They found that SO_4^{2-} concentration in drainage water
24 decreased in association with increased wetland area within the lake watershed (adj. $r^2 = 0.58$,
25 $p \leq 0.001$). They attributed this observed pattern to dissimilatory SO_4^{2-} reduction in anaerobic
26 wetland soils.

27 Sulfur storage in wetland soils to some degree prevents or delays the acidification of
28 downstream surface waters with mineral acidity. However, the water table in wetland areas
29 typically drops during drought conditions, and this allows development of aerobic conditions in
30 surface wetland soils. Under aerobic conditions, stored S is re-oxidized to SO_4^{2-} , which can then
31 be rapidly mobilized under high-flow conditions that occur in response to rainfall or snowmelt.
32 This can cause substantial episodic pulses of acidity in surface waters that receive drainage water

1 from wetlands. Thus, wetlands buffer downstream receiving waters against chronic acidity to
2 some degree, but can be an important source of periodic episodes of more extreme acidity.

3 4 **AX4.1.4.2 Nitrogen Dynamics in Transitional Ecosystems**

5 Nitrogen cycling in wetlands differ from N cycling in terrestrial ecosystems largely
6 because of the anaerobic nature of their waterlogged soils. This changes the relative importance
7 of the various microbial transformations that make up the N cycle. Organic matter
8 decomposition is reduced, which contributes to the formation of peat. Denitrification is
9 enhanced, whereby NO_3^- is converted to N_2O or N_2 and released to the atmosphere. Wetland
10 hydrology favors N exchange to and from sediments and between ecosystem compartments.
11 This can result in transport of NH_4^+ from anoxic sediments to oxidized surface sediment or the
12 water column, where nitrification occurs. The NO_3^- formed by this process is then available for
13 transport to downstream locations. The N cycle in wetlands was summarized by the U.S.
14 Environmental Protection Agency (EPA) (U.S. Environmental Protection Agency,1993).

15 Ombrotrophic bogs receive their nutrients primary from precipitation and atmospheric
16 input. Such wetlands form in locations where precipitation exceeds evapotranspiration and there
17 is a barrier that impedes drainage of the surplus water input. Bogs are typically dominated by
18 *Sphagnum* spp., and may or may not be forested. Over time, the *Sphagnum* builds a thick layer
19 of peat, which raises the bog above the surrounding landscape, preventing water entry from
20 runoff or from groundwater flux. Ombrotrophic bogs are highly sensitive to the effects of
21 N deposition. However, such effects are likely due to nutrient enrichment, rather than
22 acidification processes. See discussion in Section AX5.8.

23 24 **AX4.1.4.3 Organic Acidity in Transitional Ecosystems and Downstream Surface Waters**

25 Organic acids in fresh water originate from the degradation of biomass in upland areas,
26 wetlands, near-stream riparian zones, the water column, and stream and lake sediments
27 (Hemond, 1994). The watersheds of surface waters that have high concentrations of organic
28 matter (DOC > about 400 μM) often contain extensive wetlands and/or extensive organic-rich
29 riparian areas (Hemond, 1990; Sullivan, 2000).

30 Organic acids contributed by wetlands to downstream drainage waters can influence
31 surface water acid-base chemistry, particularly in dilute waters having moderate to high (greater
32 than about 400 μM) DOC concentrations. Organic acids in surface waters include a mixture of

1 functional groups having both strong and weak acid character. Some lakes and streams are
2 naturally acidic as a consequence of organic acids contributed to solution by wetlands. The
3 presence of organic acids also provides buffering to minimize pH change in response to changes
4 in the amount of SO_4^{2-} and NO_3^- derived from acidic deposition.

5 There are many lakes and streams that are chronically acidic or low in ANC mainly due
6 to the presence of organic acids. In many cases, the principal source of these organic acids is the
7 wetlands within the watershed. The National Acid Precipitation Assessment Program (NAPAP;
8 1991) concluded that about one-fourth of all acidic lakes and streams surveyed in the National
9 Surface Water Survey (NSWS) (Linthurst et al., 1986a; Kaufmann et al., 1988) were acidic
10 largely as a consequence of organic acids. A survey of 1400 lakes in the Adirondack Mountains
11 by the Adirondack Lake Survey Corporation (ALSC) (Kretser et al., 1989), which included many
12 small lakes and ponds (1 to 4 ha) having relatively high DOC, revealed that about 38% of the
13 lakes had $\text{pH} < 5$ due to the presence of organic acids, and that organic acids generally depressed
14 the pH of Adirondack lakes by 0.5 to 2.5 pH units in the ANC range of 0 to 50 $\mu\text{eq/L}$ (Baker
15 et al., 1990b).

16 Specification of the acid-base character of water high in DOC is somewhat uncertain.
17 Attempts have been made to describe the acid-base behavior of organic acids using a single H^+
18 dissociation constant (pK_a), despite the fact that organic acids in natural waters are made up of a
19 complex mixture of acidic functional groups. A portion (perhaps one-third) of the acidity in
20 organic acids is quite strong, with some ionization occurring at pH values well below 4.0
21 (Driscoll et al., 1994; Hemond, 1994). A number of modeling approaches have been used to
22 estimate the acidity of organic acids in fresh waters, often as simple organic acid analogs having
23 different pK_a values (Oliver et al., 1983; Perdue et al., 1984; Driscoll et al., 1994).

24 The importance of naturally occurring organic acids as agents of surface water
25 acidification was reinforced by a modeling study (Sullivan et al., 1996a) that showed that
26 inclusion of organic acids in the Model of Acidification of Groundwater in Catchments
27 (MAGIC) had a substantial effect on model predictions of surface water pH, even in waters
28 where DOC concentrations were only moderate. MAGIC hindcasts of pre-industrial lakewater
29 pH of Adirondack lakes showed poor agreement with diatom inferences of pre-industrial pH
30 when organic acids were not considered in the MAGIC model (Sullivan et al., 1996a). Revised
31 MAGIC hindcasts of pre-industrial lakewater pH that included an organic acid representation

1 (Driscoll et al., 1994) showed considerably closer agreement with diatom inferences (Figure
2 AX4.1-4). The mean difference between MAGIC and diatom estimates of pre-industrial pH was
3 reduced from 0.6 pH units to 0.2 pH units when organic acids were included in the model, and
4 the agreement for individual lakes improved by up to a full pH unit (Sullivan et al., 1996a).

5 Rosenqvist (1978) and Krug et al. (1985) hypothesized that a significant component of
6 the mobile acid anions contributed from atmospheric deposition (e.g., SO_4^{2-} , NO_3^-) replace
7 organic anions that were previously present in solution. Under this anion substitution
8 hypothesis, the net result of acidic deposition is not so much an increase in cations (including
9 potentially toxic H^+ and Al^{n+}) as much as an exchange of SO_4^{2-} and NO_3^- anions for organic
10 anions, with little or no change in ANC and pH. This hypothesis has received some support
11 from paleolimnological studies, which suggested historic decreases in DOC concentrations
12 during the period of lakewater acidification in the 1900s (Davis et al., 1985a,b; Kingston and
13 Birks, 1990; Dixit et al., 2001). Other studies have found a decrease in organic acidity which
14 was at least partly attributable to the extent of organic acid protonation. David et al. (1999)
15 measured a decrease in organic anion concentrations in stream water in response to the
16 experimental whole-watershed acidification experiment at the Bear Brook Watershed in Maine.
17 Wright et al. (1993) concluded that ANC increases in a small watershed in Norway, where rates
18 of acidic deposition were experimentally reduced, were limited by the increasing role of organic
19 acids that accompanied decreasing acid deposition load.

20 Complexation of organic acids by metals (Almer et al., 1974; Lind and Hem, 1975;
21 Dickson, 1978; Cronan and Aiken, 1985) and pH-dependent changes in dissociation of organic
22 acids (Oliver et al., 1983; Wright et al., 1988a) are probably important components of the
23 organic acidity response. Loss of DOC in response to acidic deposition can also cause a shift in
24 Al species composition towards lesser complexation with organic ligands. Such a shift from Al_o
25 to Al_i increases toxicity of the Al to aquatic biota (Baker and Schofield, 1982). Changes in pH
26 can alter the charge density of organic solutes and thus influence organic contributions to acidity
27 (e.g., Wright et al., 1988a,b). David et al. (1999) found that the charge density of organic acids
28 decreased by about 1 $\mu\text{eq/L/mg C}$ at West Bear Brook in Maine, in response to 6 years of
29 experimental acidification, probably due to greater protonation of organic acid anions at the
30 lower pH. Similar results were reported by Lydersen et al. (1996) at Lake Skjervatjern in
31 Norway. Values of the organic acid charge density in the ALSC lakes in the Adirondack

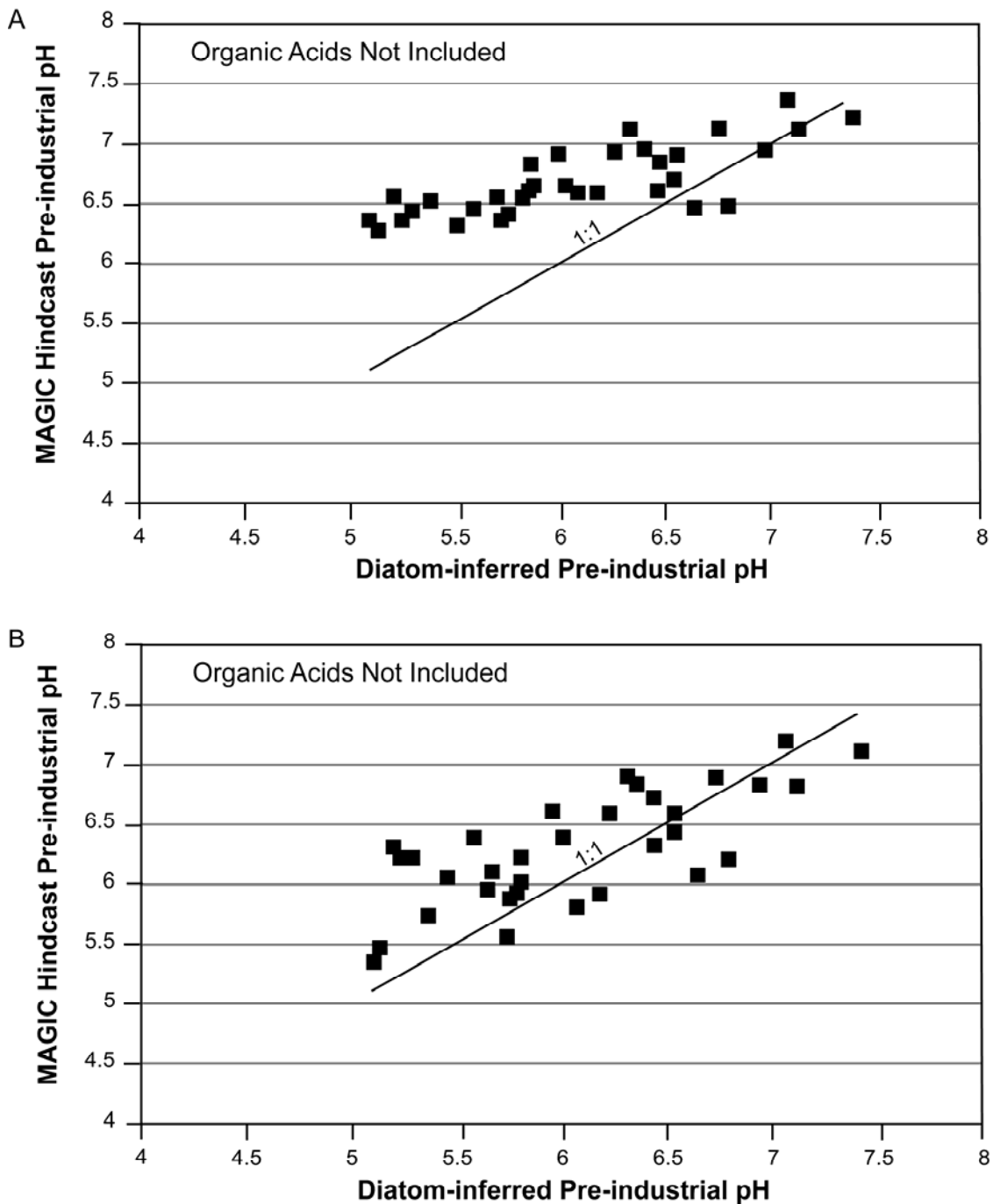


Figure AX4.1-4. MAGIC model hindcast estimates of pre-industrial pH versus diatom-inferred pH for 33 statistically selected Adirondack lakes, a) without including organic acid representation in the MAGIC simulations, and b) including a triprotic organic acid analog model in the MAGIC simulations.

Source: Sullivan et al. (1996).

1 Mountains increased with increasing pH between pH values of 5.0 to 7.0 due to the presence of
2 weakly acidic functional groups (Driscoll et al., 1994).

3 Hedin et al. (1990) artificially acidified a small, moderately high-DOC (725 $\mu\text{M C}$)
4 stream with H_2SO_4 at HBEF in New Hampshire. Streamwater pH (4.4) was near the range of
5 reported average pK_a values for organic acids, suggesting that the capacity of organic acids to
6 buffer mineral acidity should be high. The acid loading rate was adjusted to achieve an
7 increased streamwater SO_4^{2-} concentrations of 150 $\mu\text{eq/L}$ at the downstream sampling point
8 108 m below the point of acid addition. Adjustments were made for dilution by soil water or
9 inflow from small tributaries. Although streamwater DOC did not change significantly, the
10 concentration of organic anions (as calculated from the charge balance) decreased by 17 $\mu\text{eq/L}$.
11 Thus, the overall capacity of organic anions to neutralize mineral acid inputs offset about 11% of
12 the added acid (Hedin et al., 1990). This experiment only considered interactions between
13 mineral acid and organic matter within the stream. Any additional buffering that may have been
14 provided within the terrestrial catchment was not represented in the experimental design. Also,
15 any possible catchment-mediated influences of the experimental acidification on organic acid
16 properties or terrestrial DOC mobilization were excluded from the experiment because the acid
17 was not applied to the catchment soils.

18 Results of a resurvey of 485 Norwegian lakes sampled in both 1986 and 1995 provided
19 evidence in support of an increase in organic acid anion concentrations in association with
20 decreased lakewater SO_4^{2-} concentration (Skjelkvåle et al., 1998). The organic acid anion
21 concentration increased by an amount equal to between 9% and 15% of the decrease in SO_4^{2-}
22 concentration in the four regions of the country most heavily affected by the decrease in
23 S deposition during the intervening 10 year period. Lakewater SO_4^{2-} concentrations decreased
24 by 9 $\mu\text{eq/L}$ (western and northern Norway) to 20 to 21 $\mu\text{eq/L}$ (eastern and southern Norway).
25 Only in mid-Norway, where average SO_4^{2-} concentration decreased by only 6 $\mu\text{eq/L}$, did the
26 organic acid anion concentration remain unchanged between 1986 and 1995 (Skjelkvåle et al.,
27 1998).

28 Recent monitoring data have shown that DOC and organic acid anion concentrations in
29 many lakes and streams in the United States have increased in association with decreased
30 S deposition. It is likely that a high percentage of this DOC originates from wetland soils within
31 the monitored watersheds. This result appears to be partly responsible for the limited lakewater

1 ANC and pH recovery that has occurred at many locations. The response of surface waters to
2 changes in acidic deposition has included a general increase in surface water DOC (Figure
3 AX4.1-5). All regions of the eastern United States analyzed by Stoddard et al. (2003) that had
4 sufficient DOC data for analysis exhibited increases in DOC concentrations during the 1990s.
5 All regional trends were significant with the exception of the Northern Appalachian Plateau,
6 the region with the lowest median DOC concentration. The median increase in DOC of
7 0.05 mg/L/yr reported by Stoddard et al. (2003) corresponds to an overall increase of about
8 10% across study regions, similar to trends reported elsewhere in the northern hemisphere
9 (Evans and Monteith, 2001; Skjelkvåle et al., 2001). This suggests a common cause. Both
10 climate warming and decreasing acidic deposition are possible causal agents.

11

12 **AX4.1.5 Interactions with Surface Water**

13 Surface water chemistry is an indicator of adverse effect of acidification on biotic
14 integrity of fresh water ecosystems. Because surface water chemistry integrates the sum of
15 processes that occur upstream within a watershed, it also reflects the results of watershed-scale
16 terrestrial effects, such as N saturation, forest decline, or soil acidification (Stoddard et al., 2003).
17 Thus, water chemistry provides an index of soil properties and processes.

18 The scientific community has continued to make significant progress since 1982 in
19 refining understanding of surface water acidification processes and quantifying dose-response
20 relationships. In particular, knowledge has been gained regarding the role of natural organic
21 acidity, the depletion of base cation reserves from soils, and interactions between S deposition
22 and land use.

23 There are numerous sensitive chemical receptors that can be used to assess effects of
24 acidic deposition on lake or stream acid-base chemistry. These include surface water pH and
25 concentrations of SO_4^{2-} , NO_3^- , Al^{n+} , Ca^{2+} , sum of base cations, ANC, and the recently developed
26 base cation surplus. All of these are of interest, and each can provide useful information
27 regarding both sensitivity to surface water acidification and the level of acidification that has
28 occurred. Acidification effects on aquatic biota are most commonly evaluated using either Al or
29 pH as the primary chemical indicator. ANC is also used because it integrates overall acid status
30 and surface water acidification models do a better job projecting ANC than pH and Al;
31 concentrations, although ANC does not relate directly to the health of biota. The utility of the

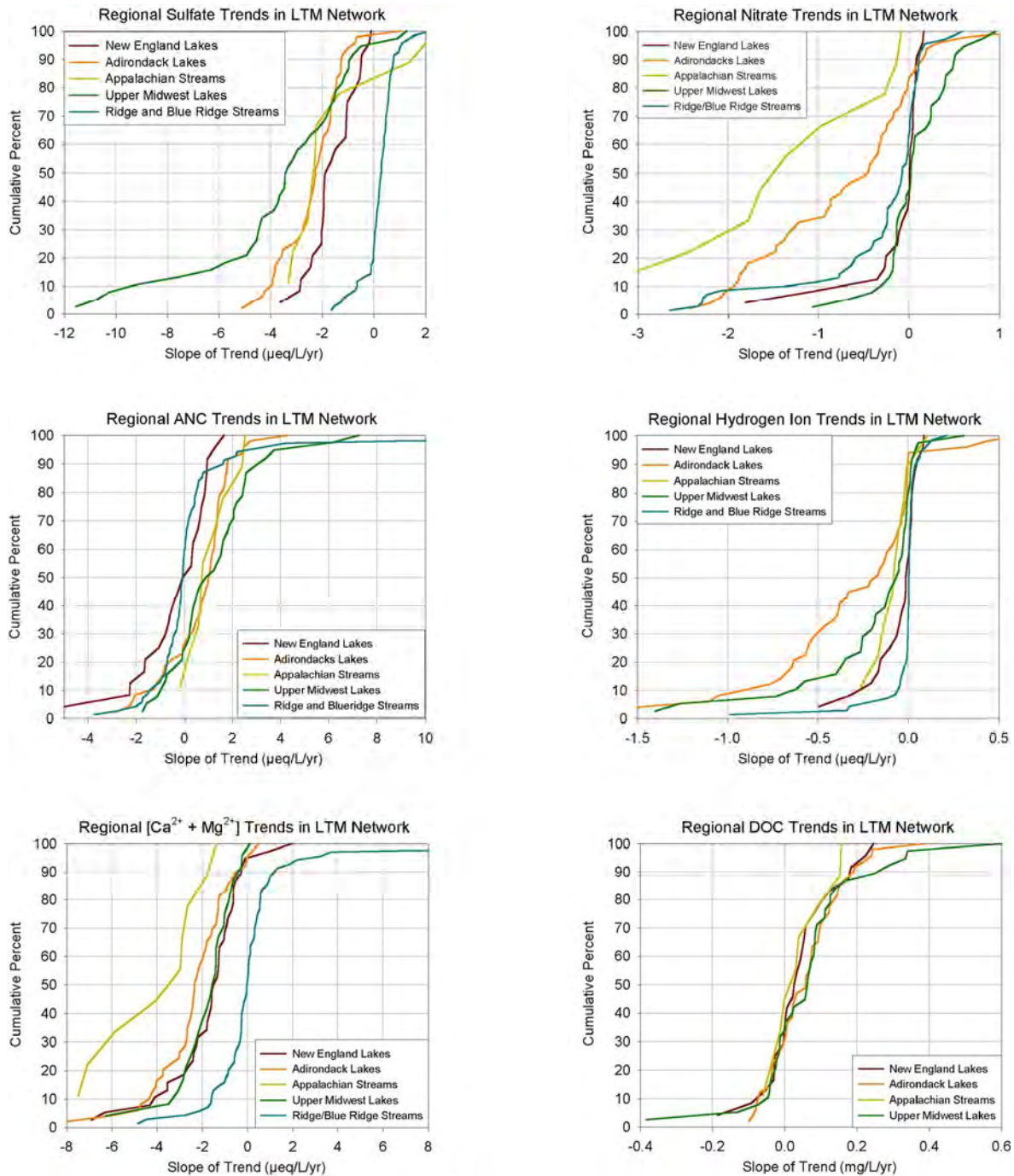


Figure AX4.1-5. Cumulative frequency diagram (distribution) of slopes for SO_4^{2-} , NO_3^- , Gran ANC, hydrogen ion, $[\text{Ca}^{2+} + \text{Mg}^{2+}]$, and DOC concentrations in LTM surface water monitoring sites, by region, for the period 1990-2000. The Ridge/Blue Ridge Province did not have sufficient DOC data to allow trend analysis.

Source: Stoddard et al. (2003).

1 ANC criterion lies in the association between ANC and the surface water constituents that
2 directly contribute to or ameliorate acidity-related stress, in particular pH, Ca²⁺, and Al_i.

3 The most widely used water chemistry indicator for both atmospheric deposition
4 sensitivity and effects over the past two decades is ANC. It can be determined by Gran titration
5 or as the difference between the measured base cation and mineral acid anion concentrations:

$$6 \quad \text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K} + \text{Na} + \text{NH}_4) - (\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-)$$

7 Field studies often rely upon the Gran titration approach. Process-based models, such as
8 MAGIC, PnET-BGC, and the Nutrient Cycling Model (NuCM) utilize the ANC calculated from
9 the charge balance. For monitoring and assessment purposes, it is always best to determine both
10 titrated and calculated ANC values. The difference between the two can yield important
11 information about data quality and reveal the influences of natural organic acidity and/or
12 dissolved Al on the overall acid-base chemistry of the water. Furthermore, measurement of full
13 ion chemistry is needed to provide sufficient information regarding:

- 14 1. the contribution of the various acidic anions (SO₄²⁻, NO₃⁻, Cl⁻) to existing
15 acidity;
- 16 2. the likelihood of confounding effects other than acidic deposition, such as road
17 salt contamination, acid mine drainage, natural organic acidity, or agricultural
18 inputs of nutrients;
- 19 3. the quality of the database; and
- 20 4. possible base cation depletion of watershed soils.

21 Surface water pH is a common alternative to ANC as an indicator of acidification.
22 However, at pH values above about 6.0, pH is not a good indicator of either sensitivity to
23 acidification or level of effect. In addition, pH measurements (especially at these higher values)
24 are sensitive to levels of dissolved carbon dioxide (CO₂) in the water. In contrast, ANC is more
25 stable and it reflects sensitivity and effect in a linear fashion across the full range of ANC values.
26 Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated
27 and calculated ANC values are commonly determined in field studies aimed at resource
28 characterization or long-term monitoring.

29 Variations in surface water chemistry can occur seasonally and episodically (hours to
30 days) as flow and biogeochemical processes within a watershed vary over time (Wigington et al.,
31 1996). These types of variations complicate the assessment of acidic deposition effects if

1 samples are collected under different flow conditions or seasons. To reduce the effects of
2 temporal variation, assessments of surface water chemistry have generally been done under non-
3 storm conditions or base flow, often in the summer, when conditions tend to be least acidic and
4 least temporally variable. Streams or lakes deemed acidic under these conditions are labeled as
5 being chronically acidic. Streams and lakes that are not acidic during base flow, but become
6 acidic during high flows are labeled episodically acidic.

7 Measurements of SO_4^{2-} concentrations in surface waters provide important information
8 on the extent of cation leaching in soils and how SO_4^{2-} concentrations relate to ambient levels of
9 atmospheric S deposition. However, the SO_4^{2-} from atmospheric deposition is not high enough
10 to degrade water quality. Assessments of acidic deposition effects dating from the 1980s to the
11 present have shown SO_4^{2-} to be the primary anion in most acid-sensitive waters (Driscoll and
12 Newton, 1985; Driscoll et al., 1988, 2001b; Webb et al., 2004). In an analysis representative of
13 over 10,000 acid-sensitive lakes in the Northeast, inorganic anions represented the majority of
14 negative charge in 83% of the lakes, and in this group of lakes, 82% of the total negative charge
15 was due to SO_4^{2-} (Driscoll et al., 2001b). In contrast, naturally derived organic anions
16 represented an average of 71% of total negative charge in the 17% of lakes in which organic
17 anions predominated (Driscoll et al., 2001b).

18 Nitrate has the same potential as SO_4^{2-} to acidify drainage waters and leach potentially
19 toxic Al from watershed soils. In most watersheds, however, N is limiting for plant growth, and
20 therefore most N inputs are quickly incorporated into biomass as organic N with little leaching of
21 NO_3^- into surface waters. A large amount of research was conducted in the 1980s and 1990s on
22 N-processing mechanisms and consequent forest effects, mainly in Europe (Sullivan, 1993). In
23 addition, concern has been expressed regarding the role of NO_3^- in acidification of surface
24 waters, particularly during hydrologic episodes. Prior to the mid-1980s, atmospheric deposition
25 effects research in the United States focused almost exclusively on S. Within the 1980 to 1990
26 NAPAP research program, relatively little attention was paid to N research.

27 Release of NO_3^- to surface waters may also affect nutrient relationships and biological
28 neutralization processes in aquatic ecosystems to a greater extent than SO_4^{2-} (Kelly et al., 1987;
29 Bukaveckas and Shaw, 1998; Momen et al., 2006). Concentrations on NO_3^- tend to vary more
30 with flow and season than SO_4^{2-} (Driscoll et al., 2003b), but generally do not reach those of
31 SO_4^{2-} on an equivalent basis in most areas during most flow conditions. Seasonality in NO_3^-

1 concentration in surface waters is generally explained by high watershed N retention due to plant
2 uptake during the growing season, and low retention during the non-growing season, when
3 biological demand is low and soil-water flux is elevated due to reduced water loss from plants by
4 transpiration (Stoddard, 1994).

5 Base cations in surface waters refer to Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . Of these four, Ca^{2+}
6 usually occurs in highest concentration. Leaching of base cations from soils into surface waters
7 is an indication of acid neutralization of soil waters and may reflect acidification of soils.
8 Concentrations of base cations relative to acid anions (SO_4^{2-} and NO_3^-) the surface waters
9 indicate the neutralizing capacity of the terrestrial system. Initial stages of acid input are
10 therefore expected to increase concentrations of base cations, a response shown by short-term
11 manipulations (Lawrence et al., 1987; Fernandez et al., 2003). Concentrations of base cations
12 are expected to decrease if continued inputs of acid deplete the terrestrial pool of available base
13 cations.

14 In assessing changes in surface water ANC, it is important to distinguish between *acidic*
15 waters and acidified waters. *Acidic* describes a condition that can be measured (i.e., Gran
16 $\text{ANC} \leq 0$). It may be due either to the effects of acidic deposition, or to other causes such as the
17 presence of organic acidity or the weathering of S-containing minerals in the watershed.
18 *Acidified* refers to the *process* of acidification (an increase in acidity observed through time). It
19 does not require that the water body be acidic, and does imply a particular cause for the change
20 in chemistry. The term *anthropogenically acidified* implies that human activity was responsible
21 for the increase in acidity that occurred.

22 Surface water ANC reflects the culmination effects of all of the ionic interactions that
23 occur as atmospheric deposition and precipitation move from the atmosphere, into the soil and
24 drainage water, to emerge in a stream or lake. ANC reflects the relative balance between base
25 cations and strong acid anions. If the sum of the equivalent concentrations of the base cations
26 exceed those of the strong acid anions, then the water will have positive ANC. To the extent that
27 the base cation sum exceeds the strong acid anion sum, the ANC will be higher. Higher ANC is
28 generally associated with higher pH and Ca^{2+} concentrations; lower ANC is generally associated
29 with higher H^+ and Al^{3+} concentrations and a greater likelihood of toxicity to biota. In response
30 to more than a century of acidic deposition, lakes and streams across broad sections of the
31 eastern United States experienced decreases in ANC to varying degrees.

1 AX4.2 FACTORS THAT DETERMINE ECOSYSTEM SENSITIVITY

3 AX4.2.1 Terrestrial Ecosystems

5 AX4.2.1.1 Forests

6 There are two primary factors that determine the sensitivity of forest ecosystems to
7 adverse acidification-related effects of acidic deposition. The most important factor is the size of
8 the soil pool of base cations available to neutralize acidic atmospheric inputs. The second
9 important factor is the distribution of plant species on the site. Each is discussed below.

10 The effects of acidification on plants are primarily mediated through the soil, and are
11 governed by Al toxicity and nutrient base cation (Ca^{2+} , Mg^{2+} , K^+) deficiencies. These two
12 factors are closely related. Aluminum is toxic to tree roots, although much higher concentrations
13 of Al in soil solution are required to elicit a toxic response as compared with the toxicity of Al to
14 fish in a stream. Plants affected by high Al concentrations in soil solution often have reduced
15 root growth, which restricts the ability of the plant to take up water and nutrients, especially Ca^{2+}
16 (Parker et al., 1989). Calcium is well known as an ameliorant for Al toxicity to roots in soil
17 solution, as well as to fish in a stream. Magnesium, and to a lesser extent Na^+ and K^+ , have also
18 been associated with reduced Al toxicity.

19 Base cations, including Ca^{2+} , Mg^{2+} , and K^+ , are taken up through plant roots in dissolved
20 form. A large fraction of the base cation stores in rocks and soils are bound in mineral structures
21 and are unavailable to plants. The available base cations in the soil are adsorbed to negatively
22 charged soil exchange sites. These exchangeable cations can become desorbed in exchange for
23 H^+ or Al^{3+} .

24 The process of weathering gradually breaks down rocks and minerals, returning their
25 stored base cations to the soil in dissolved form and thereby contributing to the pool of adsorbed
26 base cations. Base cation reserves are gradually leached from the soils in drainage water, but are
27 constantly being resupplied through weathering and atmospheric base cation deposition. It is
28 well known, however, that elevated leaching of base cations by acidic deposition might deplete
29 the soil of exchangeable bases faster than they are resupplied via weathering and base cation
30 deposition (Cowling and Dochinger, 1980).

31 Likens et al. (1996) concluded that acidic deposition enhanced the release of base cations
32 from forest soils at the HBEF from the mid-1950s until the early 1970s. As the labile pool of

1 base cations in soil became depleted, the concentrations in streamwater decreased by about one-
2 third from 1970 through 1994. The marked decrease in base cation inputs and concomitant
3 increase in net soil release of base cations in streamwater at HBEF have probably depleted soil
4 pools to the point where ecosystem recovery from decreased S deposition will be seriously
5 delayed. Moreover, Likens et al. (1996) suggested that recently observed declines in forest
6 biomass accumulation at HBEF might be attributable to Ca^{2+} limitation or Al toxicity, which can
7 be expressed by the Ca:Al ratio in soil solution (Cronan and Grigal, 1995).

8 A variety of factors predispose soils of high-elevation spruce-fir forests to potential Al
9 toxicity and Al-induced inhibition of cation uptake. These factors include features of the climate
10 (high precipitation, low temperature), vegetation (coniferous litter), bedrock (low base cation
11 production), and soil forming processes such as podzolization (Eagar et al., 1996). Because base
12 saturation in spruce-fir forests in the eastern United States tends to be very low, continued input
13 of NO_3^- and SO_4^{2-} from atmospheric deposition might further acidify the soils and contribute to
14 further Al mobilization from soils to soil solution (Johnson and Fernandez, 1992). Increased
15 mineral acid anion concentrations (NO_3^- , SO_4^{2-}) in soil solution will cause the mobilization of
16 Al ions from the exchange sites of acid soils. Although base cations normally dominate
17 exchange sites in the soil compared to Al, base cation reserves are so low in acidic soils that Al
18 exchange dominates. Dissolved Al concentrations in soil solution at spruce-fir study sites
19 frequently exceed 50 μM and sometimes exceed 100 μM (Johnson et al., 1991b; Joslin and
20 Wolfe, 1992; Eagar et al., 1996). All studies reviewed by Eagar et al. (1996) showed a strong
21 correlation between Al concentrations and NO_3^- concentrations in soil solution. They speculated
22 that the occurrence of periodic large pulses of NO_3^- in solution were important in determining Al
23 chemistry.

24 25 **AX4.2.1.2 Grasslands and Alpine Tundra**

26 Grasslands, and especially areas of alpine tundra vegetation, are thought to be particularly
27 sensitive to adverse effects of atmospheric N deposition, but this is believed to be associated with
28 nutrient enrichment, rather than acidification, processes. See discussion in AX5.3.1.2 and
29 AX5.3.1.3. It is possible that these plant communities may also be sensitive to acidification
30 effects, such as base cation deficiency and/or Al toxicity. However, data are not available with
31 which to determine the extent of such sensitivities or possible effects.

1 **AX4.2.1.3 Arid Lands**

2 Arid lands often contain plant species that are adapted to low nutrient levels. As such,
3 they can be sensitive to nutrient enrichment from atmospheric N deposition. It is not known
4 whether arid land plant communities are also sensitive to acidification effects. However, arid
5 lands are often located at relatively low elevation in areas having base-rich soils. As such, these
6 plant communities would not be expected to be adversely affected by atmospheric acid
7 contributions.

8 Arid lands by definition receive very low levels of precipitation. Therefore, the amount
9 of wet deposition of S and N tends to be low. However, dry deposition to arid lands can be high,
10 especially in proximity to the Los Angeles Basin.

11
12 **AX4.2.2 Transitional Ecosystems**

13
14 **AX4.2.2.1 Wetlands and Peatlands**

15 Wetlands and peatlands often contain highly acidic soils. Their acidity is mainly
16 attributable to the presence of large quantities of naturally occurring organic materials. Fulvic
17 and humic acids, formed during the breakdown of organic matter, contribute substantial organic
18 acidity to soil and surface waters in wetland and peatland environments. In the case of
19 ombotrophic bogs and poor fens, there is also a scarcity of base cations, which would serve to
20 buffer both organic and mineral acidity.

21 Because wetland and peatland vegetative communities are adapted to high levels of
22 natural organic acidity, it is unlikely that S or N deposition would cause any acidification-related
23 effects at levels of acidic deposition commonly found in the United States. Nevertheless,
24 wetlands are closely tied to a number of important biogeochemical processes that regulate
25 watershed response to acidic deposition. The major interactions are described below.

26 High concentrations of DOC in brownwater lakes and streams are often due to the
27 influence of wetlands on hydrography within the watershed. This presence of high
28 concentrations (higher than about 500 μM) of DOC can substantially reduce the pH and ANC of
29 surface waters, buffer those waters against pH changes in response to added mineral acidity, and
30 form stable complexes with dissolved Al, thereby reducing its toxicity to aquatic life. Therefore,
31 the response of surface waters to acidic deposition is strongly influenced by the extent of
32 upstream and shoreline wetland development.

1 Wetlands also serve as a (sometimes-temporary) sink for atmospheric S and N. Chemical
2 reduction reactions and biological uptake contribute to S and N storage in wetland soils.
3 Oxidation during drought periods, when water levels recede, followed by flushing from wetland
4 to downstream surface water during subsequent storm flow, can cause substantial pulses of
5 mineral acidity in downstream receiving waters. On a chronic basis, the concentration of SO_4^{2-}
6 (and associated acidity) in surface water can be substantially lower as a consequence of
7 dissimulatory S reduction in upslope wetlands. On an episodic basis, wetlands can contribute to
8 wide fluctuations in downstream surface water acid-base chemistry. Such fluctuations can
9 include pulses of acidity that may be toxic to aquatic biota.

10 Wetlands provide anaerobic substrate for S-reducing bacteria. These bacteria are also
11 partly responsible for the increased rate of mercury (Hg) methylation that is known to occur in
12 wetlands. As a consequence, fish in lakes drained by wetlands often have much higher
13 concentrations of tissue methyl Hg, as compared with fish in lakes that lack watershed wetlands
14 (Driscoll et al., 2007).

15 16 **AX4.2.2.2 Ponds**

17 The factors that determine the sensitivity of ponds to acidification from acidic deposition
18 are generally similar to those that determine the sensitivity of lakes (discussed in the following
19 section). In general, however, ponds and small lakes tend to exhibit low ANC and pH at a
20 greater frequency than do larger lakes (Sullivan et al., 1990). This pattern is mainly a
21 consequence of the higher concentrations of DOC frequently found in ponds as compared with
22 larger lakes. In addition, because larger bodies of water tend to have larger watersheds, there is a
23 greater likelihood that they will integrate conditions across a broader landscape, increasing the
24 possibility of receiving at least a moderate level of base cation supply (Sullivan et al., 1990).
25 Thus, where lakes are acid-sensitive, it is likely that ponds are also acid-sensitive. However,
26 synoptic databases of pond acid-base chemistry are generally not available.

27 28 **AX4.2.3 Streams and Lakes**

29 A number of factors govern the sensitivity of aquatic ecosystems to acidification from
30 S and N deposition. The most important variable is geology. The geologic composition of a
31 region plays a dominant role in influencing the chemistry and therefore sensitivity of surface
32 waters to the effects of acidic deposition. Bedrock geology formed the basis for a national map

1 of surface water sensitivity (Norton et al., 1982) and has been used in numerous acidification
2 studies of more limited extent (e.g., Bricker and Rice, 1989; Stauffer, 1990; Stauffer and
3 Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007). Most of the major
4 concentrations of low ANC surface waters are located in areas underlain by bedrock resistant to
5 weathering.

6 Other factors also contribute to the sensitivity of surface waters to acidic deposition,
7 including soil chemistry, land use, and hydrologic flowpath. Land use influences watershed
8 sensitivity to acidification mainly through land disturbance and consequent exposure of
9 S-bearing minerals to oxidation, loss of base cations through erosion and timber harvesting, and
10 change in N status of the forest through timber management. Each of these types of activity can
11 influence the relative availability of mobile mineral acid anions (SO_4^{2-} , NO_3^-) in soil solution
12 and base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) on the soil ion exchange sites and in drainage water. The
13 balance between mineral acid anions and base cations, in turn, affects the ANC and pH of soil
14 water and surface waters.

15 The effects of acidic deposition on lakes and streams are strongly controlled by the
16 flowpath of water through the terrestrial watershed. Hydrology is an important controlling factor
17 for deposition effects in all settings (Turner et al., 1991), but hydrology is of particular
18 importance in alpine and subalpine ecosystems. The depth and chemical composition of soils,
19 talus, and colluvium and the slope of the watershed collectively determine the residence time of
20 subsurface water within the watershed, extent to which snowmelt and rainfall runoff interact with
21 soils and geologic materials, and consequently the extent of NO_3^- leaching, base cation
22 mobilization, and acid neutralization within the watershed (Sullivan, 2000).

23 The movement of water through the soils into a lake or stream, and the interchange
24 between drainage water and the soils and sediments, strongly regulate the type and degree of
25 watershed response to acidic inputs (Sullivan, 2000). Surface waters in the same setting can
26 have different sensitivities to acidification depending on the relative contributions of near-
27 surface drainage water and deeper groundwater (Eilers et al., 1983; Chen et al., 1984; Driscoll
28 et al., 1991). Acidic deposition that falls as precipitation directly on the lake surface may
29 eventually be neutralized by in-lake reduction processes which are controlled in part by
30 hydraulic residence time (Baker and Brezonik, 1988). Natural hydrologic events also alter

1 acidification and neutralization processes during snowmelt and change flowpaths during
2 extended droughts (Webster et al., 1990).

3 Watershed processes control the extent of ANC contribution from soils to drainage
4 waters as acidified water moves through undisturbed terrestrial systems. These processes
5 regulate the extent to which drainage waters will be acidified in response to acidic deposition.
6 Of particular importance is the concentration of acid anions in solution, including SO_4^{2-} , NO_3^- ,
7 and organic acid anions. Naturally occurring organic acid anions, produced in upper soil
8 horizons, normally precipitate out of solution as drainage water percolates into the deeper
9 mineral soil horizons. Soil acidification processes reach an equilibrium with acid neutralization
10 processes at some depth in the mineral soil (Turner et al., 1991). Drainage waters below this
11 depth generally have high ANC. Acidic atmospheric deposition allows the natural soil
12 acidification and cation leaching processes to occur at greater depths in the soil profile, allowing
13 water that is rich in SO_4^{2-} or NO_3^- to flow from mineral soil horizons into drainage waters. If
14 these anions are charge-balanced by H^+ or Al^{n+} cations, the water will have low pH and could be
15 toxic to aquatic biota. If they are charge-balanced by base cations, the base cation reserves of the
16 soil can become depleted, but the surface water will not be acidified.

17 Leaching of base cations by acidic deposition can deplete the soil of exchangeable bases.
18 The importance of this response has recently been widely recognized because most watersheds
19 are not exhibiting much ANC and pH recovery of drainage water in response to recent large
20 decreases in S deposition. This limited recovery can be at least partially attributed to decreased
21 base cation concentrations in surface water. This understanding of the base cation response has
22 developed slowly. During the 1980s, the generally accepted paradigm of watershed response to
23 acidic deposition was analogous to a large-scale titration of ANC (Henriksen, 1984).
24 Atmospheric inputs of acidic anions were believed to result in movement of those anions through
25 soils into drainage waters with near proportional loss of surface water ANC. This view was
26 modified by Henriksen (1984), who suggested that a modest component of the added SO_4^{2-} (up
27 to a maximum of about 40%) could be charge-balanced by increased mobilization of base cations
28 from soils, and the remaining 60% to 100% of the added SO_4^{2-} resulted in loss of ANC in
29 surface waters. During the latter part of the 1980s, it became increasingly clear that a larger
30 component (> 40%) of the added SO_4^{2-} was in fact neutralized by base cation release in most
31 cases and the ANC (and therefore also pH) of surface waters typically did not change as much as

1 was earlier believed. This understanding developed in large part from paleoecological studies
2 (e.g., Charles et al., 1990; Sullivan et al., 1990), which indicated that past changes in lakewater
3 pH and ANC had been small relative to estimated increases in lakewater SO_4^{2-} concentrations
4 since pre-industrial times (Sullivan, 2000). The belief that changes in acidic deposition were
5 accompanied mainly by changes in ANC and pH has been replaced by the realization that
6 changes in SO_4^{2-} were accompanied mainly by changes in base cations. Thus, surface waters
7 have not been acidified as much by historical deposition as was earlier believed. Furthermore,
8 surface water ANC and pH should not be expected to show substantial chemical recovery upon
9 reduced emissions and deposition of S and N. The magnitude of the base cation response has
10 clearly limited the extent of surface water acidification caused by acidic deposition. However,
11 this same response has contributed to base cation deficiencies in some soils, with associated
12 adverse terrestrial effects.

13

14 **AX4.2.4 Other Types of Ecosystems**

15 There has been little work on the rates of atmospheric deposition to urban ecosystems
16 despite extensive data on concentrations and chemical reactions of air pollutants in cities (U.S.
17 Environmental Protection Agency, 2004). Nevertheless, urban ecosystems are often subjected to
18 large rates of deposition of anthropogenic pollutants (Lovett et al., 2000a). Decades of research
19 on urban air quality indicate that cities are often important sources of emissions of NO_x , SO_x ,
20 and dust. Urban N deposition may affect nutrient cycles and soil acid-base chemistry in
21 vegetated areas in and around cities, but such possible effects have not been studied sufficiently
22 to draw conclusions about sensitivities or effects.

23 To determine the patterns of atmospheric deposition and throughfall in the vicinity of a
24 large city, Lovett et al. (2000a) measured bulk deposition, oak forest throughfall, and particulate
25 dust at sites along a transect within and to the north of New York City. They found that
26 throughfall N was twice as high in the urban areas compared with suburban and rural areas.
27 Most of the urban dry deposition of NO_3^- was from gaseous NO_x . Because there is limited
28 biological uptake of throughfall N in an urban setting, it is believed that a relatively high (but
29 unknown) percentage of N deposited to the urban landscape leaches to surface waters. Aquatic
30 effects associated with N leaching from urban environments would be expected to be most
31 pronounced near coastal cities. This is because atmospheric deposition to near-coastal urban

1 environments can provide a substantial N load to estuaries and near shore oceanic environments,
2 which tend to be N-limited. See further discussion in AX5.3.3.2.

3 4 5 **AX4.3 DISTRIBUTION AND EXTENT OF ECOSYSTEM EFFECTS**

6 7 **AX4.3.1 Terrestrial Ecosystems**

8 Concerns have been cited since the early 1970s about potential forest declines that could
9 result from soil acidification and nutrient deficiency brought about by acidic deposition. In
10 addition, concerns have arisen regarding the mobilization of Al in forest soils due to inputs of
11 acidic deposition, and the potential toxicity of that Al to plant roots (Cronan and Grigal, 1995).

12 Forest resources that are potentially sensitive to the adverse impacts of acidic deposition
13 are found throughout the United States, in particular at higher-elevation sites. Some tree species
14 are more susceptible to acidification effects than others. However, NAPAP (1998) concluded
15 that the best evidence for significant forest damage in the United States due to acidic deposition
16 was the observed reduced growth of red spruce in the southern Appalachian Mountains and
17 increased mortality and decline of red spruce in the Northeast.

18 Red spruce is considered to be more highly affected by acidification than other common
19 tree species in the eastern United States, partly as a consequence of its inherent sensitivity and
20 partly as a consequence of its common distribution at high elevation, where acidic deposition
21 levels tend to be relatively high. Sugar maple (*Acer saccharum*) is also considered sensitive to
22 acidification effects related to Mg²⁺ and Ca²⁺ deficiency on the Allegheny Plateau in
23 Pennsylvania (Horsley et al., 2000). Distributions of red spruce and sugar maple are shown on
24 the map in Figure AX4.3-1. Both occur mainly in the northeastern United States and in portions
25 of the Appalachian Mountains. Forest understory plant species also probably exhibit differences
26 in sensitivity to acid and Al stress. Experimental data with which to quantify sensitivities and
27 levels of effect are generally not available for forest understory plant species in the United States.

28 The acidification effects of S and N deposition in the United States differ with location.
29 Ecosystem structure can affect the amount of local deposition and corresponding soil
30 acidification. For example, Blake et al. (1999) found higher soil acidification in woodlands than
31 in grasslands, likely due to the woodland canopy's greater interception of atmospheric pollutants.

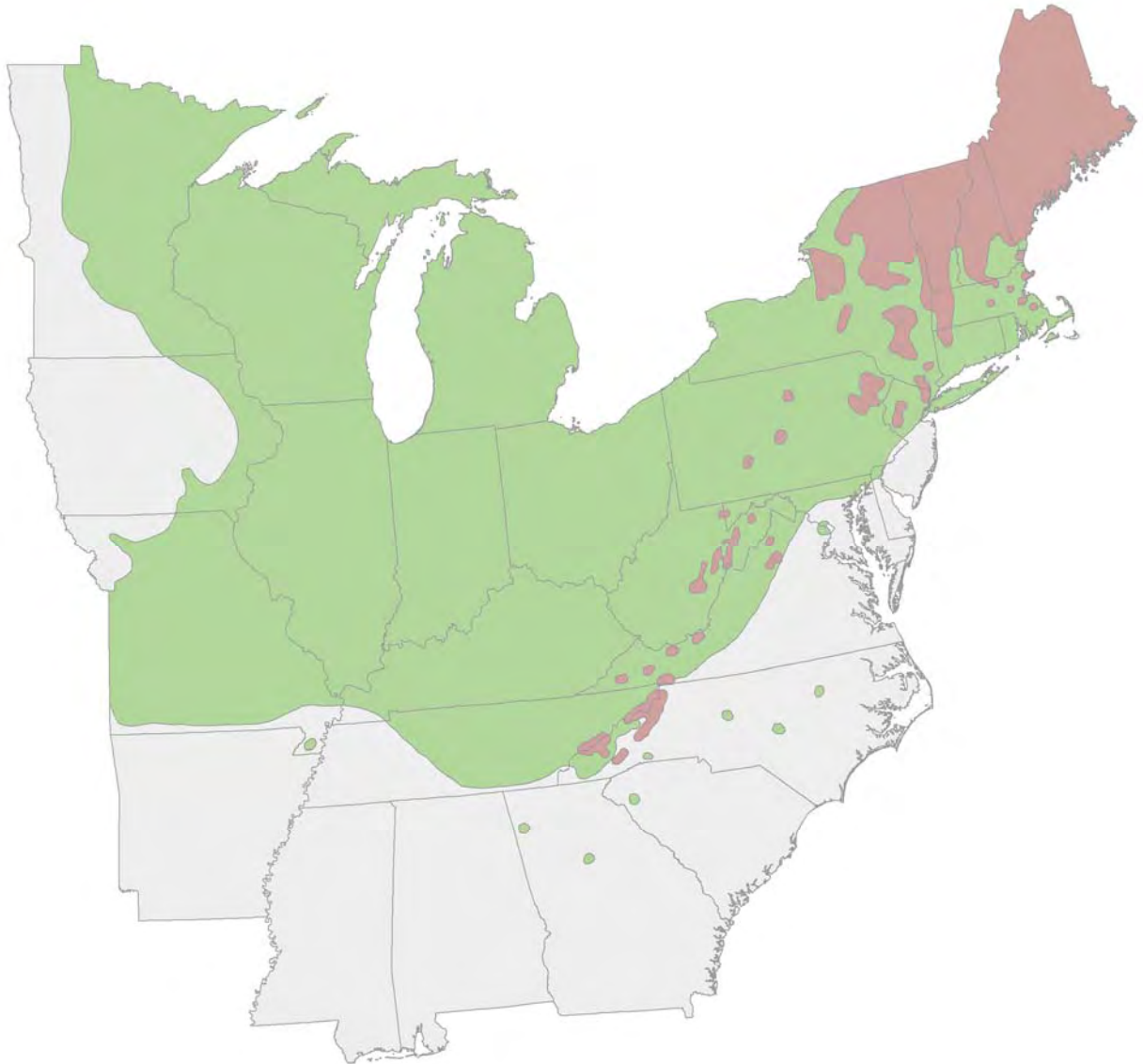


Figure AX4.3-1. Distribution of red spruce (rose) and sugar maple (green) in the eastern United States. These two tree species have experienced adverse effects in portions of their ranges that have been attributed to acidification from acidic deposition. Tree distribution data were obtained from Little's Ranges.

Source: Little (1971) (<http://esp.cr.usgs.gov/data/atlas/little/>).

- 1 In general, coniferous forests are expected to capture more dry deposition than hardwood forests,
- 2 largely because of their greater leaf area.

1 Forest soil sensitivity to acidification is largely a function of atmospheric deposition
2 level, soil age, weathering rate, and S adsorption capacity (Galloway, 1996). Coniferous forests,
3 with soils that are naturally more acidic, generally have lower pH and base saturation than soils
4 in deciduous forests (Fernandez et al., 2003). In a paired watershed study at Bear Brook
5 Watershed in Maine, one watershed with mixed coniferous and deciduous species received
6 $(\text{NH}_4)_2\text{SO}_4$ corresponding to about 25 kg N/ha/yr and 29 kg S/ha/yr. After a decade of
7 experimental acidification, the treated watershed had 66 kg/ha/yr less exchangeable Ca^{2+} and
8 27 kg/ha/yr less exchangeable Mg^{2+} than the untreated watershed (Fernandez et al., 2003). Soils
9 under conifers (red spruce, balsam fir [*Abies balsamea*], hemlock [*Tsuga canadensis*]) appeared
10 to be more sensitive to acidification than those under hardwoods (American beech [*Fagus*
11 *grandifolia*], yellow birch [*Betula alleghaniensis*], sugar, and red maples [*Acer rubrum*]). The
12 hardwoods demonstrated no significant effects from $(\text{NH}_4)_2\text{SO}_4$ addition. Differences in
13 response to acid treatment among vegetation covers were most pronounced in upper soil (O
14 horizon and upper 5 cm of the B horizon). The study did not distinguish between effects from
15 NH_4^+ versus SO_4^{2-} additions.

16 After 11 years of field application of 50 kg N/ha/yr at the Harvard Forest Long-Term
17 Ecological Research (LTER) site, S deposition of 74 kg S/ha/yr had no appreciable additive
18 effect on forest processes over N additions alone, and was subsequently discontinued (Magill
19 et al., 2004). Hardwood species (black and red oaks [*Quercus velutina* and *Q. rubra*], red maple,
20 American beech, and black cherry [*Prunus serotina*]) were generally less sensitive to excess
21 N input than red pine). Red maple suffered 72% mortality, possibly due to excess N combined
22 with drought.

23 Kozlowski (1985) suggested that plants and soils act as sinks for SO_2 deposition at low
24 exposures of 1 to 4 $\mu\text{g}/\text{m}^3$, with no discernible effects on ecosystem structure at those levels.
25 Shugart and McLaughlin (1985) cautioned that forest responses to SO_2 and other stressors are
26 strongly controlled by the successional dynamics of impacted forests. Thus, efforts to better
27 understand and quantify forest dynamics and development will be paramount to predicting
28 chronic pollution effects.

29 Moncoulon et al. (2004) suggested that forest ecosystem sensitivity to acidification varies
30 with weathering rate. In a review of 241 ecosystem types in France (classified by pedologic and

1 geologic characteristics), the ecosystems most susceptible to acidification were those with low
2 weathering rates and thus limited buffering capacity (Moncoulon et al., 2004).

3 Nitrogen is an essential nutrient for both aquatic and terrestrial organisms, and is a
4 growth-limiting nutrient in most terrestrial temperate zone ecosystems. Thus, N inputs to natural
5 systems are not necessarily harmful. For each ecosystem, there is an optimum N level which
6 will maximize ecosystem productivity without causing significant changes in species distribution
7 or abundance. Above the optimum level, harmful effects (including soil and water acidification)
8 can occur in both aquatic and terrestrial ecosystems (Aber et al., 1998).

9 The N cycle is extremely complex and controlled by many factors besides atmospheric
10 emissions and deposition (Aber et al., 1991, 1998). Also, N inputs that may be beneficial to
11 some species or ecosystems may be harmful to others (Virtuosic et al., 1997). Increased
12 atmospheric deposition of N does not necessarily cause adverse environmental impacts. In most
13 areas, added N is taken up by terrestrial biota and the most visible effects seem to be an increase
14 in primary productivity (Kauppi et al., 1992) and changes in competitive interactions among
15 species (see discussion in AX5.4.1). However, under certain circumstances, atmospherically
16 deposited N can exceed the capacity of vegetation communities to take up N. In some areas,
17 especially at high elevation, terrestrial ecosystems have become N-saturated and high levels of
18 deposition have caused elevated levels of NO_3^- in drainage waters (Aber et al., 1989, 1991;
19 Stoddard, 1994). This enhanced leaching of NO_3^- causes depletion of Ca^{2+} and other base
20 cations from forest soils and can cause acidification of soils and drainage waters in areas of base-
21 poor soils. From a review of studies throughout the northeast, Aber et al. (2003) suggested that
22 for conifer and deciduous forests, deposition above about 9 to 13 kg N/ha/yr is required to cause
23 substantial NO_3^- leaching. Leaching is generally negligible below those deposition levels.

24 Results of N fertilization studies have been used to infer the response of forests to
25 atmospheric N deposition. Such studies were reviewed by Johnson (1991) and EPA (1993),
26 illustrating that forests can respond differently to periodic large pulsed fertilizer inputs, as
27 compared with steady, low-level inputs from atmospheric deposition. For example, multiple or
28 continuous inputs of N may stimulate populations of nitrifying bacteria (U.S. Environmental
29 Protection Agency, 1993). This might be expected to modify the competitive interactions
30 between trees and microbes and affect both the forest growth response and the extent of NO_3^-
31 leaching and associated acidification.

1 **AX4.3.1.1 Coniferous Forest**

2 Spruce-fir forests are generally found at relatively high elevation, for example above
3 about 1400 m in the southern Appalachian Mountains (SAMAB, 1996). High-elevation areas
4 are often dominated by relatively unreactive bedrock, and base cation production via weathering
5 is limited (Elwood et al., 1991). Soils in such areas tend to have thick organic horizons, high
6 organic matter content in the mineral horizons, and low pH (Joslin et al., 1992). Because of the
7 largely unreactive bedrock, base-poor litter, and organic acid anions produced by the conifers,
8 high precipitation, and high leaching rates, soil base saturation in these high-elevation coniferous
9 forests often tends to be below about 10% and the soil cation exchange complex is generally
10 dominated by Al (Johnson and Fernandez, 1992).

11 Coniferous ecosystems are generally considered more susceptible to adverse impacts of
12 acidification than deciduous ecosystems, but the response varies among individual tree species.
13 Within species, other factors such as land use and topography can influence the response of a
14 particular stand to acidification from acidic deposition (Aber et al., 1998; Webster et al., 2004).

15 The terrestrial ecosystem type that has most clearly been affected by the acidifying
16 effects of S and N deposition is the red spruce or spruce-fir forest. Red spruce is common in
17 three geographic regions: high elevation in the Southeast (mainly in Tennessee and North
18 Carolina), high elevation in the Northeast (New York, New Hampshire, Vermont, and Maine),
19 and low elevation in New York and New England (Joslin et al., 1992). At low elevation in the
20 Northeast, red spruce often occurs as pure stands or in association with hardwoods or black
21 spruce (*Picea mariana* [Mill]) mixes. At high elevation, red spruce more typically occurs in
22 association with Fraser fir (*Abies fraseri* (Pursh) Poir) in the Southeast, or balsam fir in the
23 Northeast.

24 In the southern Appalachian Mountains, acidification sensitivity has been evaluated for
25 two common tree species: red spruce (sensitive) and loblolly pine (*Pinus taeda*; insensitive).
26 Dendro-chronological analyses of tree cores collected for permanent plots in the Great Smoky
27 Mountains National Park (37 trees cores from low elevation [~1500 m]; 35 tree cores from high
28 elevation sites [~2000 m]), demonstrated a positive correlation between temporal and spatial
29 trends in red spruce growth and acidic deposition, with a greater response in trees on ridges than
30 in draws. Ridges are naturally more acidified, receive higher levels of acidic deposition, and
31 have shallower soils with lower base saturation (Webster et al., 2004). From the 1940s to 1970s,

1 red spruce growth declined in the southeastern United States, as United States emissions of both
2 NO_x and SO₂ increased to maxima of about 25 and 30 × 10⁶ tons/yr. The growth decline started
3 earlier at higher elevations (around 1940s and 1950s) and was steeper, while the growth decline
4 developed 20 years later at lower elevation sites. After the 1980s, growth increased substantially
5 at both the higher and lower elevations sites, corresponding to a decrease in SO₂ emissions in the
6 United States (~20 × 10⁶ tons/yr by 2000), while NO_x emissions held fairly steady (~25 × 10⁶
7 tons/yr). At high elevation, annual emissions of SO_x + NO_x explained about 43% of the
8 variability in tree ring growth between 1940 and 1998, while climatic variability accounted for
9 about 8% of the growth variation for that period. At low elevation, changes in radial growth
10 could be explained by climatic variables only, and there was no correlation with national SO_x
11 and NO_x emissions trends. Recent reductions in SO_x emissions may have changed growth
12 trajectories (Webster et al., 2004).

13 Loblolly pine seems to have low susceptibility to adverse impacts from acidic deposition.
14 A simulated acid addition experiment showed no significant effect of acidification on foliar
15 nutrition in loblolly pine seedlings, at application levels of 21 to 26 kg/ha SO₄-S and 8 to
16 10 kg/ha NO₃-N (Baker et al., 1994). Loblolly pines grown on old agricultural fields showed
17 signs of N deficiency over 25 years of growth despite atmospheric deposition of 5 to 10 kg
18 N/ha/yr (Richter et al., 2000).

19 In the northeastern United States, two species of coniferous tree (red spruce and red pine)
20 have been shown to be sensitive to acidification. Aber et al. (2003) reported a decrease in C:N
21 ratio from about 35 to about 25 along an increasing N deposition gradient of 3 to 12 kg N/ha/yr
22 across the Northeast. At the Harvard Forest LTER site, at chronic experimental N addition
23 levels of 50 and 150 kg N/ha/yr, Magill et al. (2004) found 31% and 54% decreases,
24 respectively, in red pine growth after 15 years of chronic N application. No additive effect of S
25 was seen after 11 years of a combined N and S treatment, with an application of 74 kg S/ha/yr
26 and 50 kg N/ha/yr. There were no significant differences in baseline measurements between the
27 low N and combined N and S treatments.

28 Red spruce is common at high elevations in mountainous regions throughout the
29 Northeast. Spruce dieback has been observed and has been most severe at high elevations in the
30 Adirondack and Green Mountains, where more than 50% of the canopy trees died during the
31 1970s and 1980s. In the White Mountains, about 25% of the canopy spruce died during that

1 same period (Craig and Friedland, 1991). Dieback of red spruce trees was also observed in
2 mixed hardwood-conifer stands at relatively low elevations in the western Adirondack
3 Mountains, an area that receives high inputs of acidic deposition (Shortle et al., 1997). Results
4 of controlled exposure studies showed that acidic mist or cloud water reduced the cold tolerance
5 of current-year red spruce needles by 3 to 10 °C (DeHayes et al., 1999), and this response may
6 be at least partially responsible for the observed dieback.

7 Acidic deposition has been implicated as a causal factor for the decline of red spruce at
8 high elevation in the northeastern United States (DeHayes et al., 1999). The frequency of
9 freezing injury of red spruce has increased over the past 40 years, a period that coincided with
10 increased emissions of S and N oxides and increased acidic deposition (DeHayes et al., 1999).
11 There is a significant positive association between cold tolerance and foliar Ca^{2+} in trees that
12 exhibit deficiency in foliar Ca^{2+} . The membrane-associated pool of Ca^{2+} , although a relatively
13 small fraction of the total foliar Ca^{2+} pool, strongly influences the response of cells to changing
14 environmental conditions. The plant plasma membrane plays an important role in mediating
15 cold acclimation and low-temperature injury (U.S. Environmental protection Agency, 2004).
16 The studies of DeHayes et al. (1999) suggested that the direct deposition of acidic deposition on
17 red spruce needles preferentially removes membrane-associated Ca^{2+} . However, more recently a
18 strong link has been established between availability of soil Ca^{2+} and winter injury (Hawley
19 et al., 2006).

20 Results of the NuCM modeling exercises conducted by Sullivan et al. (2002), together
21 with the results of NuCM simulations published for other watersheds in the southern
22 Appalachian Mountain region, suggest that spruce-fir forests in the region are likely to
23 experience decreased Ca:Al ratios in soil solution under virtually all strategies of reduced future
24 acidic deposition considered. This is partly because S adsorption in soils is likely to decline,
25 even with dramatically reduced S deposition. In addition, many spruce-fir forests in the region
26 are N-saturated, and continued N deposition at moderate or high levels would be expected to
27 contribute to elevated NO_3^- concentrations in soil water, which could further enhance base cation
28 leaching and mobilization of Al from soils to soil solution. These processes will be facilitated by
29 the already low values of base saturation in the soils of many of these forests. Results of
30 modeling efforts conducted to date are consistent in suggesting that such changes to forest soils
31 and soil solutions will likely continue to occur.

1 It is not clear, however, to what extent these changes in the chemistry of soils and soil
2 solutions might actually impact forest growth and health. The state of scientific understanding
3 on this topic would suggest that such chemical changes would increase the likelihood that the
4 growth and/or health of spruce-fir forests would be adversely impacted, perhaps making them
5 more susceptible to other stressors associated with such factors as insect pests, pathogens, or
6 extreme climatic conditions. However, the occurrence of low base saturation and Ca:Al ratio in
7 soil solution will not necessarily be sufficient to cause widespread impacts. Many factors in
8 addition to soil base saturation and soil solution acid-base chemistry are important in this regard.
9 Recent evidence indicates that mortality in red spruce in the southern Appalachian Mountains is
10 not abnormal when compared to historical rates, and that Fraser fir stands killed by the balsam
11 woolly adelgid (*Adelges piceae*) are largely being replaced by vigorous re-growth of young
12 stands of that species (Van Miegroet et al., 2007). To what extent spruce or fir mortality in the
13 southern Appalachian Mountains will be replaced with a species mix similar to that existing prior
14 to the mortality remains to be seen.

15 The limited available empirical data suggest that the kinds of changes in soil solution
16 chemistry projected by NuCM for spruce-fir stands in the region will be consistent with the kinds
17 of changes that have been associated in the past with reductions in forest growth. Furthermore, a
18 strong connection between decreased availability of soil Ca^{2+} coupled with increased availability
19 of Al, and growth of Norway spruce trees, was identified in Northeast Russian (Lawrence et al.,
20 2005). The weight of evidence for spruce-fir forests suggests that adverse impacts on soil
21 solution chemistry are likely, and adverse impacts on forest growth and health are possible
22 (Sullivan et al., 2002). Changes in red spruce growth rates are potentially attributable, at least in
23 part, to base cation deficiencies caused by inhibition of base cation uptake by trees due to
24 elevated Al concentration in soil solution within the rooting zone. Other factors that could also
25 be important include depletion of base cations in upper soil horizons by acidic deposition, Al
26 toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of
27 acidic deposition, especially cloud deposition.

28 Data on the possible effects of S and N deposition on the acid-base characteristics of
29 western coniferous forest ecosystems are spotty and inconclusive. Ponderosa pine (*Pinus*
30 *ponderosa*) seedlings exposed to acidic precipitation (pH 5.3, 4.4, 3.5 of 1:1 $\text{NHO}_3:\text{H}_2\text{SO}_4$)
31 showed no significant changes in growth (Temple et al., 1992). Fenn et al. (2003) reported that

1 deposition levels of 20 to 35 kg N/ha/yr contributed to increased NO_3^- leaching and soil acidity
2 and decreased base cation saturation in southern California ecosystems, but they did not report
3 quantitative measures of growth.

4 Baron et al. (2000) showed that small differences in the N deposition regime between the
5 east (3 to 5 kg N/ha/yr) and the west (1 to 2 kg N/ha/yr) side of the Rocky Mountains were
6 associated with significant declines in foliar Mg^{2+} levels and increased foliar N/ Mg^{2+} and N/ Ca^{2+}
7 ratios in old-growth stands of Engelmann spruce (*Picea engelmannii*). It is not known whether
8 such changes in nutrient ratios affect the health or growth of these forests.

9 10 **AX4.3.1.2 Deciduous Forest**

11 The deciduous tree species most commonly associated with adverse acidification-related
12 effects of S and N deposition is sugar maple. This species is distributed throughout the
13 northeastern United States and central Appalachian Mountain region as a component of the
14 northern hardwood forest. Acidification effects have not been as widely demonstrated for sugar
15 maple as they have for red spruce. Nevertheless, several studies, mainly in Pennsylvania, have
16 indicated that sugar maple decline is linked to the occurrence of relatively high levels of acidic
17 deposition and base-poor soils.

18 Drohan et al. (2002) investigated differences in soil conditions in declining versus non-
19 declining sugar maple plots in northern Pennsylvania from the USDA Forest Service Forest
20 Inventory and Analysis (FIA) program. Soils in plots with declining sugar maple tended to have
21 lower base cation concentrations and pH, and $\text{Ca}:\text{Al} \leq 1$. Regressions between foliar and soil
22 chemistry showed that foliar nutrition was highly correlated with the chemistry of the upper
23 50 cm of soil. In general, declining sugar maple trees were found at higher elevation, on
24 geologies dominated by sandstone, with base-poor sandy soils having high percentages of rock
25 fragments (Drohan et al., 2002). Such site conditions are representative of the kinds of
26 conditions expected to be most susceptible to adverse impacts of acidic deposition because of
27 probable low initial base cation pools and high base cation leaching losses.

28 Acid deposition may be contributing to episodic dieback of sugar maple in the Northeast
29 through depletion of nutrient cations from marginal soils. Horsley et al. (1999) found that
30 dieback at 19 sites in northwestern and north central Pennsylvania and southwestern New York
31 was correlated with combined stress from defoliation and soil deficiencies of Mg^{2+} and Ca^{2+} .

1 Dieback occurred predominately on ridge tops and on upper slopes, where soil base availability
2 was much lower than at middle and lower slopes (Bailey et al., 1999). More recent research has
3 strengthened the role of soil cation nutrition in sugar maple health (Hallet et al., 2006). Because
4 multiple factors, including soil mineralogy and landscape position, affect soil base status, the
5 extent to which sugar maple dieback can be attributed to acidic deposition is not fully resolved.

6 At the Fernow Experimental Forest in West Virginia, $(\text{NH}_4)_2\text{SO}_4$ inputs of 54 kg N/ha/yr
7 and 61 kg S/ha/yr (application plus ambient atmospheric deposition), each about three times the
8 ambient deposition level, were applied to one watershed for 4 years. Few differences in soil and
9 forest floor chemistry were found in response to the N addition, although pH was significantly
10 lower in the treatment watershed, corresponding to increased base-flow concentrations of NO_3^-
11 and Ca^{2+} (Gilliam et al., 1996).

12 Deciduous forests show variable responses to acidification depending on the tree species
13 present. Along an increasing N deposition gradient in the northeastern United States, from 4.2 to
14 11.1 kg N/ha/yr, Lovett and Rueth (1999) found a twofold increase in mineralization in soils of
15 sugar maple stands, but no significant relationship between increased deposition and
16 mineralization in American beech stands. This difference might be attributable to the lower litter
17 quality in beech stands. Thus, sugar maple appears to be more susceptible to effects of
18 increasing deposition and concomitant soil acidification from either direct leaching of NO_3^- or
19 enhanced nitrification. For northeastern hardwoods, Aber et al. (2003) found a decrease in C:N
20 ratio from 24 to 17 over a deposition gradient of 3 to 12 kg N/ha/yr. This decrease was similar
21 but less steep than the decrease seen in conifers.

22 Less-sensitive forests throughout the United States are experiencing gradual losses of
23 base cation nutrients, which may reduce the quality of forest nutrition over the long-term
24 (NAPAP, 1998). However, the extent to which acidic deposition, at ambient levels, actually
25 affects the growth or health of forest types other than red spruce and sugar maple in the United
26 States is much less certain.

27 Stand age and successional stage also can affect the susceptibility of hardwood forests to
28 acidification effects. In northeastern hardwood forests, older stands exhibit greater potential for
29 Ca^{2+} depletion in response to acid deposition than younger stands. Thus, with the successional
30 change from pin cherry (*Prunus pensylvanica*), striped maple (*Acer pensylvanicum*), white ash
31 (*Fraxinus americana*), yellow birch and white birch (*Betula papyrifera*) in younger stands to

1 beech and red maple in older stands, there is an increase in sensitivity to acidification (Hamburg
2 et al., 2003).

3 Across an 800 km pollution gradient (3 to 11 kg SO₄-S/ha/yr; 2 to 4 kg NO₃-N/ha/yr)
4 in northern hardwood forests, with maples dominant, Pregitzer et al. (1992) found a 200 to
5 300 µg/g increase in foliar S, and litter fall S content ranged from 872 to 1356 µg/g. While foliar
6 N did not change across the gradient, litterfall N was correlated with changing deposition.
7 Pregitzer and Burton assert that their data did not suggest a causal link between acid deposition
8 and forest decline. Decline would be impossible to document in the short 5-year time frame of
9 their study. They did, however, assert that their results supported the plausibility of altered tree
10 nutrition across large geographic regions due to atmospheric deposition.

11 **AX4.3.1.3 Shrubs, Grasslands, and Alpine Tundra**

13 Forest trees are not the only vascular plants that are potentially sensitive to acidic
14 deposition. Available data suggest that it is possible, or perhaps likely, that a variety of shrubs
15 and herbaceous species are sensitive to base cation depletion and/or Al toxicity.

16 Westman et al. (1985) reported a decrease in the number of inflorescences for different
17 shrubs fumigated with SO₂ over ten weeks at 0, 0.05, 0.20, and 0.50 ppm. Decreased
18 inflorescences were observed at 0.05 ppm SO₂ for black sage (*Salvia mellifera*), and at 0.20 ppm
19 SO₂ for California sagebrush (*Artemisia californica*), Eastern Mojave Buckwheat (*Eriogonum*
20 *fasciculatum*), and California brittlebush (*Encelia californica*), with progressive declines as SO₂
21 concentration increased. This suggests impact of exposure and/or acidification through
22 reproduction of a species rather than solely through impacts on individual plants.

23 Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in
24 response to acidic deposition. Such effects are probably more related to the nutrient enrichment
25 effects of N deposition than to the acidification effects of S and N deposition. (See further
26 discussion in AX5.3.2). Data are insufficient in this country to allow us to use shrub or
27 herbaceous plant species as indicators of the effects of acidic deposition at this time.

28 Due to structural differences and a much lower canopy, grasslands are thought to be less
29 sensitive to acidification than woodlands (Blake et al., 1999; Köchy and Wilson, 2001). Among
30 grasslands, those with calcareous soils will be less sensitive than those with acidic soils (Bobbink
31 et al., 1998). Most literature on the effects of atmospheric deposition on grasslands documents
32 effects of fertilization from N deposition, not acidification.

1 The possible effects of acidic deposition on alpine plant communities are also of concern.
2 Especially important in this regard is the role of N deposition in regulating ecosystem N supply
3 and plant species composition. Key concerns are for listed threatened or endangered species and
4 species diversity. However, for most rare, threatened, or endangered herbaceous plant species,
5 little is known about their relative sensitivities to acidification from atmospheric deposition
6 inputs. Although plant species diversity is highly valued, it is difficult to document changes in
7 this parameter in response to acidic deposition.

8 9 **AX4.3.2 Transitional Ecosystems**

10 Wetlands are common in many areas that contain acid-sensitive surface waters. For
11 example, wetlands constitute about 14% of the land surface in the Oswegatchie/Black River
12 watershed in the southwestern Adirondack Mountains (Ito et al., 2005), one of the regions of the
13 United States most affected by surface water acidification from acidic deposition. There are no
14 studies, however, that have documented the extent or magnitude of acidification effects of S and
15 N deposition on wetland ecosystems in the United States.

16 The topic of acidification effects on wetlands is not well represented in the literature, and
17 therefore the distribution of ecosystem effects for these systems is not presented. Because levels
18 of natural organic acidity tend to be high in wetland soils and water, it is not likely that such
19 ecosystems are affected by the levels of acidic deposition commonly encountered in the United
20 States. It is more likely that atmospheric deposition affects wetlands via nutrient N enrichment
21 pathways. (See Discussion in AX5.3.2) Gorham et al. (1987) hypothesized that acidic
22 deposition to mineral-poor fens might cause depletion of exchangeable base cations and
23 decreased pH of soil water. This mechanism was suggested as a possible cause of transition
24 from mineral-poor fen to *Sphagnum* bog. Such an effect has not been observed in response to
25 acidic deposition at levels found in the United States.

26 Synoptic surveys of ponded waters generally are restricted to lakes larger than 1 ha, 4 ha,
27 or 10 ha. Reasons for this limitation are varied and can include the perception that larger lakes
28 are more important, the failure of regional topographic map coverages to include the smaller
29 lakes and ponds, and the fact that smaller lakes tend to be much more numerous than larger lakes
30 within the major lake districts of the United States. In general, if the larger lakes in a given

1 region are sensitive to acidification, the smaller ponds would also be expected to be sensitive. In
2 most cases, data to demonstrate this are not available.

3 Ponds that have been observed to be sensitive to acidic deposition have been found in the
4 Adirondack Mountains in New York (Kretser et al., 1989) and the Mount Zirkel Wilderness Area
5 located in the Colorado Rockies (Campbell et al., 2004). Acid-sensitive ponds are likely to be
6 found elsewhere as well.

7

8 **AX4.3.3 Aquatic Ecosystems**

9 In most regions of the United States, the majority of lakes and streams are not highly
10 sensitive to existing levels of ambient air pollution. In addition, air pollution levels are generally
11 decreasing in many parts of the country, especially in the eastern United States, in response to
12 federal and state air pollution control regulations. Therefore, the highly sensitive, and acidified,
13 systems tend to be restricted to a relatively small percentage of the overall aquatic resource base.
14 There are exceptions to this generalization, such as for example in Monongahela National Forest,
15 WV, where a high percentage of the streams are acid-sensitive and highly acid-affected (cf.
16 Sullivan et al., 2002). Similarly, a high percentage of Adirondack lakes (and presumably also
17 streams) are acid-sensitive and have been acidified by atmospheric deposition of S and
18 N (Driscoll et al., 1991).

19 Studies to assess relationships between atmospheric deposition loading (N and S) and the
20 estimated or expected extent, magnitude, and timing of aquatic acidification effects (U.S.
21 Environmental Protection Agency, 1995; cf. Van Sickle and Church, 1995; NAPAP, 1998) often
22 employ a “weight of evidence” evaluation of the relationships between deposition and effects, as
23 followed by NAPAP in the Integrated Assessment (IA) (NAPAP, 1991).

24 Several kinds of evidence were used in the IA to assess the extent and magnitude of
25 acidification in sensitive regions of the United States. These included:

- 26 1. results of watershed simulation models that projected past or future chemical
27 changes in response to changes in S deposition
- 28 2. empirical biological dose/response models
- 29 3. improved relationships between surface water chemistry and ambient acidic
30 deposition
- 31 4. trend analyses of long-term monitoring chemical data in regions that have
32 experienced large recent changes in acidic deposition levels

- 1 5. paleolimnological reconstructions of past water chemistry using fossil remains of
- 2 algae deposited in lake sediments
- 3 6. results from whole-watershed or whole-lake acidification or deacidification field
- 4 experiments

5 Evidence from each type of study contributes to understanding of the quantitative

6 importance of acidification and neutralization processes and their effects on the chemistry and

7 biology of affected ecosystems.

8

9 **AX4.3.3.1 Status of Surface Waters – Regional Overview**

10 Several regions of the United States contain appreciable numbers of lakes and streams

11 with low ANC (less than about 50 µeq/L) including portions of the Northeast (New England, the

12 Adirondacks, and the Catskill Mountains), the Southeast (the Appalachian Mountains and

13 northern Florida), the Upper Midwest, and the western United States (Charles, 1991). The

14 Adirondack and Appalachian Mountains, and to a lesser extent the Upper Midwest, include

15 many acidified surface waters that have been impacted by acidic deposition. Portions of

16 northern Florida also contain many acidic and low-ANC lakes and streams, although the role of

17 acidic deposition in these areas is less clear. The western United States contains many of the

18 surface waters most susceptible to potential acidification effects, but the levels of acidic

19 deposition in the West are low in most areas, acidic surface waters are rare, and the extent of

20 chronic surface water acidification that has occurred to date has likely been very limited.

21 Several national assessments have been conducted to estimate the distribution and extent

22 of surface water acidification in the United States. During summer baseflow of 2004, the EPA

23 conducted a National Wadeable Stream Assessment (WSA) survey of 1,392 randomly selected

24 sites across the conterminous 48 United States to assess the ecological condition of wadeable

25 streams (U.S. Environmental Protection Agency, 2006). Because this sampling was conducted

26 during baseflow in the summer, the least acidic conditions of the year, only the most chronically

27 acidified streams were identified as acidic. Therefore, the overall extent of acidification was

28 substantially underestimated by this approach (Lawrence et al., in review). Overall, less than 1%

29 of the 1,020,000 km of stream in the target population (based on the 1:100,000-scale U.S.

30 Geological Survey (USGS) map blue line network) was acidic due to acidic deposition. No

31 acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern

32 Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams attributable to acidic

1 deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the
2 Southern Appalachians (1.8% of 287,000 km). Very low ANC (0-25 µeq/L) streams likely
3 exposed to episodic acidification were found in the Northern Appalachians (2.7% of 96,100 km
4 of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of
5 204,000 km).

6 Even though the WSA had over 1,300 sample sites, it was still a very coarse sample of
7 the nation's streams with respect to acidic deposition effects, which are only observed in
8 spatially restrictive subpopulations. More precise survey estimates of the effects of surface water
9 acidification were made in the NSWS in the mid 1980s. The NSWS concluded that 4.2% of
10 lakes larger than 4 ha and 2.7% of stream segments in the acid-sensitive regions of the eastern
11 United States were acidic. The NSWS documented the status and extent of surface water acid-
12 base chemistry during probability surveys of lakes and streams conducted from 1984 through
13 1988 in the major acid sensitive regions of the United States (Landers et al., 1987; Kaufmann
14 et al., 1988). By statistically selecting representative lakes and streams in each surveyed region,
15 the NSWS estimated chemical conditions of 28,300 lakes and 56,000 stream reaches (Baker
16 et al., 1991a). The data collected by the NSWS have allowed EPA and the states to focus
17 monitoring efforts on those areas that contain the majority of anthropogenically acidified waters
18 in the United States, and that are most likely to respond to changes in deposition as a result of the
19 CAAA and other air pollution control legislation.

20 The stream component of the NSWS, the National Stream Survey (NSS) was focused in
21 the northern and southern Appalachians and Coastal Plain of the eastern United States
22 (Kaufmann et al., 1991). The NSS consisted of 500 stream reaches selected from
23 1:250,000 scale USGS topographic maps using a systematic, randomized sample. Sample
24 reaches were sampled at both the upstream and downstream end of each selected reach.
25 Population estimates were made for chemistry at both reach ends and for stream length by
26 interpolating chemical results between reach ends.

27 Overall, out of the estimated 57,000 stream reaches in the NSS, after excluding streams
28 acidic due to acid mine drainage, 6.2% of the upstream and 2.3% of the downstream reach ends
29 were acidic (Kaufmann et al., 1991). After interpolation, this corresponded to 2.7% of the
30 201,000 km of stream. In acidic and low-ANC NSS reaches, ANC usually increased with
31 downstream distance. Acidic (ANC ≤ 0) streams were located in the highlands of the Mid-

1 Atlantic Region (southern New York to southern Virginia, 2320 km), in coastal lowlands of the
2 Mid-Atlantic (2530 km), and in Florida (461 km). Acidic streams were rare (less than 1%) in the
3 highlands of the Southeast and Piedmont. Inorganic monomeric Al concentrations were highest
4 in acidic streams of the Mid-Atlantic Highlands where over 70% of the acidic streams had Al_i
5 greater than 100 µg/L, a concentration above which deleterious biological effects have frequently
6 been reported.

7 Anion composition of the NSS stream samples was examined to evaluate the most
8 probable sources of stream acidity in acidic and low ANC sites (Baker et al., 1991b; Herlihy
9 et al., 1991). Acidic streams that had almost no organic influence (organic anions constituted
10 less than 10% of total anions) and SO₄²⁻ and NO₃⁻ concentrations indicative of evaporative
11 concentration of atmospheric deposition were classified as acidic due to acidic deposition. These
12 acidic streams were located in small (<30 km²) forested watersheds in the Mid-Atlantic
13 Highlands (an estimated 1980 km of stream length) and in the Mid-Atlantic Coastal Plain
14 (1250 km). Acidic streams affected primarily by acidic deposition but also influenced by
15 naturally occurring organic anions accounted for another 1210 km of acidic stream length and
16 were mainly located in the New Jersey Pine Barrens, plateau tops in the Mid-Atlantic and
17 Southeast Highlands, and the Florida Panhandle. The total length of streams acidic due to acid
18 mine drainage in the NSS (4590 km) was about the same as the total length of acidic streams
19 likely affected by acidic deposition (4455 km). Acidic streams whose acid anion composition
20 was dominated by organics were mainly located in Florida and the Mid-Atlantic Coastal Plain.
21 In Florida, most of the acidic streams were organic dominated, whereas about half of the acidic
22 streams in the Mid-Atlantic Coastal Plain were organic dominated. Organic-dominated acidic
23 streams were not observed in the Mid-Atlantic and Southeast Highlands.

24 In the NSS, DOC concentrations were much higher in lowland coastal streams, compared
25 with inland streams. National Stream Survey data also supported the hypothesis that
26 atmospheric sources and watershed retention of S control regional patterns in streamwater SO₄²⁻
27 concentrations. Most NSS watersheds retained the vast majority of the total N loading from wet
28 deposition. The 1986 data suggested, however, that some atmospherically deposited N may have
29 been reaching streams in the northern Appalachians (Kaufmann et al., 1991).

30 In the 1990 NAPAP State of Science/Technology (SOS/T) summary, Baker et al. (1991a)
31 identified six high interest subpopulations that accounted for most of the U.S. surface waters that

1 were acidic with acidic deposition having been identified as the likely source (Figure AX4.3-2,
2 Table AX4.3-1).

- 3 • Southwestern Adirondacks
- 4 • New England Uplands
- 5 • Low Si Eastern Upper Midwest
- 6 • Forested Mid-Atlantic Highlands
- 7 • Mid-Atlantic Coastal Plain
- 8 • Northern Florida Highlands

9 Stream data for the NSS was unavailable for three of these high-interest areas: the
10 Adirondacks, New England, and Upper Midwest. The national WSA data indicated that acidic
11 streams in the Upper Midwest are likely to be rare but there are acidic streams in the
12 Adirondacks/New England region. Specific areas of interest within the other three high-interest
13 regions are described below.

14 Stoddard et al. (2003) presented a map of acid-sensitive regions of the eastern United
15 States where lakes and streams occur that are likely to be affected by acidic deposition (Figure
16 AX4.3-3). The map shows considerable overlap with the areas of high interest identified by
17 Baker et al. (1991a). Surface waters in most other regions of the United States are not sensitive
18 to the impacts of acidification due largely to the nature of the local geology (Stoddard et al.,
19 2003). An exception is the region surrounding the Los Angeles Basin, which receives high
20 N deposition (>20 kg N/ha/yr in some areas) and includes streams with very high NO_3^-
21 concentrations (>50 $\mu\text{eq/L}$).

22 In addition to the large water chemistry databases developed by the EPA, there are also
23 some important supplemental databases in some regions. For example, based on results of lake
24 surveys conducted during the 1980s, about 70% of the known acidic lakes in Maine were either
25 seepage type or high elevation (Kahl et al., 1991). *The Maine seepage lake* dataset includes 120
26 of the estimated 150 lakes in Maine that meet the following criteria: (1) located in sand and
27 gravel mapped by the USGS or Maine Geological Surveys; (2) depth at least 1 m; and (3) area at
28 least 0.4 ha (1 ac). Sampling was conducted in 1986-87 and 1998-2000, and included at least
29 one fall index sample for each lake. There were 87 lakes with Gran ANC less than 100 $\mu\text{eq/L}$.

30 *The Maine high elevation lake* dataset includes 90 lakes above 600 m elevation.
31 Sampling was conducted during the periods 1986-88 and 1997-99. The study included the vast

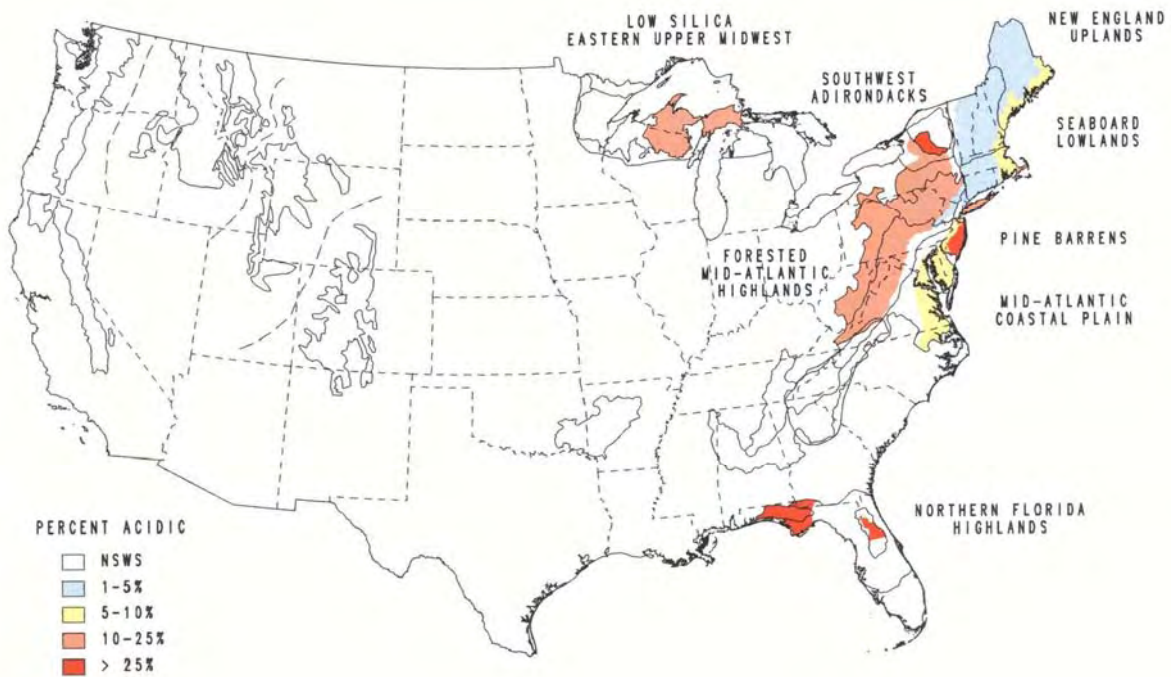


Figure AX4.3-2. Location and percentage of acidic surface waters in U.S. high-interest subpopulations with respect to acidic deposition effects. Estimates are for the upstream reach ends in the NSS data. Population estimates in the Mid-Atlantic Highlands apply only to the forested watersheds, while estimates in the eastern Upper Midwest apply only to low-silica (≤ 1 mg/L) lakes. Figure taken from Figure 9-106 in the 1990 NAPAP SOS/T report.

Source: Baker et al. (1990b).

1 majority of Maine lakes that are at least 1 m deep and at least 0.4 ha (1 ac) in area. There were
 2 64 lakes with Gran ANC less than 100 $\mu\text{eq/L}$.

3
 4 **AX4.3.3.2 Recent Changes in Surface Water Chemistry**

5 Surface water acid-base chemistry monitoring throughout the eastern United States
 6 occurs primarily in two EPA programs: the Temporally Integrated Monitoring of Ecosystems
 7 (TIME) project (Stoddard, 1990) and the Long-Term Monitoring (LTM) project (Ford et al.,
 8 1993; Stoddard et al., 1998). Both projects are operated in cooperation with numerous state

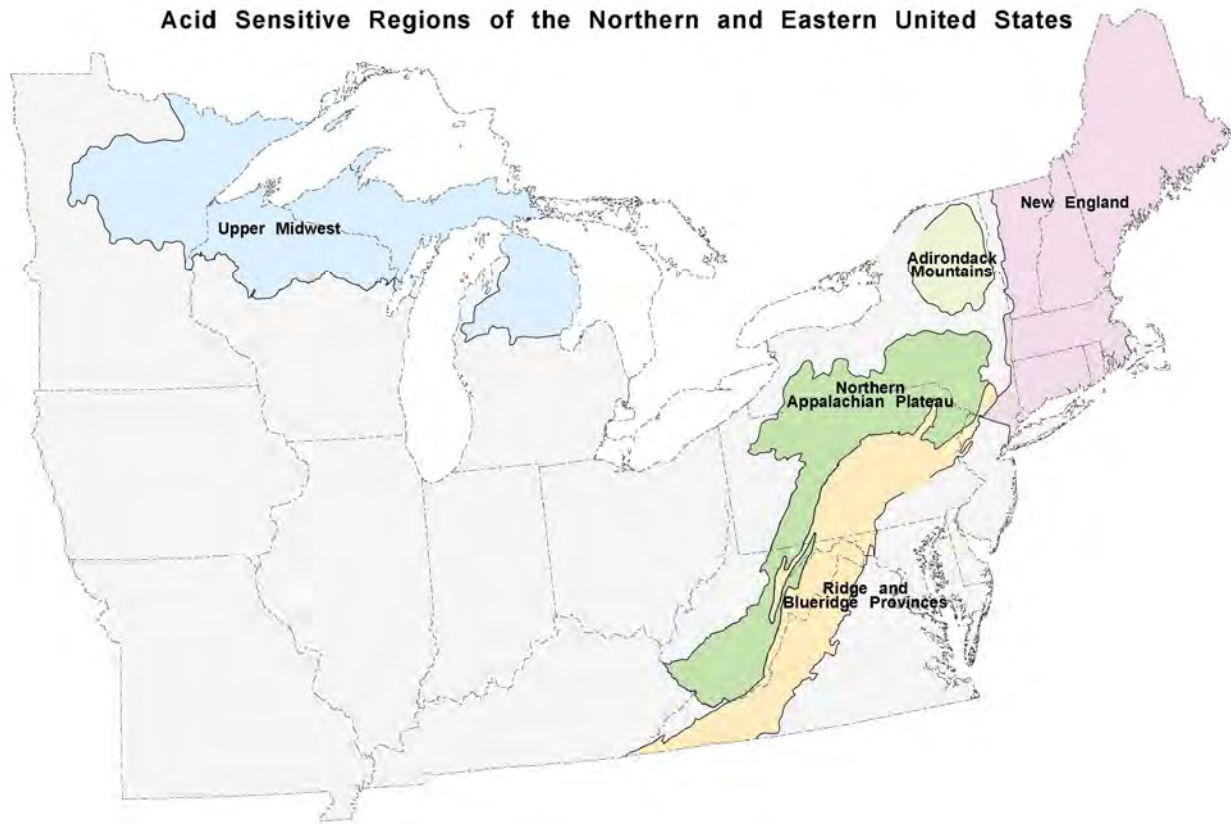


Figure AX4.3-3. Regions of the eastern United States that contain appreciable numbers of lakes and/or streams that are sensitive to acidification from acidic deposition.

Source: Stoddard et al. (2003).

1 agencies, academic institutions and other federal agencies. Each is described below.

2 The regions represented by the LTM and TIME monitoring programs (Table AX4.3-2)

3 are estimated to contain 95% of the lakes and 84% of the streams in the United States that have

4 been anthropogenically acidified by acidic deposition. The Adirondacks had a large proportion

5 of acidic surface waters (14%) in the NSWS; from 1984 to 1987, the ALSC sampled 1,469

6 Adirondack lakes greater than 0.5 ha in size and estimated that many more (26%) were acidic

7 (Driscoll et al., 1991). The higher percentage of acidic lakes in the ALSC sample was due to

8 inclusion of smaller lakes and ponds (1 to 4 ha in area), many of which were acidic as a

9 consequence of naturally occurring organic acids (Sullivan et al., 1990). The proportions of

10 lakes estimated by NSWS to be acidic were smaller in New England and the Upper Midwest

1 (5% and 3%, respectively), but because of the large numbers of lakes in these regions, there were
2 several hundred acidic waters in each of these two regions.

3 The Valley and Ridge Province and Northern Appalachian Plateau had 5% and 6% acidic
4 sites, respectively. The only potentially acid-sensitive region in the eastern United States not
5 assessed in the Stoddard et al. (2003) report was Florida, where the high proportion of naturally
6 acidic lakes, and a lack of long-term monitoring data, make assessment of the effects of acidic
7 deposition problematic (Stoddard et al., 2003).

8 The TIME project is structured as a probability sampling. Each site is chosen statistically
9 to be representative of a target population. In the Northeast (New England and Adirondacks),
10 this target population consists of lakes with Gran ANC < 100 µeq/L, which are those likely to be
11 most responsive to changes in acidic deposition. In the Mid-Atlantic, the target population is
12 upland streams with ANC < 100 µeq/L. Each lake or stream is sampled annually, and results are
13 extrapolated to the target populations (Larsen and Urquhart, 1993; Larsen et al., 1994; Stoddard
14 et al., 1996; Urquhart et al., 1998). The TIME project began sampling northeastern lakes in
15 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of about 1,000
16 lakes having ANC < 100 µeq/L, out of a total population of 1,830 lakes with surface area > 1 ha.
17 Data from 30 lakes representing about 1,500 lakes having ANC < 100 µeq/L, out of a total
18 population of 6,800 lakes, are included in the TIME program in New England.

19 As a compliment to lake and stream sampling in the statistical populations of lakes in
20 TIME, the LTM project samples a subset of sensitive lakes and streams with long-term data,
21 many dating back to the early 1980s. Each LTM site is sampled 3 to 15 times per year, and the
22 resulting data are used to characterize the response of the most sensitive aquatic systems in each
23 region to changing levels of acidic deposition. In most regions, a small number of higher ANC
24 (e.g., Gran ANC > 100 µeq/L) sites are also sampled. Because of the long-term records at most
25 LTM sites, their trends can also be placed in a better historical context than those of TIME sites,
26 where data are only available from the 1990s. Monitoring results from the LTM project have
27 been widely published (Kahl et al., 1991, 1993b; Driscoll and Van Dreason, 1993; Murdoch and
28 Stoddard, 1993; Stoddard and Kellogg, 1993; Webster et al., 1993; DeWalle and Swistock, 1994;
29 Driscoll et al., 1995; Stoddard et al., 1998). Overall results were summarized by Stoddard and
30 Kellog (1993).

1 Results of surface water chemistry monitoring in the LTM and TIME projects suggest
2 that the following important changes in lake and streamwater chemistry occurred during the
3 1990s in response to S and N emissions reductions:

- 4 • Sulfate concentration decreased as a percentage of total ion concentration in surface
5 waters.
- 6 • ANC increased modestly in three of the five regions included in surface water long-
7 term monitoring efforts.
- 8 • DOC increased, perhaps toward more natural pre-disturbance concentrations, as
9 surface water acidity contributed from acidic deposition decreased.
- 10 • Inorganic, and potentially toxic, Al concentrations appear to have decreased slightly
11 in some sensitive aquatic systems.

12 Monitoring data from the LTM and TIME projects were used to evaluate recent changes
13 in lake and stream chemistry from 1990 to 2000 in many of the sensitive areas of the eastern
14 United States including New England, the Adirondack Mountains, the Northern Appalachian
15 Plateau, the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Stoddard
16 et al., 2003). There are also substantial numbers of acid-sensitive streams in the Blue Ridge
17 Province in North Carolina and portions of South Carolina and Tennessee that have been
18 affected by acidic deposition but that were not included in this analysis. In general, the results of
19 the TIME/LTM data analysis suggest that about one-quarter to one-third of the lakes and streams
20 that were chronically acidic in the 1980s were no longer chronically acidic in the year 2000.
21 However many still had low ANC and were potentially susceptible to episodic acidification
22 (Stoddard et al., 2003).

23 Stoddard et al. (2003) found little evidence of regional change in the acidity status of
24 lakes in New England or streams in the Ridge/Blue Ridge regions. Furthermore, none of the
25 study regions showed an increase in the number of chronically acidic waters, even though there
26 was a decline in base cation concentrations and a likely increase in natural organic acidity
27 (Stoddard et al., 2003). An important caveat in this analysis is that changes in Gran ANC used in
28 the analysis were based on the median change of all sites in a region (Table AX4.3-3). However,
29 as shown in Table AX4.3-4, the rates of ANC increase were generally more rapid in chronically
30 acidic lakes with ANC less than 0 µeq/L and streams with ANC between 0 and 25 µeq/L. If

1 acidic sites are recovering more rapidly than the population of sites as a whole, then the
2 estimates of change in the number of acidic lakes and streams presented would be conservative.

3 While general estimates for large regions are useful in providing a broad picture of the
4 extent and status of surface water acidity, specific results from studies within those regions can
5 help isolate trends and determine the specific mechanisms that contribute to change. The
6 following sections report on the current status, past acidification, and potential future conditions
7 for lakes and streams in acid sensitive areas of the Northeast, Southeast, Upper Midwest, and
8 western United States

9 10 **AX4.3.3.3 Regional Assessments**

11 12 ***AX4.3.3.3.1 Northeastern Surface Waters***

13 14 ***AX4.3.3.3.1.1 Current Status***

15 The Adirondacks and New England are two of the most acid sensitive and intensively
16 studied regions in the Northeast. The glaciated soils and location downwind from emissions
17 sources have made these areas the subject of intense scientific study over the past four decades.
18 Most of this research has focused on lake ecosystems, though important stream studies have been
19 undertaken at specific research sites and more regional stream survey work is being conducted.
20 As discussed below, the surface water chemistry in these areas integrates atmospheric deposition,
21 local geology, and upland watershed characteristics.

22 Available surface water datasets for Adirondack lakes include TIME, the Environmental
23 Monitoring and Assessment Program (EMAP), and ALSC, each of which is useful for
24 documenting chemical status and recent chemical changes. Population estimates from the TIME
25 dataset suggest that 13.0% of Adirondack lakes (238 lakes) were chronically acidic in the early
26 1990s during baseflow conditions in the summer. By applying an approximate rate of change in
27 Gran ANC of +0.8 $\mu\text{eq/L/yr}$ to these estimates (based on trend slopes for TIME and LTM data,
28 Table AX4.3-5), Stoddard et al. (2003) projected that approximately 8.1% of the population
29 (149 Adirondack lakes) remained chronically acidic in 2000. This finding suggests that roughly
30 38% of lakes in the Adirondacks that were chronically acidic in the early 1990s were not
31 chronically acidic a decade later. Certain caveats need to be included with the results of this
32 analysis, however. Summertime baseflow sampling reflects the least acidic conditions

1 experienced throughout the year. In addition, LTM trends, which are based on year-round
2 sampling, may not be representative of trends in the summer-only sampling of the TIME
3 program, and the rate of change determined through the TIME program was not controlled for
4 possible differences in flow conditions between the two sample periods. Lastly, the ANC value
5 of 0 $\mu\text{eq/L/year}$ used to define acidic waters has been shown to be below the level needed to
6 protect aquatic ecosystems in the Adirondack region (Baldigo et al., 2007; Lawrence et al.,
7 2007).

8 A study by Driscoll et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the
9 extent of acidic lakes in the Adirondacks for that period. The EMAP survey is a probability
10 based survey representative of lakes with surface area greater than 1 ha (1,812 lakes). The
11 survey was conducted during low-flow summer conditions, and the results therefore likely reflect
12 the highest ANC values for the year. Results from the survey indicate that 10% of the population
13 of Adirondack lakes were chronically acidic (ANC values of less than 0) and 31% were sensitive
14 to episodic acidification (ANC values between 0 and 50) during the study period (Driscoll et al.,
15 2001b).

16 The ALSC conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in
17 surface area between 1984 and 1987 (Kretser et al., 1989). Of the 1,489 lakes surveyed, 24%
18 had summer pH values below 5.0, 27% were chronically acidic (ANC < 0), and an additional
19 21% were probably susceptible to episodic acidification (ANC between 0 and 50) (Driscoll et al.,
20 2007).

21 For the New England region, the TIME population data indicates that 5.6% of the
22 population (386 lakes) in New England exhibited Gran ANC < 0 $\mu\text{eq/L}$ during the period of
23 1991 to 1994. This result is similar to the EMAP findings which indicate that 5% of lakes in
24 New England and in the eastern Catskill region of New York had ANC values less than 0 $\mu\text{eq/L}$.
25 The EMAP analysis also estimated that an additional 10% of the population had low ANC
26 values, between 0 and 50 $\mu\text{eq/L}$, and were probably sensitive to episodic acidification (Driscoll
27 et al., 2001b).

28 Both TIME and LTM data from the New England region indicate that only a small
29 increase in Gran ANC had occurred during the reported monitoring period (+0.3 $\mu\text{eq/L/yr}$). As a
30 result, it is estimated that the proportion of chronically acidic lakes decreased only 0.1% from
31 5.6% to 5.5% over the previous 10 years (Table AX4.3-3) (Stoddard et al., 2003).

1 State surveys within New England provide additional information on the variation in
2 lakewater chemistry across the region. In Maine, approximately 100 clearwater lakes in that
3 state have been classified as acidic, based on surveys conducted by EPA and the University of
4 Maine (Kahl et al., 1999). An estimated 13% of the high-elevation lakes in Maine are acidic,
5 compared to less than 1% of Maine lakes (>4 ha) represented in EPA's Eastern Lakes Survey
6 (ELS) (Linthurst et al., 1986a; Kahl et al., 1991). Most acidic lakes in Maine are either seepage
7 lakes located in sand and gravel deposits, or high-elevation lakes located above 600 m elevation.
8 Roughly 60% of the acidic lakes are seepage lakes. The acid-sensitive seepage lakes are located
9 in mapped sand and gravel deposits, are at least 1 m deep, and are at least 0.4 ha (1 acre) in
10 surface area. About 45 of the 150 lakes of this type in Maine are acidic (Kahl et al., 1999).

11 Whereas lakes in the Adirondacks and New England have been intensively studied, there
12 are no published data which describe the status of streamwater acid-base chemistry at a regional
13 scale, except for the Catskill Mountains. A study has been conducted in the Adirondacks, and
14 results may be published in time to be included in the next draft of this report.

15 In the absence of regional streamwater studies, insights can be gained from site-specific
16 long-term studies in the region. The HBEF has one of the longest continuous records of
17 precipitation and streamwater chemistry in the United States. Compared to model hindcast
18 approximations, current conditions at HBEF indicate that soil percent base saturation has
19 decreased in response to acidic deposition and because of accumulation of nutrient cations by
20 forest vegetation. Further, acidic deposition has contributed to a nearly fourfold increase in
21 stream SO_4^{2-} concentration; a decrease in ANC from positive to negative values; a decrease in
22 stream pH to 5.0; and an increase in stream Al, largely occurring as the inorganic form which has
23 been shown by Lawrence et al. (2007) to be an unequivocal indication of the effects of acidic
24 deposition. Driscoll et al. (2001b) estimated that roughly 6% of lakes and streams in the
25 Northeast are considered more sensitive to acidic deposition than the stream monitored at HBEF
26 (Driscoll et al., 2001b).

27
28 *AX4.3.3.3.1.2 Past Acidification*

29 There are limited surface water data that directly document historic conditions and the
30 response to atmospheric deposition since the time of the Industrial Revolution (Charles, 1991).
31 To address this gap, scientists use sediment cores from lakes and detailed computer models to try

1 to reconstruct past conditions as well as understand the mechanisms that contribute to changing
2 conditions.

3
4 Paleolimnological Studies

5 Paleolimnological studies use the remains of diatoms and other algae embedded in lake
6 sediments to reconstruct historical water chemistry. In the Adirondack Mountains and northern
7 New England, both diatom and chrysophyte algal remains in sediment cores have been used to
8 evaluate patterns of past acidification in a large number of lakes.

9 Major findings of the Paleoecological Investigation of Recent Lakewater Acidification
10 (PIRLA)-I and PIRLA-II research programs in the Adirondack Mountains suggested that:
11 (1) Adirondack lakes had not acidified as much since pre-industrial times as had been widely
12 believed prior to 1990; (2) many Adirondack lakes with ambient pH greater than 6.0 had not
13 acidified historically, whereas many of the lakes having pH less than about 6.0 had acidified;
14 (3) many of the lakes having high pH and ANC had increased in pH and ANC since the previous
15 century; and (4) the average F-factor for acid-sensitive Adirondack lakes was near 0.8 (Charles
16 et al., 1990; Sullivan et al., 1990). The results of these studies had major impacts on scientific
17 understanding of the extent to which lakes had acidified in response to acidic deposition. The
18 view of surface water acidification as a large-scale titration of ANC (Henriksen, 1980, 1984) was
19 replaced by the realization that base cation concentrations typically changed more than ANC in
20 response to acidic deposition. This realization also modified expectations for chemical recovery
21 of surface waters as acidic deposition levels have decreased (Sullivan, 2000).

22 Diatom and chrysophyte reconstructions of pH and ANC for a statistically selected group
23 of Adirondack lakes suggested that about 25% to 35% of the Adirondack lakes that are larger
24 than 4 ha had acidified since preindustrial time (Cumming et al., 1992). Low-ANC lakes of the
25 southwestern Adirondacks acidified the most, probably due to low initial buffering capacity and
26 high rainfall and deposition of S and N in that area. Cumming et al. (1992) estimated that 80%
27 of the Adirondack lakes that had ambient pH ≤ 5.2 had experienced large declines in pH and
28 ANC since the previous century, and that 30% to 45% of the lakes with pH between 5.2 and 6.0
29 had also acidified.

30 Cumming et al. (1994) reported the results of chrysophyte inferences of pH in recently
31 deposited lake sediments to assess acidification timing for 20 low-ANC Adirondack lakes.

1 Lakes that were inferred to have acidified since about 1900 tended to be small, high-elevation
2 lakes with lower inferred pre-industrial pH than the group of study lakes as a whole. These were
3 probably the most acid-sensitive and were the first to acidify with increasing acidic deposition.
4 Husar and Sullivan (1991) estimated that S deposition was about 4 kg S/ha/yr at that time. These
5 lakes are located in the high peaks area and in the southwestern portion of Adirondack Park. A
6 second category of acidification response included high-elevation lakes that were historically
7 low in pH (<5.5) but that acidified further beginning about 1900. The third identified type of
8 response included lakes with pre-industrial pH in the range of about 5.7 to 6.3 that started to
9 acidify around 1900 but showed their greatest pH change around 1930 to 1950. The final
10 category included lakes that were not inferred to have acidified. They had pre-industrial pH
11 around 6.0 and are located at lower elevation.

12 Davis et al. (1994) conducted paleolimnological studies of 12 lakes in northern New
13 England that were low in pH and ANC. Past logging, forest fire, and vegetation composition in
14 the watersheds were estimated from oral and written historical information, aerial photographs,
15 and tree ring analyses. Lake sediment cores were collected and analyzed for pollen, diatoms, and
16 chemistry to reconstruct past lake conditions for several hundred years. All 12 lakes were
17 historically low in pH and ANC, with diatom-inferred pre-industrial ANC of -12 to 31 µeq/L.
18 The inferred pH and ANC values of the lakes were relatively stable throughout the one to three
19 centuries of sediment record prior to watershed disturbance by Euro-Americans. From the early
20 19th into the 20th century, however, all of the lakes showed increased diatom-inferred pH
21 changes of about 0.05 to 0.6 pH units and increased diatom-inferred ANC of about 5 to
22 40 µeq/L. Most of these inferred increases in pH and ANC coincided with watershed logging.
23 For all study lakes, recovery to pre-logging acid-base lake chemistry conditions was followed by
24 continued decline in pH by 0.05 to 0.44 pH units and ANC by up to 26 µeq/L, probably because
25 of acidic deposition. The 12-lake mean inferred decreases in pH and ANC in response to acidic
26 deposition were 0.24 pH units and 14 µeq/L, respectively (Davis et al., 1994).

27 28 Modeling Studies

29 The most extensive regional modeling study that provides estimates of past acidification
30 of Adirondack lakes is that of Sullivan et al. (2006a). They modeled past changes in the acid-
31 base chemistry of 70 Adirondack lake watersheds, including 44 that were statistically selected to

1 be representative of the approximately 1,320 lake watersheds in the Adirondacks that have lakes
2 larger than 1 ha and deeper than 1 m and that have ANC ≤ 200 $\mu\text{eq/L}$. Model hindcasts were
3 constructed using both the MAGIC and PnET-BGC models.

4 Based on MAGIC model outputs extrapolated to the regional Adirondack lake
5 population, maximum past acidification occurred by about 1980 or 1990, with median ANC of
6 the population under investigation of about 61 $\mu\text{eq/L}$ (reduced from a median of 92 $\mu\text{eq/L}$
7 estimated for the pre-industrial period). By 1990, 10% of the population target lakes had
8 decreased in ANC to below -16 $\mu\text{eq/L}$ and 25% had ANC < 28 $\mu\text{eq/L}$. Percentile values in 2000
9 illustrated limited chemical recovery (3 to 5 $\mu\text{eq/L}$) compared with simulated values in 1980 and
10 1990.

11 The MAGIC model simulations suggest that none of the target lakes were chronically
12 acidic (had ANC < 0 $\mu\text{eq/L}$) under pre-industrial conditions, but that by 1980 there were about
13 204 acidic Adirondack lakes. That number decreased by an estimated 14% between 1980 and
14 2000. Similarly, the MAGIC model simulations suggested that there were no Adirondack lakes
15 having ANC < 20 $\mu\text{eq/L}$ in 1850, but by 1990 there were 263 such lakes. Many lakes (N = 191)
16 were estimated to have had pre-industrial ANC below 50 $\mu\text{eq/L}$, and this estimate increased
17 threefold by 1990, followed by a decrease to 399 lakes in 2000.

18 PnET-BGC model simulations generated output generally similar to results provided by
19 MAGIC model simulations. PnET-BGC simulations suggested that lakewater SO_4^{2-} , NO_3^- , and
20 base cation concentrations under pre-industrial conditions were much lower than current values.
21 In 1850, simulated SO_4^{2-} concentrations in all study lakes were less than 25 $\mu\text{eq/L}$, and the
22 median value was about 15 $\mu\text{eq/L}$. By 1980, the median simulated SO_4^{2-} concentration had
23 increased more than sixfold to about 100 $\mu\text{eq/L}$. Simulated lake NO_3^- concentrations also
24 increased markedly during that time, with the median value increasing from about 4 $\mu\text{eq/L}$ in
25 1850 to 12 $\mu\text{eq/L}$ in 1980. Simulated increases in the sum of divalent base cation concentrations
26 were less than for SO_4^{2-} concentrations, with the median value increasing from 93 $\mu\text{eq/L}$ in 1850
27 to 140 $\mu\text{eq/L}$ in 1980. This large change in $\text{SO}_4^{2-} + \text{NO}_3^-$ relative to the change in the sum of
28 base cation concentrations was the major mechanism driving the decreases in ANC and pH
29 associated with historical increases in acidic deposition.

30 Simulated lakewater ANC and pH and soil base saturation decreased from pre-industrial
31 conditions to recent times. Results from PnET-BGC suggested that the median Adirondack lake,

1 from among the estimated 1,320 lakes in the population larger than 1 ha that had measured
2 recent ANC < 200 µeq/L, had pre-industrial ANC near 80 µeq/L; an estimated 10% of the lake
3 population had pre-industrial ANC < 41 µeq/L; and one-fourth had pre-industrial ANC
4 < 64 µeq/L. Percentiles for the year 2000 suggest decreases in SO₄²⁻, NO₃⁻, and sum of base
5 cations, and small increases in ANC since 1990 for lower-ANC lakes.

6 Results from PnET-BGC suggest that none of the lakes in the Adirondack population had
7 pre-industrial ANC below 20 µeq/L. By 1990, there were 289 lakes having ANC < 20 µeq/L
8 and 217 chronically acidic (ANC ≤ 0 µeq/L) lakes according to PnET-BGC simulations. There
9 were 202 lakes in the population simulated to have had pre-industrial ANC below 50 µeq/L, and
10 this number increased 2.8 times by 1980 under the PnET-BGC simulations.

11 PnET-BGC has also been used to characterize past conditions at streams within the
12 HBEF. Gbondo-Tugbawa et al. (2002) used relationships between current emissions and
13 deposition, and estimates of past emissions to reconstruct historical deposition conditions. Their
14 analysis also considered land disturbances such as logging in 1918-1920 and hurricane damage
15 in 1938. Using this approach, they estimated that past soil base saturation in the mineral soil
16 (circa 1850) was approximately 20%, stream SO₄²⁻ concentration was approximately 10 µeq/L,
17 stream ANC was about 40 µeq/L, stream pH was approximately 6.3, and stream Al_i
18 concentration was below 1 µmol/L (Driscoll et al., 2001b).

19
20 *AX4.3.3.3.1.3 Recent Trends*

21 Sulfur deposition has contributed to chronic soil and surface water acidification in the
22 eastern United States to a much greater extent than has N deposition. Nitrate concentrations in
23 acid-sensitive drainage waters in the eastern United States are generally much lower than SO₄²⁻
24 concentrations.

25 The concentration of SO₄²⁻ in precipitation has declined for about the past three decades
26 throughout the northeastern United States, in response to decreased atmospheric emissions and
27 deposition. EPA's LTM Program has been collecting monitoring data since the early 1980s for
28 many lakes and streams in acid-sensitive areas of the United States, including the Northeast.
29 These data allow evaluation of trends and variability in key components of lake and streamwater
30 chemistry prior to, during, and subsequent to Title IV implementation. Throughout the
31 northeastern United States, the concentration of SO₄²⁻ in surface waters has decreased

1 substantially (Figure AX4.3-4) in response to decreased emissions and atmospheric deposition of
2 S. Decreased concentrations of SO_4^{2-} in lakes and streams of a third, or more, have been
3 commonly observed.

4 Lakewater SO_4^{2-} concentrations have decreased steadily in Adirondack lakes, at least
5 since 1978 (Driscoll et al., 1995; Stoddard et al., 2003). Initially, there was not a systematic
6 increase in lakewater pH or ANC in response to the decreased SO_4^{2-} concentrations. Rather, the
7 decline in lakewater SO_4^{2-} during the 1980s was charge-balanced by a nearly equivalent
8 decrease in concentrations of base cations in many of the low-ANC lakes (Driscoll et al., 1995).
9 Similar findings were reported by Stoddard and Kellog (1993) for lakes in Vermont. F-factors
10 for the nine ALTM lakes that showed significant declines in both the sum of base cations (SBC)
11 and $(\text{SO}_4^{2-} + \text{NO}_3^-)$ concentration ranged from 0.55 to greater than 1.0, with a mean of 0.93
12 (Driscoll et al., 1995). These high F-factor values for chemical recovery from acidification were
13 similar to results of historical acidification obtained by Sullivan et al. (1990), based on diatom
14 reconstructions of historical change for 33 Adirondack lakes.

15 Trend analysis results for the period 1982 to 1994 were reported by Stoddard et al.
16 (1998) for 36 lakes in the northeastern United States having $\text{ANC} \leq 100 \mu\text{eq/L}$. Trend statistics
17 among sites were combined through a meta-analytical technique to determine whether the
18 combined results from multiple sites had more significance than the individual Seasonal
19 Kendall Test statistics. All lakes showed significant declining trends in SO_4^{2-} concentration
20 ($\Delta \text{SO}_4^{2-} = -1.7 \mu\text{eq/L/yr}$; $p \leq 0.001$). Lakewater ANC responses were regionally variable.
21 Lakes in New England showed evidence of ANC recovery ($\Delta \text{ANC} = 0.8 \mu\text{eq/L/yr}$; $p \leq 0.001$),
22 whereas Adirondack lakes exhibited either no trend or further acidification, largely because of
23 declines in base cation concentrations.

24 The observed changes in the concentration of NO_3^- in some surface waters have likely
25 been due to a variety of factors, including climate. During the 1980s, NO_3^- concentration
26 increased in many surface waters in the Adirondack and Catskill Mountains in New York
27 (Driscoll and Van Dreason, 1993; Murdoch and Stoddard, 1993). There was concern that
28 northeastern forests were becoming N-saturated, leading to increased NO_3^- leaching from forest
29 soils throughout the region. Such a response could negate the benefits of decreased SO_4^{2-}
30 concentrations in lake and stream waters. However, this trend was reversed in about 1990, and
31 the reversal could not be attributed to a change in N deposition. Nitrate leaching through soils to

Sulfate concentration in Lake and Stream Water ($\mu\text{eq/L}$)

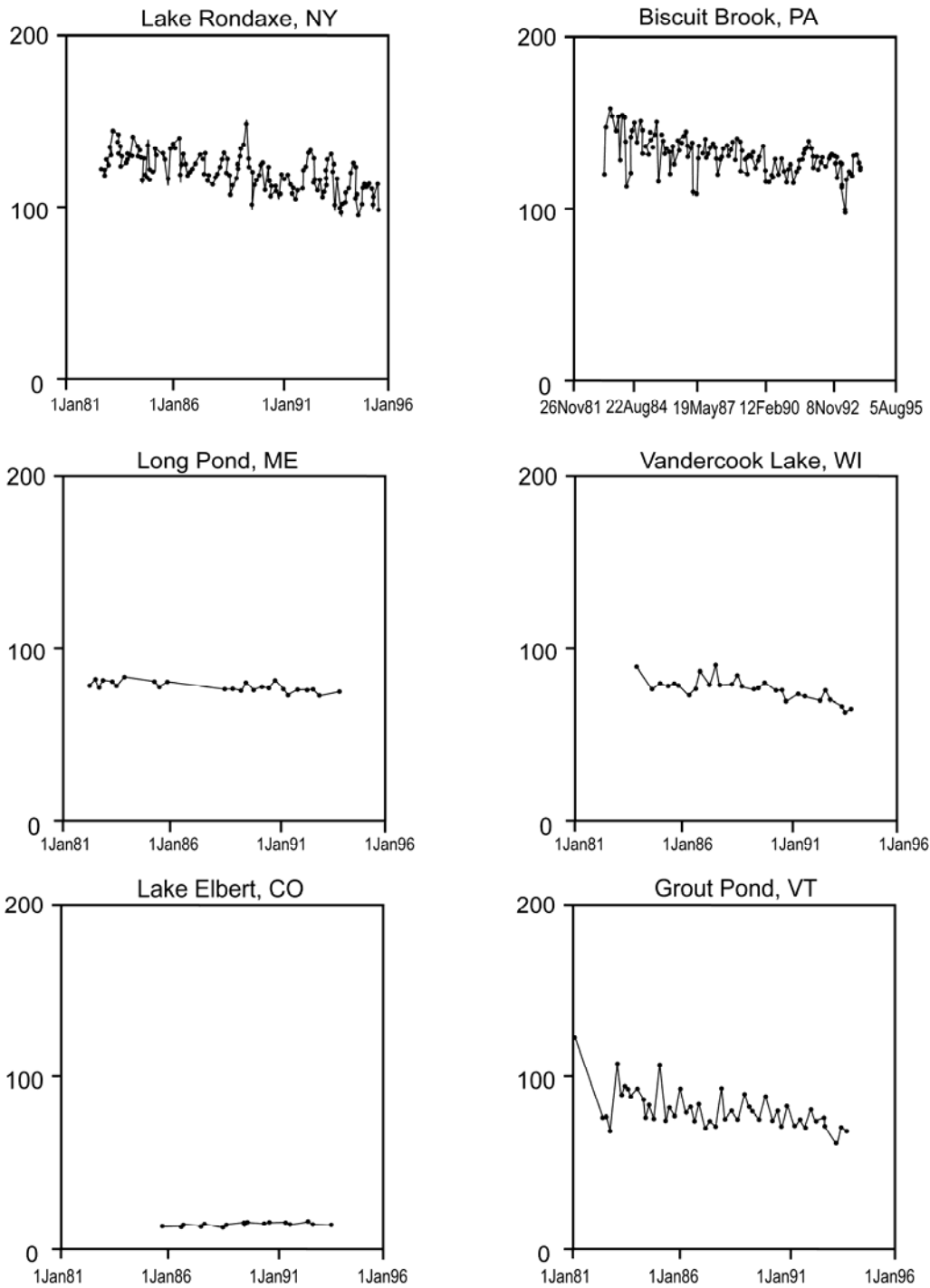


Figure AX4.3-4. Measured concentration of SO_4^{2-} in selected representative lakes and streams in six regions of the United States during the past approximately 15 years. Data were taken from EPA's Long-Term Monitoring (LTM) program.

1 drainage waters is the result of a complex set of biological and hydrological processes. Key
2 components include N uptake by plants and microbes, transformations between the various
3 forms of inorganic and organic N, and local precipitation patterns. Most of the major processes
4 are influenced by climatic factors, including temperature, moisture, and snowpack development.
5 Therefore, NO_3^- concentrations in surface waters respond to many factors in addition to
6 N deposition and can be difficult to predict. It is likely that monitoring programs of several
7 decades or longer will be needed to separate trends in NO_3^- leaching from climatic variability in
8 forested watersheds (Driscoll et al., 1995).

9 Monitoring data collected during the 1990s in the LTM and TIME projects illustrated
10 that most regions included in the monitoring efforts showed large declines in SO_4^{2-}
11 concentrations in surface waters over the 10 years of monitoring, with rates of change ranging
12 from 1.5 to 3 $\mu\text{eq/L/yr}$ (Figure AX4.3-5). These declines in lake and stream SO_4^{2-} concentration
13 were considered consistent with observed declines in S wet deposition. Surface water NO_3^-
14 concentrations also decreased, but only in the two regions that had the highest ambient surface
15 water NO_3^- concentrations (Adirondacks and Northern Appalachian Plateau), but were relatively
16 unchanged in regions with lower concentrations. DOC increased in each region over time. This
17 finding suggests an increase in the contribution of natural organic acidity, which would partially
18 offset the expected chemical recovery from decreased acidic deposition.

19 ANC increased in the Adirondacks at a rate of about +1 $\mu\text{eq/L/yr}$, despite a decline in
20 surface water base cation concentrations ($\text{Ca}^{2+} + \text{Mg}^{2+}$; Figure AX4.3-5). The decline in base
21 cations offset some of the decline in SO_4^{2-} , and thus limited the increase in ANC or pH that
22 occurred in response to lower SO_4^{2-} concentrations. Surface water ANC and pH increased
23 significantly in the 1990s; Al_i concentrations declined slightly. Regional surface water ANC did
24 not change significantly in New England (Stoddard et al., 2003).

25 Moderate increases in surface water ANC during the 1990s reduced the estimated
26 number of acidic lakes and stream segments in the northeastern United States. Stoddard et al.
27 (2003) estimated that there were 150 Adirondack lakes in the year 2000 that had ANC less than
28 0 (8.1% of the lake population), compared to 13% (240 lakes) in the early 1990s.

29 Lakewater SO_4^{2-} concentrations in the most acid-sensitive Maine lakes declined by about
30 12% to 22% during the period 1982 to 1998 (Kahl, 1999). Only in the seepage lakes, however,
31 was there evidence of a small decline in lakewater acidity during that period (Table AX4.3-6).

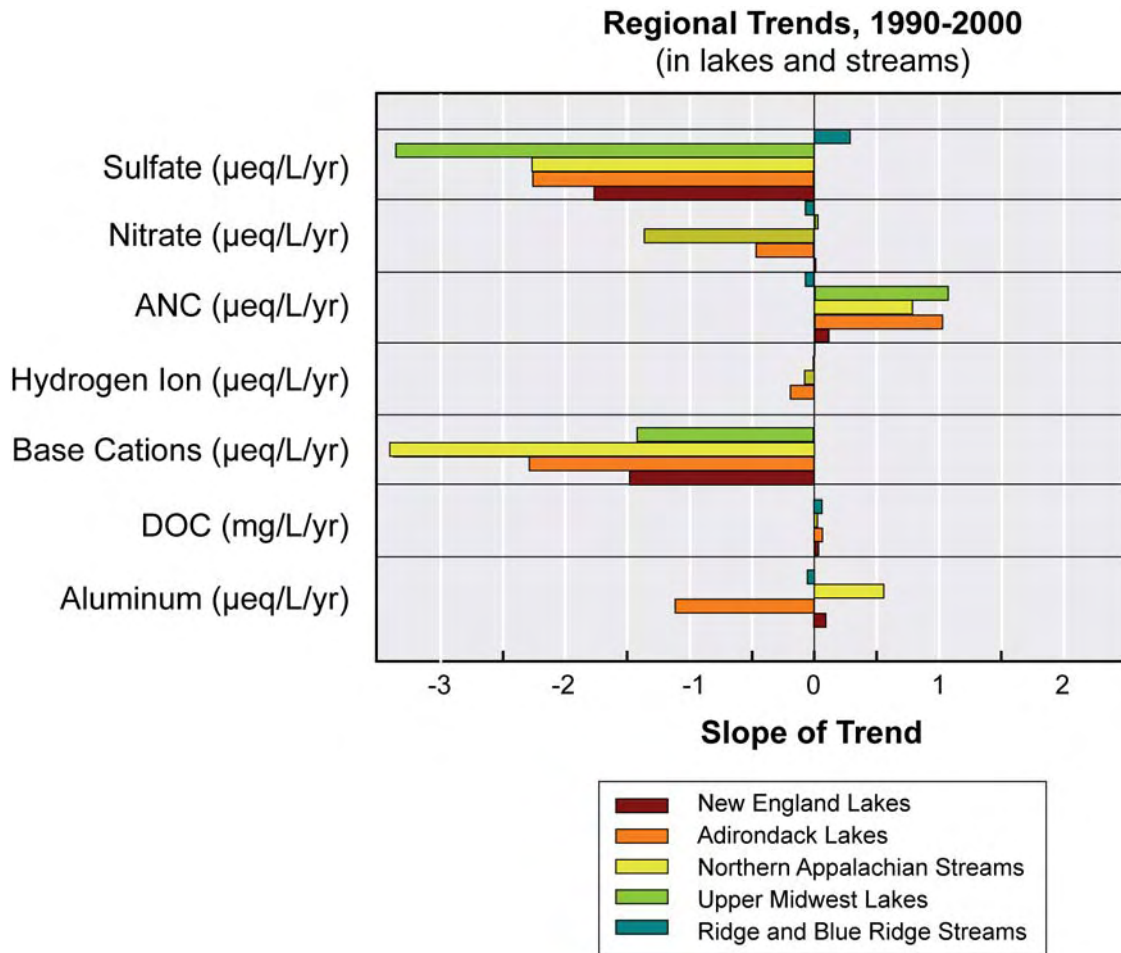


Figure AX4.3-5. Summary of regional trends in surface water chemistry from 1990 through 2000 in regions covered by the Stoddard et al. (2003) report.

Source: Stoddard et al. (2003).

1 However, evidence for reductions in lakewater ANC in seepage lakes from the mid-1980s to
 2 1998 were based on a comparison of only two sampling points, which may have been influenced
 3 by climatic variation. Therefore, the conclusion of decreasing acidity of seepage lakes is
 4 considered preliminary. The seepage lakes are generally hydrologically isolated from their
 5 surrounding soil environment. They therefore did not show a clear decreasing trend in base
 6 cation concentrations, as has been found in drainage lakes throughout the Northeast. The high-
 7 elevation lakes, in contrast, showed small declines in lakewater acidity during the 1980s, but that
 8 trend slowed or reversed in the 1990s (Kahl, 1999). Both the seepage and high elevation lakes

1 showed increased DOC concentrations of 10% to 20%, generally by about 0.5 to 1.0 mg/L. The
2 increase in dissolved organic matter would be expected to limit the extent of ANC and pH
3 recovery that would otherwise accompany the observed decreases in SO_4^{2-} concentration.

4 Whereas NO_3^- concentrations decreased during the 1990s in many lake chemistry datasets (cf.
5 Stoddard et al., 2003), the high-elevation lakes in Maine continued to show high concentrations.

6 The reference stream of the Bear Brook Watershed Study (East Bear Brook) has the
7 longest continuous, high-frequency data record of stream chemistry in Maine. Sulfate and NO_3^-
8 concentration have both declined substantially since 1987. Base cations declined by an almost
9 equivalent amount, and the increase in ANC has been limited (Kahl, 1999).

10 Long-term stream water data from the HBEF reveal a number of changes that are
11 consistent with trends in lakes and streams across Europe and eastern North America (Stoddard
12 et al., 1999, 2003; Evans and Monteith, 2001). Stream water draining the HBEF reference
13 watershed (Watershed 6) had a 32% decline in annual volume-weighted concentrations of SO_4^{2-}
14 ($-1.1 \mu\text{eq/L}$) between 1963 and 2000 (Driscoll et al., 2007). This decrease in stream SO_4^{2-}
15 concentration corresponds to both decreases in atmospheric emissions of SO_2 and to bulk
16 precipitation concentrations of SO_4^{2-} (Likens et al., 2001). In addition, there has been a long-
17 term decrease in stream concentrations of NO_3^- that is not correlated with a commensurate
18 change in emissions of NO_x or in bulk deposition of NO_3^- . The long-term declines in stream
19 concentrations of strong acids ($\text{SO}_4^{2-} + \text{NO}_3^-$; $-1.9 \mu\text{eq/L/yr}$) have resulted in small but
20 significant increases in pH, from 4.8 to 5.0 (Driscoll et al., 2007). Streams at HBEF remain
21 acidic compared to background conditions, when stream pH was estimated to be approximately
22 6.0 (Driscoll et al., 2007). The increase in stream pH has been limited because of marked
23 concurrent decreases in the sum of base cations ($-1.6 \mu\text{eq/L/yr}$; Driscoll et al., 2001b).

24 25 *AX4.3.3.3.1.4 Future Projections*

26 MAGIC model simulations were conducted for the NAPAP IA to forecast the response of
27 lakes and streams in the eastern United States to S deposition. Results were reported by NAPAP
28 (1991), Sullivan et al. (1992), and Turner et al. (1992). The projected median change in
29 lakewater or streamwater ANC during 50-year simulations was similar among regions, except in
30 the Southern Blue Ridge and Mid-Atlantic Highlands, where acidification was delayed due to
31 S adsorption on watershed soils. MAGIC projected relatively small future loss of ANC in most

1 northeastern watersheds under continued constant deposition. These modeled changes were due
2 to a simulated slight depletion of the supply of base cations from soils (Turner et al., 1992).

3 On average, each kg/ha/yr change in S deposition was projected by MAGIC to cause a
4 3 to 4 $\mu\text{eq/L}$ median change in surface water ANC. Such projected changes in ANC, while
5 considerably smaller than was generally thought to occur in the 1980s, nevertheless suggested
6 widespread sensitivity of surface water ANC to changes in S deposition throughout the
7 northeastern United States (Sullivan, 2000).

8 Since 1990, adjustments have been made to the MAGIC model and its application
9 method in response to model testing using paleolimnological data (Sullivan et al., 1992, 1996a)
10 and the results of acidification and deacidification experiments (Norton et al., 1992; Cosby et al.,
11 1995, 1996) and empirical studies (Sullivan and Cosby, 1998). The net effect has been that the
12 model projects somewhat less sensitivity of Adirondack lakes to change in S deposition as
13 compared with the version of MAGIC applied in 1990 (Sullivan and Cosby, 1998).

14 Model projections of future acid-base chemistry under three scenarios of future
15 atmospheric emissions controls were presented by Sullivan et al. (2006b) and Zhai et al. (2008)
16 for lakes in the Adirondack Mountains to evaluate the extent to which lakes might be expected to
17 continue to increase in ANC in the future. Estimated levels of S deposition at one representative
18 watershed are shown in Figure 4.3-6a for the hindcast period and in the future under the three
19 emissions control scenarios. Model simulations for 44 statistically selected Adirondack lakes
20 using the MAGIC and PnET-BGC models were extrapolated to the regional lake population.
21 Cumulative distribution frequencies of ANC response projected by MAGIC are shown in Figure
22 4.3-6b for the past (1850), peak acidification period (1990), and future (2100). Results for the
23 future are given for each of the scenarios.

24 Results suggested that the ongoing trend of increasing lakewater ANC for the most acid-
25 sensitive lakes would not continue under future emissions and deposition levels anticipated as of
26 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC below 20 and below
27 50 $\mu\text{eq/L}$ were projected to increase between 2000 and 2100 under that scenario, and the number
28 of chronically acidic Adirondack lakes (i.e., ANC less than 0) was projected to stabilize at the
29 level reached in 2000. This projected reversal of chemical recovery of acid-sensitive lakes was
30 due to a continuing decline in the simulated pool of exchangeable base cations in watershed
31 soils.

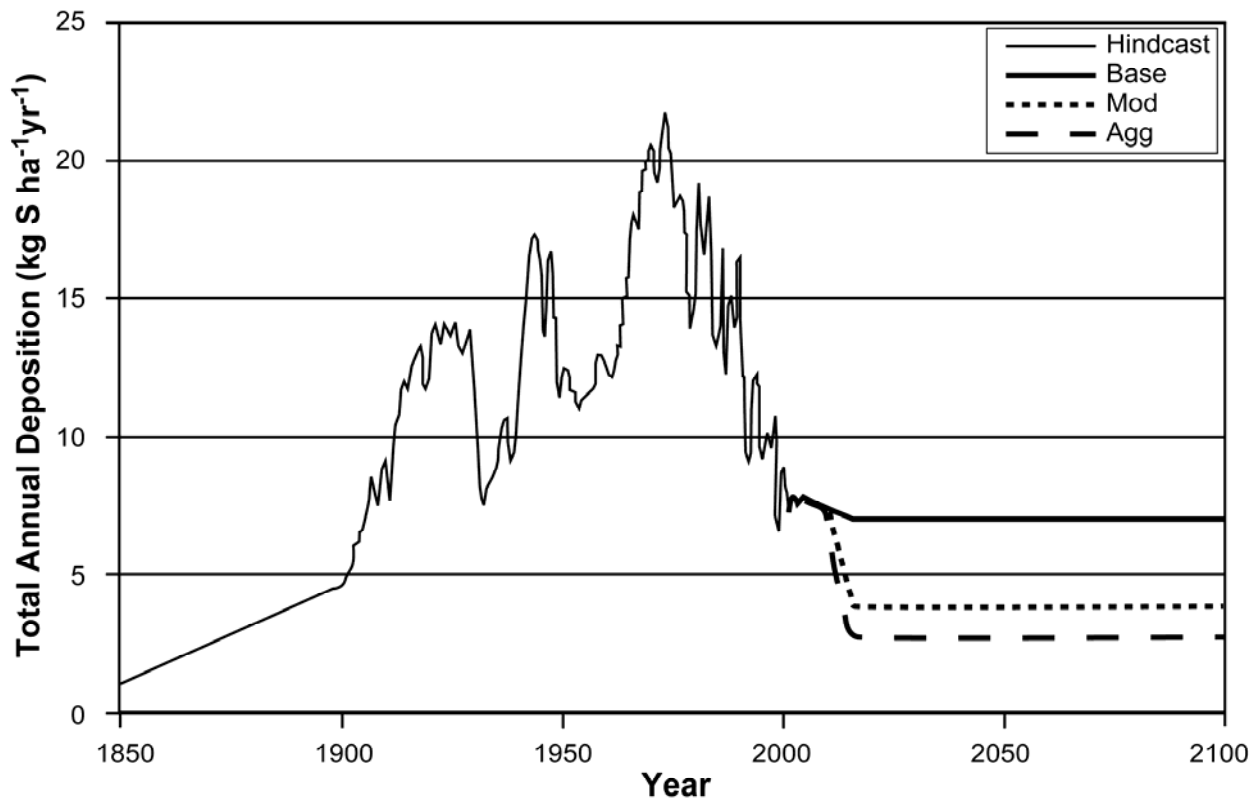


Figure AX4.3-6a. Estimated time series of S deposition at one example watershed in the SW Adirondack Mountains used by Sullivan et al. (2006) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidic deposition. Future deposition estimates were based on three emissions control scenarios (Base Case, Moderate Additional Controls, Aggressive Additional Controls).

Source: Sullivan et al. (2003).

- 1 Simulations suggested that re-acidification might be prevented with further reductions in
- 2 emissions and deposition.
- 3 Chen and Driscoll (2005) applied the PnET-BGC model to 44 EMAP lake watersheds in
- 4 the Adirondacks. PnET-BGC was used to predict the acid-base chemistry of soils and surface
- 5 waters, and to assess the fisheries status during pre-industrial conditions (~1850) and under three
- 6 future acidic deposition scenarios.

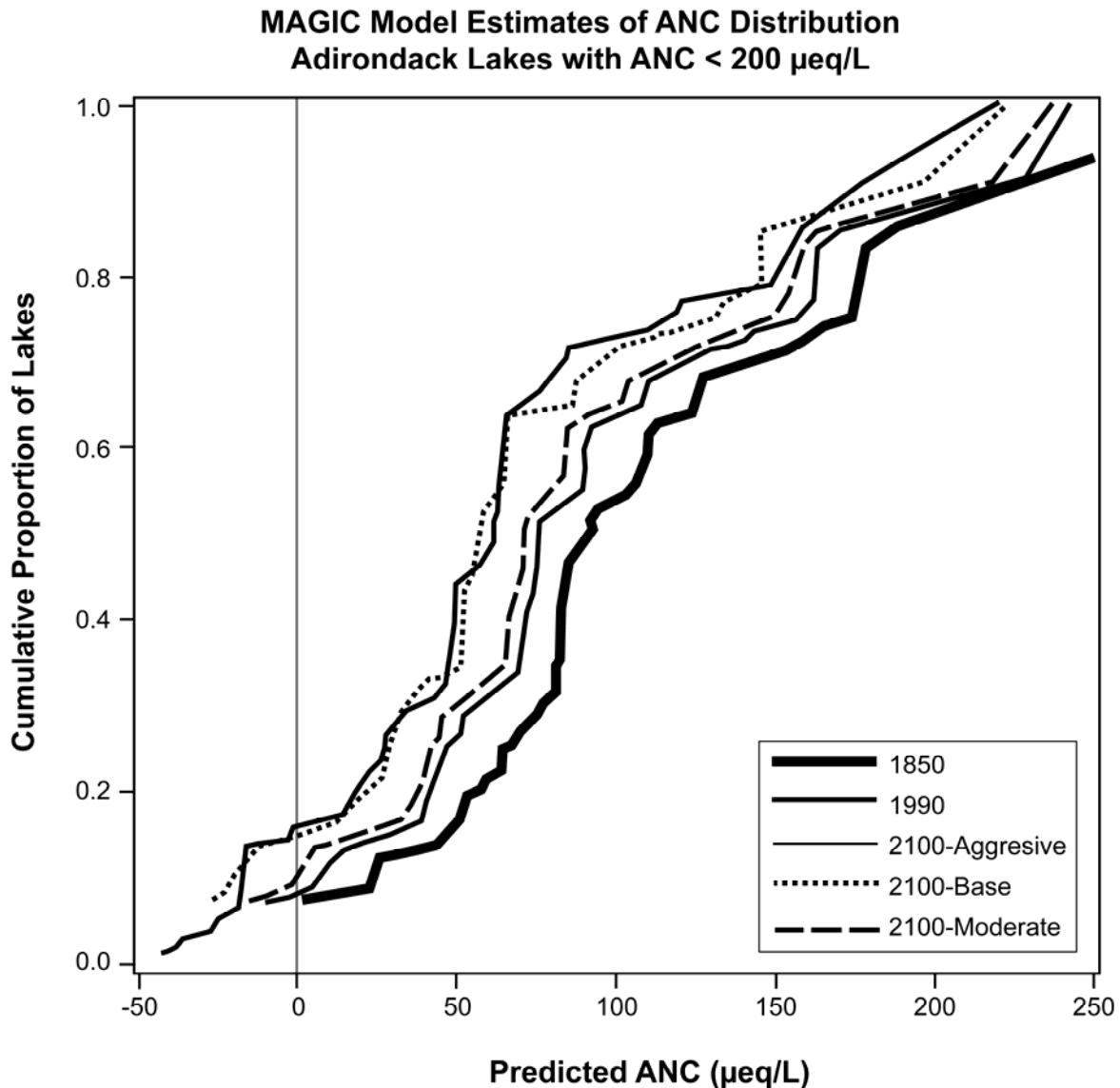


Figure AX4.3-6b. Simulated cumulative frequency distributions of lakewater ANC at three points in time for the population of Adirondack lakes.

Source: Sullivan et al. (2006b).

1 Model hindcasts using PnET-BGC indicated that acidic deposition has greatly altered
 2 surface waters and soils in the Adirondacks over the past 150 years, and that some ecosystems
 3 are continuing to acidify despite decreases in S deposition. The model was applied to three
 4 future emissions scenarios: base case, moderate emissions reductions, and aggressive emissions
 5 reductions. A case study for Indian Lake in the Adirondacks illustrated that larger reductions in

1 deposition caused greater decreases in SO_4^{2-} and base cation concentrations in stream water and
2 greater recovery in pH and ANC. Within the full population of lake-watersheds, some showed
3 decreasing ANC and pH values from 1990 to 2050 even under the moderate and aggressive
4 reduction scenarios. By 2050 to 2100, however, nearly all lakes experienced increasing ANC
5 and pH. The rate of soil base saturation regeneration increased very slowly over the modeled
6 time period, compared to changes in surface water chemistry. For 95% of the lake-watersheds
7 studied, simulated soil base saturation remained below 20% in 2100 under all emissions
8 scenarios.

9 There are few streams in the northeastern United States for which future acid-base
10 chemistry status has been modeled. One notable exception is the modeling conducted for
11 streams at the HBEF and in the Catskill Mountains. Calculations performed by Driscoll et al.
12 (2003c) using the PnET-BGC model suggested that “aggressive reductions in N emissions alone
13 will not result in marked improvements in the acid-base status of forest streams.” For example,
14 in response to an aggressive utility emissions control scenario (hypothesized 75% reduction in
15 utility N emissions beyond the CAAA), the ANC values of Watershed 6 at HBEF in New
16 Hampshire and Biscuit Brook in the Catskill Mountains in New York were only projected to
17 increase by 1 and 2 $\mu\text{eq/L}$, respectively, by the year 2050 (Driscoll et al., 2003c). Projected
18 changes in water chemistry in response to differing levels of N deposition were small in
19 comparison with model projections of variations resulting from climatic factors (Aber and
20 Driscoll, 1997; Driscoll et al., 2003c).

21 22 **AX4.3.3.4 Southeastern Surface Waters**

23 The two regions in the Southeast that were identified by Charles (1991) as containing
24 low-ANC surface waters are the Appalachian Mountains and Northern Florida. The
25 Appalachian Mountain region contains many streams that have low ANC, and it receives one of
26 the highest rates of acidic deposition in the United States (Herlihy et al., 1993). Streamwater
27 acid-base chemistry has been extensively studied in this region (e.g., Church et al., 1992; Herlihy
28 et al., 1993; Van Sickle and Church, 1995; Sullivan et al., 2002, 2003).

29 Northern Florida contains the highest percentage of acidic lakes of any lake population in
30 the United States (Linthurst et al., 1986a,b). Most lakes in Florida are located in marine sands
31 overlying carbonate bedrock and the Floridan aquifer, a series of limestone and dolomite

1 formations that underlies most of Florida. Most of the acidic and low-ANC lakes are located in
2 the Panhandle and north central lake districts.

3 The current status, past acidification and recent trends in surface waters chemistry for
4 both the Appalachian Mountains and northern Florida are discussed below.

5
6 **AX4.3.3.4.1** *Appalachian Mountains*

7
8 *AX4.3.3.4.1.1* *Current Status*

9 One of the most important processes affecting watershed acid-neutralization throughout
10 much of the Southeast is S-adsorption on soil. If S adsorption on soil is high, relatively high
11 levels of S deposition have little or no impact on stream acid-base chemistry, at least in the short-
12 term. However, this S-adsorption capacity can become depleted over time under continued
13 S deposition, and this causes a delayed acidification response.

14 Sulfur-adsorption varies by physiographic province. It is highest in the soils of the
15 Southern Blue Ridge, where typically about half of the incoming S is retained. Adsorption is
16 lower in the Valley and Ridge watersheds and especially in the Appalachian Plateau (Herlihy
17 et al., 1993). In general, S adsorption is higher in the southern portions of the Appalachian
18 Mountain region.

19 The Mid-Atlantic Highlands consists of the portions of the Blue Ridge Mountains, Ridge
20 and Valley, and Appalachian Plateau ecoregions between the Virginia-North Carolina border and
21 the Catskill Mountains in southeastern New York. Acid mine drainage (AMD) is a major source
22 of acidity to streams in the Mid-Atlantic Highlands but in many cases is easy to identify due to
23 the high concentrations of SO_4^{2-} in the streams that are influenced by AMD (Herlihy et al.,
24 1991). Acidic and low-ANC streams affected by AMD were removed before analyses of acid-
25 base chemistry population statistics.

26 Streams in the Appalachian Mountain portion of the mid-Atlantic region receive some of
27 the largest acidic deposition loadings of any region of the United States. A compilation of
28 survey data from the mid-Appalachians yields a consistent picture of the acid-base status of
29 streams. Acidic streams, and streams with very low ANC, are almost all located in small
30 (watershed area $< 20 \text{ km}^2$), upland, forested catchments in areas of base-poor bedrock. Acidic
31 surface waters in this region are nearly always found in forested watersheds because the thin

1 soils and steep slopes that make these watersheds unsuitable for agriculture and other
2 development also contribute to their sensitivity to acidic deposition (Baker et al., 1991a).

3 In the subpopulation of upland forested streams, which comprises about half of the total
4 stream population in the mid-Appalachian area, data from various local surveys showed that 5%
5 to 20% of the streams were acidic, and about 25 to 50% had ANC < 50 µeq/L (Herlihy et al.,
6 1993). NSS estimates for the whole region showed that there were 2330 km of acidic streams
7 and 7500 km of streams with ANC < 50 µeq/L. In these forested reaches, 12% of the upstream
8 reach ends were acidic and 17% had pH ≤5.5 (Table AX4.3-3). Sulfate from atmospheric
9 deposition was the dominant source of acid anions in acidic mid-Appalachian streams. In these
10 acidic streams, the low pH (median 4.9) and high levels of Al_i (median 129 µg/L) leached
11 through soils by acidic deposition were considered to be sufficiently high to cause damage to
12 aquatic biota. Acidic streams in this subpopulation typically had low DOC (mean 1.5 mg/L).

13 Localized studies have clearly shown that streamwater ANC is closely related to bedrock
14 mineralogy (Herlihy et al., 1993). Sullivan et al. (2007) delimited a high-interest area for
15 streamwater acidification sensitivity within the Southern Appalachian Mountain region
16 (Virginia/West Virginia to Georgia) based on geological classification and elevation. It covered
17 only 28% of the region, and yet included almost all known acidic and low ANC (<20 µeq/L)
18 streams, based on evaluation of about 1,000 streams for which water chemistry data were
19 available. They found that the vast majority of low ANC sample streams were underlain by the
20 siliceous geologic sensitivity class, which is represented by such lithologies as sandstone and
21 quartzite. Low ANC streamwater throughout the region was also found to be associated with a
22 number of watershed features in addition to lithology and elevation, including ecoregion,
23 physiographic province, soil type, forest type and watershed area.

24 Sulfate mass balance analyses indicated that, because of watershed SO₄²⁻ retention, soils
25 and surface waters of the region have not yet realized the full effects of elevated S deposition.
26 On average, based on NSS data, sites in the Blue Ridge Mountains retain 35% of incoming
27 SO₄²⁻ from atmospheric deposition. The amount of SO₄²⁻ retention was strongly related to
28 ecoregion in the order,

29 Piedmont > Blue Ridge and Ridge & Valley > Appalachian Plateau.

1 Herlihy et al. (1993) believed that the observed differences were due to the effects of cumulative
2 loadings from atmospheric S deposition and not due to inherent ecoregional differences in the
3 soils. They also concluded that S retention will likely continue to decrease in the future,
4 resulting in further losses of stream ANC.

5 Both mineral acids and organic acids play important roles in the acid-base status of
6 streams in the Mid-Atlantic Coastal Plain (Baker et al., 1991a). Acidic streams in the New
7 Jersey Pine Barrens (Figure AX4.3-2) are largely inorganically dominated, but most likely they
8 were naturally organically acidic in the past. It is uncertain what impact the addition of
9 inorganic acids from acidic deposition has had on these low ionic strength colored systems.
10 Over half the streams in the Pine Barrens included in the NSS were acidic, and virtually all
11 (96%) had ANC less than 50 $\mu\text{eq/L}$. Human disturbances in the Pine Barrens often result in the
12 alkalization of streams (increases in pH and ANC) that alter the natural Pine Barrens aquatic
13 biota. Outside of the Pine Barrens in the NSS, the remainder of the acidic streams in the Coastal
14 Plain were all high DOC organically dominated systems. Low DOC ($<4 \text{ mg/L}$), acidic streams
15 have been observed, however, in other Mid-Atlantic Coastal Plain surveys.

16 The Virginia Trout Stream Sensitivity Study (VTSSS) surveyed streamwater chemistry
17 for 344 (~80%) of the native brook trout (*Salvelinus fontinalis*) streams in western Virginia.
18 About half of the streams included in the VTSSS had ANC $< 50 \mu\text{eq/L}$. In contrast, the NSS
19 (Kaufmann et al., 1988) data for western Virginia suggested that only about 15% of the streams
20 in the NSS target population had ANC $< 50 \mu\text{eq/L}$. These differences may reflect the smaller
21 watershed size, more mountainous topography, and generally more inert bedrock of the VTSSS
22 watersheds, as compared with the overall NSS stream population.

23 In the Appalachian Plateau of West Virginia there are two wilderness areas located in
24 close proximity in an area of base-poor bedrock -- Dolly Sods and Otter Creek Wilderness Areas.
25 Most streams draining these wilderness areas are acidic or low in ANC.

26 In the Great Smoky Mountains National Park in North Carolina and Tennessee, Cook
27 et al. (1994) reported high NO_3^- concentrations (~100 $\mu\text{eq/L}$) in upland streams which were
28 correlated with elevation and forest stand age. The old growth sites at higher elevation showed
29 the highest NO_3^- concentrations. This pattern could have been due to the higher rates of
30 N deposition and flashier hydrology at high elevation, and also decreased N uptake by trees in

1 older forest stands. High N deposition at these sites has likely contributed to both chronic and
2 episodic acidification of streamwater (Flum and Nodvin, 1995; Nodvin et al., 1995).

3 4 *AX4.3.3.4.1.2 Recent Trends*

5 Population estimates from TIME surveys of streams in the Northern Appalachian Plateau
6 region suggested that 5014 km of streams (11.8% of the stream length) were acidic in 1993-94,
7 but that only 3600 km of streams (8.5% of the stream population) remained acidic in this region
8 in 2000. The approximate rate of estimated change in Gran ANC in the region (Table AX4.3-5)
9 was +0.79 $\mu\text{eq/L/yr}$. On this basis, Stoddard et al. (2003) estimated that roughly 3600 km of
10 stream (8.5%) remained acidic 10 years later. This represents about a 28% decrease in acidic
11 stream length over the preceding decade.

12 13 *AX4.3.3.4.1.3 Future Projections*

14 Model projections of future changes in acid-base chemistry of streams in the southeastern
15 United States were presented by Sullivan et al. (2002, 2003, 2005). In the eight-state Southern
16 Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric
17 S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for
18 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC
19 class. Simulations were based on assumed constant future atmospheric deposition at 1995 levels
20 and on three regional strategies of emissions controls provided by the Southern Appalachian
21 Mountains Initiative (SAMI), based on the Urban to Regional Multiscale One-Atmosphere
22 model (Odman et al., 2002).

23 The NSS statistical frame (Kaufmann et al., 1991) was used to estimate the number and
24 percentage of stream reaches in the region that were projected to change their chemistry in
25 response to the emissions control strategies. There was a small decline in the estimated length of
26 projected acidic ($\text{ANC} \leq 0$) streams in 2040 from the least to the most restrictive emissions
27 control strategy, but there was little difference in projected stream length in the other ANC
28 classes as a consequence of adopting one or another strategy. However, projections of continued
29 future acidification were substantially larger under a scenario in which S and N deposition were
30 held constant into the future at 1995 levels. Turner et al. (1992) also reported MAGIC model
31 simulation results that suggested substantial acidification ($\sim 20 \mu\text{eq/L}$) of aquatic systems would

1 occur in the southeastern United States if deposition remained constant at 1985 levels. Those
2 model analyses were conducted as part of the NAPAP (1991) IA.

3 The SAMI emissions control strategies used in the modeling represented air regulatory
4 requirements being implemented at the time of SAMI's formation, expected reductions under
5 recent federal regulatory actions, and additional emissions controls applied to all emissions
6 sectors in the eight SAMI states. The spatial variability of these emissions controls resulted in
7 varying estimated future changes in S and N deposition at different locations within the SAMI
8 region. The SAMI strategies were designated A2, B1, and B3. A2 is the reference strategy that
9 represented SAMI's best estimates for air emission controls under regulations for which
10 implementation strategies were relatively certain at the time of the study (about the year 2000).
11 Emissions reductions under the A2 strategy included the acid rain controls under Title IV of the
12 1990 Amendments to the CAAA, the 1-h O₃ standard, NO_x reductions required under EPA's call
13 for revised State Implementation Plans (Sips), and several highway vehicle and fuel reductions.
14 The A2 strategy was applied for all eastern states and focused on the utility and highway vehicle
15 sectors. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted
16 only to the eight SAMI states but covering all emissions sectors.

17 Streams exhibited a broad range of response to the cumulative S deposition loadings
18 received to date and the large simulated decreases in S deposition in the future under the
19 emissions control strategies (Figure AX4.3-7). Some streams showed modeled stream water
20 SO₄²⁻ concentrations increasing in the future, even while S deposition was reduced by more than
21 two-thirds. These were mostly sites that had relatively low SO₄²⁻ concentrations in 1995
22 (≤ about 50 µeq/L) because of S adsorption on soils. They generally showed simulated future
23 acidification, which was most pronounced for the A2 strategy. Other streams were simulated to
24 show relatively large decreases in future stream water SO₄²⁻ concentrations and concurrent
25 increases in ANC in response to the strategies, with progressively larger changes from the A2 to
26 the B3 strategy. These tended to be streams that had relatively high concentrations of SO₄²⁻
27 (>50 µeq/L) in 1995, suggesting that they were closer to steady state with respect to S inputs and
28 outputs. Some streams were projected to exhibit future decreases in both SO₄²⁻ and NO₃⁻
29 concentrations but nevertheless to continue to acidify. This response was attributed by Sullivan
30 et al. (2004) to large simulated decreases in base cation concentrations at these sites due to soil
31 base cation depletion.

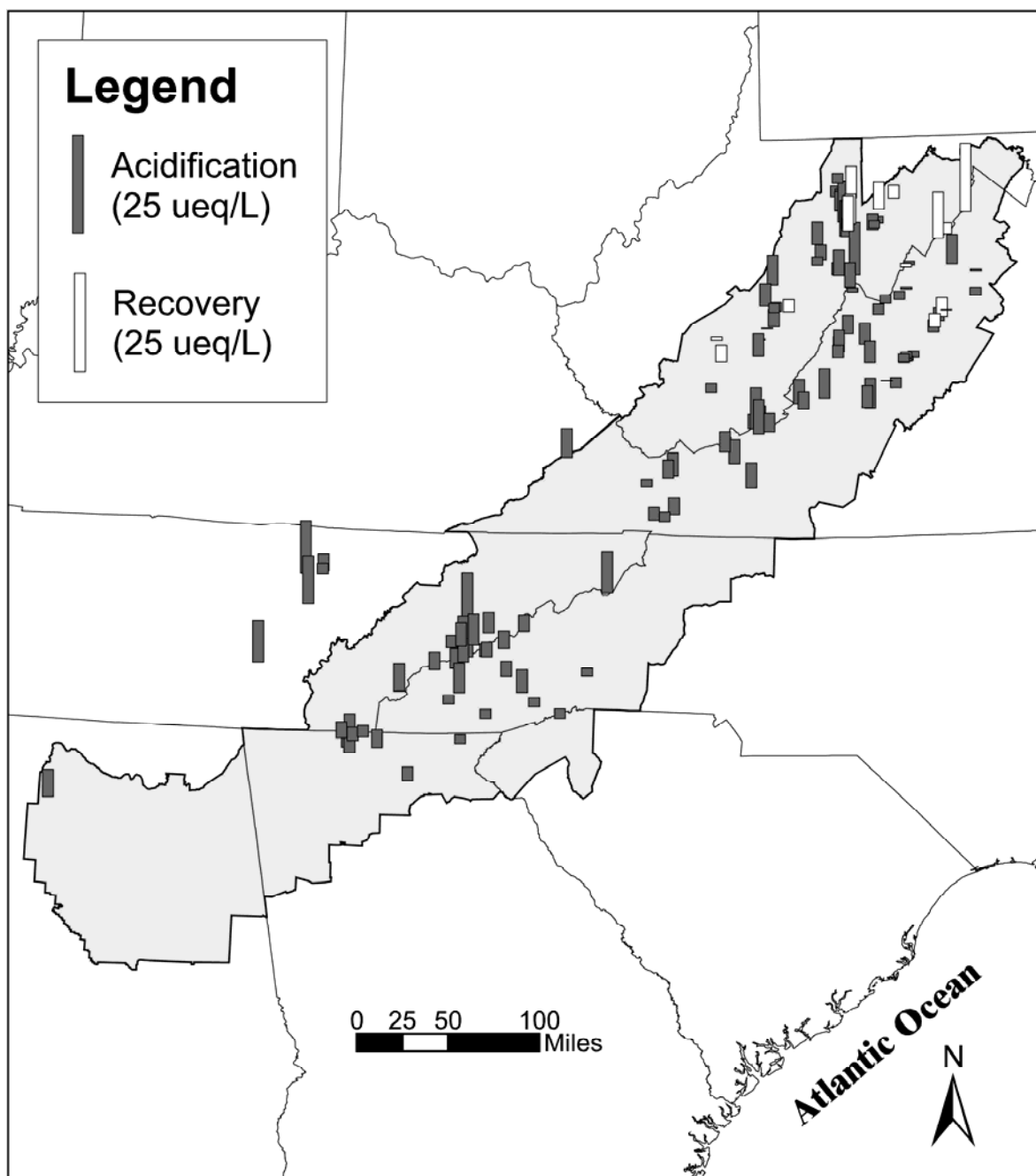


Figure AX4.3-7. Map showing simulated changes in streamwater ANC from 1995 to 2040 in response to the SAMI A2 emissions control strategy, representing existing emissions control regulations.

Source: Sullivan et al. (2004).

1 Most simulated changes in stream water ANC from 1995 to 2040 were rather modest
2 (Table AX4.3-7), given the very large estimates of decreased S deposition. Few modeled
3 streams showed projected change in ANC of more than about 20 µeq/L. Some of the largest
4 changes were simulated for some of the streams that were most acidic in 1995. For such
5 streams, however, even relatively large increases in ANC would still result in negative ANC
6 stream water, and therefore little biological benefit would be expected from the simulated
7 improvement in chemistry. The model results suggested, however, that benefits would continue
8 to accrue well beyond 2040 for all strategies, even if deposition was held constant at 2040 levels
9 into the future.

10 11 **AX4.3.3.4.2 Florida Surface Waters**

12 13 *AX4.3.3.4.2.1 Current Status*

14 According to the ELS survey conducted in 1984, 75% of the Florida Panhandle lakes
15 were acidic at that time, as were 26% of the lakes in the northern peninsula. Most of the acidic
16 lakes were clearwater (DOC < 400 µmol) seepage lakes in which the dominant acid anions were
17 Cl⁻ and SO₄²⁻. Most of the acidic and low-ANC lakes are located in the Panhandle and north
18 central lake districts. In these areas, the Floridan aquifer is separated from overlying sand
19 deposits by a confining layer called the Hawthorne formation. The major lake districts are
20 located in karst terrain, where lakes formed through dissolution of the underlying limestone
21 followed by movement of surficial deposits into solution cavities (cf. Arrington et al., 1987).

22 Flow of water from most of the lakes is downward, recharging the Floridan aquifer. Lake
23 stage varies in response to long-term trends in precipitation, and perhaps in response to
24 groundwater withdrawals. ANC generation in most lakes that have been studied appears to be
25 due primarily to in-lake SO₄²⁻ and NO₃⁻ reduction (Baker et al., 1988; Pollman and Canfield,
26 1991). Retention of SO₄²⁻ by watershed soils may also be important. Lakes can be highly
27 alkaline where groundwater interacts with the deeper aquifer. Lakes with hydrologic
28 contributions from shallow aquifers in highly weathered sands can be quite acidic and may be
29 sensitive to acidic deposition.

30 DOC concentrations are high in many Florida lakes, but organic anions are less important
31 than SO₄²⁻ in most low-ANC and acidic lakes (Pollman and Canfield, 1991). Aluminum
32 concentrations tend to be very low in Florida lakes despite the high lakewater acidity because

1 most of the Al^{3+} is removed from soil solution by precipitation and ion exchange reactions within
2 75 cm depths (Grates et al., 1985), and relatively little Al^{3+} is transported in groundwater to lake
3 waters.

4 Baker et al. (1988) reported that retention of inorganic N is nearly 100% in most Florida
5 lakes. ANC generation from SO_4^{2-} retention may approach 100 $\mu\text{eq/L}$ in some Florida lakes
6 (Pollman and Canfield, 1991). These in-lake processes are important for generating ANC. Base
7 cation deposition and NH_4^+ assimilation can also influence the acid-base status of lakes in
8 Florida.

9 The Northern Florida Highlands high interest area identified by Baker et al. (1991a)
10 consists of the northern portion (north of 29°N latitude) of the Central Lake District and the
11 Florida Panhandle (Figure AX4.3-2). Acidic streams were located in the Florida Panhandle
12 and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-corrected
13 SBC (mean 21 $\mu\text{eq/L}$) and sea salt corrected SO_4^{2-} concentrations (mean 16 $\mu\text{eq/L}$). One-fourth
14 of these acidic Panhandle streams were organic-dominated but the remaining sites all had
15 $\text{DOC} < 2 \text{ mg/L}$ and were inorganically dominated. Inorganic monomeric Al concentrations in
16 these acidic streams were very low (mean 11 $\mu\text{g/L}$). In these low DOC, low ANC Panhandle
17 streams, it was suggested that the degree of SO_4^{2-} and NO_3^- retention was an important control
18 on streamwater ANC (Baker et al., 1991a).

19
20 *AX4.3.3.4.2.2 Past Acidification*

21 Considerable research has been conducted on past acidification in Florida lakes.
22 Historical analyses of lake chemistry (Battoe and Lowe, 1992), inferred historical deposition
23 (Hendry and Brezonik, 1984; Husar and Sullivan, 1991), and paleolimnological reconstructions
24 of lake pH (Sweets et al., 1990; Sweets, 1992) suggest evidence that some Florida lakes have
25 acidified in response to acidic deposition. However, the role of acid deposition in lakewater
26 acidification is not entirely clear (cf. Pollman and Canfield, 1991), and the interpretation is
27 complicated by regional and local changes in land use and hydrology (Sullivan, 2000).

28 An alternative explanation for the apparent acidification of some lakes is the regional
29 decline in the potentiometric surface of the groundwater (Sweets et al., 1990). Large
30 groundwater withdrawals of the Floridan aquifer for residential and agricultural purposes may
31 have reduced groundwater inflow of base cations into seepage lakes, and therefore caused less

1 buffering of acidity. Other land use changes may have increased lake pH by providing inputs of
2 fertilizer, which would increase lake productivity. Paleolimnological evidence of this effect was
3 provided by Brenner and Binford (1988) and Deevey et al. (1986).

4 It is likely that lake chemistry in Florida has been heavily impacted by land use changes.
5 More than half of the Florida lakes included in the ELS showed evidence of disturbance based on
6 deviations from expected geochemistry (Pollman and Canfield, 1991). Such impacts complicate
7 efforts to determine the role of acidic deposition in controlling lakewater acid-base chemistry.

8 Diatom-inferred pH reconstructions of lakewater chemistry of six seepage lakes in
9 Florida were calculated as part of the PIRLA-I project and reported by Sweets et al. (1990). An
10 additional 10 seepage lakes were cored as part of PIRLA-II, and results of those analyses were
11 reported by Sweets (1992). Paleolimnological study lakes are located in the Panhandle, the Trail
12 Ridge Lake District, and Ocala National Forest, generally in terraces of highly weathered loose
13 sand that were deposited on top of the clay-confining layer.

14 Of the six lakes analyzed in PIRLA-I, two (Barco and Suggs) were inferred to have
15 acidified since 1950 (Sweets et al., 1990). The timing of the onset of inferred acidification
16 correlated with increases in SO₂ emissions and S deposition, which increased consistently
17 between about 1945 and 1985 (Husar and Sullivan, 1991).

18 Of the 16 Florida seepage lakes studied in the PIRLA-II projects, 5 were located in or
19 near the Trail Ridge Lake District, and all showed diatom-inferred acidification of at least 0.2 pH
20 units (Sweets, 1992). Lakes located in the Panhandle region and Ocala National Forest generally
21 did not show evidence of recent acidification. The exception was Lake Five-O, which was
22 inferred to have decreased by 2 pH units. However, the diatom data suggested that this pH
23 decline was associated with a sudden change in chemistry, probably caused by a catastrophic
24 disturbance such as sinkhole development, rather than by acidification from atmospheric
25 deposition (Pollman and Sweets, 1990; Sweets, 1992).

26 27 **AX4.3.3.5 Upper Midwest**

28 The Upper Midwest contains numerous lakes created by glaciation. The region has little
29 topographic relief and with its deep glacial overburden, it also has little or no exposed bedrock.
30 Acid-sensitive surface waters in the Upper Midwest are mainly seepage lakes (Eilers et al.,
31 1983). Most drainage lakes and some of the seepage lakes in the Upper Midwest region receive
32 substantial inflow from groundwater, which is generally high in base cation concentrations from

1 dissolution of carbonate and silicate minerals. Relatively high concentrations of base cations in
2 these lakes make them insensitive to acidification from acidic deposition. The seepage lakes that
3 have low base cation concentrations, and that are therefore more acid-sensitive, generally receive
4 most of their water input from precipitation directly on the lake surface (Baker et al., 1991b).

5 6 **AX4.3.3.5.1 Current Status**

7 Based on the ELS survey, the Upper Midwest has a large population of low ANC lakes,
8 but relatively few chronically acidic ($\text{ANC} \leq 0$) lakes (Linthurst et al., 1986a,b). Acidic lakes in
9 the Upper Midwest are primarily small, shallow, seepage lakes that have low concentrations of
10 base cations and Al and moderate SO_4^{2-} concentrations. Organic anions, estimated by both the
11 Oliver et al. (1983) method and the anion deficit, tend to be less than half the measured SO_4^{2-}
12 concentrations in the acidic lakes (Eilers et al., 1988), but much higher in many of the drainage
13 lakes that are less sensitive to acidification from acidic deposition.

14 Groundwater flow-through lakes in the Upper Midwest can be identified on the basis of
15 having Si concentration greater than about 1 mg/L (Baker et al., 1991b). They generally have
16 high pH and ANC, due to groundwater inputs of base cations (e.g., Baker et al., 1991b). Based
17 on results from the ELS survey, only 6% of these lakes had $\text{ANC} \leq 50 \mu\text{eq/L}$ and none were
18 acidic. Groundwater recharge lakes (those having Si concentration less than 1 mg/L) constituted
19 71% of the seepage lakes in the Upper Midwest, and were more frequently low pH and ANC.
20 Five percent were acidic and 9% had $\text{pH} \leq 5.5$. Nearly 90% of Upper Midwestern lakes that had
21 $\text{ANC} \leq 50 \mu\text{eq/L}$ were in this category (Baker et al., 1991b). Such lakes tend to be susceptible to
22 acidification from acidic deposition.

23 Sullivan (2000) summarized patterns in lakewater chemistry across the Upper Midwest
24 from the ELS survey. Lakewater pH, ANC, base cations, and DOC all decreased from west to
25 east across the region. Lakewater SO_4^{2-} concentrations did not show a comparable change,
26 despite a substantial increase in wet SO_4 deposition from Wisconsin to Michigan. Cook and
27 Jager (1991) attributed the absence of a more pronounced gradient in lakewater SO_4^{2-}
28 concentration across the region to watershed sources of S in Minnesota and high anion retention
29 in seepage lakes, which predominate in the eastern portion of the region. The retention of SO_4^{2-}
30 by dissimilatory reduction is generally high for seepage lakes because of their long hydraulic
31 retention times (τ_w). For example, an Upper Midwestern seepage lake with mean depth of 3 m

1 and hydraulic retention time of 7.5 years would be expected to lose about 50 $\mu\text{eq/L}$ of SO_4^{2-}
2 from the water column by this process (Cook and Jager, 1991).

3 Lakewater concentrations of inorganic N reported by the ELS were low throughout
4 the Upper Midwest. In addition, snowmelt would not be expected to provide any significant
5 NO_3^- influx to lakes in the Upper Midwest because most snowmelt infiltrates the soil before
6 reaching the drainage lakes, and because snowmelt input of N into seepage lakes would be
7 limited mainly to the snow on the lake surface and immediate near-shore environment.
8 Aluminum concentrations are far lower in the Upper Midwest than in lakes of similar pH in the
9 Northeast.

10 Wetlands are common throughout the Upper Midwest. They contribute to high
11 production of organic matter which is reflected in high DOC concentrations in many lakes.
12 Despite the abundant wetlands, SO_4^{2-} is the dominant anion in the low-ANC ($\leq 50 \mu\text{eq/L}$)
13 groundwater recharge seepage lakes.

14 Base cation production is the dominant ion-enrichment process in most Upper
15 Midwestern lakes. Even in low-ANC groundwater-recharge seepage lakes, base cation
16 production accounts for 72% to 86% of total ANC production (Cook and Jager, 1991).

17 18 ***AX4.3.3.5.2 Past Acidification***

19 Space-for-time substitution analysis was used to infer the general levels of past change in
20 lake water acid-base chemistry in the Upper Midwest. Such an analysis assumes that study lakes
21 were generally similar in acid-base chemistry prior to the onset of acidic deposition and that the
22 only substantial driver of recent change in acid-base chemistry has been the level of acidic
23 deposition. Across an increasing S depositional gradient from eastern Minnesota eastward to
24 eastern Michigan, ANC expressed as $(\text{HCO}_3^- - \text{H}^+)$ decreased and the ratio SO_4^{2-} to SBC
25 increased in the groundwater recharge seepage lakes. In Michigan and Wisconsin, many lakes
26 had $\text{SO}_4^{2-} > \text{SBC}$, indicating that the acidity was due to high SO_4^{2-} relative to SBC
27 concentration. There were also many lakes that had high concentrations of DOC, and organic
28 acidity probably accounted for many of these lakes having $\text{ANC} < 0$. The spatial pattern in
29 $(\text{HCO}_3^- - \text{H}^+)$ could not be attributed to DOC, which generally showed a decreasing trend with
30 increasing acidic deposition.

1 The concentration of lakewater ($\text{Ca}^{2+} + \text{Mg}^{2+}$) also decreased with increasing acidic
2 deposition, probably due to lower levels of base cation deposition and greater amounts of
3 precipitation in the eastern portion of the region. Atmospheric deposition is an important source
4 of base cations for groundwater recharge seepage lakes because of minimal groundwater inputs.
5 In the eastern portion of the region, such lakes are more sensitive to pH and ANC depression in
6 response to either elevated SO_4^{2-} or DOC. The spatial patterns for low ANC groundwater
7 recharge lakes in the Upper Midwest are consistent with the following hypotheses (Sullivan,
8 1990, 2000):

- 9 1. Sensitivity to mineral and organic acidity increased from west to east because of
10 decreasing lakewater base cation concentrations, and this may have been due, in
11 part, to changes in base cation deposition and precipitation volume along this
12 gradient.
- 13 2. High concentrations of DOC were responsible for the acidic conditions in some of
14 the lakes, and DOC may have decreased in response to acidic deposition.
- 15 3. Many of the lakes in eastern Michigan, and some in Wisconsin, were acidic
16 because of high SO_4^{2-} relative to base cation concentration, and had probably
17 been acidified by acidic deposition.

18 Diatom-inferred pH reconstructions were completed for 15 lakes in the Upper Midwest
19 region, and summarized by Kingston et al. (1990) and Cook and Jager (1991). Four lakes, all of
20 which had measured $\text{pH} < 5.7$, showed a diatom-inferred pH decline of 0.2 to 0.5 pH units
21 during the preceding 50 to 100 years. Diatom-inferred pH increased in one lake by 0.2 pH units.
22 No change was inferred for the other 10 lakes, including 4 lakes with $\text{pH} > 6.0$. No major,
23 recent, regional acidification was indicated by the diatom-inferred pH reconstructions. Inferred
24 changes in most lakes were small, and were no greater during the industrial period than during
25 the pre-industrial period (Sullivan, 2000).

26 Although diatom data suggested that some Upper Midwestern lakes may have acidified
27 since pre-industrial times, there is little paleolimnological evidence indicating substantial
28 widespread acidification in this region (Cook et al., 1990; Kingston et al., 1990). Land use
29 changes and other human disturbances of Upper Midwestern lakes and their watersheds have
30 probably exerted more influence on the acid-base chemistry of lakes than has acidic deposition
31 (Kingston et al., 1990; Sullivan, 1990, 2000). The portion of the region most likely to have
32 experienced acidification from acidic deposition is the Upper Peninsula of Michigan, where
33 acidic seepage lakes are particularly numerous (Baker et al., 1991a); acidic deposition is highest

1 for the region, and the $[\text{SO}_4^{2-}]/[\text{SBC}]$ ratio is commonly >1.0 . The percentage of acidic lakes in
2 the eastern portion of the Upper Peninsula of Michigan (east of longitude 87°) was estimated to
3 be 18% to 19% in 1984 (Schnoor et al., 1986; Eilers et al., 1988).

4 5 **AX4.3.3.5.3 Recent Trends**

6 Regional trend values for long-term monitoring lakes during the period 1990 to 2000
7 suggested that SO_4^{2-} declined in lakewater by $3.63 \mu\text{eq/L/yr}$, whereas lakewater NO_3^-
8 concentrations were relatively constant. The large decrease in SO_4^{2-} concentration was mainly
9 balanced by a large decrease in base cation concentrations ($-1.42 \mu\text{eq/L/yr}$) and an increase in
10 ANC ($+1.07 \mu\text{eq/L/yr}$). All of these trends were significant at $p < 0.01$ (Stoddard et al., 2003).
11 In the Upper Midwest, an estimated 80 of 251 lakes that were acidic in the mid-1980s were no
12 longer acidic in 2000. This change may be due to reduced levels of S deposition (Stoddard et al.,
13 2003).

14 15 **AX4.3.3.6 West**

16 Portions of the mountainous West contain large areas of exposed bedrock, with little soil
17 or vegetative cover to neutralize acidic inputs. This is particularly true of alpine regions of the
18 Sierra Nevada, northern Washington Cascades, the Idaho batholith, and portions of the Rocky
19 Mountains in Wyoming and Colorado. However, the percentage of exposed bedrock in a
20 watershed does not always indicate acid-sensitivity. If the bedrock contains even small deposits
21 of calcareous minerals or if physical weathering such as that caused by glaciers causes a high
22 production of base cations within the watershed (Drever and Hurcomb, 1986), surface waters
23 may be alkaline, and are not sensitive to acidification from acidic deposition.

24 The areas that are sensitive to adverse effects from acidic deposition in the western
25 United States form two nearly continuous ranges, the Sierra Nevada, which extends through
26 most of the length of California, and the Cascade Mountains, which extend from northern
27 California to northern Washington (Figure AX4.3-8). The sensitivity of the Rocky Mountains
28 varies widely because the ranges are discontinuous with highly variable geological composition.
29 For that reason, assessments of the sensitivity of Rocky Mountain aquatic resources to
30 acidification should be specific to individual ranges (Turk and Spahr, 1991).

31 The NAPAP SOS/T Reports and the IA (NAPAP, 1991) provided only a cursory
32 treatment of aquatic effects issues in the West, largely because it was well known that

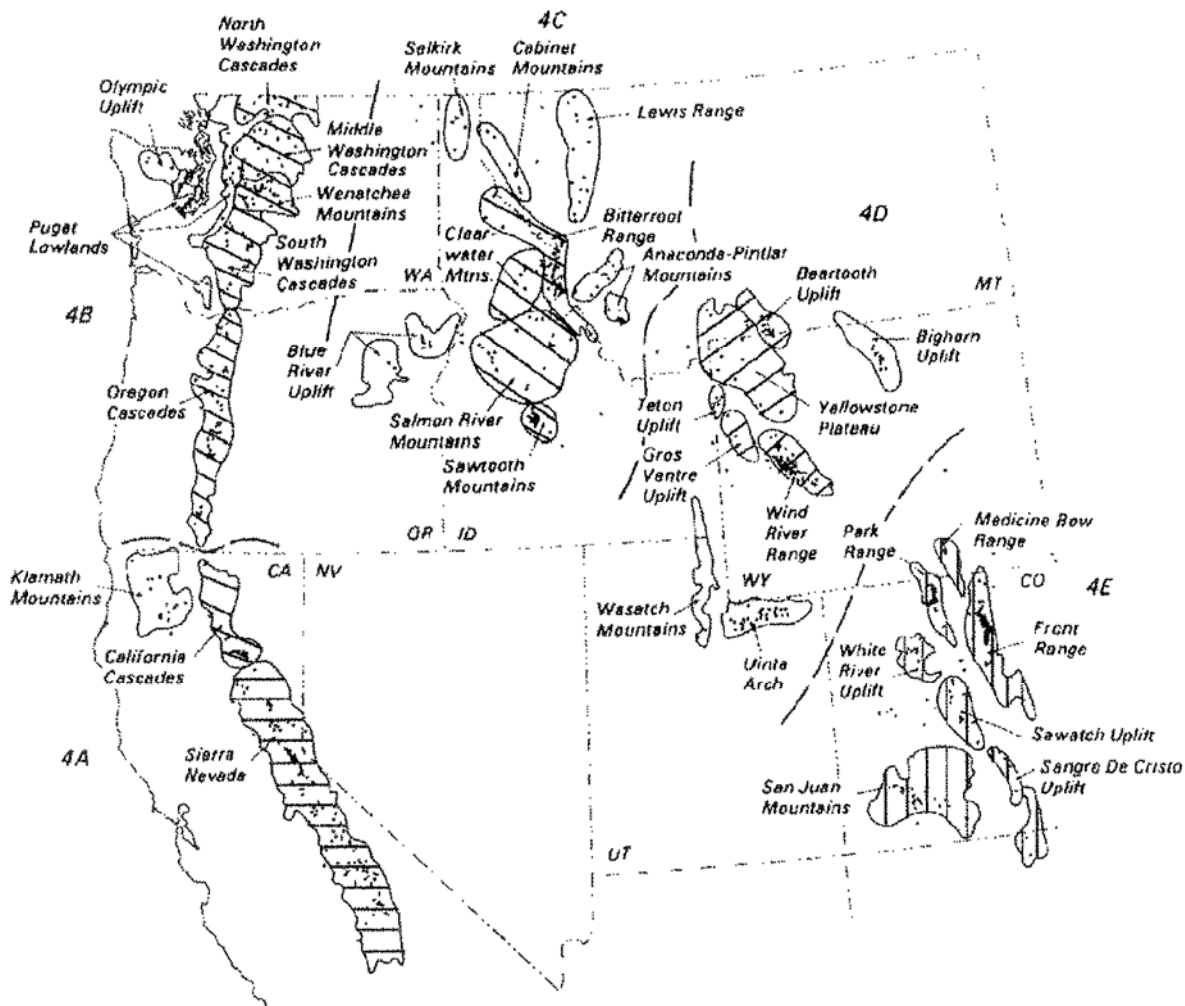


Figure AX4.3-8. Major geomorphic units and locations of lakes sampled in the Western Lake Survey. Those areas known to contain sensitive lake resources are shaded with cross-hatching.

Source: Landers et al. (1987).

1 atmospheric deposition of S and N were generally low compared to highly affected areas in the
 2 East (Sullivan, 2000) and because results from the WLS (Landers et al., 1987) indicated that
 3 there were virtually no acidic ($ANC \leq 0$) lakes in the West. NAPAP (1991) indicated, however,
 4 that high-elevation areas of the West contained many of the watersheds most sensitive to the
 5 potential effects of acidic deposition.

6 Because of the proximity of western urban and industrial pollution sources to individual
 7 mountain ranges, it is important to consider emissions in the immediate vicinity of sensitive

1 resources as well as regional emissions. Atmospheric deposition in the far western ranges (i.e.,
2 Sierra Nevada, Cascade Mountains) is largely influenced by local emissions, particularly
3 emission sources to the west (upwind) of sensitive resources. In the Rocky Mountains,
4 deposition chemistry is often influenced by a more complex collection of emission sources. For
5 example, in the Mt. Zirkel Wilderness of northwestern Colorado, SO_4^{2-} and NO_3^- in the snow
6 appeared to originate largely from sources in the Yampa Valley, about 75 km to the west (Turk
7 et al., 1992). Rocky Mountain National Park is affected by emissions from the Front Range to
8 the southeast.

9 The acid base chemistry of lake and stream waters in Rocky Mountain National Park
10 appears to be primarily a function of the interactions among several key parameters and
11 associated processes: atmospheric deposition, bedrock geology, the depth and composition of
12 surficial deposits and associated hydrologic flowpaths, and the occurrence of soils, tundra, and
13 forest vegetation (Sullivan, 2000). Potential biological effects of acidic deposition on lakes in
14 the Rocky Mountains are primarily attributable to acidification from high NO_3^- concentration.
15 In general, such effects tend to be episodic, rather than chronic. Highest NO_3^- concentrations in
16 both precipitation and surface waters are found above timberline in Colorado, where biological
17 activity, and therefore NO_3^- uptake, by terrestrial and aquatic biota is lowest.

18
19 **AX4.3.3.6.1 Current Status**

20 The available information on acid-base chemistry of surface waters in the West is based
21 mostly on synoptic data from the WLS (Landers et al., 1987) and some more localized studies.
22 Acid anion concentrations in most western lakes are low during fall, but can be higher during
23 snowmelt (Williams and Melack, 1991). Available data from intensive study sites in the West
24 (e.g., Loch Vale, CO, Emerald Lake Basin, CA, and the Glacier Lakes Watershed, WY) suggest
25 that episodic depression of stream pH may be more pronounced than for lakes. However, there
26 are no available systematic regional stream chemistry data with which to assess regional
27 sensitivity of streams to acidic deposition.

28 In most western lakes concentrations of SO_4^{2-} are low, although watershed sources of
29 S are substantial in some cases (Table AX4.3-8). Turk and Spahr (1991) presented a conceptual
30 model for expected SO_4^{2-} distributions in lakewaters in the West that can be used as an aid in
31 identifying the proportion of watersheds with significant watershed sources of S. Considering

1 that atmospheric sources can account for generally $< 30 \mu\text{eq/L}$ of SO_4 in the West, it appears that
 2 many lakes, particularly in Colorado, receive variable amounts of watershed S (Sullivan, 2000;
 3 Figure AX4.3-9).

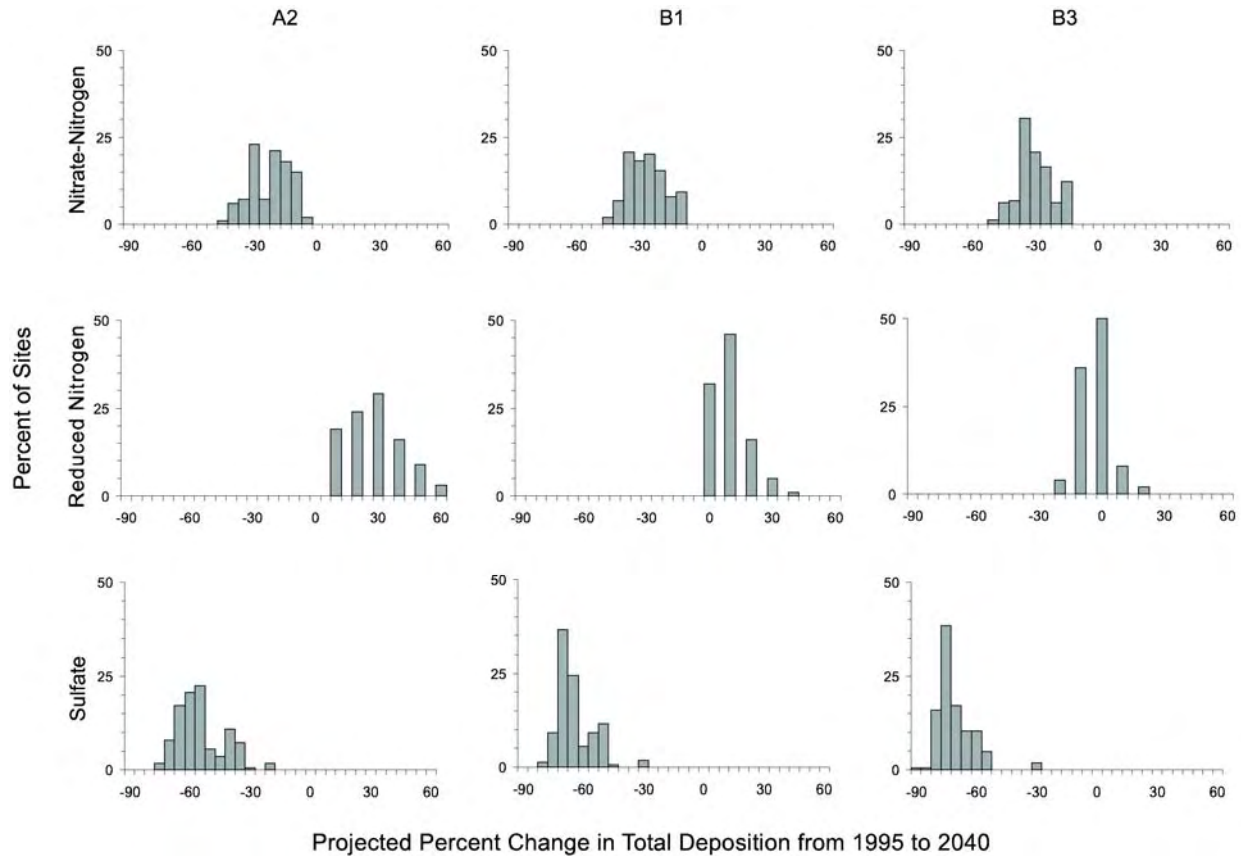


Figure AX4.3-9. Estimated percent changes in the total deposition of sulfur, reduced nitrogen, and nitrate-nitrogen at MAGIC modeling sites from 1995 to 2040 under each of the emissions control strategies.

Source: Sullivan et al. (2004).

4 Nitrate concentrations in most WLS lakes were near 0 during fall (Landers et al., 1987),
 5 although fall NO_3^- concentrations were high in some cases (Table AX4.3-8). For example,
 6 nearly one fourth of the lakes in northwest Wyoming had $\text{NO}_3^- > 5 \mu\text{eq/L}$ and almost 10% had
 7 $\text{NO}_3^- > 10 \mu\text{eq/L}$ (Table AX4.3-9). In both the Sierra Nevada and Colorado Rockies subregions,
 8 about 10% of the lakes had fall NO_3^- concentrations above $5 \mu\text{eq/L}$ (Table AX4.3-9).

1 It is important to note that even low to moderate concentrations of NO_3^- in western lakes might
2 be significant in view of: (1) the low base cation concentrations in many lakes; (2) potential for
3 continuing N deposition to eventually exhaust natural assimilative capabilities; and (3) the fact
4 that these distributions are based on fall data. Time-intensive discharge and chemical data for
5 two alpine streams in Loch Vale watershed identified strong seasonal control on streamwater
6 NO_3^- concentrations (Campbell et al., 1995). In spite of the paucity of soil cover, the chemical
7 composition of streams is regulated much as in typical forested watersheds. Soils and other
8 shallow groundwater matrices such as boulder fields are more important in controlling surface
9 water chemistry than their abundance would indicate. Spring streamwater NO_3^- concentrations
10 ranged to 40 $\mu\text{eq/L}$, compared with summer minimum values near 10 $\mu\text{eq/L}$. Elution of acidic
11 waters from snowpack along with dilution of base cations originating in shallow groundwater
12 caused episodes of decreased ANC in alpine streams (Campbell et al., 1995). A subalpine
13 stream in the same watershed similarly displayed decreased ANC and elevated monomeric Al
14 concentrations during snowmelt over 2 years of intensive sampling, related to elevated
15 concentrations of SO_4^{2-} , NO_3^- , and DOC (Denning et al., 1991). Limited data collected during
16 snowmelt suggest that spring concentrations could be several times higher than samples collected
17 during the fall (e.g., Reuss et al., 1995).

18 The surface water chemistry data for the West indicate that the Sierra Nevada and
19 Cascade Mountains constitute the mountain ranges with the greatest number of sensitive
20 resources (Tables AX4.3-8 and AX4.3-9). Lakes in the Sierra Nevada are especially sensitive to
21 impacts from acidic deposition because of the predominance of granitic bedrock, thin acidic
22 soils, large amounts of precipitation, coniferous vegetation, and dilute nature of the lakes
23 (Melack et al., 1985; Melack and Stoddard, 1991). Surface waters in this region are among the
24 poorly buffered surface waters in the United States (Landers et al., 1987; Melack and Stoddard,
25 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute,
26 mildly acidic (pH about 5.5) snowpack.

27 During the 1980s, an Integrated Watershed Study (IWS) was conducted at seven lakes in
28 the Sierra Nevada, including Emerald Lake and surrounding watersheds (~3,000 m elevation) to
29 determine the effects of acidification on surface waters (Tonnessen, 1991). Three lakes (Lost,
30 Pear, and Emerald) had volume-weighted mean ANC in the range of 15 to 30 $\mu\text{eq/L}$. Moderate

1 ANC waters (Topaz, Spuller, and Marble Fork) exhibited mean ANC in the range of 30 to
2 50 $\mu\text{eq/L}$. Crystal and Ruby Lakes had mean annual ANC $> 50 \mu\text{eq/L}$.

3 Many Cascade and Rocky Mountain lakes are also highly sensitive to potential acidic
4 deposition effects (Nelson, 1991; Turk and Spahr, 1991). It does not appear that chronic
5 acidification has occurred to any significant degree, although episodic acidification has been
6 reported for lakes in the Colorado Front Range (Williams and Tonnessen, 2000). The data that
7 would be needed for determining the extent and magnitude of episodic acidification have not
8 been collected to a sufficient degree in acid-sensitive areas of the West to support regional
9 assessment of episodic acidification (Sullivan, 2000).

10 Along the eastern edge of the Continental Divide in Colorado and southeastern
11 Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in
12 the mountainous areas that are exposed to relatively high (by western standards) deposition of N.
13 A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed
14 bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically
15 acidic (ANC < 0), although several had ANC $< 10 \mu\text{eq/L}$, and more than 10% of the lakes had
16 ANC $< 50 \mu\text{eq/L}$. The WLS data for lakes in Colorado and Wyoming demonstrate that surface
17 waters in this area had fall concentrations of NO_3^- in the range of 10 to 30 $\mu\text{eq/L}$, and likely had
18 substantially higher NO_3^- concentrations during spring.

19 The weight of evidence suggests many high-elevation lakes in the West receive
20 N deposition sufficiently high to cause chronic NO_3^- leaching, and likely some degree of
21 associated chronic and episodic acidification. However, existing data are insufficient to make a
22 conclusive determination (Sullivan, 2000).

23 24 ***AX4.3.3.6.2 Past Acidification***

25 The limited paleolimnological data available for lakes in the western United States
26 suggest that widespread chronic acidification probably has not occurred. Some lakes may have
27 experienced recent pH declines, but the magnitude of such changes has likely been small
28 (Sullivan, 2000).

29 In the Sierra Nevada, paleolimnological reconstructions of lakewater pH and ANC were
30 calculated by Holmes et al. (1989) at 24 depth intervals at Emerald Lake, for the period 1825 to
31 the present. Significant trends were not found for either pH or ANC, and the authors concluded

1 that Emerald Lake had not been acidified by acidic deposition. Whiting et al. (1989) completed
2 paleolimnological analyses of three additional lakes in the Sierra Nevada. Eastern Book Lake
3 (pH = 7.06) showed evidence of both long-term alkalization (~0.3 pH units over the past
4 200 years) and pH fluctuations since 1970. Lake 45 (pH = 5.16) may have acidified slightly
5 (~0.2 pH units) over the last 60 years. Lake Harriet (pH = 6.52) showed no significant change.

6 In Rocky Mountain National Park, Colorado, Baron et al. (1986) investigated metal
7 stratigraphy, diatom stratigraphy, and inferred pH profiles of four subalpine lakes. They found
8 no evidence of historical influence on pH attributable to atmospheric deposition. Other
9 paleolimnological studies of Rocky Mountain lakes report similar results: metals (primarily
10 lead) exhibit temporal dynamics related to the increase and decline of precious metal mining in
11 the region, but these are asynchronous with other metal or biological indicators of acidification
12 (Wolfe et al., 2003). Both the study by Wolfe et al. (2003) and a study by Saros et al. (2003)
13 showed no evidence of acidification of lake waters over time, but increasing evidence of
14 eutrophication from atmospheric N deposition (see AX5.3.3.1).

15 DayCent-Chem, a model that simulates the daily dynamics of plant production, soil
16 organic matter, cation exchange, mineral weathering, elution, stream discharge, and stream
17 solute concentrations, was able to recreate daily stream chemistry dynamics over 13 years for an
18 alpine watershed in the Colorado Front Range (Hartman et al., 2007). Using the model to
19 hindcast stream chemical dynamics back to 1900 revealed changes in simulated pH coincident
20 with maximum SO₂ emissions in the late 1960s and early 1970s. Model simulations suggested
21 annual mean pH values decreased to 5.6 to 5.8 during the years of maximum regional SO₂
22 emissions, and have since recovered to circumneutral values. Simulated ANC responded to both
23 SO₂ and NO_x emissions, decreasing to annual values of 20 to 25 µeq/L during years of highest
24 SO₂ or NO_x emissions compared with current mean annual ANC values near 50 µeq/L (Hartman
25 et al., 2007).

26 27 **AX4.3.3.6.3 Recent Trends**

28 Limited monitoring data are available on recent trends in surface water chemistry in the
29 western regions and are mostly limited to the recent past and a number of reconnaissance studies
30 (Melack and Stoddard, 1991; Nelson, 1991; Turk and Spahr, 1991). Existing information on
31 recent trends in surface water chemistry since the 1980s suggests that conditions vary widely

1 across the West. Parts of Colorado, Wyoming and the western Cascades showed decreased
2 ANC, while Emerald Lake experienced reduced NO_3^- concentrations.

3 Turk et al. (1993) reported the results of 5 years of monitoring for ten lakes in the
4 Mt. Zirkel and Weminuche Wilderness areas in Colorado. Based on lake concentrations of
5 SO_4^{2-} and Cl^- and on wet deposition concentrations of SO_4^{2-} , NO_3^- , and H^+ , Turk and Spahr
6 (1991) concluded that low-ANC lakes had lost no more than 5 $\mu\text{eq/L}$ ANC in the Bitterroot
7 Range of the Northern Rocky Mountains, 12 $\mu\text{eq/L}$ ANC in the Wind River Range of Wyoming,
8 and 10 $\mu\text{eq/L}$ ANC in the Front Range of Colorado. It is likely that the actual ANC losses had
9 been much less than these estimates (Sullivan, 2000).

10

11 **AX4.3.3.6.4 Future Projections**

12 The DayCent-Chem model was used to project a timeline to acidification for an alpine
13 watershed of Rocky Mountain National Park (Hartman et al., 2007). At current levels of
14 N deposition of 4 to 6 kg N/ha/yr, acidification does not occur over 48 years of simulation, but
15 increasing deposition amounts lead to first episodic acidification over time at deposition of 7.0
16 to 7.5 kg N/ha/yr. MAGIC model simulation results suggested that a sustained N deposition load
17 of 12.2 kg N/ha/yr would be required over a period of 50 years to cause chronic acidification of
18 the Andrews Creek watershed in Rocky Mountain National Park (Sullivan et al., 2005).

19

20 **AX4.3.3.7 Temporal Variability in Water Chemistry**

21 Water chemistry changes on both intra-annual and inter-annual time scales in response to
22 changes in environmental conditions. Because of this variability, many years of data are
23 required to establish the existence of trends in surface water chemistry. Assignment of causality
24 to changes that are found to occur is even more difficult.

25 Temporal variability in surface water and soil solution chemistry, and patterns in nutrient
26 uptake by terrestrial and aquatic biota, influence acidification processes and pathways. Thus,
27 conditions are constantly changing in response to episodic, seasonal, and inter-annual cycles and
28 processes. In particular, climatic fluctuations that govern the amount and timing of precipitation
29 inputs, snowmelt, vegetative growth, depth to groundwater tables, and evapoconcentration of
30 solutes influence soil and surface water chemistry and the interactions between pollution stress
31 and sensitive aquatic and terrestrial biological receptors.

1 Decreases in pH with increases in flow are nearly ubiquitous in drainage waters
2 throughout the United States (Wigington et al., 1991). Chemical changes during episodes are
3 controlled in part by acidic deposition and in part by natural processes, including dilution of base
4 cation concentrations, nitrification, flushing of organic acids from terrestrial to aquatic systems,
5 and the neutral salt effect. Episodic acidification pulses may last for hours to weeks, and
6 sometimes result in depletion of ANC in acid-sensitive streams and lakes to negative values and
7 concomitant increases in Al_i in solution to toxic levels.

8 During episodes, which are driven by rainstorms and/or snowmelt events, both discharge
9 (streamflow volume per unit time) and water chemistry change, sometimes dramatically. This is
10 important because streams may in some cases exhibit chronic chemistry that is still suitable for
11 aquatic biota, but nevertheless experience occasional episodic acidification with lethal
12 consequences (cf. Wigington et al., 1993).

13 The most important factor governing watershed sensitivity to episodic acidification is the
14 pathways followed by snowmelt water and stormflow water through the watershed. These
15 pathways determine the extent of acid neutralization provided by the soils and bedrock in that
16 watershed. High-elevation watersheds with steep topography, extensive areas of exposed
17 bedrock, deep snowpack accumulation, and shallow, base-poor soils tend to be most sensitive to
18 episodic acidification.

19 Rainfall and snowmelt typically pass through the soil profile prior to reaching a stream
20 channel. The typical soil profile in acid-sensitive watersheds has lowest pH in upper organic soil
21 horizons, increasing down the profile to higher pH at depth. Drainage water chemistry during
22 baseflow conditions is generally reflective of conditions in the lower soil horizons and the
23 subsoil. During high flows during snowmelt or rainfall events, however, flow-routing favors
24 water flowpaths through upper horizons. During such events, drainage water chemistry,
25 therefore, typically reflects the lower pH, higher organic content, and lower ANC of these upper
26 soil horizons (Sullivan, 2000). As such, storm flow and snowmelt are often associated with
27 episodes of extreme surface water acidity due to an increase in the proportion of flow derived
28 from water that has moved laterally through the surface soil without infiltration to deeper soil
29 horizons (Wigington et al., 1991).

30 The routing of water as it flows through a watershed determines the degree of contact
31 with acidifying or neutralizing materials and therefore influences (along with soils and bedrock

1 characteristics) the amount of episodic acidification that occurs. In any given watershed, surface
2 water ANC may vary in time depending upon the proportion of the flow that has contact with
3 deep versus shallow soil horizons; the more subsurface contact, the higher the surface water
4 ANC (Turner et al., 1991). This can be attributed in part to higher base saturation and (in some
5 watersheds) greater SO_4^{2-} adsorption capacity in subsurface soils. It may also relate to the
6 accumulation in the upper soil horizons of acidic material derived from atmospheric deposition
7 and decay processes (Lynch and Corbett, 1989; Turner et al., 1991). Episodic acidification is
8 often the limiting condition for aquatic organisms in streams that can be suitable for aquatic life
9 under baseflow conditions.

10 Episodes are generally accompanied by changes in at least two or more of the following
11 chemical parameters: ANC, pH, base cations, SO_4^{2-} , NO_3^- , Al^{3+} , organic acid anions, and DOC
12 (Sullivan, 2000). The EPA's Episodic Response Project (ERP) confirmed the chemical and
13 biological effects of episodic pH depressions in lakes and streams in parts of the United States
14 (Wigington et al., 1993). The ERP illustrated that episodic processes are mostly natural, that
15 SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition play important roles in the
16 episodic acidification of some surface waters, and that the chemical response that has the greatest
17 effect on biota is increased Al_i concentration. Similar findings had been reported elsewhere,
18 especially in Europe, but the ERP helped to clarify the extent, causes, and magnitude of episodic
19 acidification in portions of the United States (Sullivan, 2000).

20 Water chemistry trends documented by long-term monitoring programs and reported here
21 represent recovery from chronic acidification. Most surface waters exhibit seasonally lower
22 ANC and pH values than would be captured by trend analysis that considers only chronic
23 chemistry data. In many cases, sites that are relatively low in ANC, but not chronically acidic,
24 undergo short-term episodic acidification to negative ANC values during spring snowmelt, or
25 during intense rain events. Lawrence found that 16% of total stream reaches in the West Branch
26 Neversink River, in the Catskill Mountains of New York, were chronically acidic, whereas 66%
27 of total stream reaches has a high likelihood of becoming acidic during high flows.

28 Most research on episodic processes has been conducted on stream systems, which tend
29 to be more susceptible to such effects than lakes. Spatial variability can be considerable in lakes,
30 and this complicates efforts to quantify the magnitude of episodic effects (Gubala et al., 1991).
31 Moreover, synoptic lake surveys are typically conducted during the autumn "index period,"

1 during which time lakewater chemistry exhibits low temporal variability. Although autumn is an
2 ideal time for surveying lakewater chemistry in terms of minimizing variability, lakewater
3 samples collected during autumn provide little relevant data on episodic processes, and in
4 particular on the dynamics or importance of N as an agent of acidification. Nitrate
5 concentrations in lakewater are elevated during the autumn season only in lakes having
6 watersheds that exhibit fairly advanced symptoms of N saturation (Stoddard, 1994).

7 Mixing zones have received little attention despite the fact that they can be acutely toxic
8 to aquatic biota. Whether an area of acidic water that comes in contact with non-acidic water is a
9 safe haven or a toxic zone depends on many parameters, one of the most important of which is
10 the amount and form of Al species produced at the boundaries. For example, Al hydroxide
11 ($\text{Al}(\text{OH})_3$) can precipitate out of solution if pH is suddenly increased within a mixing zone. This
12 form of Al is acutely toxic to fish.

13 The mechanisms that produce acidic episodes can include dilution of base cations and
14 flushing of NO_3^- , SO_4^{2-} and/or organic acids from forest soils to drainage water (Kahl et al.,
15 1992; Wigington et al., 1996; Wigington, 1999; Lawrence, 2002). Acidic deposition can
16 contribute to episodic acidification of surface water both by supplying N which can produce
17 pulses of NO_3^- during high flow periods, contributing hydrologically mobile SO_4^{2-} through dry
18 deposition, and by lowering baseline pH and ANC, so that episodes are sufficient to produce
19 biologically harmful conditions (Stoddard et al., 2003).

20 Episodic acidification due to atmospheric deposition is most commonly associated with
21 N deposition, and effects tend to be most pronounced during snowmelt. However, snowmelt can
22 flush into surface waters N that was deposited from the atmosphere to the snowpack and also
23 N that was mineralized within the soil under the snowpack during winter. A substantial
24 component of the NO_3^- flux may have been derived from mineralization of organic N (Ley et al.,
25 2004). Much of the N released from the snowpack during the melting period is retained in
26 underlying soils and only a component of that is flushed to surface waters. Where soils are
27 sparse, as in alpine regions of the western United States, most snowpack N is flushed to surface
28 waters, and even though there is evidence through use of isotopic tracers that much of the N was
29 cycled microbially, snowpack N has been reported to caused temporary acidification of alpine
30 streams (Williams and Tonnessen, 2000; Campbell et al., 2002).

1 Episodic pH and ANC depressions during snowmelt are largely driven by base cation
2 dilution and NO_3^- enrichment in most areas (cf. Wigington et al., 1991, 1993; Campbell et al.,
3 1995; Stoddard, 1995), although Denning et al. (1991) found a significant decline of both pH and
4 ANC associated with DOC flushing from forest soils. Pulses of increased SO_4^{2-} during
5 hydrological episodes are usually attributable to S storage and release in soils (for example, in
6 the southeastern United States) or wetlands. More commonly, lake and streamwater
7 concentrations of SO_4^{2-} decrease or remain stable during snowmelt. This is probably because
8 most stream flow during episodes is derived from water previously stored in watershed soils that
9 is then forced into streams and lakes by the piston effect.

10 In the Northeast, the most severe acidification of surface waters generally occurs during
11 spring snowmelt (Charles, 1991). Stoddard et al. (2003) found that on average, spring ANC
12 values in New England, the Adirondacks, and the Northern Appalachian Plateau were about
13 $30 \mu\text{eq/L}$ lower than summer values during the period 1990 to 2000 (Figure AX4.3-10). This
14 implies that lakes and streams in these regions would need to recover to chronic Gran ANC
15 values above about $30 \mu\text{eq/L}$ before they could be expected to not experience acidic episodes
16 (Stoddard et al., 2003). However, the estimate of $30 \mu\text{eq/L}$ is certain to be low because the
17 comparison was made with non-episodic sampling in spring.

18 In the West, episodic acidification is an especially important issue for surface waters
19 throughout high-elevation areas. A number of factors pre-dispose western systems to potential
20 episodic effects (Peterson et al., 1998; Sullivan, 2000), including:

- 21 1. the abundance of dilute to ultradilute lakes which exhibit very low concentrations
22 of base cations, and therefore ANC, throughout the year;
- 23 2. large snowpack accumulations at the high-elevation sites, thus causing substantial
24 episodic acidification via the natural process of base cation dilution; and
- 25 3. short hydraulic retention times for many of the high-elevation drainage lakes, thus
26 enabling snowmelt to rapidly flush lake basins with highly dilute meltwater.

27 Based on measurements of microbial biomass, CO_2 flux through the snowpack, and soil N pools,
28 Williams et al. (1996b) concluded N cycling under the snowpack in Colorado during the winter
29 and spring was sufficient to supply the NO_3^- measured in stream waters. Brooks et al. (1996)
30 investigated soil N dynamics throughout the snow-covered season on Niwot Ridge, CO. Sites
31 with consistent snow cover had a 3 to 8 cm layer of thawed soil under the snowpack for several
32 months before snowmelt began. Nitrogen mineralization in this thawed layer contributed to Nr

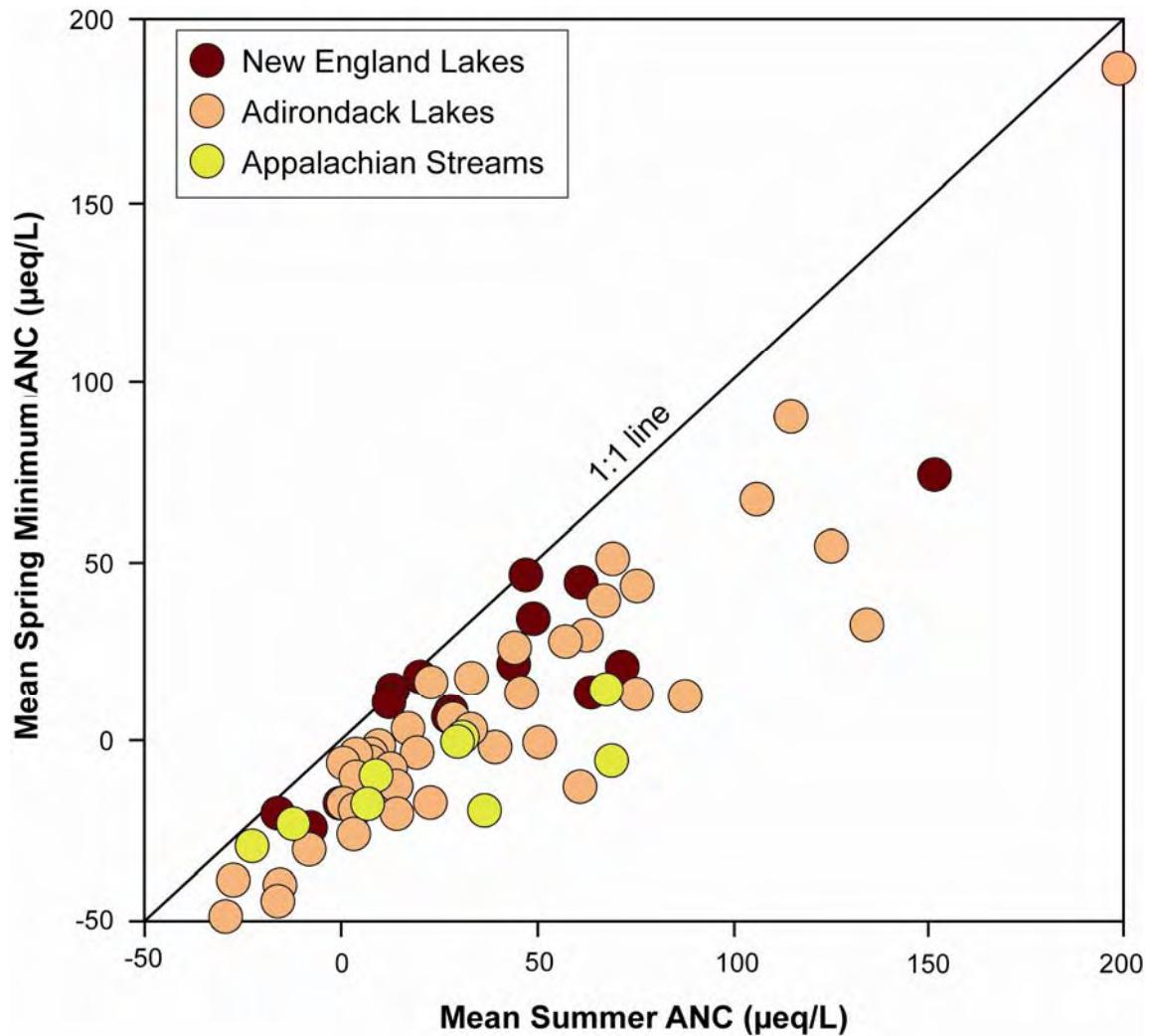


Figure AX4.3-10. Relationship between mean summer and spring ANC values at LTM sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

Source: Stoddard et al. (2003).

1 pools that were significantly larger than the pool of N stored in the snowpack. As snowmelt
 2 began, soil inorganic N pools decreased sharply, concurrent with a large increase in microbial
 3 biomass N. As snowmelt continued, both microbial N and soil inorganic N decreased,
 4 presumably due to increased demand by growing vegetation (Brooks et al., 1996).

5 In the Sierra Nevada, the hydrology of alpine and subalpine ecosystems is dominated by
 6 snowfall and snowmelt, with over 90% of the annual precipitation falling as snow. The
 7 relatively small loads of acidic deposition can supply relatively high concentrations of SO_4^{2-} and

1 NO₃⁻ to lakes and streams during the early phase of snowmelt (Stoddard, 1995) through the
2 process of preferential elution (Johannessen and Henriksen, 1978).

3 Lakewater pH and ANC in the Sierra Nevada generally decrease with increasing runoff,
4 reaching minima near peak snowmelt discharge. Most other solutes exhibit temporal patterns
5 that indicate dilution or a pulse of increased concentration followed by either dilution or
6 biological uptake. Williams and Melack (1991) and Williams et al. (1995) documented ionic
7 pulses (2 to 10 days in duration) in meltwater concentrations in the Emerald Lake watershed
8 twofold to twelvefold greater than the snowpack average. Sulfate and NO₃⁻ concentrations in
9 meltwater decreased to below the initial bulk concentrations after about 30% of the snowpack
10 had melted. The initial meltwater draining from the snowpack had concentrations of NO₃⁻ and
11 NH₄⁺ as high as 28 µeq/L, compared to bulk snowpack concentrations < 5 µeq/L (Williams et al.,
12 1995). Streamwater NO₃⁻ concentrations peaked during the early snowmelt period, with
13 maximum streamwater concentrations of 18 µeq/L. During summer, streamwater NO₃⁻
14 concentrations were always near or below detection limit.

15 Stoddard (1995) reported results for two lakes in the Sierra Episodes Study, one of which
16 (Treasure Lake) typified the response of the majority of high elevation lakes in the study and one
17 whose response was most extreme (High Lake). At Treasure Lake, ANC began to decline at the
18 onset of snowmelt and reached a minimum at peak runoff, corresponding with minimum base
19 cation, NO₃⁻, and SO₄²⁻ concentrations. The lakewater did not become acidic. High Lake
20 watershed contained a deeper snowpack, and began melting later in the season. ANC fell to 0
21 and below twice during the first 10 days of snowmelt. The ANC minimum corresponded with
22 maximum concentrations of base cations, NO₃⁻ and Al. Nitrate concentrations increased to
23 values greater than 40 µeq/L, exceeding concurrent increases in base cations and causing the lake
24 to become acidic for brief periods. Stoddard (1995) concluded that High Lake appeared to be
25 representative of the most extreme conditions of episodic acid-sensitivity in the Sierra Nevada.

26 Data regarding episodic variability in streamwater ANC for six intensively studied sites
27 within Shenandoah National Park for the period 1993 to 1999 are presented in Figure AX4.3-11.
28 The minimum measured ANC each year at each site (which generally is recorded during a large
29 rain or snowmelt episode) is plotted against the median spring ANC for that year at that site.
30 Sites that exhibited median spring ANC below about 20 µeq/L (Paine Run, White Oak Run,

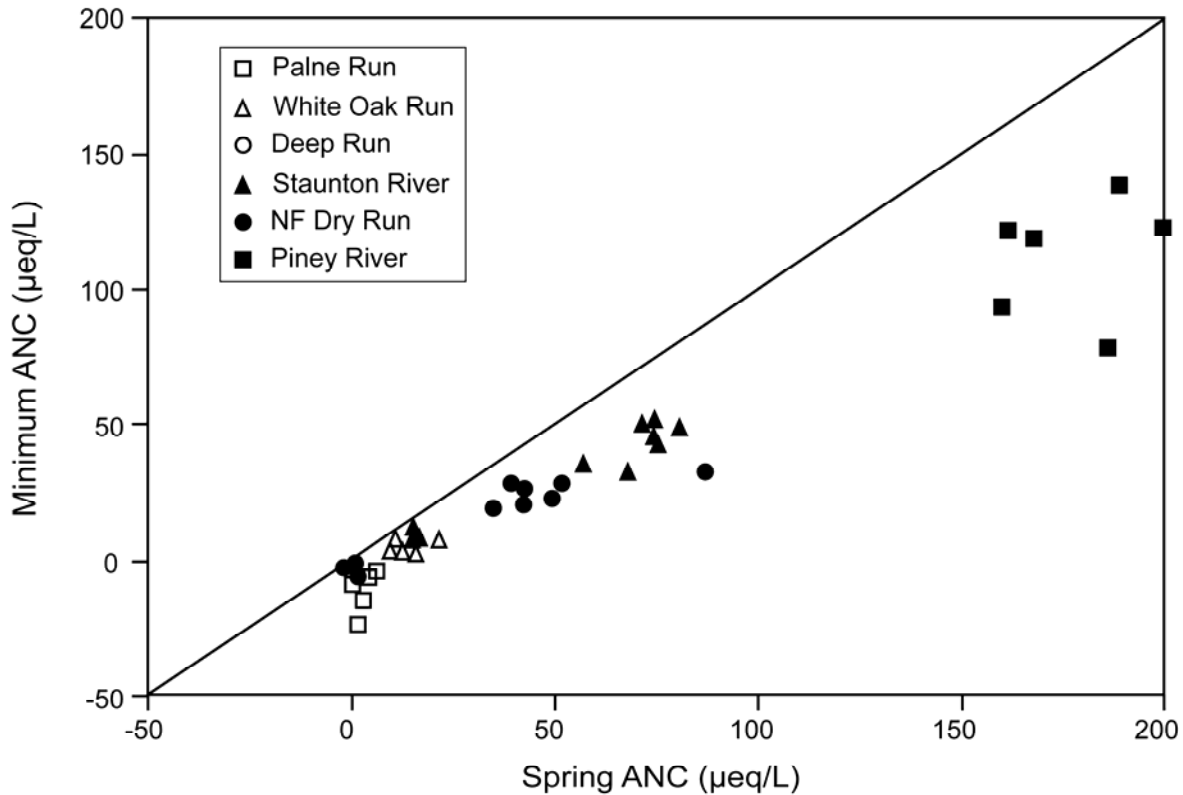


Figure AX4.3-11. Minimum streamwater ANC sampled at each site during each year versus median spring ANC for all samples collected at that site during that spring season. Data are provided for all intensively studied streams within Shenandoah National Park during the period 1993-1999. A 1:1 line is provided for reference. The vertical distance from each sample point upwards to the 1:1 line indicates the ANC difference between the median spring value and the lowest sample value for each site and year.

Source: Sullivan et al. (2003).

1 Deep Run) generally had minimum measured ANC about 10 µeq/L lower than median spring
 2 ANC.

3 In contrast, at the high-ANC Piney River site (median spring ANC > 150 µeq/L), the
 4 minimum measured ANC was generally more than about 40 µeq/L lower than the respective
 5 median spring ANC. At sites having intermediate ANC values, with median spring ANC in the
 6 range of about 30 to 90 µeq/L, the minimum ANC measured each year was generally about 20 to
 7 30 µeq/L lower than the respective median spring ANC. Thus, there is a rather clear pattern of
 8 larger episodic ANC depressions in streams having higher median ANC and smaller episodic

1 ANC depressions in streams having lower median ANC. The two sites that had median spring
2 ANC between about 0 and 10 $\mu\text{eq/L}$ consistently showed minimum measured values below 0.
3 Streams having low chronic ANC can be expected to experience relatively small episodic ANC
4 depressions. However, those depressions can result in minimum ANC values that are associated
5 with toxicity to aquatic biota.

6 A recent study by Deviney et al. (2006) used hourly ANC predictions over short time
7 periods to compute recurrence intervals of annual water-year minimum ANC values for periods
8 of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the Shenandoah National
9 Park catchments using catchment geology and topography. On the basis of the models, they
10 conclude that large number of Shenandoah National Park streams have 6- to 168-h periods of
11 low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically,
12 on the basis of a 4-year recurrence interval, approximately 23% of the land area (44% of the
13 catchments) can be expected to have conditions that are indeterminate (ANC 20 to 50),
14 episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous
15 hours. Many catchments are predicted to have successive years of low-ANC values potentially
16 sufficient to extirpate some species (Deviney et al., 2006). The authors of the study reported that
17 smaller catchments are more vulnerable to episodic acidification than large catchments underlain
18 by the same bedrock. Catchments with similar topography and size are more vulnerable if
19 underlain by less basaltic and carbonate bedrock.

20 There are several different mechanisms of episodic acidification in operation in the
21 streams in Shenandoah National Park, depending at least in part on the bedrock geology of the
22 stream. The most acidic conditions in Shenandoah National Park streams occur during high-flow
23 periods, in conjunction with storm or snowmelt runoff. The general relationship between flow
24 level and ANC is evident in Figure AX4.3-12, which plots ANC measurements against flow for
25 three intensively studied streams representing the major bedrock types in the park. The response
26 of all three streams is similar in that most of the lower ANC values occur in the upper range of
27 flow levels.

28 Consistent with observations by Eshleman (1988), the minimum ANC values that occur
29 in response to high flow are related to baseflow ANC values. Paine Run (siliciclastic bedrock)
30 had a mean weekly ANC value of about 6 $\mu\text{eq/L}$ and often had high-flow ANC values that were
31 less than 0 $\mu\text{eq/L}$. Staunton River (granitic bedrock) had a mean weekly ANC value of about

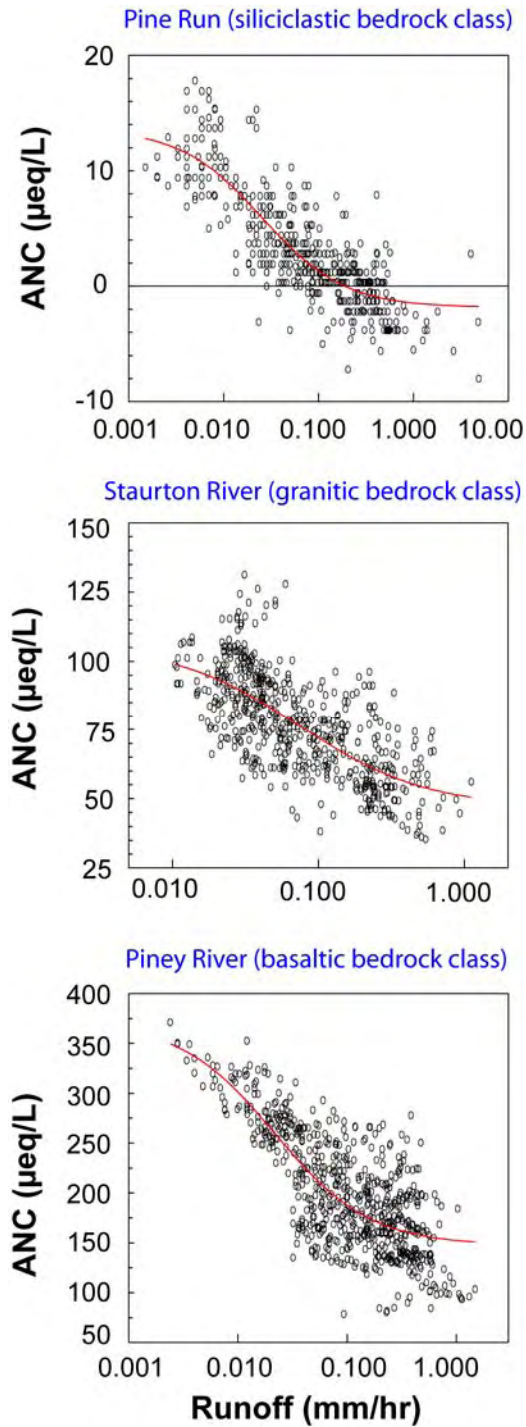


Figure AX4.3-12. Relationship between ANC and runoff for streamwater samples collected at intensively studied sites in Shenandoah National Park. The data represent samples collected during the 1992-1997 period.

Source: Sullivan et al. (2003).

1 82 $\mu\text{eq/L}$ and had only a few high-flow ANC values less than 50 $\mu\text{eq/L}$. Piney River (basaltic
2 bedrock) had a mean weekly ANC value of 217 $\mu\text{eq/L}$ and no values as low as 50 $\mu\text{eq/L}$.

3 Eshleman and Hyer (2000) estimated the contribution of each major ion to observed
4 episodic ANC depressions in Paine Run, Staunton River, and Piney River during a 3-year period.
5 During the study, 33 discrete storm events were sampled and water chemistry values were
6 compared between antecedent baseflow and the point of minimum measured ANC (near peak
7 discharge). The relative contribution of each ion to the ANC depressions was estimated using
8 the method of Molot et al. (1989), which normalized the change in ion concentration by the
9 overall change in ANC during the episode. At the low-ANC (~ 0) Paine Run site on siliciclastic
10 bedrock, increases in NO_3^- and SO_4^{2-} , and to a lesser extent organic acid anions, were the
11 primary causes of episodic acidification. Base cations tended to compensate for most of the
12 increases in acid anion concentration. ANC declined by 3 to 21 $\mu\text{eq/L}$ (median 7 $\mu\text{eq/L}$) during
13 the episodes studied.

14 At the intermediate-ANC (~ 60 to 120 $\mu\text{eq/L}$) Staunton River site on granitic bedrock,
15 increases in SO_4^{2-} and organic acid anions, and to a lesser extent NO_3^- , were the primary
16 causes of episodic acidification. Base cation increases compensated these changes to a large
17 degree, and ANC declined by 2 to 68 $\mu\text{eq/L}$ during the episodes (median decrease in ANC was
18 21 $\mu\text{eq/L}$).

19 At the high-ANC (~ 150 to 200 $\mu\text{eq/L}$) Piney River site on basaltic (69%) and granitic
20 (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other
21 two sites where base cation concentrations increased). Sulfate and NO_3^- usually increased. The
22 change in ANC during the episodes studied ranged from 9 to 163 $\mu\text{eq/L}$ (median 57 $\mu\text{eq/L}$;
23 Eshleman and Hyer, 2000).

24 Previous studies have shown that mobilization of dissolved Al during episodic
25 acidification is a primary cause of fish mortality in streams that have low ANC under baseflow
26 conditions (Wigington et al., 1993). Streams with higher ANC during baseflow are less likely to
27 become sufficiently acidic during episodes to bring much Al into solution.

28 Figure AX4.3-13 provides an example of changes in ANC, pH, and total monomeric Al
29 that occurred in Paine Run, Staunton River, and Piney River during a high-flow episode in
30 January 1995. Under baseflow conditions, ANC at the Paine Run site was above 0 $\mu\text{eq/L}$, pH
31 was above 5.5, and Al concentration was less than about 1 μM . Discharge levels increased

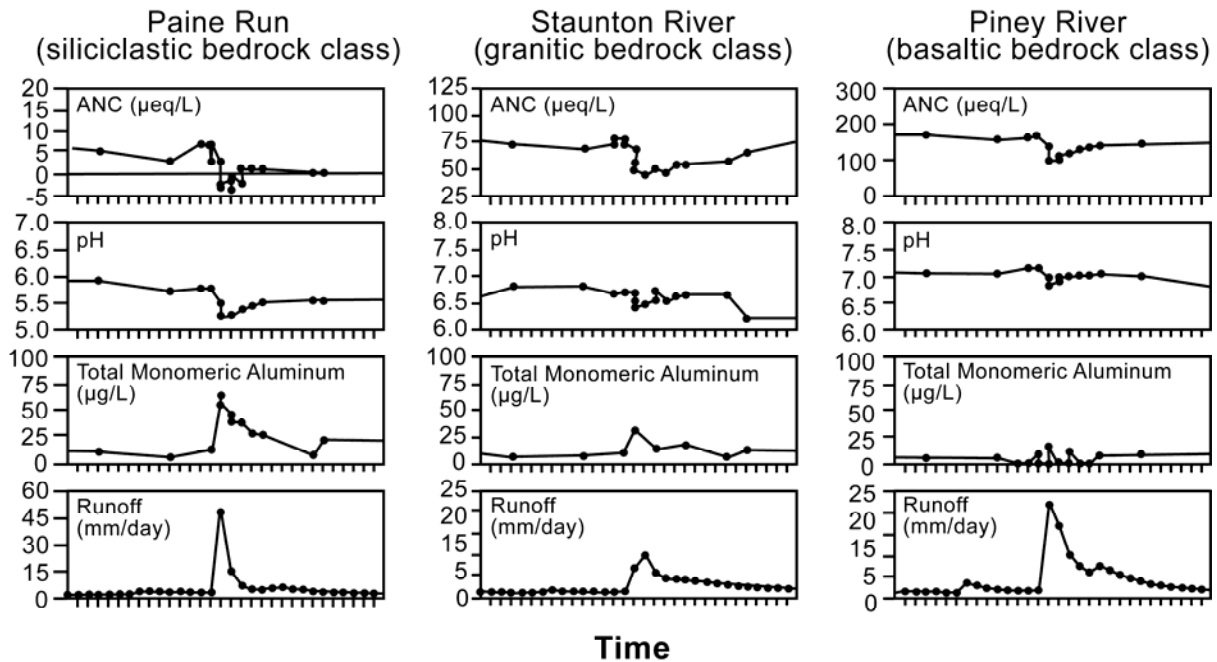


Figure AX4.3-13. Decrease in ANC and pH and increase in dissolved aluminum in response to a sharp increase in streamflow in three watersheds within Shenandoah National Park during a hydrological episode in 1995. The watersheds were selected to be representative of the three geologic sensitivity classes within the park. Data are shown for the month of January 1995.

Source: Sullivan et al. (2003).

1 dramatically during the episode, resulting in depression of ANC to less than 0 µeq/L, pH values
 2 less than 5.5, and an increase in Al concentration to near 3 µM, above the threshold for adverse
 3 effects on some species of aquatic biota.

4 The same episode also resulted in substantial declines in ANC in the granitic (Staunton
 5 River) and basaltic (Piney River) watersheds. However, ANC values at these two sites were
 6 relatively high prior to the episode (about 75 and 175 µeq/L, respectively) and did not decline to
 7 below about 50 µeq/L during the episode at either site, and pH values remained above 6.0 and
 8 6.5, respectively (Figure AX4.3-13).

9 In general, pre-episode ANC is a good predictor of minimum episodic ANC and also a
 10 reasonable predictor of episodic ΔANC. Higher values of pre-episode ANC lead to larger
 11 ΔANC values, but minimum ANC values of such streams are generally not especially low.

1 Lowest minimum ANC values are reached in streams that have low pre-episode ANC, but the
2 Δ ANC values for such streams are generally small.

3 Webb et al. (1994) developed an approach to calibration of an episodic acidification
4 model for VTSSS long-term monitoring streams in western Virginia that was based on the
5 regression method described by Eshleman (1988). Median, spring quarter ANC concentrations
6 for the period 1988 to 1993 were used to represent chronic ANC, from which episodic ANC was
7 predicted. Regression results were very similar for the four lowest ANC watershed classes, and
8 they were therefore combined to yield a single regression model to predict the minimum
9 measured ANC from the chronic ANC. Extreme ANC values were about 20% lower than
10 chronic values, based on the regression equation:

$$11 \quad \text{ANC}_{\text{min}} = 0.79 \text{ANC}_{\text{chronic}} - 5.88 \quad (r^2 = 0.97; \text{se of slope} = 0.02, p = 0.001)$$

12 Because the model was based on estimation of the minimum ANC measured in the
13 quarterly sampling program, it is probable that the true minimum ANC values were actually
14 somewhat lower than 20% below the measured chronic ANC. Nevertheless, regression
15 approaches for estimation of the minimum episodic ANC of surface waters, such as was
16 employed by Webb et al. (1994) for western Virginia, provide a basis for predicting future
17 episodic acidification. It must be recognized, however, that future episodic behavior might vary
18 from current behavior if chronic conditions change dramatically.

19 The relative importance of the major processes that contribute to episodic acidification
20 varies among the streams within Shenandoah National Park, in part as a function of bedrock
21 geology and baseflow streamwater ANC. Sulfur-driven acidification was an important
22 contributor to episodic loss of ANC at all three study sites, probably because S adsorption by
23 soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to
24 diminished contact between drainage water and potentially adsorbing soils surfaces. Dilution of
25 base cation concentrations was most important at the high-ANC site.

26 The documented importance of NO_3^- to episodic acidification was a relatively recent
27 development, attributed to the effects of gypsy moth (*Lymantria dispar*) infestation in many
28 watersheds within Shenandoah National Park (Webb et al., 1995). Consumption of foliage by
29 the moth larvae converted foliar N, which is normally tied up in long-term N cycling processes,
30 into more labile N forms on the forest floor.

1 Thus, episodic acidification of streams in Shenandoah National Park can be attributed to
2 a number of causes, including dilution of base cations and increased concentrations of sulfuric,
3 nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-
4 episodic ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can
5 have adverse effects on fish populations. Not all of the causes of episodic acidification are
6 related to acidic deposition. Base-cation dilution and increase in organic acid anions during
7 high-flow conditions are natural processes. The contribution of nitric acid, indicated by
8 increased NO_3^- concentrations, has evidently been (at least for streams in the park) related to
9 forest defoliation by the gypsy moth (Webb et al., 1995; Eshleman et al., 1998). However,
10 significant contributions of sulfuric acid, indicated by increased SO_4^{2-} concentrations during
11 episodes in some streams, is an effect of atmospheric deposition and the dynamics of S
12 adsorption on soils (Eshleman and Hyer, 2000).

13
14

15 **AX4.4 EFFECTS ON BIOTA**

16 Soil and surface water acidification involve changes in a number of chemical parameters,
17 each of which has the potential to influence the health and vigor of biological communities and
18 the species that comprise them. In most cases where biological effects of acidification have been
19 documented, the most important chemical parameters involved in those effects have been pH,
20 Al_i , and Ca^{2+} . Less commonly, one or more base cations other than Ca^{2+} (e.g., Mg^{2+} , K^+) or C
21 are also involved. This is true for both aquatic and terrestrial effects.

22 A number of authors have examined the complex interactions between pH, Al, and Ca^{2+}
23 that must be considered when attempting to determine the effects of acidification on both aquatic
24 and terrestrial biota (e.g., Mount et al., 1988; Ingersoll et al., 1990b; Wood et al., 1990).

25 Calcium concentration significantly affects the distribution of species and their ability to survive
26 in acidified environments. Aluminum, leached by acid precipitation from soils in the watershed,
27 complicates the response considerably because some forms of Al are highly toxic to both aquatic
28 and terrestrial species. Aluminum and hydrogen ions interact both synergistically and
29 antagonistically depending on conditions (Havas, 1985; Rosseland and Staurnes, 1994). In the
30 presence of naturally occurring organic acids, Al toxicity can be reduced or eliminated. A
31 number of authors have examined the complex interactions between pH, Al, and Ca^{2+} that must

1 be considered when attempting to determine the effects of acidification on both aquatic and
2 terrestrial biota (e.g., Mount et al., 1988; Ingersoll et al., 1990a; Wood et al., 1990).

3 4 **AX4.4.1 Types of Effects of Acidification on Biota**

5 Ecological effects occur at four levels of biological organization: (1) the individual,
6 (2) the population, comprised of many individuals, (3) the biological community, composed of
7 many species, (Billings, 1978), and (4) the ecosystem. Several metrics have been developed to
8 describe the effects of acidification at each of these levels of organization. For the individual,
9 impacts are assessed in terms of sublethal effects on condition. At the population level, effects
10 are measured by changes in the population of a certain species. At the community level, species
11 richness and community structure can be used to evaluate effects, and at the ecosystem level,
12 changes in nutrient cycling and ecosystem processes are assessed. Most of these indices have
13 been applied primarily to aquatic ecosystems. Each is discussed below.

14 Baker et al. (1990a) conducted a rigorous review of the effects of acidification on aquatic
15 biota for the 1990 NAPAP State of Science/Technology reports. They evaluated hundreds of
16 laboratory, *in situ* bioassay, field surveys, whole-system field experiments, and smaller
17 mesocosm studies on the effects of acidification on aquatic biota. Their 381-page report is the
18 most exhaustive source summarizing the aquatic biological effects of acidification from acidic
19 deposition. The summaries provided here in sections AX4.4 and AX4.6 rely heavily on this
20 source.

21 In Shenandoah National Park, a statistically robust relationship between acid-base status
22 of streams and fish species richness was documented. The 3-year Fish in Sensitive Habitats
23 (FISH) study of stream acidification in Shenandoah National Park demonstrated negative effects
24 on fish from both chronic and episodic acidification (Bulger et al., 1999). Biological differences
25 in low- versus high-ANC streams included species richness, population density, condition factor,
26 age, size, and field bioassay survival. Of particular note was that both episodic and chronic
27 mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC
28 stream (MacAvoy and Bulger, 1995), and that blacknose dace (*Rhinichthys atratulus*) in low-
29 ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis
30 et al., 1995; Dennis and Bulger, 1995).

1 **AX4.4.1.1 Individual Condition Factor**

2 Relatively little is known about changes in the condition of fish or other aquatic biota
3 resulting from acidification. It is expected that sublethal effects will occur in acid-sensitive
4 species well before the species is eliminated from a particular lake, stream, or terrestrial habitat.
5 For that reason, loss of an acid-sensitive species is not necessarily an ideal indicator of acid
6 stress. Clearly, stress begins to occur prior to species elimination. Sublethal effects are more
7 difficult to quantify, but are nevertheless important.

8 Condition factor is one measure of sublethal effect that has been used to quantify effects
9 of acidification on fish. Condition factor is an index to describe the relationship between fish
10 weight and length. Expressed as fish weight/length³, multiplied by a scaling constant, this index
11 reflects potential depletion of stored energy reserves (Everhart and Youngs, 1981; Goede and
12 Barton, 1990; Dennis and Bulger, 1995). Condition factor is interpreted as depletion of energy
13 resources such as stored liver glycogen and body fat (Goede and Barton, 1990). Fish with higher
14 condition factor are more robust than fish having low condition factor.

15 Field studies have shown lower condition factor in fish found in more acidic streams
16 (Dennis and Bulger, 1995). Condition factor has been developed and applied mainly for
17 blacknose dace. This species is widely distributed in Appalachian Mountain streams and is
18 moderately tolerant of low pH and ANC, relative to other fish species in the region. However,
19 the concept is probably applicable to other species as well. Condition factor may be a useful
20 metric for many species in aquatic ecosystems that are only marginally affected by acidification.

21 Bulger et al. (1999) observed a positive relationship between condition factor and pH in
22 streams in Shenandoah National Park (Figure AX4.4-1). Dennis and Bulger (1995) found a
23 reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations
24 shown in Figure AX4.4-1 with the lowest condition factor have mean habitat pH values within or
25 below the range of critical pH values at which Baker and Christensen (1991) estimated that
26 negative population effects for blacknose dace are likely for the species. The mean length-
27 adjusted condition factor of fish from the study stream with the lowest ANC was about 20%
28 lower than that of the fish in best condition. Comparisons with the work of Schofield and
29 Driscoll (1987) and Kretser et al. (1989) suggest that pH in the low-pH Shenandoah National
30 Park streams is near or below the limit of occurrence for blacknose dace populations in the
31 Adirondack region of New York (Sullivan et al., 2003).

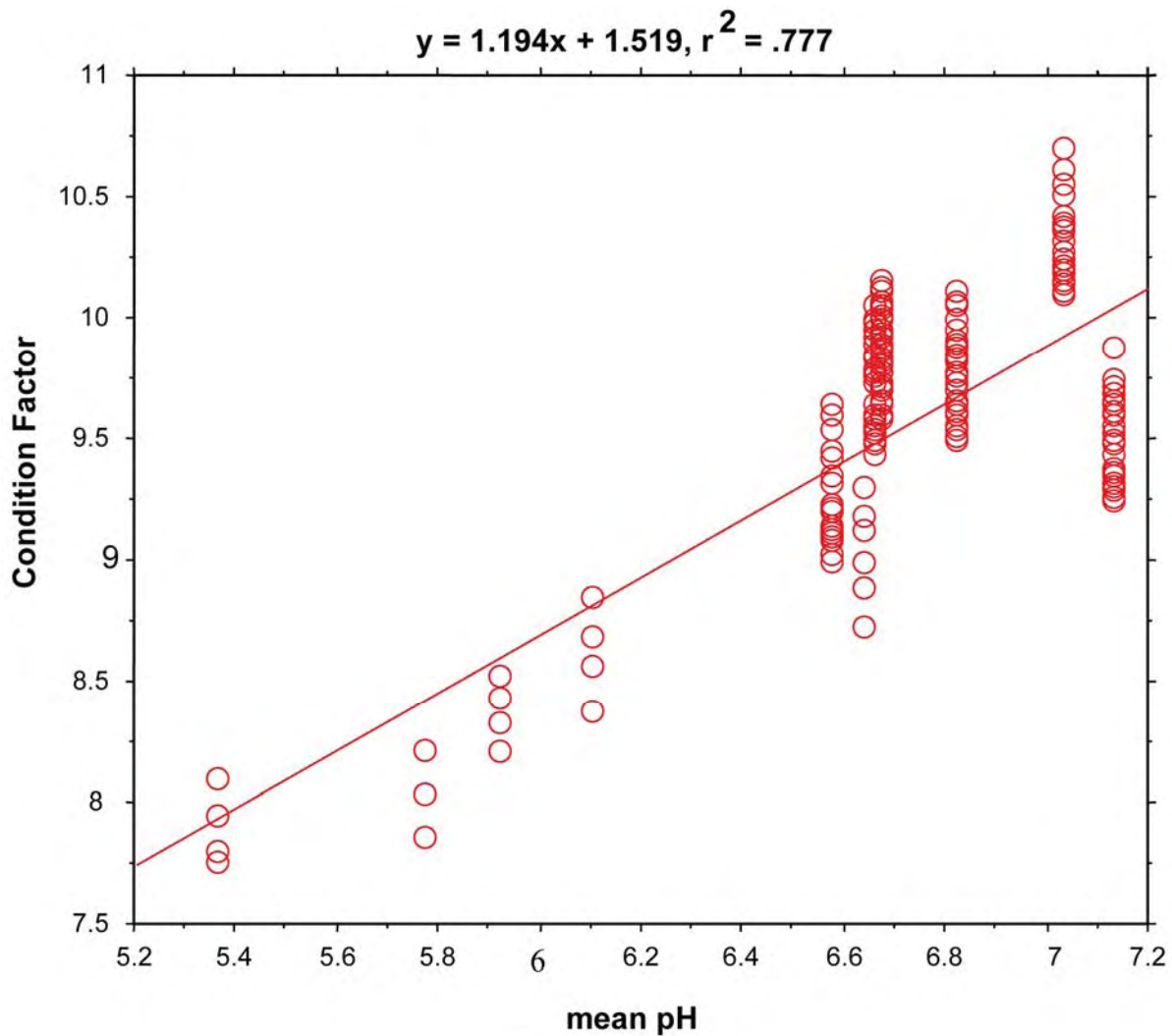


Figure AX4.4-1. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The regression analysis showed a highly significant relationship (p < 0.001) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams.

Source: Bulger et al. (1999).

- 1 Chronic sublethal stress caused by pH below about 6.0 may have serious effects on a
- 2 variety of wild fish populations. There is an energy cost in maintaining physiological
- 3 homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and

1 are unavailable for other functions, such as growth and reproduction (Schreck, 1981, 1982;
2 Wedemeyer et al., 1990).

3 Observed differences in condition factor may occur because maintenance of internal
4 chemistry in the more acidic streams would require energy that otherwise would be available for
5 growth and weight gain (Dennis and Bulger, 1999; Sullivan et al., 2003). The energy costs to
6 fish for active iono-osmoregulation can be substantial (Farmer and Beamish, 1969; Bulger,
7 1986). Because of the steep gradient in Na^+ and Cl^- concentrations between fish blood and
8 freshwater, there is constant diffusional loss of these ions, that must be replaced by energy-
9 requiring active transport. Low pH increases the rate of passive loss of blood electrolytes
10 (especially Na^+ and Cl^-), and AI elevates losses of Na^+ and Cl^- above the levels that occur due to
11 acid stress alone (Wood, 1989).

12 It is also possible that the loss of sensitive individuals or early life stages within species
13 may reduce competition for food among the survivors, resulting in better growth rates, survival,
14 or condition. Similarly, competitive release (increase in growth or abundance subsequent to
15 removal of a competitor) may result from the loss of a sensitive species, with positive effects on
16 the density, growth, or survival of competitor population(s) of other species (Baker et al.,
17 1990b). However, in some cases where acidification continued, transient positive effects on size
18 of surviving fish were shortly followed by extirpation (Bulger et al., 1993).

19 Acid stress is at least partly responsible for the lower condition of blacknose dace
20 populations in Shenandoah National Park, though reduced access to food or lower food quality
21 (Baker et al., 1990b), either resulting from the nature of soft water streams or exacerbated by
22 acidification, cannot be ruled out. Primary productivity is low in headwater streams and lower
23 still in soft water headwaters, which are more likely to be acidified. Production of invertebrates
24 is likely to be low in such streams as well (Wallace et al., 1992). Thus, lower food availability
25 cannot be discounted as a potential contributor to lowered condition in Shenandoah National
26 Park blacknose dace populations in low-pH streams. Nevertheless, reduced growth rates have
27 been attributed to acid stress in a number of other fish species, including Atlantic salmon (*Salmo*
28 *salar*), Chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*),
29 rainbow trout (*Oncorhynchus mykiss*), brook trout, brown trout (*Salmo trutta*), and Arctic char
30 (*Salvelinus alpinus*).

31

1 **AX4.4.1.2 Species Composition**

2 Species composition refers to the mix of species that are represented in a particular
3 ecosystem. Acidification alters species composition in aquatic ecosystems. There are a number
4 of species common to many oligotrophic waters that are sensitive to acidic deposition and that
5 cannot survive, compete, or reproduce in acidic waters. In response to small to moderate
6 changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species,
7 resulting in changes in community composition, but little or no change in total community
8 abundance or biomass. The effects of acidification are continuous, with more species being
9 affected at higher degrees of acidification. Therefore, the degree of alteration of surface water
10 biological community composition increases as surface waters become more acidic. There is a
11 consistent pattern of lower community diversity with increased acidification.

12

13 **AX4.4.1.3 Taxonomic Richness**

14 Taxonomic richness is a metric that is commonly used to quantify the effects of an
15 environmental stress such as acidification or eutrophication. The richness metric can be applied
16 at various taxonomic levels. For example, the number of fish species can be used as an index of
17 acidification (cf. Bulger et al., 1999). Similarly, acidification effects on aquatic insects can be
18 evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera)
19 (Sullivan et al., 2003).

20 Acidification results in the loss of acid-sensitive species, with more species lost with
21 higher degrees of acidification. A direct outcome of population loss caused by acidification is a
22 decline in species richness (the total number of species in a stream or lake). This is a highly
23 predictable outcome of regional acidification, although the pattern and rate of species loss varies
24 from region to region.

25 Decreases in ANC and pH and increases in Al_i concentration contribute to declines in
26 species richness and abundance of zooplankton, macroinvertebrates, and fish (Schindler et al.,
27 1985; Keller and Gunn, 1995). Species richness is positively correlated with pH and ANC (Rago
28 and Wiener, 1986; Kretser et al., 1989) because of the elimination of acid-sensitive species
29 (Schindler et al., 1985). Knowledge of the spatial distribution of pH and other water quality
30 variables is necessary to explain the presence or absence of species within heterogeneous
31 environments. Organisms that are mobile and can sense the pH of their environment can move
32 to areas (called refugia) that have more favorable water chemistry. Although some species are

1 favored by increased acidity, species diversity generally decreases as surface water acidity
2 increases.

3 Decreases in species richness have been observed for all major trophic groups of aquatic
4 organisms (Baker et al., 1990a). Baker et al. (1990a) discussed 10 selected studies that
5 documented this phenomenon, with sample sizes ranging from 12 to nearly 3,000 lakes and
6 streams analyzed per study.

7 Lake and stream size can be an important complicating factor in interpreting species
8 richness data. Larger lakes and streams in larger watersheds would generally be expected to
9 contain more species than smaller lakes or streams in smaller watersheds, irrespective of acid-
10 base chemistry. Nevertheless, when adjusted for lake size, lakes with pH less than
11 approximately 6.0 contain significantly fewer species than lakes with pH above 6.0 (Figure
12 AX4.4-2) (Frenette et al., 1986; Rago and Wiener, 1986; Schofield and Driscoll, 1987; Matuszek
13 and Beggs, 1988).

14 Studies in the Adirondack Mountains demonstrated the effect of acidification on species
15 richness; of the 53 fish species recorded in Adirondack lakes by the ALSA, about half (26
16 species) were absent from lakes with pH below 6.0. Those 26 species included important
17 recreational species, such as Atlantic salmon, tiger trout (*Salmo trutta* X *Salvelinus fontinalis*),
18 redbreast sunfish (*Lepomis auritus*), bluegill (*Lepomis macrochirus*), tiger musky (*Esox*
19 *masquinongy* X *lucius*), walleye (*Sander vitreus*), alewife (*Alosa pseudoharengus*), and kokanee
20 (*Oncorhynchus nerka*) (Kretser et al., 1989), plus ecologically important minnows that serve as
21 forage for sport fish. Fully 346 of 1,469 lakes surveyed by the ALSA supported no fish at all at
22 the time of the survey. These lakes were significantly lower in pH, dissolved Ca²⁺, and ANC,
23 and had higher concentrations of Al_i than lakes hosting one or more species of fish (Gallagher
24 and Baker, 1990). Among lakes with fish, there was an unambiguous relationship between the
25 number of fish species and lake pH, ranging from about one species per lake for lakes having pH
26 less than 4.5 to about six species per lake for lakes having pH > 6.5 (Kretser et al., 1989; Driscoll
27 et al., 2001a). Figure AX4.4-3 shows the mean number of fish species for pH classes from 4.0 to
28 8.0 in lakes in the Adirondacks. It is important to note, however, that there are many possible
29 causes of fish absence in addition to acidification. These include lack of suitable habitat
30 (especially for spawning), winter kill, blocked access, etc.

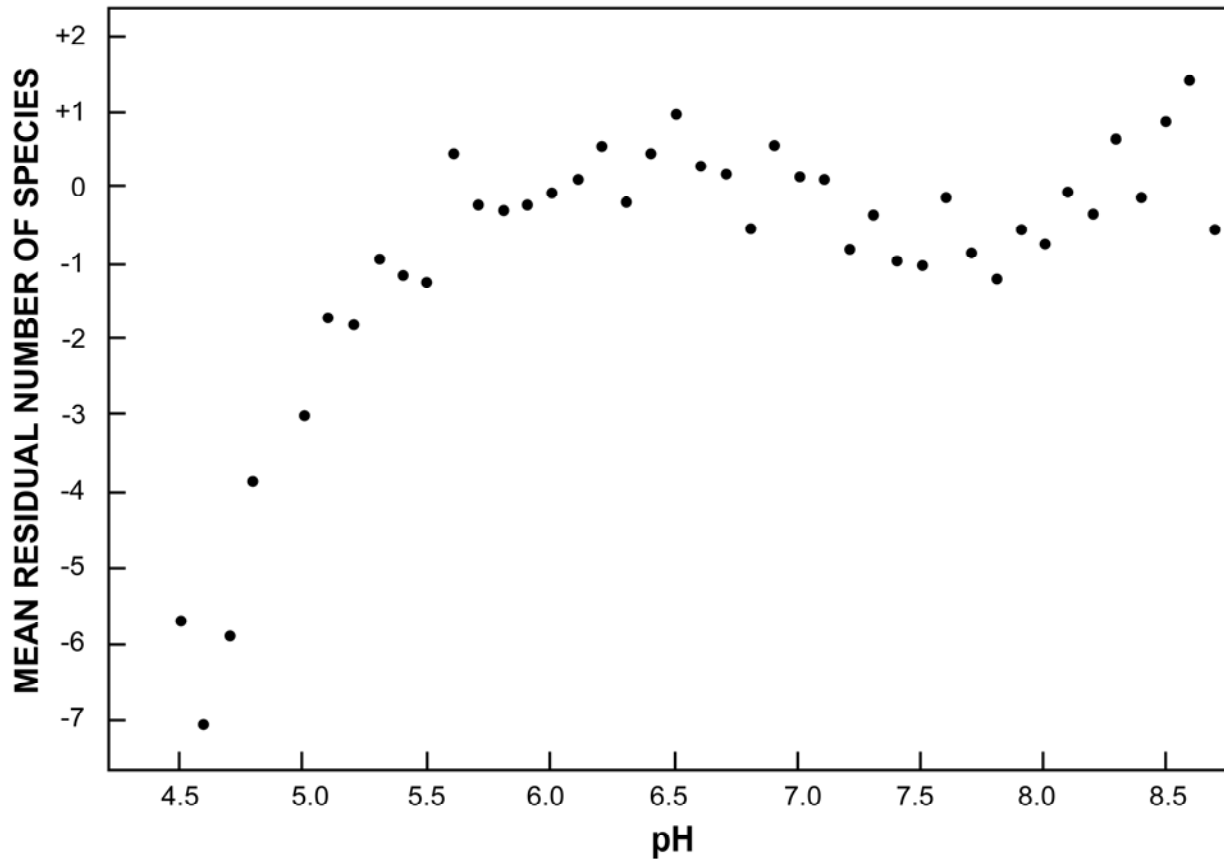


Figure AX4.4-2. Mean residual number of species per lake for lakes in Ontario, by pH interval. The residual number of species for a lake is the deviation of the observed number from the number predicted by lake area.

Source: Matuszek and Beggs (1988).

- 1 Sullivan et al. (2006a) developed a relationship between fish species richness and ANC class for
- 2 Adirondack lakes. Fish species richness observations, as a function of ANC ($\mu\text{eq/L}$) class, were
- 3 fit to a logistic relationship by a non-linear regression analysis. Under chronically acidic
- 4 conditions (summer index or annual average ANC $< 0 \mu\text{eq/L}$), Adirondack lakes are generally
- 5 fishless. There was a marked increase in mean species richness with increases in ANC up to
- 6 values of approximately $100 \mu\text{eq/L}$. The asymptote for the fish species equation was 5.7 species.
- 7 This analysis suggests that there could be loss of fish species with decreases in ANC below
- 8 approximately $100 \mu\text{eq/L}$. It does not account, however, for the possibility that lakes having

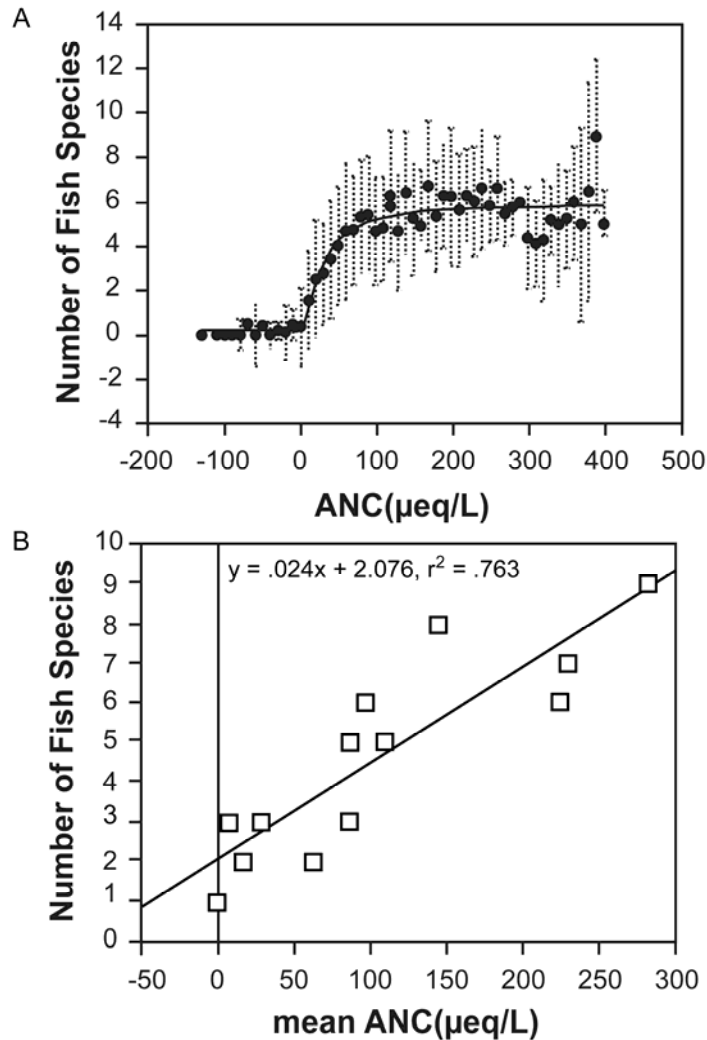


Figure AX4.4-3. Number of fish species per lake or stream versus acidity status, expressed either as pH or ANC. (a) Adirondack lakes (Sullivan et al., 2006a); (b) streams in Shenandoah National Park (Bulger et al., 1999). The data for the Adirondacks are presented as mean and range of species richness within 10 µeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

1 higher ANC are often larger, and therefore support more fish species because of increased
 2 habitat diversity and complexity.

3 As an element of the FISH project (Bulger et al., 1999), numbers of fish species were
 4 compared among 13 Shenandoah National Park streams spanning a range of pH and ANC
 5 conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base

1 status (during the 7-year period of record) and fish species richness among the 13 streams. The
2 streams with the lowest ANC hosted the fewest species (Figure AX4.4-4).

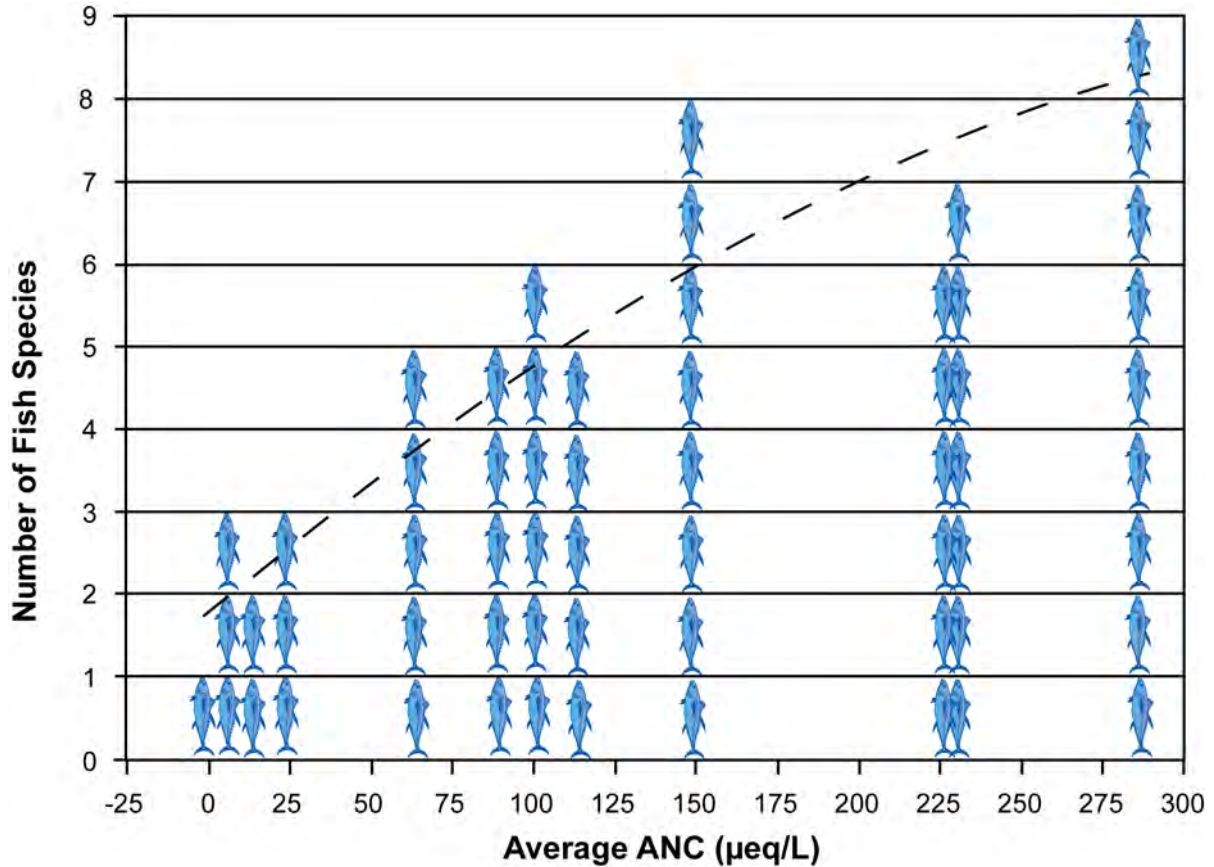


Figure AX4.4-4. Number of fish species among 13 streams in Shenandoah National Park. Values of ANC are means based on quarterly measurements, 1987-94. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently $< 75 \mu\text{eq/L}$ had three or fewer species.

Source: Redrawn from Bulger et al. (1999).

3 Median stream ANC values and watershed areas are shown in Table AX4.4-1 for the 14
4 streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species
5 richness shown in Figure AX4.4-4. Despite the overall similarities, these study streams vary in
6 watershed area by a factor of 10. The streams that have larger watershed areas generally have

1 more fish species than the streams having smaller watershed areas. All of the “rivers” have
2 watersheds larger than 10 km² and ANC higher than 75 µeq/L. In contrast, the majority (but not
3 all) of the “runs” have watershed area smaller than 10 km² and ANC less than 20 µeq/L. All of
4 the streams that have watershed areas smaller than 10 km² have three or fewer known species of
5 fish present. All of the streams having larger watersheds (>10 km²) have three or more known
6 fish species; seven of nine have five or more species; and the average number of fish species is
7 six. There is no clear distinction between river and run, but it is clear that as small streams in
8 Shenandoah National Park combine and flow into larger streams and eventually to rivers, two
9 things happen: acid-sensitivity generally declines, and habitat generally becomes suitable for
10 additional fish species (Sullivan et al., 2003).

11 South of Shenandoah National Park the effects of surface water acidification on fish
12 species richness have been studied in some detail in the St. Marys River in Virginia. Fish
13 species richness was closely associated with surface water acid-base chemistry. Bugas et al.
14 (1999) conducted electrofishing in the St. Marys River in 1976, and every 2 years from 1986
15 through 1998. Systemic stream acidification occurred during the study period. Sampling
16 occurred at six sites between the downstream end of the St. Marys Wilderness and the
17 headwaters over a distance of about 8 km. The number of fish species in the St. Marys River
18 within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in
19 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*]) are tolerant of low pH
20 and are typically the only fish species present in streams having similar levels of acidity in
21 Shenandoah National Park, which is also located in Virginia (Bulger et al., 1999). Bugas et al.
22 (1999) reported that successful brook trout reproduction in the St. Marys River occurred only 1
23 year out of 4 during the period 1995 through 1998. Eight of the fish species recorded in one or
24 more early years have not been observed in more recent years. Several, including blacknose
25 dace, rainbow trout, and torrent sucker (*Thoburnia rhotroeca*), showed a pattern of being
26 progressively restricted over time to lower river reaches, which generally have higher ANC. The
27 number of fish species decreased with decreasing minimum ANC, from nine species at ANC of
28 about 160 µeq/L to one to three species at ANC near 0. The best fit regression line suggested, on
29 average, a loss of one species for every 21 µeq/L decline in annual minimum recorded ANC
30 value.

1 Dynamic water chemistry model projections have been combined with biological dose-
2 response relationships to estimate declines in fish species richness with acidification. A
3 relationship derived from the data in Figure AX4.4-4 was used by Sullivan et al. (2003) with
4 stream ANC values predicted by the MAGIC model to provide estimates of the expected number
5 of fish species in each of the modeled streams for the past, present, and future chemical
6 conditions simulated for each stream. The coupled geochemical and biological model
7 predictions were evaluated by comparing the predicted species richness in each of the 13 streams
8 with the observed number of species that occur in each stream. The agreement between
9 predicted and observed species numbers was good, with a root mean squared error (RMSE) in
10 predicted number of species across the 13 streams of 1.2 species. The average error was 0.3
11 species, indicating that the coupled models were unbiased in their predictions. Model
12 reconstructions of past species richness in the streams suggested that historical loss of species
13 had been greatest in the streams located on the most sensitive geological class (siliciclastic). The
14 average number of species lost from streams on the three bedrock types examined were
15 estimated as: 1.6 species on siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4
16 species on basaltic bedrock. In the case of the siliciclastic streams, the projected past changes
17 were much larger than the average error and RMSE of the coupled models, suggesting that the
18 projections were reasonably robust.

19 It appears that fish species richness is controlled by multiple factors, of which both
20 acidification and watershed area can be important. Watershed area might be important in this
21 context because smaller watersheds may contain smaller streams having less diversity of habitat,
22 more pronounced effects on fish from high-flow periods, or lower food availability. Such issues
23 interact with other stresses, including acidification, to determine overall habitat suitability.

24 For Shenandoah National Park, Bulger et al. (1999) concluded that the most important
25 cause of the observed decline in species richness with decreasing ANC was acid stress associated
26 with acidification. However, an additional causal factor may have been the decrease in the
27 number of available aquatic niches when moving from downstream locations (which are seldom
28 low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region;
29 Sullivan et al. 2003). The relative importance of this latter factor, compared with the importance
30 of acid stress, in determining this relationship is unknown.

1 In the Adirondack region, Driscoll et al. (2001b) concluded that high-elevation lakes are
2 more likely to be fishless than larger lakes at low elevation (Gallagher and Baker, 1990) because
3 they have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may
4 be susceptible to periodic winter kills. Nevertheless, small, high-elevation Adirondack lakes
5 with fish also had significantly higher pH compared with fishless lakes; acidity is likely to play
6 an important role in the absences of fish from such lakes (Driscoll et al., 2001b).

7 8 **AX4.4.1.4 Community Structure**

9 Ecosystem response to pollutant deposition is a direct function of the ecosystem's ability
10 to ameliorate resulting changes in individual species (Strickland et al., 1993). In order to
11 determine ecosystem response and the possible effects on community structure, species
12 responses must be scaled in both time and space and be propagated from the individual to the
13 more complex levels of community interaction within an ecosystem.

14 Individuals within a population vary in their ability to withstand a stress. The response of
15 each individual is based on its genetic constitution (genotype), its stage of growth at time of
16 exposure to the stress, and the microhabitat in which it lives (Levlin, 1998). The range within
17 which individuals in the population can exist and function determines the ability of the
18 population to survive when exposed to a chronic stress. Those individuals that are able to cope
19 with the stress survive and reproduce. The same kinds of pressures act on populations of
20 different species. Competition among species results in community change over time and
21 eventually produces ecosystems composed of populations of species that have the capability to
22 tolerate the stress (Guderian et al., 1985; Rapport and Whitford, 1999; U.S. Environmental
23 Protection Agency, 2004).

24 Work conducted on the biological effects of acidification has largely been focused on the
25 response of fish, especially salmonids (trout and salmon). This focus tends to be driven by the
26 value people place on fish and fishing, rather than any ecological consideration. Other
27 vertebrate, invertebrate, plant, and algal communities are also sensitive to acidification. In
28 general, higher order trophic groups are more susceptible to acidification. Thus, in terms of
29 changes in community structure in response to aquatic acidification, the general progression of
30 sensitivity is as follows: fish > invertebrates (benthic and zooplankton) > algae > microbes
31 (Baker et al., 1990a). Population-level fish response to acidification is primarily through
32 recruitment failure, a result of increased mortality of early life stages or indirect effects through

1 the food chain (loss of prey species). Al_i , pH, and Ca^{2+} have been identified as the variables
2 most likely to have the greatest influence on fish community structure.

3 4 **AX4.4.1.5 Indices of Ecological Effects**

5 The most widely used index of acidification effect is the Acid Stress Index (ASI)
6 developed by Baker et al. (1990a). This index uses fish bioassay survival data fitted to a
7 maximum likelihood logistic regression model as a function of exposure to pH, Al, and Ca^{2+} to
8 predict the probability of fish survival expressed as a percent mortality. This approach can aid in
9 determination of effects on species composition by predicting the probability of occurrence of
10 species of varying acid sensitivity. Separate ASI models were developed for tolerant,
11 intermediate, and sensitive fish species. Approximate ASI reference levels were established for
12 various species based on logistic regression of fish presence as a function of the sensitive,
13 intermediate, and tolerant ASI values for brown bullhead (*Ameiurus nebulosus*), brook trout, lake
14 trout, and common shiner (*Luxilus cornutus*). They are presented in Table AX4.4-2.

15 The ASI was deemed a useful index of stress by Baker et al. (1990a), even though the
16 relationships between ASIs and fish population status could not be quantified precisely because
17 of confounding factors. Such factors included the abundance and types of food species,
18 competitors and predators present, variations in habitat quality, and density-dependent effects on
19 fecundity.

20 21 **AX4.4.2 Timing of Effects**

22 23 **AX4.4.2.1 Life Stage Differences in Sensitivity**

24 Episodic and chronic changes in the chemistry of surface waters can have different
25 effects on aquatic organisms and populations depending on species and the life history stages
26 present. More is known about the sensitivity to acidification of the life stages of fish than is
27 known for other aquatic organisms. In general, early life stages are more sensitive to acidic
28 conditions than the young-of-the-year, yearlings, and adults (Baker and Schofield, 1985; Johnson
29 et al., 1987; Baker et al., 1990a). Also, small fish, especially swim-up fry, are probably less
30 mobile and less able to avoid exposure to adverse chemical conditions than the relatively larger
31 adults (Baker et al., 1996).

1 There are a number of issues of acidification timing that are important to determination of
2 the extent and magnitude of effects. One important issue concerns the timing of acidity exposure
3 relative to life stage. For example, adult fish are generally more tolerant of acidity than early life
4 stages such as eggs, fry and juveniles. There could be substantial differences in effect based on
5 small differences in age or timing of exposure to acidity. No definite pattern was observed by
6 Baker et al. (1990a) across all studies or species. This may reflect either differences in the test
7 conditions or actual differences among species.

8 The presence of early life stages of brook trout, which are most sensitive to adverse
9 effects from acidification (Bulger et al., 2000), varies with season. For example, the most acid-
10 sensitive stages of brook trout development are present in Virginia streams throughout the cold
11 season in general, and the winter in particular (Figure AX4.4-5).

Acid-Sensitive Life Stages of the Brook Trout

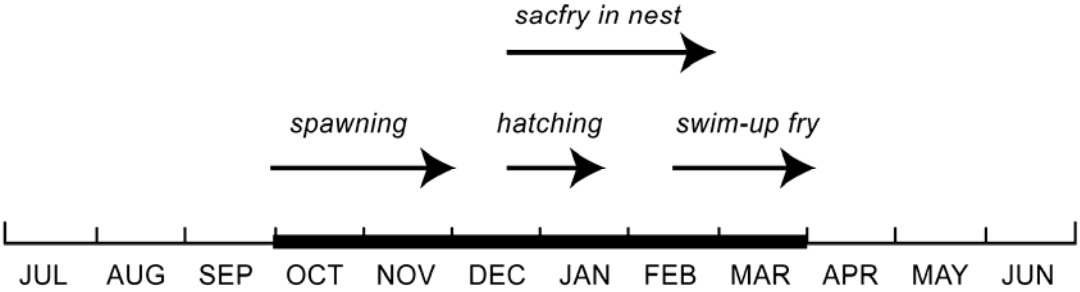


Figure AX4.4-5. Life stages of brook trout.

Source: Sullivan et al. (2003).

12 The processes of oogenesis and fertilization in fish and aquatic invertebrates are
13 especially sensitive to low pH (Muniz, 1991; Havas et al., 1995). In fish, this sensitivity is most
14 likely due to adverse effects on the female spawner. For instance, Beamish et al. (1976) reported
15 that reduced serum and plasma Ca^{2+} in female fish in acidified Canadian lakes lead to a higher
16 probability for failure in producing viable eggs. A depletion of Ca^{2+} from bone and increased

1 numbers of females with unshed eggs have also been linked to sensitivity at this life stage (cf.
2 Rosseland, 1986; Muniz, 1991).

3 After fertilization, the embryo seems to be susceptible to acidic waters throughout the
4 whole period of development. The periods shortly after fertilization and prior to hatching seem
5 to be most critical (Rosseland, 1986). The susceptibility of the embryo can be the result of direct
6 exposure to elevated H^+ concentrations and also to the toxic effects of Al_i at intermediate pH-
7 values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to
8 either a prolongation of the hatching or to a reduced hatching success (Rosseland, 1986). Eggs
9 lying in gravel on stream and lake beds are to some extent protected from exposure to rapid
10 changes in pH (Gunn and Keller, 1984b; Lacroix, 1985b). Nevertheless they can experience
11 high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a).

12 In fish, emergent alevins show susceptibility to the adverse effects of Al_i and H^+ that
13 increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland (1986)
14 indicated that this increasing sensitivity results from changes that take place in the respiratory
15 system. Shortly after hatch, alevins still respire through their skin but gradually gills become the
16 primary organ of gas and ion exchange. Gills are the locus for interference of H^+ and Al_i with
17 iono-regulatory exchange. Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus*
18 *clarki*) from the Snake River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory.
19 Fertilized egg, eyed embryo, alevin, and swim-up larval stages were exposed to low pH for a
20 period of seven days. Each life stage was monitored for mortality, growth, and development for
21 40 days after hatching. Reductions in pH from 6.5 to 6.0 in low- Ca^{2+} water (70 $\mu eq/L$) did not
22 affect survival, but reduced growth of swim-up larvae. The eggs, alevin, and swim-up larval
23 stages showed significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher
24 at pH 5.0 than at pH 6.5, but only statistically higher for eggs.

25 Woodward (1991) exposed greenback cutthroat trout (*Oncorhynchus clarki stomias*) in
26 the laboratory to 7-day pH depressions. Low- Ca^{2+} (65 $\mu eq/L$) water at pH 6.5 was
27 experimentally reduced to pH values of 6.0, 5.5, 5.0, and 4.5. Four life stages were exposed:
28 freshly fertilized egg, eyed embryo, alevin, and swim-up larva. Alevin survival was reduced at
29 pH 5.0, whereas survival of eggs, embryos, and swim-up larvae was reduced at pH 4.5.
30 Swim-up larvae showed feeding inhibitions at pH 4.5. The authors concluded that the threshold

1 for effects of acidity on greenback cutthroat trout in the absence of Al was pH 5.0 (Woodward,
2 1991).

3 Yellowstone cutthroat trout (*O. c. bouveri*) were exposed to 7-day pH depressions by
4 Farag et al. (1993). Of the four life stages studied, eggs were most sensitive to low pH. Eggs
5 exposed for seven days to pH 5.0 test water showed a statistically significant reduction in
6 survival compared with eggs exposed for seven days to pH 6.5 water. Survival of alevin and
7 swim-up larvae were significantly reduced from near 100% at pH 6.5 to near 0% at pH 4.5.
8 Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control
9 (6.5) but not by statistically significant amounts. Eyed embryos were not sensitive to any of the
10 exposures.

11 According to Bulger et al. (1999), adult brook trout in Shenandoah National Park streams
12 are more tolerant of acidity than are adult blacknose dace. For both species, the early life stages
13 are more sensitive than the adults, and brook trout young are actually more sensitive than
14 blacknose dace adults (Bulger et al., 1999). Blacknose dace spawn during summer and the eggs
15 and very young fry are therefore somewhat protected from the most acidic episodes, which
16 typically occur during cold-season, high-flow conditions.

17 18 **AX4.4.2.2 Biological Effects of Episodes**

19 Episodic decreases in pH and ANC can produce chemical conditions in lakes, and
20 especially in streams, that are as harmful to biota as chronic acidification (Baker et al., 1996).
21 Adverse effects on biota occur particularly when changes involve pH, Al_i, or Ca²⁺ (Baker et al.,
22 1990a). Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases
23 in Al_i in waters having low Ca²⁺ concentration. However, Baker et al. (1990a) concluded that
24 episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above
25 5.5 and minimum pH during the episode of less than 5.0.

26 Results from the ERP demonstrated that episodic acidification can have long-term
27 adverse effects on fish populations. Streams with suitable chemistry during low flow, but low
28 pH and high Al_i levels during high flow, had substantially lower numbers and biomass of brook
29 trout than in non-acidic streams (Wigington et al., 1996). Streams having acidic episodes
30 showed significant mortality of fish.

31 Some brook trout avoided exposure to stressful chemical conditions during episodes by
32 moving downstream or into areas with higher pH and lower Al_i. This movement of brook trout

1 only partially mitigated the adverse effects of episodic acidification, however, and was not
2 sufficient to sustain fish biomass or species composition at levels that would be expected in the
3 absence of acidic episodes. Just as spatially heterogeneous environments or refugia enable some
4 species to survive in otherwise unfavorable conditions, temporal heterogeneity often has the
5 opposite effect. These findings suggest that stream assessments based solely on chemical
6 measurements during low-flow conditions will not accurately predict the status of fish
7 populations and communities in small mountain streams unless some adjustment is made for
8 episodic processes (Baker et al., 1990a, 1996; Wigington et al., 1996; Sullivan, 2000).

9 In Shenandoah National Park, MacAvoy and Bulger (1995) used multiple bioassays over
10 3 years in one of the low-ANC streams as part of the FISH project to determine the effect of
11 stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry.
12 Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acid episodes
13 (with associated low pH and elevated Al_i concentrations, and high streamwater discharge)
14 induced rapid mortality in the low-ANC stream, while the test fish in the higher-ANC stream
15 survived (Bulger et al., 1999).

16 In the West, it has also been shown that native trout are sensitive to short-term increases
17 in acidity. For example, Woodward et al. (1989) exposed native western cutthroat trout to pH
18 depressions (pH 4.5 to 6.5) in the laboratory. Reductions in pH from 6.5 to 6.0 in low- Ca^{2+}
19 water (70 $\mu eq/L$) did not affect survival, but did reduce growth of swim-up larvae. Eggs,
20 alevins, and swim-up larvae showed significantly higher mortality at pH 4.5 as compared to pH
21 6.5. Mortality was also somewhat higher at pH 5.0, but only statistically higher for eggs. Some
22 species of aquatic biota in western aquatic ecosystems have been shown to be somewhat more
23 sensitive to pH and ANC change than are cutthroat trout (Baker et al., 1990a).

24 Multiple logistic regression models were used by Van Sickle et al. (1996) to relate fish
25 bioassay mortality rates to summary statistics of time-varying stream chemistry over the 20-day
26 bioassay periods. Higher mortality of all three test fish species (brook trout, dace, sculpin
27 [*Cottus* spp.]) during the *in situ* bioassays was clearly associated with increased Al_i . In addition,
28 individual bioassays conducted during chronically or episodically acidified conditions had higher
29 median mortality than did those during non acidic conditions, but no mortality differences were
30 detected between chronically acidic and episodically acidic conditions. Time-weighted median

1 Al_i was the best single predictor of 20-day mortality for both brook trout and sculpin, whereas
2 the number of days with Al_i > 200 µg/L provided the best prediction of blacknose dace mortality.

3 In the Northeast, Baker et al. (1996) studied the effects of episodic acidification on fish in
4 13 small streams in the Adirondack and Catskill Mountains of New York and the Northern
5 Appalachian Plateau in Pennsylvania. They conducted *in situ* bioassays with brook trout and
6 blacknose dace, mottled sculpin (*Cottus bairdi*) or slimy sculpin (*Cottus cognatus*) depending on
7 the region, to measure direct toxicity. Movements of brook trout individuals in relation to stream
8 chemistry were tracked using radiotelemetry. Electrofishing surveys assessed fish community
9 status and the abundance and biomass of brook trout in each stream. Streams with suitable
10 conditions during low flow, but moderate-to-severe episodic acidification during high flow, had
11 higher fish mortality in bioassays, higher net downstream movement of brook trout during
12 events, and lower brook abundance and biomass compared to nonacidic streams. These streams
13 lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into
14 refugia (areas with higher pH and lower Al) during episodes partially mitigated the adverse
15 effects of episodes.

16 Chemical measurements by ERP during high flow correlated with fish community status.
17 In general, reduced trout abundance occurred in ERP streams with median high flow pH < 5.0
18 and Al_i > 100 to 200 µg/L. Acid -sensitive fish species were absent from streams with median
19 high flow pH < 5.2 and Al_i > 100 µg/L. More recently, Baldigo et al. (2007) found that mortality
20 of brook trout young of the year occurred at concentrations as low as 54 µg/L .Al_i was the single
21 best predictor of fish mortality in ERP bioassays (Van Sickle et al., 1996) and has been identified
22 as an important toxic factor in other bioassays and field studies (Mount et al., 1988; Ingersoll
23 et al., 1990b; Rosseland et al., 1990). The relationships between pH and Al_i or ANC and Al_i
24 vary among streams (Wigington et al., 1996), and therefore predictions of potential effects on
25 fish based solely on pH or ANC may be misleading. High Al_i concentrations during episodes are
26 probably the dominant cause of adverse effects on fish during episodic acidity events.

27 28 **AX4.4.2.2.1 Biological Effects of Chronic Acidification**

29 Changes in surface water acid-base chemistry, including pH, ANC, Al_i, and Ca²⁺, can
30 affect in-stream and in-lake biota. Adverse biological effects may be seen at pH less than about
31 6.0 to 6.5 and Al_i greater than about 30 to 50 µg/L (1 to 2 µM). It tends to increase with
32 decreasing pH, and reaches potentially toxic concentrations (> ~2 µM) in surface drainage waters

1 having pH less than about 5.5. Effects vary substantially by organism, life stage, and the
2 concentration of DOC. Inorganic Al in solution is also toxic to plants.

3 Calcium can ameliorate the toxic effects of acidity and Al on biota. Most organisms can
4 tolerate lower pH and higher Al_i at higher Ca²⁺ concentrations, but in natural environments,
5 elevated concentrations of Al_i are only found in Ca²⁺-depleted systems. This effect is most
6 important at low Ca²⁺ levels. Overall biological effects noted with decreasing pH are described
7 in Table AX4.4-3 (Baker et al., 1990a). The organisms most likely to respond to such changes in
8 water chemistry include fish, aquatic insects, zooplankton, and diatoms. In some cases,
9 amphibians are also important sensitive biological receptors. Most available data are for fish
10 response.

11 In most stream or lake survey areas, direct quantification of biological responses to
12 surface water acidification is not possible, given the scarcity or absence of biological long-term
13 monitoring and dose-response data. Few biological long-term monitoring studies have been
14 conducted. Much of the available *in situ* dose-response data have been generated from studies of
15 streams in Virginia and Pennsylvania and lakes in New York. Data with which to evaluate
16 acidification relationships have been scarce in most other regions.

17 18 **AX4.4.2.2.2 Lakes**

19 Fish status assessments for the eastern and upper midwestern United States were
20 conducted by Baker et al. (1990a), by region, using a variety of assessment methods. For the
21 northeast region, two water chemistry models were linked to fish response models: the Integrated
22 Lake-Watershed Acidification Study (ILWAS) model and MAGIC. For the Adirondack
23 subregion, three process models were used: ILWAS, MAGIC, and Regional MAGIC. For other
24 areas in the eastern United States and for the Upper Midwest, analysis of fish status was limited
25 to application of the sensitive, intermediate, and tolerant toxicity models.

26 Assessment results reported by Baker et al. (1991a) for the Adirondack region are
27 presented in Table AX4.4-4 showing results based on the ASI. Table AX4.4-5 shows the
28 estimated percentage of Adirondack lakes with acid-base chemistry unsuitable for fish
29 population survival according to various assessment models based on responses for brook trout,
30 lake trout, and common shiner. Assessment results for the Northeast region are presented in
31 Tables AX4.4-6 and AX4.4-7.

1 In acid-sensitive lakes in the western United States, the focus is often mainly on native
2 cutthroat trout. It is important to note, however, that many high-elevation western lakes and
3 streams were historically fishless. The top predators in such aquatic ecosystems were often
4 amphibians or crustaceans. Thus, even though cutthroat trout might be considered native to the
5 region, they are not necessarily native to a particular lake or stream.

6 7 **AX4.4.2.2.3 Streams**

8 In streams, the major organisms of concern with respect to water acidification are fish,
9 amphibians, benthic macroinvertebrates, and periphyton (attached algae). All of these groups
10 have shown adverse effects in response to acidification (see section AX4.6). Most available data
11 are for fish and aquatic insects, mainly in the southeastern United States. Streams affected by
12 acidic deposition tend to occur at high elevation. They are often high-gradient and flow through
13 base-poor geology.

14 Baker et al. (1991a) presented assessment results for the mid-Appalachian region as the
15 distribution (percent) of NSS lower node, upper node, and total streams classified in various ASI
16 values (Table AX4.4-8) (Baker et al., 1991a). Most of the streams were classified in the lowest
17 ASI category (Table AX4.4-8). Assessment results for the interior Southeast region were similar
18 (Table AX4.4-9).

19 Some fish response research has also been conducted for streams in the Catskill
20 Mountains. Baker and Christensen (1991) estimated that the fish species found in the Neversink
21 River Basin in the Catskill Mountains are typically lost when pH decreases to the range of 4.7 to
22 5.2 (brook trout), 5.5 to 5.9 (slimy sculpin), 4.7 to 5.7 (brown trout), 5.6 to 6.2 (blacknose dace),
23 and 4.9 to 5.3 (Atlantic salmon).

24 The Shenandoah National Park FISH Project evaluated the effects of streamwater
25 acidification on fish populations and communities in streams in Shenandoah National Park. Fish
26 species richness, population density, condition factor, age distribution, size, and bioassay
27 survival were all lower in streams having low-ANC compared to intermediate-ANC and high-
28 ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and
29 Bulger, 1995).

30 Bulger et al. (2000) developed model-based projections using the MAGIC model to
31 evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels
32 using data from VTSSS and SWAS. Projections were based on four brook trout stream

1 categories: Suitable, ANC > 50 µeq/L; Indeterminate, ANC 20 to 50 µeq/L; Marginal, ANC 0 to
2 20 µeq/L; and Unsuitable, ANC < 0 µeq/L. Three scenarios of future acidic deposition were
3 modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and
4 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values,
5 approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout
6 because they were either episodically (24%) or chronically (6%) acidic. In addition, another
7 20% of the streams were classified as indeterminate, and brook trout in these streams may or
8 may not have been affected. Based on the model simulations, 82% of these streams would not
9 have been acidic prior to the onset of acidic deposition and would likely have been suitable for
10 brook trout.

11 The model projections suggested that neither the 40% nor the 70% reductions in acidic
12 deposition would be expected to increase the number of streams that were suitable for brook
13 trout above the ambient 50%. In fact, the results suggested that a 70% reduction in deposition
14 would be needed in the long-term just to maintain the number of streams that were considered
15 suitable for brook trout. Because of the length of time required to restore buffering capacity in
16 watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or
17 unsuitable for the foreseeable future.

18 To develop projections of probable past and future responses of aquatic biota to changing
19 S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al.
20 (2003) with several empirical models that linked biological response to past and future model
21 projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the
22 biological effects estimates were based on observed empirical relationships rooted in correlation
23 and expressed as linear relationships. Correlation does not necessarily imply cause, but an
24 observed pattern of co-variation between variables does provide a context for analysis of a
25 possible relationship. In this case, the projections did not require extrapolation and are,
26 therefore, statistically robust. To the extent that the observed empirical relationships used in the
27 coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were
28 also biologically robust.

29 The geochemical and biological response models also differ in that MAGIC is a dynamic
30 model and explicitly predicts the time course of changing water quality, whereas the empirical
31 relationships used for estimating biological response were static. These relationships reflected a

1 point in time (when the observations were made) and provided no information concerning the
2 dynamics of biological response. That is, the empirical models predicted a new biological status
3 for a new water chemistry, but gave no indication of the time required to achieve the biological
4 status once the water quality change had occurred.

5 There are thus two considerations that must be kept in mind when interpreting the
6 biological responses predicted using a combination of process-based and empirical modeling
7 approaches: the causality of the relationship between water quality and response, and the
8 dynamics of biological response. With respect to the issue of causality, acidification is a
9 disturbance and disturbance usually lowers species richness. In turn, loss of species usually
10 lowers ecosystem stability. Biodiversity loss is a predictable and proven consequence of
11 acidification, and there are abundant examples of this in North America and Europe (cf. Bulger
12 et al., 2000). With respect to the timing of biological response, it can be variable and difficult to
13 predict.

14 **AX4.4.2.3 Timing of Recovery from Acidification**

16 Lakes and streams show spatial and temporal variability in response to a host of biotic
17 and abiotic factors. Against this background of variability, it is difficult to detect changes in
18 biological communities in response to changes in an individual environmental stressor without
19 long-term biological data (Schindler, 1990; Lancaster et al., 1996). Long-term data sets are rare,
20 and there are few well-documented instances of temporal changes in biological communities in
21 response to changes in water chemistry. Regardless, it is known that surface water acidification
22 affects virtually all trophic levels (e.g., Flower and Battarbee, 1983; Økland and Økland, 1986;
23 Rundle and Hildrew, 1990; St. Louis et al., 1990; Ormerod and Tyler, 1991; Siminon et al.,
24 1993; Lancaster et al., 1996; Sullivan, 2000).

25 Biological recovery can occur only if chemical recovery is sufficient to allow survival
26 and reproduction of acid-sensitive plants and animals. The time required for biological recovery
27 is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored
28 because of the long life of many plant species and the complex interactions of soil, roots,
29 microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate
30 populations may recover relatively rapidly (within approximately 3 years), whereas lake
31 populations of zooplankton recover more slowly (Gunn and Mills, 1998).

1 The timing of fish recovery is highly uncertain, and probably will depend heavily on
2 dispersal opportunities. Stocking could accelerate fish population recovery (Driscoll et al.,
3 2001b). Fish populations have recovered in acidified lakes when the pH and ANC have been
4 raised through liming or reduction of acidic deposition (Hultberg and Andersson, 1982; Beggs
5 and Gunn, 1986; Dillon et al., 1986; Keller and Pitblado, 1986; Raddum et al., 1986; Gunn et al.,
6 1988; Kelso and Jeffries, 1988).

7 Studies in Canada have improved understanding of the feasibility and complexity of
8 biological recovery in response to chemical recovery from acidification. Biological recovery of
9 previously acidified lakes is expected to be a slower process than chemical recovery. Sometimes
10 there are other environmental stresses in addition to acidity, such as metal contamination
11 (Gundersen and Rasmussen, 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al.,
12 1995; Yan et al., 1996b). Barriers can be imposed by water drainage patterns between lakes that
13 hinder re-colonization by some fish species (Jackson and Harvey, 1995). Predation by non-acid-
14 sensitive fish species can affect the recovery of zooplankton and macroinvertebrate communities
15 (McNicol et al., 1995). Finally, tributary-spawned fish can be preyed upon when they move
16 downstream into lakes inhabited by predatory fish and birds (Schofield and Keleher, 1996).

17 Changes in surface water chemistry as a direct response to changes in S and N deposition
18 are difficult to predict. Both chemical and biological effects of changing deposition can lag as
19 the ecosystem comes into equilibrium with the modified deposition inputs. Soils or wetlands
20 may continue to release S at a high rate for many years subsequent to a decrease in S deposition.
21 As a result, surface water SO_4^{2-} concentrations may decrease in the future as a consequence of
22 deposition changes that have already occurred. If soil base cations have become depleted, base
23 cation concentrations in some surface waters could decrease in the future irrespective of any
24 further changes in SO_4^{2-} concentrations. This would be expected to contribute to additional
25 acidification.

26 Studies in the United States, Canada, and Europe have illustrated the feasibility and
27 complexity of biological recovery in response to decreased surface water acidity. There is
28 currently no theoretical basis on which to predict the paths of biological recovery. At some
29 scale, each stream or river is unique. The null hypothesis is that recovery will proceed in the
30 same fashion as acidification, only backwards. Thus, for example, the last species lost (the most
31 acid-tolerant) would be the first to return. However, time lags are expected to differ widely

1 among species and among water bodies. Biological recovery of previously acidified lakes or
2 streams can lag behind chemical recovery because of such factors as (a) limits on dispersal and
3 recolonization; (b) barriers imposed by water drainage patterns (Jackson and Harvey, 1995); (c)
4 the influence of predation (McNicol et al., 1995); and (d) other environmental stresses (Gunn
5 et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al.,
6 1996a,b).

7 Limitations on dispersal and recolonization can hamper biological recovery from chronic
8 and episodic acidification. If fish move into refugia areas during low pH and then return,
9 behavioral avoidance would reduce the overall effect of acidification on fish populations.
10 However, if fish move out of the stream system in response to sublethal episodes, as suggested
11 by Baker et al. (1996), and do not return or return in smaller numbers, then the population level
12 effects of episodic acidification would be greater than predicted based on mortality tests alone.

13 Stream macroinvertebrate communities are often dominated by immature life stages of
14 flying insects, such as mayflies, dragonflies, and stoneflies. Such species have rather rapid
15 colonization times, such that a functional stream macroinvertebrate community may return in
16 only a few years in response to improved chemistry. However, fish community recovery is
17 expected to be quite variable, depending on sources of colonists. In streams, fish could be
18 introduced as soon as the water quality becomes suitable or the macroinvertebrate community
19 becomes established. In streams that had simple fish communities in the past, a fish community
20 might become rapidly established. It might take decades for complex communities without
21 species introductions.

22 The Sudbury region of Ontario, Canada has been important for studying the chemical and
23 biological effects of S deposition. Mining and smelting of copper-nickel ore began in the 1880s.
24 By the 1950s and 1960s, SO₂ emissions from the mining and smelting operations peaked at over
25 5,000 tons/day and extensive acidification of nearby surface waters was documented (Beamish
26 and Harvey, 1972). Emissions of SO₂ then decreased during the 1970s to less than one-third of
27 the peak values. This region has been the focus of extensive chemical and biological effects
28 work since the 1980s (Keller, 1992). Sulfur emission reductions resulted in improved water
29 quality in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries
30 recovery was also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and
31 Keller (1992) found changes in the occurrence and abundance of benthic invertebrates that were

1 consistent with a direct effect of reduced lakewater acidity. A more recent assessment of
2 recovery of ecosystems in Canada provided further evidence of biological recovery, but also
3 showed that the spatial extent of recovery was limited to lakes that had been severely acidified
4 by the Sudbury smelter (Jeffries et al., 2003).

5 Whitepine Lake, located 90 km north of Sudbury, had low pH (5.4) and ANC (1 $\mu\text{eq/L}$)
6 in 1980 and its fish populations displayed symptoms of acid stress. Acid-tolerant yellow perch
7 (*Perca flavescens*) were abundant, but the more acid-sensitive species lake trout and white
8 sucker (*Catostomus commersoni*) were rare and not reproducing. Fish populations were studied
9 by Gunn and Keller (1990) from 1978 through 1987, and zooplankton were sampled at least
10 monthly during the open-water periods of 1980 through 1988. During the period between 1980
11 and 1988, pH increased to 5.9 and ANC increased to 11 $\mu\text{eq/L}$. Young lake trout first reappeared
12 in 1982 and became increasingly abundant throughout the study. The number of benthic
13 invertebrate taxa increased from 39 in 1982/83 to 72 in 1988, and the relative abundance of
14 many of the invertebrates found in 1982 changed along with the changes in water chemistry
15 (Gunn and Keller, 1990). Research at Sudbury clearly documented that chemical recovery of
16 lakes was possible upon reduced emissions and deposition of S, and also that biological
17 recovery, involving multiple trophic levels, would soon follow.

18 Baker et al. (1990a) used field-based models to test the potential for biological recovery.
19 The models were calibrated from the observed among-lake or among-stream associations
20 between fish status and the chemical and physical characteristics measured in the surface water.
21 The models were generally calibrated using chemistry data collected in conjunction with surveys
22 of fish status. It was assumed that the systems surveyed were at steady state and that the
23 observed status of the fish community was determined by the observed chemical and physical
24 conditions in the lake or stream. For each species considered, the current presence or absence of
25 the species was analyzed as a function of the water quality variables associated with acidification
26 (e.g., pH, Al, Ca^{2+} , ANC, and DOC) using maximum likelihood logistic regression (Reckhow
27 et al., 1987). Models developed from data from the ELS and the ALSC were calibrated against
28 data from Ontario lakes.

29 The results from the various models were compared to their prediction of the change in
30 the number of Adirondack lakes with unsuitable acid-base chemistry, given a 50% decrease or a
31 30% increase in S deposition relative to the existing conditions. All the models provided similar

1 results (Figure AX4.4-6) with the exception of those that relied on the pCa/pH term to predict
 2 fish status. Those models seemed to overestimate the effect of Ca^{2+} , and thus underestimate
 3 predicted fish response to changes in acidic deposition.

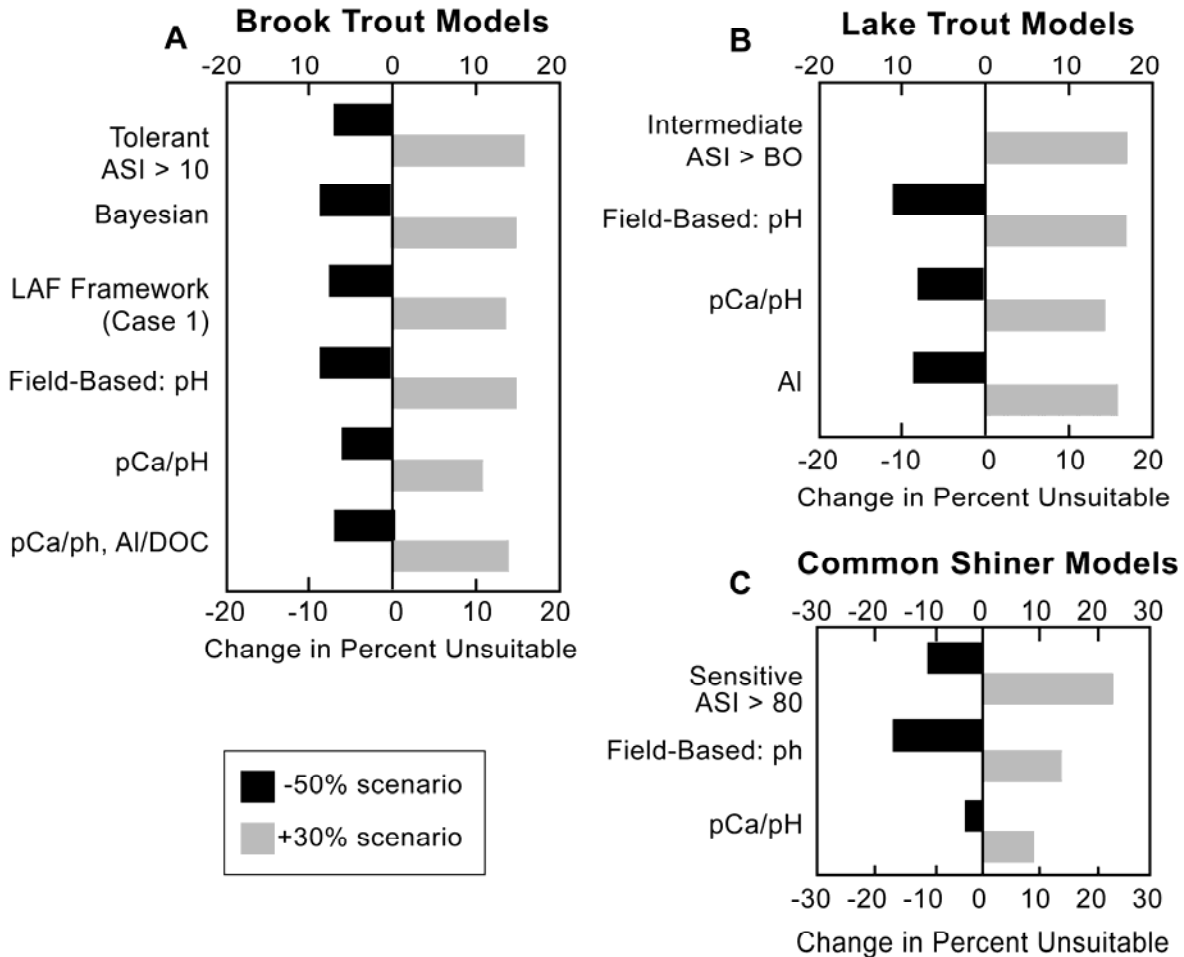


Figure AX4.4-6. Example model application: Projected changes in the percentage of Adirondack lakes (Direct/Delayed Response project target population) with acid-base chemistry unsuitable for the survival of fish populations in the year 2034, versus current simulated conditions, based on projected changes in water chemistry from the Model of Acidification of Groundwater in Catchments (MAGIC) and using alternative models of fish response, given a 50% decrease in deposition or a 30% increase in deposition. (a) brook trout, (b) lake trout, (c) common shiner.

Source: Baker et al. (1990a).

1 An important consideration for measuring the success of S and N emissions controls is
2 the development of appropriate expectations for the *magnitude* of potential chemical recovery.
3 Most lakes inferred to have been measurably acidified by atmospheric deposition were already
4 marginally acidic, typically with pH less than about 6, before anthropogenic atmospheric
5 pollution began prior to 1900. Therefore, full recovery of currently acidic lakes would not be
6 expected to yield neutral pH. Nevertheless, increases in ANC may allow recovery of fish
7 populations even if pH remains relatively low (Stoddard et al., 2003).

8 9 **AX4.4.3 Effects by Ecosystem Type**

10 11 **AX4.4.3.1 Terrestrial Ecosystems**

12 The effects of atmospheric deposition of S and N on terrestrial ecosystems are manifested
13 at the individual plant level. However, individual plants do not exist in isolation. Each is a
14 member of an ecosystem, which is a structurally complex entity that is comprised of populations
15 of plants, animals, and other life forms that interact with each other and with the non-living
16 environment in which they exist (Odum, 1989; U.S. Environmental Protection Agency, 1993).
17 All life on Earth is dependent on chemical energy that flows through ecosystems in the form of C
18 compounds. Terrestrial vegetation, through the process of photosynthesis, accounts for about
19 half of the C that cycles between the Earth and its atmosphere (Chapin and Ruess, 2001).

20 The responses of plant species and populations to environmental perturbations, such as
21 those caused by atmospheric deposition of NO_x and SO_x, are governed by plant genetics, life
22 cycles, and habitats. An environmental stress applies selection pressures on individual plants
23 (Treshow, 1980). A common response in a community under stress is the elimination of the
24 more sensitive populations or species and an increase in abundance of those that tolerate or are
25 favored by that stress (Woodwell, 1970; Guderian et al., 1985).

26 27 **AX4.4.3.1.1 Forests**

28 Scientists are concerned about the potential effects of soil acidification on forest health.
29 However, forest health is a complicated concept. It can be reflected by a variety of physiological
30 indicators, including, for example, changes in the growth rate of trees, foliar damage,
31 susceptibility to insects or disease, or tree mortality. Similarly, forest health can be affected by a
32 host of potential stressors, of which air pollution is only one possibility. Climate, stand

1 competition, outbreak of non-native pathogens, and forest management (alone or in combination)
2 often contribute greatly to observed forest health problems. Attempts to document and, in
3 particular, to quantify the effects of air pollution on forest health have encountered considerable
4 complexity and uncertainty. Nevertheless, such efforts have produced some evidence that
5 suggests in some areas in the eastern United States red spruce and sugar maple have experienced
6 declining health as a consequence of acidic deposition. Available evidence for the southern
7 Appalachian Mountains was reviewed by Eagar et al. (1996) and Sullivan et al. (2002). In the
8 western United States, the health of ponderosa and Jeffrey pines have been affected by air
9 pollution, but such effects have been attributed to O₃ exposure, not acidic deposition.

10 It is important to note that, at most forested locations in the United States, it is unlikely
11 that terrestrial effects of atmospheric deposition can be documented by conducting vegetation
12 studies. This is because levels of atmospheric deposition of S and N are usually below expected
13 damage thresholds for most tree species, assessment of forest health is extremely complex, and
14 trees typically respond to a wide variety of stressors in addition to atmospheric deposition. It is
15 therefore more likely that the results of vegetative studies will be useful as corroborating
16 evidence, to be used in conjunction with results of analysis of soil and/or drainage water
17 chemistry when assessing acidification effects on terrestrial ecosystems.

18 Species vary in the extent to which they can tolerate environmental change. The ability
19 of a given species to survive any environmental change is governed by the range of variation in
20 that environmental attribute within which individual organisms can exist and thrive. Plant
21 species compete for nutrients, light, water, and growing space. Different species possess
22 different abilities to withstand stresses, including stress associated with climatic features,
23 herbivory, disease, and disturbance. Human-caused stresses, including air pollution, are
24 superimposed on the natural stresses to which species are adapted. A disturbance such as air
25 pollution can change the plant species composition of the vegetative community by reducing or
26 eliminating species that are most sensitive to that stress. Species able to cope with the stress
27 survive, reproduce, and become more dominant. This can result in changes in species
28 composition and elimination of some highly sensitive species from the plant community.

29 Atmospheric deposition of S and/or N can have disproportionate effects on the more
30 sensitive plant species, making it more difficult for them to effectively compete for limited
31 resources and increasing their susceptibility to natural disturbances such as disease, cold

1 temperature, insect pest attack, wind or ice-storm damage, or drought. Such effects are
2 commonly manifested through acidification and nutrient enrichment. The end result can be
3 reduced growth, health, or distribution of the more sensitive species, and enhanced growth or
4 distribution of the more tolerant species.

5 Ecosystems respond to environmental stress in part through the response of each
6 organism that makes up the ecosystem. Plant communities can react to a stress such as air
7 pollution, at levels typically encountered in the United States, with no response, physiological
8 accommodation, or differential response (Taylor and Pitelka, 1992). Differential response results
9 in some individuals exhibiting better growth and reproduction than others. Over multiple
10 generations, sensitive individuals can be eliminated, causing a shift toward greater resistance of
11 the population to that environmental stressor. The primary effect of air pollution on the more
12 susceptible members of the plant community is that they can no longer compete as effectively for
13 essential nutrients, water, light, and space (U.S. Environmental Protection Agency, 1993). Over
14 time, the more susceptible individuals of the plant populations and the more susceptible
15 populations of the plant community are eliminated.

16 The effects of atmospheric N deposition on vegetation are mediated either through the
17 soil or foliage. Nitrogen deposition in the United States is generally not high enough to reach
18 phytotoxic levels. Thus, N deposition effects generally entail modification of the N cycle and
19 associated soil chemical properties (U.S. Environmental Protection Agency, 1993). Increased
20 N loads to the soil can alleviate N deficiencies and allow increased plant growth because most
21 plant communities are N-limited. Excessive N inputs can also lead to deficiencies in other
22 elements, especially Ca^{2+} or Mg^{2+} .

23 The major effects of acidic deposition on vegetation occur through the soil (NAPAP,
24 1998) and are considered to be indirect effects. Acidic deposition has contributed to a decline in
25 the availability of Ca^{2+} and other base cations in the soils of acid-sensitive forest ecosystems by
26 the leaching of base cations from foliage and from the primary rooting zone, and by the
27 mobilization of Al from soils to soil solution and drainage water (Eagar and Adams, 1992;
28 NAPAP, 1998). Aluminum mobilization from acid soils can impede Ca^{2+} and Mg^{2+} uptake by
29 plant roots and potentially induce deficiencies in these nutrients. Both N and S deposition have
30 contributed to these effects. As a consequence, foliar Ca^{2+} levels and soil and root Ca:Al ratios

1 are considered low to deficient over large portions of the spruce-fir region in the eastern United
2 States (Joslin et al., 1992; Cronan and Grigal, 1995; NAPAP, 1998).

3 Calcium must be dissolved in soil water to be taken up by roots. Aluminum in soil
4 solution reduces Ca^{2+} uptake by competing for binding sites in the cortex of fine roots. Tree
5 species may be adversely affected if high Al-to-nutrient ratios limit the uptake of Ca^{2+} and Mg^{2+}
6 (Shortle and Smith, 1988; Garner, 1994). A reduction in Ca^{2+} uptake suppresses cambial growth,
7 reduces the rate of wood formation, decreases the amount of functional sapwood and live crown,
8 and predisposes trees to disease and injury when the functional sapwood becomes less than 25%
9 of the cross-sectional stem area (Smith, 1990). Cronan and Grigal (1995) summarized results of
10 studies that examined the influence of Al and Ca^{2+} on trees (Table AX4.4-10).

11 Included among the direct responses of forest trees to acidic deposition are increased
12 leaching of nutrients from foliage; accelerated weathering of leaf cuticular surfaces; increased
13 permeability of leaf surfaces to toxic materials, water, and disease agents; and altered
14 reproductive processes (Altshuller and Linthurst, 1984; Cape, 1993; U.S. Environmental
15 Protection Agency, 2004). As noted above, acidification results in the loss of acid-sensitive
16 species, and there is more loss with higher degrees of acidification. The overall species pool
17 decreases as surface water acidity increases. Thus, acidification can result in decreasing species
18 richness.

19 Patterns of change in tree ring chemistry, principally at high-elevation sites in the eastern
20 United States, are believed to reflect the changing inputs of atmospheric pollutants to forests. A
21 temporal sequence of change in uptake patterns, and possibly in tree growth, would be expected
22 if significant base cation mobilization and subsequent depletion of base cations from eastern
23 forest soils has occurred (U.S. Environmental Protection Agency, 2004). Temporal changes in
24 the chemistry of the tree rings of red spruce were examined as indicators of historical changes in
25 the red spruce's soil chemical environment (Bondietti and McLaughlin, 1992). Available data
26 suggested that Ca^{2+} mobilization increased about 60 years ago, followed by reduced
27 accumulation rates in wood, presumably associated with decreasing Ca^{2+} availability in soil. The
28 period of Ca^{2+} mobilization coincided with a region-wide increase in the growth rate of red
29 spruce. The period of decreasing levels of Ca^{2+} in wood corresponded temporally with patterns
30 of decreasing radial growth at high elevation sites throughout the region. The decline in wood
31 Ca^{2+} suggests that soil Ca^{2+} loss may have increased to the point at which base saturation of soils

1 was reduced. Increases in Al and iron (Fe) typically occur as base cations are removed from the
2 soils by tree uptake (Bondietti and McLaughlin, 1992). The changes are spatially and temporally
3 consistent with changes in the emissions of SO_x and NO_x across the region and suggest that
4 increased acidification of soils has occurred (U.S. Environmental Protection Agency, 2004).

5 The content of base cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) in soils can increase in response to
6 base cation additions via atmospheric deposition, decomposition of vegetation, and geologic
7 weathering; losses from the soil may occur through plant uptake and leaching. Increased loss of
8 base cations may result in nutrient deficiencies in soils, as has occurred in some sensitive forest
9 ecosystems (NAPAP, 1998).

10 Ambient levels of N deposition range from about 1 to 4 kg N/ha/yr throughout most of
11 the western United States, essentially acting as a low-level fertilizer to western forests and other
12 vegetative communities. For most western ecosystems, these low-level N additions probably
13 serve to slightly increase N availability and plant growth. However, some sensitive species,
14 including lichens, can be affected by deposition inputs as low as 3 to 8 kg N/ha/yr (Fenn et al.,
15 2003). Levels of N deposition can be much higher and have more pronounced effects on
16 ecosystems near depositional hot spots such as metropolitan, industrial, or agricultural centers or
17 large point sources of pollution (Fenn et al., 2003).

18 Due to a strong dependency on atmospheric deposition and exposure to gaseous
19 compounds as the major sources of nutrients, lichens are affected by changes in these conditions.
20 Vulnerability of lichens to increased N input is generally greater than that of vascular plants
21 (Fremstad et al., 2005). Even in the Pacific Northwest, which receives uniformly low levels of
22 N deposition, changes from acid-sensitive and N-sensitive to pollution-tolerant and nitrophilic
23 lichen taxa are occurring in some areas (Fenn et al., 2003). In eastern North America and central
24 Europe, areas experiencing relatively high levels of acidic deposition have experienced
25 noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees
26 (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely
27 (McCune, 1988; Van Haluwyn and van Herk, 2002).

28 Fenn et al. (2007) speculated that large, pollution-sensitive macrolichens, including
29 epiphytic cyanolichens, will be replaced by N-tolerant species in areas where development
30 expands in western Oregon and Washington into N-limited Coast Range forests. Currently, in
31 the Pacific Northwest, nitrophilic lichen species are common in and around Seattle, Portland,

1 Spokane, the Tri-cities, Salem, Oregon's agricultural lands in the northeast and southwest, and
2 the Willamette Valley (Fenn et al., 2007). The USDA Forest Service website contains
3 information about lichen species pollution tolerance, diversity, and preferred habitat in relation to
4 exposure to N (<http://www.nacse.org/lichenair>).

5 In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas
6 where NO₂ surpassed 40 µg/m³ and NO_x surpassed 70 µg/m³. Lichens remaining in areas
7 affected by these levels of exposure contained almost exclusively families *Candelariaceae*,
8 *Physciaceae* and *Teloschistaceae* (Davies et al., 2007).

9 Typically, lichens and other bryophytes are among the first components of the terrestrial
10 ecosystem to be affected by acidic deposition. Nevertheless, recovery in response to reduced
11 inputs is inconsistent. Improvement for bryophytes has been reported to occur in 1 year by
12 Power et al. (2006) and Mitchell et al. (2004), 5 years by Gordon et al. (2001), and 49 years by
13 Strengbom et al. (2001).

14 Scott (1989a,b) concluded that the S:N exposure ratio was as important as pH in causing
15 toxic effects on lichens, based on experiments on *Cladina rangiferina* and *C. stellaris*. Thus, it is
16 not clear to what extent acidity is the principal stressor under high levels of air pollution
17 exposure. However, the toxicity of SO₂ is greater under acidic conditions than under neutral
18 conditions to *Lobaria spp.* (containing cyanobacteria) and *Usnea spp.* (containing green algae).
19 Cyanobacteria are considered to be more sensitive than green algae to nitrite and bisulphite
20 (Wodzinski et al., 1977). The toxic effects of atmospheric deposition of SO₂ are lessened when
21 lichen are attached to a substrate, typically bark or rock, having high pH or superior buffering
22 capacity (Richardson and Cameron, 2004). Van Herk (2001) evaluated relationships between
23 bark pH and air pollution levels as two significant variables affecting epiphytic lichen
24 composition, and concluded that bark pH was the primary factor regulating the distribution of
25 nitrophilic species and acidophilic species in The Netherlands. In studies of unpolluted areas,
26 differences in bark chemistry also affect the presence and distribution of epiphytes (Farmer et al.,
27 1992). Indirect effects on bark pH, caused by acidification and high SO₂ concentrations, also
28 affect lichen distribution (Farmer et al., 1992).

29 Damage caused to lichens in response to SO₂ exposure includes reduced photosynthesis
30 and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition

1 of N fixation, reduced K^+ absorption, and structural changes (Wetmore, 1985; Farmer et al.,
2 1992; Belnap et al., 1993; Hutchinson et al., 1996).

3 Ambient levels of acidic deposition probably affect the health of red spruce trees,
4 especially at high elevation throughout the northeastern United States and Appalachian
5 Mountains. (See discussion in Section AX4.4.3.1.1). California mixed coniferous forests seem
6 less susceptible to N deposition stress than coniferous forests in the eastern United States. For
7 example, ponderosa pine and black oak demonstrated increased bole growth with additions of
8 50 kg N/ha/yr (Bytnerowicz, 2002).

9 Although the weight of evidence suggests the likelihood of adverse impacts of
10 acidification from atmospheric S and N deposition on some coniferous forests in the eastern
11 United States, the state of scientific understanding is less clear with respect to hardwood forests.
12 Acidification can affect the base saturation, availability, and leaching loss of important nutrients
13 in hardwood forests. In a study of sugar maple decline throughout the Northeast, Bailey et al.
14 (2004) found threshold relationships between base cation availability in the upper B soil horizon
15 and sugar maple mortality at Ca^{2+} saturation less than 2%, and Mg^{2+} saturation less than 0.5%.
16 Bailey et al. (2004) did not attempt to establish connections between low base saturation and
17 acidic deposition. They interpreted base saturation as a function of topography, parent material
18 and acidic deposition. Nevertheless, their work could have implications for the effects of acidic
19 deposition.

20 A long-term decrease in pH since 1960 (0.78 pH unit decrease in the O horizon, and
21 0.23 pH unit decrease in the A horizon) in Pennsylvania hardwood forests has been documented,
22 along with decreases in soil Ca^{2+} and Mg^{2+} concentrations. Declining sugar maples were shown
23 to be deficient in foliar Ca^{2+} and Mg^{2+} , and decreased Mg^{2+} has been associated with crown
24 defoliation and discoloration in Norway spruce (*Picea abies*) (Drohan and Sharpe, 1997).

25 Progressive decline in ectomycorrhizal fungal (EMF) community structure and species
26 richness was observed at five Alaskan coniferous forest sites (white spruce [*Picea glauca*]
27 dominant) along an N deposition gradient (1 to 20 kg N/ha/yr) downwind from a large industrial
28 complex on the Kenai Peninsula. The effects were attributed to both acidification and
29 fertilization processes (Lilleskov et al., 2002). EMF communities are important in tree nutrition
30 and C balance, and EMF trees tend to be dominant in N-limited forest ecosystems. A shift in
31 EMF community structure could result in changes in tree species.

1 Westman et al. (1985) summarized the literature of negative effects of SO₂ on native
2 plants, including decreased pollen germination and tube elongation in both angiosperms and
3 gymnosperms. It is often difficult to separate the effects of SO₂ exposure on plants from the
4 effects of S deposition. This is because areas that experience high SO₂ exposure generally also
5 receive high S deposition. Kozlowski (1985) summarized relative susceptibility of different
6 trees, lichens, and bryophytes to SO₂.

7 Available information is not sufficient to draw conclusions regarding the increased
8 likelihood of future effects on the condition of hardwood forests in the Southern Appalachian
9 Mountain region (Sullivan et al., 2002). Certainly, such effects are less likely for hardwood
10 forests than for spruce-fir forests. Red oak seedlings grown in a greenhouse in deciduous forest
11 soils exhibited no response to acidified soil (pH 4.0 from 9:1 H₂SO₄:HNO₃) or to high or low
12 SO₄²⁻ inputs (12.8 to 24.8 mg/L). The lack of response suggested that red oak seedlings are not
13 sensitive indicators of acidification impacts from S deposition (McClenahan, 1987).

14 15 **AX4.4.3.1.2 Grasslands and Alpine Tundra**

16 Alpine communities are considered very sensitive to changes in N deposition, but
17 documented effects in the scientific literature have been attributed to nutrient enrichment, rather
18 than acidification (Seastedt et al., 2004; Bowman et al., 2006). Lower-elevation grasslands,
19 especially those in semi-arid environments, would be expected to be even less sensitive to
20 acidification because of low water leaching potential and the common presence of base-rich
21 Mollisol and Aridisol soils. However, some effects of acidification may be manifested in mesic
22 grasslands.

23 In a review of SO₂ effects on grasses in the United Kingdom, Bell (1985) suggested that
24 damage can occur at levels as low as 150 µg/m³. However, he asserted that any ubiquitous
25 critical load value must be modified to include variations due to environmental conditions and
26 combined effects with other pollutants. He also suggested that many grass species exhibit a
27 tolerance to SO₂, resulting from more intraspecific competition in agricultural grasslands.
28 Westman et al. (1985) also provided evidence of the evolution of a tolerant grass species,
29 *Bromus rubens*, in southern California coastal sage scrub, influenced by an average of
30 3.7 µmol/m³ of SO₂ over 25 years.

1 Studies of SO₂ effects on timothy grass (*Phleum pratense*) showed diminished leaf
2 production and increased leaf senescence in seedlings exposed to 0.120 ppm SO₂ for 35 days
3 (Mansfield and Jones, 1985). In another experiment, Mansfield and Jones (1985) reported that
4 exposure to 0.120 ppm SO₂ in seedlings over 40 days resulted in a 62% reduction in the dry
5 weight of roots and 51% reduction in the dry weight of shoots, as well as a significant decline in
6 leaf-area ratio (LAR) and specific leaf area (SLA) by the end of the experiment. They suggested
7 that decreased growth and shifts in LAR and SLA could lead to decreased hardiness and
8 increased susceptibility to water stress.

9 In a 5-year exposure of native mixed prairie grassland in Montana, Lauenroth and
10 Milchunas (1985) exposed grasses to a control (~20 µg/m³) and three elevated levels of SO₂
11 (~60, 106, 184 µg/m³). Year-to-year S accumulation did not appear to occur over the 5-year
12 course of the treatment, though progressive increases in root and rhizome S concentrations were
13 observed seasonally. No significant negative effects on either above-ground net primary
14 productivity or below-ground biomass dynamics in grasses were observed, except a decrease in
15 biomass for *Bromus japonicus*. However, lichen cover declined after 1 year of exposure at the
16 low treatment level. Though no biomass or cover effects were observed at the community level,
17 there were minor population changes. These results are consistent with the nature of semi-arid
18 grasslands that typically adjust well to perturbations (Lauenroth and Milchunas, 1985).

19 20 **AX4.4.3.1.3 Arid Lands**

21 At the time of the previous AQCD, it was believed that arid and semi-arid ecosystems
22 were not as susceptible to soil acidification and high NO₃⁻ leaching as are forested ecosystems.
23 This is because of a scarcity of water for NO₃⁻ leaching, except on an episodic basis, and
24 because arid soils tend to be more alkaline than soils in more humid environments. No new
25 research has altered that conclusion. Arid lands in the United States generally receive low levels
26 of S deposition. However, N deposition can be quite high, especially in southern California in
27 the vicinity of the Los Angeles Basin. Little work has been done on the effects of acidification
28 on arid land ecosystems. As reviewed by Fenn et al. (2003), acidification effects have not been
29 demonstrated at the Central Arizona-Phoenix LTER site, despite the almost 30 kg N/ha/yr of
30 deposition received. Nevertheless, N deposition has the potential to increase plant growth and
31 denitrification and alter community composition in arid environments (Egerton-Warburton and

1 Allen, 2000; Allen et al., 2005). Such changes could alter key ecosystem processes and, as such,
2 merit consideration. There has been little research to examine these issues and, therefore, the
3 state of knowledge is similar to what it was in 1993.

4 5 **AX4.4.3.2 Transitional Ecosystems**

6 There are no data available with which to evaluate the extent to which atmospheric
7 deposition of acidifying substances has affected wetland ecosystems in the United States. We
8 expect that such effects, if they occur at all, are only minor.

9 10 **AX4.4.3.3 Aquatic Ecosystem**

11 12 ***AX4.4.3.3.1 Chronic Effects***

13 The NSWS documented the status and extent of surface water acid-base chemistry during
14 base flow with probability surveys of lakes and streams conducted from 1984 through 1988 in
15 the major acid sensitive regions of the United States (Linthurst et al., 1986a,b; Landers et al.,
16 1987; Kaufmann et al., 1988). By statistically selecting representative lakes and streams in each
17 surveyed region, the NSWS estimated chemical conditions of 28,300 lakes and 56,000 stream
18 reaches (Baker et al., 1991a). The data collected by the NSWS have allowed EPA and the states
19 to focus monitoring efforts on those areas that contain the majority of anthropogenically
20 acidified waters in the United States, and that are most likely to respond to changes in deposition
21 as a result of the CAAA and other air pollution control legislation.

22 The NSWS concluded that 4.2% of lakes larger than 4 ha and 2.7% of stream segments in
23 the acid-sensitive regions of the eastern United States were acidic. The regions represented by
24 the LTM and TIME monitoring programs (Table AX4.3-2) are estimated to contain 95% of the
25 lakes and 84% of the streams that have been anthropogenically acidified in the United States by
26 acidic deposition. The Adirondacks had a large proportion of acidic surface waters (14%) in the
27 NSWS; from 1984 to 1987, the ALSC sampled 1,469 Adirondack lakes greater than 0.5 ha in
28 size and estimated that many more (26%) were acidic (Driscoll et al., 1991). The higher
29 percentage of acidic lakes in the ALSC sample was due to inclusion of smaller lakes and ponds
30 (1 to 4 ha in area), many of which were acidic as a consequence of naturally occurring organic
31 acids (Sullivan et al., 1990). The proportions of lakes estimated by NSWS to be acidic were
32 smaller in New England and the Upper Midwest (5% and 3%, respectively), but because of the

1 large numbers of lakes in these regions, there were several hundred acidic waters in each of these
2 two regions.

3 The Valley and Ridge province and Northern Appalachian Plateau had 5% and 6% acidic
4 sites, respectively. The only potentially acid-sensitive region in the eastern United States not
5 assessed in the Stoddard et al. (2003) report was Florida, where the high proportion of naturally
6 acidic lakes, and a lack of long-term monitoring data, make assessment of the effects of acidic
7 deposition problematic (Stoddard et al., 2003).

8 Surface water acid-base chemistry monitoring throughout the eastern United States
9 occurs primarily in two EPA programs: the TIME project (Stoddard, 1990) and LTM project
10 (Ford et al., 1993; Stoddard et al., 1998). Both projects are operated in cooperation with
11 numerous state agencies, academic institutions and other federal agencies. Each is described
12 below.

13 The TIME project is structured as a probability sampling. Each site is chosen statistically
14 to be representative of a target population. In the Northeast (New England and Adirondacks),
15 this target population consists of lakes with Gran ANC < 100 $\mu\text{eq/L}$, which are those likely to be
16 most responsive to changes in acidic deposition. In the Mid-Atlantic, the target population is
17 upland streams with ANC < 100 $\mu\text{eq/L}$. Each lake or stream is sampled annually, and results are
18 extrapolated to the target populations (Larsen and Urquhart, 1993; Larsen et al., 1994; Stoddard
19 et al., 1996; Urquhart et al., 1988). The TIME project began sampling northeastern lakes in
20 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of about 1,000
21 lakes having ANC < 100 $\mu\text{eq/L}$, out of a total population of 1,830 lakes with surface area > 1 ha.
22 Data from 30 lakes representing about 1,500 lakes having ANC < 100 $\mu\text{eq/L}$, out of a total
23 population of 6,800 lakes, are included in the TIME program in New England.

24 As a compliment to lake and stream sampling in the statistical populations of lakes in
25 TIME, the LTM project samples a subset of sensitive lakes and streams with long-term data,
26 many dating back to the early 1980s. Each LTM site is sampled 3 to 15 times per year, and the
27 resulting data are used to characterize the response of the most sensitive aquatic systems in each
28 region to changing levels of acidic deposition. In most regions, a small number of higher ANC
29 (e.g., Gran ANC > 100 $\mu\text{eq/L}$) sites are also sampled. Because of the long-term records at most
30 LTM sites, their trends can also be placed in a better historical context than those of TIME sites,
31 where data are only available from the 1990s. Monitoring results from the LTM project have

1 been widely published (Kahl et al., 1991; Driscoll and Van Dreason, 1993; Murdoch and
2 Stoddard, 1993; Stoddard and Kellogg, 1993; Webster et al., 1993; DeWalle and Swistock, 1994;
3 Driscoll et al., 1995). Overall results were summarized by Stoddard et al. (2003).

4 Results of surface water chemistry monitoring in the LTM and TIME projects suggest
5 that the following important changes in lake and streamwater chemistry occurred during the
6 1990s in response to S and N emissions reductions:

- 7 • Sulfate concentration decreased as a percentage of total ion concentration in surface
8 waters.
- 9 • ANC increased modestly in three of the five regions included in surface water long-
10 term monitoring efforts.
- 11 • DOC increased, perhaps toward more natural pre-disturbance concentrations, as
12 surface water acidity contributed from acidic deposition decreased.
- 13 • inorganic, and potentially toxic, Al concentrations appear to have decreased slightly
14 in some sensitive aquatic systems.

15 In addition to the large water chemistry databases, developed by the EPA, there are also
16 some important supplemental databases for some regions. For example, based on results of lake
17 surveys conducted during the 1980s, about 70% of the known acidic lakes in Maine were either
18 seepage lakes (no inlet or outlet stream) or high elevation (Kahl et al., 1991). The *Maine*
19 *seepage lake* dataset includes 120 of the estimated 150 lakes in Maine that meet the following
20 criteria: (1) located in sand and gravel mapped by the USGS or Maine Geological Survey and;
21 (2) depth at least 1 m; and (3) area at least 0.4 ha (1 ac). Sampling was conducted in 1986-87
22 and 1998-2000, and included at least one fall index sample for each lake. There were 87 lakes
23 with Gran ANC less than 100 µeq/L.

24 The *Maine high elevation lake* dataset includes 90 lakes above 600 m elevation.
25 Sampling was conducted during the periods 1986-88 and 1997-99. The study included the vast
26 majority of Maine lakes that are at least 1 m deep and at least 0.4 ha (1 ac) in area. There were
27 64 lakes with Gran ANC less than 100 µeq/L.

28 Details on trends and current status of the key measurements used to assess acidification
29 are presented in the following sections.

30

1 AX4.4.3.3.1.1 Sulfate

2 Atmospheric deposition of SO_4^{2-} is widely acknowledged as causing increases in
3 concentrations of SO_4^{2-} in surface water. In seven streams in the Catskill region of New York,
4 Stoddard (1991) identified increasing trends in SO_4^{2-} concentrations from 1952-54 to 1970 in
5 three streams and no trend in the four other streams. For the period from 1971 to 1987, Stoddard
6 (1991) identified decreasing trends in SO_4^{2-} concentrations in 5 of 13 Catskill streams and no
7 trend in the other 8 streams. Concentrations of SO_4^{2-} at the HBEF did not show a trend from
8 1963 to 1975, but decreased linearly from 1975 to 1997 (Likens et al., 2002).

9 The study of Clow and Mast (1999) is unique in that SO_4^{2-} trends were evaluated with
10 both raw data and data adjusted for existing trends in flow. From 1967 to 1983, Clow and Mast
11 (1999) showed a decreasing trend in SO_4^{2-} concentrations in a Catskill river, no trend in three
12 rivers in Maine, Pennsylvania, and Virginia, and an increasing trend in a river in Ohio. The
13 Maine river did show a decreasing trend before flow adjustment of the data. From 1984 to 1996,
14 however, Clow and Mast (1999) found decreasing trends in SO_4^{2-} concentrations in all five
15 rivers, both with and without flow adjustment. The rivers in Pennsylvania, Ohio, and Virginia
16 were south of the maximum southern extent of glaciation, and therefore were more likely to be
17 subject to the effects of SO_4^{2-} adsorption in soils of their watersheds. In such streams,
18 decreasing S-adsorption on soils would be expected to counteract the effects of decreasing
19 S deposition in terms of effects on stream SO_4^{2-} concentration.

20 Additional analyses of trends in SO_4^{2-} concentrations in surface waters has been
21 conducted to evaluate the effects of the 1990 CAAA. Stoddard et al. (2003) found that surface
22 waters monitored in the LTM showed consistent decreases in SO_4^{2-} concentrations from 1990 to
23 2000 in New England lakes (1.77 $\mu\text{eq/L/yr}$), Adirondack lakes (2.26 $\mu\text{eq/L/yr}$), Appalachian
24 streams (2.27 $\mu\text{eq/L/yr}$), and Upper Midwest lakes (3.36 $\mu\text{eq/L/yr}$). The only exception to the
25 pattern of decreasing SO_4^{2-} concentrations in surface waters during this period were streams in
26 the Blue Ridge Mountain region of Virginia that showed a significant increase in SO_4^{2-}
27 concentrations (0.29 $\mu\text{eq/L/yr}$) during this period. The increasing trend in Virginia streams is
28 presumably the result of decreased S-adsorption and/or net desorption in the soil in response to
29 decreased S deposition. In contrast, surface waters in other unglaciated regions exhibited
30 decreasing trends in SO_4^{2-} by the 1980s. Concentrations of SO_4^{2-} in 130 northeastern lakes in
31 1984 were compared to those in the same lakes in 2001 (Warby et al., 2005). Median

1 concentrations in each subregion were lower in 2001 than 1984, and in the region as a whole, the
2 overall median decrease was 1.53 $\mu\text{eq/L/yr}$. A decrease in SO_4^{2-} concentrations that averaged
3 2.16 $\mu\text{eq/L/yr}$ was also observed in 47 of 48 Adirondack lakes from 1992 to 2004, and a similar
4 decrease of 2.09 $\mu\text{eq/L/yr}$ was observed in a subset of these lakes from 1982 to 2004 (Driscoll
5 et al., 2007).

6 Stoddard et al. (2003) noted that the percent declines in SO_4^{2-} concentrations were
7 generally steeper in precipitation than in surface waters in New England, the Adirondacks, and
8 the Northern Appalachians. This result suggests that SO_4^{2-} recovery of surface waters lags
9 behind deposition. Nevertheless, the lakes and streams that exhibited the steepest declines in
10 SO_4^{2-} concentration had similar decline rates to those in precipitation. Thus, the most responsive
11 watersheds responded approximately proportionately to the decrease in SO_4^{2-} concentration in
12 precipitation. As expected, there was little correspondence between rates of SO_4^{2-} decline in
13 streams and precipitation in the Ridge and Blue Ridge provinces and this finding can be
14 attributed to S adsorption on soils in this region. In the upper Midwest, the rate of decline in
15 lakes was actually greater than the decline in precipitation, which could reflect errors in
16 measurement, the influence of dry deposition, or the residual effects of the drought of the late
17 1980s.

18 In summary, the pattern of increasing concentrations of SO_4^{2-} in surface waters before
19 the year of peak S emissions in 1973, followed by widespread decreasing trends in SO_4^{2-}
20 concentrations after the peak (with the only exception being the Blue Ridge Mountain region in
21 Virginia), provides convincing evidence of the link between S emissions and SO_4^{2-}
22 concentrations in surface waters. A similar link has been shown in Europe (Stoddard et al.,
23 1999). On this basis, continued decreases in S emissions would be expected to result in further
24 decreases in SO_4^{2-} concentrations in surface waters, although the rate of response is uncertain
25 due to an incomplete knowledge of S retention mechanisms in terrestrial systems. Also, in a
26 detailed analysis of flow effects on SO_4^{2-} trends, Murdoch and Shanley (2006) found SO_4^{2-} that
27 higher concentrations of SO_4^{2-} occurred at corresponding high, medium and low flows in 2000
28 to 2002 than in 1997 to 1999 in two of the rivers studied by Clow and Mast (1999), and at high
29 and medium flows in a third river. Continued monitoring of surface waters will be needed to
30 verify a future link between emissions and SO_4^{2-} concentrations in surface waters.

1 Declines in S deposition have contributed to nearly universal declines in SO_4^{2-}
2 concentrations in surface waters. This is one measure of chemical recovery of surface waters in
3 response to implementation of the CAAA and efforts by industry to reduce SO_2 emissions.
4 Nevertheless, the anticipated decrease in surface water acidity in acid-affected areas has been
5 modest.

6
7 *AX4.4.3.3.1.2 Nitrate*

8 Driscoll et al. (1985) found that NO_3^- concentrations in 20 lakes in the early 1980s in the
9 Adirondack region of New York averaged 12% of SO_4^{2-} concentrations, whereas Lovett et al.
10 (2000b) found that baseflow NO_3^- concentrations in 1994-97 were an average of 37% of SO_4^{2-}
11 concentrations in 39 streams in the Catskill region of New York. Average concentrations of
12 NO_3^- in most southeastern streams also tend to be considerably less than SO_4^{2-} concentrations
13 (Webb et al., 2004).

14 High-frequency sampling in the study of Murdoch and Stoddard (1993) demonstrated the
15 importance of NO_3^- during high-flow conditions in Catskill streams in which concentrations
16 periodically equaled or exceeded SO_4^{2-} concentrations. This study also reported increasing
17 trends in NO_3^- concentrations during the period of 1970 to 1990 in all 16 Catskill streams for
18 which data were available. A similar increase in NO_3^- concentrations was reported for
19 Adirondack lakes in the 1980s (Stoddard et al., 1999). These increasing trends in NO_3^-
20 concentrations were attributed to N saturation in response to atmospheric deposition (Aber et al.,
21 1998).

22 The relationship between N deposition and surface water NO_3^- concentrations up through
23 the 1980s suggested that continued N deposition would further the accumulation of N in
24 terrestrial ecosystems and drive continued increases in surface water NO_3^- concentrations.
25 However, more recent information on NO_3^- concentrations have been less consistent with the
26 concept of N saturation. Goodale et al. (2003) resampled New Hampshire streams in 1996-97
27 that had been previously sampled in 1973-74 and found substantially lower NO_3^- concentrations
28 in the more recent sampling, despite two decades of relatively stable levels of deposition to
29 otherwise undisturbed forests. The lower NO_3^- concentrations could not be accounted for by
30 differences in flow or forest succession, but interannual climate variation was proposed as a
31 possible cause. The long-term record of dissolved inorganic N (which is largely NO_3^-)

1 concentrations at the HBEF showed a similar pattern; high concentrations in the late 1960s and
2 1970s, followed by decreases to minimum values in the mid-1990s (Aber et al., 2002). These
3 authors attributed this pattern to a combination of environmental factors, but did not identify a
4 single most important control variable. A reversal from increasing trends in NO_3^- concentrations
5 in the 1980s to decreasing trends in the 1990s was also observed in Adirondack lakes (Driscoll
6 et al., 2003a). A small decrease in atmospheric deposition of N also occurred in this region
7 through the 1990s, but was not considered sufficient by these authors to explain the decreasing
8 trend in lakewater NO_3^- concentrations. Rather, they proposed that increased concentrations of
9 atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation
10 (Driscoll et al., 2007).

11 In general, trends in surface water NO_3^- concentrations during the 1990s were much
12 smaller than trends in SO_4^{2-} , with the only ecologically significant changes occurring in the two
13 regions with the highest ambient NO_3^- concentrations (Figure AX4.1-5). Lakes in the
14 Adirondacks and streams in the Northern Appalachian Plateau both exhibited small but
15 significant downward trends in NO_3^- in the 1990s (Table AX4.3-5). Both of these regions are
16 central to the debate over whether N saturation is a legitimate threat to the health of forests and
17 surface waters (Stoddard, 1994; Aber et al., 1998). While declining NO_3^- concentrations in these
18 regions is a positive development for these ecosystems, we clearly do not know if these trends
19 will continue, especially because they do not appear to reflect changes in N emissions or
20 deposition. The presence of strong *upward* trends in NO_3^- in these same regions in the 1980s
21 (Murdoch and Stoddard, 1992; Stoddard, 1994) suggests that trends measured on the scale of a
22 single decade may reflect variability in long-term patterns of changing NO_3^- leakage from
23 forested watersheds. Such patterns are controlled by factors that may take many years of
24 additional research to determine. While great uncertainty exists and the time scales of N
25 saturation may be longer than previously considered (e.g., centuries rather than decades), the
26 long-term retention of N deposition in forested regions is unlikely to continue indefinitely (Aber
27 et al., 2003).

28 In New England and the Upper Midwest, where ambient NO_3^- concentrations are much
29 lower than in the Adirondacks and Northern Appalachian Plateau (Figure AX4.4-7), NO_3^-
30 concentrations in surface waters were unchanged during the 1990s. The Ridge/Blue Ridge
31 province registered a small, but significant, decrease in NO_3^- during the 1990s, but interpretation

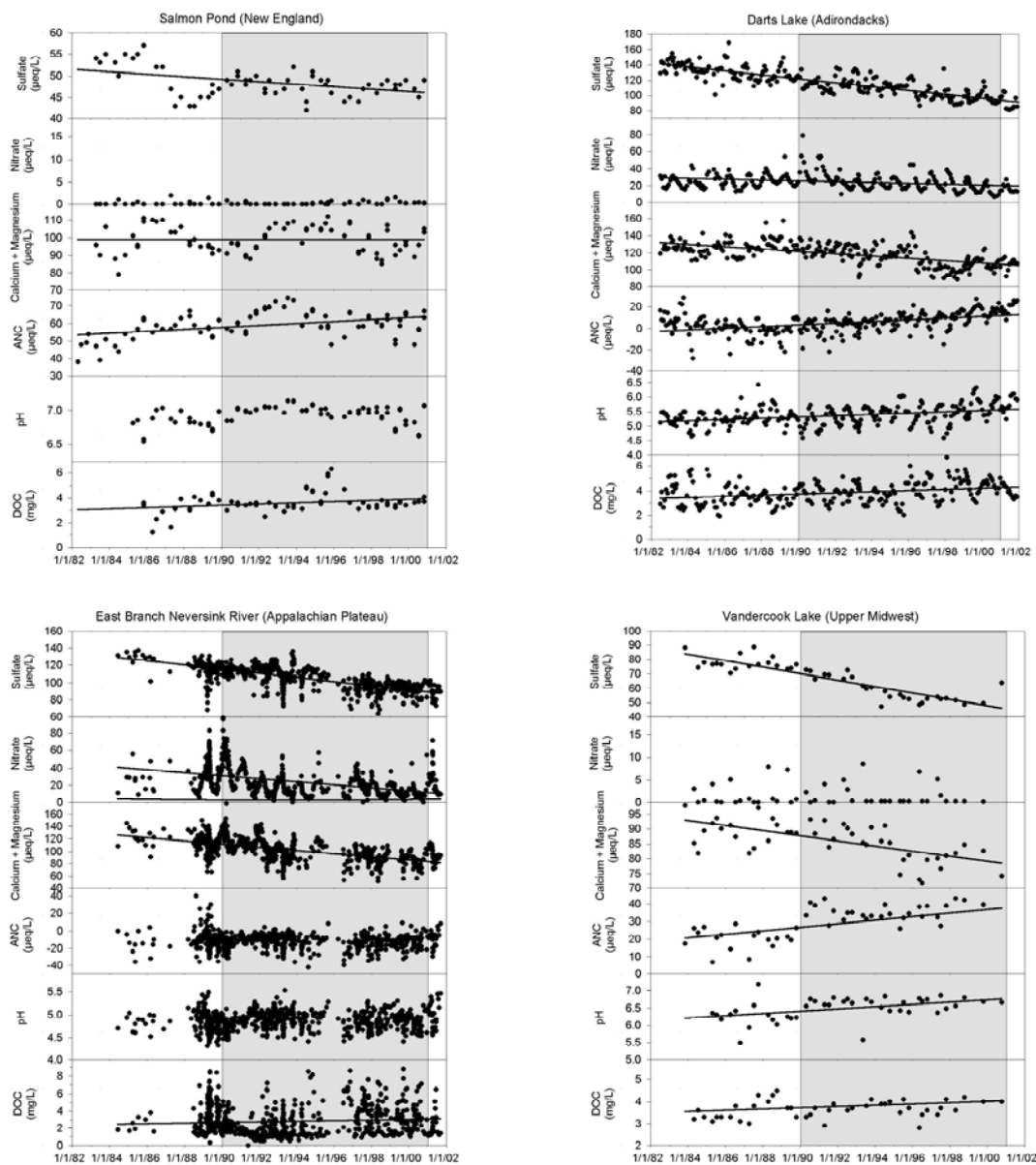


Figure AX4.4-7. Time series data for SO_4^{2-} , NO_3^- , base cations [$\text{Ca}^{2+} + \text{Mg}^{2+}$], Gran ANC, pH, and DOC in example Long Term Monitoring Lakes and streams that have relatively low ANC. The example surface waters include Salmon Pond, Maine (New England region); Darts Lake, NY (Adirondack region); East Branch Neversink River (Appalachian Plateau region); and Vandercook Lake, Wisconsin (Upper Midwest region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Source: Stoddard et al. (2003).

1 of trends for NO_3^- in this region is complicated by an outbreak of gypsy moths that also occurred
2 during this period. Forest defoliation by gypsy moths was the most likely cause of a pulse in
3 NO_3^- export from many streams in this region in the mid-1990s (Eshleman et al., 1998).

4 Some evidence of climate effects on long-term trends in NO_3^- concentrations in surface
5 waters was provided by studies of Mitchell et al. (1996) and Murdoch et al. (1998). A
6 synchronous pattern in NO_3^- concentrations was observed from 1983 to 1993 in four small
7 watersheds in New York, New Hampshire, and Maine, which included anomalously high
8 concentrations during the snowmelt period of 1990. The region-wide spike in NO_3^-
9 concentrations followed an unusually cold December that may have disrupted soil N cycling
10 processes (Mitchell et al., 1996). Murdoch et al. (1998) also found that mean annual air
11 temperatures were strongly related to average annual NO_3^- concentrations in most years in a
12 Catskill watershed with elevated NO_3^- concentrations in stream water. Those relationships were
13 explained by microbial control of N release in watersheds that were considered to be
14 N-saturated.

15 Efforts to explain the decreasing trends in NO_3^- concentrations under conditions
16 of reasonably stable atmospheric N deposition have focused on terrestrial N cycling and
17 N-saturation theory. However, processes within lakes may have also played a role in the
18 trends in Adirondack lakes. In a study of 30 of the 48 lakes studied by Driscoll et al.
19 (2003a; 2007), Momen et al. (2006) found that concentrations of NO_3^- were inversely correlated
20 with concentrations of chlorophyll *a* in 11 lakes, and that chlorophyll *a* was increasing in
21 concentration in 9 lakes. The increase in pH observed in most of these lakes may have
22 stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

23 Thus, there is little or no apparent relationship between recent trends in N deposition and
24 trends of NO_3^- concentrations in surface waters, in sharp contrast to S deposition and SO_4^{2-}
25 concentrations. Rather than disprove the concept of N-saturation; however, these studies more
26 likely reflect the complexities of N utilization within terrestrial and aquatic ecosystems. These
27 complexities create considerable uncertainty with regard to how future trends in NO_3^-
28 concentrations in surface waters will respond to changing levels of deposition.

29

1 AX4.4.3.3.1.3 *Base Cations*

2 The earliest trends of base cation concentrations in acid-sensitive surface waters of the
3 United States were presented by Stoddard (1991) for 12 streams in the Catskill region. In 5 of 12
4 streams, concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ increased from 1915-22 to 1945, but decreased from
5 1945-46 to 1990. In the remaining seven streams, concentrations increased during both periods,
6 but at a lower rate in the more recent period in five of the seven streams. In streams that showed
7 an increase in concentrations during both periods, the average rate of increase from 1915 to 1922
8 was 2.8 $\mu\text{eq/L}$, whereas the average rate of increase from 1945 to 1990 was 1.2 $\mu\text{eq/L}$. Data on
9 SO_4^{2-} trends were not available for the early period, but the trends in $(\text{Ca}^{2+} + \text{Mg}^{2+})$
10 concentrations were consistent with the expected pattern of high rates of cation leaching during
11 the early stages of acidification from S deposition.

12 Clow and Mast (1999) observed trends in $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations that were
13 generally consistent with SO_4^{2-} trends in five eastern rivers from 1968 to 1983. Decreasing
14 trends in concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and SO_4^{2-} concentrations were observed in a Maine
15 river, and increasing trends in $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and SO_4^{2-} concentrations were observed in an Ohio
16 river. None of the three other rivers showed a decrease in concentrations of $(\text{Ca}^{2+} + \text{Mg}^{2+})$, and
17 only one showed a decreasing trend in SO_4^{2-} concentrations. For the period 1984 to 1996, the
18 trend in SO_4^{2-} concentrations was negative in the Ohio river and the concentrations of $(\text{Ca}^{2+} +$
19 $\text{Mg}^{2+})$ showed no trend. Also, a negative trend in $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations in a Virginia
20 river was coupled with a negative trend in SO_4^{2-} concentrations. Relations for the other three
21 rivers were similar to the earlier period of 1984 to 1996.

22 The study of Likens et al. (1996) evaluated trends in base cations in relation to trends in
23 $(\text{SO}_4^{2-} + \text{NO}_3^-)$ in the long-term record for the HBEF. This record showed an approximately
24 linear, increasing relationship between concentrations of base cations and $(\text{SO}_4^{2-} + \text{NO}_3^-)$ from
25 1964 to 1969, then a reversal in 1970 to a decreasing trend up to 1994. The slope of the phase
26 with increasing anion concentrations was steeper than the slope for the phase with decreasing
27 anion concentrations. This indicates lower base cation leaching per equivalent of mobile anion,
28 and therefore suggests depletion of base cations stored in soil. The study of Lawrence et al.
29 (1999b) showed decreased concentrations of base cations at a rate that exceeded decreases in
30 $(\text{SO}_4^{2-} + \text{NO}_3^-)$ in Catskill streams from 1984 to 1997. In streams within western Virginia and
31 in Shenandoah National Park, concentrations of base cations did not exhibit significant trends

1 from 1988 to 2001, perhaps due to the influence of S adsorption on streamwater SO_4^{2-}
2 concentrations.

3 Regional declines in base cation concentrations were measured in the LTM Program from
4 1990 to 2000 in New England lakes, Adirondack lakes, Appalachian streams, and upper Midwest
5 lakes (Stoddard et al., 2003). These results were consistent with decreased Ca^{2+} concentrations
6 measured by Warby et al. (2005) in 130 acid-sensitive lakes in the Northeast between 1984 and
7 2001. The rate of decrease identified by Warby et al. (2005) for base cations ($1.73 \mu\text{eq/L}$) was
8 somewhat less than the rate of decrease in SO_4^{2-} concentrations ($1.53 \mu\text{eq/L}$). Driscoll et al.
9 (2007), also documented decreasing trends in base cation concentrations in 16 Adirondack Lakes
10 from 1982 to 2004, and similar rates of decrease in 48 lakes (including the 16) from 1992 to
11 2004.

12 In summary, decreases in base cation concentrations over the past two to three decades
13 are ubiquitous and closely tied to trends in SO_4^{2-} concentrations in acid-sensitive regions of the
14 United States. Reports of increases in concentrations of base cations in acid-sensitive regions
15 were not found in the literature. In most regions, rates of decrease for base cations have been
16 similar to those for SO_4^{2-} and NO_3^- , with the exception of streams in Shenandoah National Park.
17 Decreasing trends of base cation concentrations do not necessarily indicate further acidification
18 or recovery of surface waters, but do indicate lower leaching rates in soils, a prerequisite for
19 recovery of soil base saturation. However, decreased concentrations of base cations, particularly
20 Ca^{2+} , would also be expected to lower productivity in oligotrophic surface waters.

21
22 *AX4.4.3.3.1.4 Acid Cations*

23 Measurements of pH (sometimes expressed as H^+) have been routinely collected in
24 surface waters in the United States where effects of acidic deposition have been monitored, but a
25 long-standing reliance on titrated ANC rather than pH as the primary chemical measurement has
26 limited the amount of pH data published. The longest continuous record of pH in surface waters
27 dates back to 1963 at the HBEF (Driscoll et al., 2001b). This record shows an overall increasing
28 trend from 1963 to 1994, although most of the increase occurred after 1980. In Adirondack
29 lakes, 12 of 16 monitored from 1982 to 2004 showed an increase in pH, but the rates of change
30 among lakes were highly variable, and one lake showed a decrease in pH (Driscoll et al., 2007).
31 When expressed as H^+ concentration, the average increase for the 12 lakes was $0.18 \mu\text{eq/L/yr}$. In

1 this same region, pH also increased in 31 of 48 lakes (including the 16 lakes monitored from
2 1982) from 1992 to 2004. Two lakes showed increases in pH over the 12 years.

3 Comparison of pH measurements of 130 lakes in 1984 and in 2001, in the northeastern
4 United States, showed an overall average increase in pH of 0.002 units (Warby et al., 2005).
5 However, in this assessment, lakes in the Adirondack region did not show a significant increase,
6 nor did lakes in central New England, or Maine. The Catskill/Poconos region of New York and
7 Pennsylvania showed an average increase of 0.008 pH units per year, and southern New England
8 showed an average increase of 0.002 pH units per year. Through continuous monitoring from
9 1990 to 2000, Stoddard et al. (2003) found a decrease in H⁺ (0.19 µeq/L/yr) similar to that
10 observed in the same Adirondack lakes by Driscoll et al. (2007) from 1992 to 2004 (0.18 µeq/L),
11 and an increase in Appalachian streams (0.08 µeq/L/yr) and Midwest lakes (0.01 µeq/L/yr). No
12 trends were found in New England lakes or Blue Ridge streams in Virginia in this study. Stream
13 monitoring in the Adirondack region from 1991 to 2001 showed an increase in H⁺ in one stream,
14 no trend in a second stream, and also an increase in a third stream near the outlet of a lake
15 (Lawrence et al., 2004). In summary, decreasing trends in pH in surface waters are common
16 through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have
17 been small.

18 The discovery that Al_i was toxic to aquatic life resulted in a considerable amount of data
19 on Al concentrations in surface waters in the 1980s, but most of this sampling was done either
20 once or for a limited period of time (Johnson et al., 1981; Driscoll and Newton, 1985; Driscoll
21 et al., 1987; Lawrence et al., 1987; Cronan et al., 1990). Monitoring of Al_i concentrations was
22 begun in 16 Adirondack lakes in 1982 and expanded to 48 lakes in 1990. From 1982 to 2004,
23 5 of the original 16 Adirondack monitoring lakes showed decreasing trends in Al_i concentrations
24 at rates that ranged from 0.02 µM/yr to 0.18 µM/yr (Driscoll et al., 2007). From 1992 to 2004,
25 24 of the 48 lakes showed decreasing trends in Al_i concentrations (Driscoll et al., 2007). The
26 analysis of Stoddard et al. (2003) also observed an average decrease in Al_i concentrations from
27 1990 to 2000 in the same group of Adirondack lakes reported on by Driscoll et al. (2007), but
28 observed no trend for this period in New England lakes, Appalachian streams, or Midwest lakes.

29 Monthly stream chemistry monitoring at the HBEF showed decreases in Al_i
30 concentrations at four locations along the reference stream for the experimental forest from 1982
31 to 2000, but no trends at two other locations along this stream (Palmer et al., 2004). These data

1 also showed a surprising decrease in pH at two of the locations where Al_i decreased, and no pH
2 trend at the other two locations where Al_i decreased (Palmer et al., 2004). Comparison of total
3 Al concentrations in 130 lakes in the northeastern United States in 1984 with those measured in
4 2001 showed lower average concentrations in 2001 in the Adirondack region, the
5 Catskill/Pocono region, central New England, southern New England, and Maine (Warby et al.,
6 2005). Because these measurements are of total Al, they are not directly comparable to Al_i .
7 Most recently, Lawrence et al. (in review) found that 49 of 195 streams (25%) during August
8 base flow in the western Adirondack region had Al_i concentrations above 2.0 μM , the level
9 above which toxic effects on biota have been shown (Driscoll et al., 2001b; Baldigo et al., 2007).

10 11 *AX4.4.3.3.1.5 Acid Neutralizing Capacity*

12 In response to reduced levels of acidic deposition required by the CAA and other
13 emissions control legislation, Stoddard et al. (2003) found trends during the 1990s toward
14 increasing Gran ANC (Figure AX4.1-5) in all of the glaciated regions of the eastern United
15 States (i.e., New England, Adirondacks, Northern Appalachian Plateau) and Upper Midwest, and
16 decreasing Gran ANC in the Ridge/Blue Ridge province. Changes were relatively modest
17 compared with observed reductions in SO_4^{2-} concentrations. Only the regional increases in the
18 Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant
19 (Table AX4.3-4). Median increases of about +1 $\mu eq/L/yr$ in the Northern Appalachian Plateau,
20 Adirondacks and Upper Midwest represent significant movement towards ecological recovery
21 from acidification (Stoddard et al., 2003).

22 It has been hypothesized that decreases in acidic deposition will yield the most chemical
23 recovery in lakes and streams that have experienced the most severe acidification. Using data
24 from all of the sites in regions where decreases in surface water SO_4^{2-} and NO_3^- have occurred,
25 Stoddard et al. (2003) found that acidic lakes and streams exhibited a highly significant median
26 increase in Gran ANC of +1.3 $\mu eq/L/yr$ during the 1990s. Low-ANC sites (0 to 25 $\mu eq/L$)
27 showed a smaller significant median ANC increase of +0.8 $\mu eq/L/yr$. Moderate ANC sites, those
28 with mean ANC values greater than 25 $\mu eq/L$, showed no significant change in Gran ANC
29 (Table AX4.3-5).

30 All of the glaciated regions in the eastern United States showed declines in base cation
31 ($Ca^{2+} + Mg^{2+}$) concentrations during the 1990s, with the average changes in the range of -1.5 to

1 -3.4 $\mu\text{eq/L/yr}$. All of the regional trends were highly significant (Table AX4.3-4). Across the
2 eastern United States, surface water SO_4^{2-} has decreased at a rate of about $-2.5 \mu\text{eq/L/yr}$ (the
3 mean of regional median slopes), and NO_3^- at a rate of $-0.5 \mu\text{eq/L/yr}$, in surface waters on
4 glaciated terrain during the 1990s. These rates of change set an upper limit to our expectation of
5 ANC recovery of $+3 \mu\text{eq/L/yr}$ (i.e., the sum of SO_4^{2-} and NO_3^- trend magnitudes). The Gran
6 ANC increase reported by Stoddard et al. (2003) was actually about one-third of this maximum,
7 $+1 \mu\text{eq/L/yr}$. The difference between the observed Gran ANC trend and the maximum trend
8 estimated from rates of acid anion change can largely be explained by the average regional
9 median decline in $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations, which was about $-2.0 \mu\text{eq/L/yr}$ (Stoddard et al.,
10 2003).

11 12 **AX4.4.3.3.2 Episodic Effects**

13 Episodic acidification can result naturally from the mobilization of organic acids and
14 from dilution of base cation concentrations, but decreases in pH and ANC associated with
15 increases in SO_4^{2-} and NO_3^- are largely attributable to acidic deposition (Wigington et al., 1996).
16 Episodic acidification is most common in the early spring and late fall as a result of snowmelt
17 and rainstorms, and is least common in summer, when high flows tend to be infrequent.
18 Seasonal variations in stream flow also result in seasonal patterns of surface water chemistry at
19 base flow. Lakes and streams at base flow tend to be more acidic in early spring than at other
20 times of the year and low flows in late summer tend to be least acidic (Lawrence et al., 2007).

21 The transient nature of high flows makes episodic acidification difficult to measure.
22 Therefore, assessments have generally estimated the number of lakes and streams prone to
23 episodic acidification by combining episode information from a few sites with base flow values
24 of ANC determined in large surveys (Eshleman et al., 1995; Bulger et al., 2000; Driscoll et al.,
25 2001b). Inclusion of episodically acidified water bodies in regional assessments substantially
26 increases estimates of the extent of surface water acidification. For example, baseflow samples
27 collected from 1991 to 1994 through the EPA TIME Program indicated that 10% of the 1,812
28 lakes (>1 ha surface area) in the Adirondack region of New York could be considered
29 chronically acidic on the basis of ANC values less than $0 \mu\text{eq/L}$, but that an additional 31% of
30 these lakes had baseflow ANC values less than $50 \mu\text{eq/L}$ and were, therefore, estimated to be
31 susceptible to episodic acidification (Driscoll et al., 2001b). Lawrence (2002) also estimated the

1 extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km²)
2 through the use of an index site at the base of the watershed that became episodically acidified at
3 high flows. Upstream sites with a lower base flow ANC than the index site at the same date and
4 time were found to have a high likelihood of becoming episodically acidified. Base flow
5 sampling of 122 upstream sites indicated that approximately 16% of the total upstream reaches
6 were chronically acidified (ANC < 10 µeq/L), but that 66% of the stream reaches became
7 episodically acidified.

8 Stoddard et al. (2003) compared seasonal data from New England lakes, Adirondack
9 lakes and Northern Appalachian streams, collected monthly to quarterly, to evaluate the
10 difference between the chemistry of surface waters in the summer and in the spring. Results
11 indicated that spring values of ANC were an average of 30 µeq/L lower than summer ANC.
12 This study referred to samples collected in spring as “episodic samples”, although sampling was
13 done independent of flow. Therefore, the 30 µeq/L difference should be considered a seasonal
14 effect rather than an episodic effect.

15 The most thorough characterization of episodic variations in stream chemistry was
16 conducted through the ERP, in which 13 low-order streams (watershed areas less than 24 km²) in
17 the Adirondack and Catskill regions of New York, and the Appalachian Plateau in Pennsylvania
18 were monitored from 1988 to 1990 (Wigington et al., 1996). Acid episodes with chemical
19 concentrations within the 90th percentile involved decreases in ANC of up to 200 µeq/L,
20 decreases in pH of up to one unit, and increases in concentrations of Al_i of up to 15 µM
21 (Wigington et al., 1996). Results also showed that acid episodes reduced the size of fish
22 populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and
23 Al_i concentrations exceeded 3.7 µM, despite the relatively short duration of episodes (Baker
24 et al., 1996). Baker et al. (1996) concluded that impact on biota from episodic acidification were
25 likely to be similar to those from chronic acidification. Elimination of an annual age class can
26 result from an episode that occurred in the presence of a sensitive life stage. Largely on the basis
27 of this study, the EPA concluded that reversal of effects from episodic acidification could be
28 used as a key ecological endpoint for an acid deposition standard for protection of the
29 environment (U.S. Environmental Protection Agency, 1995).

30 Despite the significance of the findings of ERP, little assessment or monitoring of
31 episodes was done in the 1990s. One exception was the work of Hyer et al. (1995) in three

1 watersheds of differing geology in Shenandoah National Park. Results suggested that episodic
2 acidification was occurring throughout the park on all bedrock types, although acidification was
3 not sufficient to cause elevated Al concentrations. Lawrence (2002) also documented severe
4 episodic acidification in August 1998 in a tributary of an ERP stream, where Al_i concentrations
5 increased from 1.6 to 7.3 μM in 6.5 h.

6 In the first large-scale study designed to sample streams during high-flow conditions,
7 Lawrence et al. (2007) found that 124 out of 188 (66%) western Adirondack streams were prone
8 to acidification to the level at which Al_i becomes mobilized. Only streams accessible with less
9 than a 60-min hike were sampled in this study. The March, 2004 survey was chosen to represent
10 episodic conditions, and a survey conducted August 16-18, 2004 was chosen to represent base
11 flow conditions. Based on this comparison, 35% of the streams were chronically acidified, 30%
12 of the streams were episodically acidified, and 34% were not acidified. Survey results were also
13 used to estimate that 718 km of stream reaches were prone to acidification, although 3085 km of
14 stream reaches within the study region could not be assessed because of inaccessibility.

15 There have been no studies in the United States that determine if either the severity or
16 frequency of episodic acidification has lessened. In a study of two streams in Nova Scotia
17 (Laudon et al., 2002), trends in ANC in four phases of storm hydrographs from 1983 to 1998,
18 were not detected other than in the peak-flow phase of one stream (an increase of 0.87 μeq/L).
19 In Sweden, the anthropogenic contribution to episodic decreases in ANC were estimated to range
20 from 40 to 80% in five streams from 1990 to 1999 (Laudon et al., 2002).

21 22 23 **AX4.5 EFFECTS ON WATERSHEDS AND LANDSCAPES**

24 25 **AX4.5.1 Interactions Among Terrestrial, Transitional, and Aquatic** 26 **Ecosystems**

27 Acidification has pronounced effects on nutrient cycling in terrestrial, transitional, and
28 aquatic ecosystems. Of particular importance in this regard is the role of N deposition in
29 influencing N cycling. This topic is discussed in detail in Section 5. Also important are the
30 influences of acidification on the availability of Ca²⁺ and other nutrient base cations (Mg²⁺, K⁺).

31 In general, decomposition, nutrient cycling, productivity, and other system-level
32 processes in surface waters are not as sensitive as species composition and richness to relatively

1 small amounts of acidification. Such effects only seem to occur at high levels of acidification
2 (e.g., pH < 5). This is because acid-sensitive species are often replaced by more acid-tolerant
3 species that perform the same function until acidification becomes severe. For example, whereas
4 changes in microbial composition and abundance have been observed with acidification, they
5 appear to have minimal effect on overall microbial respiration and nutrient cycling. At extreme
6 levels of acidity, however, these system-level functions may also decrease. Thus, system-level
7 functions are not generally good indicators of light to moderate levels of acidification.

8 Integrating the effects of atmospheric deposition across spatial scales is difficult. The
9 response of a single plant, or small group of plants, cannot be easily scaled up to examine effects
10 on plant communities, ecosystems, watersheds, or geographic regions. Integration typically
11 requires a combination of approaches, including ecosystem modeling, experimental manipulation
12 studies, surveys across pollution deposition gradients, and long-term monitoring studies.
13 Similarly, aquatic effects at the population level can be readily quantified, but extrapolation to
14 the community or aquatic ecosystem level is problematic. Linking research results across scales
15 will be an important component of future research. Measurements that correlate with ecosystem
16 processes, such as foliar N concentration, leaf area index, or spectral reflectance, can in some
17 cases be remotely sensed. They offer great promise for future assessment of terrestrial effects
18 across spatial scales.

19 Effects of atmospheric deposition of acidifying substances on soil, vegetation, and
20 surface water are manifested in specific processes, affecting energy, water and nutrient flow,
21 intra- and inter-species competitive interactions, and ecosystem primary production. Therefore,
22 effects on sensitive species (only some of which have been documented) have the potential to
23 cascade throughout the ecosystem and become manifested at a variety of scales. Such
24 ecosystem- to landscape-scale effects from atmospheric deposition of acidifying substances are
25 known to occur, but the results of these interacting processes have not been conclusively
26 demonstrated.

27 It is also evident that acidification from natural and human-caused disturbances,
28 including climatic stressors (temperature, moisture availability, wind), insect infestation, disease,
29 fire, and timber harvest, can affect the severity of effect of atmospheric deposition of SO_x and
30 NO_y. Although it is clear that such interactions can occur, there are no studies that have clearly
31 documented that acidic deposition at levels that commonly occur across broad landscapes in the

1 United States has conclusively altered ecosystem structure or function. Similarly, although it is
2 widely believed that acidic atmospheric deposition can make plants more susceptible to the
3 adverse effects of other natural and human-caused stressors, such effects have not been
4 conclusively demonstrated in more than a few cases. The data demonstrating and quantifying
5 the extent to which SO_x and NO_y deposition are altering natural terrestrial ecosystems via
6 acidification pathways are sparse. In particular, effects of soil and soil water acidification on soil
7 ecosystem processes and nutrient cycling are poorly known. Even less is known about effects on
8 soil microorganisms and food webs, or how such effects interact with the above-ground
9 vegetation community.

10 **AX4.5.2 Interactions with Land Use and Disturbance**

12 The prevailing scientific consensus during the 1980s held that the majority of lakes in
13 eastern North America that had pH less than about 5.5 to 6.0 had been acidified by acidic
14 deposition. Reports that acidic lakes and streams were rare or absent in similar areas not
15 receiving acidic deposition were used as evidence of acidification by acidic deposition in many
16 regions (e.g., Neary and Dillon, 1988; Sullivan et al., 1988; Baker et al., 1991a). An alternative
17 hypothesis had been advanced by Rosenqvist (1978), Krug (1989, 1991), and Krug and Frink
18 (1983) that land use changes could explain recent lake acidification in southern Norway and the
19 northeastern United States. According to this hypothesis, natural soil processes and changes in
20 vegetation can generate more acidity than is received from atmospheric deposition. For
21 example, an increase in acidic humus formation in response to decreased upland agriculture was
22 suggested as being responsible for regional acidification in southern Norway, rather than acidic
23 deposition (Rosenqvist, 1978). Subsequent acidic deposition effects research in some cases
24 seemed to be designed to refute this hypothesis rather than to explore the relationships between
25 land use and acid-base chemistry (cf. Havas et al., 1984; Birks et al., 1990). Research intended
26 to discriminate between acidic deposition and land use as the major cause of acidification
27 generally concluded that acidic deposition was the principal cause of regional acidification in
28 certain areas of North America and Europe. Perhaps more appropriate research questions might
29 have focused on quantifying the relative importance of land use activities or landscape change in
30 exacerbating or ameliorating acidic deposition effects. The importance of acidic deposition as an

1 agent of acidification does not preclude the importance of land use and landscape changes which,
2 in some cases, may actually be more important than acidic deposition (Sullivan et al., 1996b).

3 There has not been a regional evaluation of land use changes in areas of the United States
4 susceptible to surface water acidification from acidic deposition. It has therefore not been
5 possible to quantify the extent or magnitude of land use effects on acidification. It is clear,
6 however, that such changes can have important effects on acid-base status (Sullivan, 2000),
7 especially as influenced by N deposition (Goodale and Aber, 2001).

8 Changes in human land use activity, and associated changes in vegetative structure,
9 influence ecosystem response to external stressors such as acidic deposition, exposure to O₃,
10 natural disturbance factors such as wind and fire, and climatic changes. Some activities
11 contribute to the acidification of soil and surface waters; other activities decrease acidity
12 (Sullivan et al., 1996b) (Table AX4.5-1).

13 Forest management practices, especially those that have occurred over many generations
14 of trees, can have important effects on soil erosion, nutrient supplies, and organic material. Such
15 effects can influence the availability of base cations for acid neutralization and/or aspects of
16 N cycling.

17 Forests are efficient at scavenging S and N from the atmosphere. Differences in forest
18 canopy, particularly between deciduous and coniferous trees, can cause large differences in dry
19 deposition, and therefore total deposition of S and N. In regions that receive high levels of acidic
20 deposition, the presence of forest vegetation, especially coniferous trees, enhances total
21 deposition of acid-forming precursors (Rustad et al., 1994). In addition to the enhanced
22 deposition caused by the presence of large trees, there are also differences in nutrient uptake. In
23 particular, younger trees take up larger quantities of N and other nutrients than do trees in older
24 forests. Therefore, changes in the occurrence and age or species composition of the forest can
25 influence the rates of atmospheric deposition to the site as well as the fate of atmospherically
26 deposited substances.

27 Landscape processes and watershed disturbance can influence soil and water acidification
28 in many ways. Land use practices and vegetation patterns have been changing in various parts of
29 the United States for decades to centuries. These changes in human activity can influence the
30 response of forested ecosystems to external stressors, including atmospheric deposition of S or
31 N, natural disturbance factors such as wind and fire, and climatic changes. Some processes

1 contribute to the acidification of soil and surface waters or reduce the base saturation of the soils
2 thereby increasing their sensitivity to acidic deposition. Other processes cause decreased acidity
3 (Sullivan et al., 1996b; Sullivan, 2000).

4 Watershed disturbance from logging, blowdown, and fire disrupts the normal flow of
5 water and can cause increased contact between runoff water and soil surfaces, leading to
6 increased base cation concentration and ANC in drainage water. Recovery from disturbance can
7 cause a decrease in drainage water ANC as the system returns to pre-disturbance conditions. In
8 particular, soil loss through erosion can reduce the base cation pool size, thereby limiting the
9 capacity of soils to neutralize atmospheric acidity. In addition, forest harvesting has an
10 important effect on forest N-demand, thereby reducing the likelihood of future N-saturation in
11 response to high N deposition. Forest management practices, especially those that have occurred
12 over many generations, have had important effects on soil chemistry, nutrient supplies, and
13 organic material.

14 Watershed disturbances, including road building, agriculture, mining, urbanization,
15 logging, blowdown, and fire can alter various aspects of ecosystems biogeochemistry. Such
16 disturbances can influence the water budget, base cation mobilization, routing of drainage water,
17 nutrient input, and S and N cycling in ways that affect the acid-base chemistry and nutrient
18 dynamics of soils and drainage waters (Sullivan et al., 1996b). The effects of such disturbances
19 can greatly modify the response of a given watershed to atmospheric inputs of S and N.

20 21 **AX4.5.2.1 Timber Harvest**

22 Removal of the forest affects drainage water quality in several ways. Deposition of S and
23 N are reduced; leaching of NO_3^- increases and, in some cases, causes a pulse of surface water
24 acidification. Base cations tied up in wood are lost when wood is transported off-site. Regrowth
25 of the forest may further affect drainage water quality through vegetative uptake of N and base
26 cations. Trees accumulate base cations to a greater degree than anions. To balance the charge
27 discrepancy, roots release an equivalent amount of protons and acidify the soil. Base cation
28 accumulation by trees is age-dependent. Young forests grow faster and are therefore more
29 acidifying than older forests (Nilsson et al., 1982; Nilsson, 1993). They also retain greater
30 amounts of N.

1 Most forests in the northeastern United States are recovering from extensive human
2 disturbance that occurred over a period of about 200 years. Landscapes were mainly forested
3 during pre-colonial times, logged or cleared for agriculture in the mid to late 19th century, and
4 are now largely early to mid-seral stage regenerating forests (Niering, 1998).

5 In some areas that experience relatively high levels of acidic deposition, there is growing
6 concern about sustainable timber productivity (cf. Adams, 1999). Harvest-induced leaching
7 losses have been estimated to range from 6 to 60 kg/ha/yr of N, 28 to 48 kg/ha/yr of Ca^{2+} , and
8 7 to 16 kg/ha/yr of Mg^{2+} (Federer et al., 1989). Timber harvesting also increases leaching losses
9 from the site because of the reduction in transpirational water loss. The increased water flux
10 after tree removal increases the opportunity to leach base cations from the soil.

11 If base cations sequestered in tree wood are removed from the site by tree harvesting, the
12 result is a decrease in the available base cation pool on the site. Physical disturbances to forest
13 soils during logging operations and increased soil temperature that results from exposure of the
14 forest floor to sunlight may also cause a short-term increase in the rates of N mineralization and
15 nitrification (Joslin et al., 1992). The resulting increase in NO_3^- production and leaching further
16 depletes base cations from the soil pool.

17 Johnson et al. (1991a) measured short-term (3 years) effects of logging at HBEF in New
18 Hampshire on soil acid-base chemistry. Base saturation of the mineral soil Bh horizon decreased
19 from 14 to 11% and pH decreased by 0.24 pH units.

20 Likens et al. (2002) reported results of a 34-year study of the biogeochemistry of forest
21 ecosystems at HBEF. Part of the study evaluated the effects of tree removal on S cycling and
22 related biogeochemical processes. Vegetation removal resulted in increased decomposition of
23 organic matter and nitrification. These changes, in turn, lowered soil water pH, enhanced SO_4^{2-}
24 adsorption on mineral soil, and therefore decreased the flux of SO_4^{2-} in stream water. With
25 subsequent vegetation regrowth, the adsorbed SO_4^{2-} was released from the soil to drainage
26 water, and streamwater SO_4^{2-} concentrations increased.

27 Baldigo et al. (2005) compared the effects of clear-cut and timber-stand improvement
28 (TSI) harvests on water chemistry and mortality of caged brook trout in three Catskill Mountain
29 streams. Harvests removed 73% of tree basal area from a clearcut subbasin, 5% basal area from
30 a TSI subbasin, and 14% basal area at a site below the confluence of both streams (the combined
31 effect of the two harvest methods). Water quality and trout mortality were affected only in the

1 clearcut stream. Acidity and concentrations of NO_3^- and Al_i increased sharply during high flows
2 after the first growing season (1997). Acid- Al_i episodes were severe during this period and
3 decreased steadily in magnitude and duration thereafter. All trout at the clearcut site died within
4 7 days during spring 1998, and 85% died during spring 1999. Only background mortality was
5 observed in other years at this site and at the other three sites during all tests. The effects of tree
6 harvests on fish communities are of concern because they might interact with effects of acidic
7 deposition and produce more substantial effects on biota than either stress factor on its own.

8

9 **AX4.5.2.2 Insect Infestation**

10 Effects of insect-caused defoliation on the N cycle can be pronounced. The foliar
11 N consumed by insects is deposited on the forest floor as insect feces (frass), greenfall, and
12 insect biomass. Some of this deposited N is subsequently taken up by tree roots and soil
13 microbes, with little effect on the nutritional condition of the trees or the site. Where a sizable
14 component of this N is leached in drainage water, the nutritional consequences can be more
15 significant. There are also various feedback mechanisms. For example, low N supply can slow
16 the population growth of defoliating insects (Mason et al., 1992) and enhance the tree's chemical
17 defenses against insects (Hunter and Schultz, 1995). The amount of N leaching loss is generally
18 small, relative to atmospheric deposition inputs and relative to the amount of N transferred to the
19 forest floor with the defoliation (Lovett and Ruesink, 1995; Lovett et al., 2002). Nevertheless, it
20 can be high enough to contribute to base cation depletion of soils and effects on downstream
21 receiving waters. The extent of NO_3^- leaching may be partly related to the extent of defoliation
22 and tree mortality that occurs and also the amount of precipitation that occurs immediately after
23 the defoliation (Lovett et al., 2002).

24 Forest insect infestation can have profound effects on the acid-base and nutrient
25 chemistry of soils and drainage waters. Effects of a gypsy moth infestation in Shenandoah
26 National Park provide a good example. Between the mid-1980s and the early 1990s, the
27 southward expanding range of the European gypsy moth traversed Shenandoah National Park
28 and affected all of the University of Virginia's SWAS study watersheds (Webb, 1999). Some
29 areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed,
30 for example, was more than 90% defoliated in both 1991 and 1992. This insect infestation of
31 forest ecosystems in Shenandoah National Park resulted in substantial effects on streamwater

1 chemistry. The most notable effects of the defoliation on park streams were dramatic increases
2 in the concentration and export of N and base cations in streamwater. Following defoliation,
3 NO_3^- export increased to previously unobserved levels and remained high for over 6 years before
4 returning to predefoliation levels. The very low levels of pre-disturbance NO_3^- export in park
5 streams were consistent with expectations for N-limited, regenerating forests (Aber et al., 1989;
6 Stoddard, 1994). Release of NO_3^- to surface waters following defoliation was likewise
7 consistent with previous observations of increased N export due to forest disturbance (Likens
8 et al., 1970; Swank, 1988). The exact mechanisms have not been determined, but it is evident
9 that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the
10 ordinarily tight cycling of N in Shenandoah National Park forests.

11 Although N is thought to play an important role in the chronic acidification of surface
12 waters in some areas (cf. Sullivan et al., 1997), the elevated concentrations of NO_3^- in
13 Shenandoah National Park streams following defoliation did not appear to contribute to baseflow
14 acidification in White Oak Run. This was due to a concurrent increase in concentrations of base
15 cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation concentrations increased
16 during high-runoff conditions, although the increase in base cations did not fully compensate for
17 the episodic increase in NO_3^- . Episodic acidification following defoliation thus became more
18 frequent and more extreme in terms of observed minimum ANC (Webb et al., 1995).

19 The full effect of the gypsy moth on aquatic resources in Shenandoah National Park is
20 not well understood. One consequence may be a reduction in the supply of available soil base
21 cations and associated effects on streamwater ANC. Repeated periods of defoliation would
22 probably increase the effect of episodic acidification on sensitive aquatic fauna and may
23 determine the conditions under which some species are lost. Ultimately such effects may depend
24 upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount
25 of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic
26 outbreaks and collapse (Cambell, 1981). It remains to be seen what the long-term pattern will be
27 (Sullivan et al., 2003).

28 Webb et al. (1994) compared pre- and post-defoliation streamwater chemistry for 23
29 VTSSS watersheds. Nitrate concentrations, measured quarterly, increased in most of the streams
30 in response to defoliation, typically by 10 to 20 $\mu\text{eq/L}$ or more. The increased streamwater NO_3^-
31 concentration was probably derived from the N content of the foliage that had been consumed by

1 the gypsy moth larvae and converted to feces on the forest floor. Sulfate concentrations and
2 ANC also decreased in streamwater. Although the mechanism for decreased SO_4^{2-} was not
3 totally clear, Webb et al. (1994) hypothesized that increased nitrification in response to the
4 increased soil N pool may have caused soil acidification, which would be expected to have
5 increased soil S adsorption (cf. Johnson and Cole, 1980). Decreased S deposition during the
6 comparison period may also have contributed to the SO_4^{2-} response.

7 Eshleman et al. (1998) reported NO_3^- outputs from five small (<15 km²) forested
8 watersheds in Virginia and Maryland from 1988 to 1995. The study watersheds varied in
9 geology, vegetation, and acid sensitivity, with baseflow ANC typically in the range of 0 to
10 10 µeq/L in Paine Run to the range of 150 to 350 µeq/L in Piney River. Oak species
11 (*Quercus* spp.), which are a preferred food source of gypsy moth larvae, occupied about 60% to
12 100% of the study watersheds. Nitrate concentrations increased in at least three of the
13 watersheds in association with intense defoliation by the gypsy moth larva during the late 1980s
14 to early 1990s, to peak annual average NO_3^- concentrations of about 30 to 55 µeq/L. Most of the
15 increased NO_3^- leaching occurred during storm flow conditions.

16 A number of other studies have been conducted that examined the effects of gypsy moth,
17 or other forest insect pests, on watershed biogeochemistry. Defoliation of poplars (*Populus* sp.)
18 by gypsy moth larvae in southwestern Michigan did not result in appreciable NO_3^- leaching
19 (Russell et al., 2004).

20 Other pest species can have similar effects. For example, spruce-fir forests throughout
21 the southern Appalachian Mountains have been subjected to significant disturbance, especially
22 from the balsam wooly adelgid, a European pest which has infested Fraser fir since about the
23 1960s. Severe fir mortality has occurred in many areas. This disturbance factor has the potential
24 to interact with acidic deposition and other ecosystem stresses, and contribute to multiple-stress
25 tree mortality and to changes in biogeochemical cycling.

26 Defoliation by the elm spanworm (*Ennomos subsignarius* Hübner) larvae in old-growth
27 hemlock-hardwood forests on the Allegheny High Plateau of northwestern Pennsylvania
28 increased streamwater NO_3^- concentrations from pre-defoliation levels of about 29 µeq/L to
29 peak values the summer after defoliation of about 100 µeq/L (Lewis and Likens, 2007).

30

1 **AX4.5.2.3 Wind or Ice Storm Damage**

2 Forest blowdown might affect surface water acid-base chemistry by changing the
3 pathway followed by drainage water through watershed soils (Dobson et al., 1990). Pipes
4 formed in the soil by decaying tree roots can alter hydrologic flow so that less water enters the
5 soil matrix, where neutralization processes buffer the acidity of rainwater and snowmelt. Pipes
6 tend to occur most commonly in near-surface soil horizons where most tree rooting occurs.
7 Contact between drainage water and mineral soil is reduced when runoff is routed through them.
8 If enhanced pipeflow, resulting from sudden extensive tree mortality, affects a large portion of a
9 watershed, runoff water may have less opportunity for acid neutralization than would be the case
10 in the absence of such pipeflow.

11 Severe canopy damage occurred in 1998 in response to an ice storm at HBEF and
12 surrounding areas in the White Mountains. Houlton et al. (2003) reported effects of this
13 disturbance on N cycling and leaching losses. Subsequent to the ice storm, drainage water NO_3^-
14 concentrations increased sevenfold to tenfold. Peak streamwater NO_3^- concentrations during
15 spring months reached or exceeded 50 $\mu\text{eq/L}$ at many sites. There were no significant
16 differences, however, in N mineralization, nitrification, or denitrification rates between damaged
17 and undamaged areas. Houlton et al. (2003) interpreted these results as an indication that
18 increased NO_3^- leaching was probably due to decreased root uptake rather than accelerated
19 N cycling by soil microbes. The amount of NO_3^- leaching loss was estimated to be more than
20 half of the entire year's worth of atmospheric N deposition.

21
22 **AX4.5.2.4 Fire**

23 Fire can increase concentrations of NO_3^- and SO_4^{2-} in soils and drainage water (cf.
24 Chorover et al., 1994; Riggan et al., 1994). Fenn and Poth (1998) hypothesized that successful
25 fire suppression efforts may have contributed to the development of N-saturation in fire-adapted
26 ecosystems in southern California by allowing N to accumulate in soil and in the forest floor, and
27 by maintaining dense mature stands with reduced N demand.

28 The effects of fire on NO_3^- leaching in chaparral stands in the San Gabriel Mountains,
29 CA that received high atmospheric N deposition were investigated by Riggan et al. (1994).
30 Study watersheds were burned with fires of different intensity and, after rainfall, NO_3^- and NH_4^+
31 were measured in watershed streams. Nitrogen release was up to 40 times greater in burned

1 watersheds than in unburned watersheds, and the amount and concentration of N release were
2 found to be related to fire intensity.

3 Chorover et al. (1994) evaluated the effects of fire on soil and stream water chemistry in
4 Sequoia National Park, CA. Burning increased concentrations of NO_3^- and SO_4^{2-} in soil water
5 and stream water. Sulfate concentrations increased 100 fold. Nitrate concentrations also
6 increased and remained higher in soils and stream water for about 3 years. These results suggest
7 that successful fire suppression may have contributed to the development of N saturation in fire-
8 adapted ecosystems in southern California by allowing N to accumulate in the soil and forest
9 floor, and by maintaining dense mature stands with reduced N demand (Fenn and Poth, 1998).

10

11 **AX4.5.2.5 Multiple Stress Response**

12 Acidification-related effects of S and N deposition do not occur in isolation; they interact
13 with disturbances of various types, both natural and human-caused. They also influence a range
14 of biogeochemical processes that may be difficult to predict. Overall, the interactions between
15 disturbance and ecosystem acidification as a consequence of acidic deposition are not well
16 understood.

17 It is believed that high rates of N deposition cause increased susceptibility of forests to
18 other stressors, including reducing the resistance of some tree species to frost, insect damage, or
19 drought. The effects of acidic deposition can interact with a variety of stressors, both natural and
20 human-caused. The end result might include adverse effects that would not occur solely in
21 response to acidic deposition, or in response to any one of the other stressors.

22 Watershed disturbance might also impact Hg cycling and its relationship to S deposition.
23 For example, Garcia and Carignan (2000), in a study of 20 watersheds in Quebec, Canada, found
24 that the average Hg concentration in 560-mm northern pike (*Esox lucius*) was significantly
25 higher in lakes whose watersheds had recently (1995) been logged (3.4 $\mu\text{g/g}$), as compared with
26 reference lake watersheds (1.9 $\mu\text{g/g}$), that had remained undisturbed for at least 40 years. Fish
27 tissue Hg concentration also increased with increasing DOC and lakewater SO_4^{2-} concentration,
28 and with decreasing pH.

29

30

31 **AX4.6 ECOLOGICAL INDICATORS OF ACIDIFICATION**

32

1 **AX4.6.1 Chemical Indicators**

2 Chemical indicators generally refer to chemical measurements that quantify the
3 acidification status of terrestrial and aquatic ecosystems in a way that can be related to effects on
4 biota. Numerous studies have been conducted to establish critical levels or thresholds for these
5 measurements that have biological importance. Accurate identification of the critical values for
6 these measurements is a key step in setting targets for recovery.

7 **AX4.6.1.1 Terrestrial Ecosystems**

8 **AX4.6.1.1.1 Soil Base Saturation**

9
10
11 There are several chemical indicators that provide useful information about the base
12 status of soils. These include CEC, exchangeable Ca^{2+} , exchangeable $\text{Ca}^{2+} + \text{Mg}^{2+}$, and base
13 saturation. The most useful of these measurements is base saturation, which expresses the
14 concentration of exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ , Na^+) as a percent of the total CEC (which
15 includes exchangeable H^+ and Al^{n+}). In soils with a base saturation less than 20%, exchange
16 chemistry is dominated by Al (Reuss, 1983). Under this condition, inputs of sulfuric and nitric
17 acid are buffered, in large part, by release of inorganic Al through cation exchange. This is the
18 form of Al that interferes with uptake of Ca by roots and is toxic to many forms of aquatic biota.

19 Release of Ca^{2+} , Mg^{2+} , and K^+ through mineralization of organic matter, and a high CEC
20 due to abundant organic matter, results in much higher concentrations of exchangeable bases in
21 the O horizon than in the B horizon. The O horizon also tends to have a much higher base
22 saturation than the B horizon, despite a much lower pH due to organic acids. The base saturation
23 of the B horizon is therefore more sensitive to base cation depletion from leaching by SO_4^{2-} and
24 NO_3^{--} , and is therefore particularly useful for assessing base status with regard to acidic
25 deposition. Little direct work has been done to relate base saturation to stand or forest health,
26 but Cronan and Grigal (1995) determined that base saturation values below 15% in the B horizon
27 could lead to impacts from Al stress. Lawrence et al. (2005) also observed pronounced
28 decreases in diameter growth of Norway spruce in northwestern Russia where base saturation
29 decreased from 30% to 20% in the upper 10 cm of the B horizon in 37 years.

30 Base saturation values less than 10% predominate in the B horizon in the areas where soil
31 and surface water acidification from acidic deposition have been most pronounced, including the
32 Adirondack Mountains (Sullivan et al., 2006a), red spruce forests throughout the Northeast

1 (David and Lawrence, 1996), hardwood forests in the Allegheny Plateau (Bailey et al., 2004),
2 and the southern Appalachian Mountains (Sullivan et al., 2003).

3 4 ***AX4.6.1.1.2 Soil Solution Calcium-to-Aluminum Ratio***

5 The negative effects of Al mobilization on uptake of Ca by tree roots was first proposed
6 by Shortle and Smith (1988), and substantial evidence of this relationship has accumulated over
7 the past 2 decades through field studies (McLaughlin and Tjoelker, 1992; Schlegel et al., 1992;
8 Minocha et al., 1997; Shortle et al., 1997; Kobe et al., 2002) and an extensive number of
9 laboratory studies (e.g., Cronan and Grigal, 1995). As a result, considerable effort has been
10 focused on determining a threshold value for the ratio of Ca to Al that could be used to identify
11 soil conditions that put trees under physiological stress. From an exhaustive literature review,
12 Cronan and Grigal (1995) estimated that there was a 50% risk of adverse effects on tree growth
13 if the molar ratio of Ca to Al in soil solution was as low as 1.0 They estimated that there was a
14 100% risk for adverse effects on growth at a molar ratio value of 0.2 in soil solution.

15 The information available to define levels of risk for the Ca to Al ratio is derived almost
16 entirely from laboratory experiments. Because natural soil conditions cannot be fully duplicated
17 in controlled laboratory settings, these experiments were conducted by growing seedlings
18 hydroponically or in artificial soils with little or no DOC (Cronan and Grigal, 1995). However,
19 DOC (1) ameliorates the harmful effects of Al by forming Al-organic complexes, and (2) occurs
20 in high concentrations in the rooting zone of most forest soils. Accurate speciation of Al in soil
21 solutions of the rooting zone is therefore needed to calculate the Ca to Al ratio, but only a limited
22 number of studies have developed this type of data. The method in which soil water is collected
23 also can affect Al speciation and concentrations (David and Lawrence, 1996). Other
24 complications include the much higher ratios of Ca to inorganic Al that occur in the O horizon
25 than in the upper B horizon (Lawrence et al., 1995). Trees may adjust the distribution of fine
26 roots between these horizons to minimize stress (Wargo et al., 2003). Furthermore, the
27 chemistry of the rhizosphere may be modified by root processes so that standard soil sampling
28 does not fully characterize the chemistry experienced by the roots (Phillips and Yanai, 2004).

29 As a result of these complications, the risk levels for the ratio defined in the laboratory
30 experiments have not been successfully applied to natural systems. Johnson et al. (1994a,b)
31 measured Ca:Al ratios above 1.0 through most of 4 years in the Oa and B horizon of a high-
32 elevation red spruce stand experiencing high mortality. In the 3-year study of De Wit et al.

1 (2001), Al additions lowered molar Ca to inorganic Al ratios in soil solutions of a Norway spruce
2 stand below 0.5, but saw no response other than reduced Mg concentrations in needles in the
3 third year, which was a possible precursor to damage. It is unclear if extending the duration of
4 the experiment would have led to eventual harm. In the study of Kobe et al. (2002), addition of
5 Al to forest plots lowered the Ca:Al ratio of the O horizon only to a mean value of 7.15, but
6 resulted in significant mortality of transplanted seedlings.

7 In summary, a molar ratio of Ca^{2+} to Al^{n+} in soil solution can be used as a general index
8 that suggests an increasing probability of stress to forest ecosystems as the ratio decreases, but
9 the ratio value of 1.0 cannot be interpreted as a generally applicable threshold in natural systems.
10 Tree species vary widely in their sensitivity to Al stress. In addition, Al concentrations in soil
11 solution often have pronounced spatial and temporal variability that is difficult to relate to root
12 activity. Finally, the form of Al present in solution plays an important role in determining
13 toxicity. For example, organically complexed Al, which predominates in upper, organic-rich soil
14 horizons, is essentially nontoxic.

15

16 ***AX4.6.1.1.3 Carbon-to-Nitrogen Ratio***

17 Mechanisms of retention and release of N in forest ecosystems are not fully understood,
18 but the adverse effects of nitrification and associated acidification and cation leaching have
19 been consistently shown to occur only in soils with a C to N ratio below 20-25 (Aber et al.,
20 2003; Ross et al., 2004). This relationship makes the C to N ratio especially useful because
21 N mineralization and nitrification rates cannot be measured under natural conditions. All
22 available measurement approaches disturb the soil and often cause artificially high rates, that
23 makes these measurements a relative index rather than a realistic rate (Ross et al., 2004).
24 Approaches for measuring N mineralization and nitrification also are subject to high degrees of
25 variability, both temporally (hourly to seasonal) and spatially (down to the sub meter level).
26 Measurements of total organic C and N however, are less variable in space and time and
27 therefore more straightforward to measure than N mineralization and nitrification rates. Also,
28 ratios of C to N in the forest floor are inversely related to acidic deposition rates, although the
29 relation is stronger for hardwood stands than conifer stands (Aber et al., 2003). In sum, these
30 factors make the C to N ratio a reliable and relatively straightforward measure for identifying
31 forest ecosystems that are experiencing soil acidification and base leaching as a result of
32 nitrification.

1 **AX4.6.1.2 Transitional Ecosystems**

2 There are no commonly used chemical indicators of acid stress to transitional
3 ecosystems.

4
5 **AX4.6.1.3 Aquatic Ecosystems**

6 The most common indicators of surface water acidification are ANC, pH, and the
7 concentration of Al_i . Recently, the base-cation surplus (BCS) was also developed to better
8 account for the effects of natural organic acidity. To date, the BCS has only been applied to
9 stream chemistry data collected in the western Adirondacks from 2001 to 2005. Each indicator
10 is discussed briefly below.

11
12 **AX4.6.1.3.1 Surface Water ANC**

13 Chronic acidification of surface waters generally refers to loss of ANC that is often
14 accompanied by a reduction in pH. Chronic acidification is documented by measuring changes
15 in surface water chemistry during periods when that chemistry is expected to be relatively stable.
16 These are generally summer or fall (before turnover) for lakes and spring base flow for streams.

17 There have been many advances in scientific ability to quantify chronic surface water
18 acidification since publication of the previous AQCDs for SO_x and NO_y . Most of the NAPAP
19 research was conducted between about 1982 and 1991 and mainly focused on S-driven
20 acidification; research results from those programs were published throughout the 1980s and
21 1990s. Major research efforts were conducted in Europe during the 1990s regarding the
22 dynamics of N-driven acidification and related processes in both terrestrial and aquatic
23 ecosystems. New predictive models were developed, tested, and improved. Data from long-
24 term monitoring programs and experimental manipulation studies contributed critical
25 quantitative dose-response data, providing the foundation for establishment of standards for the
26 protection of acid-sensitive resources.

27 Sensitivity of surface waters to chronic and episodic acidification is not solely a function
28 of surface water chemistry, but depends also upon watershed soils, mineralogy, and hydrologic
29 flow paths (Chen et al., 1984; Cosby et al., 1985), as well as on the current and historic
30 atmospheric depositional loadings of acids and bases. Nevertheless, surface water ANC provides
31 an initial point of departure from which to assess quantitatively the current status of streams on a
32 synoptic scale. Baker et al. (1991a) used ANC cutoffs of 0, 50, and 200 $\mu\text{eq/L}$ for reporting on

1 national lake and stream population estimates. ANC < 0 µeq/L is of significance because
2 waters at or below this level have no capacity to neutralize acid inputs. Surface waters with
3 ANC < 50 µeq/L have been termed “extremely acid sensitive” (Schindler, 1988), are prone to
4 episodic acidification in some regions (DeWalle et al., 1987; Eshleman, 1988), and may be
5 susceptible to future chronic acidification at current or increased rates of acidic deposition.

6
7 *AX4.6.1.3.1.1 Titrated ANC*

8 The most widely used measure of surface-water acidification is ANC, determined by
9 Gran titration (titrated ANC). This measurement is the primary chemical indicator used by EPA
10 for assessing past effects of acidic deposition, and the recovery expected from decreasing
11 atmospheric deposition (Bulger et al., 2000; Stoddard et al., 2003). Titrated ANC is useful
12 because it reflects the ANC of the complete chemical system, which is typically reduced by
13 acidic deposition in acid-sensitive landscapes. However, titrated ANC also reflects the influence
14 of acids and bases associated with DOC and inorganic Al (Munson and Gherini, 1993a,b). The
15 use of titrated ANC to assess the effects of acidic deposition on aquatic ecosystems can,
16 therefore, be complicated by natural acidity derived from acidic functional groups of DOC, and
17 hydrolyzed Al, which increases titrated ANC, but is caused by acidic deposition and is harmful
18 to both aquatic and terrestrial biota. As the concentration of DOC decreases, the influence of
19 organic acidity on titrated ANC also decreases. Hydrolyzed Al influences titrated ANC
20 primarily in waters with low DOC concentrations and pH values in the range of 4.7 to 5.1, where
21 concentrations are typically highest (Driscoll and Bisogni, 1984). Application of a triprotic
22 model of organic acidity showed that an increase in DOC concentration of 183 µmol L⁻¹ would
23 decrease Gran ANC by 10 µeq/L in Adirondack lakes (Driscoll et al., 1994). The influence of
24 organic acidity also complicates assessments of recovery from acidification because
25 concentrations of DOC have increased over the past 10 to 15 years in the Adirondack region,
26 as well as in other regions in the eastern U.S (Stoddard et al., 2003) at the same time that
27 S deposition has been decreasing.

28
29 *AX4.6.1.3.2 Base Cation Surplus*

30 European assessments of surface-water acidification use an alternative to titrated ANC, in
31 which acidification status is measured by the sum of base cation concentrations (Ca²⁺, Mg²⁺,
32 Na⁺, K⁺) minus the sum of inorganic strong-acid anion concentrations (SO₄²⁻, NO₃⁻, Cl⁻), which

1 has been termed both ANC (Wright et al., 2005), and calculated ANC (Cosby et al., 2001). The
2 sum of base-cation concentrations reflects the ability of a watershed to neutralize acid inputs
3 through the release of base cations, and the sum of inorganic strong-acid anions largely reflects
4 the input of acidic deposition. The difference in these two quantities provides a relative measure
5 of acidic deposition effects. However, because organic acidity is not included in the formulation,
6 this version of ANC does not relate to inorganic Al concentrations in a consistent manner if DOC
7 concentrations vary (Lawrence et al., 2007).

8 The recently developed BCS provides a new approach for distinguishing between the
9 effects of organic acidity and acidic deposition (Lawrence et al., 2007). The BCS is similar to
10 the European formulation of ANC, but explicitly accounts for strongly acidic organic acids. The
11 BCS is defined as the difference between the summed concentrations of base cations (Ca^{2+} ,
12 Mg^{2+} , Na^+ , K^+) and strongly acidic anions (SO_4^{2-} , NO_3^- , Cl^- , and RCOO-s), where RCOO-s
13 refers to the concentration of strongly acidic organic anions. When the BCS is plotted against
14 inorganic Al concentrations, a distinct threshold for Al mobilization occurs at a BCS value that
15 closely approximates 0, regardless of the DOC concentration (Lawrence et al., 2007). This
16 threshold provides an unambiguous reference point for evaluating the effects of acidic deposition
17 on mobilization of inorganic Al.

18 The role of weakly acidic organic acids in mobilizing organic forms of Al has long been
19 recognized, but the BCS is the first indicator that accounts for the role of strong organic acids in
20 the mobilization of inorganic Al (Lawrence et al., 2007). However, the BCS formulation does
21 not imply that mobilization of inorganic Al occurs in the absence of acidic deposition. If the sum
22 of base-cation concentrations exceeds the concentration of strong organic anions, excess H^+ will
23 not be available for mobilization of inorganic Al without contributions of SO_4^{2-} and NO_3^- from
24 acidic deposition. This was shown to be the case for 388 out of the 389 stream samples collected
25 in approximately 200 Adirondack streams during spring snowmelt and high DOC concentrations
26 in the fall (Lawrence et al., 2007). The sum of base-cation concentrations exceeded the estimate
27 of strong organic anions by an average of 178 $\mu\text{eq/L}$ for all samples collected in October 2003
28 and March 2004 surveys. In combination with inorganic strong acids from acidic deposition,
29 however, strongly acidic organic acids further decrease the value of the base-cation surplus.
30 Production of strongly acidic organic acids therefore increases the sensitivity of a watershed to
31 acidic deposition in a manner analogous to base-poor bedrock and till. To date, the BCS has

1 only been used in one large-scale assessment of acidic deposition effects on surface waters
2 (Lawrence et al., 2007).

3
4 **AX4.6.1.3.3 *Surface Water pH***

5 The pH of water quantifies the H⁺ concentration, which is toxic to many forms of aquatic
6 life and is frequently used as an index of biological response to acidification of surface waters.
7 In addition, pH correlates with other biologically important components of surface water acid-
8 base chemistry, including ANC, Al_i, Ca²⁺ concentrations, and organic acidity. Common
9 reference values for pH are 5.0, 5.5, and 6.0 and low pH can have direct toxic effects on aquatic
10 species (Driscoll et al., 2001b). Only the most acid tolerant fish species can survive below pH
11 5.0, and Kretser et al. (1989) found that half the total number of fish species that occur in the
12 Adirondack region were present in lakes with pH less than 6.0. A pH value of 6.0 is often
13 considered the level below which biota are at risk from acidification (Driscoll et al., 2001b).
14 Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic
15 organisms (Haines and Baker, 1986; Baker et al., 1990a). The effects of natural acidity also
16 complicate the use of pH as an indicator of acidic deposition effects, however. Most species of
17 plants and animals are sensitive to certain ranges of pH, but naturally acidic environments with
18 indigenous species often occur in areas affected by acidic deposition (Dangles et al., 2004). The
19 effects of low pH are specific to the organism and region under consideration and depend also
20 upon the concentrations of other chemical constituents in the water, notably Al_i and Ca²⁺.

21
22 **AX4.6.1.3.4 *Surface Water Inorganic Aluminum***

23 Considerable work has been done to define pH sensitivity ranges for a wide variety of
24 aquatic organisms, but when pH values fall below approximately 5.5, inorganic Al becomes the
25 greater health risk to biota. Although organically complexed Al (organic Al) can occur in
26 surface waters as a result of natural soil and hydrologic processes, this form of Al is not harmful
27 to aquatic life (Gensemer and Playle, 1999). Inorganic Al, however, has been found to be toxic
28 to plant and animal species throughout the food web (Gensemer and Playle, 1999). The
29 concentration of inorganic Al in surface waters is an especially useful indicator of acidic
30 deposition effects because it is widely toxic and also because it does not move from the
31 terrestrial environment to surface waters in the absence of acidic deposition, with exceptions
32 such as acid mine drainage and rare geologic deposits (Lawrence et al., 2007).

1 Earlier studies have demonstrated reduced growth and survival of various species of fish
2 (Baker and Schofield, 1982; Baker et al., 1996) between approximately 2 and 7.5 $\mu\text{mol/L}$ of
3 inorganic Al. Most recently, 20% mortality of brook trout young-of-the year was documented
4 *in situ* during a 30-day period with a median inorganic Al concentration of 2 $\mu\text{mol/L}$ (Baldigo
5 et al., 2007). Because brook trout are one of the most acid-tolerant fish species, and young-of-
6 the year are not the most acid-sensitive life stage, negative effects of inorganic Al concentrations
7 on fish communities are likely to occur at concentrations below 2 $\mu\text{mol/L}$ (Baldigo et al., 2007).
8 This same study estimated that 90% mortality would occur over 30 days with a median inorganic
9 Al concentration of 4.0 $\mu\text{mol/L}$.

10 11 **AX4.6.2 Biological Indicators**

12 Surface water acidification from acidic deposition causes effects on organisms at all
13 trophic levels. Early studies focused on the loss of fish populations, especially salmonids. Later
14 studies also reported that many species of phytoplankton, zooplankton, insect larvae, crayfish,
15 snails, and freshwater mussels are sensitive and are often reduced or absent from acidified lakes
16 and streams (Havas, 1986; Baker et al., 1990a). Similarly, many species of microrhizal fungi
17 and lichens have been reported to be particularly sensitive to acidic deposition in terrestrial
18 ecosystems.

19 Effects of acidification on aquatic biota have been demonstrated in laboratory and field
20 bioassays (e.g., Baker et al., 1996), whole-ecosystem acidification experiments (e.g., Schindler
21 et al., 1985), and field surveys (e.g., Baker and Schofield, 1982; Gallagher and Baker, 1990).
22 Many of the species that commonly occur in acid-sensitive surface waters susceptible to acidic
23 deposition cannot reproduce or survive if the water is acidic. Some sensitive species of fish,
24 invertebrates, and algae cannot survive at moderate levels of acidity. For example, some
25 zooplankton predators, sensitive mayfly species, and sensitive fish species are affected at pH
26 values below the range of 5.6 to 6.0 (Baker and Christensen, 1991). Such pH values generally
27 equate to ANC below about 25 to 50 $\mu\text{eq/L}$.

28 There are few published examples of long-term monitoring data for biological
29 assemblages in acid-sensitive surface waters, and none in the United States. Therefore,
30 conclusions about the effect of acidic deposition on the distribution of sensitive species are based
31 on other kinds of data (Stoddard et al., 2003). For example, the number of fish species increases

1 with increasing pH and ANC when evaluated for multiple water bodies across the landscape.
2 This result has been shown for streams in Virginia, lakes in the Adirondacks, and both high-
3 elevation and seepage lakes in Maine (Figure AX4.4-3).

4 Given the available data, it is clear that acidification from acidic deposition limits the
5 distribution of acid-sensitive fish, benthic invertebrate, phytoplankton, and zooplankton species,
6 but a lack of adequate data makes it difficult to quantify the magnitude of change in biota from
7 historical condition or in response to recent (past two to three decades) decreases in acidic
8 deposition in individual lakes or streams. Studies in Canada and Europe have illustrated the
9 feasibility and complexity of biological recovery in response to decreased acidity.

10 Threshold pH levels for adverse biological effects have been summarized for a variety of
11 aquatic organisms (Haines and Baker, 1986; Baker et al., 1990a). The effects of low pH are
12 specific to the organism, and perhaps region, under consideration and depend also upon the
13 concentrations of other chemical constituents in the water, notably Al_i and Ca^{2+} . In general,
14 populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass
15 (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.2 to 5.5
16 (Haines and Baker, 1986). A number of synoptic surveys indicate loss of species diversity and
17 absence of many other fish species in the pH range of 5.0 to 5.5 (Haines and Baker, 1986).
18 Levels of pH less than 6.0 to 6.5 have been associated with adverse effects on populations of
19 dace, minnows, and shiners (family Cyprinidae), and bioassays suggest that given sufficient Al
20 concentrations, pH less than 6.5 can lead to increased egg and larval mortality in blueback
21 herring (*Alosa aestivalis*) and striped bass (*Morone saxatilis*) (Hall, 1987; Klauda et al., 1987).

22 Mycorrhizal fungi have been suggested as possible biological indicators of atmospheric
23 deposition effects by Løkke et al. (1996) because they are intimately associated with tree roots,
24 depend on plant assimilates, and play essential roles in plant nutrient uptake. Thus, mycorrhizal
25 fungi can influence the ability of their host plants to tolerate different anthropogenically
26 generated stresses. Mycorrhizae and associated fine roots have short lifespans and their turnover
27 appears to be controlled by environmental factors. Changes in mycorrhizal species composition,
28 or the loss of dominant mycorrhizal species in areas where diversity is already low, may cause
29 increased susceptibility of plants to stress (Løkke et al., 1996).

30 Mycorrhizal fungi are dependent for their nutrition on the supply of assimilates from the
31 host plant. Stresses that shift the allocation of C reserves to the production of new leaves at the

1 expense of supporting tissues will be reflected rapidly in decreased fine root and mycorrhizal
2 biomass (Winner and Atkinson, 1986). Decreased C allocation to roots could also affect soil
3 carbon and rhizosphere organisms. For example, earthworms are believed to decrease in
4 abundance, and in species number, in acidified soils (Løkke et al., 1996). Soil dwelling animals,
5 including earthworms, are important for decomposition, soil aeration, and nutrient redistribution
6 in the soil. They contribute to decomposition and nutrient availability, mainly by increasing the
7 accessibility of dead plant material to microorganisms.

8

9 **AX4.6.2.1 Phytoplankton**

10 Phytoplankton are the small microscopic plants or plant-like organisms that live
11 suspended in the water column of lakes and large rivers. Acidification results in decreased
12 species richness and diversity of phytoplankton communities. There is also a shift in the
13 composition of dominant taxa, but species composition shifts cannot be accurately predicted
14 (though it is clear that community restructuring occurs with acidification). This effect is most
15 prevalent in the pH 5 to 6 range (Baker et al., 1990a). Acidification has also been found to cause
16 decreases in food web complexity (indicated by the number of trophic links or species) in the
17 Adirondack Mountains (Havens and Carlson, 1998). Both Al toxicity and P limitation may also
18 be responsible for shifts in phytoplankton community composition. Neither grazing pressure nor
19 changes in water clarity associated with acidification seem to have a major effect on
20 phytoplankton community structure. There is no consistent pattern of acidification effects on
21 phytoplankton biomass. Various lakes have shown increases, decreases, or no change in
22 phytoplankton biomass with acidification (Baker et al., 1990a). Leavitt et al. (1999) suggested
23 that the complex interactions between pH, DOC, and light explain the high variability in the
24 algal biomass-acidification relationship. In most lakes, acidification has a negligible effect on
25 primary productivity.

26 Diatoms, which comprise an important component of the phytoplankton, are excellent
27 indicators of environmental change in aquatic ecosystems, including acidity, nutrient status,
28 salinity, and climatic features (Sullivan and Charles, 1994; Stoermer and Smol, 1999). There are
29 thousands of different species, many of which have rather narrow ecological tolerance ranges.
30 Diatoms have been widely used as indicators of past lake acidification. Inference based on
31 diatom fossil remains preserved in lake sediments is an excellent approach for quantifying
32 historical chemical change (Charles and Norton, 1986).

1 Paleolimnological reconstructions of past lakewater chemistry are based on transfer
2 functions derived from relationships between current lakewater chemistry and diatom (or, in
3 some cases, chrysophyte) algal remains in surface sediments. Predictive relationships are
4 developed using regional lake datasets, and are then applied to diatom assemblage data collected
5 from horizontal slices of lake sediment cores to infer past lakewater conditions (Charles et al.,
6 1989; Husar and Sullivan, 1991).

7 Periphyton are the small microscopic plants (or plant-like organisms) that live on
8 submerged substrates in aquatic systems (e.g., stream or lake bottoms). As seen in
9 phytoplankton communities, acidification results in decreased species richness, community
10 alteration, and emergence of new dominant species in periphyton communities. Many diatom
11 and blue-green bacterial periphyton species cannot tolerate acidic conditions. On the other hand,
12 green algae, particularly the filamentous Zygnemataceae, increase in relative abundance at lower
13 pH (Baker et al., 1990a). Unlike for phytoplankton, there is evidence that the biomass of
14 attached periphyton increases at lower pH.

15 Studies of phytoplankton recovery from acidification indicate that there is an increase in
16 phytoplankton species richness and diversity as pH increases. In the Experimental Lakes area of
17 Ontario, previously acidified lakes have been experimentally de-acidified. In Lake 223, there
18 was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong
19 recovery of diversity at pH above 6 (Findlay and Kasian, 1996). In Lake 302S, profound change
20 began at pH 5.5; phytoplankton assemblages at pH below 5.5 resembled acidified lakes.
21 Cyanobacteria were among the first to recover at pH 5.5 to 5.8 (Findlay et al., 1999). In the
22 Killarney Park area of Ontario, Findlay (2003) reported that lakes that were previously low in pH
23 (5.0 to 5.5) and are now above pH 6 have shifted towards phytoplankton assemblages typical of
24 circumneutral environments.

25 26 **AX4.6.2.2 Zooplankton**

27 Field survey and experimental lake studies both indicate that acidification reduces
28 zooplankton species richness. Effects of acidification on community biomass and abundance,
29 however, were not definitive. Some studies indicated a lower biomass under low pH conditions,
30 whereas other studies showed no consistent pattern in the biomass-pH relationship. Limited data
31 indicated that acidification does not alter zooplankton community grazing rates. Zooplankton
32 species that have been shown to be sensitive to low pH include *Diatomus sicilis*, *Epischura*

1 *lacustris*, *Tropocyclops parsinus mexicanus*, *Daphnia galeata mendotae*, *Daphnia rosea*,
2 *Diaphanosoma birgei*, *Leptodora kindtii*, *Asplanchna priodonta*, and *Conochilus unicornis*. In
3 North America, species reported to have increased dominance in acidic lakes (acid-tolerants)
4 include *Keratella taurocephala*, *Bosmina longirostris*, and *Diatomus minutus*. Possible
5 mechanisms for zooplankton sensitivity to low pH include ion regulation failure, reduced oxygen
6 uptake, inability to reproduce, and Al toxicity. Indirect effects of acidification on zooplankton
7 communities are also possible due to pH-induced shifts in higher trophic level zooplankton
8 predators. This mechanism is probably of less importance than the direct effects of low pH. It is
9 also probable that under acidic conditions, zooplankton communities are less able to ameliorate
10 nutrient additions or control algal densities (Baker et al., 1990a).

11 Reported pH thresholds for zooplankton community alteration range from 5 to 6. Holt
12 and Yan (2003) reported a threshold of community change at pH 6 for lakes in southern Ontario.
13 Locke and Sprules (1994) reported that acidification below pH 5 in the 1970s overcame the
14 resistance stability of the zooplankton community in Ontario Precambrian Shield lakes. The
15 subset of study lakes that showed pH recovery from acidification 20 years later in 1990 also
16 showed recovery in the stability of the zooplankton community. Holt and Yan (2003) also noted
17 recovery in zooplankton community composition (based on similarity to neutral lakes) in the
18 subset of Killarney Park (Ontario) lakes in which the pH increased to over 6 during the 1971 to
19 2000 study period. They did not, however, note any time trend of increasing species richness
20 between recovering lakes and non-recovering lakes.

21 Recovery in experimentally acidified Lake 223 back to pH 6.1 was studied by Malley
22 and Chang (1995). They reported that the zooplankton community was still in a state of flux.
23 Species diversity that had been reduced during the acidification phase had partially returned to
24 preacidification levels. Rotifers had recovered less than crustaceans. One decade after cessation
25 of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton
26 community was complete (Frost et al., 2006). Recovery did not follow the same trajectory as the
27 initial acidification, however, indicating a substantial hysteresis in zooplankton community
28 recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to
29 recover to levels noted in the neutral reference basin.

30 *In situ* enclosure studies were conducted for 35 days at Emerald Lake in the Sierra
31 Nevada by Barmuta et al. (1990). The lake sediments were included within the experimental

1 enclosures. This allowed the investigators to document the response of zoobenthos as well as
2 zooplankton. Treatments included a control (pH 6.3) and acid addition to reach pH levels of 5.8,
3 5.4, 5.3, 5.0, and 4.7. Results indicated that zooplankton were sensitive to acidification but
4 zoobenthos were unaffected by the experimental treatment. *Daphnia rosea* and *Diaptomus*
5 *signicauda* decreased in abundance below the range of pH 5.5 to 5.8 and were eliminated below
6 about pH 5.0. *Bosnia longirostris* and *Keratella taurocephala* generally became more abundant
7 with decreasing pH. Barmuta et al. (1990) concluded that even slight acidification of high-
8 elevation lakes in the Sierra Nevada might alter the structure of the zooplankton community.

9 Sullivan et al. (2006a) found that zooplankton taxonomic richness varied with ANC in
10 Adirondack lakes (Table AX4.6-1). Taxonomic richness expressed as number of species of
11 crustaceans, rotifers, and total zooplankton, increased with increasing ANC. In general,
12 lakewater ANC explained nearly half of the variation in total zooplankton and crustacean
13 taxonomic richness, but less for rotifer richness. These results (Table AX4.6-1) provided the
14 basis for estimating changes in zooplankton richness in response to past or future changes in
15 lakewater ANC. Several zooplankton species found in lakes in the Sierra Nevada are also known
16 to be sensitive to acidity status (Gerritsen et al., 1998).

17 18 **AX4.6.2.3 Benthic Invertebrates**

19 Within stream systems, macroinvertebrate communities are among the most sensitive life
20 forms to disturbances, including those associated with atmospheric deposition (Cairns and Pratt,
21 1993). In addition, they are relatively easy to sample in the field (Plafkin et al., 1989; Resh
22 et al., 1995; Karr and Chu, 1999).

23 Acidification results in the loss of acid-sensitive benthic invertebrates and decreases in
24 pH of one unit or more typically result in species loss. Invertebrate taxa that are most sensitive
25 to acidification are mayflies, amphipods, snails, and clams. At low levels of acidification (pH
26 5.5 to 6.0), acid-sensitive species are replaced by more acid-tolerant species, yielding little or no
27 change in total community species richness, diversity, density, or biomass. If pH decreases are
28 larger, more species will be lost without replacement, resulting in decreased richness and
29 diversity. Many sites also note decreases in invertebrate biomass and productivity (more so in
30 streams than lakes). High levels of acidification (pH < 5) were found to virtually eliminate all
31 mayflies, crustaceans and mollusks from French streams (Guerold et al., 2000). Examples of
32 sensitive benthic invertebrate species include *Baetis rhodani*, *Gammarus lacustris*, *Hyaella*

1 *azteca*, *Asellus aquaticus*, *Orconectes rusticus*, and *O. propinquus*. Stoneflies are generally
2 more acid-tolerant than mayflies and caddisflies.

3 Possible mechanisms for acidification effects on invertebrates include direct toxicity of
4 H^+ and Al, disruption of ion regulation, and reproductive failure. Indirect effects due to
5 acidification-induced changes to invertebrate predator populations are also possible (Baker et al.,
6 1990a). Acidic episodes in streams can cause increased downstream drift of acid-sensitive
7 species, particularly *Baetis* (Kratz et al., 1994; Smock and Gazzera, 1996).

8 It has been well documented that low streamwater pH can be associated with reductions
9 in invertebrate species richness or diversity (Townsend et al., 1983; Raddum and Fjellheim,
10 1984; Burton et al., 1985; Kimmel et al., 1985; Hall and Ide, 1987; Peterson and Van Eechhaute,
11 1992; Rosemond et al., 1992; Sullivan et al., 2003), and sometimes density (Hall et al., 1980;
12 Townsend et al., 1983; Burton et al., 1985; Kimmel et al., 1985). Effects on invertebrate density
13 are not universal; a number of studies have found no density effects (Harriman and Morrison,
14 1982; Simpson et al., 1985; Ormerod and Tyler, 1987; Winterbourn and Collier, 1987).
15 However, a decrease in species richness with decreasing pH has been found in almost all such
16 studies (Rosemond et al., 1992), and this finding has been especially pronounced in streams for
17 order Ephemeroptera (mayflies).

18 The Ephemeroptera-Plecoptera-Tricoptera (EPT) Index is a common measure of stream
19 macroinvertebrate community integrity. The EPT metric is the total number of families present
20 in those three insect orders (mayflies, stoneflies, and caddisflies, respectively). The total number
21 of families is generally lower at acidified sites because species within those families tend to
22 exhibit varying acid sensitivity (cf. SAMAB, 1996). Mayflies tend to be most sensitive of the
23 three, and stoneflies tend to be least sensitive (Peterson and Van Eechhaute, 1992).

24 There has been some recovery in benthic invertebrate communities in surface waters
25 exhibiting chemical recovery from acidification. In Scotland, Soulsby et al. (1995) reported an
26 increase in acid-sensitive mayflies in some streams that showed recent ANC increases.
27 However, no increases in invertebrates were observed in the most acidic streams despite
28 observed increases in ANC. They suggested that further acidic deposition reductions and
29 sufficient time for reversal of soil acidification may be required before biotic recovery can occur.
30 Tipping et al. (2002) noted increases of invertebrate richness and diversity in the English Lake
31 District in their study streams that had pH increases of 0.3 to 0.5 units since about 1970.

1 Responses of aquatic macroinvertebrates to acidification were evaluated by Kratz et al.
2 (1994) in 12 streamside channels in Sequoia National Park, CA. Replicated treatments included
3 a control (pH 6.5 to 6.7) and experimental exposure at pH levels of 5.1 to 5.2 and 4.4 to 4.6.
4 Invertebrate drift was monitored continuously and benthic densities were determined before and
5 after acidification. Single 8-hr acid pulses increased the drift of sensitive taxa, and benthic
6 densities were reduced. *Baetis* showed reduced density post-treatment to less than 25% of
7 control densities in both pH reduction treatments (5.2, 4.6) and two different experimental
8 exposures. Densities of *Paraleptophlebia* appeared to be reduced by the acidification, but most
9 treatment effects were not statistically significant. Kratz et al. (1994) suggested that the effects
10 of acid inputs on benthic species densities depended on microhabitat preferences. *Baetis* nymphs
11 are epibenthic and active. They are often found on the upper surfaces of rocks where they are
12 directly exposed to acidified water. This may have been responsible for their greater response to
13 acidification.

14 15 **AX4.6.2.4 Fish**

16 By 1990 it was well established that pH in the range of 4.0-6.5 could cause significant
17 adverse biological effects on fish. Low pH was one of the most important factors resulting in
18 adverse effects. The toxicity of pH was, in most cases, the result of impaired body salt
19 regulation. Decreased pH in the water inhibited the active uptake of Na⁺ and Cl⁻ and stimulated
20 the passive loss of these ions (Baker et al., 1990a).

21 The response to acidification was not uniform, however. Some species and life stages
22 experienced significant mortality in bioassays at relatively high pH (e.g., pH 6.0-6.5 for eggs and
23 fry of striped bass and fathead minnow) (Buckler et al., 1987; McCormick et al., 1989), whereas
24 others were able to persist at quite low pH without adverse effect (Mudminnow; [*Umbra* spp.] at
25 pH 4.0 and *Umbra pygmaea* at pH 3.5) (Dederen, 1987). Many minnows and dace (Cyprinidae)
26 are sensitive to acidity (threshold effects at pH < 5.5 to 6.0), but some common game species
27 such as brook trout, largemouth bass, and small mouth bass are relatively insensitive (threshold
28 effects at pH < 5.0 to 5.5). A summary of studies that demonstrated the difference among
29 species is shown in Table AX4.6-2. Table AX4.6-3 summarizes the results from a variety of
30 studies that determined the threshold values of pH for various taxa and kinds of effects.

1 The effect of acidification on aquatic organisms, especially fish, is due in large part to the
2 toxic effect of Al_i that is released from watershed soils. A number of studies reviewed by Baker
3 et al. (1990a) reported threshold values of Al_i for various species and effects. Those results are
4 presented in Table AX4.6-4. The effects of low pH and high Al_i can be ameliorated to an extent
5 in the presence of increased Ca^{2+} concentration. A summary of the effect of increasing Ca^{2+}
6 concentration is presented in Table AX4.6-5.

7 Fish populations in acidified streams and lakes of Europe and North America have
8 declined, and some have become extinct as a result of atmospheric deposition of acids and the
9 resulting changes in water quality (Baker et al., 1990a). A variety of factors, including Al_i ,
10 DOC, and Ca^{2+} , along with the timing and magnitude of episodic fluctuations in toxic acid and
11 Al_i concentrations, are related to the degree to which surface water acidification influences fish
12 survival in natural systems (Baker et al., 1990a; Gagen et al., 1993; Siminon et al., 1993; Van
13 Sickle et al., 1996; Baldigo and Murdoch, 1997). Aluminum fractionation and Al_i concentration
14 are directly dependent upon pH levels (Driscoll et al., 1985).

15 Fish communities of acid-sensitive streams and lakes may contain a variety of species,
16 but are often dominated by trout. Across the eastern United States, brook trout is often selected
17 as an indicator of acidification effects on aquatic biota because it is native to many eastern
18 streams and lakes and because residents place great recreational and aesthetic value on this
19 species. It must be emphasized, however, that brook trout is a relatively acid-tolerant species.
20 Many other fish species, including rainbow and brown trout, as well as a variety of other fish
21 species, are more acid-sensitive than brook trout. In many Appalachian Mountain streams that
22 have been acidified by acidic deposition, brook trout is the last species to disappear; it is
23 generally lost at pH near 5.0 (MacAvoy and Bulger, 1995), which usually corresponds in these
24 streams with ANC near 0 (Sullivan et al., 2003).

25 Although there are known differences in acid sensitivity among fish species,
26 experimentally determined acid sensitivities are available for only a minority of freshwater fish
27 species. Baker and Christensen (1991) reported critical pH values for 25 species of fish. They
28 defined critical pH as the threshold for significant adverse effects on fish populations. The
29 reported range of pH values represents the authors' estimate of the uncertainty of this threshold.
30 The range of response within species depends on differences in sensitivity among life stages, and
31 on different exposure concentrations of Ca^{2+} and Al. To cite a few examples, blacknose dace is

1 regarded as very sensitive to acid stress, because population loss due to acidification has been
2 documented in this species at pH values as high as 6.1; in field bioassays, embryo mortality has
3 been attributed to acid stress at pH values as high as 5.9. Embryo mortality has occurred in
4 common shiner at pH values as high as 6.0. Although the critical pH range for rainbow trout is
5 designated as 4.9-5.6, adult and juvenile mortality have occurred at pH values as high as 5.9.
6 Brown trout population loss has occurred over the pH range of 4.8-6.0, and brook trout fry
7 mortality has occurred over the range of 4.8-5.9 (Baker and Christensen, 1991). Relative
8 sensitivities can be suggested by regional surveys as well, although interpretation of such data is
9 complicated by factors that correlate with elevation. Such factors, including habitat complexity
10 and refugia from high-flow conditions, often vary with elevation in parallel with acid sensitivity.
11 It is noteworthy, however that about half of the 53 fish species found in Adirondack Mountain
12 waters in New York never occur at pH values below 6.0 (Kretser et al., 1989; Driscoll et al.,
13 2001b); for those species whose acid tolerances are unknown, it is probable that acid sensitivity
14 is responsible for at least some of these absences. It is the difference in acid tolerance among
15 species that produces a gradual decline in species richness as acidification progresses, with the
16 most sensitive species lost first.

17 Effects on biota can be assessed as effects on a particular sensitive species or species
18 perceived to be important, or as effects on the richness or diversity of fish or other potentially
19 sensitive life form. For example, Bulger et al. (2000) developed ANC thresholds for brook trout
20 in Virginia, which are presented in Table AX4.6-6. These values were based on annual average
21 stream water chemistry, and therefore represent chronic exposure conditions. The likelihood of
22 additional episodic stress is incorporated into the response categories in the manner in which
23 they are interpreted. For example, the episodically acidic response category, which has chronic
24 ANC in the range of 0 to 20 $\mu\text{eq/L}$, represents streams that are expected to acidify to ANC near
25 or below 0 during rainfall or snowmelt episodes. In such streams, sublethal and/or lethal effects
26 on brook trout are possible (Bulger et al., 2000; Sullivan et al., 2003).

27 Fish species richness, population density, condition factor, age distribution, size, and
28 bioassay survival have all been shown to be reduced in low-ANC streams as compared to
29 intermediate-ANC and high-ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis
30 and Bulger, 1995; MacAvoy and Bulger, 1995). Fish species richness is a good indicator of
31 acidification response. Lakes or streams having pH below about 5.0 or ANC below about

1 0 generally do not support fish. Depending on the region, waters having pH above about 6.5
2 and ANC above about 50 $\mu\text{eq/L}$ support large, but variable, numbers of species. There is often a
3 positive relationship between pH and number of fish species, at least for pH values between
4 about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 $\mu\text{eq/L}$ (Bulger et al., 1999;
5 Sullivan et al., 2006a). Such observed relationships are complicated, however, by the tendency
6 for smaller lakes and streams, having smaller watersheds, to also support fewer fish species,
7 irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of
8 available niches as stream or lake size decreases. Nevertheless, fish species richness is one of
9 the most useful indicators of biological effects of surface water acidification.

10 Acidification and the associated elevated concentrations of Al_i in surface waters have
11 adversely affected fish populations and communities in parts of the Adirondack Mountains of
12 northern New York (Baker and Schofield, 1982; Johnson et al., 1987; Schofield and Driscoll,
13 1987; Kretser et al., 1989; Siminon et al., 1993) and in acid-sensitive streams of the Catskill
14 Mountains of southeastern New York (Stoddard and Murdoch, 1991) and the Appalachian
15 Mountains from Pennsylvania to Tennessee and South Carolina (SAMAB, 1996; Bulger et al.,
16 1999, 2000).

17 Adverse effects of low pH and high Al_i concentration on fish include increased mortality,
18 decreased growth, decreased reproductive potential, and ionoregulatory impairment. A partial
19 list of studies demonstrating such effects is provided in Table AX4.6-7 from Baker et al. (1990a).
20 It has been shown, however, that there is marked variability among species and among life stages
21 within species in the specific levels of pH and Al_i that produce measurable responses.

22 Surface-water acidification can affect fish populations by a number of mechanisms
23 ranging from increased mortality and emigration to decreased food supplies (Baker et al., 1990a).
24 The primary reason for population decline and extinction, however, is usually the failure of a
25 species to successfully recruit young-of-the-year fish (Mills et al., 1987; Brezonik et al., 1993).
26 The response of aquatic communities to acidification, therefore, should appear first as changes in
27 age distribution and decreased health of individual fish (growth and condition), then as decreased
28 biomass and density in populations of acid-intolerant fish species, and finally as elimination of
29 sensitive species (Baker et al., 1990a).

30 The primary mechanism for the toxic effects of low pH and elevated Al on fish involves
31 disruption of normal ion regulation at the gill surface resulting in increased rates of ion loss and

1 inhibition of ion uptake (McWilliams and Potts, 1978; Leivestad, 1982; Wood and McDonald,
2 1987; Bergman et al., 1988). Additional effects might include disruption of Ca^{2+} metabolism
3 (Peterson and Martin-Robichaud, 1986; Gunn and Noakes, 1987; Reader et al., 1988), and
4 decreased hatching success (Runn et al., 1977; Peterson et al., 1980; Haya and Waiwood, 1981;
5 Waiwood and Haya, 1983).

6 Prominent physiological disturbance for fish exposed to acid waters are iono- and
7 osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure.
8 Most of these effects can be directly attributed to effects on gill function or structure. The acute
9 toxicity of low pH in acidic waters results in the loss of Ca^{2+} from important binding sites in the
10 gill epithelium, which reduces the ability of the gill to control membrane permeability
11 (McDonald, 1983; Havas, 1986; Exley and Phillips, 1988).

12 The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and
13 Beamish, 1969; Bulger, 1986). The concentrations of serum electrolytes (such as Na^+ and Cl^-)
14 are many times higher (often 100-fold higher) in fish blood than in the fresh waters in which they
15 live. The active uptake of these ions occurs at the gills. Because of the steep gradient in Na^+ and
16 Cl^- concentrations between the blood and fresh water, there is constant diffusional loss of these
17 ions, which must be replaced by energy-requiring active transport. Low pH increases the rate of
18 passive loss of blood electrolytes (especially Na^+ and Cl^-); and Al elevates losses of Na^+ and Cl^-
19 above the levels due to acid stress alone (Wood, 1989). For example, dace in an acidified stream
20 maintain whole-body Na^+ at levels similar to dace in a high-ANC stream (Dennis and Bulger,
21 1995), despite probable higher gill losses of electrolytes due to acid/Al stress. Therefore, the
22 homeostatic mechanisms at the gill responsible for maintaining blood electrolyte levels must
23 work harder and use more energy to maintain these levels for dace in the acidified stream.

24 Whole lake experiments and artificial stream channel experiments have shown that
25 acidification can lead to loss of fish species. A summary of the work on Lake 223 in the
26 Experimental Lakes Area in Canada is provided in Table AX4.6-8. Work at Little Rock Lake
27 in Wisconsin suggested that rock bass suffered recruitment failure at pH 5.6 or below.
28 Artificial channel studies showed poor survival and reproductive success for fathead minnow
29 at pH 5.9 to 6.0.

30 ANC criteria have been used for evaluation of potential acidification effects on fish
31 communities. The utility of these criteria lies in the association between ANC and the surface

1 water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH,
2 Ca^{2+} , and Al. Bulger et al. (2000) developed ANC thresholds for brook trout response to
3 acidification in forested headwater catchments in western Virginia (Table AX4.6-6). Note that
4 because brook trout are comparatively acid tolerant, adverse effects on many other fish species
5 should be expected at relatively higher ANC values.

6 Streams with chronic ANC greater than about 50 $\mu\text{eq/L}$ are generally considered suitable
7 for brook trout in southeastern United States streams because they have a large enough buffering
8 capacity that persistent acidification poses no threat to this species, and there is little likelihood
9 of storm-induced acidic episodes lethal to brook trout. In such streams, reproducing brook trout
10 populations are expected if the habitat is otherwise suitable (Bulger et al., 2000), although some
11 streams may periodically experience episodic chemistry that affects species more sensitive than
12 brook trout. Streams having annual average ANC from 20 to 50 $\mu\text{eq/L}$ may or may not
13 experience episodic acidification during storms that can be lethal to juvenile brook trout, as
14 well as other fish. Streams that are designated as episodically acidic (chronic ANC from 0 to
15 20 $\mu\text{eq/L}$) are considered marginal for brook trout because acidic episodes are likely (Hyer et al.,
16 1995), although the frequency and magnitude of episodes vary. Streams that are chronically
17 acidic (chronic ANC less than 0 $\mu\text{eq/L}$) are not expected to support healthy brook trout
18 populations (Bulger et al., 2000).

19 Field surveys provided a regional context for fish response to acidification. Although
20 there were some variations, the results of field surveys generally confirmed the results of
21 bioassays, field experiments, and other intensive field studies. The results of many field surveys
22 were summarized in Baker et al. (1990a) and are compiled in Table AX4.6-9.

23 It is important to note, however, that the absence of fish from a given lake or stream in an
24 area that experiences surface water acidification does not necessarily imply that acidification is
25 responsible for the absence of fish. For example, results of fisheries research in the Adirondacks
26 has indicated that many Adirondack lakes always had marginal spawning habitat for brook trout
27 (Schofield, 1993), and some of the currently fishless acidic lakes probably never supported fish.

28 Many of the data for the assessment of fish status in the Adirondack region of New York
29 come from the reports by Kretser et al. (1989) and Baker et al. (1990a). The status of fish and of
30 the presence of individual species were related to a variety of lake characteristics. Of the lakes
31 without fish, 42% had high organic acid content that may have caused the observed low pH, 13%

1 were bog lakes of high acidity and naturally poor fish habitat, 9% had pH > 5.5 suggesting other
2 factors were likely responsible for the lack of fish, and 3% were small high-elevation lakes that
3 were unlikely to have fish regardless of acid-base chemistry. However, 34% of the lakes
4 surveyed (112 lakes) that had no fish at the time of survey had low pH that was most likely the
5 result of acid deposition and no other obvious explanation for the lack of fish.

6 Multivariate regression of the presence/absence of brook trout in Adirondack waters
7 produced a ranking of factors that appeared to influence the presence of brook trout when
8 biological factors were excluded from the analysis (stocking, presence of associated species,
9 presence of competitors). Among contributing factors, including SiO₂, ANC, DOC, substrate,
10 and distance to the nearest road, pH ranked first as a predictor of brook trout presence
11 (Christensen et al., 1990). The results of this analysis supported the hypothesis that 1990 levels
12 of pH and related variables restricted the distribution of some fish in Adirondack waters.

13 Fish toxicity models have been developed as mathematical regression functions fit to
14 observations of fish mortality when exposed to constant levels of pH, Al_i, and Ca²⁺ in laboratory
15 toxicity tests. These models had the advantage that they dealt directly with the interaction effects
16 of pH, Al, and Ca²⁺, but they did not account for the effects of variations in other aspects of
17 surface water quality, and they could not be directly interpreted in terms of population-level
18 response.

19 The many bioassays conducted of pH effects were screened by Baker et al. (1990a) to
20 provide data most suitable for model development. Bioassays selected for inclusion were those
21 that measured the mortality of early life stages, those that incorporated different combinations of
22 pH, Al, and Ca²⁺, and those that used fish of varying sensitivity (Bergman et al., 1988).

23 Acidity and Al toxicity are not the only stress factors that influence the distribution of
24 fish in acid-sensitive streams. Other habitat characteristics, including water temperature and
25 stream channel morphology, can be important (Sullivan et al., 2003). In addition, it is probable
26 that some trout populations have been affected by competition with other introduced species (cf.
27 Larson and Moore, 1985).

28 29 **AX4.6.2.5 Amphibians**

30 Some species of amphibians are considered to be highly sensitive to changes in
31 environmental conditions and some species have probably been adversely impacted by acidic
32 deposition in some areas. Furthermore, several species of amphibian have exhibited marked

1 declines in abundance throughout the western United States in recent decades and there has been
2 much speculation concerning the cause(s) of these declines in abundance.

3 Populations of many species of amphibians have declined or become eradicated
4 throughout the world in recent decades (Barinaga, 1990; Wake, 1991). The causes have not been
5 evident and some of the declines have occurred in remote pristine areas. For example, in the
6 Sierra Nevada, at least two of five species of aquatic-breeding amphibians, *Rana muscosa*
7 (mountain yellow-legged frog) and *Bufo canorus* (Yosemite toad) have been declining (Phillips,
8 1990). A number of hypotheses have been proposed for amphibian decline, including acidic
9 deposition. In the western United States, however, acidic deposition has been discounted as the
10 primary cause of the decline of *R. muscosa* and *B. canorus* in the Sierra Nevada and of *R. pipiens*
11 and *B. boreas* in the Rocky Mountains (Corn et al., 1989; Bradford et al., 1992). Grant et al.
12 (2005) reported little relationship between streamwater ANC and the adjacent salamander
13 community in Shenandoah National Park.

14 In some cases, population fragmentation as a consequence of fish predation may be a
15 more likely cause (Bradford et al., 1993). It is generally recognized that *R. muscosa* was
16 eliminated by introduced fish early in the 20th century in many lakes and streams in Sequoia and
17 Kings Canyon National Parks. The amphibians have been eliminated from nearly all waters
18 inhabited by fish, presumably by predation on tadpoles. Prior to 1870, virtually all of the high-
19 elevation (>2500 m) lakes in the Sierra Nevada were barren of fish, but have since been stocked
20 with fish. Fish introductions may have contributed to recent amphibian declines because
21 amphibian populations are now more isolated from each other than formerly. The role of
22 atmospheric deposition as an additional stressor is not clear.

23 The acidification sensitivity of temporary ponds, where many amphibians live or
24 reproduce, have not been well studied. These ponds tend to fill directly from rain or snowmelt
25 and thus can be more acidic than surrounding lakes and streams. There is a correlation between
26 pond acidity and amphibian abundance.

27 There are both acid-sensitive and acid-tolerant amphibians. Examples of acid-sensitive
28 amphibians include the spotted salamander (*Ambystoma maculatum*) and Jefferson salamander
29 (*Ambystoma jeffersonianum*). Embryos of acid-sensitive species are killed by water with pH less
30 than about 4.5. Acid-tolerant embryos may survive at a pH of 3.7. Toxicity is not solely a
31 matter of pH, but is also influenced by Ca^{2+} , Al_i , and DOC concentrations. It is also dependent

1 on the life stages present and water temperature (Baker et al., 1990a). Large-scale amphibian
2 extinctions in any geographic region due to acidic deposition have not been detected.

3 Although acidic deposition may play a role in some areas, there is no evidence to suggest
4 that it is a primary factor. Other issues, including fish introductions, are probably more
5 important as stressors on amphibian populations across broad regional to national scales.

6 7 **AX4.6.2.6 Fish-Eating Birds**

8 Relative to other trophic groups, there are few studies assessing acidification effects on
9 fish-eating birds. Limited data suggest that fish-eating birds are adversely affected by
10 acidification. Acidification effects on birds may be indirect, related to changes in the quantity
11 and quality of food. Other potential causal pathways include delayed egg laying, lighter/thinner
12 egg shells, and reduced chick growth in acidic waters (Tyler and Ormerod, 1992). There is also
13 concern about increased metal and Hg concentrations in fish-eating birds associated with
14 bioaccumulation from contaminated fish in known areas of acidification (Baker et al., 1990a).

15 Fish-eating birds can serve as biological indicators of lakes affected by acidic deposition
16 (McNicol, 2002). Lack of prey resources, decreased food quality, and elevated lake water
17 methylmercury (MeHg) concentrations that could be associated with acidification may
18 negatively impact foraging, breeding, and/or reproduction for the common loon (*Gavia immer*),
19 common merganser (*Mergus merganser*), belted kingfisher (*Ceryle alcyon*), osprey (*Pandion*
20 *haliaetus*), American black duck (*Anas rubripes*), ring-necked duck (*Aythya collaris*), eastern
21 kingbird (*Tyrannus tyrannus*), and tree swallow (*Tachycineta bicolor*) (Table AX4.6-10)
22 (Longcore and Gill, 1993). Breeding distribution for the common goldeneye (*Bucephala*
23 *clangula*), an insectivorous bird, may be positively impacted by acidic deposition (Longcore and
24 Gill, 1993). Reduced prey diversity and quantity have been observed to create feeding problems
25 for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

26 Since the mid 1980s, a statistically significant increase in fish-eating birds has been
27 observed in the Sudbury region of Ontario, Canada, which has corresponded with a decreasing
28 abundance of common goldeneye (McNicol, 2002). This interaction has been attributed to an
29 increase in prey for piscivorous birds and a decrease in available prey for insectivorous birds as a
30 result of stricter S emissions controls in the United States and Canada (McNicol, 2002). Logistic
31 regression modeling with measured pH and species occurrence data for acid-sensitive lakes in
32 the Algoma region of Ontario showed that the occurrence of fish, common loons, and common

1 mergansers is positively related to lake water pH (McNicol, 2002). Predictions of common loon
2 and merganser recovery for this area were made using the Waterfowl Acidification Response
3 Modeling System (WARMS) under varying S emissions control scenarios targeted for 2010
4 (McNicol, 2002). The modeled emissions scenarios include:

- 5 • S1: sulfate emissions equal to those in the early 1980's (base case)
- 6 • S2: sulfate emissions equal to that in 1994 (full Canadian emissions reductions based
7 on the 1991 Canada/U.S. Air Quality Agreement)
- 8 • S3: expected sulfate emissions in 2010 (full implementation of U.S. emissions
9 reductions based on the 1991 agreement)
- 10 • S4: a hypothetical 50% reduction in expected 2010 sulfate emissions
- 11 • S5: a hypothetical 75% reduction in expected 2010 sulfate emissions

12 The number of lakes projected to be suitable for supporting breeding pairs and broods increased
13 with lake pH and stricter emissions controls (Table AX4.6-11) (McNicol, 2002).

14 Marginal improvements to fish-eating bird habitat were predicted to occur by 2010 (S3),
15 with more significant improvements expected under hypothetical S emissions reductions of 50%
16 and 75% (S4 and S5) for lakes with pH below 6.5 (McNicol, 2002). Fundamental to the
17 predicted improvement of these fish-eating bird populations is the expected increase in food
18 availability with lake pH recovery.

19 Elevated MeHg accumulation in fish-eating birds in Wisconsin and the northeastern
20 United States has been linked to lake acidification (Meyer et al., 1995; Hrabik and Watras, 2002;
21 Evers et al., 2007). This form of Hg is toxic, bioavailable, and accumulates in top predators to
22 levels of concern for both human health and the environment (Table AX4.6-12) (Evers et al.,
23 2007).

24 Acidic deposition might contribute to Hg toxicity in fish-eating birds because SO_4^{2-}
25 addition to wetland environments could stimulate the production of MeHg, thereby increasing
26 lake water concentrations of MeHg (Jeremiason et al., 2006). Kramar et al. (2005) determined
27 that the extent of wetland located in close proximity (less than 150 m) to loon territory was
28 positively correlated with Hg concentrations in loon blood. Wetland MeHg production is
29 discussed in greater detail in Section 6.3.

30 Accumulation of MeHg in fish-eating birds can result in damage to nervous, excretory,
31 and reproductive systems (Wolfe et al., 1998). Table AX4.6-13 (Wolfe et al., 1998) lists several

1 studies indicating effects related to mercury bioaccumulation in avian eggs and tissues.
2 Reproduction is considered one of the most sensitive endpoints to chronic low-level MeHg
3 exposure for fish-eating birds (Wolfe et al., 1998). Reduced clutch size, increased number of
4 eggs laid outside the nest, eggshell thinning, and increased embryo mortality have all been
5 documented (Wolfe et al., 1998).

6
7

8 **AX4.7 SUMMARY**

9 Sulfur, in the form of SO_4^{2-} is the greatest anthropogenic agent of soil acidification in the
10 United States. By leaching base cations, SO_4^{2-} reduces the base saturation of the soil, which
11 increases the susceptibility of the soil to acidification and decreases the ability of the soil to
12 neutralize acidity deposited from the atmosphere. Retention of S in the soil through anion
13 adsorption or incorporation into organic matter prevents SO_4^{2-} leaching, at least temporarily.
14 Sulfur retention in soils is most pronounced in the southeastern United States, where it
15 contributes to a substantial delay in water acidification effects.

16 Some acid-sensitive forest soils have been acidified by SO_x and NO_x deposition. Effects
17 have mainly been limited to the northeastern United States and portions of the Appalachian
18 Mountains. Effects have been most pronounced at high elevation in areas occupied by
19 coniferous forests and have included reduced exchangeable Ca^{2+} and reduced soil base
20 saturation, and decreased Ca:Al ratio in soil solution. Soil acidification has probably also
21 occurred in localized areas of mixed conifer forest and chaparral vegetation in, and near, the Los
22 Angeles Basin, in response to high levels of dry atmospheric N deposition.

23 Soil acidification, Al toxicity, and exposure of foliage to acidic deposition have
24 collectively contributed to decline in red spruce, sugar maple, and perhaps other tree species in
25 portions of the northeastern United States and Appalachian Mountains that have experienced soil
26 acidification as a consequence of SO_x and NO_x deposition. Effects have included reduced
27 growth and increased stress to overstory trees, and likely changes in the species distributions of
28 understory plants.

29 Decreases in concentrations of exchangeable base cations in the Oa and B soil horizons
30 over the past several decades are common and widespread in the eastern United States. Acidic
31 deposition has been shown to be an important factor causing the observed decreases in
32 concentrations of exchangeable base cations on soils. To some degree, soils can recover their

1 base cation reserves over time in response to reduced future levels of acidic deposition.
2 However, the recovery potential of soil exchangeable base cation concentrations is dependent on
3 weathering rates, which can only be estimated with a high degree of uncertainty.

4 The natural downward movement and deposition of Al within the soil profile has been
5 altered by acidic deposition, resulting in greater availability of inorganic Al within soil and
6 transport of this form of Al from the soil to surface waters. Increases in concentrations of
7 exchangeable Al in soil over the past several decades have been documented at several locations
8 in North America and Europe. Inorganic Al, in sufficiently high concentrations in soil solution
9 or surface water can be toxic to plant roots and to aquatic life, respectively.

10 Atmospheric deposition of N has decreased C:N ratios in soils and contributes to an
11 increase in net nitrification and associated production of acidity in soils. Nitrogen availability in
12 excess of ecological demand (N saturation) has become common and widespread, as evidenced
13 by elevated NO_3^- concentrations in surface waters during the growing season in many areas.

14 Leaching of NO_3^- to surface waters during the growing season occurs above a threshold
15 of atmospheric deposition of about 10 kg N/ha/yr. This threshold is lower (as low as about 4 kg
16 N/ha/yr) in watersheds that contain little soil development, such as alpine regions of the western
17 United States. The relationship between atmospheric deposition and NO_3^- loss from terrestrial
18 ecosystems is confounded by land-use history dating back a century or more. It is also modified
19 by such factors as climate change, forest insect infestation and disease, and land management.
20 Consequently, future projections of changes in N retention and release from terrestrial
21 ecosystems in response to changing levels of atmospheric N deposition are highly uncertain.

22 Lakes and streams in some regions of the United States are sensitive to episodic and
23 chronic acidification in response to SO_x , and to a lesser extent, NO_x deposition. Sensitive lakes
24 and streams tend to occur at relatively high elevation in areas that have base-poor bedrock, high
25 relief, and shallow soils. Sensitive waters are numerous in some regions of the United States,
26 including much of the Northeast, Appalachian Mountains, and mountainous West, and portions
27 of the Upper Midwest. Aquatic acidification has been most pronounced in the Adirondack,
28 Appalachian, and Catskill Mountains, with more than 25% of the surface waters affected in some
29 areas. Aquatic acidification in the West has been minimal because levels of acidic deposition
30 have been low in most areas.

- 1 Aquatic biota have been affected by acidification at virtually all levels of the food web.
- 2 Effects have been clearly documented for fish, aquatic insects, other invertebrates, and algae.
- 3 Some species, and some life stages within species, are more sensitive than others. In some
- 4 acidified waters, sensitive species have been eliminated and taxonomic richness has decreased.
- 5 In some cases, all fish species have been eliminated from acidified waters.

TABLE AX4.1-1. NITROGEN-SATURATED FORESTS IN NORTH AMERICA, INCLUDING ESTIMATED N INPUTS AND OUTPUTS

Location	Forest Type	Elevation (m)	N Input (kg/ha/yr)	N Output (kg/ha/yr)	Reference
Adirondack Mts., northeastern New York	Northern hardwoods or hardwood/conifer mix	396-661	9.3 ^a	Stage 1 N loss ^b	Driscoll and Van Dreason (1993)
Catskill Mts., southeastern New York	Mainly hardwood; some eastern hemlock	335-675	10.2 ^a	Stage 1 and 2 N loss ^b	Stoddard (1994)
Turkey Lakes Watershed, Ontario, Canada	Sugar maple and yellow birch	350-400	7.0-7.7 (as throughfall)	17.9-23.6	Foster et al. (1989); Johnson and Lindberg (1992a)
Whitetop Mt., southwestern, Virginia	Red spruce	1,650	32 ^c	47 ^c	Joslin and Wolfe (1992); Joslin et al. (1992)
Fernow, West Virginia	Mixed hardwood	735-870	15-20	6.1	Gilliam et al. (1996); Peterjohn et al. (1996)
Great Smoky Mts. National Park, Tennessee	American beech	1,600	3.1 ^d	2.9	Johnson and Lindberg (1992b)
Great Smoky Mts. National Park, Becking Site, North Carolina	Red spruce	1,800	10.3 ^d	19.2	Johnson et al. (1991c)
Great Smoky Mts. National Park, Tower Site, North Carolina	Red spruce	1,740	26.6	20.3	Johnson et al. (1991c)
Front Range, Colorado	Alpine tundra, subalpine conifer	3,000-4,000	7.5-8.0	7.5	Williams et al. (1996)
San Dimas, San Gabriel Mts., southern California	Chaparral and grasslands	580-1,080	23.3 ^e	0.04-19.4	Riggan et al. (1985)
Camp Paivika, San Bernardino Mts., southern California	Mixed conifer	1,600	30	7-26	Fenn et al. (1996)

TABLE AX4.1-1 (cont'd). NITROGEN-SATURATED FORESTS IN NORTH AMERICA, INCLUDING ESTIMATED N INPUTS AND OUTPUTS

Location	Forest Type	Elevation (m)	N Input (kg/ha/yr)	N Output (kg/ha/yr)	Reference
Klamath Mts., northern California	Western coniferous	NA	Mainly geologic ^g	NA ^g	Dahlgren (1994)
Thompson Forest, Cascade Mts., Washington	Red alder	220	4.7 plus > 100 as N ₂ fixation	38.9	Johnson and Lindberg (1992b)

^a Estimated total N deposition from wet deposition data is from Driscoll et al. (1991) for the Adirondacks, and from Stoddard and Murdoch (1991) for the Catskills. Total deposition was estimated based on the wet deposition: total N deposition ratio (0.56) at Huntington Forest in the Adirondacks (Johnson and Lindberg, 1992b). Nitrogen deposition can be higher in some areas, especially at high-elevation sites such as Whiteface Mountain (15.9 kg/ha/yr); Johnson and Lindberg, 1992b).

^b Stage 1 and 2 of N loss according to the watershed conceptual model of Stoddard (1994). Nitrogen discharge (kg/ha/yr) data are not available, only stream water NO₃⁻ concentration trend data were collected.

^c Values appear high compared to other sites, especially N leaching losses. Joslin and Wolfe (1992) concede that "there is considerable uncertainty associated with the estimates of atmospheric deposition and leaching fluxes." However, elevated NO₃⁻ concentrations in soil solution and lack of a growth response to N fertilization ratio (Joslin and Wolfe, 1994) support the hypothesis that the forest at Whitetop Mountain is N saturated.

^d Estimated total N deposition from throughfall data. Total deposition was estimated based on the throughfall/total N deposition ratio from the nearby Smokes Tower site (Johnson and Lindberg, 1992b).

^e Annual throughfall deposition to the chaparral ecosystem.

^f Nitrogen output is from unpublished stream water data (Fenn and Poth, 1999). The low value represents a year of average precipitation, and the high value is for 1995, when precipitation was nearly double the long-term average. Nitrogen output includes N export in stream water and to groundwater.

^g Annual input and output data are not known, although N deposition in this forest is probably typical for much of the rural western United States (2-3 kg N/ha/yr; Young et al., 1988). Excess N is from weathering of ammonium in mica schist bedrock. The ammonium was rapidly nitrified, leading to high NO₃⁻ concentrations in soil solution (Dahlgren, 1994).

**TABLE AX4.3-1. SUMMARY OF MEASURED ANC, pH, AND Al
CONCENTRATIONS COMPARED WITH REFERENCE VALUES IN THE SIX
HIGH-INTEREST AREAS**

Area	n*	N*	Percent of Population with		
			ANC ≤0	pH ≤5.5	Al _i > 100 µg/L
ADIRONDACKS					
Southwest lakes	52	450	38	51	36
Other lakes	84	707	0	3	0
NEW ENGLAND					
Seaboard Lowlands lakes	94	848	8	11	0
Highland lakes	354	3,574	2	5	2
MID-ATLANTIC HIGHLANDS					
Forested lakes	91	433	10	9	1
Other lakes	52	791	0	0	0
Forested streams	78	11,631	12	17	8
Other streams	69	10,172	0	2	0
ATLANTIC COASTAL PLAIN					
Northeast lakes	22	187	11	15	7
Pine Barrens streams	12	675	56	92	56
Other streams	31	7,452	10	24	15
FLORIDA					
Northern Highland lakes	32	522	63	53	10
Northern Highland streams	18	669	28	55	0
EASTERN UPPER MIDWEST					
Low silica lakes	155	1,254	16	19	1
High silica lakes	125	1,673	3	4	2

* n = sample size, N = estimated number of lakes or upstream reach ends in population.

Source: Baker et al. (1990b).

TABLE AX4.3-2. SOURCES OF DATA AND SAMPLE SIZES FOR DATASETS ANALYZED BY STODDARD ET AL. (2003), ALONG WITH ESTIMATES OF THE CONDITION OF SURFACE WATERS IN EACH REGION IN THE 1980S. STATISTICAL SURVEY DATA ARE FROM THE EMAP AND TIME PROJECTS. SENSITIVE SURFACE WATER DATA ARE FROM THE LTM PROJECT, AS WELL AS OTHER CONTRIBUTED STUDIES.

Source of Data and Region	No. of Sites¹	Size of Population²	Percent Acidic in 1980s³
Statistical Surveys			
New England Lakes ⁴	30	4,327 lakes	5%
Adirondack Lakes ⁴	43	1,290 lakes	14%
Appalachian Plateau Streams	31	72,000 stream miles	6%
Sensitive Surface Waters			
New England Lakes	24	N.A.	5%
Adirondack Lakes	48	N.A.	14%
Northern Appalachian Streams	9	N.A.	6%
Upper Midwest Lakes	38	N.A.	3%
Ridge/Blue Ridge Streams	69	N.A.	5%

¹ Number of monitoring sites with monitoring data available (1990-2000)

² Total number of lakes, or stream length, for which statistical survey results can be inferred. Site selection for LTM (sensitive surface waters) is not statistically based, and results cannot be expanded to population level.

³ Estimates of extent of acidification, based on National Surface Water Survey results (Linthurst et al., 1986; Kaufmann et al., 1988).

⁴ Estimates are for lakes with surface areas > 4 ha; estimates based on populations including smaller lakes are likely to be higher, due to the increased incidence of acidification in small lakes.

Source: Stoddard et al. (2003).

TABLE AX4.3-3. ESTIMATES OF CHANGE IN NUMBER AND PROPORTION OF ACIDIC SURFACE WATERS IN ACID-SENSITIVE REGIONS OF THE NORTH AND EAST, BASED ON APPLYING CURRENT RATES OF CHANGE IN GRAN ANC TO PAST ESTIMATES OF POPULATION CHARACTERISTICS FROM PROBABILITY SURVEYS

Region	Results of Regional Survey				Results of Monitoring during 1990s			
	Population Size	Number Acidic ¹	% Acidic ²	Time Period of Estimate	Rate of ANC change ³	Estimated Number Acidic in 2000	% Acidic in 2000	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991-94	+0.3	374 lakes	5.5%	-2%
Adirondacks.	1830 lakes	238 lakes	13.0%	1991-94	+0.8	149 lakes	8.1%	-38%
No. Appalachians	42,426 km	5014 km	11.8%	1993-94	+0.7	3600 km	8.5%	-28%
Ridge/Blue Ridge	32,687 km	1634 km	5.0%	1987	-0.0	1634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	-68%

¹ Number of lakes/streams with Gran ANC < 0 in past probability survey by EPA (data collected at "Time Period of Estimate", in column 5)

² Percent of population (from column 2) with Gran ANC < 0 in past probability survey (data collected at "Time Period of Estimate", in column 5)

³ Based on regional trends presented in the Stoddard et al. (2003) report, in µeq/L/year, for the 1990s

Source: Stoddard et al. (2003).

TABLE AX4.3-4. REGIONAL TREND RESULTS FOR LONG-TERM MONITORING SITES FOR THE PERIOD 1990 THROUGH 2000

Region	SO₄²⁻ (µeq/L/yr)	NO₃⁻ (µeq/L/yr)	Base Cations [Ca²⁺ + Mg²⁺] (µeq/L/yr)	Gran ANC (µeq/L/yr)	Hydrogen (µeq/L/yr)	DOC (mg/L/yr)	Aluminum (µg/L/yr)
New England Lakes	-1.77**	+0.01 ^{ns}	-1.48**	+0.11 ^{ns}	-0.01 ^{ns}	+0.03*	+0.09 ^{ns}
Adirondack Lakes	-2.26**	-0.47**	-2.29**	+1.03**	-0.19**	+0.06**	-1.12**
Appalachian Streams	-2.27*	-1.37**	-3.40**	+0.79*	-0.08*	+0.03 ^{ns}	+0.56 ^{ns}
Upper Midwest Lakes	-3.36**	+0.02 ^{ns}	-1.42**	+1.07**	-0.01*	+0.06**	-0.06 ^{ns}
Ridge/Blue Ridge Streams	+0.29**	-0.07**	-0.01 ^{ns}	-0.07 ^{ns}	+0.01 ^{ns}	NA	NA

^{ns} regional trend not significant (p > 0.05)

* p < 0.05

** p < 0.01

NA insufficient data

Note: Values are median slopes for the group of sites in each region.

Source: Stoddard et al. (2003).

TABLE AX4.3-5. SLOPES OF TRENDS IN GRAN ANC IN ACIDIC, LOW ANC AND MODERATE ANC LAKES AND STREAMS FOR THE PERIOD 1990-2000

ANC Class	Number of Sites	Change in Gran ANC ($\mu\text{eq/L/yr}$)
Acidic (ANC < 0 $\mu\text{eq/L}$)	26	+1.29**
Low ANC (0 < ANC < 25 $\mu\text{eq/L}$)	51	+0.84**
Moderate ANC (25 < ANC < 200 $\mu\text{eq/L}$)	43	+0.32 ^{ns}

^{ns} trend not significant ($p > 0.05$)

** $p < 0.01$

Note: Analysis includes all sites in New England, Adirondacks, Appalachian Plateau, and Upper Midwest; Ridge and Blue Ridge sites excluded.

Source: Stoddard et al. (2003).

TABLE AX4.3-6. CHANGES IN KEY CHEMICAL CHARACTERISTICS DURING PERIODS OF RECORD IN AQUATIC SYSTEMS IN MAINE

	Years	Change in (all in $\mu\text{eq/L}$)					
		Sulfate	Nitrate	Base Cations	Calculated ANC ^a	ANC	DOC ^b
Acadia NP lakes (22)	17	-10	0	-17	-7	0	-2
LTM lakes @ Tunk Mtn (6) - spring	17	-9	0	-10	-1	1	1
LTM lakes @ Tunk Mtn (6) - fall	17	-7	0	-9	-2	-2	1
LTM lakes since 1990 - fall only	8	-9	0	-10	-1	-1	0
High elevation lakes (90)	12	-16	1	-23	-8	-2	4
Seepage lakes (120)	12	-9	1	-1	7	7	4
East Bear Brook at BBWM	11	-22	-16	-44	-6	-4	1
RLTM lakes (16)	7	-6	1	-17	-12	-4	2

^a Calculated ANC = [change in base cations] minus [change in (sulfate + nitrate)]

^b DOC ($\mu\text{eq/L}$) = DOC in $\text{mg/l} \times 4$ (e.g., Kahl et al., 1999).

Source: Kahl et al. (1999).

TABLE AX4.3-7. PROJECTED CHANGES ($\mu\text{eq/L}$) IN MEDIAN VALUES OF STREAMWATER CHEMISTRY AT THE REGIONAL MODELING SITES FROM 1995 TO 2040 IN EACH OF THE THREE EMISSIONS CONTROL STRATEGIES, STRATIFIED INTO TWO SEGMENTS OF THE SAMI REGION (NORTHEAST AND SOUTHWEST) AND BY PHYSIOGRAPHIC PROVINCE

Physiographic Province	Number of Sites	Δ Sulfate	Δ Nitrate	Δ SBC	ΔANC
A2 STRATEGY¹					
Virginia and West Virginia					
Blue Ridge	16	1.8	0.03	-2.2	-4.0
Valley and Ridge	41	-0.45	0.02	-6.8	-6.6
Appalachian Plateau	34	-31.2	-3.5	-33.8	-4.4
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					
Blue Ridge	33	8.8	0.15	1.0	-8.0
Appalachian Plateau	6	15.3	0.15	-1.2	-15.9
B1 STRATEGY¹					
Virginia and West Virginia					
Blue Ridge	16	-2.7	-0.04	-3.0	-1.0
Valley and Ridge	41	-5.6	-0.37	-8.2	-4.7
Appalachian Plateau	34	-36.3	-4.9	-38.4	-1.4
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					
Blue Ridge	33	5.6	-0.48	-0.60	-5.4
Appalachian Plateau	6	11.6	-0.23	-1.9	-13.3
B3 STRATEGY¹					
Virginia and West Virginia					
Blue Ridge	16	-7.4	-0.09	-5.1	2.9
Valley and Ridge	41	-13.8	-0.36	-10.3	-0.83
Appalachian Plateau	34	-40.4	-5.8	-39.3	2.6
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					
Blue Ridge	33	3.2	-1.0	-2.3	-3.2
Appalachian Plateau	6	7.2	-0.53	-3.1	-10.4

¹ Emissions control strategies were based on existing regulations (A2), moderate additional controls (B1), and more aggressive additional controls (B3)

Source: Sullivan et al. (2004).

TABLE AX4.3-8. POPULATION ESTIMATES OF WATER CHEMISTRY PERCENTILES FOR SELECTED LAKE POPULATIONS IN THE WESTERN UNITED STATES^a

Population	n	N	pH		ANC ($\mu\text{eq/L}$)		SBC ($\mu\text{eq/L}$)		SO ₄ ²⁻ ($\mu\text{eq/L}$)		NO ₃ ⁻ ($\mu\text{eq/L}$)		DOC (mg/L)	
			P ₁	P ₅	P ₁	P ₅	P ₁	P ₅	P ₉₅	P ₉₉	P ₉₅	P ₉₉	P ₅₀	P ₉₉
Sierra Nevada	114	2,119	5.84	6.31	15	16	21	26	90	386	8	10	0.8	2.7
Cascades	146	1,473	5.95	6.25	11	18	20	31	60	97	3	6	1.3	2.6
Idaho Batholith	88	937	6.34	6.42	21	33	30	45	30	43	3	4	1.2	2.4
NW Wyoming	38	648	6.56	6.56	38	38	64	66	41	2,909	13	32	1.0	4.8
Colorado Rockies	121	1,173	6.02	6.65	25	42	58	80	915	2,212	10	13	1.3	5.7

^aData from Landers et al. (1987).

^bExcluding Fern Lake (4D3-017) which is naturally acidic

Note: The 1st and 5th percentiles (P₁, P₅) are presented for pH, ANC ($\mu\text{eq/L}$), and SBC ($\mu\text{eq/L}$) and the 95th and 99th (P₉₅, P₉₉) percentiles are shown for SO₄²⁻ ($\mu\text{eq/L}$) and NO₃⁻ ($\mu\text{eq/L}$). The median (P₅₀) and 90th percentiles are shown for DOC (mg/L).

TABLE AX4.3-9. POPULATION ESTIMATES OF THE PERCENTAGE OF LAKES IN SELECTED SUBREGIONS OF THE WEST WITH ANC AND NO₃⁻ WITHIN DEFINED RANGES

	ANC (µeq/L)			NO ₃ ⁻ (µeq/L)	
	<0	<25	<50	>5	>10
Sierra Nevada	0	8.7	39.3	10.6	1.5
Cascades	0	10.2	22.4	1.5	0.0
Idaho Batholith	0	2.0	23.6	4.6	3.9
NY Wyoming ^a	0	2.3	12.8	22.8	8.9
Colorado Rockies	0	0.9	5.5	9.8	1.8

^aExcluding Fern Lake (4D3-017) which is a naturally acidic lake

Source: Landers et al. (1987).

TABLE AX4.4-1. MEDIAN STREAMWATER ANC AND WATERSHED AREA OF STREAMS IN SHENANDOAH NATIONAL PARK THAT HAVE WATER CHEMISTRY AND FISH SPECIES RICHNESS DATA

Site ID	Watershed Area (km ²)	Median ANC (µeq/L)	Number of Fish Species
Smaller Watersheds (<10 km ²)			
North Fork Dry Run	2.3	48.7	2
Deep Run	3.6	0.3	N.D. ^a
White Oak Run	4.9	16.2	3
Two Mile Run	5.4	10.0	2
Meadow Run	8.8	-3.1	1
Larger Watersheds (>10 km ²)			
Brokenback Run	10.1	74.4	3
Staunton River	10.6	76.8	5
Piney River	12.4	191.9	7
Paine Run	12.7	3.7	3
Hazel River	13.2	86.8	6
White Oak Canyon	14.0	119.3	7
N. Fork Thornton River	18.9	249.1	9
Jeremy's Run	22.0	158.5	6
Rose River	23.6	133.6	8

^a No data were available regarding the number of fish species in Deep Run

Source: Sullivan (2003) #2430.

TABLE AX4.4-2. REFERENCE LEVELS FOR THE ACIDIC STRESS INDEX (ASI) BASED ON LOGISTIC REGRESSION OF FISH PRESENCE AS A FUNCTION OF THE SENSITIVE INTERMEDIATE AND TOLERANT ASI VALUES FOR BROWN BULLHEAD, BROOK TROUT, LAKE TROUT, AND COMMON SHINER

Reference Acid Stress Index		Fish Response
Lakes	Streams	
Tolerant ASI > 30	Intermediate ASI > 30	Loss of all fish species
Tolerant ASI > 10	Sensitive ASI > 30	Loss of brook trout
Intermediate ASI > 80		Loss of other sport fish, such as smallmouth bass and lake trout
Sensitive ASI > 80	Sensitive ASI > 10	Loss of acid-sensitive species, such as minnows.

Source: Baker et al. (1990a).

**TABLE AX4.4-3. GENERAL SUMMARY OF BIOLOGICAL CHANGES
ANTICIPATED WITH SURFACE WATER ACIDIFICATION, EXPRESSED
AS A DECREASE IN SURFACE WATER pH**

pH Decrease	General Biological Effects
6.5 to 6.0	<p>Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.</p> <p>Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).</p>
6.0 to 5.5	<p>Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.</p> <p>Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.</p> <p>Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.</p> <p>Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.</p>
5.5 to 5.0	<p>Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.</p> <p>Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.</p> <p>Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.</p> <p>Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.</p> <p>Inhibition of nitrification.</p>
5.0 to 4.5	<p>Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass).</p> <p>Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.</p>

TABLE AX4.4-3 (cont'd). GENERAL SUMMARY OF BIOLOGICAL CHANGES ANTICIPATED WITH SURFACE WATER ACIDIFICATION, EXPRESSED AS A DECREASE IN SURFACE WATER pH

pH Decrease	General Biological Effects
5.0 to 4.5 (cont'd)	<p>Substantial decrease in number of species of plankton and benthic invertebrates and further decline in species richness of plankton and periphyton communities; measurable decrease in total community biomass of plankton and benthic invertebrates of most waters.</p> <p>Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans.</p> <p>Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.</p>

Source: Baker et al. (1990a).

TABLE AX4.4-4. ESTIMATED PERCENTAGE OF ADIRONDACK LAKES WITH AND ACIDIC STRESS INDEX EXCEEDING THE REFERENCE LEVELS FOR EFFECTS ON FISH POPULATIONS, BASED ON DIATOM-INFERRED HISTORICAL (PRE-INDUSTRIAL) CHEMISTRY AND PRESENT-DAY MEASURED AND INFERRED ACID-BASE CHEMISTRY

ASI Reference Level	DDRP Target Population			Measured	ELS/NSWS Target Population Measured
	Diatom Inferred				
	Historical	Current	Net Change		
Tolerant ASI > 30	0.0	3.6	+3.6	1.8	2.2
Tolerant ASI > 10	0.0	9.1	+9.1	10.9	6.5
Intermediate ASI > 80	7.3	21.8	+14.5	21.8	15.2
Sensitive ASI > 80	28.5	41.2	+12.7	32.7	20.0

Source: Baker et al. (1990a).

TABLE AX4.4-5. ESTIMATED PERCENTAGE OF ADIRONDACK LAKES WITH ACID-BASE CHEMISTRY UNSUITABLE FOR FISH POPULATION SURVIVAL, BASED ON DIATOM-INFERRED HISTORICAL (PRE-INDUSTRIAL) CHEMISTRY AND PRESENT-DAY MEASURED AND INFERRED ACID-BASE CHEMISTRY

Fish Species Model ^a	DDRP Target Population ^b				ELS/NWS Target Population ^b	ALSC
	Diatom-Inferred ^c				Measured	Measured
	Historical	Current	Net Change	Measured		
<u>Brook Trout</u>						
Bayesian	2.7	13.0	+10.3	14.2	10.1	21.8
LAF framework	-	-	-	-	15.8	24.6
pH	2.3	11.3	+9.0	12.8	9.3	22.2
pCa/pH	16.0	13.3	-2.6	14.5	10.3	23.0
pCa/pH, Al/DOC	16.6	15.6	-1.0	19.2	13.9	23.5
<u>Lake Trout</u>						
pH	6.4	18.1	+11.2	21.4	14.4	30.9
pCa/pH	31.7	25.1	-6.6	29.0	18.9	-
Inorg. Al	23.9	38.6	+14.7	26.2	17.1	-
<u>Common Shiner</u>						
pH	19.2	29.6	+10.5	33.5	21.3	42.3
pCa/pH	45.8	37.7	-8.1	40.2	29.1	-

^a All models, except the brook trout Bayesian model (Section 3.5) and LAF framework (Section 3.4), are field-based acidification response models as defined in Section 3.3.3.

^b ELS/NSWS target population in Subregion 1A, defined in Section 3.1 (N = 1,290 lakes); a subset of these lakes was considered for the DDRP and sediment diatom analyses, for example, excluding lakes with ANC > 400 µeq/L and with site depths < 1.5 m (N = 675 lakes). See Sullivan (1990) for further details.

^c Estimates of acid-base chemistry inferred from sediment diatom analysis; methods and water chemistry described in Sullivan (1990).

- Analysis not conducted.

Source: Baker et al. (1990a).

TABLE AX4.4-6. ESTIMATED PERCENTAGE OF THE LAKES IN THE NORTHEAST AND UPPER MIDWEST, ELS/NSWS TARGET POPULATION WITH AN ACIDIC STRESS INDEX EXCEEDING THE REFERENCE LEVELS FOR FISH POPULATIONS DEFINED IN TABLE AX 4.4-2

ASI Reference Level	Subregion 1A	Northeast Region	Upper Midwest Region
Tolerant ASI > 30	2.2	1.0	0.5
Tolerant ASI > 10	6.5	2.4	1.0
Intermediate ASI > 80	15.2	5.7	2.0
Sensitive ASI > 80	20.0	8.6	3.1

Source: Baker et al. (1990a).

TABLE AX4.4-7. ESTIMATED PERCENTAGE OF LAKES IN THE NORTHEAST, ELS/NSWS TARGET POPULATIONS WITH ACID-BASE CHEMISTRY UNSUITABLE FOR FISH POPULATION SURVIVAL

Fish Species/Model	Subregion 1A	Entire Northeast
Brook trout		
Bayesian	10.1	3.7
LAF Framework	15.8	8.9
pH	9.3	3.5
pCa/pH	10.3	4.4
pCa/pH, Al/DOC	13.9	7.0
Lake trout		
pH	14.4	5.8
pCa/pH	18.9	8.9
Inorganic Al	17.1	6.3
Common shiner		
pH	21.3	9.5
pCa/pH	29.1	19.7

Source: Baker et al. (1990a).

**TABLE AX4.4-8. DISTRIBUTION OF ACIDIC STRESS INDEX VALUES AMONG
THE NSS-1 TARGET POPULATIONS FOR THE MID-APPALACHIAN REGION**

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
<u>Sensitive ASI</u>			
≤10	84.6	66.7	76.1
10-30	10.1	18.9	14.0
30-50	1.4	1.9	1.9
50-80	1.8	2.6	1.6
>80	2.0	9.8	6.4
<u>Intermediate ASI</u>			
≤10	97.8	89.3	88.9
10-30	0.2	2.5	0.7
30-50	0.6	1.3	0.4
50-80	0.1	1.4	0.4
>80	1.3	5.4	1.9
<u>Tolerant ASI</u>			
≤10	99.4	97.1	98.1
10-30	0.6	1.4	0.9
30-50	0.0	0.6	0.3
50-80	0.0	0.9	0.7
>80	0.0	0.0	0.0

Source: Baker et al. (1990a).

**TABLE AX4.4-9. DISTRIBUTION OF ACIDIC STRESS INDEX VALUES AMONG
THE NSS-1 TARGET POPULATIONS FOR THE INTERIOR SOUTHEAST REGION**

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
<u>Sensitive ASI</u>			
≤10	79.4	70.1	75.9
10-30	18.8	21.1	18.8
30-50	0.0	1.7	2.0
50-80	1.7	5.2	2.5
>80	0.0	1.7	0.7
<u>Intermediate ASI</u>			
≤10	100.0	98.3	99.3
10-30	0.0	0.0	0.0
30-50	0.0	0.0	0.0
50-80	0.0	0.0	0.0
>80	0.0	1.7	0.7
<u>Tolerant ASI</u>			
≤10	100.0	100.0	100.0
10-30	0.0	0.0	0.0
30-50	0.0	0.0	0.0
50-80	0.0	0.0	0.0
>80	0.0	0.0	0.0

Source: Baker et al. (1990a).

TABLE AX4.4-10. COMPARISON OF SOLUTION AND TISSUE CHEMISTRIES AT THRESHOLD TREATMENT LEVELS WHERE SIGNIFICANT IMPACTS ON TREE GROWTH OR NUTRIENT CONTENT WERE FIRST OBSERVED. IN MANY CASES, ADVERSE IMPACTS WERE OBSERVED AT THE LOWEST AI TREATMENT LEVEL. HENCE, THE ACTUAL THRESHOLD Ca/AI RATIO MAY BE HIGHER THAN THAT REPORTED. RESULTS ARE FROM A VARIETY OF STUDIES REPORTED IN THE LITERATURE.

Study	Solution Al (µmol/L)	Solution Ca/AI (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/AI (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/AI (M)	Type of Study or Experiment ^a	Response Variable ^b	AI Analysis Used in Ratio ^c
Norway spruce											
Godbold et al. (1988)	100	1.3							H	N	Al _i
Matzner et al. (1989)	100+	0.3 to 1.8							F	N	Al _t
Stienen and Bauch (1988)	1500	0.66	1470	32	31	770	1890	0.28	H	N,B	Al _t
Schroder et al. (1988)	2000	1							H	N	Al _i
Red spruce											
Thornton et al. (1987)	250	1	1100	65	11.4	650	6000	0.07	H	B	Al _i
Hutchinson et al. (1986)	185	2.2							S	B	Al _t
Joslin and Wolfe (1988)	200	nd	~3000			~2000			S	B	Al _i
Schier (1985)	1850	1.35			12.9			0.43	H	B,N	Al _i
Ohno et al. (1988)	250	0.8			14				S	N	Al _a in soil paste
Joslin and Wolfe (1992)		0.45							F	B	Al _t
White spruce											
Nosko et al. (1988)	50	0.2							H	B	Al _t

TABLE AX4.4-10 (cont'd). COMPARISON OF SOLUTION AND TISSUE CHEMISTRIES AT THRESHOLD TREATMENT LEVELS WHERE SIGNIFICANT IMPACTS ON TREE GROWTH OR NUTRIENT CONTENT WERE FIRST OBSERVED. IN MANY CASES, ADVERSE IMPACTS WERE OBSERVED AT THE LOWEST AI TREATMENT LEVEL. HENCE, THE ACTUAL THRESHOLD Ca/AI RATIO MAY BE HIGHER THAN THAT REPORTED. RESULTS ARE FROM A VARIETY OF STUDIES REPORTED IN THE LITERATURE.

Study	Solution Al ($\mu\text{mol/L}$)	Solution Ca/AI (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/AI (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/AI (M)	Type of Study or Experiment ^a	Response Variable ^b	AI Analysis Used in Ratio ^c
Red oak											
Joslin and Wolfe (1989)	300	4.05			11.9			0.06	S	B	Al _i in SrCl ₂
DeWald et al. (1990)	115	4.48	3630	75	32.4	3630	6415	0.38	S	B	Al _i
McCormick and Steiner (1978)	7405	0.54							H	B	Al _i
Honeylocust											
Thornton et al. (1986b,c)	50	1.1			8.4			0.21 to 0.32	H	B	Al _i
Sucoff et al. (1990)	100	1.4						0.35	S	B	Al _i
Wolfe and Joslin (1989)	100	4.3						0.71	S	B	Al _i
Sugar maple											
Thornton et al. (1986a)	100-600	0.42 to 2.5	~2000	~190	9.9	~1500	~2700	0.4	H	B,N	Al _i
Loblolly pine											
Cronan et al. (1989) Thornton (unpubl.)	500-3000	0.5	900	260	2.3	3700	7770	0.32	H	N	Al _i
American beech											
Cronan et al. (1989)	500-3000	0.5	2670	69	26.1	1140	7930	0.1	H	N	Al _i

TABLE AX4.4-10 (cont'd). COMPARISON OF SOLUTION AND TISSUE CHEMISTRIES AT THRESHOLD TREATMENT LEVELS WHERE SIGNIFICANT IMPACTS ON TREE GROWTH OR NUTRIENT CONTENT WERE FIRST OBSERVED. IN MANY CASES, ADVERSE IMPACTS WERE OBSERVED AT THE LOWEST AI TREATMENT LEVEL. HENCE, THE ACTUAL THRESHOLD Ca/AI RATIO MAY BE HIGHER THAN THAT REPORTED. RESULTS ARE FROM A VARIETY OF STUDIES REPORTED IN THE LITERATURE.

Study	Solution Al ($\mu\text{mol/L}$)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al (M)	Type of Study or Experiment ^a	Response Variable ^b	Al Analysis Used in Ratio ^c
European beech											
Asp and Berggren (1990)	300	0.35			3.8			0.2	H	N	Al _i
Cronan et al. (1989)	500	0.5							H	N	Al _i
Peach											
Edwards and Horton (1977)	222				10.8			0.008	H	N	Al _i
Scotch pine											
Ilvesniemi (1992)	185	nd	400	300	0.9		2300		S	N,B	Al _t
McCormick and Steiner (1978)	2960	1.35							H	B	Al _t
Virginia pine											
McCormick and Steiner (1978)	2960	1.35							H	B	Al _t
Pitch pine											
McCormick and Steiner (1978)	2960	1.35							H	B	Al _t
Cumming and Weinstein (1990)	50	20							S	N,B	Al _t

TABLE AX4.4-10 (cont'd). COMPARISON OF SOLUTION AND TISSUE CHEMISTRIES AT THRESHOLD TREATMENT LEVELS WHERE SIGNIFICANT IMPACTS ON TREE GROWTH OR NUTRIENT CONTENT WERE FIRST OBSERVED. IN MANY CASES, ADVERSE IMPACTS WERE OBSERVED AT THE LOWEST AI TREATMENT LEVEL. HENCE, THE ACTUAL THRESHOLD Ca/AI RATIO MAY BE HIGHER THAN THAT REPORTED. RESULTS ARE FROM A VARIETY OF STUDIES REPORTED IN THE LITERATURE.

Study	Solution Al ($\mu\text{mol/L}$)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al (M)	Type of Study or Experiment ^a	Response Variable ^b	Al Analysis Used in Ratio ^c
Birches: gray, paper and yellow McCormick and Steiner (1978)	4444	0.9							H	B	Al _t
European birch Goransson and Eldhuset (1987)	1000	0.02						0.17	H	N	Al _i
Radiata pine Truman et al. (1986)	17	10.5	2120	800	1.8	1320	1850	0.48	H	N	Al _t
Douglas-fir Keltjens and Van Loenen (1989)	370	0.54	2300	300	5.2				H	B	Al _t
Larch Keltjens and Van Loenen (1989)	555	0.36	1800	250	4.9				H	B	Al _t

^a Types of study include hydroponic (H), soil or sand culture (S), or existing forest (F).

^b Response variables include biomass (B), or nutrient content (N).

^c Aluminum measurements include Al_i (Al_i), monomeric Al (Al_o), and total Al (Al_t). Since most of the lab studies were conducted under conditions of low pH and minimal DOC, measurements of total Al, Al_i, and labile Al are very comparable.

Source: Cronan and Grigal (1995).

**TABLE AX4.5-1. OVERVIEW OF SELECTED MAJOR PROCESSES BY WHICH
LANDSCAPE CHANGE CAN ALTER DRAINAGE
WATER ACID-BASE CHEMISTRY**

Landscape Change	Effect on Acid-Base Chemistry
Logging, blowdown	Dilution Lower deposition, less acidity Pulse of NO ₃ ⁻ acidity initially Less base cation neutralization, more acidity Less water contact with mineral soils, less neutralization of acidic deposition inputs
Road building and construction	More base cation neutralization, less acidity initially Depletion of base cation reserves in soils, more acidity long-term
Drainage of wetlands	Re-oxidation of stored S, pulses of acidity with increased discharge
Drought	Reduced groundwater inputs to seepage lakes with consequent increased acidity Increased relative baseflow to drainage waters with consequent decreased acidity
Lake shore development	Decreased acidity
Insect damage	Pulse of NO ₃ ⁻ acidity initially

Source: Sullivan (2000).

**TABLE AX 4.6-1. OBSERVED RELATIONSHIPS BETWEEN ZOOPLANKTON
SPECIES RICHNESS (R) AND LAKEWATER ANC**

Taxonomic Group	Equation	r ²	p
Total Zooplankton	R = 15.65 + 0.089ANC	0.46	0.001
Crustaceans	R = 6.35 + 0.028ANC	0.47	0.001
Rotifers	R = 9.04 + 0.053ANC	0.30	0.001

Source: Sullivan et al. (2006a).

TABLE AX4.6-2. THRESHOLD RESPONSE OF INCREASED MORTALITY OF FISH TO LOW pH LISTED FROM LEAST SENSITIVE TO MOST SENSITIVE (after Baker et al., 1990)

Study	Species	Increased Mortality Threshold, pH	Study Conditions
Johnson et al. (1987)	Blacknose dace, creek chub	5.9 - 6.0	In situ bioassay with early life stages in Adirondack surface waters
	Brook trout	4.8 - 5.1	
Holtze and Hutchinson (1989)	Common shiner	5.4 - 6.0	Laboratory exposure of early life stages to pH and Al.
	Lake whitefish, white sucker, walleye	5.1 - 5.2	
	Smallmouth bass	4.8	
Johansson et al. (1977)	Atlantic salmon	5.0	Laboratory tests with eggs exposed to low pH, no Al.
	Brown trout	4.5 - 5.0	
	Brook Trout	4.5	
Swenson et al. (1989)	Black crappie	5.5	Laboratory tests with early life stages exposed to pH and Al.
	Rock bass	5.0	
	Yellow perch, largemouth bass	4.5	
Mills et al. (1987)	Fathead minnow	5.9	Whole-lake treatment (fish population recruitment failure)
	Slimy sculpin	5.6 - 5.9	
	Lake Trout	5.6	
	Pearl dace	5.1	
	White sucker	5.0 - 5.1	

Source: Baker et al. (1990a).

TABLE AX4.6-3. THRESHOLD VALUES OF pH FOR VARIOUS TAXA AND EFFECTS

Reference	Type of Study	Taxa	pH	Observed Effects
Buckler et al. (1987)	Lab bioassay	Striped bass	6.5	>50% larval mortality
McCormick et al. (1989)	Lab bioassay	Fathead minnow	6.0	Significant decrease in embryo survival
Mills et al. (1987)	Whole-lake experiment	Fathead minnow	5.9	Population recruitment failure
Klauda et al. (1987)	Lab bioassay	Blueback herring	5.7	>50% mortality of larvae
Holtze and Hutchinson (1989)	Lab bioassay	Common shiner	5.4	>50% embryo mortality
Baker and Schofield (1980)	Lab bioassay	White sucker	5.2	Substantial reduction in embryo survival
Kane and Rabeni (1987)	Lab bioassay	Smallmouth bass	5.1	>50% mortality of larvae after 30-day exposure
Leino et al. (1987)	Whole-Lake experiment	Adult fathead minnow	5.2-5.8	Increased numbers of chloride (ionoregulatory) cells on the gills
Lacroix (1985a)	Field survey	Atlantic salmon parr (age 1+)	4.9-5.3	Significantly lower blood Cl levels; high K levels
McDonald and Milligan (1988)	Lab bioassay	Adult brook trout	5.2	Reduced Na transport activity
McWilliams and Potts (1978)	Lab bioassay	Adult brown trout	5.0	Net Na loss; major shift in the gill tansepthelial potential
Tietge et al. (1988)	Lab bioassay	Adult brook trout	4.9	Increased volume density of lamellar chloride cells on gills
Booth et al. (1988)	Lab bioassay	Adult brook trout	4.8	Net loss of Na and Cl
Audet and Wood (1988)	Lab bioassay	Adult rainbow trout	4.8	Decreased plasma Na and Cl levels
Peterson and Martin-Robichaud (1986)	Lab experiment	Atlantic salmon larvae	4.5	Reduced accumulation of Na, K, and Ca
Powell and McKeown (1986)	Lab bioassay	Coho salmon parr and smolts	4.4	Net decrease in plasma Na

Source: Baker et al. (1990a).

TABLE AX4.6-4. THRESHOLD VALUES OF AI FOR VARIOUS SPECIES AND EFFECTS (form of AI not specified for most studies)

Reference	Type of Study	Taxa	pH	AI (µg/L)	Observed Effect (at similar pH without added AI)
Sadler and Lynam (1988)	LB	Brown trout	5.2	30	Significant reduction in fish growth
Turnpenny et al. (1987)	Field survey	Broen trout	---	40	Fish absent or rare in streams in Wales and England
Holtze and Hutchinson (1989)	LB	Walleye	4.9	50	>50% mortality of embryos to 4-d post-hatch
Skogheim and Roseland (1986)	Field mesocosm experiment	Atlantic salmon	5.1	75	>50% mortality of smolts
Klauda and Palmer (1987)	LB	Blueback herring	5.5-5.6	100	>50% larval mortality
Rosseland and Skogheim (1984)	LB	Atlantic salmon	4.9-5.0	130	Significant increase in mortality of presmolts
Baker and Schofield (1982)	LB	White sucker	5.2	200	>50% larval mortality
Fjellheim et al. (1985)	LB	Eel	5.1	230	Significant increase in elver mortality
Brown (1983)	LB	Brown trout	4.5-5.4	250	>50% fry mortality
Schofield and Trojnar (1980)	Field study	Brook trout	4.9	286	No survival of trout stocked into lakes with higher total AI (even after accounting for pH effects).
Ormerod et al. (1987)	Whole-stream experiment	Atlantic salmon and brown trout	5.0	350	>50% mortality of young-of-the-year.

Source: Baker et al. (1990a).

TABLE AX4.6-5. THE EFFECTS OF INCREASING Ca²⁺ TO AMELIORATE LOW pH AND HIGH Al

Reference	Type of Study	Taxa	pH	Al Range (µg/L)	Ca ²⁺ Range (µeq/L)	Observed Response to Increasing Ca ²⁺
Brown (1982, 1983)	LB	Brown trout	4.5-5.1	---	12-400	Increased embryo survival and hatch
Wright and Snekvik (1978)	Field survey	Brown trout	4.5-7.5	---	20-200	Trout status significantly correlated with log Ca ²⁺ and pH.
Brown (1983)	LB	Brown trout	4.5-5.4	0-500	12-100	Increased fry survival in low pH or high Al waters
McDonald (1983)	LB	Rainbow trout	4.3	---	69-223	Decreased adult mortality and net loss of Na and Cl
Edwards et al. (1987)	LB	Brown trout	4.2	---	100-5600	Lower loss of plasma Na and Cl ions
Freda and McDonald (1988)	LB	Common shiner, rainbow trout	4.0	---	70-1000	Significant decrease in Na loss
Mount et al. (1988)	LB	Brook trout	5.0-6.3	0-500	25-400	Increased survival and growth of adults; increased progeny survival with adult exposure to low and high Al
Sadler and Lynam (1988)	LB	Brown trout	5.2	0-80	8-800	Increased yearling survival and growth in waters with elevated Al.

Source: Baker et al. (1990a).

TABLE AX 4.6-6. BROOK TROUT ACIDIFICATION RESPONSE CATEGORIES DEVELOPED BY BULGER ET AL. FOR STREAMS IN VIRGINIA (2000)

Response Category	Chronic ANC Range (µeq/L)	Expected Response
Suitable	>50	Reproducing brook trout expected if other habitat features are also suitable
Indeterminate	20 to 50	Brook trout response expected to be variable
Episodically acidic	0 to 20	Sub-lethal and/or lethal effects on brook trout are possible
Chronically acidic	<0	Lethal effects on brook trout probable

**TABLE AX4.6-7. PARTIAL LISTING OF BIOASSAYS DEMONSTRATING
DECREASED FISH SURVIVAL IN WATERS WITH LOW pH AND (OR)
ELEVATED ALUMINUM**

Reference	Species	Life Stage	Lab/Field
Johansson and Kihlström (1975)	Northern pike	Fry	Lab
Johansson and Milbrink (1976)	Roach European perch	Egg	Lab, field
Johansson et al. (1977)	Brown trout Brook trout	Egg and fry	Lab
Trojnar (1977)	White sucker	Egg and fry	Lab
Peterson et al. (1980)	Atlantic salmon	Egg	Lab
Schofield and Trojnar (1980)	Brook trout	Fry	Lab
Baker and Schofield (1982)	Brook trout White sucker	Egg and fry	Lab
Brown (1983)	Brown trout	Fry	Lab
Hulsman et al. (1983)	Walleye Rainbow trout	Egg Fry	Field
Sharpe et al. (1983)	Brook trout Brown trout Rainbow trout Mottled sculpin	Fry and adult	Field
Jago et al. (1984)	Arctic char	Egg and fry	Lab
Lacroix (1985b)	Atlantic salmon	Egg and fry	Field
Ingersoll (1986)	Brook trout	Egg and fry	Lab
Buckler et al. (1987)	Striped bass	Fry	Lab
Johnson et al. (1987)	Brook trout Lake trout Creek chub Blacknose dace	Egg, fry, and young-of-year	Field
Klauda and Palmer (1987)	Blueback herring	Egg and fry	Lab
Lacroix and Townsend (1987)	Atlantic salmon	Juvenile	Lab
Wales and Liimatainen (1987)	Walleye	Egg	Field
Palmer et al. (1988)	Bluegill Fathead minnow	Juvenile	Lab
Gunn (1989)	Lake trout	Egg and fry	Lab, field

**TABLE AX4.6-7 (cont'd). PARTIAL LISTING OF BIOASSAYS
 DEMONSTRATING DECREASED FISH SURVIVAL IN WATERS WITH
 LOW pH AND (OR) ELEVATED ALUMINUM**

Reference	Species	Life Stage	Lab/Field
Holtze and Hutchinson (1989)	Common shiner Lake whitefish White sucker Walleye Smallmouth bass Largemouth bass	Egg and fry	Lab
Hutchinson et al. (1989)	Lake trout Brook trout	Egg and fry	Lab

TABLE AX4.6-8. RESPONSE OF FISH IN ELA LAKE 223 TO EXPERIMENTAL pH (Schindler et al., 1985; Mills et al., 1987. SHOWS EFFECT OF VARIOUS pH ON FISH FORAGE FISH AND LAKE TROUT.

Biota	1977 pH 6.13	1978 pH 5.93	1979 pH 5.64	1980 pH 5.59	1981 pH 5.02	1982 pH 5.09	1983 pH 5.13
Forage fish		Fathead minnow experience recruitment failure	Fathead minnow near extinction; slimy sculpin decline in abundance	Increase in abundance of pearl dace, Suckers very abundant.	White sucker recruitment failure; no effect on adult growth and survival	Recruitment failure for all species	Recruitment failure for all species
Lake trout	Increase in condition i.e., "fatter"		Increased abundance of young-of-the-year	Lake trout recruitment failure; condition similar to preacidification	Recruitment failure; no effect on adult growth and survival	Lake trout condition poor; recruitment failure; reduced adult survival	Lake trout condition very poor; recruitment failure; reduced adult survival

Source: Baker et al. (1990a).

**TABLE AX4.6-9. RANGE OF MINIMUM pH OF FISH SPECIES OCCURRENCE
IN 11 LAKE SURVEYS**

Family and Species	High Minimum pH	Low Minimum pH
<i>Cyprinidae</i>		
Bluntnose minnow	6.6	5.6
Fathead minnow	6.3	5.1
Blacknose dace	6.8	5.6
Pearl dace	5.9	4.7
Northern redbelly dace	5.9	4.7
Common shiner	6.2	4.9
Golden shiner	5.5	4.5
Creek chub	5.9	4.6
<i>Salmonidae</i>		
Brook trout	5.6	4.6
Lake trout	5.2	4.9
Brown trout	5.0	4.6
Atlantic salmon	6.3	5.3
<i>Centrarchidae</i>		
Smallmouth bass	7.0	4.9
Largemouth bass	5.0	4.6
Pumpkinseed	6.6	4.6
Bluegill	4.5	4.5
Rock bass	6.2	4.6
Black crappie	5.6	5.6
<i>Percidae</i>		
Yellow perch	5.8	4.4
Walleye	6.9	5.2
Johnny darter	6.2	4.9
Iowa darter	6.2	4.6
<i>Esocidae</i>		
Northern pike	5.9	4.0
<i>Catostomidae</i>		
White sucker	5.5	4.6
<i>Ictaluridae</i>		
Brown bullhead	5.6	4.5
<i>Umbridae</i>		
Central mudminnow	4.5	4.2
<i>Gasterosteidae</i>		
Brook stickleback	5.4	4.6

Source: Baker et al. (1990a).

TABLE 4.6-10. STUDIES^a THAT EITHER DID (YES) OR DID NOT (NO) YIELD EVIDENCE THAT ACIDIC DEPOSITION AFFECTED CERTAIN SPECIES OF BIRDS

Species	Diet/ Foraging		Breeding Distribution		Reproductive Measures		Reference ^a
	Yes	No	Yes	No	Yes	No	
Common loon	x		x	x	x	x	1-3, 19,20
Common merganser			x		x		19
Belted kingfisher			x				4
Osprey	x		x		x		5,6
Black duck	x		x		x ^b		7-9
Common goldeneye			x ^b				8
Ring-necked duck	x				x		10,11
Eurasian dipper	x		x		x		12-14
Eastern kingbird				x	x		15
Tree swallow	x			x	x		16-18

^a1= Alvo et al. (1988); 2 = Parker (1988); 3 = Wayland and McNicol (1990); 4 = Goriup (1989);

5 = Eriksson (1983); 6 = Eriksson (1986); 7 = Hunter et al. (1986); 8 = DesGranges and Darveau (1985);

9 = Rattner et al. (1987); 10,11 = McAuley and Longcore (1988a,b)

12,13 = Ormerod et al. (1985, 1986); 14 = Ormerod and Tyler (1987); 15 = Glooschenko et al. (1986);

16,17 = Blancher and McNicol (1988, 1991); 18 = St. Louis et al. (1990); 19 = Blancher and McNicol (1991); 20 = Blair (1990).

^bThe effect was beneficial

Source: Longcore and Gill (1993).

TABLE AX4.6-11. PREDICTED HABITAT SUITABILITY FOR LAKES IN THE ALGONA MODEL DATASET IS PRESENTED. RESULTS ARE EXPRESSED AS THE NUMBER OF LAKES WITH SUITABLE HABITAT FOR FISH, COMMON LOONS (PAIRS AND BROODS) AND COMMON MERGANSERS (PAIRS AND BROODS) UNDER EACH EMISSION SCENARIO (S1, S2, S3, S4, S5) ACCORDING TO CURRENT pH CLASSES (<6, 6-6.5, >6.5). HABITAT SUITABILITY IS CALCULATED BY PROBABILITY OF PRESENCE AT TIME T FROM WARMS OUTPUT (# OF SUITABLE LAKES AT TIME T/TOTAL NUMBER OF LAKES), FOR FISH [N = 526], AND FOR LOONS AND MERGANSERS [N = 433].

Group	Total Model Lakes	Current Suitable Lakes	Number of Lakes with Suitable Habitat Under Each Emission Scenario														
			Current pH < 6					Current pH 6-6.5					Current pH > 6.5				
			S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Fish	526	338	29	34	40	77	100	97	100	107	124	133	196	196	197	197	197
Common loon pairs	433	100	12	14	14	16	17	22	22	23	24	24	66	66	66	67	67
Common loon broods	433	36	2	2	2	2	2	6	6	7	7	7	28	28	28	28	28
Common merganser pairs	433	52	6	12	27	68	86	14	17	20	33	44	31	31	32	34	35
Common merganser broods	433	31	6	10	18	69	89	14	15	16	21	29	12	11	10	10	10

TABLE AX4.6-12. SUMMARY STATISTICS OF BIOLOGICAL DATA LAYERS FOR MERCURY (Hg) CONCENTRATIONS IN FISH AND WILDLIFE ($\mu\text{g/g}$) IN THE NORTHEASTERN UNITED STATES AND SOUTHEASTERN CANADA

Category/Species	Sample Size	Data layer Designation	Hg Concentrations		Hg Level of Concern (Tissue Type)	Percentage of Samples with Concentration > Level of Concern
			Mean \pm Standard Deviation	Range		
<i>Human health</i>						
Yellow perch ^a	4089	Primary	0.39 \pm 0.49	< 0.05-5.24	0.30 (fillet)	50
Largemouth bass ^b	934	Secondary	0.54 \pm 0.35	<0.05-2.66	0.30 (fillet)	75
<i>Ecological health</i>						
Brook trout	319	Secondary	0.31 \pm 0.28	<0.05-2.07	0.16 (whole fish)	75
Yellow perch ^c	(841) ^d	Secondary	0.23 \pm 0.35	<0.05-3.18	0.16 (whole fish)	48
Common loon ^e	1546	Primary	1.74 \pm 1.20	0.11-14.20	3.0 (blood)	11
Bald eagle	217	Secondary	0.52 \pm 0.20	0.08-1.27	1.0 (blood)	6
Mink	126	Secondary	19.50 \pm 12.1	2.80-68.50	30.0 (fur)	11
River otter	80	Secondary	20.20 \pm 9.30	1.14-37.80	30.0 (fur)	15

Note: All data are in wet weight except for fur, which is on a fresh-weight basis

^aFillet Hg in yellow perch is based on individuals with a standardized length of 20 cm.

^bFillet Hg in largemouth bass is based on individuals with a standardized length of 36 cm.

^cWhole-fish Hg in yellow perch is based on individuals with a standardized length of 13 cm. Whole-fish Hg for yellow perch was converted to fillet Hg.

^dThe sample population of 841 yellow perch examined for whole-fish Hg is included with the 4089 fillets (i.e., the total number of all biotic data layers does not double-count yellow perch).

^eEgg Hg for the common loon was converted to the adult blood equivalent

TABLE AX4.6-13. MERCURY CONCENTRATIONS IN AVIAN EGGS AND TISSUES AND RELATED EFFECTS

Tissue	Concen. (ppm)	Wet (w) or Dry (d)	Endpoint	Species	Reference
Liver	1.06	w	No effect	Common tern	Gochfeld (1980)
Liver	22.2	w	Abnormal feather loss in juveniles	Common tern	Gochfeld (1980)
Liver	5	w	<i>Conservative threshold for major toxic effects</i>	Water birds	Zillioux et al. (1993)
Liver	7.2	w	Increased disease and emaciation	Common tern	Spalding and Forrester (1991)
Liver	9.08	w	Nesting success	Common tern	Finley and Stendall (1978)
Liver	20.7	w	Hatching success	Common tern	Finley and Stendall (1978)
Liver	30	w	Neurologic effects	Osprey	Heinz (1974)
Liver	35	w	Death	Common loon	Wiemeyer et al. (1987)
Liver	54.5	w	LD33 ^a	European starling	Finley et al. (1979)
Liver	97.7	w	Death	Gannet	
Liver	103.6	w	LD33	European starling	Finley et al. (1979)
Liver	126.5	w	LD33	Red-winged blackbird	Finley et al. (1979)
Liver	306 total/ 20.4 MeHg	d	No adverse effects observed	Black-footed albatross	Gochfeld (1980)
Brain	4-6	w	Failure to hatch	Black duck	Hoffman and Moore (1979)
Brain	20	w	25% mortality	Zebra finch	Scheuhammer (1988)
Egg	1-5/0.2-1.0	d	Reduced productivity in one half of the population	Merlin	Newton and Hass (1988)

TABLE AX4.6-13 (cont'd). MERCURY CONCENTRATIONS IN AVIAN EGGS AND TISSUES AND RELATED EFFECTS

Tissue	Concen. (ppm)	Wet (w) or Dry (d)	Endpoint	Species	Reference
Egg	0.5-1.5	w	Decreased hatchability	Pheasant	Heinz (1979)
Egg	0.86	w	Aberrant nesting behavior	Common loon	Heinz (1979)
Egg	1.0	w	Successful reproduction	Common tern	Finley and Stendall (1978)
Egg	1.0-3.6	w	<i>Residue threshold for significant toxic effects</i>	<i>Variety of water birds</i>	Zillioux et al. (1993)
Egg	2-16	w	No decreased hatchability	Herring gull	Finley and Stendall (1978)
Egg	3.65	w	27% hatching, 10-12% fledging	Common tern	Finley and Stendall (1978)
Kidney	37.4 total/ 6.2 MeHg	d	No adverse effect observed	Black-footed albatross	Kim et al. (1996)
Kidney	40.4	w	LD33	Grackle	Finley et al. (1979)
Kidney	74.3	w	LD33	Red-winged blackbird	Finley et al. (1979)
Kidney	86.4	w	LD33	European starling	Finley et al. (1979)

^aLD33 = lethal dose, 33%

Source: Wolfe et al. (1998).

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1 **AX5. NUTRIENT ENRICHMENT EFFECTS FROM N**

2
3
4 Nitrogen deposition can affect terrestrial, transitional, and aquatic ecosystems at multiple
5 levels and in multiple ways. Ecosystem effects can be broadly classified into two groups:
6 acidification effects and nutrient enrichment effects. Acidification effects include aspects of soil
7 acidification, base cation nutrient depletion from soil, drainage water acidification, and
8 aluminum (Al) mobilization from soil to water. Those topics are addressed in Annex 4. In this
9 annex, we consider nutrient enrichment effects, which include eutrophication and changes that
10 occur in species composition as a consequence of differing nitrogen (N)-demand among the
11 various species that occur in natural ecosystems. Some nutrient enrichment effects can occur
12 within terrestrial, transitional, and aquatic (fresh water, estuarine, and marine) ecosystems.

13 14 15 **AX5.1 THE NITROGEN CASCADE**

16 Nitrogen is one of the most important, and often limiting, nutrients in virtually all
17 ecosystems on earth (Vitousek and Howarth, 1991). It is mainly because of its importance as a
18 limiting nutrient that N deposition from air pollution causes ecological problems. The N cycle,
19 and the basic mechanisms by which the cycle can be perturbed by atmospheric deposition, were
20 described in the previous Air Quality Criteria Document (AQCD) for Oxides of Nitrogen (U.S.
21 Environmental Protection Agency, 1993).

22 Nitrogen is required by all organisms because it is a major constituent of both the nucleic
23 acids that determine the genetic character of all living things and the enzyme proteins that drive
24 the metabolism of every living cell (U.S. Environmental Protection Agency, 1993; Galloway,
25 1998; Galloway and Cowling, 2002). Nitrogen is typically the most important nutrient for plant
26 growth, especially in temperate and boreal regions. It is of critical importance in plant
27 metabolism and it often governs the utilization of phosphorus (P), potassium (K), and other
28 nutrients.

29 For convenience, N can be divided into two groups: nonreactive (N_2) and reactive (N_r).
30 Nitrogen (as N_2) composes 80% of the total mass of the Earth's atmosphere, but most
31 atmospheric N is not biologically available. Nitrogen fixation converts N_2 to biologically active
32 reduced forms of N. Reactive N includes all biologically active N compounds in the Earth's

1 atmosphere and biosphere (Galloway et al., 2003). The N_r class includes inorganic reduced
2 forms of N (e.g., ammonia [NH_3] and ammonium [NH_4]), inorganic oxidized forms (e.g., NO_x ,
3 HNO_3 , N_2O , and NO_3^-), and organic N compounds (e.g., urea, amine, proteins, and nucleic
4 acids) (Galloway et al., 2003). Given the many forms of N that occur in natural environments,
5 this assessment of ecosystem effects of NO_x and NH_4 deposition requires consideration of
6 multiple forms of N, including but not limited to oxidized forms. Nitrogen species that are
7 contained in atmospheric deposition, and that influence nutrient dynamics, include both multiple
8 oxidized and reduced forms of inorganic N and also carbon (C)-bonded N.

9 An increase in global N_r has occurred over the past century, largely due to three main
10 causes: (1) widespread cultivation of legumes, rice, and other crops that promote conversion of
11 N_2 to organic N through biological N fixation; (2) combustion of fossil fuels, which converts
12 both atmospheric N_2 and fossil N to reactive NO_x ; and (3) synthetic N fertilizer production via
13 the Haber-Bosch process, which converts nonreactive N_2 to N_r to sustain food production and
14 some industrial activities (Galloway and Cowling, 2002; Galloway et al., 2003). Food production
15 accounts for much of the conversion from N_2 to N_r .

16 Reactive N is accumulating in the environment on local, regional, and global scales
17 (Galloway, 1998; Galloway and Cowling, 2002; Galloway et al., 2003). Reactive N
18 accumulation occurs in the atmosphere, soil, and water (Galloway and Cowling, 2002), with a
19 multitude of effects on humans and ecosystems (Galloway, 1998; Rabalais, 2002; Van Egmond
20 et al., 2002; Townsend et al., 2003). A single atom of new NH_x or NO_x can alter a wide array of
21 biogeochemical processes and exchanges among environmental reservoirs. The sequence of
22 transfers, transformations, and environmental effects is referred to as the “N cascade”
23 (Figure AX5.1-1) (Galloway and Cowling, 2002; Galloway et al., 2003).

24 The results of the N cascade and the various transformations in the N cycle can be both
25 beneficial and detrimental to humans and ecosystems (Galloway and Cowling, 2002; Galloway
26 et al., 2003). Synthetic fertilizers and cultivation-induced bacterial N fertilization (BNF) have
27 sustained dramatic increases in human population. However, there have been, and will continue
28 to be, environmental consequences resulting from increased fertilization with N, including
29 (1) wide dispersal of N_r by hydrological and atmospheric transport, (2) accumulation of N_r in the
30 environment because the rates of creation exceed rates of removal through denitrification to
31 nonreactive N_2 , (3) projected continued increase in N_r creation and accumulation in the future,

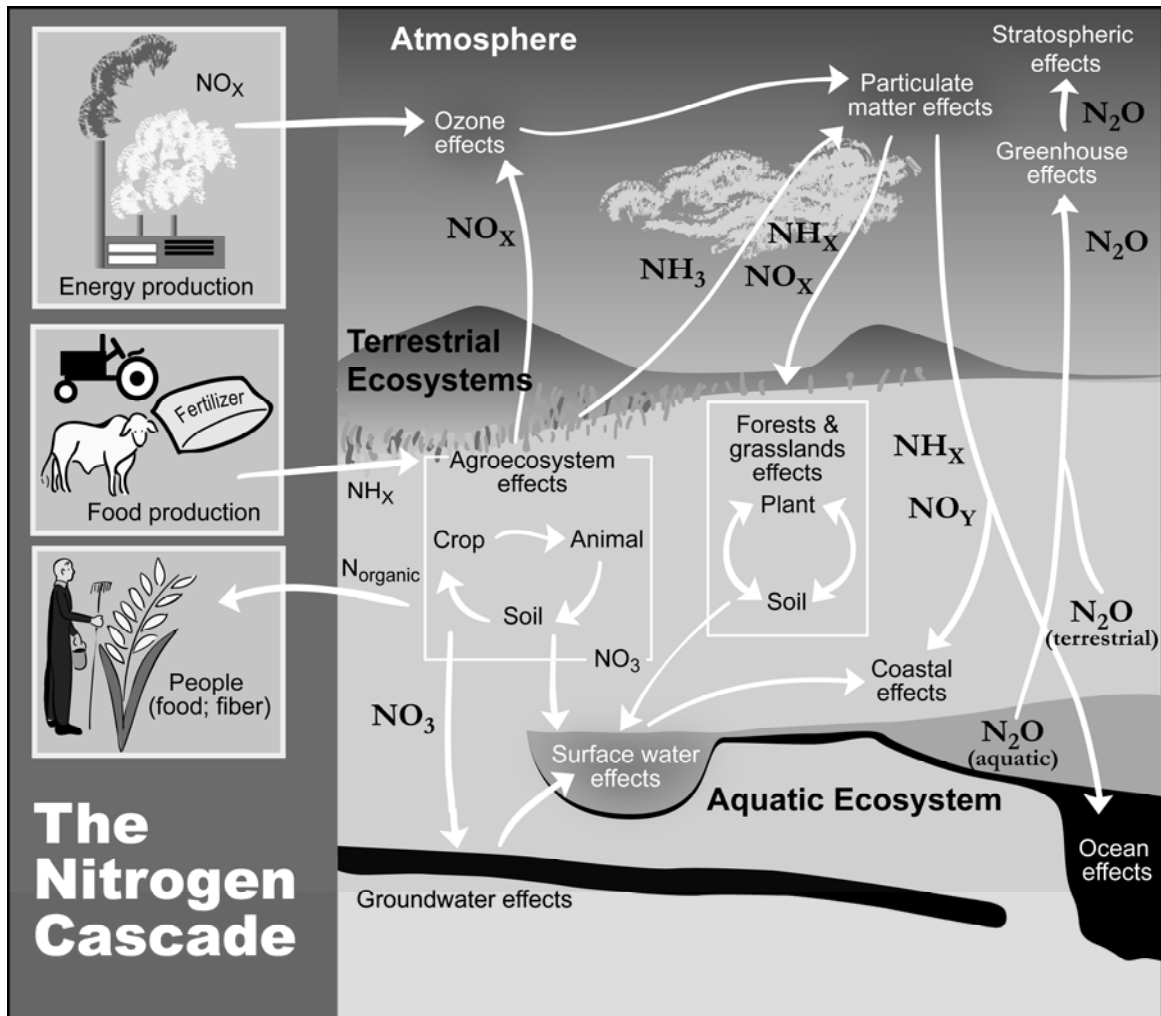


Figure AX5.1-1. Illustration of the N cascade showing the movement of the human-produced reactive N (N_r) as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and the aquatic ecosystems.

Source: Galloway et al. (2003).

1 and (4) the fact that N_r accumulation contributes to many contemporary environmental problems
 2 (Galloway et al., 2003; U.S. Environmental Protection Agency, 2004). Among the most
 3 important effects of chronic N deposition are eutrophication and changes in the composition of
 4 plant communities, disruptions in nutrient cycling, increased soil emissions of nitrous oxide
 5 (N_2O ; a potent greenhouse gas), accumulation of N compounds in the soil with enhanced
 6 availability of nitrate (NO_3^-) or NH_4^+ , soil-mediated effects of acidification, and increased

1 susceptibility of plants to stress factors (Aber et al., 1989, 1998; Bobbink et al., 1998; Driscoll
2 et al., 2003a; Fenn et al., 1998).

3 Changes in N supply can also affect an ecosystem's nutrient balance. Nitrogen addition
4 disrupts normal nutrient cycling and alters plant and soil processes (Aber et al., 1989). Among
5 the processes expected to be most affected are (1) nutrient uptake and allocation in plants, (2)
6 litter production, (3) N immobilization, (4) nitrification, (5) NO₃⁻ leaching, and (6) trace gas
7 emissions (Figure AX5.1-2) (Aber et al., 1989). Changes in N supply can also interact with C
8 cycling and the effects of global carbon dioxide (CO₂) fertilization. See further discussion of this
9 issue in Annex 7. This annex summarizes the effects of added N on terrestrial, transitional, and
10 aquatic ecosystems, beginning with changes to biogeochemical pathways and cycles.

11
12

13 **AX5.2 EFFECTS ON BIOGEOCHEMICAL PATHWAYS AND CYCLES**

14

15 **AX5.2.1 Cycling and Storage of Nitrogen Compounds**

16 The nutrient enrichment effects of N deposition are largely determined by the retention
17 and release of Nr in terrestrial and transitional ecosystems and the relationships between N and
18 other nutrients. Ecosystem retention and loss of N are regulated mainly by biological processes
19 the response of ecosystems to N inputs from atmospheric deposition that greatly complicate the
20 N cycle. The basic features of the cycle are well understood and were summarized by the U.S.
21 Environmental Protection Agency (EPA) in the previous AQCD for NO_x (U.S. Environmental
22 Protection Agency, 1993).

23 Given the complexity of the N cycle, a broadly applicable and well-tested predictive
24 model had not been developed at the time of the last AQCD. Substantial progress has been made
25 since that time, and while this goal has not yet been fully achieved, knowledge has developed
26 with which to make many generalizations about how ecological and biogeochemical processes
27 respond to N deposition. Significant scientific advancements in recent years have included
28 refinement of theoretical foundations of nutrient limitation, development and improvement of
29 analytical technologies, and improved understanding of the role of N in regulating or influencing
30 the cycling of other elements, especially C. Central to this understanding is the basic process of
31 N cycling in terrestrial, transitional, and aquatic ecosystems.

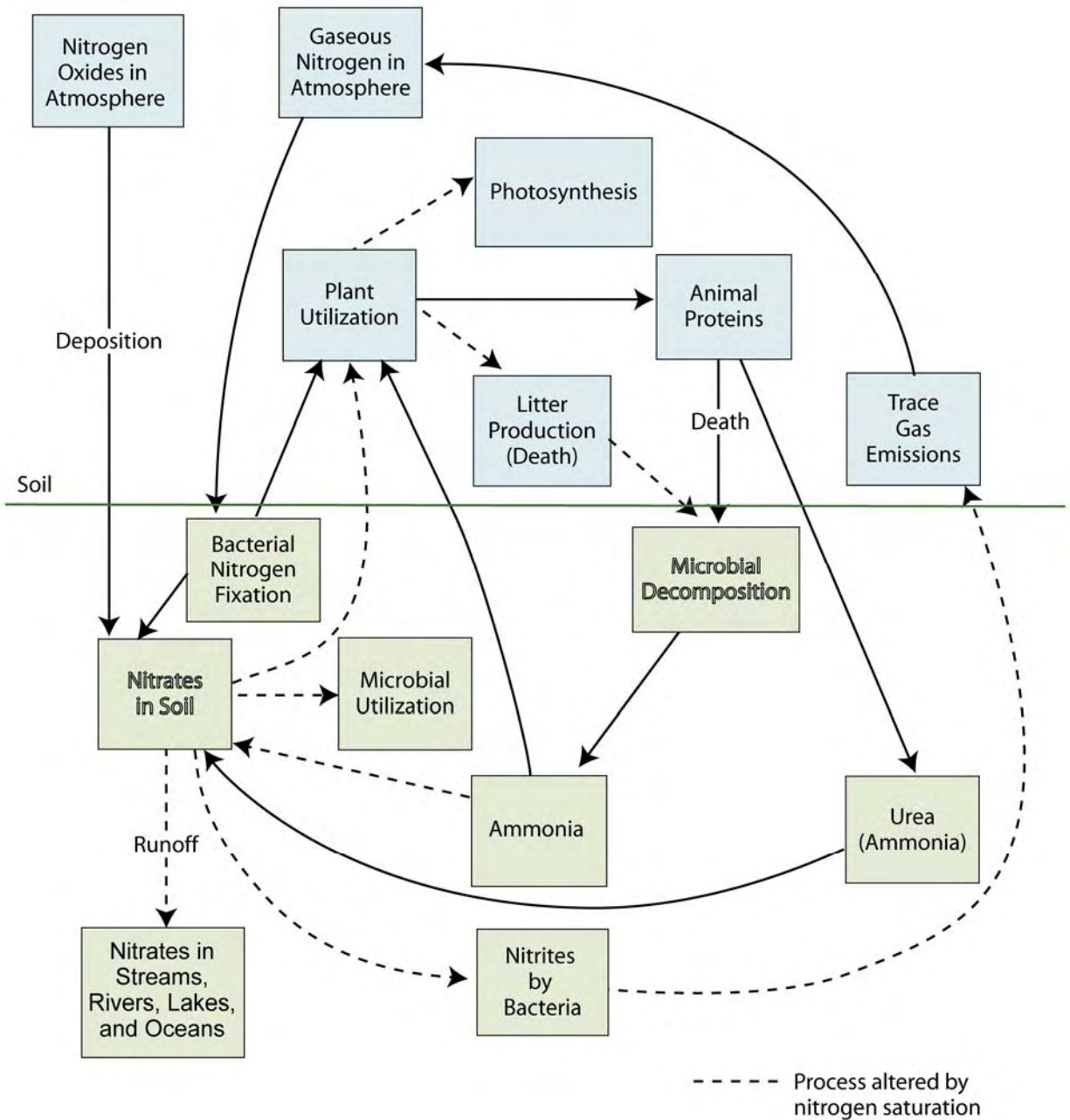


Figure AX5.1-2. Nitrogen cycle (dotted lines indicated processes altered by N saturation).

Source: Garner (1994).

- 1 The key steps in the N cycle include N fixation, assimilation, mineralization (conversion
- 2 of organic N to simple inorganic forms), nitrification (conversion of reduced inorganic N to

1 oxidized inorganic N), and denitrification (the reduction of NO_3^- to NO, N_2O , and N_2 gas by
2 microbes under anaerobic conditions). These steps generally require biologically mediated
3 transformations. Key organisms involved in transforming N from one form to another include
4 plants and microbes. The following sections outline the fundamentals of N cycling in terrestrial,
5 transitional, and aquatic ecosystems.

6 7 **AX5.2.1.1 Nitrogen Cycling in Terrestrial Ecosystems**

8 Nitrogen deposition has a potentially important effect on terrestrial ecosystems
9 throughout large areas of the United States because, under natural conditions, it is an important
10 limiting nutrient. The availability of N to plants is largely controlled by the process of N
11 mineralization, or the microbial conversion from organic N to simple amino acids and then to
12 inorganic forms such as NH_4^+ and NO_3^- (Schimel and Bennett, 2004). The two-step, aerobic,
13 microbial process of autotrophic nitrification converts NH_4^+ to NO_3^- . Nitrification is an
14 acidifying process, releasing 2 mol hydrogen ion (H^+) per mol NH_4^+ converted to NO_3^- (Reuss
15 and Johnson, 1986). As the N cycle becomes enriched through cumulative N addition, N
16 becomes more abundant, competition among organisms for N decreases, net nitrification rates
17 often increase, and NO_3^- can leach from the ecosystem (Aber et al., 1989, 2003).

18 Nitrogen in forest ecosystems is stored primarily in the soil, and soil N often exceeds
19 85% of the total ecosystem N (cf. Bormann et al., 1977; Cole and Rapp, 1981). Most soil N is
20 contained in organic matter, typically bound in humic material or organo-mineral complexes that
21 are resistant to microbial degradation. This N is not directly available for biological uptake by
22 plants or microbes or for leaching loss into ground water or surface water.

23 Only what is termed the mineralizable, or labile, pool of N_f is considered to be
24 biologically active (Aber et al., 1989). Bioavailable N often controls photosynthesis and net
25 primary productivity (NPP) (e.g., Field and Mooney, 1986). Plants obtain N from the soil by
26 absorbing NH_4^+ , NO_3^- , or simple organic N compounds through their roots, or N is taken up by
27 symbiotic organisms (e.g., fungi, bacteria, cyanobacteria) in plant roots (cf. Lilleskov et al.,
28 2001; Schimel and Bennett, 2004). Plant roots, nitrifying bacteria, and microbial decomposers
29 within the soil utilize, and compete for, this available soil N pool. Plant uptake of N can be
30 energetically costly, as NO_3^- must be reduced to NH_4^+ , and NH_4^+ fixed into amino acids before
31 N can be used in plant processes. Plants use the enzyme NO_3^- reductase to reduce NO_3^- to

1 NH_4^+ . Some species reduce NO_3^- in their leaves, taking advantage of excess energy from
2 photosynthesis, whereas other species are restricted to the more energy expensive approach of
3 reducing NO_3^- in their roots.

4 Dozens of experimental ^{15}N -addition studies have been conducted as a way of
5 understanding how N cycles through terrestrial ecosystems. These studies have shown that trees
6 typically take up only a small fraction of added ^{15}N ; the vast preponderance is retained in the soil
7 (e.g., Tietema et al., 1998; Nadelhoffer et al., 1999; Providoli et al., 2005; Templer et al., 2005).
8 This pattern persists even a decade after ^{15}N application (Nadelhoffer et al., 2004). These
9 experiments have been criticized for applying ^{15}N directly to the soil surface, thereby precluding
10 direct canopy uptake of N from wet, dry, or gaseous deposition (Sievering, 1999; Sievering et al.,
11 2000). Canopy ^{15}N experiments are now underway, but have not yet been published.
12 Comparisons of rates of N deposition in throughfall and in total deposition suggest that forest
13 canopies can take up an average of 16% of total atmospheric N input (Lovett, 1992), but this
14 interception can be considerably higher (up to 90%) in some N-limited forests with large
15 epiphyte loads (e.g., Klopatek et al., 2006). Of that N from deposition that is retained in
16 vegetation, it remains unclear if, or how much of, it is used in photosynthetic enzymes (e.g.,
17 Bauer et al., 2004).

18 19 **AX5.2.1.2 Nitrogen Cycling in Transitional Ecosystems**

20 Nitrogen dynamics in wetland ecosystems are variable in time and with type of wetland
21 and environmental factors, especially water availability (Howarth et al., 1996). A wetland can
22 act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and
23 these functions can vary with season and with hydrological conditions. Vegetation type,
24 physiography, local hydrology, and climate all play significant roles in determining source/sink
25 N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren,
26 1994; Mitchell et al., 1996).

27 Where a wetland acts as a net sink for N via denitrification, it may have the ability to
28 “buffer” increased atmospheric N inputs. This is especially true if N supply is limiting the rate
29 of denitrification in wetland soils (Hayden and Ross, 2005). Previous studies suggest that
30 elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and
31 Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process increases the contribution

1 of nitrous greenhouse gasses to the atmosphere, but limits other environmental effects that are
2 typically associated with increased N supply to soils and drainage waters. However, increased N
3 inputs to wetland systems would only be expected to stimulate denitrification if there is an
4 adequate C supply (Groffman, 1994). Although denitrification has been observed to increase
5 with N addition, N mineralization has also been shown to increase, and this can cause an increase
6 in wetland N export to adjacent surface water (Groffman, 1994). Denitrification appears to be
7 negligible in wetland environments that are typically nutrient (including N) poor, such as bogs
8 and fens (Morris, 1991).

9 Increased N loading to transitional ecosystems can affect both methane (CH₄)-producing
10 and CH₄-oxidizing microbial activity. The difference between the CH₄ production and oxidation
11 determines the magnitude of CH₄ emission from soils. Nitrate can decrease CH₄ production by
12 acting as a redox buffer during organic decomposition in anaerobic sediments. Ammonium
13 compounds are generally considered to reduce CH₄ oxidation (Steudler et al., 1989; King and
14 Schnell, 1994; Gullledge et al., 1997), but have also been observed to increase methanotropic
15 bacterial activity (Bodelier et al., 2000).

16 Methane emissions from saturated soils have been observed to increase with N addition
17 (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). The prevailing hypothesis for
18 explaining this effect is that increased vegetative cover increases C availability through root
19 exudates, which in turn stimulates methanogenic bacteria and CH₄ emissions (Granberg et al.,
20 2001; Saarnio et al., 2003; Zhang et al., 2007). Saarnio et al. (2003) observed moderate
21 increases in CH₄ emissions from boreal wetland soils with N fertilization rates of 30 kg N/ha/yr
22 as ammonium nitrate (NH₄NO₃). Comparable N application rates and effects on CH₄ emissions
23 were also observed by Granberg et al. (2001) in a similar ecosystem type. Zhang et al. (2007)
24 observed elevated CH₄ emissions from freshwater wetland soils with experimental N additions of
25 240 kg N/ha/yr. They postulated that additional N increased abundance of *Deyeucia angustifolia*
26 which increased CH₄ emissions by supplying methanogenic bacteria with additional substrate in
27 the form of root exudates. Other studies have shown that N addition had little or no effect on
28 CH₄ emissions across a variety of ecosystem types (Saarnio et al., 2000; Silvola et al., 2003;
29 Ambus and Robertson, 2006).

30 It is important to note that the N enrichment rates employed in all of the above reported
31 studies related to N effects on soil CH₄ emissions were much greater (30 to 240 kg N/ha/yr) than

1 atmospheric N inputs in most areas of the United States that are heavily impacted by elevated
2 atmospheric N deposition. Nevertheless, an increase in CH₄ emissions from wetland soils in
3 response to N loading is important, especially because CH₄ is an effective greenhouse gas
4 contributing to global warming (Saarnio et al., 2000). Changes in the C cycle in wetlands,
5 especially within the geographically extensive boreal zone, could have an important influence on
6 climate. The reason(s) for the observed difference in response are not known.

7

8 **AX5.2.1.3 Nitrogen Cycling in Aquatic Ecosystems**

9 Eutrophication, or nutrient enrichment, is a potential consequence of N deposition to both
10 freshwater and marine aquatic ecosystems. Many freshwater ecosystems are P-limited, and
11 therefore would not be expected to increase primary productivity in response to increased
12 atmospheric inputs of N (Elser et al., 1990). However, there are many examples of fresh waters
13 that are N-limited or N and P co-limited (e.g., Elser et al., 1990; Fenn et al., 2003a; Tank and
14 Dodds, 2003; Baron, 2006; Bergström and Jansson, 2006). In such aquatic systems, atmospheric
15 inputs of N would be expected to increase productivity and alter biological communities,
16 especially phytoplankton.

17 Estuaries and coastal marine environments tend to be N-limited, and many currently
18 receive high levels of N input from human activities (Vitousek and Howarth, 1991; Howarth
19 et al., 1996). Eutrophication is an important problem in many coastal areas of the United States.
20 Atmospheric N deposition contributes to this problem. The relative importance of the various N
21 sources varies from estuary to estuary. Atmospheric sources are proportionately more important
22 to estuaries that exhibit large surface area relative to watershed drainage area, and in those
23 estuaries that drain watersheds that are dominated by natural ecosystems rather than agricultural
24 or urban lands (Boyer et al., 2002). The nature and extent of the impacts on estuarine and coastal
25 environments is, in part, related to the export of N from upland systems to coastal environments,
26 as discussed below.

27

28 **AX5.2.2 Export of Nitrogen**

29 In addition to direct effects on the ecosystem where it is deposited, N can be exported
30 from the system and cause environmental effects (eutrophication or acidification) in other
31 ecosystem compartments. The two principal mechanisms for N export or loss from ecosystems
32 are leaching and denitrification. Leaching removes N from terrestrial or transitional ecosystems,

1 but adds it to aquatic ecosystems. Thus, an export from one ecosystem becomes an import to
2 another. Denitrification removes N from terrestrial, transitional, and aquatic ecosystems and
3 adds it to the atmosphere (Davidson et al., 2000; Seitzinger et al., 2006). Although
4 denitrification provides a pathway for removing excess N_r from ecosystems, incidental
5 production of NO and N_2O during denitrification is of concern due to the roles of NO as a
6 precursor to ozone (O_3) production, and N_2O as a potent greenhouse gas. Here we discuss
7 leaching and denitrification processes as a window into the environmental transfer and
8 ecosystem effects of N.

9 10 **AX5.2.2.1 Export from Terrestrial Ecosystems**

11 12 **AX5.2.2.1.1 Leaching**

13 In most upland forested areas in the United States, most N received in atmospheric
14 deposition is retained in soil (Nadelhoffer et al., 1999). Several different data compilations
15 indicate that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems
16 that receive less than about 10 kg N/ha/yr (Dise and Wright, 1995; Sullivan, 2000; MacDonald
17 et al., 2002; Aber et al., 2003; Kristensen et al., 2004).

18 Nitrogen-related adverse effects on aquatic life occur despite retention of most
19 atmospheric N deposition within the terrestrial environment (Driscoll et al., 2003a). For
20 example, although 70% to 88% of atmospheric N deposition was retained in the Catskill
21 Mountains watersheds in upstate New York, fish populations could not be sustained because
22 high NO_3^- concentrations in stream water during high flows caused the concentrations of
23 inorganic Al to exceed the toxicity threshold (Lawrence et al., 1999).

24 Two of the primary indicators of N enrichment in forested watersheds are the leaching of
25 NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the
26 growing season (Stoddard, 1994). The concentration of NO_3^- in surface water provides an
27 indication of the extent to which atmospherically deposited (or otherwise added) N leaches from
28 the terrestrial ecosystem. Some N fertilization experiments suggest that increasing N deposition
29 drives an increase in production of dissolved organic nitrogen (DON) in soil (e.g., Seely and
30 Lajtha, 1997; McDowell et al., 2004), but there is little evidence that elevated N deposition
31 increases the export and loss of DON from terrestrial ecosystems. Essentially all of the increase
32 in N export across gradients of N deposition occurs as an increase in NO_3^- rather than DON

1 export. The latter is typically less than 2 kg N/ha/yr from most northeastern-forested watersheds
2 (Campbell et al., 2000; Goodale et al., 2000; Lovett et al., 2000; Aber et al., 2003).

3 In an analysis of data collected during the mid- to late 1990s from lakes and streams
4 throughout the northeastern United States, Aber et al. (2003) suggested that nearly all N
5 deposition is retained or denitrified in northeastern watersheds that receive less than about 8 to
6 10 kg N/ha/yr. An analysis of N deposition to forestland in the northeastern United States based
7 on Ollinger et al. (1993) suggested that approximately 36% of the forests in the region received
8 8 kg N/ha/yr or more and may therefore be susceptible to elevated NO_3^- leaching (Driscoll et al.,
9 2003a).

10 Aber et al. (2003) further found that surface water NO_3^- concentrations exceeded 1 $\mu\text{eq/L}$
11 in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition (Figure AX5.2-1).
12 The lakes and streams found to have high NO_3^- concentration were those receiving N deposition
13 above this range, but responses were variable among those receiving high N deposition. Above
14 this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg
15 $\text{NO}_3\text{-N/ha/yr}$ for every 1 kg N/ha/yr increase in deposition, although there was considerable
16 variability in N retention among watersheds at higher rates of deposition (Figure AX5.2-2) (Aber
17 et al., 2003).

18 In other studies, the isotopic signature of ^{18}O in streamwater NO_3^- indicates that only a
19 small percentage of the incoming NO_3^- from atmospheric deposition leached directly to drainage
20 waters (e.g., Spoelstra et al., 2001; Burns and Kendall, 2002; Pardo et al., 2004). The rest of the
21 NO_3^- that leached from the terrestrial ecosystem had been cycled by biota in soils or streams
22 prior to being exported. It is possible, however, that the cycled N was originally derived from
23 atmospheric deposition.

24 Experimental studies have shown that NO_3^- leaching can be induced by chronic addition
25 of N. Ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$) fertilization of a forested watershed at Bear Brook, ME,
26 resulted in long-term increases in NO_3^- concentration in stream water and high annual export of
27 N, although the fertilized catchment retained 80% of N inputs, mostly in soil (Kahl et al., 1999;
28 Norton et al., 1999). Similar results were observed in response to $(\text{NH}_4)_2\text{SO}_4$ fertilization to the
29 Fernow Experimental Forest, WV (Edwards et al., 2002) and NH_4NO_3 fertilization at Harvard
30 Forest, MA (Magill et al., 2004). Several N-exclusion studies in Europe demonstrated that

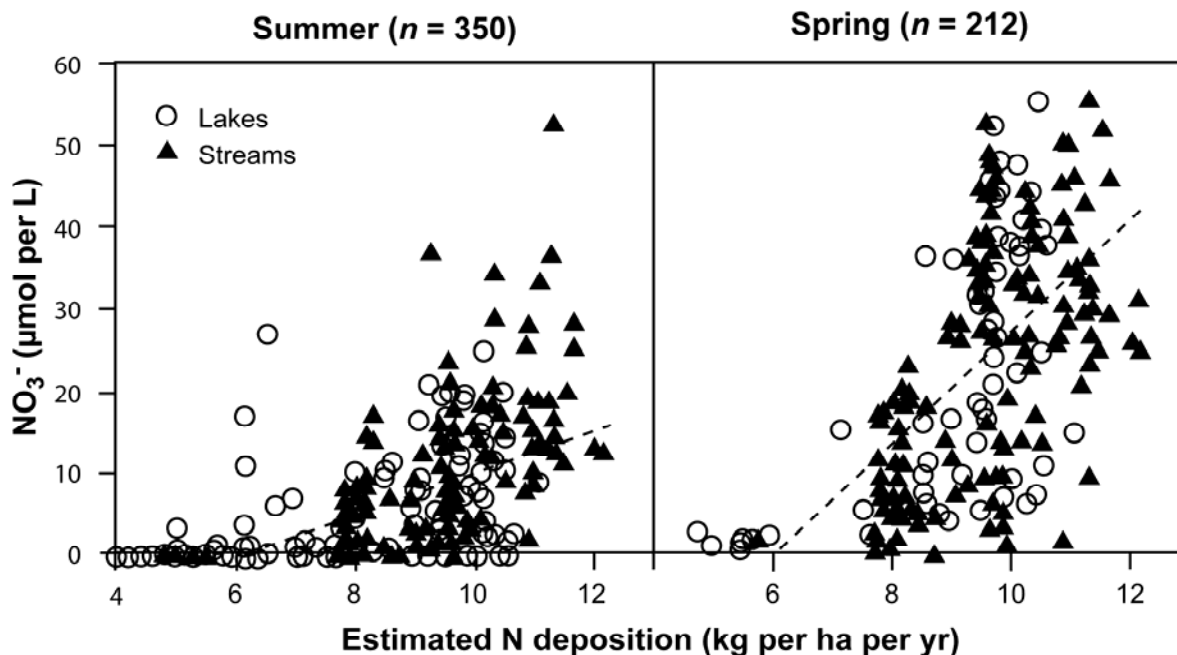


Figure AX5.2-1. Surface water nitrate (NO_3^-) concentrations as a function of nitrogen deposition at the base of each watershed in summer and spring. Nitrogen deposition to the whole watershed may be 2 to 6 kg/ha/yr greater than at the base.

Source: Aber et al. (2003).

1 decreases in N deposition produced immediate reductions in NO_3^- leaching from forest stands
 2 (Gundersen et al., 1998; Quist et al., 1999).

3 At a regional scale, the leaching transport of N from terrestrial to freshwater systems has
 4 important implications beyond its impact on upland lakes and streams, because N exports can
 5 ultimately also contribute to the eutrophication of coastal ecosystems (Howarth et al., 1996;
 6 Driscoll et al., 2003c). In general, because much of the atmospherically deposited N is retained
 7 within the terrestrial ecosystem or denitrified during export, a relatively small fraction of this N
 8 reaches downstream estuaries (Castro et al., 2001; Alexander et al., 2002; Seitzinger et al., 2002;
 9 van Breemen et al., 2002).

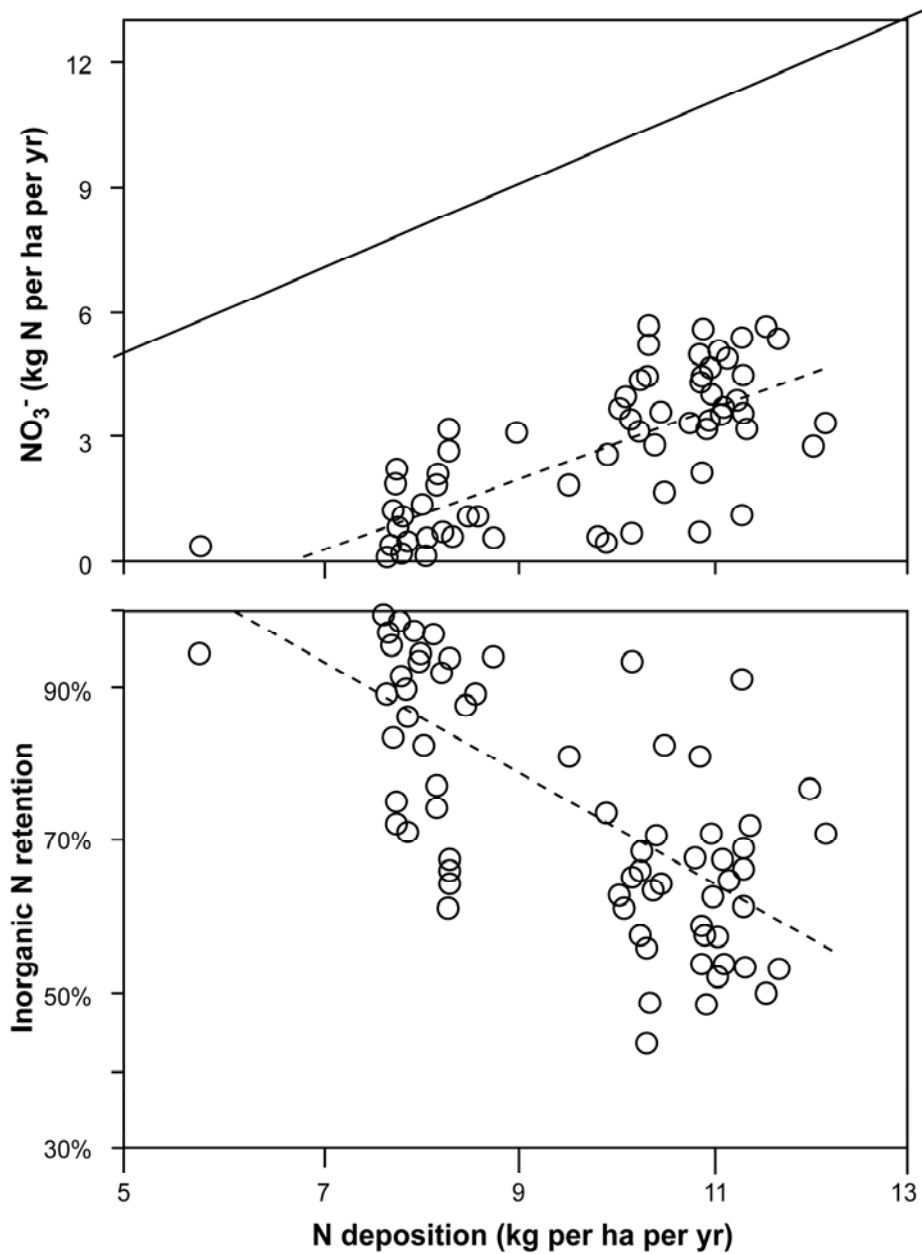


Figure AX5.2-2. (a) Nitrogen export in stream water as a function of N deposition at the base of sampled watersheds. Nitrogen export is represented by the equation $NB_{\text{exp}} = 0.85 N_{\text{dep}} - 5.8$; $r^2 = 0.56$; $p < 0.001$. (b) Watershed N retention decreases as N deposition at the base of the watersheds increases (N retention = $-0.07 N_{\text{deposition}} + 1.44$; $r^2 = 0.50$).

Source: Aber et al. (2003).

1 **AX5.2.2.1.2 Denitrification**

2 The role of denitrification in terrestrial ecosystems is important in understanding what
3 fraction of the atmospheric deposition is returned to the atmosphere and therefore does not have
4 direct effects on terrestrial and aquatic ecosystems. Denitrification has been difficult to measure
5 directly in most ecosystems, due to the difficulty of measuring small changes in N_2 and to the
6 great degree of spatial and temporal heterogeneity inherent in the denitrification process
7 (Davidson and Seitzinger, 2006). There are a variety of methods for measuring denitrification
8 rates in freshwater and marine sediments, including measurements of NO_3^- loss, N_2 production,
9 N_2O accumulation in response to acetylene inhibition of N_2O reduction, isotopic methods, and
10 N_2 :argon (Ar) measurement by membrane inlet mass spectrometry (MIMS) (Smith et al., 2006).
11 The majority of direct measurements of denitrification have measured only rates of production of
12 N_2O , or used the “acetylene block” technique of inhibiting transformation of N_2O to N_2 and
13 monitoring the accumulation of N_2O as a surrogate of the sum of N_2O and N_2 . The acetylene
14 block method is highly problematic, however, as it also inhibits rates of nitrification, and so
15 denitrification rates are strongly underestimated where nitrification and denitrification processes
16 are coupled closely in space or time (Groffman et al., 2006).

17 Techniques can be based on laboratory incubation of sediment cores or *in situ* studies.
18 Each method has advantages and disadvantages. Many studies have been conducted to compare
19 results among the various methods (e.g., Seitzinger, 1988; Seitzinger et al., 1993, 2002; Bernot
20 et al., 2003; Groffman et al., 2006; Smith et al., 2006). Kana et al. (1998) described the MIMS
21 method to measure small changes in dissolved N_2 caused by denitrification in sediments. This
22 technique allows measurement of N_2 flux in unperturbed sediment cores with high temporal
23 resolution (Kana et al., 1998). This is especially useful during summer conditions when NO_3^-
24 concentration in the water is typically low, but the high temperature can support high rates of
25 denitrification. Under such conditions, it is likely that a coupled sequence of nitrification and
26 denitrification accounts for substantial N loss from estuarine sediments (Kemp et al., 1990).
27 Constraints regarding field and analytical methods have seriously limited understanding of the
28 magnitude and controls on denitrification (Groffman et al., 2006). Groffman et al. (in press)
29 recently reviewed the major approaches to measuring denitrification in both aquatic and
30 terrestrial ecosystems.

1 Denitrification occurs only under anaerobic conditions, where and when there is also
2 sufficient NO_3^- and organic C to fuel the facultatively anaerobic denitrifying bacteria. Hence,
3 most terrestrial denitrification occurs in “hotspots,” that is, in sporadically wet places or times or
4 in anaerobic soil microsites (McClain et al., 2003; Seitzinger et al., 2006). The high organic
5 matter content of terrestrial soils presents an ample supply of C, and so the factors that typically
6 limit rates of denitrification in terrestrial ecosystems are rates of NO_3^- supply and the occurrence
7 of anaerobic conditions. Davidson et al. (2000) described N gas loss from terrestrial ecosystems
8 using a conceptual model called “hole-in-the-pipe.” In this model, production of NO, N_2O , and
9 N_2 gas are functions of the general rate of N cycling processes through soil (i.e., the N flux
10 “flowing through the pipe”), combined with information on soil water content, a key determinant
11 of the ratio of NO: N_2O (relative “hole size” for NO and N_2O gas “leakage”). The model
12 formulation has been supported by a range of field measurements in temperate and especially
13 tropical ecosystems (Davidson et al., 2000), and suggests that processes that increase the rate of
14 N cycling through soils should also increase the rate of N gas loss from these systems.
15 Production of NO and N_2O tend to be lower in temperate than in tropical ecosystems, largely
16 because of colder temperatures and slower rates of N cycling in temperate systems, and the
17 frequency of P rather than N limitation in tropical systems. However, increased availability of N
18 through fertilization can increase the rate of NO and N_2O gas loss from temperate forests.

19 Early studies of N gas emission in response to N fertilization experiments at the Harvard
20 Forest, MA, found small increases in N_2O production in response to the highest N treatment
21 (150 kg N/ha/yr) to a red pine (*Pinus resinosa*) stand, but N_2O losses accounted for <0.4% of N
22 additions (Magill et al., 2000). However, later studies found that NO emission rates can be more
23 than an order of magnitude greater than N_2O emissions, with NO emissions amounting to 3-4%
24 to 8% (4 to 5 kg N/ha/yr) of the N additions to the fertilized pine stands (Venterea et al., 2003,
25 2004). Emissions of NO and N_2O increased with fertilization rate (0, 50, and 150 kg N/ha/yr) in
26 both the red pine and a nearby red oak (*Quercus rubra*)/red maple (*Acer rubrum*) stand
27 (Venterea et al., 2003, 2004). A study of the response of Scots pine (*Pinus sylvestris*) stands
28 across a gradient of N deposition in Germany found a threefold to fourfold increase in the rate of
29 NO and N_2O production as N deposition increased from 15 to 22 N/ha/yr. In these forests, both
30 gases were produced in roughly equal amounts, although as N deposition increased, the rate of

1 NO production increased more steeply than did the rate of N₂O production (Butterbach-Bahl
2 et al., 2002a).

3 At Höglwald, a German site receiving 20 to 30 kg N/ha/yr in throughfall, Butterbach-
4 Bahl et al. (2002b) reported higher emissions of NO than N₂O in both a spruce and a beech
5 stand, with N oxide emissions totaling 4.5 to 6.8 kg N/ha/yr. Intensive laboratory studies
6 suggested additional emissions of N₂ gas amounting to 7.2 and 12.4 kg N/ha/yr in the spruce and
7 beech stands, respectively. This is the only known forest site for which a complete (NO, NO₂,
8 N₂O, and N₂) N gas budget has been estimated, and in total, these measurements suggest that soil
9 emissions may balance 46% to 78% of the N received in throughfall at this site. This result
10 suggests somewhat higher rates of N gas loss than might be inferred from a series of ¹⁵N tracer
11 studies in conifer stands across Europe, which spanned a range of rates of N input from
12 atmospheric and experimental sources of 3 to 91 kg N/ha/yr. Across all sites, total recovery of
13 added ¹⁵N in soil, vegetation, and lysimeter leachate after 9 to 21 months amounted to 65% to
14 105% of added ¹⁵N (Tietema et al., 1998), providing a broad constraint on N gas emissions of no
15 more than 35% of added ¹⁵N. The lowest rates of ¹⁵N recovery (65% to 67%) occurred at Speuld
16 and Ysselsteyn, two sites in The Netherlands with the highest rates of chronic throughfall N
17 input (35 to 53 kg N/ha/yr). Although much more work is needed on complete N gas budgets,
18 several lines of evidence suggest that trace gas emissions of N may constitute an increasing
19 pathway of N loss with increasing rates of N deposition.

20 Using a simple model of the fate of global N inputs to terrestrial ecosystems, Seitzinger
21 et al. (2006) estimated that denitrification in terrestrial soils removed 46% (124 Tg/yr) of global
22 N inputs from all sources (N deposition, fertilizer, and N fixation). Half of this denitrification
23 (66 Tg/yr) was estimated to have occurred in agricultural systems. However, this model
24 assumed that all N entering terrestrial systems was leached as NO₃⁻ if it was not taken up by
25 plants; hence, the model overestimated the potential for denitrification by the extent to which N
26 accumulated in soils or ground water (Seitzinger et al., 2006).

27

28 **AX5.2.2.2 Export from Transitional Ecosystems**

29

30 **AX5.2.2.2.1 Leaching**

31 Leaching losses from wetlands are rarely considered as explicitly distinct from leaching
32 losses from upland terrestrial environments and the wet environments that occur in upland

1 catchments. That is, when leaching losses from terrestrial ecosystems are quantified based on
2 stream exports, estimated leaching losses inherently include the net loss of NO_3^- from both
3 terrestrial ecosystems and adjacent wetlands. Leaching losses of NO_3^- in water derived directly
4 from wetlands are often small because of NO_3^- removal by denitrification. However, hydrologic
5 flowpaths that deliver water to streams by bypassing wetland soils can deliver substantial
6 quantities of NO_3^- -rich water from terrestrial uplands.

7
8 **AX5.2.2.2.2 Denitrification**

9 Transitional ecosystems can remove significant quantities of NO_3^- from water because
10 they represent a convergence of conditions of NO_3^- , oxygen (O_2), and C that are requisite for
11 denitrification. Denitrification is frequently optimized when NO_3^- from more oxic upland areas
12 passes through wet, often C-rich and anoxic conditions in wetlands. For example, Groffman
13 (1994) used the acetylene block technique to measure rates of denitrification of 1 to 135 kg
14 N/ha/yr in Rhode Island wetlands. They found the highest rates of denitrification (4 to 135 kg
15 N/ha/yr) in very poorly drained soils on nutrient-rich parent material, with lower rates (1.2 to
16 5.3 kg N/ha/yr) in soils that were better drained or less nutrient-rich. Denitrification was best
17 predicted by soil NO_3^- concentration rather than soil moisture status.

18 For a range of Catskill Mountain soils, Ashby et al. (1998) used the acetylene block
19 technique to measure denitrification rates, and found higher rates of denitrification per unit area
20 associated with soils with higher organic matter content and water-filled pore spaces.
21 Instantaneous NO_3^- concentration did not correlate with denitrification rate, suggesting that the
22 rates of NO_3^- supply through microbial production or hydrologic transport were more important
23 than *in situ* NO_3^- concentration. Denitrification was most stimulated by amendments with
24 glucose alone or glucose plus NO_3^- , suggesting limitation by labile C and NO_3^- supply.

25 In a review of the effects of riparian zones on NO_3^- removal from ground water, Hill
26 (1996) concluded that there is consensus that there are large losses of NO_3^- to denitrification
27 within riparian zones. However, there are important caveats to the generalization that riparian
28 wetlands prevent the leaching of NO_3^- to streams. Not all water entering streams passes directly
29 through adjacent riparian zones, and denitrification in deep subsurface flowpaths is often limited
30 by the supply of labile C.

1 In a review of denitrification in wetlands, Hill (1996) also warned that not all
2 streamwater necessarily passes through riparian zones, and that large amounts of water may
3 follow flowpaths beneath organic-rich riparian zones, allowing significant transport of NO_3^- to
4 streams. For example, McHale et al. (2004) found strong effects of peatlands on local N
5 concentrations, but little effect of peatlands on adjacent stream chemistry, since peatland ground
6 water contributed little to streamflow. In an agricultural catchment in Michigan, Hedin et al.
7 (1998) used both spatial patterns of water chemistry and additions of labile C to demonstrate that
8 the supply of degradable C from shallow flowpaths limited rates of NO_3^- removal via
9 denitrification in near-stream zones. Wetland soils can be hotspots of NO_3^- removal by
10 denitrification in anoxic sites rich in NO_3^- and labile C, but denitrification rates can be limited by
11 suboptimal conditions of any single biogeochemical factor, and deep water flowpaths can bypass
12 wetland denitrification altogether.

13

14 **AX5.2.2.3 Export from Aquatic Ecosystems**

15

16 ***AX5.2.2.3.1 Leaching and Transport***

17 The transport of N via rivers and streams represents an important source of N to
18 downstream ecosystems. The transport and loss of N is determined by the net balance of
19 delivery of N by direct atmospheric deposition and from upland terrestrial and associated
20 transitional ecosystem sources, minus the uptake and gaseous loss of that N during transport.
21 Net transport of N from headwater streams, large catchments, and entire watersheds is discussed
22 in this section; a discussion of loss processes follows in the section on denitrification.

23 Alexander et al. (2002, 2007) applied the statistical model SPARROW (SPAtially
24 Referenced Regression On Watershed attributes) to rivers in New England, and concluded that
25 first-order headwaters contributed 65%, 55%, and 40% of the N flux to 2nd, 4th, and higher-
26 ordered catchments, respectively (Alexander et al., 2007). Atmospheric deposition accounted for
27 almost 70% of the total simulated N load to these headwater streams. Hence, understanding the
28 factors driving N export in small catchments is crucial for predicting the effects on downstream
29 water quality.

30 In most cases, atmospheric N combines with fertilizer N in agricultural areas and with N
31 from wastewater treatment facilities in urban areas, and the role of atmospheric deposition in
32 residential and urban ecosystems has rarely been explicitly addressed. There is considerable

1 uncertainty regarding the extent to which atmospheric N deposition to areas of mixed land use
2 actually contributes to the N load of large rivers and to estuarine inputs of N.

3 Urbanization entails alteration of the land surface in ways that dramatically affect runoff
4 and nonpoint source pollution processes. In particular, along with urbanization, there is an
5 increase in the amount of roads and other impervious surfaces, and these enhance surface runoff
6 and reduce infiltration of precipitation into soil. Roadside ditches route precipitation directly
7 from roads into streams. Furthermore, urbanization often involves substantial clearing of
8 vegetation and soil compaction (Poff et al., 1997; Burges et al., 1998; Jones et al., 2000;
9 Trombulak and Frissell, 2000; Alberti et al., 2007). Runoff is transmitted much more efficiently
10 downstream in the urban environment, altering the magnitude of discharge and the flux of
11 contaminants from urban landscape surfaces to the stream system (Arnold and Gibbons, 1996;
12 Montgomery and Buffington, 1998). The reduction in riparian and wetland coverage and
13 functionality also diminishes the ability of the urban watershed to filter contaminants from
14 runoff, including atmospherically deposited N (Peterjohn and Correll, 1984).

15 Numerous studies have illustrated correlations between water quality or ecological
16 conditions and various measures of the extent of urbanization, such as human population density
17 or percent impervious surface (Hachmoller et al., 1991; Charbonneau and Kondolf, 1993;
18 Johnson et al., 1997; Thorne et al., 2000; Alberti et al., 2007). Alberti et al. (2007) hypothesized
19 that the influence of urbanization on stream and watershed condition is controlled largely by the
20 extent, spatial distribution, intensity, and frequency of disturbance. They found strong statistical
21 relationships between patterns in urbanization and stream ecological condition, as reflected in the
22 benthic index of biological integrity (B-IBI) (Fore et al., 1996; Morley and Karr, 2002).
23 Although percent impervious surface explained much of the variation in B-IBI in 42 Puget
24 Sound, WA lowland sub-basins, Alberti et al. (2007) found that mean urban patch size and
25 number of road crossings explained much of the variation that was not captured by percent
26 impervious surface. These additional variables provide information regarding the configuration
27 and connectivity of the urban landscape.

28 Burkholder et al. (2006) concluded that the observed trends in N and P concentrations in
29 the Neuse Estuary, NC from 1998 to 2002 could be explained mainly by a combination of
30 climate, management policies, and urban/agricultural development. Nutrient loading reductions
31 did occur in response to imposed management practices in the watershed, but they were affected

1 by increases in human and livestock population in the watershed. Thus, goals for estuarine and
2 coastal nutrient loading reduction must consider the influence of within-watershed development
3 (Burkholder et al., 2006).

4 In lowland areas, other terrestrial sources of N, such as fertilizer, livestock waste, septic
5 effluent, and wastewater treatment plant outflow, often become much more important than they
6 are in upland areas. In these areas, it is difficult to determine the percent of atmospheric N that
7 actually leaches to drainage water because there are too many other ill-defined sources of N to
8 drainage waters.

9 Fisher et al. (2006) presented two case studies of cultural eutrophication from the
10 Chesapeake Bay system. The Choptank watershed (1756 km²) is dominated by agricultural land
11 use (62%), with only 5% urban development. The Patuxent watershed (2260 km²) is dominated
12 by forest (64%), with a significant urban land use coverage (16%) and less intensive agricultural
13 development (20%). Sewage is a major cause of nutrient enrichment in the Patuxent watershed;
14 fertilizer is a major cause in the Choptank. Oxygen concentration in bottom waters of the
15 Patuxent estuary is consistently below 3 mg/L in summer; oxygen levels have been steadily
16 decreasing in the Choptank estuary over the past two decades and now approach 3 mg/L in wet
17 years (Fisher et al., 2006). The authors estimated that nutrient inputs to these estuaries increased
18 by a factor of between 4 and 20 over the previous century. Efforts to control nutrient sources
19 within these watersheds have resulted in point source reductions that amount to about 18% of the
20 total watershed inputs in the Patuxent watershed. However, nutrient inputs to the Choptank
21 watershed are still increasing (Fisher et al., 1998, 2006). Atmospheric deposition of N to the
22 estuary surfaces and to the terrestrial watershed interact with the other anthropogenic sources of
23 N to make up the total anthropogenic N load to the system.

24 25 **AX5.2.2.3.2 Denitrification**

26 Denitrification in aquatic ecosystems has been most intensively studied in small streams,
27 though some work has also been done at larger scales. Nitrogen is cycled rapidly within streams,
28 especially small streams with large relative areas for contact with benthic surfaces and hyporheic
29 zones. For example, Peterson et al. (2001) found that ¹⁵N-NH₄⁺ added to a range of streams was
30 taken up most rapidly in the smallest streams, and that these headwater streams exported less
31 than 50% of their added NH₄⁺. Nevertheless, the long-term fate of this removed or transformed
32 and recycled N is more difficult to assess. Mulholland et al. (2004) found that addition of

1 $^{15}\text{N-NO}_3^-$ to a headwater stream at Walker Branch, TN, indicated a mean uptake length of 35 m
2 under ambient conditions. The uptake length extended three-fold (i.e., reduced uptake) under a
3 modest fertilization treatment, which employed NO_3^- addition of approximately 500 $\mu\text{g N/L}$.
4 Direct measurements of denitrification of added ^{15}N indicated that denitrification accounted for
5 16% of the NO_3^- loss under the ambient treatment, and only 1% of NO_3^- uptake under the
6 fertilized treatment. Nearly all of the denitrification occurred as reduction to N_2 gas rather than
7 to N_2O .

8 Hyporheic losses of NO_3^- to denitrification may be largely controlled by supplies of
9 labile dissolved organic carbon (DOC). Bernhardt and Likens (2002) found that adding 6 mg/L
10 of DOC as acetate to a small stream at Hubbard Brook, NH, reduced stream NO_3^- concentrations
11 from ~ 5 to $< 1 \mu\text{mol/L}$. In experimental mesocosms designed to mimic hyporheic flowpaths of a
12 small river in the Catskill Mountains, NY, Sobczak et al. (2003) found that adding just 0.5 to
13 1.0 mg/L DOC from leaf litter resulted in the net consumption of nearly all of the 40 $\mu\text{mol/L}$
14 NO_3^- in solution. Acetylene block measurements indicated that the majority of this NO_3^- loss
15 was due to microbial assimilation rather than denitrification, consistent with the isotopic tracer
16 results of Mulholland et al. (2004).

17 At large spatial scales, water residence time is the variable most frequently identified as a
18 controller of N loss from aquatic ecosystems examined, for example, for a range of lakes
19 (Howarth et al., 1996) or for large river basins spanning the northeastern United States
20 (Seitzinger et al., 2002). Compiling N loss data sets from a wide range of aquatic ecosystems,
21 Seitzinger et al. (2006) found that water residence time alone explained 56% of the variance in
22 rates of N loss across lakes, rivers, estuaries, and continental shelves, from fast-flowing river
23 reaches (residence time of h) with 0% to 15% N loss to century-scale turnover lakes that
24 eventually incur 80% to 100% N loss.

25 Denitrification is a major factor governing the loss of N from estuarine ecosystems.
26 Collection of quantitative data on this process has been hampered, however, by the complexity of
27 environmental controls on the denitrification process and difficulties in measuring denitrification
28 rates (Kana et al., 1998). Major environmental controls include temperature and the availability
29 of NO_3^- , O_2 , and organic materials (Seitzinger, 1988; Rysgaard et al., 1994). Measurement of
30 denitrification requires measurement, or estimation, of the ultimate end product of denitrification
31 (N_2).

1 Anaerobic ammonium oxidation (anammox) also accounts for substantial loss of N from
2 estuarine and marine sediments and water columns to the atmosphere. This reaction uses nitrite
3 as the primary electron acceptor and is catalyzed by planctomycete bacteria of the genera
4 *Brocadia*, *Kuenenia*, and *Scalindua*. That NH_4^+ could be oxidized under anoxic conditions was
5 theorized several decades ago based on calculations of the ratios among N, P, and C in marine
6 ecosystems. Nevertheless, the process was not experimentally documented until the 1990s (van
7 de Graaf et al., 1995). More recently, anammox has been detected in a variety of freshwater,
8 estuarine, and marine waters and sediments (Devol, 2003; Jetten et al., 2003; Ward, 2003;
9 Rysgaard et al., 2004; Dalsgaard et al., 2005; Engstrom et al., 2005; Jetten et al., 2005; Kuypers
10 et al., 2005; Pilcher, 2005; Op Den Camp et al., 2006).

11 Marine microbes are responsible for a major component of global N cycling (Arrigo,
12 2005). Marine microbial ecology is highly complex and poorly understood. This relatively new
13 knowledge about anammox bacteria has completely altered scientific understanding of N cycling
14 in the oceans (Devol, 2003). Previously it was believed that denitrification was responsible for
15 virtually all of the transfer of N_r in the ocean to the atmosphere as N_2 gas. It now appears that
16 anammox may account for up to 50% of the N_2 production in the oceans (Devol, 2003; Ward,
17 2003; Dalsgaard et al., 2005; Kuypers et al., 2005).

18

19 **AX5.2.3 Timing of Chemical Change**

20

21 **AX5.2.3.1 Interannual Change**

22 Interannual changes in N cycling are in part reflected in changes in streamwater
23 chemistry. Many of the original lakes in EPA's Adirondack Long Term Monitoring (ALTM)
24 program reflected increased NO_3^- leaching from terrestrial ecosystems throughout the 1980s
25 (cf. Driscoll and Van Dreason, 1993), which was followed by a decline during the 1990s. As a
26 consequence of this subsequent decline, Driscoll (2003b) reported an overall significant ($p < 0.1$)
27 *decrease* in NO_3^- concentration for the period 1982 to 2000 for 8 of the 16 original ALTM
28 monitoring sites. Only the one mounded seepage lake in the study (Little Echo Pond) had a
29 small, but statistically significant, increase in NO_3^- concentration ($0.01 \mu\text{eq/L/yr}$, $p < 0.06$). It is
30 not clear why many Adirondack watershed soils leached NO_3^- to a lesser extent during the 1990s
31 than they did during the 1980s (Driscoll et al., 2003b). Decreasing stream NO_3^- concentrations
32 during the 1990s was also observed in the Catskill Mountains (Stoddard et al., 2003) and in New

1 Hampshire (Goodale et al., 2003). There was not a substantial change in N emissions or
2 deposition in the Northeast region over that period. Climatic factors, insect defoliation, increases
3 in atmospheric CO₂, and interactions with increasing availability of DOC have been proposed as
4 possible contributing factors to regional decreases in NO₃⁻ leaching (cf. Mitchell et al., 1996;
5 Aber et al., 2002; Driscoll et al., 2003b; Goodale et al., 2003, 2005), but the driver of this
6 decadal scale pattern remains uncertain.

7

8 **AX5.2.3.2 Episodic Change**

9 Nutrient enrichment effects of N deposition are controlled to a large degree by biological
10 and hydrological processes that operate on episodic (hours to days), seasonal, and interannual
11 time scales. Nitrogen uptake and transformation reactions and processes vary greatly with
12 season and with climatic factors. In particular, N export from terrestrial and transitional
13 ecosystems to aquatic ecosystems is governed by seasonal fluctuations in temperature and
14 biological uptake, and episodic fluctuations in water movement associated with rainstorms and
15 snowmelt. The role of N in driving biotic change in stream ecosystems due to episodic pulses of
16 NO₃⁻ associated with spring snowmelt are discussed in detail in section AX4.3.3.7.

17

18 **AX5.2.3.3 Future Cumulative Impacts**

19 Changes in N addition and cycling can prompt conditions of N saturation. Nitrogen
20 saturation reflects a set of gradually developing changes in ecosystem processes which govern
21 the integrated response of a system to increased N_r availability over time (Aber, 1992). Nitrogen
22 saturation occurs when N_r inputs exceed the capacity of plants and soil microorganisms to utilize
23 and retain N (Aber et al., 1989, 1998; U.S. Environmental Protection Agency, 1993). Under
24 conditions of saturation, some resource other than N becomes growth-limiting. High
25 concentration of NO₃⁻ in soil solution or streamwater is a symptom of N saturation. See further
26 discussion of N saturation in Section AX4.1.2.5.

27 The timing of chemical and biological changes that result from atmospheric N deposition
28 is highly variable. The overall process of N saturation is expected to result from a series of
29 cumulative effects, as N availability gradually increases beyond the capacity for biotic retention
30 and results in increased losses of N gases to the atmosphere and NO₃⁻ to drainage water (Aber
31 et al., 1989, 1998). The time required for many ecosystems to reach saturation at current rates of
32 deposition may well be decades to centuries. Nevertheless, some ecosystems in regions of high

1 deposition or low N uptake capacity have experienced considerable leaching losses in recent
2 years (e.g., Peterjohn et al., 1996).

3
4 **AX5.2.3.4 Reversibility of Impacts**

5 Although there are relatively few studies of the reversibility of the biogeochemical
6 impacts of elevated N deposition, the few to date suggest the possibility of rapid recovery.
7 Species shifts that might occur in response to reductions in N deposition would be expected to
8 exhibit greater lag periods. In areas where N is very tightly cycled, multi-year cycling of species
9 composition and abundance towards, and then away from, conditions comparable to undisturbed
10 vegetation denotes strong biological regulation of ecosystems subject to N enrichment
11 (Milchunas and Lauenroth, 1995).

12 Experimental studies in Europe suggest that some ecosystem processes and
13 characteristics are likely to recover rapidly following a reduction in N deposition. At a study in
14 northern Sweden, high levels of fertilization (90 kg N/ha/yr) over 20 years induced substantial
15 soil acidification, including loss of over half of the base cations in the mineral soil, a decrease in
16 pH, and an increase in soluble Al (Högberg et al., 2006). However, 10 years after this treatment
17 was stopped, the pH of the mineral soil had increased, and extractable NO_3^- was no higher than
18 in the control plot. Stem volume growth did not substantially increase relative to the
19 acidification period. “Clean roof” experiments that prevent N deposition inputs at sites receiving
20 >40 kg N/ha/yr ambient atmospheric N deposition in The Netherlands increased wood and root
21 production soon after the roof was installed (Boxman et al., 1998a), and NO_3^- exports below the
22 rooting zone were reduced dramatically within 2 years (Bredemeier et al., 1998).

23 A study of alpine lake sediment cores in Rocky Mountain National Park, CO (Wolfe
24 et al., 2003) suggested the possible reversibility of N enrichment effects on lake biota. Although
25 increased dominance of mesotrophic diatom species was correlated with increased N inputs
26 during the 20th century, it did not appear that any of the oligotrophic species had been totally lost
27 from study lakes. Thus, reduced future N loading may allow renewed dominance by
28 oligotrophic diatom species.

29 It is not necessarily true, however, that nutrient enrichment effects of N deposition will,
30 in all cases, be easily reversible. For example, it has been suggested that vegetation conversion
31 in the coastal sage scrub community in California has altered hydrologic function to an extent

1 that may be difficult to reverse. The depth of rainwater percolation into soil has been reduced as
2 a result of invasion of non-native annual grasses. This hydrologic change inhibits the growth of
3 deep-rooting native shrubs (Wood et al., 2006). As a consequence, active management, in
4 addition to reduced N deposition, may be required to restore the native flora in this area.

5 The importance of controlling nonpoint sources of nutrients to estuaries in the United
6 States is well recognized, but strategies to do so are often not effective (NRC, 2000). For
7 example, in the late 1980s the Chesapeake Bay Program targeted a 40% reduction in controllable
8 N sources to the bay. Nevertheless, less than a 20% reduction in N loading was accomplished
9 over a period of about 15 years despite major decreases in point sources (Burkholder et al.,
10 2006). Subsequently, Hagy et al. (2004) recommended that a 40% reduction in N loading would
11 still be required in order to significantly reduce the size of the area of the bay affected by
12 seasonal anoxia related to N enrichment.

13 14 15 **AX5.3 FACTORS THAT DETERMINE SENSITIVITY**

16 In general, ecosystems that are most responsive to nutrient enrichment from atmospheric
17 N deposition are those that receive high levels of N loading, are N-limited, or contain species
18 that have evolved in nutrient-poor environments. In general, high N loading is associated with
19 proximity to large N sources and conditions that enhance N deposition (such as dense forest
20 cover). Based on a review of the literature, the ecosystems that appear to be particularly
21 sensitive include alpine and other grassland ecosystems, arid lands, nutrient-poor wetlands, N-
22 limited oligotrophic freshwaters, and estuarine ecosystems. Changes in productivity and
23 interspecies competition, resulting from increased N inputs, can change the character and
24 functioning of these ecosystems in complex ways.

25 Several sensitive receptors have been identified which receive most of their nutrient
26 inputs directly from the atmosphere and are therefore sensitive to N deposition changes. These
27 receptors include high-elevation protected areas that may contain tundra and alpine and
28 subalpine lakes, perched seepage lakes, ombrotrophic bogs, and epiphytic lichens. In addition,
29 endemic species are also often sensitive to excess N because they are generally adapted to low N
30 levels, and are therefore sensitive to competition from nitrophilous (sometimes non-native)
31 opportunistic invaders when exposed to high N supply. The following sections describe the

1 factors that make specific terrestrial, transitional, and aquatic ecosystems more sensitive to N
2 deposition than others.

3 4 **AX5.3.1 Factors that Determine the Sensitivity of Terrestrial Ecosystems**

5 Since the 1980s, it has been well known that atmospheric N deposition affects sensitive
6 terrestrial ecosystems. However, development of an understanding of the magnitude and nature
7 of the affects has developed slowly. At the time of the previous AQCD for NO_x effects, there
8 was growing concern that N deposition was contributing to N saturation of ecosystems that had
9 previously been considered N-limited. There was also concern regarding the possible effects on
10 species composition and richness, especially of relatively fast-growing plant communities that
11 have historically developed in nutrient-poor environments. Recent research results have helped
12 to clarify which ecosystems are most responsive to adverse impacts of nutrient enrichment from
13 N deposition.

14 15 **AX5.3.1.1 Forest Sensitivity**

16 Nitrogen deposition poses a substantial potential for nutrient enrichment to temperate
17 forest ecosystems because the growth of trees in these systems is often N-limited (Vitousek and
18 Howarth, 1991), and forest canopy structure can enhance rates of N deposition to terrestrial
19 ecosystems by scavenging dry N deposition for the atmosphere (Lovett, 1992). Forests
20 considered sensitive to N deposition include high-elevation red spruce and sugar maple forests
21 which receive high rates of N deposition, and where effects of N deposition on root allocation or
22 late-season growth may exacerbate other stresses from acid deposition and harsh climate. The
23 effects of excess N on sensitive forests can be exacerbated in forests that have already
24 experienced base cation depletion from soils due to the acidifying effects of acidic deposition.

25 In some areas, particularly in high-elevation terrestrial ecosystems which have become
26 N-saturated, high levels of deposition have caused elevated levels of NO₃⁻ in drainage waters,
27 making these areas potentially more sensitive to added N deposition (Aber et al., 1989, 1998;
28 Stoddard, 1994; Campbell et al., 2002; Bowman et al., 2006). Elevated NO₃⁻ leaching
29 contributes to depletion of base cations from forest soils, causing adverse effects on sensitive tree
30 species and acidification of drainage waters in base-poor soils (Aber et al., 1989, 1998; Stoddard,
31 1994). In general, sites receiving high N deposition also are subject to other pollutant exposures.

1 Interactions of the nutrient enrichment effects of N deposition with O₃ and acid rain make it
2 difficult to attribute specific effects to nutrient N effects alone.

3 Conifer forests that receive high inputs of N_r appear to exhibit decreases in productivity
4 and increases in mortality (Fenn et al., 1998). For example, fertilization experiments at Mount
5 Ascutney, VT suggested that N saturation may lead to the replacement of slow-growing spruce-
6 fir forest stands by fast-growing deciduous forests that cycle N more rapidly (McNulty et al.,
7 1996, 2005).

8 Plants balance their allocations of sunlight and nutrients in order to grow above ground to
9 maximize light and C capture and to grow below ground to maximize capture of water and other
10 nutrients, including N. Therefore, high nutrient availability should be associated with high plant
11 shoot:root ratio (Sterner and Elser, 2002). As a consequence, light availability, nutrient balance,
12 and C:N:P stoichiometry are closely related, and largely help to determine the mix of autotrophic
13 species that will occupy a particular habitat. The resulting stoichiometric balance of C:N:P in the
14 autotrophic community can have additional feedbacks on nutrient cycling by herbivores,
15 detritivores, and decomposers (Sterner and Elser, 2002).

16

17 **AX5.3.1.2 Grassland Sensitivity**

18 Grasslands can exhibit substantial sensitivity to nutrient enrichment effects of N
19 deposition. It is expected that the most important factor is the occurrence of grassland
20 communities that are adapted to low nutrient supply. For example, acid grasslands in the United
21 Kingdom adapted to low-nutrient conditions decreased significantly in diversity as N deposition
22 increased from 5 to 35 kg N/ha/yr (Stevens et al., 2004).

23 Wedin and Tilman (1996) conducted studies of N enrichment over a 12-year period on
24 Minnesota grasslands and found that plots initially dominated by native warm-season grasses
25 shifted to low-diversity mixes of species dominated by cool-season grasses at all but the lowest
26 rates of N addition. Grasslands with high N retention and C storage rates were the most
27 vulnerable to loss of species and major shifts in N cycling in response to experimental N
28 enrichment.

29 Experimental studies in successional fields in Cedar Creek Natural History Area in
30 Minnesota have shown that N is the major limiting resource. Terrestrial plant biomass increases
31 and community composition changes after N addition to grasslands (Tilman, 1987; Tilman and
32 Wedin, 1991). Increased availability of N to grasses can also affect herbivores that feed on

1 grasses by altering food quality, quantity, and phenology, and also perhaps by changing the
2 relationships between herbivores and their predators (Throop and Lerdau, 2004).

3 4 **AX5.3.1.3 Arctic and Alpine Tundra Sensitivity**

5 Arctic tundra terrestrial ecosystems are adapted to cold temperature, short growing
6 season, high soil moisture, and periodically low soil O₂ level. Poor soil aeration is caused by
7 permafrost, resulting in poor water drainage and the development of anaerobic conditions.
8 Vegetation composition and primary productivity vary in response to differences in soil moisture
9 and aeration (Everett and Brown, 1982; Gebauer et al., 1995). Reduced soil O₂ can limit nutrient
10 availability. For example, N mineralization and nitrification rates decrease, and denitrification
11 increases under anaerobic conditions (Ponnamperuma, 1972; Gebauer et al., 1995). Plants
12 respond to reduced N availability by changing the allocation of biomass to favor root growth
13 (Bloom et al., 1985) or changing the efficiency with which N is used or stored (Chapin, 1980).
14 Gebauer et al. (1995) demonstrated that different species of arctic sedge (*Eriophorum*
15 *angustifolium* and *E. vaginatum*) use different strategies to accommodate limited N supply. For
16 example, flood tolerance in *E. vaginatum* appeared to depend on high soil N availability. This
17 species may be unable to successfully compete in the typically N-poor, anaerobic environment of
18 wet tundra sites.

19 Factors that govern the sensitivity of alpine tundra to N deposition include lower rates of
20 primary production, short growing season, low temperature, and wide variation in moisture
21 availability in the alpine environment (Bowman and Fisk, 2001). Alpine plant communities have
22 also developed under conditions of low nutrient supply, in part because soil-forming processes
23 are poorly developed, and this also contributes to their N-sensitivity. Alpine plant communities
24 are sensitive to changes in species composition in response to added N (Bowman et al., 1995;
25 Seastedt and Vaccaro, 2001). See discussion of this topic in Section AX5.5.4.1.2.

26 Nitrogen cycling in alpine environments is strongly tied to variations in moisture regime
27 (Bowman et al., 1993; Bowman, 1994; Fisk et al., 1998). Blowing snow is transported across
28 alpine landscapes by wind and tends to accumulate in certain depression areas. These areas
29 receive much higher levels of moisture and winter season N deposition than other more wind-
30 swept portions of the alpine environment (Bowman, 1992). Fenn et al. (2003a) suggested that as
31 much as 10 kg N/ha/yr may leach through the snow during the initial phases of snowmelt in
32 some of the alpine areas in Colorado that accumulate substantial snowpack. It is these moist

1 meadow areas that may be most affected by N deposition and are also the areas most likely to
2 show changes in plant species composition and impacts on N cycling (Bowman and Steltzer,
3 1998).

4 **AX5.3.1.4 Arid Land Sensitivity**

6 Some arid and semi-arid ecosystems in the United States are believed to be sensitive to
7 nutrient enrichment effects from atmospheric N deposition due to the high levels of atmospheric
8 N deposition and because N tends to be limiting to plant growth where adequate moisture is
9 available. Much of the arid land data are from the coastal sage scrub (CSS) communities of
10 southern California, down-wind of the Los Angeles Basin, where dry N deposition is very high.
11 Native shrub and forb seedlings in the CSS community are unable to compete with dense stands
12 of exotic grasses, and thus are gradually replaced by the grasses, especially following
13 disturbances such as fire (Eliason and Allen, 1997; Yoshida and Allen, 2001; Cione et al., 2002).
14 It has been hypothesized, but not demonstrated, that the decline in CSS community species could
15 be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and
16 Allen, 2000). Nitrogen-induced changes in arbuscular mycorrhizal fungi may affect the growth
17 of native seedlings. Larger-spored fungal species (*Scutellospora* and *Gigaspora*) have decreased
18 in number due to a failure to sporulate, with a concomitant proliferation of small-spored species,
19 including *Glomus aggregatum*, *G. leptotichum*, and *G. geosporum*. This suggests selective
20 pressure favoring the smaller-spored species of fungi (Egerton-Warburton and Allen, 2000), and
21 that N enrichment of the soil might alter the arbuscular mycorrhizal species composition and
22 diversity.

23 **AX5.3.2 Factors that Determine the Sensitivity of Transitional Ecosystems**

25 Wetlands considered sensitive to N deposition typically contain plants species that have
26 evolved under N-limited conditions. It is believed that the balance of competition among plant
27 species in some sensitive wetland ecosystems can be altered by N addition, with resulting
28 displacement of some species by others that can utilize the excess N more efficiently (U.S.
29 Environmental Protection Agency, 1993). This effect has been well documented in heathlands in
30 the Netherlands, where *Calluna vulgaris* has been replaced by grass species (Heil and Bruggink,
31 1987; Tomassen et al., 2003). It is important to note, however, that N deposition in the
32 Netherlands has been much higher (about 20 to 60 kg N/ha/yr) than levels commonly

1 encountered in wetland areas in the United States (usually, but not always, less than 20 kg
2 N/ha/yr) (See Section AX4.1.1, Figure AX4.1-3).

3 The sensitivity of wetlands is particularly important given that they contain a
4 disproportionately high number of rare plant species (Figure AX5.3-1) (Moore et al., 1989).
5 EPA reported that, of the 130 plant species from the conterminous United States that were listed
6 as threatened or endangered in 1987, 14% occurred principally in wetlands (U.S. Environmental
7 Protection Agency, 1993). Bedford and Godwin (2003) indicated that a disproportionately high
8 number of rare plant species occur in fens relative to their percent land cover (Table AX5.3-1)
9 (Bedford and Godwin, 2003). For example, fens comprise only 0.01% of northeastern Iowa but
10 contain 12% of the region's rare plant species and 17% of the listed endangered, threatened, and
11 species of concern (Table AX5.3-1).

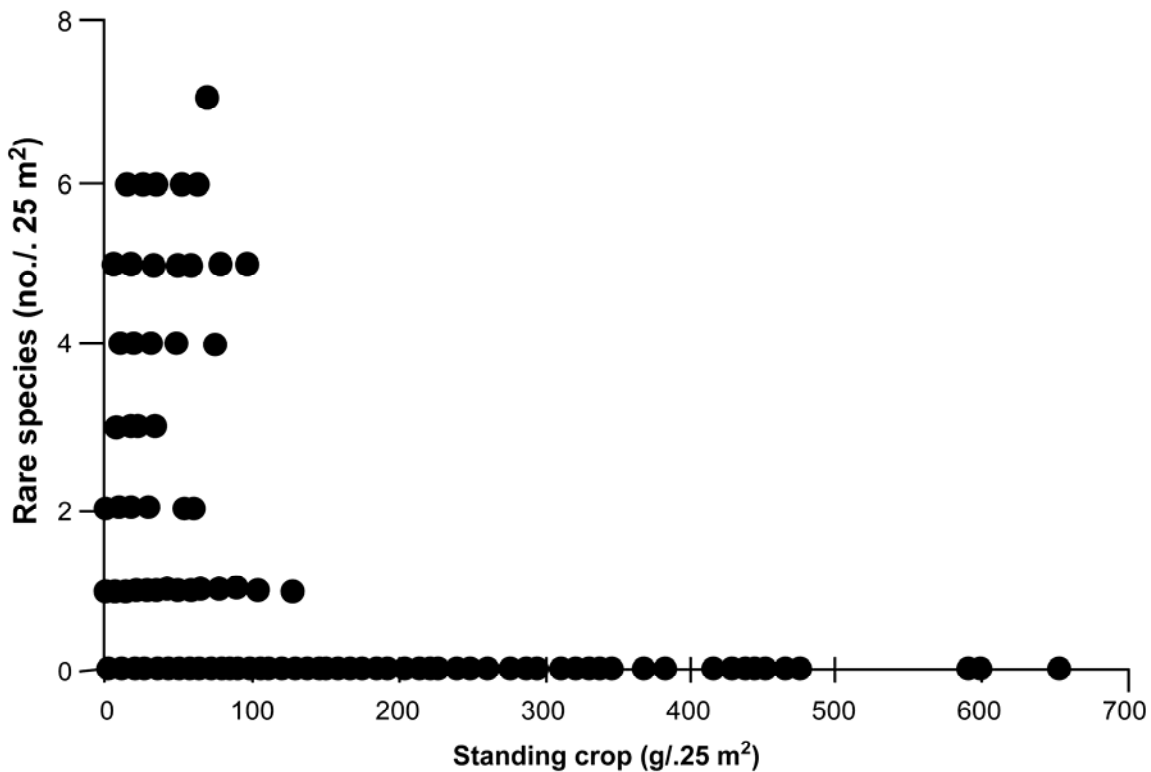


Figure AX5.3-1. Number of nationally rare species versus standing crop in each of 401 quadrants from wetlands in Ontario, Quebec, and Nova Scotia.

Source: Moore et al. (1989).

1 **AX5.3.3 Factors that Determine the Sensitivity of Aquatic Ecosystems**

3 **AX5.3.3.1 Fresh Water Sensitivity**

4 Some freshwater aquatic ecosystems in the United States are sensitive to nutrient
5 enrichment effects from atmospheric N deposition. In order to be sensitive to such effects, the
6 lake or stream must be N-limited. Conventional wisdom holds that most lakes and streams in the
7 United States are P-, rather than N-limited. As discussed below, new research suggests that this
8 may not always be the case. There is increasing evidence from surveys and paleolimnological
9 research suggesting N limitation is common, or was common, in many lakes prior to human
10 settlement. This shift in understanding is an important advancement in knowledge since the last
11 NAAQS review of the effects of NO_x emissions.

12 Surveys of the literature of fertilization experiments and lake studies found that
13 oligotrophic waters are commonly N-limited, especially undisturbed northern temperate or
14 boreal lakes that receive low levels of atmospheric N deposition (Elser et al., 1990; Bergström
15 et al., 2005). An examination of EPA Western Lakes Survey (WLS) data (Eilers et al., 1987)
16 found enhanced N concentrations in high elevation lakes adjacent to and downwind of urban
17 centers (Fenn et al., 2003a). A survey of 62 lakes that were the subject of N-enrichment studies
18 reported a mean increase in phytoplankton biomass of 79% in response to N-enrichment
19 (average of 46.3 µeq/L N) (Elser et al., 1990). Long-term measurements at Lake Tahoe, CA
20 showed that primary productivity has doubled, while water clarity has declined, mostly as a
21 result of atmospheric N deposition (Goldman, 1988; Jassby et al., 1994). A meta-analysis of
22 lakes from 42 regions of Europe and North America concluded that atmospheric N deposition
23 was responsible for increased concentrations of N in lake water, and elevated phytoplankton
24 biomass (Bergström and Jansson, 2006). Bergström et al. (2005) found a consistent pattern of
25 nutrient limitation showing N limitation for deposition below approximately 2.5 kg N/ha/yr, co-
26 limitation of N and P for deposition between ~2.5 and 5.0 kg N/ha/yr, and P limitation in areas
27 with N deposition greater than 5.0 kg N/ha/yr.

28 Based on current understanding, eutrophication effects on freshwater ecosystems from
29 atmospheric deposition of N are of greatest concern in lakes and streams that have very low
30 productivity and nutrient levels and that are located in remote areas. In more productive and less
31 remote fresh waters, nutrient enrichment from N deposition does not necessarily stimulate

1 productivity or community changes because P is more commonly the limiting nutrient. Also, in
2 many places with even minor levels of human disturbance, nutrient enrichment with both N and
3 P from non-atmospheric anthropogenic sources is common.

4 In a review covering the Rocky Mountains of Colorado and Wyoming, Burns (2004)
5 concluded that the effects of atmospheric N deposition on aquatic ecosystems in the region were
6 uncertain and that a widespread shift from N to P limitation had not been clearly demonstrated.
7 Burns (2004) stated that recent studies did suggest a change in diatom species dominance in the
8 1950s, but widespread species changes across lakes in the region and the role of N deposition in
9 these changes needed confirmation. Thus, the available data were not clear at that time, but
10 suggested that some changes had likely occurred in some aquatic ecosystems.

11 Recent research (e.g., Wolfe et al., 2001, 2003, 2006; Lafrancois et al., 2003; Das et al.,
12 2005; Saros et al., 2005) has provided additional evidence indicating that N deposition has
13 played an important role in influencing the productivity of oligotrophic, high-elevation lakes in
14 the western United States and Canada, and the Canadian arctic. There is evidence suggesting
15 historical N-limitation of some lakes based on paleolimnological studies conducted in
16 mountainous regions of the western United States that have been the recipient of elevated levels
17 of N, but not S, deposition over background values. A study of lakes in the Beartooth Mountains
18 of Montana-Wyoming by Saros et al. (2005) combined evaluation of resource requirements for
19 dominant diatom species with paleolimnological reconstructions and contemporary surveys of
20 the flora of seven lakes. Results reinforced the likelihood that recent increases in dominant
21 diatom numbers have been the result of N enrichment rather than climatic change (Saros et al.,
22 2005). Available data suggest that the increases in total N deposition do not have to be large in
23 order to elicit an ecological effect; a hindcasting exercise determined that the change in Rocky
24 Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an
25 increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes
26 inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at
27 about 1.5 kg N/ha deposition (Saros et al., 2003). Pre-industrial inorganic N deposition is
28 estimated to have been only 0.1 to 0.7 kg N/ha based on measurements from remote parts of the
29 world (Galloway et al., 1995; Holland et al., 1999). In the western United States, pre-industrial,
30 or background, inorganic N deposition was estimated by Holland et al. (1999) to range from 0.4
31 to 0.7 kg N/ha/yr.

1 The paleolimnological method of taxonomic identification of fossil diatoms in lake
2 sediments has been augmented in recent years with cell counts and pigment concentrations of
3 chlorophyll and chlorophyll derivatives, rendering inferences about trophic state from proxies
4 preserved in sediments more robust than before (Das et al., 2005). Paleolimnological studies of
5 mountain lakes that have only been disturbed by atmospheric deposition and climate change
6 have reported changes in diatom species assemblages, increases in cell numbers, and pigment-
7 inferred increases in whole lake primary production. These inferred changes have been
8 coincident with regional surrogates for increased N deposition. Such changes have included
9 increases in human population, industrial animal production, and fossil fuel combustion
10 emissions (Wolfe et al., 2001, 2003; Saros et al., 2003; Das et al., 2005). In most, but not all, of
11 these studies, the observed changes in ecology were inconsistent with changes in climate and
12 more concordant with effects from increased atmospheric N deposition.

13 A series of *in situ* meso- or microcosm N amendment experiments going back more than
14 30 years showed increases in lake algal productivity. Lake 226S in Ontario's Experimental
15 Lakes Area (ELA) showed doubling of average epilimnetic chlorophyll *a* over 5 years of
16 fertilization. However, because the response to P fertilization was much greater, the effects of N
17 were ignored (Schindler, 1980). Other ELA lakes with N:P ratios of 5:1 and 15:1 had 3 to 10
18 times greater increases in chlorophyll *a* than Lake 226S (Schindler, 1980). Similar experiments
19 at Castle Lake, CA, the Snowy Range of southern Wyoming, and Alaskan arctic foothill lakes
20 yielded measurable increases in chlorophyll *a* and primary productivity with N amendments
21 (Axler and Reuter, 1996; Levine and Whalen, 2001; Nydick et al., 2003, 2004a; Lafrancois et al.,
22 2004). Experiments conducted with mesocosms in lakes where NO_3^- was below detection found
23 a strong response in phytoplankton biomass with additions of N (bringing concentrations to
24 ~ 1.0 mg N/L) and even stronger responses to additions of N+P, but not P alone (Lafrancois et al.,
25 2004). The reverse was also found in Colorado Front Range lakes with ambient NO_3^-
26 concentrations of ~ 1.0 mg/L: productivity increased with additions of N+P or P only, but not N
27 alone (Lafrancois et al., 2004).

28 Lake bioassay experiments that enriched the water column down into the sediments
29 found enhancement of productivity in pelagic and benthic algae, in addition to stimulating
30 periphyton growth on bioassay walls in experiments in California, Wyoming, and Massachusetts
31 (Axler and Reuter, 1996; Nydick et al., 2004b; Smith and Lee, 2006). Many studies have shown

1 N-limitation of stream periphyton. Nitrogen amendment experiments with 6.4 μM N to small
2 arctic Alaskan streams elicited responses throughout the ecosystem, including enhanced primary
3 production, enhanced fungal biomass and elevated leaf litter decomposition rates, and a fourfold
4 to sevenfold greater benthic macroinvertebrate abundance (Benstead et al., 2005). A study in
5 Texas found some instances where the rivers were found to be seasonally N-limited, and other
6 instances of year-round N-limitation (Stanley et al., 1990). Strong N limitation of benthic algae
7 has also been inferred in streams of Arizona (Grimm and Fisher, 1986), California (Hill and
8 Knight, 1988), Missouri (Lohman et al., 1991), and Montana (Lohman and Priscu, 1992; Smith
9 and Nicholas, 1999).

10 A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America,
11 including many of the studies described above, found algal growth enhancement from N
12 amendments to be common in slightly less than half the studies (Elser et al., 1990). There was
13 a mean increase in phytoplankton biomass of 79% in response to N enrichment (average of
14 46.3 $\mu\text{eq/L}$ N) (Elser et al., 1990). This meta-analysis was recently repeated with a much large
15 data set and similar results (Elser et al., 2007). Freshwater enrichment bioassay studies from 990
16 separate studies worldwide were gleaned from the literature. The \ln -transformed response ratio
17 (RR_X), a frequently used effect metric in ecological meta-analysis, was equal at about 0.3 for N
18 and P experiments with stream benthos (periphyton) bioassays, and approximately equal at about
19 0.2 for lake phytoplankton. There was a stronger response to P than N in lake benthos studies,
20 but the RR_X for N was still about 0.3, showing that many sites increased productivity when
21 fertilized with N alone (Elser et al., 2007).

22 High-elevation lakes in the Sierra Nevada are primarily oligotrophic. Even small
23 changes in the nutrient supply can impact algal productivity (Sickman et al., 2003a). Changes in
24 other environmental parameters can also be important. Measurement of nutrient concentrations
25 in Emerald Lake over a period of 19 years suggested that NO_3^- concentration declined between
26 1983 and 1995. This was likely caused by changes in the snow regime induced by a drought
27 during the period 1987 to 1992 (Sickman et al., 2003a). Years that had shallow and early
28 melting snowpacks generally had lower snowmelt NO_3^- concentration. In addition, declines in
29 NO_3^- concentration during the growing season even in the wet years of 1993 through 2000 were
30 likely the result of increased P loading to Emerald Lake and the consequent release of
31 phytoplankton from P limitation (Sickman et al., 2003a).

1 Data from 28 Sierra Nevada lakes sampled in 1985 and again in 1999 also suggested that
2 NO_3^- concentrations decreased during that period and total P concentrations increased in more
3 than 70% of the lakes sampled. Sickman et al. (2003a) concluded that lakes throughout the
4 Sierra Nevada appear to be experiencing measurable eutrophication in response to atmospheric
5 deposition of nutrients, but N deposition is only part of the process.

6 Because there was evidence of increased P loading throughout the Sierra Nevada,
7 Sickman et al. (2003a) concluded that site-specific P sources were unlikely to be the cause of
8 observed trends. They proposed that atmospheric deposition and accelerated internal cycling of
9 P in response to changes in climatic factors were the most likely sources of increased P loading
10 to the Sierra Nevada Lakes. It is not known why atmospheric deposition of P to these lakes has
11 increased over time. Possibilities include use of organo-phosphate pesticides and aeolian
12 transport of soils and dust that are high in P from the San Joaquin Valley to the Sierra Nevada
13 Mountains (Bergametti et al., 1992; Lesack and Melack, 1996; Sickman et al., 2003a).

14 The implications of all these studies are that the productivity of many freshwater
15 ecosystems is limited by the availability of N, European and North American lakes may have
16 been N-limited before human-caused disturbance, and remote lakes remained N-limited until
17 slight increases in atmospheric N deposition brought about an increase in phytoplankton
18 biomass. Increases in algal biomass are associated with changes in algal assemblages that favor
19 certain species over others. A widespread increase in the relative abundance of *Asterionella*
20 *formosa* and *Fragilaria crotonensis* has occurred in oligotrophic lakes across the western United
21 States; these changes have been documented from both lake sediments and limnological surveys
22 (Goldman, 1988; Interlandi et al., 1999; Wolfe et al., 2001; Saros et al., 2003).

23 24 **AX5.3.3.2 Estuary and Coastal Water Sensitivity**

25 Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to
26 increased N loading (D'Elia et al., 1986; Howarth and Marino, 2006). This is at least partly
27 because the rate of denitrification by microbes found in estuarine and marine sediments releases
28 much of the added N inputs back into the atmosphere (Vitousek et al., 1997a). There is a
29 scientific consensus that N-driven eutrophication of shallow estuaries has increased over the past
30 several decades and that environmental degradation of coastal ecosystems is now a widespread
31 occurrence (Paerl et al., 2001). For example, the frequency of phytoplankton blooms and the

1 extent and severity of hypoxia have increased in the Chesapeake Bay (Officer et al., 1984) and
2 Pamlico estuaries in North Carolina (Paerl et al., 1998) and along the continental shelf adjacent
3 to the Mississippi and Atchafalaya rivers discharges to the Gulf of Mexico (Eadie et al., 1994).
4 It is partly because many estuaries and near-coastal marine waters are degraded by N enrichment
5 that they are highly sensitive to potential adverse impacts from N addition from atmospheric
6 deposition. Thus, non-atmospheric sources of N have increased the sensitivity of estuarine and
7 marine waters to atmospheric sources of N enrichment. Such sensitivity is most pronounced in
8 areas that include extensive agricultural and/or urban land uses that constitute substantial non-
9 atmospheric watershed sources of N. The implications to society of this development are severe,
10 in part because estuaries constitute the most valuable of all ecosystems with respect to services
11 provided, including fish and shellfish harvest, waste assimilation, and recreational activities
12 (Costanza et al., 1997).

13 There are a variety of factors that govern the sensitivity of estuaries and near-coastal
14 marine waters to eutrophication from atmospheric N deposition. Of critical importance is the
15 total N input from all sources, including both atmospheric and non-atmospheric sources. Other
16 key elements include the dilution capacity of the watershed and flushing time. Dilution capacity
17 reflects the volume of water available to dilute added N. Flushing rate reflects the time required
18 for inflowing water to replace the estuary volume (Bricker et al., 1999; NRC, 2000). Other
19 potentially important factors can include the following (NRC, 2000):

- 20 • Physiography (geomorphology, dominant biological communities, biogeographic
21 province);
- 22 • Type of primary production base (i.e., seagrasses, phytoplankton, coral, attached
23 intertidal algae, etc.);
- 24 • Stratification and extent to which phytoplankton occupy the nutrient-rich photic zone;
25 and
- 26 • Allochthonous inputs of organic matter.

27 A number of factors control the N loading rates to estuaries and the potential effects of N
28 deposition on nutrient loading and algal blooms. Estuaries communicate with fresh water on the
29 upstream side and with the ocean on the downstream side. The flushing of fresh river water
30 through the system and the movement and mixing of salt water from the ocean are complicated
31 and are always changing in response to weather and tidal cycles. The surface area, volume, and
32 depth of the estuary are also critical factors governing the sensitivity of an estuary to N inputs.

1 Decreases in grazer, filter-feeder, and higher trophic level populations of fish and shellfish
2 exacerbate problems associated with nutrient over-enrichment (Jackson et al., 2001).

3 At the upstream end of an estuary, the water is primarily fresh much of the time.
4 Discharge of N from the land surface, only a part of which is of atmospheric origin (mainly as
5 deposition to the land that subsequently leached to the river water), dominates new N inputs.
6 Further downstream within the estuary, where fresh water is more thoroughly mixed with
7 saltwater, much of the terrestrial N load is assimilated by phytoplankton and benthic flora or
8 removed by microbes in the process of denitrification (Paerl, 2002). The importance of
9 atmospheric N as a contributor to the total N load beyond this zone probably increases, but there
10 are no data to evaluate that.

11 The principal watershed features that control the amount of increased N flux to estuaries
12 in the United States include human population, agricultural production, and the size of the
13 estuary relative to its drainage basin (Peierls et al., 1991; Caddy, 1993; Fisher et al., 2006).
14 Dense human populations generate large volumes of nutrient-rich wastewater. Tertiary sewage
15 treatment can reduce effluent N concentrations to less than 35 μM , but these technologies have
16 not been promoted as aggressively in the United States as elsewhere (Conley et al., 2002; U.S.
17 Environmental Protection Agency, 2003). Agricultural production is heavily dependent on
18 fertilizer application to generate high yields from small areas. Fertilizer application has
19 dramatically increased NO_3^- concentrations in ground water in many agricultural areas (Bohlke
20 and Denver, 1995), which can leach to surface waters. Large terrestrial drainage basins that
21 drain into small estuaries tend to have high nutrient flux if the land is heavily populated or used
22 for agriculture.

23 In addition to estuaries, coastal marine ecosystems are highly susceptible to nutrient
24 enrichment, especially from N. Land clearing, agricultural land use, sewage treatment discharge,
25 and atmospheric deposition can all result in high loadings of N to the coastal zone. Excessive N
26 inputs contribute to a range of impacts, including enhanced algal blooms, decreased distribution
27 of seagrasses, and decreased dissolved oxygen (DO) concentration (Valiela et al., 1992; Nixon,
28 1995; Borum, 1996; Bricker et al., 1999). Because of human population growth and the great
29 popularity of coastal areas, there is substantial potential for increased N loading to coastal
30 ecosystems from both atmospheric and non-atmospheric sources.

1 There is a strong scientific consensus that N is the principal cause of coastal
2 eutrophication in the United States (NRC, 2000). On average, human activity has likely
3 contributed to a sixfold increase in the N flux to the coastal waters of the United States, and N
4 now represents the most significant coastal pollution problem (Howarth et al., 2002; Howarth
5 and Marino, 2006). Atmospheric deposition is responsible for a portion of the N input.

6 Results of empirical observations and short-term (3 week) marine mesocosm experiments
7 suggest that there can be wide variation in the response of autotroph biomass to nutrient addition
8 (Cloern, 2001; Olsen et al., 2006). Such variation may be attributable to the time scale of the
9 observations, rate of water exchange, grazing pressure, and other environmental factors (Olsen
10 et al., 2006).

11 **AX5.3.4 Sensitivity of Other Types of Ecosystems**

13 Agricultural lands are excluded from this discussion of ecosystems sensitive to nutrient
14 enrichment effects of N deposition because crops are routinely fertilized with amounts of N (100
15 to 300 kg/ha) that far exceed air pollutant inputs even in the most polluted areas (U.S.
16 Environmental Protection Agency, 1993). High rates of fertilization can contribute to ground
17 water NO₃⁻ contamination and eutrophication of some surface waters, especially estuaries.
18 However, assessment of the environmental effects of agricultural N fertilization is beyond the
19 scope of this annex. Agricultural crops can also be damaged by exposure to high atmospheric
20 concentrations of ground-level O₃, the formation of which is catalyzed by atmospheric NO_x.

21 22 **AX5.4 DISTRIBUTION OF MOST SENSITIVE ECOSYSTEMS**

23 **AX5.4.1 Distribution of Sensitive Terrestrial Ecosystems**

24 25 **AX5.4.1.1 Forest Ecosystems**

26
27 In general, the most affected forest ecosystems in the United States are expected to be
28 those that now receive relatively high levels of N deposition, that are naturally adapted to very
29 low nutrient supply, or that have already experienced depletion of soil base cations associated
30 with high levels of acidic deposition. These types of forests are known to exist in the greater Los
31 Angeles area, in the red spruce and northern hardwood forests of the northeastern United States,
32

1 at high-elevation in the southeastern United States, and in the unglaciated regions of the mid-
2 Atlantic that have been impacted by acidic deposition.

3 Mixed conifer forests and chaparral plant communities directly exposed to air pollution
4 from greater Los Angeles receive sufficiently high levels of atmospheric N deposition to be N
5 saturated. Fenn et al. (1996) concluded that symptoms of N saturation were evident in mixed
6 conifer or chaparral sites receiving atmospheric deposition of 20 to 25 kg N/ha/yr or higher.
7 This is double the N deposition levels commonly encountered in forest ecosystems in the eastern
8 United States, and is likely to be high enough to cause nutrient enrichment effects on plants.

9 In northeastern and some southeastern forests that receive atmospheric N deposition
10 higher than about 10 kg/ha/yr, elevated concentrations of NO_3^- in surface waters are common
11 (Aber et al., 2003), which suggests that their watersheds are also receiving excess N input above
12 vegetative demand. However, little information on direct effects on plant communities in the
13 eastern United States is available. Beyond this basic overview, there is insufficient basis for
14 ranking eastern forests according to their sensitivity to nutrient enrichment effects from N
15 deposition.

16 The boreal forest represents the largest terrestrial biome on Earth, and as such can have a
17 large influence on global cycling of N and other nutrients. Plant growth in the boreal forest is
18 limited mainly by N availability, in part because of slow mineralization of organic materials in
19 the harsh climate (Vitousek and Howarth, 1991). Högberg et al. (2006) reported the effects of
20 long-term (30 year) N fertilization at high loading rates (34 and 68 kg N/ha/y) on an unpolluted
21 boreal forest in northern Sweden. They found a gain of 50 m³/ha stemwood at the higher loading
22 rate and a gain of 100 m³/ha stemwood at the lower loading rate. Conceptual models of N
23 cycling in the boreal forest have typically assumed that mineralization of organic N is required
24 for plant uptake of N (Näsholm et al., 1998). However, it has been demonstrated in laboratory
25 studies (Chapin et al., 1993) and field studies (Näsholm et al., 1998) that some boreal plants are
26 capable of directly taking up amino acids from the soil, and therefore bypassing the need for
27 prior mineralization. The interactions among soil abiotic processes, mycorrhizal associations,
28 microbes, and plants are complex and poorly understood. Nevertheless, these interactions are
29 important to global N cycling and to boreal plant species composition because organic N
30 concentrations are typically high in the soil of boreal forests. It appears that atmospheric N

1 deposition and climate warming have the potential to alter boreal forest plant communities by
2 shifting nutritional processes from organic to inorganic N uptake (Näsholm et al., 1998).

3 4 **AX5.4.1.2 Grasslands**

5 Grasslands are sensitive to nutrient enrichment from N deposition. Data with which to
6 quantify grassland sensitivity in the United States are largely not available. Increased N supply
7 can alter species composition, increase productivity, and contribute to increased herbivory
8 (Tilman and Wedin, 1991; Wedin and Tilman, 1996; Stevens et al., 2004; Throop and Ler dau,
9 2004). It is not clear whether atmospheric N deposition to grasslands in this country is
10 commonly high enough to cause adverse effects.

11 12 **AX5.4.1.3 Alpine Tundra**

13 The western United States contains extensive land areas that receive low levels of
14 atmospheric N deposition, interspersed with hot spots of relatively higher N deposition
15 downwind of large metropolitan centers and agricultural areas (Fenn et al., 2003a). Alpine plant
16 communities occur in some of the areas that receive moderately elevated atmospheric N
17 deposition. Because alpine plant species are typically adapted to low nutrient availability, they
18 often are sensitive to effects from N enrichment.

19 The alpine areas most likely subject to adverse impact are the alpine vegetation zones
20 located in proximity to the major urban and agricultural emissions source areas. These are
21 located in the Sierra Nevada in southern California, the Front Range in Colorado, and the
22 Cascade Mountains in Washington (Figure AX5.4-1).

23 24 **AX5.4.2 Distribution of Sensitive Transitional Ecosystems**

25 Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the
26 effects of N deposition. In the conterminous United States, peat-forming bogs are most common
27 in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S.
28 Environmental Protection Agency, 1993). In Alaska, these ecosystems are common in poorly
29 drained locations throughout the state. Other types of wetlands occur across broad areas of the
30 United States (Figure AX5.4-2). It is not clear whether current levels of N deposition cause
31 extensive eutrophication to these ecosystems.

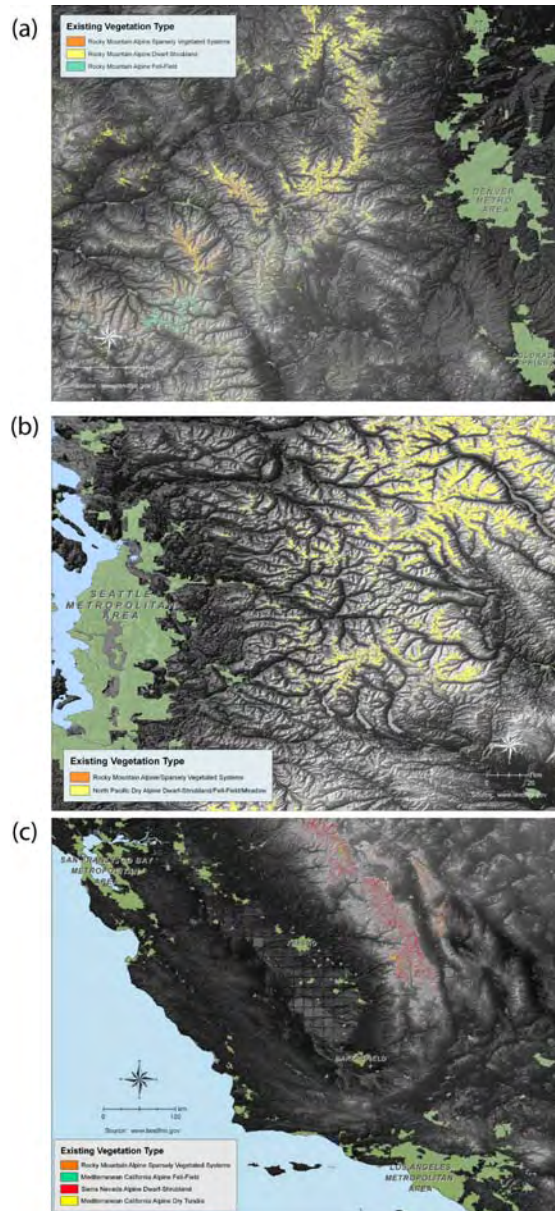
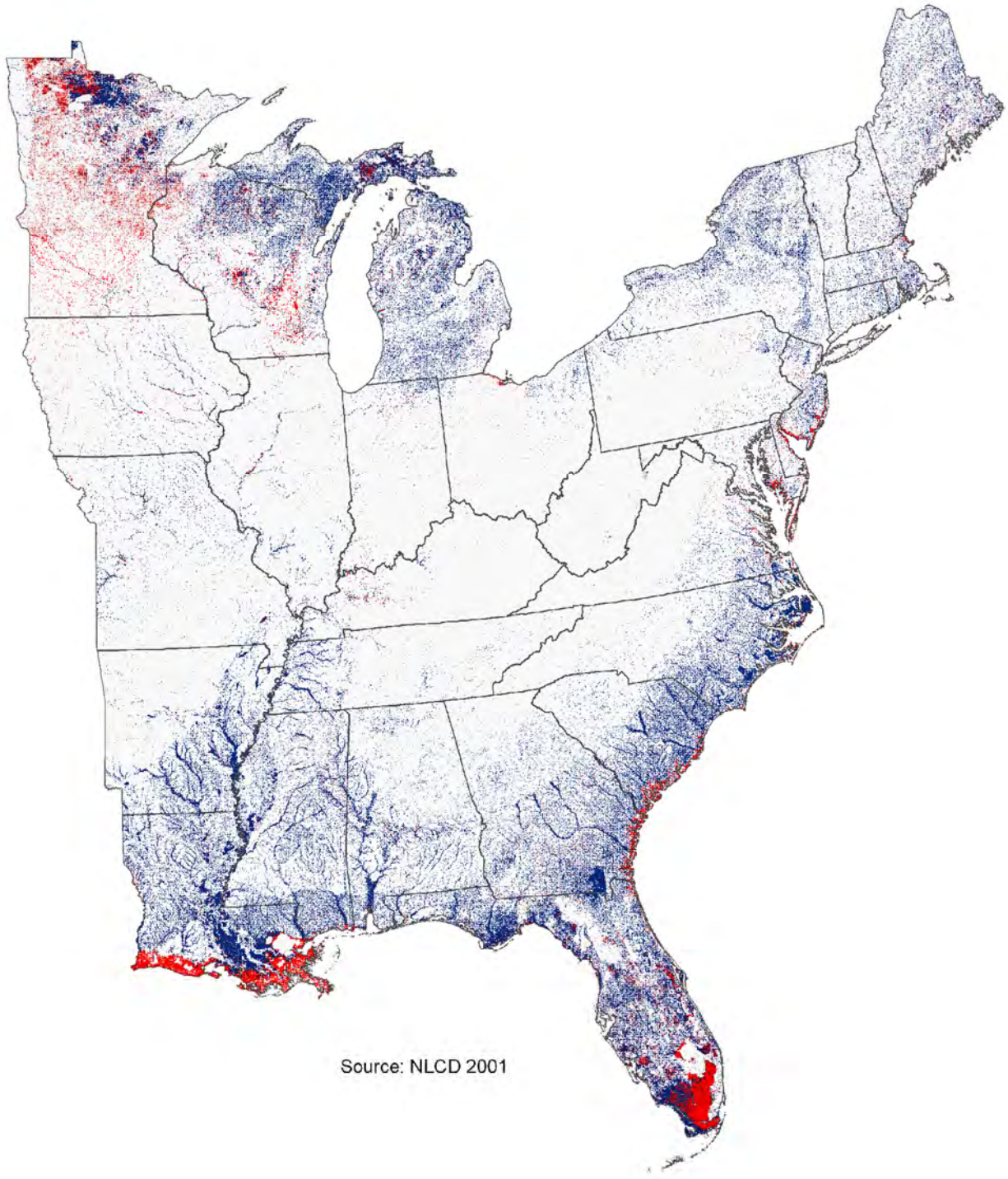


Figure AX5.4-1. Distribution of alpine vegetation in three western regions that are in close proximity to urban and agricultural sources of atmospheric nitrogen emissions: a) the Denver-Fort Collins region of Colorado, b) the Seattle-Tacoma region of Washington, and c) the Fresno-Los Angeles area of California (the blue line on the map is the California/Nevada border). Alpine vegetation in these areas is sensitive to nutrient enrichment effects from atmospheric nitrogen deposition.

Source: Vegetative distribution data were taken from the national map LANDFIRE (September 2006) (<http://gisdata.usgs.net/website/landfire/>).



Source: NLCD 2001

Figure AX5.4-2. Map of location of wetlands in the eastern United States. Woody wetlands are coded blue and emergent herbaceous wetlands are coded red.

Source: Data were obtained from the National Land Cover Data (NLCD) (2001) (<http://www.mrlc.gov/>).

1 Coastal marsh ecosystems, unlike bog ecosystems, often receive large N inputs in tidal
2 water, ground water, and surface runoff. At many locations, especially along the Atlantic and
3 Gulf coasts, atmospheric N inputs probably contribute to eutrophication problems in coastal
4 marshes. Atmospheric inputs to these systems are important because any N addition has the
5 potential to contribute to eutrophication of coastal marshes and nearby marine and estuarine
6 ecosystems.

7 Nutrient concentrations in wetland waters associated with the Laurentian Great Lakes
8 suggest that coastal Great Lakes wetlands are N-limited. Hill et al. (2006) found that more
9 wetlands were N- than P-limited at each of the five Laurentian Great Lakes. This result is
10 consistent with the apparent general N-limitation of North American marsh lands (Bedford et al.,
11 1999). Nutrient loading to coastal wetlands is a concern throughout the lower lakes (Lakes Erie
12 and Ontario, and the southern part of Lake Michigan) and in some localized areas of the upper
13 lakes (Hill et al., 2006). Both agricultural and atmospheric sources of nutrients contribute to this
14 stress.

15 **AX5.4.3 Distribution of Sensitive Aquatic Ecosystems**

16 **AX5.4.3.1 Fresh Waters**

17 High elevation lakes in the western United States are considered some of the most
18 sensitive aquatic ecosystems to N deposition. The aquatic biota most likely to show rapid
19 eutrophication effects from N deposition are algae. Such effects are most likely to occur in fresh
20 waters that historically received low levels of nutrient inputs.

21 Studies have shown an increase in lake phytoplankton biomass with increasing N
22 deposition in the Snowy Range in Wyoming (Lafrancois et al., 2003), the Sierra Nevada
23 Mountains in California (Sickman et al., 2003a), Sweden (Bergström et al., 2005), and across
24 Europe (Bergström and Jansson, 2006). Community shifts in phytoplankton were observed in
25 the Snowy Range, with chrysophytes favored in lakes having lower N and cyanophytes and
26 chlorophytes favored in lakes having higher N (Lafrancois et al., 2003). Sediment cores from
27 lakes in the Colorado Front Range showed increasing representation of mesotrophic diatoms in
28 recent times, as compared with pre-development conditions (Wolfe et al., 2001). In Lake Tahoe,
29 CA, there has been a sharp increase in the ratio of araphidinate pennate to centric diatoms since
30 about 1950 (largely due increases in *Fragilaria crotenensis*), associated with increased N loading
31
32

1 to the lake (Goldman, 1988). Jassby et al. (1994) showed that atmospheric deposition supplies
2 most of the N to Lake Tahoe.

3 It is generally believed that the Laurentian Great Lakes are P-Limited (Schelske, 1991;
4 Downing and McCauley, 1992; Rose and Axler, 1998). Water quality in the open waters of
5 these lakes has been improving in recent years in response to controls on point sources of P
6 (Nicholls et al., 2001). Work by Levine et al. (1997), however, suggested a more complicated
7 pattern of response to nutrient addition for Lake Champlain. They added nutrients to *in situ*
8 enclosures and measured indicators of P status, including alkaline phosphatase activity and
9 orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during
10 summer, N addition also resulted in algal growth stimulation. Phosphorus sufficiency appeared
11 to be as common as P deficiency. During spring, phytoplankton growth was not limited by P, N,
12 or silica (Si), but perhaps by light or temperature (Levine et al., 1997).

13 14 **AX5.4.3.2 Estuaries and Coastal Waters**

15 Nitrogen over-enrichment is a major environmental problem for coastal regions of the
16 United States, especially in the eastern and Gulf Coast regions, where atmospheric N deposition
17 is generally highest (See Section AX4.1.1, Figure AX4.1-3). Effects are especially pronounced
18 in estuaries. For example, of 138 estuaries examined by Bricker et al. (1999), 44 were identified
19 as showing symptoms of nutrient over-enrichment. Estuaries are among the most biologically
20 productive ecosystems on Earth and provide critical habitat for an enormous diversity of life
21 forms, especially fish. Of the 23 estuaries examined in the Northeast, 61% were classified as
22 moderately to severely degraded (Bricker et al., 1999).

23 Increased N deposition can enhance estuarine and marine primary productivity and favor
24 growth of specific phytoplankton functional groups and size categories. Nitrogen contribution
25 also changes the nutrient ratios of N:P:Si, which can affect phytoplankton community
26 composition and growth. These changes are most likely to occur in areas that receive high inputs
27 of both atmospheric and non-atmospheric N. Estuarine and coastal waters that receive drainage
28 from areas with extensive urban and agricultural land use are generally most susceptible to
29 adverse impacts from atmospheric N deposition.

30 The sensitivity of estuarine and coastal marine waters to eutrophication from atmospheric
31 N deposition depends on the supply of, and relative availability of, N and P. The data for 92
32 worldwide coastal marine sites analyzed by Smith (2006), for which measurements of both total

1 N and total P were available, illustrated that about half of the sites had total nitrogen (TN):total
2 phosphorus (TP) above the Redfield ratio, which is commonly used to evaluate nutrient
3 limitation in freshwater (TN:TP = 16). That analysis provided additional support for the
4 hypothesis (Downing, 1997) that more pristine marine environments (annual mean TP < 0.8 μM)
5 tend to have TN:TP ratios in excess of the Redfield ratio, suggesting the possibility of P
6 limitation (Smith, 2006). In general, it is expected that the upper sections of estuaries, which are
7 commonly dominated by fresh water, tend to be P-limited. The lower sections contain primarily
8 marine water, and tend to be N-limited.

9 River discharge has a huge influence on the hydrology and nutrient cycling of estuaries.
10 For example, discharge from the large watershed of the Susquehanna River is important to the
11 seasonal and interannual variability in the hydrology of Chesapeake Bay (Fisher et al., 1988;
12 Malone et al., 1988). When discharge from the Susquehanna River is low, summer
13 phytoplankton biomass in Chesapeake Bay tends to be low compared to spring conditions, and
14 the phytoplankton community is dominated by small and flagellated forms (Marshall and
15 Lacouture, 1986). Under higher river flows, summer phytoplankton biomass in the bay is higher,
16 and has an increased prevalence of diatoms (Paerl et al., 2006).

17 Hydrologic variation interacts with nutrient supply to control phytoplankton seasonal
18 patterns in Chesapeake Bay. High biomass during the spring diatom bloom leads to consequent
19 sedimentation of organic material out of the photic zone during the transition to summer (Malone
20 et al., 1996; Harding et al., 2002). Microbial decomposition of this material then fuels the
21 pattern of summer anoxia in bottom waters (Paerl et al., 2006).

22 At upstream freshwater locations in Chesapeake Bay, P is often the limiting nutrient
23 (Larson et al., 1985). At the transition between fresh water and salt water, N and P may be co-
24 limiting, whereas the saltwater environments of the outer bay are usually N-limited (Fisher et al.,
25 1988; Rudek et al., 1991). Nutrient limitation varies in space and over time, in response to
26 changes in discharge and temperature that interact with estuarine morphology and hydrology
27 (Paerl et al., 2006).

28 Smith (2006) evaluated nutrient limitation and trophic state data from 92 estuarine and
29 marine coastal zone ecosystems worldwide. Average concentrations of chlorophyll *a* were
30 strongly dependent on the mean concentrations of TN and TP in the water column. The identity
31 of the primary limiting nutrient for marine phytoplankton growth was generally predictable

1 based on the molar ratio of TN:TP. There was a large amount of scatter at any given nutrient
2 condition, reflecting the influence of other physical and biological factors that enhance or
3 depress algal biomass. Nevertheless, the threshold TN:TP ratio below 20 was associated with
4 strong N limitation on phytoplankton. As was emphasized in earlier work on nutrient limitation
5 in fresh waters by Redfield (1958) and Reiners (1986), elemental stoichiometry is a fundamental
6 property of life that probably stems from the shared phylogenetic histories of marine and
7 freshwater autotrophs (Sterner and Elser, 2002; Smith, 2006).

8 The scientific community is at an early stage in development of an understanding of the
9 effects of anthropogenic activities on the stoichiometry of nutrient loading to estuaries and
10 marine waters (Turner, 2002; Dodds, 2006). Changes in nutrient stoichiometry in estuarine and
11 marine ecosystems could alter algal assemblages and cascade to higher trophic levels (Frost
12 et al., 2002).

13 14 15 **AX5.5 EFFECTS ON BIOTA**

16 17 **AX5.5.1 Kinds of Effects**

18 Excess N can produce a range of effects on biota within terrestrial and aquatic
19 ecosystems. Some of the more pronounced potential effects include changes in productivity,
20 species composition, and species richness. These general types of effects are described below,
21 followed by a description of the species thought to be most sensitive to these effects within
22 terrestrial, transitional, and aquatic ecosystems.

23 24 **AX5.5.1.1 Productivity**

25 The concentration of NO_x in the atmosphere and the N load contributed to aquatic
26 environments by atmospheric deposition in the United States are generally not considered high
27 enough to induce direct injury or toxicity to vegetation or aquatic biota. However, atmospheric
28 deposition of N, and the associated production of ground-level O₃, can have indirect effects on
29 the productivity of terrestrial and aquatic ecosystems. These changes are discussed below and
30 represent a subtle shift in scientific understanding that has occurred since the previous AQCD
31 for N.

1 In general, atmospheric nutrient (e.g., N) deposition on an ecosystem that is deficient in
2 that nutrient will often cause an increase in growth, at least initially, especially of the primary
3 producers. If that same nutrient is deposited on an ecosystem that has an adequate supply of that
4 nutrient, there may be no appreciable nutrient enrichment effect, at least up to a point. Nutrient
5 input that is greatly in excess of biological demand will often cause toxicity, reduced growth, or
6 problems other than those associated with nutrient enrichment (i.e., N-saturation, acidification,
7 base cation depletion) (Figure AX5.5-1).

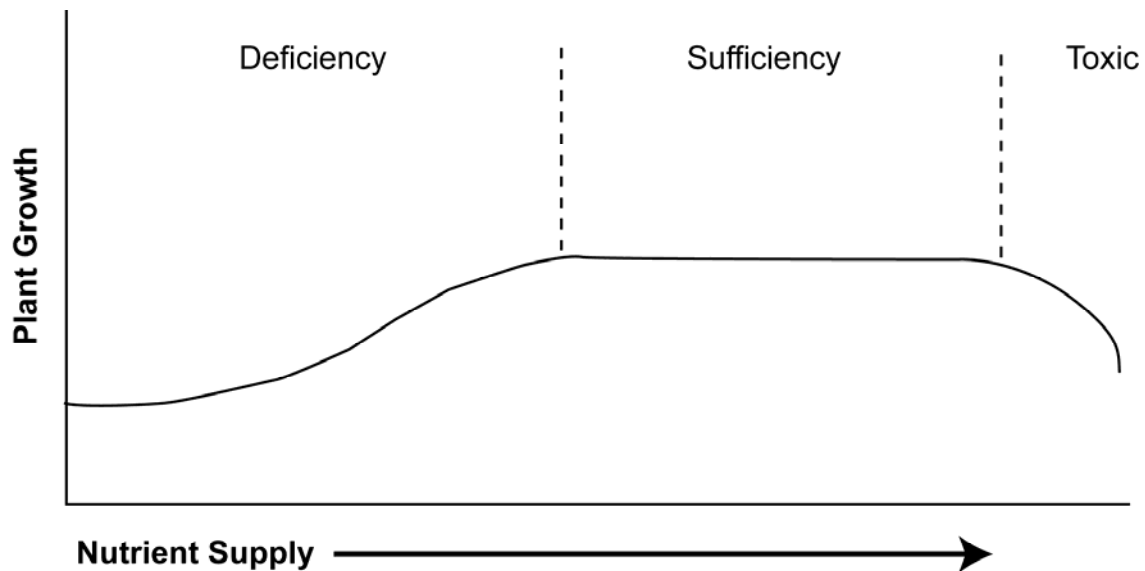


Figure AX5.5-1. Schematic representation of the response of vegetation to nutrient addition.

Source: U.S. Environmental Protection Agency (1993).

8 In terrestrial ecosystems, productivity can be affected by ground-level O₃, which is
9 formed by the interaction of NO_x and volatile organic compounds (VOCs). In the eastern United
10 States, ground level O₃ formation is controlled to a greater extent by NO_x emissions than by
11 VOCs (NRC, 1991; Ryerson et al., 2001). Indirect effects of NO_x emissions through ground-
12 level O₃ production include reduction in net photosynthetic capacity (Reich, 1987) and
13 associated changes in biomass production and C allocation (Laurence et al., 1994). Ozone
14 related decreases in above-ground forest growth appear to be in the range of 0% to 10% per year

1 (Chappelka and Samuelson, 1998). Extrapolation from seedling-level experiments is
2 complicated and uncertain, but process-level modeling offers promise for combining
3 physiological effects with stand- and site-level factors. One such analysis involving the PnET
4 ecosystem model estimated that O₃ exposure in the northeastern United States reduces annual
5 rates of NPP by 2% to 16%. Variation resulted mainly from differences in O₃ exposure levels,
6 and interactions with other atmospheric pollutants (Ollinger et al., 1997, 2002).

7 In freshwater ecosystems, excess contribution of N to N-limited systems can stimulate
8 algal productivity, which in turn can reduce DO levels. Extreme cases of DO reduction can
9 cause O₂ depletion, fish mortality, odor problems, and other aspects of water quality degradation.
10 To our knowledge, current atmospheric N deposition level in the United States is not high
11 enough to cause such extreme effects on fresh waters. The extent of effect is determined by the
12 level of N input in combination with characteristics of the receiving body of water and its
13 watershed. Especially important are the supply of P, which is often limiting in freshwater
14 ecosystems, and light availability. The most common, and easiest to document, indicators of
15 change in algal productivity are measures of water clarity and the concentration of chlorophyll *a*.
16 Clarity is also strongly influenced by erosional inputs of fine sediment to the lake or stream
17 system. Chlorophyll *a* concentration is generally more directly tied to algal productivity than is
18 water clarity.

19 Productivity investigations have included gradient studies in which the relationship
20 between lake N concentration and primary productivity (reported as chlorophyll *a*, NPP, or an
21 index such as the lake chemistry ratio of dissolved inorganic N [DIN] to total P, DIN:TP) was
22 surveyed and correlated with atmospheric N deposition. Productivity studies have also included
23 lake and stream bioassays in which N was added to waters in field or laboratory in order to
24 measure the response. We only found one long-term study that has documented observed
25 changes; 28 years of study in Lake Tahoe, CA showed that primary productivity has doubled
26 during that period, while water clarity has declined, mostly as a result of eutrophication from N
27 deposition (Goldman, 1988; Jassby et al., 1994).

28 Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive
29 low levels of atmospheric N deposition found strong relationships between N-limitation and
30 productivity where N deposition was low, and P and N+P limitations where N deposition was
31 higher (Fenn et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006). Chemical data

1 from 3,907 lakes and phytoplankton biomass data from 225 lakes from Swedish monitoring
2 programs were used to identify a clear north-south gradient of increasing lake concentrations and
3 algal productivity related to the pattern of increasing N deposition input (Bergström et al., 2005).
4 The lowest productivity was found at sites where wet N deposition was about 1.3 kg N/ha/yr;
5 increasing productivity occurred at greater than 2.2 kg N/ha/yr (Bergström et al., 2005).
6 Although these lakes are all in Sweden, the sheer number of them used to derive a strong
7 correlation between productivity and atmospheric N deposition makes the results of interest to
8 North American audiences.

9 Under oligotrophic conditions, bacteria generally compete better than phytoplankton for
10 the nutrients that tend to limit both autotrophs and heterotrophs. As nutrient availability
11 increases, conditions become increasingly more favorable for larger celled phytoplankton
12 (Roberts and Howarth, 2006). The total biomass of both phytoplankton and heterotrophic
13 bacteria increases along a trophic gradient. However, the biomass of heterotrophic bacteria
14 appears to increase more slowly than the biomass of phytoplankton with increasing nutrient
15 availability (Del Giorgio et al., 1997; Roberts and Howarth, 2006).

16 In coastal marine ecosystems, the nutrients most commonly associated with
17 phytoplankton growth are N, P, and Si. Interactions among the supplies of these nutrients can
18 affect phytoplankton species composition in ways that might impact ecosystem function
19 (Riegman, 1992; Paerl et al., 2001). The relative proportions of these nutrients are important
20 determinants of primary production, food web structure, and energy flow through the ecosystem
21 (Dortch and Whittedge, 1992; Justic et al., 1995a,b; Turner et al., 1998).

22 Nitrogen enrichment of marine waters can alter the ratios among nutrients and affect
23 nutrient limitation. For example, excessive N loading to Chesapeake Bay and its tributaries
24 during spring high-runoff periods contributes to periods of P limitation and co-limitation
25 (Boynton et al., 1995). The system then returns to N limitation during low-flow summer months
26 (Paerl, 2002). High loadings of N and P can increase the potential for Si limitation, with
27 associated changes in diatoms. Such changes to the phytoplankton community can also affect
28 higher trophic levels. For example, Officer and Ryther (1980) and Turner et al. (1998) suggested
29 that a shift in the Si:N atomic ratio to less than 1 would alter the marine food web. Specifically,
30 the diatom-to-zooplankton-to-higher trophic level ratios would decrease, whereas flagellated algae
31 (including those that can contribute to hypoxia) would increase (Paerl et al., 2001).

1 Perhaps the most important environmental effect of N input to coastal waters is the
2 development of hypoxia. The largest zone of hypoxic coastal water in the United States is in the
3 northern Gulf of Mexico on the Louisiana-Texas continental shelf. During midsummer, the
4 hypoxic zone has regularly been larger than 16,000 km² (Rabalais, 1998). The timing, duration,
5 and spatial extent of hypoxia are related mostly to the nutrient flux from the Mississippi River
6 (Justic et al., 1993, 1997; Rabalais et al., 1996; Lohrenz et al., 1997; Paerl et al., 2001).
7 Atmospheric deposition contributes a portion of the N load, but that portion is probably limited
8 (Paerl et al., 2001).

9 10 **AX5.5.1.2 Species Composition**

11 A common response to environmental stress is the tendency for the more sensitive
12 species to decrease in abundance, or to be eliminated, while the more tolerant species increase in
13 abundance (Woodwell, 1970). Selective removal of certain species can result in an impairment
14 of ecosystem function, change in community structure and food web dynamics, and decrease in
15 species richness and diversity. Such changes in species composition can occur in response to N
16 addition to terrestrial, aquatic, and transitional ecosystems.

17 In terrestrial ecosystems, changes in plant species occurrence in response to increased N
18 deposition will be most obvious in ecosystems that are deficient in N. This is because species
19 that are adapted to low N supply will often be more readily outcompeted by species that have
20 higher N demand (Aerts, 1990; Tilman and Wedin, 1991; Krupa, 2003). As a consequence,
21 some native species can be eliminated by N-enhanced eutrophication (Ellenberg, 1987;
22 Falkengren-Grerup, 1986, 1989; Roelofs, 1986; Stevens et al., 2004).

23 In high-elevation freshwater ecosystems that are N-limited, N deposition can contribute
24 to the changes in diatom species abundance to favor species more typical of mesotrophic
25 conditions. Similarly, in coastal ecosystems, eutrophication can cause changes in marine
26 biodiversity and species composition. There are few data documenting the long-term response of
27 coastal ecosystems to N loading. One such data set is available at Waquoit Bay, MA. Driscoll
28 et al. (2003a) reported a strong negative relationship between modeled N loading and measured
29 eelgrass area in Waquoit Bay based on measurements of eelgrass coverage from 1951 to 1992.

30 Phytoplankton production and community composition in estuarine and marine
31 environments also respond to differences in the form of atmospheric N input. Major algal
32 functional groups, including diatoms, dinoflagellates, cyanobacteria, and chlorophytes, may

1 show different responses to changing mixtures of added N (Paerl et al., 2002). Differential
2 phytoplankton responses, in turn, may cause changes in the species composition of zooplankton,
3 herbivorous fish, and higher trophic levels of aquatic biota.

4 5 **AX5.5.1.3 Species Richness and Biodiversity**

6 Reductions in species richness that occur as a consequence of nutrient enrichment from N
7 deposition contribute to an overall decline in biodiversity. Such effects can occur in sensitive
8 terrestrial, transitional, and aquatic ecosystems. Weis et al. (2006) presented an overview of
9 potential biodiversity loss from N enrichment. A survey by Stohlgren et al. (1999) of variables
10 that contribute to species richness and invasibility of sites found positive relationships of soil N
11 with species richness and numbers of nonnative plant species. The implication of this work is
12 that N fertilization can enhance plant species richness and resource availability, at least up to a
13 certain point, after which competitive interactions occur, such as shading. Some of the native
14 species can then be lost due to these competitive interactions, with subsequent decrease in
15 species richness.

16 Wet N deposition in the western portion of the Pacific Northwest region has increased
17 from generally less than 1 kg N/ha/yr in the mid-1980s to the range of 1 to 3 kg N/ha/yr, mainly
18 due to increased NH_4^+ deposition (NADP/NTN, 2006; Geiser and Neitlich, 2007). Lichen
19 communities are beginning to show evidence of changes in response to increased N pollution,
20 including decreased distribution of sensitive lichen taxa, and their replacement with nitrophilous
21 species (Geiser and Neitlich, 2007).

22 Atmospheric N inputs also have the potential to influence soil microbial communities,
23 with feedbacks on ecosystem nutrient dynamics. Hill et al. (2006) linked microbial enzyme
24 activity to regional-scale anthropogenic stressors and suggested that the quantities and ratios of
25 microbial enzymes are directly related to the concentrations and ratios of limiting nutrients.
26 Compton et al. (2004) investigated the effects of 11 years of experimental N addition on forest
27 soil microbial ecology. They measured soil microbial biomass, microbial composition, and
28 utilization of N-containing substances as indicators of altered microbial N cycling. This work
29 was conducted in pine and hardwood stands at Harvard Forest, MA. Experimental N addition
30 decreased the C content of microbial biomass in the O-horizon of both stands, based on
31 chloroform fumigation-extraction. In addition, the use of N-containing substrates by microbes
32 appeared to be reduced by N addition in the pine stand, but not in the hardwood stand. The

1 mechanisms responsible for such changes are not clear (Arnebrandt et al., 1990; Compton et al.,
2 2004). It is possible that added N has both direct (nutrient) and indirect (soil chemistry, organic
3 matter quality, and quantity) effects on microbial ecology. Effects can be manifested on
4 mycorrhizal fruiting body abundance, hyphal networks, and community composition (Lilleskov
5 et al., 2002; Frey et al., 2004).

6 Microbial biodiversity can also be affected by N enrichment. Interactions between
7 atmospherically deposited N and terrestrial vegetation frequently occur in the rhizosphere. The
8 rhizosphere includes the soil that surrounds and is influenced by plant roots (Wall and Moore,
9 1999). Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N
10 cycling and for the growth and health of plants. The plant provides shelter and C; the fungi and
11 bacteria provide access to potentially limiting nutrients, particularly N and P. Changes in soil N
12 can influence mycorrhizal-plant relationships in the rhizosphere. Mycorrhizal fungal diversity
13 has been shown to be associated with above-ground plant biodiversity and ecosystem
14 productivity (Wall and Moore, 1999) and to be adversely affected by increased N availability
15 (Egerton-Warburton and Allen, 2000).

16 Organisms in their natural environment are commonly adapted to a specific regime of
17 nutrient availability. If one important nutrient suddenly becomes more or less available, the
18 result can be a nutrient imbalance, which in turn can affect ecosystem processes. Ecological
19 stoichiometry (Sterner and Elser, 2002) addresses the consequences of changing the supply of
20 nutrients to organisms that differ in their ability to sequester limiting elements.

21

22 **AX5.5.2 Timing of Effects**

23 The timing of biological effects from increased N deposition is highly variable. There
24 are many factors, in addition to the level of N deposition, that exert substantial controls on the
25 development of both chemical and biological effects. These include, in particular, climatic
26 factors such as temperature and associated soil freezing processes, hydrological factors such as
27 rainstorms and snowmelt, and disturbance factors such as forest management and insect or storm
28 damage. In response to these, and other, confounding variables, biological responses to nutrient
29 enrichment can develop very quickly (<1 year) or develop gradually over many decades or
30 longer.

1 Climatic perturbations can also affect nutrient-phytoplankton interactions and the effects
2 of anthropogenic nutrient contributions on estuarine productivity and health. Such effects were
3 examined by Paerl et al. (2006) for the Chesapeake Bay in Maryland and Virginia and Neuse
4 River Estuary/Pamlico Sound system in North Carolina, the two largest estuary systems in the
5 United States. Nutrient enrichment processes and eutrophication effects are strongly influenced
6 by such climatic events as prolonged drought and increased frequency and intensity of
7 hurricanes. For example, fast-growing diatoms are favored during periods of high discharge and
8 short residence time in Chesapeake Bay. In the longer residence time Neuse River
9 Estuary/Pamlico Sound system, summer cyanobacterial populations were enhanced during years
10 having high discharge.

11 Hurricanes Dennis, Floyd, and Irene in the fall of 1999 dropped up to 1 m of rainfall on
12 coastal North Carolina, causing a 100- to 500-year flood, depending on location, in Pamlico
13 Sound. Sediment and nutrient-laden floodwaters displaced over 80% of the estuary volume and
14 delivered more than half of the annual N load to the estuary (Paerl et al., 2001, 2006). The
15 effects of this sequence of hurricanes included a threefold increase in algal biomass, hypoxic
16 bottom waters (<4 mg O₂/L), changes in fish distribution and fish catches, and increased
17 prevalence of fish disease (Paerl et al., 2001, 2006; Adams et al., 2003; Tester et al., 2003).
18 Higher rates of discharge from the watershed, such as is associated with hurricane activity,
19 reduce the salinity, increase the sediment load, and contribute nutrients from the watershed to the
20 estuary.

21 22 **AX5.5.3 Most Sensitive Species**

23 A variety of sensitive receptors have been identified for evaluating the likelihood of
24 nutrient effects of N deposition on natural ecosystems. Sensitive receptors for effects of excess
25 nutrient N deposition on surface water could include water chemistry, productivity, and the
26 response of important life forms, including fish, zooplankton, benthic macroinvertebrates, and
27 phytoplankton. Key sensitive receptors for assessing impacts on soil include soil chemistry and
28 soil solution chemistry. Sensitive receptors for flora include macro-lichens and vascular plant
29 species that are adapted to nutrient-poor environments. Thus, the sensitive receptors can be
30 chemical or biological. In some cases, the chemical receptors may be easier to characterize,

1 although they likely also reflect important biological changes that may be more difficult to
2 document.

3 Here we outline what is known about species sensitivity in terrestrial, transitional, and
4 aquatic ecosystems. A more complete description of the effects is provided in section AX5.5.4.

5 6 **AX5.5.3.1 Most Sensitive Terrestrial Species**

7 8 **AX5.5.3.1.1 *Lichens and Fungi***

9 Lichens are frequently used as indicators of air pollution and atmospheric deposition
10 levels. In addition to being good subjects for biomonitoring, they constitute important
11 components of the forest ecosystem by contributing to biodiversity, regulating nutrient and
12 hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997).
13 There are several potential uses of lichens for air pollution and deposition monitoring, including
14 measurement of tissue lichen concentrations of specific pollutants (i.e., use lichens as passive
15 monitors of air pollution), determination of changes in species composition or the
16 presence/absence of sensitive species, and identification of areas having relatively high levels of
17 air pollution, where monitoring instrumentation could be installed to more quantitatively
18 measure pollution levels.

19 Epiphytic macro lichens (those that grow attached to trees or other plants) are good
20 indicators of air pollution. Their tissue content of contaminants is generally reflective of the
21 amount of ambient atmospheric pollution. Individual species exhibit different sensitivities to
22 atmospheric pollutants, with some species being adversely impacted at air pollution levels that
23 may not be considered high relative to other sensitive receptors. Particularly sensitive genera
24 include *Alectoria*, *Bryoria*, *Ramalina*, *Lobaria*, *Pseudocyphellaria*, *Nephroma*, and *Usnea*
25 (McCune and Geiser, 1997).

26 Lichens that include a cyanobacterium as the photobiont are adversely affected by N
27 deposition as well as acidity. In contrast, those that include a green algal photobiont tend to be
28 only sensitive to acidity. The decline of lichens containing cyanobacteria in parts of northern
29 Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr (Bobbink et al.,
30 1998). In fact, epiphytic cyanobacteria-containing lichens may be among the most sensitive
31 species in humid forested ecosystems to atmospheric N deposition (Hallingbäck, 1991; Bobbink
32 et al., 1998).

1 Assessment of long-term change in the epiphytic lichen community can be especially
2 valuable to provide an early indication of either improving or deteriorating air quality and
3 atmospheric deposition. Such monitoring was incorporated in 1994 into the USFS Forest
4 Inventory and Analysis (FIA) Program.

5 Community composition of epiphytic lichens can be altered by relatively small increases
6 in N deposition (Fenn et al., 2003a). Most epiphytic lichens meet their nutritional requirements
7 from atmospheric deposition and can store N in excess of their nutritional needs (van Herk,
8 1999). In the San Bernardino Mountains, CA, up to 50% of lichen species that occurred in the
9 region in the early 1900s have disappeared, with a disproportionate number of locally extinct
10 species being epiphytic cyanolichens (Nash and Sigal, 1999; Fenn et al., 2003a).

11 The Pacific Northwest retains widespread populations of pollution-sensitive lichens
12 (Fenn et al., 2003a). However, in urban areas, intensive agricultural zones, and downwind of
13 major urban and industrial centers in the Pacific Northwest, there are few air pollution-sensitive
14 lichen species, such as epiphytic cyanolichens, and high N concentrations have been measured in
15 lichen tissue (Fenn et al., 2003a). With N enrichment, especially around urban and agricultural
16 areas, there is a shift towards weedy, nitrophilous lichen species (Fenn et al., 2003a).
17 Replacement of sensitive lichens by nitrophilous species has undesirable ecological
18 consequences. In late-successional, naturally N-limited forests of the Coast Range and western
19 Cascade Mountains, for example, epiphytic cyanolichens make important contributions to
20 mineral cycling and soil fertility (Pike, 1978; Sollins et al., 1980), and together with other large,
21 pollution-sensitive macrolichens, are an integral part of the food web for mammals, insects, and
22 birds (McCune and Geiser, 1997; U.S. Environmental Protection Agency, 2005). Sensitive
23 lichen species appear to be negatively affected by N inputs as low as 3 to 8 kg/ha/yr (Fenn et al.,
24 2003a).

25 Lichen communities in the Pacific Northwest now receive sufficient levels of air
26 pollution that they are beginning to show signs of air pollution damage, with decreases in the
27 occurrences of sensitive taxa and replacement by pollution-tolerant and nitrophilous taxa (Fenn
28 et al., 2003a; Geiser and Neitlich, 2007). Indicators of clean sites and polluted sites (Table
29 AX5.5-1) were used by Geiser and Neitlich (2007) to create six lichen zones of air quality within
30 the region, from worst (all sensitive species absent) to best (all sensitive species present).

1 Air pollution was associated with effects on community composition of lichens, rather
2 than species richness. The most widely observed effects included paucity of sensitive, endemic
3 species, and enhancement of nitrophilous and non-native species (Geiser and Neitlich, 2007).
4 The strongest relationship was with wet NH_4^+ deposition, consistent with findings in California
5 (Jovan and McCune, 2005) and Europe (van Dobben et al., 2001). The zone of worst air quality
6 was associated with absence of sensitive lichens, enhancement of nitrophylous lichens, mean
7 wet NH_4^+ deposition > 0.06 mg N/L, lichen tissue N and S concentrations > 0.6% and 0.07 %,
8 and SO_2 levels harmful to sensitive lichens.

9 Mycorrhizal fungi are also highly sensitive to N supply (Egerton-Warburton and Allen,
10 2000). This relationship is important because the diversity of mycorrhizal fungi is often closely
11 tied to the diversity of above-ground plants (Wall and Moore, 1999).

12 Progressive decline in ectomycorrhizal fungal (EMF) species richness in Alaskan
13 coniferous forest [white spruce (*Picea glauca*) dominant] occurred along a local N deposition
14 gradient, from 1 to 20 kg N/ha/yr, downwind from an industrial complex (Lilleskov et al., 2002).
15 EMF communities are important in tree nutrition, and EMF trees tend to be dominant in N-
16 limited forest ecosystems. A shift in EMF community structure could result in a shift in
17 dominant tree species and in nutrition. Changes in species composition and abundance of
18 bryophytes and lichens have also been demonstrated in European ecosystems that receive high
19 levels of N deposition (Bobbink et al., 1998; Mitchell et al., 2005).

20 Nitrogen fertilization at rates of 54 and 170 kg N/ha/yr (as NH_4NO_3) led to a decline in
21 EMF diversity and species composition in an oak savanna at Cedar Creek Natural History Area
22 Long Term Ecological Research (LTER) site in Minnesota (Avis et al., 2003). In the control
23 plots, five species collectively accounted for more than 40% cover versus four plant species in
24 the lower N addition plots. In the higher N addition plots, a single plant species accounted for
25 more than 40% cover.

26 27 **AX5.5.3.1.2 *Herbaceous Species***

28 N deposition can also affect the relative abundance and competitive interactions of
29 herbaceous plant species if their growth is limited by N, rather than light or some other nutrient.
30 Gilliam (2006) summarized what is currently known about the effects of excess N on the
31 herbaceous layer of forests, based on the few studies that have been conducted in Europe and the

1 United States. Studies in Europe have generally been based on natural gradients, whereas
2 findings in the United States have mostly been based on experimental N addition.

3 Negative effects of increasing N deposition reviewed by Gilliam (2006) included species
4 shifts towards nitrophilous and more acid-tolerant plant species along a deposition gradient from
5 6 to 20 kg N/ha/yr in Swedish oak forests, decline in abundance and cover of ericaceous shrubs
6 along a deposition gradient from less than 3 to more than 12 kg N/ha/yr in the boreal forest in
7 Sweden, decline in species diversity and biomass in several experimental N applications to pine
8 between 50 and 150 kg N/ha/yr for at least 7 years, and decline in herbaceous cover under
9 hardwoods following 3 years of N additions applied as $(\text{NH}_4)_2 \text{SO}_4$ at rates ranging from 14 to
10 28 kg N/ha/yr. The decline in herbaceous cover was attributed to increased shading by ferns, and
11 the effect was more pronounced at sites that experienced lower atmospheric N inputs.

12 Gilliam (2006) proposed that dominance of inorganic NO_3^- in soil can increase
13 invasibility of sites by exotics, and predicted a loss of biodiversity with increasing N availability.
14 Research at Fernow, WV, indicated that applications of 35 kg N/ha/yr applied as $(\text{NH}_4)_2 \text{SO}_4$ for
15 6 years had no significant impact on the herbaceous layer in an Appalachian hardwood forest
16 (Gilliam et al., 2006). Fernow has been the recipient of high level of N deposition for decades,
17 raising the possibility that the herbaceous layer responded long ago to changes in N availability.

18 Nitrogen additions of 120 kg N /ha/yr in Michigan old fields, applied as NH_4NO_3 pellets,
19 had a significant positive growth effect on annual dicot biomass but no significant growth effect
20 on annual grass biomass (Huberty et al., 1998). In tallgrass prairie, C_3 grasses (*Elymus*
21 *virginicus* L., *E. Canadensis* L.) showed a greater positive growth response to N additions than
22 C_4 grasses (*Andropogon gerardii* Vitmanm, *Schizachyrium scoparium* Michx.) and forbs
23 (*Solidago nemoralis* Ait., *S. rigida* L.) (Lane and BassiriRad, 2002). Species with smaller initial
24 biomass exhibited the greatest increase in biomass, with a sevenfold to eightfold increase in *S.*
25 *nemoralis* and *E. canadensis* and only a threefold increase in *S. rigida* (Lane and BassiriRad,
26 2002). In experiments where N fertilization to simulate increased N deposition was applied to
27 common ragweed (*Ambrosia artemisifolia*), simulated N deposition led to increased vegetative
28 and seed biomass and decreased root:shoot ratios (Throop, 2005).

29 Herbaceous plants in alpine communities are considered very sensitive to changes in N
30 deposition. A combination of short growing season, strong seasonal variation in moisture and
31 temperature, shallow and poorly developed soils, steep terrain, sparse vegetation, and low rates

1 of primary productivity generally limit the N uptake and retention capacity of herbaceous plant
2 species in alpine ecosystems (Fisk et al., 1998; Burns, 2004). Alpine herbaceous plants are
3 generally considered N-limited and changes in alpine plant productivity and species composition
4 have been noted in response to increased N inputs (Vitousek et al., 1997a; Bowman et al., 2006).

5 6 **AX5.5.3.1.3 Trees**

7 Few studies have been conducted on the relative sensitivity of different tree species to the
8 nutrient enrichment effects of N deposition. However, based on research at Harvard Forest
9 (Magill et al., 2004), conifers seem more sensitive (as evidenced by growth declines) to the
10 effects of N addition than hardwood species (which often exhibited increased production).
11 Among hardwoods, red maple appeared to be particularly sensitive to N addition, indicated by
12 high mortality, but the effects of this study were complicated by drought conditions. In the
13 eastern United States, the nutrient enrichment effects of N deposition on trees can be difficult to
14 separate from the acidification effects (see discussion in Annex 4).

15 16 **AX5.5.3.2 Most Sensitive Transitional Species**

17 Increased N availability in nutrient-poor wetland environments may lead to a decrease in
18 species diversity and increased risk of extinction for some of the more sensitive and rare species
19 (Moore et al., 1989). Peatlands and bogs are among the most vulnerable transitional ecosystems
20 to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland
21 *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse
22 et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to
23 be negatively affected by experimentally elevated atmospheric N and S inputs in Europe
24 (Kooijman and Bakker, 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to
25 elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and
26 broadly distributed across, the United States and is federally listed as endangered in Illinois and
27 Iowa, threatened in Tennessee, and vulnerable in New York (<http://plants.usda.gov/> accessed
28 3/30/07).

29 For two ombrotrophic bogs in the northeastern United States (Vermont and
30 Massachusetts), model estimates of extinction risk for the northern pitcher plant (*Sarracenia*
31 *purpurea*) were calculated under varying N deposition scenarios (Gotelli and Ellison, 2002).
32 Modeled extinction risk within the next 100 years was relatively low under precipitation N

1 concentrations equivalent to those at the time of the study (0.391 to 0.477 mg N/L/yr). However,
2 model estimates showed increased extinction risk under elevated N deposition scenarios (Gotelli
3 and Ellison, 2002).

4 In wet heathlands in Europe, changes in plant species composition have been attributed to
5 elevated atmospheric N deposition (Roem and Berendse, 2000). Diverse plant communities
6 consisting of *Erica tetralix*, *Calluna vulgaris*, *Gentiana pneumonanthe*, *Drosera intermedia*, and
7 *Lycopodium inundatum* have been replaced by monospecific stands of the grass *Molina caerulea*
8 or *Deschampsia flexuosa* in Dutch wet heathlands (Aerts and Berendse, 1988; Houdijk et al.,
9 1993). Responses can be complex.

10 In other studies, wetland species such as *Calluna vulgaris* can successfully compete with
11 grasses even at relatively high rates of N deposition, as long as the vegetative canopies are closed
12 (Aerts et al., 1990). However, N deposition causes nutrient imbalances, including increase in the
13 shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost
14 stress, and attack by insect pests (Heil and Diemont, 1983). These can result in gaps in the
15 canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in
16 using the additional N and therefore gain a competitive advantage (Krupa, 2003).

17 In riparian wetlands, Marler et al. (2001) evaluated the potential impacts of
18 experimentally elevated stream water nutrient concentrations on three plant species: Fremont
19 cottonwood (*Populus fremontii*), Goodding willow (*Salix gooddingii*), and exotic saltcedar
20 (*Tamarix ramosissima*) collected from the riparian zone of the Salt River near Phoenix, AZ. The
21 results from this 43-day experiment showed that growth of all three riparian plant species
22 responded positively to increased nutrient supply (treatments 3 and 4) (Figure AX5.5-2) (Marler
23 et al., 2001). Only slight increases in biomass were observed between treatments 1 and 2. The
24 exotic and invasive saltcedar (*T. ramosissima*) showed the greatest increases in biomass at high
25 (treatments 3 and 4) nutrient supply. Other studies have also found that exotic plant species
26 often respond more rapidly than native vegetation to increased nutrient supply (Milberg et al.,
27 1999; Paschke et al., 2000). This experiment was conducted to simulate impacts of wastewater
28 effluent on riparian zones, and N additions were therefore very large. Elevated nutrient supply to
29 riparian systems via atmospheric N deposition in the United States is more typically in the range
30 of treatments 1 and 2, which showed minimal response to N addition.

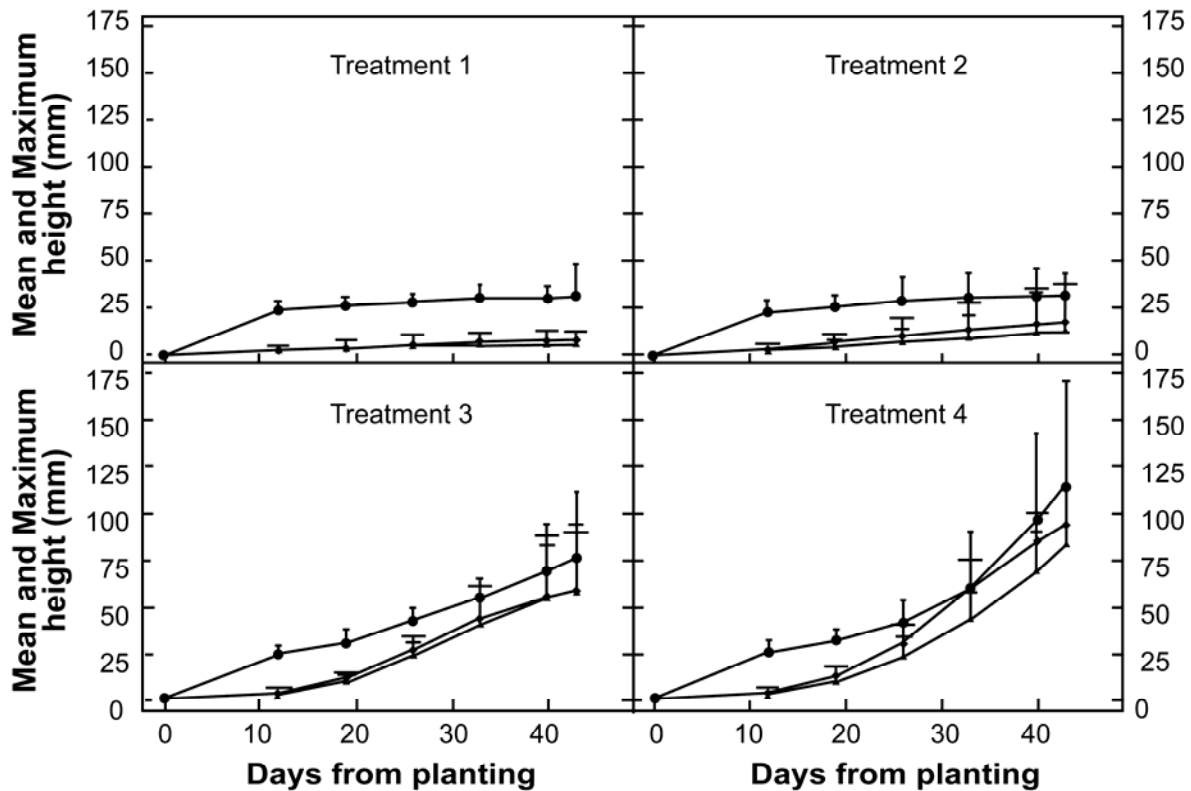


Figure AX5.5-2. Nutrient effect at four treatments on stem height of *Populus fremontii* (---●---), *Salix gooddingii* (---▲---) and *Tamarix ramosissima* (---◆---) seedlings over a 43-day period. Values shown are means with maximum height.

Source: Marler et al. (2001).

1 AX5.5.3.3 Most Sensitive Aquatic Species

2 Bioassay, mesocosm, and laboratory experiments have been conducted on algae (both
 3 phytoplankton and periphyton), invertebrates, amphibians, and fish, in order to determine effects
 4 of N on sensitive aquatic organisms (Table AX5.5-2). Based on these studies, we describe what
 5 is known about the sensitive species in aquatic ecosystems. Our literature search included only
 6 studies in which the amount of N added was less than the EPA Safe Drinking Water Standard
 7 (10 mg NO₃-N/L, or 714 μM), and most studies tested the effects of 5 mg NO₃⁻-N/L or less. The
 8 Drinking Water Standard is more than 30 times higher than the concentration of surface water
 9 NO₃⁻ commonly attributable to atmospheric N deposition in the United States.

1 Overall, several major effects were noted: (1) the effects on algae included growth
2 stimulation, increased cell densities, decline or stimulation of individual taxa, and decline in
3 diversity; (2) the amount of N required to stimulate growth in phytoplankton is extremely low:
4 3 μM or less; and (3) animal responses included no response, decreased reproductive capability,
5 declines in growth rate and biomass, mortality, and in one case, increased fitness because NO_3^-
6 was detrimental to a fungal parasite.

7 The dose-response data for aquatic organisms such as those cited here are generally
8 expressed in concentration units, as mg/L or $\mu\text{mol/L}$ of N, for example. Such exposure
9 concentration data cannot be directly related to ecosystem exposure, which is generally
10 expressed in such units as kg/ha. This is because a given N deposition exposure can result in
11 widely varying concentrations of N compounds (especially NO_3^-) in water. For convenience, a
12 concentration of 1 mg/L of N (as, for example, in the case of NO_3^- -N or NH_4^+ -N) is equal to
13 71.4 $\mu\text{mol/L}$ or 71.4 $\mu\text{eq/L}$ of NO_3^- or NH_4^+ .

14 15 **AX5.5.3.3.1 *Phytoplankton and Plants***

16 Some aquatic algae are particularly sensitive to the effects of added nutrient N. Two
17 species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at
18 least several alpine and montane Rocky Mountain lakes (Interlandi and Kilham, 1998; Baron
19 et al., 2000; Wolfe et al., 2001, 2003; Saros et al., 2003, 2005). These species are opportunistic
20 algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in
21 many parts of the world. They were among the first diatoms to increase in abundance following
22 watershed settlement and agricultural development in European lake watersheds in the 12th and
23 13th centuries (Anderson et al., 1995; Lotter, 1998), and North American settlements in the 18th
24 and 19th centuries (Christie and Smol, 1993; Hall et al., 1999). In these studies, as well as in a
25 Swedish lake influenced by acidic deposition, these two diatom species expanded following
26 initial disturbance, and were later replaced by other species more tolerant of either acidification
27 or eutrophication (Renberg et al., 1993; Hall et al., 1999). Moreover, the growth of *A. formosa*
28 has been stimulated with N amendments during *in situ* incubations, using bioassays and
29 mesocosms (6.4 to 1616 $\mu\text{M N/L}$) (McKnight et al., 1990) (76 $\mu\text{M N/L}$) (Lafrancois et al., 2004)
30 (18 $\mu\text{M N/L}$) (Saros et al., 2005).

1 *In situ* incubations in large lakes of Yellowstone National Park also stimulated
2 *F. crotonensis* (Interlandi and Kilham, 1998), although this publication did not reveal how much
3 N was added to the incubations. The N requirements for *A. formosa* and *F. crotonensis* were
4 determined to be 0.041 μM N and 0.006 μM N, respectively, and higher concentrations
5 stimulated growth (Michel et al., 2006). Other species have shown negative growth responses to
6 increased N; two of these, *Tetracyclus glans* and *Staurosirella pinnata*, were reported by Michel
7 et al. (2006). In studies of lake sediment diatom remains, typical oligotrophic species such as
8 *Aulacoseria perglabra*, *Cyclotella steligera*, and *Achnanthes spp.* declined coincident with the
9 rise in dominance of *A. formosa* and *F. crotonensis* (Wolfe et al., 2001, 2003).

10 It may seem obvious that additions of N stimulate cell growth, but not all species of
11 diatoms or other algae are equally responsive to N supply. *A. formosa* and *F. crotonensis* have
12 extremely low resource requirements for P, enabling them to outcompete other algae for
13 resources. Differences in resource requirements allow some species to gain a competitive edge
14 over others upon nutrient addition, and as a consequence, shifts in assemblages have been
15 observed (Wolfe et al., 2001, 2003; Lafrancois et al., 2004; Saros et al., 2005). This is in
16 keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species
17 diversity was maintained when N levels were extremely low ($<3 \mu\text{M}$ N) in lakes in the
18 Yellowstone National Park (Wyoming, Montana) region. The implication is that species
19 diversity declines with increasing availability of N, and this finding complements the results of
20 terrestrial studies that also showed a negative relationship between species diversity and N
21 availability (Stevens et al., 2004; Suding et al., 2005; Gilliam, 2006).

22 Experimental examination of the resource requirements of *A. formosa* and *F. crotonensis*
23 found low requirements for P and moderate requirements for N, allowing for rapid response to
24 increased N availability (Michel et al., 2006). These results corroborate earlier work on resource
25 requirements for these algal species (Tilman, 1981).

26 Mesocosm enrichments in Wyoming lakes similarly found positive responses of *A.*
27 *formosa* and *F. crotonensis* to N, but not to P or Si enrichment (Saros et al., 2005). Mesocosm
28 experiments in oligotrophic Snowy Range lakes changed algal assemblages as well.
29 Phytoplankton shifted away from a general dominance by chrysophyte species to dominance
30 primarily by large chlorophytes and the dinoflagellate *Gymnodinium* (Lafrancois et al., 2004).
31 A similar positive correlation between the proportion of the phytoplankton comprised of

1 chrysophytes and the concentration of NO_3^- in lakewater was found in a survey of 15 Snowy
2 Range lakes (Lafrancois et al., 2003). Chlorophytes, like the two diatoms identified above, have
3 generally high preferences for N and are able to rapidly dominate the flora when N
4 concentrations increase (Findlay et al., 1999). This occurs in both circumneutral and acidified
5 waters (Wilcox and Decosta, 1982; Findlay et al., 1999).

6 Phosphorus limitation and co-limitation of both N and P are reported for fresh waters in
7 the literature, particularly during summer (Morris and Lewis, 1988; Elser et al., 1990; Downing
8 and McCauley, 1992; Sickman et al., 2003b). Because diatoms in northern temperate
9 freshwaters respond rapidly and favorably to N enrichment and also have relatively high Si
10 requirements, Si can be depleted, at least seasonally, from waters that are relatively high in N
11 and P.

12 Silica depletion due to nutrient enrichment has been reported for the Great Lakes (Conley
13 et al., 1993). Increased growth of silicate-utilizing diatoms as a result of NO_3^- and phosphate
14 (PO_4^-)-induced eutrophication, and subsequent removal of fixed biogenic Si via sedimentation
15 has brought about changes in the ratios of nutrient elements Si, N, and P. In turn, such changes
16 can cause shifts from diatoms to non-siliceous phytoplankton in large rivers and coastal marine
17 regions (Ittekkot, 2003). Reduction in dissolved Si in lakewater corresponded to phytoplankton
18 blooms under ice and large numbers of diatoms during spring in Loch Vale Watershed, Rocky
19 Mountain National Park (Campbell et al., 1995). This is a potential seasonal issue in water
20 bodies underlain by aluminosilicate rocks because mineral weathering can replenish the Si
21 supply.

22 In addition to diatoms, N effects have been observed on periphyton. Periphyton grow on
23 rocks or sediment in lakes and streams where there is sufficient light for photosynthesis. We
24 found no studies that documented resource requirements for periphyton, although several papers
25 described stimulated growth with N amendments from ecosystems throughout the United States
26 (Table AX5.5-2). Growth stimulation occurred with N additions ranging from 8 to 50 $\mu\text{M/L}$, or
27 with exposure to 0.5 M N concentrations on agar substrate (cf. Bushong and Bachmann, 1989;
28 Allen and Hershey, 1996; Wold and Hershey, 1999; Smith and Lee, 2006). *Anabaena circinalis*,
29 an obligate N-fixing cyanobacterium, was suppressed with additions of 500 $\mu\text{M/L}$ N (Higley
30 et al., 2001), and DIN levels $>\sim 200$ $\mu\text{M/L}$ N completely inhibited N fixation in Castle Lake, CA
31 (Reuter et al., 1985).

1 **AX5.5.3.3.2 Invertebrates**

2 Toxic responses to N exposure by aquatic invertebrates have been identified in a number
3 of studies. Toxic response thresholds are typically much higher than the levels of N in surface
4 waters that could be attributable to N deposition in the United States. Safe concentrations (SC),
5 or threshold values of N, were determined by Camargo and Ward (1995) for several aquatic
6 insects at different life stages. Early instars are generally more sensitive to N in solution than
7 later or adult stages. The SC for late instars of *Hydropsyche occidentalis*, a caddis fly, was found
8 to be 171 $\mu\text{M/L}$, and concentrations greater than this value induced mortality. The SC was
9 100 $\mu\text{M/L}$ for early instars of the same species (Camargo and Ward, 1995). Another caddis fly,
10 *Cheumatopsyche pettiti*, tolerated higher concentrations, with safe concentrations of 171 and
11 250 $\mu\text{M N/L}$, respectively for early and late instars (Camargo and Ward, 1995). Two species of
12 amphipod did not survive after 120-hr exposure to NO_3^- concentrations of 200 $\mu\text{M N/L}$ for one
13 species, and 314 $\mu\text{M N/L}$ for the other (Camargo et al., 2005). No observable effect
14 concentrations above which *Ceriodaphnia dubia* exhibited reduced reproductive capability
15 ranged broadly in laboratory experiments, but some effects were seen at concentrations greater
16 than 507 $\mu\text{M N/L}$ (Scott and Crunkilton, 2000). A decline in *Daphnia spp.* was observed in
17 mesocosm nutrient enrichment experiments where 75 $\mu\text{M N/L}$ was added, but this was attributed
18 to lower food quality of the algal assemblage that replaced the original species as a result of
19 fertilization (Lafrancois et al., 2004). Thus, toxic responses seem to occur at N concentrations
20 that are much higher than the concentrations required to elicit a response in competitive
21 interactions.

22 A whole-ecosystem experiment at the Bear Brook watershed, ME simulated the effects of
23 N and S deposition by means of experimental $(\text{NH}_4)_2\text{SO}_4$ addition over a period of 10 years.
24 Researchers found that elevated N inputs had minimal effect on stream detritus processing
25 (Chadwick and Huryn, 2003). They also found that N additions had no significant effect on
26 stream macroinvertebrate secondary production or varying production by functional feeding
27 groups. They concluded that climate-related variables such as flow duration and litter inputs
28 controlled secondary production when N was not limiting (Chadwick and Huryn, 2005).

29 Changes to aquatic food webs have not been as thoroughly explored as changes to algal
30 assemblages, but a few studies have shown declines in zooplankton biomass (Paul et al., 1995;
31 Lafrancois et al., 2004) in response to N-related shifts in phytoplankton biomass toward less

1 palatable taxa with higher C:P ratios (Elser et al., 2001). Nitrogen enrichment of arctic streams
2 not only increased periphyton biomass and productivity, but also stimulated the entire ecosystem,
3 increasing decomposition rates, fungal biomass, and invertebrates (Benstead et al., 2005).

4 5 **AX5.5.3.3.3 Amphibians and Fish**

6 It appears that very high NO_3^- concentrations in surface water are required to elicit a
7 toxic response in amphibian populations. Concentrations that caused no observed effects and no
8 observed adverse effects ranged from 357 to 714 $\mu\text{M N/L}$ for frogs, salamanders, and the
9 American toad (*Bufo americanus*) (Hecnar, 1995; Laposata and Dunson, 1998; Johansson et al.,
10 2001; Romansic et al., 2006). In one experiment, the red-legged frog (*Rana aurora*) exhibited a
11 decreased susceptibility to *Saprolegnia* mold when exposed to elevated NO_3^- concentrations
12 (Romansic et al., 2006).

13 According to one review, adverse direct effects of N deposition on fish due to nutrient
14 enrichment are probably minimal (Burns, 2004). Nitrogen concentrations alone are not high
15 enough to influence fish metabolism, and the extent of eutrophication is insufficient (due to
16 induced P limitation in oligotrophic waters) to cause O_2 depletion.

17 Other research suggests that the eggs and fry of rainbow trout (*Oncorhynchus mykiss*;
18 including steelhead), cutthroat trout (*O. clarki*), and chinook salmon (*O. tshawytscha*) are
19 susceptible to elevated concentrations of NO_3^- , with rainbow trout mortality occurring after 30
20 day incubations in concentrations $>79 \mu\text{M N/L}$ (Kincheloe et al., 1979). There were no observed
21 effects reported below this concentration. Chinook salmon and cutthroat trout eggs and fry
22 responded to slightly higher concentrations; no observed effects occurred below 164 $\mu\text{M N/L}$,
23 but mortality occurred at higher concentrations (Kincheloe et al., 1979). Lake whitefish
24 (*Coregonus clupeaformis*) and lake trout (*Salvelinus namaycush*) embryos displayed
25 developmental delays at concentrations greater than 446 and 114 $\mu\text{M N/L}$, respectively (McGurk
26 et al., 2006). All of these toxic threshold concentrations are much higher than the concentrations
27 of NO_3^- in surface water that would routinely be expected to occur solely in response to
28 atmospheric N deposition in the United States. Nevertheless, such high concentrations of
29 streamwater NO_3^- have been measured in the Great Smoky Mountains, NC (Cook et al., 1994)
30 and in mixed conifer forests in southern California (Fenn and Poth, 1999).

1 **AX5.5.4 Effects by Ecosystem Type**

2
3 **AX5.5.4.1 Effects on Terrestrial Ecosystems**

4 Nitrogen deposition affects terrestrial ecosystems throughout large areas of the United
5 States due to the importance of N as a limiting nutrient. Because N acts as a fertilizer, the most
6 immediate impact in most areas has probably been increased above-ground growth of vegetation,
7 which can cause changes in the shoot-to-root ratio with potentially adverse long-term
8 consequences for the tree. Atmospheric N inputs in many areas may have been high enough to
9 cause some plant species to outcompete others.

10 Atmosphericly deposited N can act as a fertilizer to soil that is low in N. Not all plants,
11 however, are equally capable of utilizing added N. Plants vary in their ability to absorb NH_4^+
12 and NO_3^- (Chapin et al., 1987). Atmospheric inputs of N can alleviate deficiencies and increase
13 growth of some plants at the expense of others. Thus, N deposition can alter competitive
14 relationships between plant species, which can alter species composition and diversity
15 (Ellenberg, 1987; Kenk and Fischer, 1988; U.S. Environmental Protection Agency, 1993). In the
16 United Kingdom, Stevens et al. (2004) found a decrease in diversity in acid grassland plant
17 species of approximately 12 species per 4-m² plot, correlating with an increase in N deposition
18 from 5 to 35 kg N/ha/yr. Wholesale shifts in species composition are more probable in short-
19 lived ecosystems such as annual grasslands or in the forest understory or mycorrhizal
20 associations than for forest trees. These kinds of species shifts and ecosystem changes can occur
21 even if the ecosystem does not exhibit signs of N saturation.

22 As discussed previously, N saturation reflects a set of gradually developing changes in
23 ecosystem processes which govern the integrated response of a system to increased N_r
24 availability over time (Aber, 1992). Nitrogen saturation occurs when N_r inputs exceed the
25 capacity of plants and soil microorganisms to utilize and retain N (Aber et al., 1989, 1998; U.S.
26 Environmental Protection Agency, 1993). Under conditions of saturation, some resource other
27 than N becomes growth-limiting. High concentration of NO_3^- in soil solution or streamwater is
28 an early symptom of N saturation. During N saturation, soil microbial communities change from
29 being dominated by fungi to being dominated by bacteria.

30 A meta-analysis of the effect of N and P fertilization on mycorrhize observed a 15%
31 decrease in mycorrhizal abundance due to N fertilization across 16 studies at 31 sites, covering a

1 range of grassland, shrubland, temperate and boreal forest ecosystems (Treseder, 2004).
2 Declines in mycorrhizal abundance were slightly higher at higher rates of N fertilization, but
3 there was significant variation across all studies. The loss of mycorrhizal function has been
4 hypothesized as a key process contributing to reduced N uptake by vegetation and increased
5 NO_3^- mobility from soil into drainage water (U.S. Environmental Protection Agency, 2004).

6 Long-term effects of increased N deposition have been more thoroughly studied in
7 European plant communities than in plant communities in the United States (Bobbink, 1998).
8 Changes in plant species composition have been observed in regions of Europe with high N
9 loadings or in field experiments after years of N addition (Bobbink et al., 1998; Stevens et al.,
10 2004). The increased input of N typically increased N availability in the soil, which has caused
11 increased litter decomposition and mineralization rates. Faster growth and greater height of
12 nitrophilic species enabled these plants to shade out the slower growing species (Bobbink, 1998;
13 Bobbink et al., 1998). Van Breemen and Van Dijk (1988) also noted that over the previous
14 several decades the composition of plants in forest herb layers in The Netherlands had shifted
15 toward species commonly found in N-rich areas.

16 Brunet et al. (1998) and Falkengren-Grerup (1998) reported the effects of excessive N
17 deposition on mixed-oak forest vegetation along a depositional gradient. Results of this study,
18 which employed multivariate methods, suggested that N deposition had affected non woody
19 vegetation directly by increased N availability and, indirectly, by accelerating soil acidity. Time
20 series studies indicated that 20 of the 30 non woody plant species that were associated most
21 closely with high N deposition had increased in abundance in those areas in Europe that received
22 high N deposition.

23 In a European study involving 15 herb and 13 grass species, Falkengren-Grerup (1998)
24 found that species with relatively high N demand were particularly competitive in areas with
25 acidic soils and high N deposition. In general, grasses grew better than herbs in response to
26 experimental addition of N. At the highest experimental N deposition rates, growth was limited
27 for most species by the supply of nutrients other than N. At intermediate N deposition, grass
28 species were more efficient than herbs in utilizing available N.

29 Joint effects of NH_3 and other pollutants such as NO_3^- and O_3 are not well understood.
30 Plants also exhibit different degrees of response to NO_3^- versus NH_4^+ deposition. In general,
31 fast-growing annual species, including many agricultural crops, and fast growing pioneer trees

1 such as birch (*Betula* spp.) prefer NO_3^- (Pearson and Stewart, 1993). Slow-growing perennial
2 plant species generally prefer NH_4^+ . There are also many plant species which readily utilize both
3 NO_3^- and NH_4^+ (Krupa, 2003). These include members of the family Ericaceae (e.g., *Calluna*,
4 *Erica*, *Vaccinium*), conifer trees, and climax species such as *Quercus* and *Fagus* (Krupa, 2003).

5 6 **AX5.5.4.1.1 Forests**

7 Over 50% of plant N is used for photosynthetic enzymes. Because N is so crucial to
8 photosynthesis, rates of photosynthesis and NPP typically correlate with metrics of N availability
9 such as leaf N content and net N mineralization rate (Field and Mooney, 1986; Reich et al.,
10 1997a,b; Smith et al., 2002). Because N availability often limits rates of NPP, many modeling
11 analyses expect atmospherically deposited N to increase growth of vegetation (e.g., Townsend
12 et al., 1996; Holland et al., 1997; Ollinger et al., 2002).

13 In order to understand the effects of added N to forest ecosystems, it is helpful to
14 examine the results of modeling projects and experimental N additions. Experimental N
15 additions to forest ecosystems have elicited positive growth responses in some, but certainly not
16 all, organisms (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006).
17 Forest growth enhancement, to the extent that it occurs, can potentially exacerbate other nutrient
18 deficiencies, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), or potassium (K^+), thereby causing
19 problems with forest health. Multiple long-term experiments have demonstrated transient
20 growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir
21 et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).

22 One of the longest of these fertilization studies examined a Scots pine forest in northern
23 Sweden, and found that chronic fertilization at 30 kg N/ha/yr continued to stimulate stemwood
24 production even after 30 years, whereas a higher application (90 kg/ha/yr) decreased stem
25 volume growth, and an intermediate application (60 kg/ha/yr) had little positive or negative
26 effect relative to the control plots (Högberg et al., 2006). Note that the lower rates of application
27 in this study are low by fertilization standards, but are still higher than the level of atmospheric N
28 deposition in almost all areas of the United States (See Section AX4.1.1, Figure AX4.1-3).

29 At the Bear Brook, ME, watershed acidification study site, basal area increment of sugar
30 maple was enhanced 13% to 104% by addition of 25 kg N/ha/yr as $(\text{NH}_4)_2\text{SO}_4$, whereas red
31 spruce was not significantly affected (Elvir et al., 2003). In a comparable experiment at the

1 Fernow Experimental Forest, WV, application of 35 kg N/ha/yr as $(\text{NH}_4)_2\text{SO}_4$ enhanced growth
2 of black cherry (*Prunus serotina*) and yellow poplar (*Liriodendron tulipifera*) during the first
3 seven years, but led to reduced growth of these species relative to control trees in years 9 to 12,
4 with no change in red maple or sweet birch (*Betula lenta*) (DeWalle et al., 2006). Chronic
5 fertilization combined with drought led to significant mortality in a 70-year old red pine stand at
6 Harvard Forest, MA (Magill et al., 2004). As red pine has died, striped maple
7 (*Acer pensylvanicum*), black cherry, and black birch (*Betula lenta*) have increased their
8 contributions to annual litterfall production. Parallel fertilization of a 50-year-old red-oak/red
9 maple stand largely stimulated productivity, although the drought in 1995 induced significant
10 mortality in small red maple trees. Fine root biomass was slightly, but not significantly, lower in
11 highly fertilized stands relative to controls in both red pine and oak/maple ecosystems (Magill
12 et al., 2004). These results are broadly consistent with a series of N manipulation (fertilization
13 and deposition exclusion) experiments in Europe, which demonstrated improvements in wood
14 accumulation rate, root production, and mycorrhizal associations when a “clean roof” was
15 installed at the site receiving the highest rate of N deposition (>40 kg N/ha/yr; Ysselsteyn, The
16 Netherlands) (Boxman et al., 1998b; Emmett et al., 1998). Decreased production of fine roots
17 may predispose N-fertilized plants to be more sensitive to intermittent drought, as well as to
18 nutrient depletion exacerbated by acid deposition.

19 Increased growth of trees, to the extent that it occurs, could be considered a desirable
20 outcome by forest managers. There are, however, also ecological effects from N deposition that
21 would be considered undesirable and that could negate positive tree growth responses (Fenn
22 et al., 2003a). Fertilization with N often causes trees to allocate less photosynthate to roots and
23 mycorrhizal fungi. The resulting decreased capacity to take up water and other potentially
24 limiting nutrients may exacerbate limitation by other nutrients, and make fertilized plants more
25 sensitive to drought.

26 The typical immediate response to NH_Y addition is enhanced plant growth (Krupa, 2003).
27 Enhanced growth is usually observed as long as the NH_Y concentrations are below toxic levels.
28 Such enhanced growth generally occurs mainly above ground level (Dueck et al., 1991). This
29 can cause changes in the shoot-to-root ratio after NH_Y uptake. These changes can be detrimental
30 to the plant because they can decrease resistance to environmental stresses such as drought.
31 Addition of NH_Y is believed to decrease resistance to drought stress for at least two reasons.

1 First, the demand for C to accompany the assimilated NH_Y increases CO_2 uptake through plant
2 leaves and therefore stomata opening and water loss. Second, because shoot growth is more
3 enhanced than root growth by the addition of NH_Y , the water supply from the roots can become
4 insufficient during periods of drought to support water loss via transpiration (Fangmeier et al.,
5 1994; Krupa, 2003). Deposition of NH_Y is also believed to reduce frost hardiness of plants
6 (Dueck et al., 1990). This is likely because the addition of NH_Y prolongs the growth phase of the
7 plants during autumn and delays winter hardiness. This can cause detrimental effects if the first
8 frost occurs early in the autumn period (Cape et al., 1991). Plants also appear to be more
9 susceptible to fungal infection under high N status or changed nutrient balance such as an
10 increase in the ratio of N to K^+ (Ylimartimo, 1991; Krupa, 2003).

11 There is little direct evidence for regional growth enhancement of forest ecosystems in
12 the United States in response to atmospheric deposition of N. However, detection and attribution
13 of growth trends across heterogeneous systems is difficult (cf. Joos et al., 2002), and exposure to
14 O_3 or other pollutants may offset N-induced growth enhancement (Ollinger et al., 2002).
15 Evaluation of tree growth rates in five states (Minnesota, Michigan, Virginia, North Carolina,
16 Florida) found little evidence for growth enhancement due to any factor (e.g., N deposition, CO_2
17 fertilization, or climate change) (Caspersen et al., 2000). Analyses of satellite observations of
18 canopy greenness over the last 20 years across North America suggest enhancement of NPP in
19 some regions corresponding to observed changes in climate and forest management, but few
20 changes in NPP in the northeastern United States, where rates of N deposition are relatively high
21 (Hicke et al., 2002). In Europe, forest biomass is accumulating largely in response to increases
22 in forest area and improved management, but other possible mechanisms of growth enhancement
23 cannot be ruled out (Kauppi et al., 1992; Spiecker et al., 1996). One of the most comprehensive
24 analyses of regional growth trends was an analysis of increment cores from more than 31,000
25 plots in Norway. In this study, growth increased during the 1960s and 1970s and then declined
26 in the 1990s, especially in southern regions exposed to the highest rates of N deposition (Figure
27 AX5.5-3) (Nellemann and Thomsen, 2001). Evidence for growth enhancement in the United
28 States from atmospheric N deposition is limited at present, but suggests modest, transient
29 enhancement at most sites, often followed by growth declines or increased mortality in the long
30 term, especially at the highest rates of N deposition. The potential for synergistic effects on

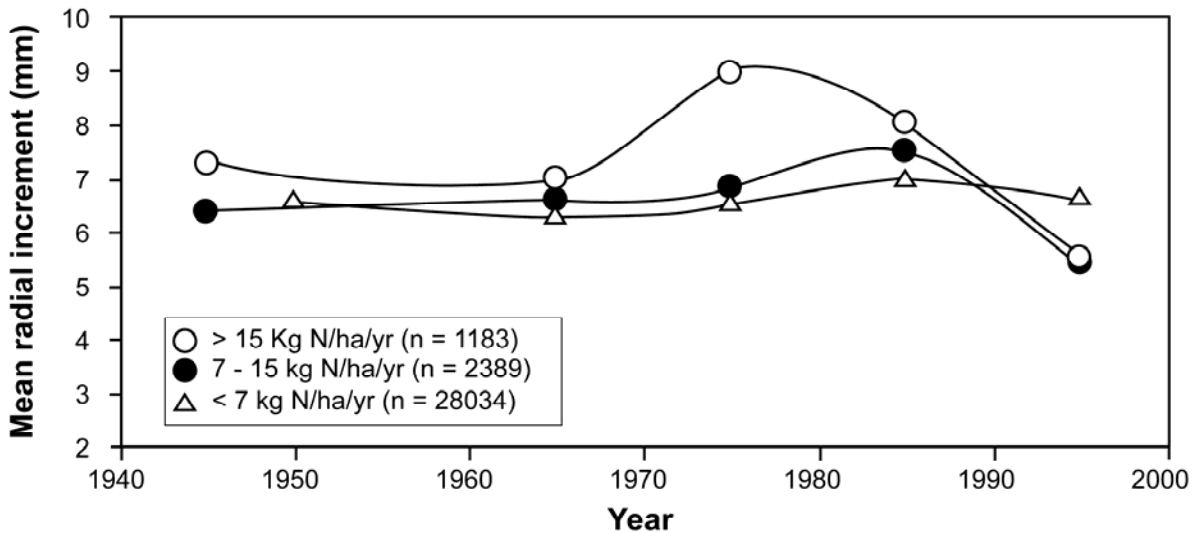


Figure AX 5.5-3. Mean 5-year radial increment from 31,606 core samples from *Picea abies* during the period 1945 to 1996 for three atmospheric N deposition zones (high, medium, and low wet N-deposition in 1990), respectively. Note that the decline in radial increment after 1975 corresponds with the peak in exceedances for critical loads for the same areas. The increase and subsequent decline from 1965-1996 is significant ($p < 0.01$) using Kruskal-Wallis analysis with Dunn's tests. S.E.s are all below 5% or 1-3.5 mm increment.

Source: Nellemann and Thomsen (2001).

1 terrestrial productivity due to the combination of N deposition and rising atmospheric CO₂
 2 concentrations remains an active area of research and uncertainty.

3 It is also important to note that emissions of NO_x are involved in the formation of
 4 ground-level O₃, which can have serious consequences to the health and function of terrestrial
 5 vegetation (Reich, 1987; Taylor and Hanson, 1992; Laurence et al., 1994; Gundhardt-Goerg
 6 et al., 2000). Ozone effects are not included in this assessment. The combined effects of N and
 7 other air pollutants such as O₃ are not well understood, although studies in regions where both
 8 are important stressors demonstrate effects that include both additive and negative (cancelling
 9 each other out) components (Ollinger et al., 2002).

10 Because the competitive equilibrium of plants in any community is finely balanced, the
 11 alteration of any important environmental parameter has the potential to change the vegetation

1 structure (Skeffington and Wilson, 1988; Bobbink, 1998). This is especially true when the
2 variable is as important as N is to terrestrial ecosystems.

3
4 *AX5.5.4.1.1.1 Coniferous Forest*

5 There are several examples of studies in Europe and the United States that have evaluated
6 the effects of excess N on coniferous forests. In areas of Europe that have received very high
7 levels (>30 kg N/ha/yr) of atmospheric NH_Y deposition, observations in the vicinity of NH₃
8 emissions sources (e.g., livestock farms, manure storage facilities, fertilizer plants) have shown
9 damage to coniferous trees by needle necrosis, followed by needle loss, and finally death of the
10 trees. There may be few areas in the United States where NH_Y deposition would be high enough
11 to cause these kinds of damages.

12 In a high-elevation red spruce-balsam fir (*Abies balsamea*) forest in the northeastern
13 United States, N fertilization over 14 years led to a decrease in live basal area (LBA) with
14 increasing N additions. In control plots, LBA increased by 9% over the course of the study,
15 while LBA decreased by 18% and 40% in plots treated, respectively, with 15.7 kg N/ha/yr and
16 31.4 kg N/ha/yr (McNulty et al., 2005). At the Harvard Forest LTER site, at chronic N addition
17 levels of 50 and 150 kg/ha/yr for 15 years, Magill et al. (2004) found a 31% and 54% decrease,
18 respectively, in red pine growth.

19 Areas of chaparral and mixed conifer forests that receive very high levels of air pollution
20 in southern California have experienced significant environmental change over the past several
21 decades (Fenn et al., 1996, 2003a). There are a number of substantial differences in
22 environmental characteristics and pollution dynamics of these forests as compared to forests in
23 the eastern United States that are exposed to relatively high levels of N deposition (Fenn et al.,
24 2003a). Chaparral watersheds in close proximity to N emissions sources in southern California
25 are characterized by very high N deposition and concentrations of NO₃⁻ in streamwater during
26 high-flow events (Riggan et al., 1985; Fenn and Poth, 1999). In a review of acidic deposition
27 effects on mixed conifers in California, Takemoto et al. (2001) reported that southern California
28 forests experience N deposition up to 45 kg/ha/yr. For Jeffrey (*Pinus jeffreyi*) and ponderosa
29 pine (*Pinus ponderosa*) stands, increased N deposition caused increased growth. Additionally, N
30 fertilization has been shown to cause increased litter accumulation and C storage in above-

1 ground woody biomass, which in turn may lead to increased susceptibility to more severe fires
2 (Fenn et al., 2003a).

3 Wet N deposition is generally low throughout the region, in the range of 1 to 3 kg
4 N/ha/yr. However, dry deposition is highly variable, but ranges up to about 30 kg N/ha/yr or
5 more (Bytnerowicz and Fenn, 1996; Fenn and Bytnerowicz, 1997; Takemoto et al., 2001).
6 Available data (e.g., Minnich et al., 1995) suggest progression toward less needle retention,
7 higher shoot:root biomass ratios, increasing depth of litter, and high NO_3^- in soil solution in
8 response to high N deposition. These changes may eventually lead to replacement of pine
9 species with nitrophilous and O_3 -tolerant species such as fir and cedar (Takemoto et al., 2001).

10 Streamwater NO_3^- concentrations in montane watersheds that are downwind of the
11 greater Los Angeles area are the highest in North America. Some streams in the San Gabriel and
12 the San Bernardino Mountains have been documented to have levels of NO_3^- in stream water
13 with peaks as high as 370 $\mu\text{eq/L}$ (Fenn and Poth, 1999), reflecting very high N deposition and N-
14 saturation of the terrestrial ecosystem. In contrast, N leaching is low in most watersheds in the
15 Sierra Nevada, and NO_3^- concentrations in streams are usually below 1 $\mu\text{eq/L}$. Nevertheless,
16 some of the higher elevation watersheds in the Sierra Nevada export appreciable NO_3^- from the
17 terrestrial environment, particularly during the early phases of snowmelt. Fenn et al. (2002)
18 reported springtime peaks of NO_3^- concentration in lakewater up to 38 $\mu\text{eq/L}$ at high elevation
19 and for watersheds dominated by talus. At lower elevation areas, however, most of the inorganic
20 N deposition loading is retained within the watersheds and concentrations of NO_3^- in stream and
21 lake waters are low (Fenn et al., 2003a). Surface water NO_3^- concentrations in these areas
22 provide an index reflecting the general levels of N deposition. Where surface water NO_3^-
23 concentrations are high, N deposition to the terrestrial watershed is also high.

24 Vegetation in the southern Rocky Mountains responds to increased N supply by
25 increasing plant productivity for some species, but this increase in productivity is also
26 accompanied by changes in species composition and abundance (Bowman et al., 1993). Many of
27 the dominant plant species do not respond to additional N supply with increased production.
28 Rather, many subdominant species, primarily grasses and some forbs, increase in abundance
29 when the N supply is increased (Fenn et al., 2003a).

30 Rueth and Baron (2002) compared Engleman spruce (*Picea engelmannii*) forest stands
31 east and west of the Continental Divide in Colorado. Nitrogen deposition, arising mainly from

1 agricultural and urban areas of the South Platte River Basin, was moderate (3 to 5 kg N/ha/yr) on
2 the east slope, but only 1 to 2 kg N/ha/yr on the west slope. East slope sites showed lower soil
3 organic horizon C:N, lower foliar C:N, higher potential net mineralization, and higher percent N,
4 N:Mg, and N:P ratios in foliage. These results suggested that even moderate levels of N
5 deposition input can cause measurable changes in spruce forest biogeochemistry. It is unclear,
6 however, to what extent such biogeochemical changes affect forest growth or health.

7 Potential effects of N deposition on boreal forests of North America are of concern in
8 part due to the large size of this terrestrial biome. There is also concern that changes in N
9 cycling in the boreal forest may interact with effects of climate warming in ways that are difficult
10 to predict. Such changes have important implications for global C budgets (Mäkipää et al.,
11 1999). For example, climate warming and N deposition may increase NPP and C sequestration
12 in the boreal forest, but may also stimulate decomposition of soil organic matter, potentially
13 leading to a net loss of C from the ecosystem (Kirschbaum, 1994; Mäkipää et al., 1999).

14 Experimental additions of N at low levels (6 kg N/ha/yr) have been shown to cause
15 increased growth of *Deschampsia flexuosa*, which can affect the growth of other species. In
16 areas of Sweden that receive N deposition higher than about 6 kg N/ha/yr, the abundance of two
17 common boreal forest understory species (*Vaccinium myrtillus* and *V. vitis-idea*) is lower than in
18 areas to the north where N deposition is lower (Nordin et al., 2005). Experimental N application
19 has also been shown to increase damage to *V. myrtillus* by natural enemies. The severity of
20 parasitic fungal disease and herbivory by Lepidoptera larvae both increased with N addition
21 (Nordin et al., 1998).

22 23 AX5.5.4.1.1.2 *Deciduous Forest*

24 There is only limited evidence of negative effects of N enrichment on deciduous trees.
25 Aspen (*Populus tremuloides*) have been reported to show positive growth effects from
26 fertilization at N deposition rates as low as 10 kg N/ha/yr (Bytnerowicz, 2002). In a mixed
27 hardwood stand dominated by oaks at the Harvard Forest LTER, growth increased by 11% and
28 30%, respectively, with N additions (NH₄NO₃) of 50 and 150 kg N/ha/yr for 15 years (Magill
29 et al., 2004).

30 The effects of increased nutrient availability to deciduous forests are not restricted to the
31 primary producers. Such effects also extend to herbivores, and likely other members of the food
32 web. Forkner and Hunter (2000) altered plant growth of oak (*Quercus prinus* and *Q. rubra*)

1 saplings through fertilizer (N, P, K) addition. They then censused the densities of insect
2 herbivore guilds and predaceous arthropods on experimental and control trees. In general, leaf
3 chewers, phloem feeders, and leaf miners were more common on fertilized, as compared with
4 non-fertilized, trees. Predaceous arthropods were also more numerous on fertilized trees and
5 their densities were correlated with herbivore densities.

6 7 **AX5.5.4.1.2 Arctic and Alpine Areas**

8 Plant species distributions in arctic tundra are often N-limited (Shaver and Chapin, 1980).
9 Soluble N in tundra soil solution is dominated by organic N, including free amino acids, rather
10 than NH_4^+ or NO_3^- (Kielland, 1995). Tundra plants appear to exhibit a range of interspecific
11 differences that allow coexistence under conditions that reflect a single limiting element.
12 Species differ in rooting depth, phenology, and uptake preferences for organic and inorganic
13 forms of N (Shaver and Billings, 1975; Chapin et al., 1993; Kielland, 1994; McKane et al.,
14 2002). McKane et al. (2002) demonstrated, based on ^{15}N field experiments, that arctic tundra
15 plant species were differentiated in timing, depth, and chemical form of N utilization.
16 Furthermore, the species that exhibited greatest productivity were those that efficiently used the
17 most abundant N forms.

18 Ericoid mycorrhizae provide host plants with the capacity to take up N in the form of
19 amino acids (Stribley and Read, 1980; Bajwa and Read, 1985). This is important in arctic plant
20 communities that occur on acidic organic soils because amino acids are typically readily
21 available in such soils, and N availability generally limits primary productivity.

22 Future climate warming could have important effects on N cycling in arctic tundra
23 ecosystems. In the past, organic materials have accumulated in tundra soils, largely because
24 decomposition has been slower than plant growth. Climate warming may increase the
25 decomposition of soil organic matter, thereby increasing the availability of stored N (Weintraub
26 and Schimel, 2005). The distributions of woody plant species are also increasing in response to
27 warming, with likely feedbacks on C and N cycling. For example, the dominant shrub species in
28 the arctic tundra in Alaska is *Betula nana*; it is expanding its distribution in tussock vegetation
29 communities (Weintraub and Schimel, 2005).

30 Research on N enrichment effects on alpine and subalpine ecosystems in the western
31 United States has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain

1 National Park and the Niwot Ridge LTER site, both located east of the Continental Divide in
2 Colorado (see review by Burns, 2004). Biomass production responses of alpine communities to
3 increased N deposition are dependent on moisture regimes (Fisk et al., 1998) and are driven by
4 shifts in species composition. Addition of 25 kg N/ha during summer caused a community shift
5 towards greater dominance of hairgrass (*Deschampsia* sp.) in wet alpine meadows, but the
6 increase in plant biomass (+67%) and plant N content (+107%) following N fertilization was
7 higher in graminoid-dominated dry meadows than in forb-dominated wet meadows (+53% plant
8 biomass, +64% standing N crop, respectively) (Bowman et al., 1995; Burns, 2004).

9 Seastedt and Vaccaro (2001) showed that 4 years of N addition to alpine vegetation at
10 rates ranging between 100 and 200 kg N/ha (depending on the year) caused marginal increases in
11 alpine plant foliage productivity but reduced species richness.

12 In a follow-up study at Niwot Ridge, additions of 20, 40, and 60 kg N/ha/yr (on top of
13 ambient N deposition near 5 kg N/ha/yr) over an 8-year period to a dry alpine meadow led to a
14 change in plant species composition, an increase in species diversity and plant biomass, and an
15 increase in tissue N concentration at all treatment levels within 3 years of application. Much of
16 the response was due to increased cover and total biomass of sedges (*Carex* spp.). There was a
17 significant decrease in *Kobresia* biomass with increasing N input. Vegetation composition
18 appeared to respond at lower N input levels than those that caused measurable changes in soil
19 inorganic N content.

20 Bowman et al. (2006) concluded that alpine plants may be more sensitive indicators of
21 the effects of increased N inputs than soils. Changes in plant species composition occurred at all
22 treatment levels within 3 years. Changes in an individual species (*Carex rupestris*) were
23 estimated to occur at deposition levels near 4 kg N/ha/yr. Changes in the plant community,
24 based on the first axis of a detrended correspondence analysis, were estimated to occur at
25 deposition levels near 10 kg N/ha/yr. In contrast, increases in NO₃⁻ leaching, soil solution NO₃⁻
26 concentration, and net nitrification occurred at levels above 20 kg N/ha/yr. The authors
27 concluded that changes in vegetation composition preceded detectable changes in soil indicators
28 of ecosystem response to N deposition.

29 Effects of N_r deposition to alpine ecosystems in the western United States are thought to
30 include community-level changes in plants, lichens, mycorrhizae, and phytoplankton. Subtle
31 effects have been shown to occur at what would be considered relatively low levels of N

1 deposition in the eastern United States (about 4 kg N/ha/year) (Bowman et al., 2006). More
2 pronounced effects have been documented in hot spot areas that receive much higher levels of N
3 deposition (Fenn et al., 2003a).

4 Nitrogen deposition to the alpine tundra of Niwot Ridge in the Colorado Front Range
5 altered N cycling and provided the potential for replacement of some native plant species by
6 more competitive, faster-growing native species (Bowman and Steltzer, 1998; Baron et al., 2000;
7 Bowman, 2000). Many plants that grow in alpine tundra, as is true of plants growing in other
8 low resource environments (e.g., infertile soil, desert), tend to have some similar characteristics,
9 including slow growth rate, low photosynthetic rate, low capacity for nutrient uptake, and low
10 soil microbial activity (Bowman and Steltzer, 1998; Bowman, 2000). Such plants generally
11 continue to grow slowly when provided with an optimal supply and balance of resources (Pearcy
12 et al., 1987; Chapin, 1991). In addition, plants adapted to cold, moist environments grow more
13 leaves than roots as the relative availability of N increases. These patterns of vegetative
14 development and their response to added N affect plant capacity to respond to variation in
15 available resources and to environmental stresses such as frost, high winds, and drought.

16 Changes in alpine plant species composition on Niwot Ridge have included increased
17 cover of the plant species that tend to be most responsive to N fertilization in some of the long-
18 term monitoring plots (Korb and Ranker, 2001; Fenn et al., 2003a). These changes have
19 probably developed in response to changes in N deposition. However, the influences of climatic
20 change, particularly changes in precipitation (Williams et al., 1996), and pocket gopher
21 disturbance (Sherrod and Seastedt, 2001) could not be ruled out as contributors to vegetation
22 change (Fenn et al., 2003a). Other environmental factors also affect the species make-up of
23 alpine ecosystems, but long-term experimental fertilization plots demonstrate a clear response of
24 alpine flora to N, including shifts toward graminoid plants that shade smaller flowering species,
25 and accompanying changes in soil N cycling (Bowman et al., 2006).

26 Changes in plant species in response to N deposition to the alpine zone can result in
27 increased leaching of NO_3^- from the soils because the plant species favored by higher N supply
28 are often associated with greater rates of N mineralization and nitrification than the pre-existing
29 species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al., 2006).

30 Total organic N pools in the soils of dry alpine meadows are large compared to pools of
31 NH_4^+ and NO_3^- (Fisk and Schmidt, 1996). However, positive response to inorganic N

1 fertilization has been demonstrated, and thus some plant species appear to be restricted in their
2 ability to take up organic N from the soil and are growth-limited by the availability of inorganic
3 N (Bowman et al., 1993, 1995; Theodose and Bowman, 1997). Miller and Bowman (2002)
4 analyzed patterns of foliar ^{15}N , NO_3^- reductase activity, and mycorrhizal infection compared
5 with N uptake quantified by stable isotope tracer additions in the greenhouse. ^{13}C enrichment
6 subsequent to ^{13}C , ^{15}N -glycine addition indicated that all of the 11 genera studied were able to
7 take-up labeled glycine to some extent. Glycine uptake ranged from about 35% to more than
8 100 % of NH_4^+ uptake. Only *Festuca* (fescue grass) showed glycine uptake exceeding both
9 NH_4^+ and NO_3^- uptake (Miller and Bowman, 2002).

10 11 **AX5.5.4.1.3 Grasslands**

12 Grasses are well known to respond to increased N availability. Under high N supply,
13 grasses will often out-compete other species, and cause changes in plant community
14 composition. In European grasslands, change in species composition in response to N deposition
15 have been observed regardless of soil type. Such effects have been found in calcareous, neutral,
16 and acidic environments, species-rich heaths, and montane-subalpine grasslands (Bobbink et al.,
17 1992, 1998; Stevens et al., 2004).

18 Lowe et al. (2002) tested the response of two native (blue grama and western wheatgrass)
19 and four exotic (cheatgrass, leafy spurge, Canada thistle, and Russian knapweed) grassland
20 species to increased N availability (0, 10, 40, 70, or 100 kg N/ha) in a 75-day greenhouse
21 experiment. They found that all of the grass species exhibited increased growth with increased N
22 availability. Native species did not consistently grow better at low N levels than the exotic
23 species. Two of the exotic grasses exhibited the greatest increase in growth, while another of the
24 exotics exhibited the smallest increase in growth. For these species, the authors found no
25 generalizable relationship between life-history (weedy exotic versus non-weedy native) and
26 growth response to N.

27 In the San Francisco Bay area, which receives N deposition levels of 10 to 15 kg N/ha/yr,
28 exotic nitrophilous grasses have displaced native grass species, likely due to greater N
29 availability from deposition and from the cessation of grazing, which previously exported N out
30 of the system (Fenn et al., 2003a). Since this change in species composition, populations of the
31 rare and threatened bay checkerspot butterfly (*Euphydryas editha bayensis*) have declined

1 greatly. It has been hypothesized that the response of the butterfly has been due to the vegetative
2 changes.

3 In old agricultural fields in Michigan, increased N deposition changed neither the
4 successional timing nor the gain or loss of species numbers (Huberty et al., 1998). A lack of
5 response in species richness may have been due to mid-growing season fertilization. Huberty
6 et al. (1998) suggested that N additions may change the dominance structure of these
7 successional old-field communities. Other studies in Michigan also indicated that successional
8 grasslands were not N-saturated (Ambus and Robertson, 2006) and showed no response to N
9 application of 1 g N/m²/yr, equivalent to about 2.5 times ambient deposition rates. Ambus and
10 Robertson (2006) suggested that the small projected increases in future N deposition would have
11 little effect on these grasslands.

12 From studies of N additions in tallgrass prairie (0.1, 1, 3 mmol N addition/80 days), Lane
13 and BassiriRad (2002) suggested that increasing N deposition levels could cause species-specific
14 growth and plant tissue quality changes, which in turn could lead to changes in ecosystem
15 dynamics and community structure. In interior coastal grasslands at Jasper Ridge Biological
16 Preserve in California, additions of 70 kg N/ha/yr over 3 years led to declines in plant diversity,
17 forb production, and forb abundance, concomitant with increased grass productivity (Zavaleta
18 et al., 2003). Increased N deposition led to a decline in total species richness. Specifically,
19 *Bromus hordeaceus* abundance increased while *Avena barbata* declined during the experiment.

20 Grasslands of the Great Plains of North America have experienced invasions of woody
21 plant species (Kleb and Wilson, 1997). The limiting soil resource in this plant community is
22 generally N (Tilman, 1987). Fertilization may increase the water use efficiency of woody
23 species (Bert et al., 1997), and enable them to colonize temperate grassland sites (Köchy and
24 Wilson, 2001). Accelerated rates of N cycling (Carreiro et al., 2000) may increase competition
25 for light (Wilson and Tillman, 1991) and give advantage to trees (Aerts et al., 1999; Köchy and
26 Wilson, 2001). High N deposition has been shown to be correlated with an increase of tall plant
27 species in nutrient-poor European grasslands (Bobbink et al., 1998). Köchy and Wilson (2001)
28 quantified forest invasion of aspen trees into grasslands in six national parks in western Canada
29 that received a range of levels of atmospheric N deposition. The rate of aspen expansion was
30 measured from aerial photographs taken over a period of six decades. Forests in high-deposition

1 parks expanded 10 times faster than forests in low-deposition parks. The average forest
2 expansion rate was 1% per year in high-deposition parks (Köchy and Wilson, 2001).

3 4 **AX5.5.4.1.4 Arid Lands**

5 In desert ecosystems, water is generally more limiting than N. However, enhanced N
6 could play a role in the observed invasion of some exotic plant species. In the Mojave desert, the
7 shrub *Larrea tridentata* showed no increased growth response to N additions (at 10 and 40 kg
8 N/ha/yr as $(\text{Ca}(\text{NO}_3)_2)$) but did respond to increased water (Barker et al., 2006). Invasive
9 annuals showed a greater response to elevated N than native species, and have recently invaded
10 parts of the Mojave and Sonoran deserts. Though their invasion is correlated with greater N
11 deposition, no causation has been established (Fenn et al., 2003a).

12 In a greenhouse experiment with native shrubs and exotic grasses from the California
13 coastal sage scrub (CSS) ecosystem, N (as 5.4 g/L NH_4Cl or 10g/L KNO_3) was added to obtain
14 soil N concentrations of 2, 20, 40, and 80 $\mu\text{g/g}$. The grasses demonstrated a 1.5- to 2.5-fold
15 growth increase when soil N levels increased from 20 to 40 $\mu\text{g/g}$. To achieve a comparable
16 growth increase, shrubs required higher soil N levels (between 20 and 80 $\mu\text{g/g}$) (Padgett and
17 Allen, 1999). These lab experiments agree with observations in the field, where exotic grasses,
18 especially once established, have replaced native shrubs under elevated N deposition (Padgett
19 and Allen, 1999).

20 Changes in plant root-to-shoot growth ratios were observed in studies of the CSS
21 community, which is composed largely of the drought-resistant deciduous shrubs *Artemisia*
22 *californica*, *Encelia farinosa*, and *Eriogonum fasciculatum*. The CSS community in California
23 has been declining in land area and in shrub density over about the past 60 years and is being
24 replaced in many areas by Mediterranean annual grasses (Padgett and Allen, 1999; Padgett et al.,
25 1999). Nitrogen deposition is considered a possible cause or contributor to this ecosystem
26 alteration. More than 30 kg N/ha/year of atmospheric N is deposited to portions of the Los
27 Angeles Air Basin (Bytnerowicz and Fenn, 1996). The CSS community is of particular interest
28 because about 200 sensitive plant species and several federally listed threatened or endangered
29 animal species are found in the area.

30 In CSS ecosystems along a deposition gradient (2 to 57 $\mu\text{g N/g}$ as soil NO_3^-), Egerton-
31 Warburton and Allen (2000) discerned a shift in arbuscular mycorrhizal community composition

1 with decreased species richness and diversity. Larger-spored species were displaced as smaller-
2 spored species proliferated. These shifts in mycorrhizal fungal communities may facilitate
3 replacement of native CSS plant communities by Mediterranean annual grasslands.

4 In a sagebrush (*Artemisia tridentata*) steppe ecosystem, N additions of 6 or 12 kg N/ha/yr
5 as NH_4NO_3 for 6 years (in addition to ambient inputs of 1.3 to 1.4 kg N/ha/yr) resulted in a
6 decrease in soil moisture caused by shifts in plants species composition and cover. However,
7 there were no effects on perennial grass cover in response to experimental N additions (Inouye,
8 2006).

9 *Sarcobatus vermiculatus*, a desert shrub found in the Great Basin Desert, demonstrated a
10 twofold to threefold increase in stem growth, a 2.5 to 4 fold increase in viable seed production,
11 and a 17% to 35% increase in leaf N with N additions at sites around Mono Lake, CA. Nitrogen
12 was applied in March and November as NH_4NO_3 , at a cumulative addition rate of 233.6 g N per
13 plant (Drenovsky and Richards, 2005).

14 In the Chihuahuan desert, greater N losses in shrublands (0.33 kg/ha/yr) versus grasslands
15 (0.15 kg/ha/yr) corresponded with greater runoff in shrublands. Even with runoff nutrient losses,
16 both systems showed a net accumulation of total dissolved N, just over 2 kg N/ha/yr, with
17 atmospheric N deposition of about 2.5 kg/ha/yr (Schlesinger et al., 2000).

18 A fertilization experiment in the Chihuahuan desert, with inputs of 100 kg N/ha/yr over
19 about a decade, resulted in a 30% increase in cover of warm season grasses and a 52% reduction
20 in cover of legumes (Baez et al., 2007). From 1989 to 2004, Baez et al. (2007) observed a 43%
21 increase in ambient N deposition, from 1.71 to 2.45 kg N/ha/yr, resulting in an additional 5.88 kg
22 N/ha deposition over that time period. They suggest that these deposition trends may result in
23 significant plant community changes, as indicated by fertilization studies of blue gramma
24 (*Bouteloua gracilis*) and black gramma (*B. eriopoda*). With additions of 20 kg N/ha in one
25 season, blue gramma was favored over black gramma, the current dominant species (Baez et al.,
26 2007).

27 Another fertilization experiment in an arid grassland on the Colorado Plateau
28 demonstrated a large difference in the response of native and non-native plants. For 2 years,
29 plots were treated with 0, 10, 20, or 40 kg N/ha/yr as a KNO_3 solution (Schwinning et al., 2005).
30 Galleta (*Hilaria jamesii*) and Indian ricegrass (*Oryzopsis hymenoides*) showed no increase in leaf
31 photosynthesis or tiller size, but ricegrass showed a 50% increase in tiller density in the second

1 year at the 20 and 40 kg N/ha/yr application levels. For both species, the increased N application
2 hastened the onset of water stress. Unexpectedly, a non-native species, Russian thistle (*Salsola*
3 *iberica*) showed a rapid growth response to the highest fertilization rate in the first summer,
4 when rainfall was above average. Schwinning and colleagues (2005) suggested that the timing
5 and amount of N deposition could facilitate noxious weed invasion and thus change community
6 composition in arid grasslands.

7 Fertilization experiments in the Mojave desert also showed that increased levels of N
8 deposition could favor the establishment of non-native species where non-natives are already
9 prevalent (Brooks, 2003). At application rates of 32 kg N/ha/yr over 2 years, both density and
10 biomass of non-native plants increased (54% increased biomass), while native species biomass
11 declined by about 39%. Brooks (2003) found that plant responses were influenced by rainfall
12 events rather than by average annual rainfall, with the annual plants thriving in a year when high
13 rainfall events triggered germination.

14 Allen et al. (in press) measured N_f in the atmosphere and soils in Joshua Tree National
15 Park, CA, which receives moderate levels of air pollution from the Los Angeles Basin. Possible
16 effects on native and invasive plant species were examined. The park is located at the boundary
17 between the Mohave and Colorado deserts. Extractable soil N was generally higher at study sites
18 that received higher atmospheric N deposition. Nitrogen fertilizer was applied at levels of 5 and
19 30 kg N/ha/yr at four sites over a 2-year period. Low-elevation sites were dominated by creosote
20 bush scrub and higher-elevation sites by pinyon-juniper woodland. Non-native grass biomass
21 increased significantly at three of four treatment sites that received 30 kg N/ha/yr, but not at the
22 sites that received 5 kg N/ha/yr. Nitrogen fertilizer studies by Brooks et al. (2003) in the
23 Mohave Desert also showed increased productivity of invasive grasses with increased N loading.

24 25 **AX5.5.4.2 Effects on Transitional Ecosystems**

26 As discussed previously, ombrotrophic bogs, peatlands, and coastal marshes are the
27 transitional ecosystems that appear to be most sensitive to the effects of excess N. Many bogs
28 receive the majority of their nutrients, including N, from atmospheric deposition. If atmospheric
29 N loading increases substantially to a bog ecosystem, it is expected that productivity will
30 increase and may be accompanied by changes in species composition to favor those species that
31 are adapted to higher nutrient levels. U.S. EPA (1993) reviewed field experiments involving N

1 fertilization of wetlands. Results of those experiments confirmed the belief that wetland
2 vegetation is commonly limited by N availability.

3 The form of added N may regulate wetland response to N deposition. Experimental
4 applications of NO_3^- appear to have been less effective at stimulating wetland plant productivity
5 than applications of NH_4^+ (U.S. Environmental Protection Agency, 1993). This may reflect
6 higher rates of denitrification in response to the added NO_3^- , suggesting the importance of
7 competition between plants and microbes for bioavailable N. Plants appear to compete more
8 successfully for NH_4^+ and microbes to compete more successfully for NO_3^- . An important
9 caveat expressed by U.S. EPA (1993), however, was that the results of relatively short-term N
10 fertilization experiments are not necessarily good predictors of long-term wetland community
11 responses to increased N inputs.

12 Data are not available with which to evaluate the extent to which wetlands in the United
13 States have been affected by nutrient enrichment from N deposition. Wetlands are widely
14 distributed (Figure AX5.4-2) including some areas that receive moderate levels of N deposition.
15 In general, however, wetlands are not common in areas of the United States that experience the
16 highest levels of N deposition: near the Los Angeles Basin and at high elevation in the Great
17 Smoky Mountains. The moderate levels of N deposition commonly found in areas that contain
18 appreciable areas of wetland may or may not be sufficiently high to cause species shifts in
19 wetland plants. If such effects do occur, they are most likely in wetlands such as bogs and poor
20 fens that normally receive most of their nutrients from atmospheric inputs.

21 22 **AX5.5.4.3 Effects on Aquatic Ecosystems**

23 24 **AX5.5.4.3.1 Lakes and Streams**

25 Aquatic systems can be subdivided into major types based on hydrology. At the broadest
26 level, freshwater aquatic ecosystems can be classified as riverine, lacustrine, and palustrine
27 systems. Riverine systems can be identified at varying scales, including valley segment, river
28 reach, and channel unit. Lacustrine systems include deepwater habitats associated with lakes and
29 reservoirs. Palustrine systems include small, shallow, or intermittent water bodies, including
30 ponds. Each type of aquatic ecosystem is potentially sensitive to nutrient enrichment effects
31 from N deposition. Nevertheless, available data documenting such effects are limited.

1 A number of things have conspired to prevent extensive evaluation of the effects of
2 atmospheric N deposition on aquatic organisms via nutrient-enrichment pathways. These
3 include assumptions, or prevailing paradigms, that have channeled scientific thought in one
4 direction and away from others. First were the assumptions for many years that atmospheric
5 deposition was caused primarily by sulfur (S) emissions and that effects on aquatic ecosystems
6 were primarily caused by acidification processes. Only after S emissions began to decrease
7 substantially in response to the Clean Air Act amendments did the role of NO_x, and still later,
8 NH₃, emissions become recognized as potential agents of environmental change. And even then,
9 that role was assumed to be restricted mainly to acidification from NO₃⁻, a strong acid anion, not
10 eutrophication (Reuss and Johnson, 1985). Second, because N is the nutrient most limiting to
11 primary production in most ecosystems, it was assumed until fairly recently that N was tightly
12 cycled in terrestrial systems, and that excess NO₃⁻ leaching rarely occurred in natural
13 environments (Vitousek and Howarth, 1991). Finally, the attention of aquatic biologists has
14 been strongly focused on the role of P in eutrophication of freshwaters for the past 40 years,
15 largely due to the demonstrated role of P in causing large increases in algal productivity
16 worldwide (Schindler et al., 1971; Schindler, 1974). Phosphorus is an essential, and often
17 limiting, nutrient to aquatic organisms. A large number of highly influential studies in the 1960s
18 and 1970s exposed the role of wastewater, in particular phosphate detergents, in causing
19 excessive algal production and anoxia in Lake Mendota (Wisconsin), Lake Washington
20 (Washington), Lake Erie, and many other locations (Hasler, 1947; Vollenweider, 1968;
21 Edmondson, 1969, 1991). Because of the emphasis on P as a major cause of fresh water
22 eutrophication, Downing and McCauley (1992) wrote as recently as 1992: “opinions differ on
23 the role of N as a limiting nutrient in lakes.”

24 The role of N deposition in freshwater eutrophication and acidification processes has
25 been considered secondary to P and S, and only within the past 20 years have there been studies
26 questioning the established science and showing N-limitation in some fresh waters, N excess in
27 some terrestrial systems, and N-caused acidification in poorly buffered fresh waters. A recent
28 meta-analysis of 990 freshwater field experiments to determine the patterns of autotrophic
29 nutrient limitation found that N-limitation of stream benthos, lake benthos, and phytoplankton
30 was as common as P-limitation from sites in all biomes worldwide (Elser et al., 2007). In other

1 words, experimental additions of N to these systems stimulated primary production. Many other
2 individual studies are described below, and are tabulated in Table AX5.5-3.

3 Recently, a comprehensive study of available data from the northern hemisphere found
4 unequivocal evidence of N limitation in lakes with low ambient inputs of N, and increased N
5 concentrations in lakes receiving N solely from atmospheric N deposition (Bergström and
6 Jansson, 2006). These authors suggested that the majority of lakes in the northern hemisphere
7 may have originally been N-limited, and that atmospheric N deposition has changed the balance
8 of N and P in lakes so that P-limitation is generally observed today. If this is correct, the role of
9 atmospheric N deposition as an influence on aquatic primary production may have been
10 underestimated throughout the entire history of limnology.

11 A cascade of environmental effects occurs in response to excess available N, but in
12 freshwater systems effects can be grouped under the two categories of eutrophication and
13 acidification. Aquatic systems in which N has been observed to influence ecological processes
14 either receive extremely high inputs (e.g., Dumont et al., 2005), or have very low initial N
15 concentrations, and respond rapidly to additional inputs (Baron et al., 2000; Bergström and
16 Jansson, 2006). Some ecosystems are seasonally enhanced with N from atmospheric deposition,
17 either from snowmelt flushing of accumulated N in winter snow, or from flushing during
18 dormancy of terrestrial vegetation (Stoddard, 1994). While many eutrophic and hypereutrophic
19 freshwater ecosystems have seasonal or perennial cyanobacteria that fix atmospheric N,
20 obviating the need for an external source of N (Wetzel, 2001), we found only one study of an
21 oligotrophic lake with obligate N-fixing bacteria (Reuter et al., 1985). N-fixation is energy
22 expensive and sometimes limited by trace metal availability, so obligate N-fixing cyanobacteria
23 (formerly called blue-green algae) are rarely found in ultra-oligotrophic waters (McKnight et al.,
24 1990; Vitousek and Howarth, 1991). Because of this, oligotrophic and ultraoligotrophic waters
25 are extremely sensitive to even low inputs of N from atmospheric deposition. A review paper on
26 the impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems provides
27 evidence for N-caused eutrophication, and states that nutrient loading restriction is the essential
28 cornerstone of aquatic eutrophication control (Smith et al., 1999).

29 We explored the eutrophication effects of excess N to lakes and streams, addressing
30 responses to individual species of aquatic organisms, including fungi, algae, zooplankton,
31 aquatic insects, amphibians, and fish. A literature search revealed 60 studies in which species'

1 tolerances to different N concentrations were studied. We also addressed ecosystem processes
2 influenced by excess N, including primary productivity, community composition, and trophic
3 state (31 studies). These analyses illustrate three important scientific findings: (1) primary
4 productivity in many freshwaters today can be increased with the addition of even very low
5 concentrations of N; (2) the eutrophication that ensues increases algal biomass, alters algal
6 species assemblages, and possibly affects food webs; and (3) lakes and streams remote from
7 direct inputs of N from runoff historically have been, and currently are, susceptible to N-caused
8 eutrophication via atmospheric N deposition.

9 Individual algal taxa are stimulated at low N concentrations, and several, including
10 *Asterionella formosa* and *Fragilaria crotonensis*, have come to dominate some lakes that have
11 received elevated N deposition. Other species have declined commensurate with increased
12 available N, but we found only one study (Interlandi et al., 1999) that addressed the question of
13 effects of N deposition on freshwater aquatic diversity. Clearly, more work is needed in this
14 field.

15 Results from surveys, paleolimnological reconstructions of past conditions, experimental
16 results, and meta-analyses of hundreds of studies all consistently show N-limitation to be
17 common in fresh waters, especially in remote areas, and a nearly universal eutrophication
18 response to N-enrichment in lakes and streams that are N-limited. Paleolimnological records
19 similarly show increases in productivity and changes in algal assemblages in the recent past
20 (since 1950) that are correlated with increased societal use of synthetic N fertilizers and human
21 population increases. The paleolimnological evidence is strongest in regions with the highest N
22 deposition, and is weaker where N deposition is lower (Wolfe et al., 2001, 2003, 2006; Saros
23 et al., 2003).

24 Surveys of lake N concentrations and trophic status along gradients of N deposition show
25 increased inorganic N and productivity to be strongly related to atmospheric N deposition.
26 Where N-enrichment has occurred, P limitation, N+P colimitation, and a few instances of Si
27 depletion have been reported. Algal community reorganization has been observed in the
28 paleolimnological record, experiments, and observations of N-enriched lakes, especially those
29 where enrichment has come from N deposition.

30 Nitrogen deposition appears to have stimulated productivity and altered algal species
31 assemblages at low deposition rates of 1.5 to 2.2 kg N/ha/yr. Data from a survey of 44 lakes east

1 and west of the Continental Divide in Colorado indicated that lakes on the western side of the
2 Continental Divide averaged 6.6 $\mu\text{eq/L}$ of NO_3^- , whereas lakes on the eastern side of the
3 Continental Divide averaged 10.5 $\mu\text{eq/L}$ of NO_3^- concentration. In the Colorado Front Range,
4 NO_3^- concentrations in lakes above 15 $\mu\text{eq/L}$ have commonly been measured, suggesting some
5 degree of N-saturation (Baron, 1992). A meta-analysis of 42 regions in Europe and North
6 America suggested that a majority of lakes in the northern hemisphere were limited by N in their
7 natural state. While many of these lakes now receive sufficient N from deposition that they are
8 no longer N-limited, some lakes in remote regions still maintain their original oligotrophic or
9 ultra-oligotrophic status.

10

11 ***AX5.5.4.3.2 Estuaries and Near-Coastal Marine Waters***

12 Estuarine and coastal ecosystems experience a range of ecological problems associated
13 with nutrient enrichment. Because the productivity of estuarine and saltwater ecosystems is
14 naturally limited by the availability of N_r , excessive contribution of N_r from sources of water and
15 air pollution can cause eutrophication. Environmental effects include increased algal blooms,
16 depletion of DO in bottom waters, and reduction in fisheries and sea grass habitats (Valiela and
17 Costa, 1988; Valiela et al., 1990; Boynton et al., 1995; Paerl, 1995, 1997; Howarth et al., 1996).
18 Each of these potential impacts carries ecological and economic consequences. An algal bloom
19 can cost local fishing and tourism economies millions of dollars. In most cases, the excess
20 nutrient inputs to estuarine and near-coastal environments are largely derived from point and
21 nonpoint source pollution contributions in upstream watersheds. A small, but sometimes
22 quantitatively important, portion of the riverine N load is derived from atmospheric N
23 deposition.

24 The form of N input to coastal ecosystems has an important influence on its effects.
25 Atmospheric deposition of reduced N has increased relative to oxidized N in the eastern United
26 States, and this trend is expected to continue in the future under existing emissions controls.
27 Such patterns can influence marine eutrophication responses. Large diatoms tend to dominate
28 coastal waters when NO_3^- is supplied (Stolte et al., 1994; Paerl et al., 2001), whereas smaller
29 diatom species have a greater preference for NH_4^+ uptake. Thus, ongoing trends of decreasing
30 NO_3^- deposition and increasing NH_4^+ deposition might lead to changes in species distributions

1 and size distributions of phytoplankton, with cascading effects on trophic structure and
2 biogeochemical cycling (Paerl et al., 2001).

3 Smith et al. (1997) applied the SPARROW model to streamwater chemistry data from the
4 National Stream Quality Accounting Network in order to evaluate NO_3^- leaching in large river
5 basins. Leaching losses of N in large river systems provide important sources of N to estuaries
6 and coastal marine waters. Smith et al. (1997) concluded that much of the United States
7 probably exports less than 5 kg N/ha/yr, but that N export in watersheds of the northeastern
8 United States is probably higher. For the watersheds that export more than 10 kg N/ha/yr, Smith
9 et al. (1997) concluded that fertilizer was the largest source of N (48%), followed by atmospheric
10 deposition (18%) and livestock wastes (15%). In this analysis, fertilizer used for human food
11 production was considered to be the ultimate source of N contributed to waterways through
12 wastewater treatment plants. If the analysis of N sources to estuarine water is restricted to only
13 nonpoint sources of N, atmospheric deposition is often considered to be the largest individual
14 source (Howarth et al., 1996; Jaworski et al., 1997; Smith et al., 1997; NRC, 2000).

15 Direct atmospheric deposition to the surfaces of estuaries and coastal marine waters
16 provides additional N loading to these ecosystems. There is no evidence suggesting that fish
17 kills or other severe ecological consequences have been caused solely by atmospheric N inputs to
18 estuarine or marine water in the United States. It is clear, however, that atmospheric N
19 deposition has contributed to the N supply that has caused such effects.

20 Nitrogen is an essential nutrient for estuarine and marine fertility. However, excessive N
21 contributions can cause habitat degradation, algal blooms, toxicity, hypoxia (reduced dissolved
22 oxygen), anoxia (absence of dissolved oxygen), fish kills, and decrease in biodiversity (Paerl,
23 2002). In the estuaries and coastal ecosystems in the United States that experience varying levels
24 of N over-enrichment, the importance of atmospheric deposition as a cause of eutrophication is
25 determined by the relative contribution of atmospheric versus non-atmospheric sources of N
26 input.

27 Atmospheric N deposition has been estimated to account for only a few percent to more
28 than 40% of total external N loading to estuaries in North America and Europe. Valigura et al.
29 (2000) estimated that direct atmospheric deposition to the estuary surface generally constitutes at
30 least 20% of the total N load for estuaries that occupy more than 20% of their watershed. U.S.
31 EPA (1999b) estimated that between 10% and 40% of the total N input to estuaries in the United

1 States is typically derived from atmospheric deposition. NRC (2000) judged that U.S. EPA
2 (1999a) underestimated the importance of atmospheric deposition as a contributor to the total N
3 load. These estimates of the relative importance of atmospheric deposition, compared to non-
4 atmospheric sources of N, are highly uncertain. It is clear, however, that the relative contribution
5 of atmospheric deposition to total N loading varies with atmospheric N deposition, land use,
6 watershed and estuary area, and hydrological and morphological characteristics that influence
7 water retention time (Paerl et al., 2001).

8 The greatest uncertainty in the development of detailed N budgets for coastal ecosystems
9 is how much of the N deposited on the watershed is transferred through the terrestrial watershed
10 to the estuary. For example, published estimates of the percent of the total N loading to the
11 estuary contributed by atmospheric deposition exhibit wide variability. Such estimates for a
12 specific estuary commonly differ by more than a factor of two, and sometimes differ by much
13 more than that. For example, published estimates of the percent of the total N load contributed
14 to two east coast estuaries by atmospheric deposition are summarized in Table AX5.5-4.

15 It has been difficult to quantify the magnitude of the various watershed N sources as
16 contributors to the load of N that enters a specific estuary. This difficulty stems from a number
17 of uncertainties, the most important of which concern (1) the existence of multiple agricultural
18 and mobile and stationary fuel combustion emission sources, (2) the difficulty in quantifying dry
19 deposition to the estuary surface and to the watershed, (3) the difficulty in measuring gaseous
20 losses of NH₃ and NO_x compounds to the atmosphere, and (4) the complexity of N flow
21 pathways through the watershed (NRC, 2000).

22 Despite the variability, it appears that atmospheric sources of N loading to estuaries in the
23 United States can be quantitatively important. The major sources of N to estuaries and near-
24 coastal marine waters in the United States, in addition to atmospheric deposition, include
25 wastewater effluent derived mainly from food imports and consumption, fertilizer application,
26 livestock feed imports, and N-fixing crops (Boyer et al., 2002; Driscoll et al., 2003a). Driscoll
27 et al. (2003a) estimated annual net anthropogenic N inputs to eight large watersheds in the
28 Northeast for the year 1997. Input values of total atmospheric plus non-atmospheric
29 anthropogenic N ranged from 14 kg N/ha/yr in the watershed of Casco Bay in Maine to 68 kg
30 N/ha/year in the watershed of Massachusetts Bay (Driscoll et al., 2003a). In all eight
31 watersheds, net import of N in food for humans was the largest anthropogenic input.

1 Atmospheric deposition was estimated to be the second largest anthropogenic N input, ranging
2 from 5 to 10 kg N/ha/year, or 11% to 36% of the total inputs, with four watersheds ranging from
3 34% to 36% (Driscoll et al., 2003a). These results are broadly consistent with estimates by
4 Boyer et al. (2002), who used a similar N budgeting approach for 16 large northeastern United
5 States river basins and reported that N deposition contributes approximately 31% of the total N
6 load to large river basins, although this fraction varies regionally (Boyer et al., 2002). Boyer
7 et al. (2002) considered only the portions of each basin above USGS gauging stations, which
8 often occurred above large population centers. Hence, the Driscoll et al. (2003a) budgets
9 included regions with greater human food consumption than those considered by Boyer et al.
10 (2002).

11 Boyer et al. (2002) estimated that, over the combined area of the 16 northeastern river
12 basins, atmospheric deposition averaged 31% of total N inputs, the largest of the N input terms.
13 Contributions from atmospheric deposition ranged from 60% of N inputs for the basins in
14 northern Maine to 15 to 20% for the Schuylkill and Potomac River Basins, the latter of which
15 had large agricultural N inputs. Across all basins, estimated riverine export of N amounted to
16 25% of total N inputs, and ranged from 11% to 40%. This result is consistent with a similar
17 analysis by Howarth et al. (1996), who found that basins draining to the North Atlantic exported
18 approximately 25% of anthropogenic N inputs on average.

19 Turner et al. (2001) found a strong correlation between population density (persons per
20 km²) and the total N loading from watershed to estuary ($r^2 = 0.78$) for coastal watersheds in the
21 United States. This finding is likely due to the prevalence of automobiles in heavily populated
22 areas, and their associated N emissions and deposition, plus the myriad non-atmospheric sources
23 of N from human activities, particularly sewage releases. They also determined that direct
24 atmospheric deposition becomes increasingly more important as a contributor to the total N
25 loading to an estuary as the water surface area increases relative to total watershed area
26 (terrestrial plus water surfaces). Turner et al. (2001) found that, on average, direct atmospheric
27 deposition of N accounted for more than an estimated 25% of the estuarine N load when the
28 estuary surface occupied 20% or more of the overall watershed area. Few of the estuaries in the
29 eastern United States comprise such a large percentage of their watershed (Castro et al., 2001).

30 The estimates of the effect of direct atmospheric deposition to estuary surfaces are
31 hampered by uncertainties in dry deposition rates. Many published studies have assumed that

1 dry N deposition is equal to measured wet deposition (e.g., Fisher and Oppenheimer, 1991;
2 Hinga et al., 1991; Scudlark and Church, 1993), and this is probably biased high (cf. Baker,
3 1991). However, other studies have assumed lower dry N deposition rates for estuarine and near
4 coastal areas, equal to 40% of wet (Jaworski et al., 1997) or 67% of wet (Meyers et al., 2001).
5 Of particular importance, the rate of dry deposition to open water surfaces is much lower than
6 the rate of dry deposition to vegetated terrestrial surfaces. Paerl et al. (2001) estimated that dry
7 deposition to open estuarine surfaces is three to five times lower. This difference is seldom
8 considered in N-budgeting studies, and can have a substantial impact on estimates of direct
9 atmospheric loading to estuary surfaces, which is especially important for estuaries having low
10 watershed area to estuary surface area ratio.

11 Overall, a significant fraction of atmospherically deposited N is retained within terrestrial
12 ecosystems. Only a relatively small percentage typically reaches an estuary or coastal marine
13 waters. The loading of N to the watershed from various sources does not necessarily reflect the
14 importance of N sources to the portion of the total N loading that is actually transported to
15 estuaries or marine waters. If all of the N that is added to the watershed actually leached to the
16 estuary, environmental damage to many estuaries in the United States would be catastrophic.
17 Fortunately, most of the atmospherically deposited N is retained within watershed soils and
18 vegetation. It is difficult to estimate the percentage of atmospherically deposited N that leaches
19 to estuaries and marine environments under mixed land use conditions. Nevertheless, the
20 fraction that is exported from upland watersheds to estuaries in the eastern United States is
21 ecologically significant.

22 In an effort to evaluate the contribution of atmospheric N deposition to the future
23 reduction in N loading to estuaries, Castro and Driscoll (2002) reported model calculations that
24 suggested that considerable reductions (more than 25%) in atmospheric N deposition will be
25 needed to significantly reduce the contribution made by atmospheric N deposition to the total N
26 loads to their study estuaries in the northeastern United States. A simulated reduction in
27 atmospheric deposition of 25% of ambient deposition rates reduced the contribution made by
28 atmospheric deposition to the total estuarine N loads by only 1% to 6% (Castro and Driscoll,
29 2002). In a later study, Driscoll et al. (2003a) estimated that the implementation of aggressive
30 controls on both mobile N emissions sources and electric utilities would produce an estimated
31 reduction in estuarine loading in Casco Bay, ME of 13% (Driscoll et al., 2003a).

1 Better knowledge of the relative contribution of the various N sources to river systems is
2 needed to understand the importance of atmospheric sources to coastal waters and to provide the
3 foundation for basin-scale nutrient management. A number of empirical approaches have been
4 developed to quantify N fluxes to the coastal zone. They rely on estimates of N sources within
5 the watershed and characteristics of the landscape. Alexander et al. (2002) compared several of
6 these empirical methods. The most accurate and least biased approach examined was that of
7 Howarth et al. (1996). A modified version of the Howarth et al. (1996) methodology was
8 published by Boyer et al. (2006). More mechanistic approaches include those of Bouwman et al.
9 (2005), Van Drecht et al. (2003), and Green et al. (2004).

10 11 12 **AX5.6 EFFECTS ON WATERSHEDS AND LANDSCAPES**

13 14 **AX5.6.1 Interactions among Terrestrial, Transitional, and Aquatic** 15 **Ecosystems**

16 Streams, and to a lesser extent lakes, can serve as indicators of regional environmental
17 change (Seastedt et al., 2004), partly because they integrate conditions within their watersheds,
18 including atmospheric, edaphic, geologic, and hydrologic conditions. Streams reflect the
19 terrestrial environment most closely during high flow, when much of the stream water enters the
20 channel from the upper soil, where most of the biological activity occurs. The terrestrial signal
21 can be less clear in lakes because they have the capacity to store water and modify water
22 chemistry through internal processes to a greater degree than streams (Lawrence et al., in
23 review).

24 Young and Sanzone (2002) provided a checklist of ecological attributes that should be
25 considered when evaluating the effects of an environmental stressor on the integrity of ecological
26 systems (Table AX5.6-1). The Essential Ecological Attributes (EEAs) listed in the table
27 represent groups of related ecological characteristics (Harwell et al., 1999), including landscape
28 condition, biotic condition, chemical and physical characteristics, ecological processes,
29 hydrology and geomorphology, and natural disturbance regimes. The first three ecological
30 attributes listed in Table AX5.6-1 can be classified primarily as “patterns,” whereas the last three
31 are “processes” (cf. Bormann and Likens, 1979). They can be affected by a variety of
32 environmental stressors (Figure AX5.6-1).

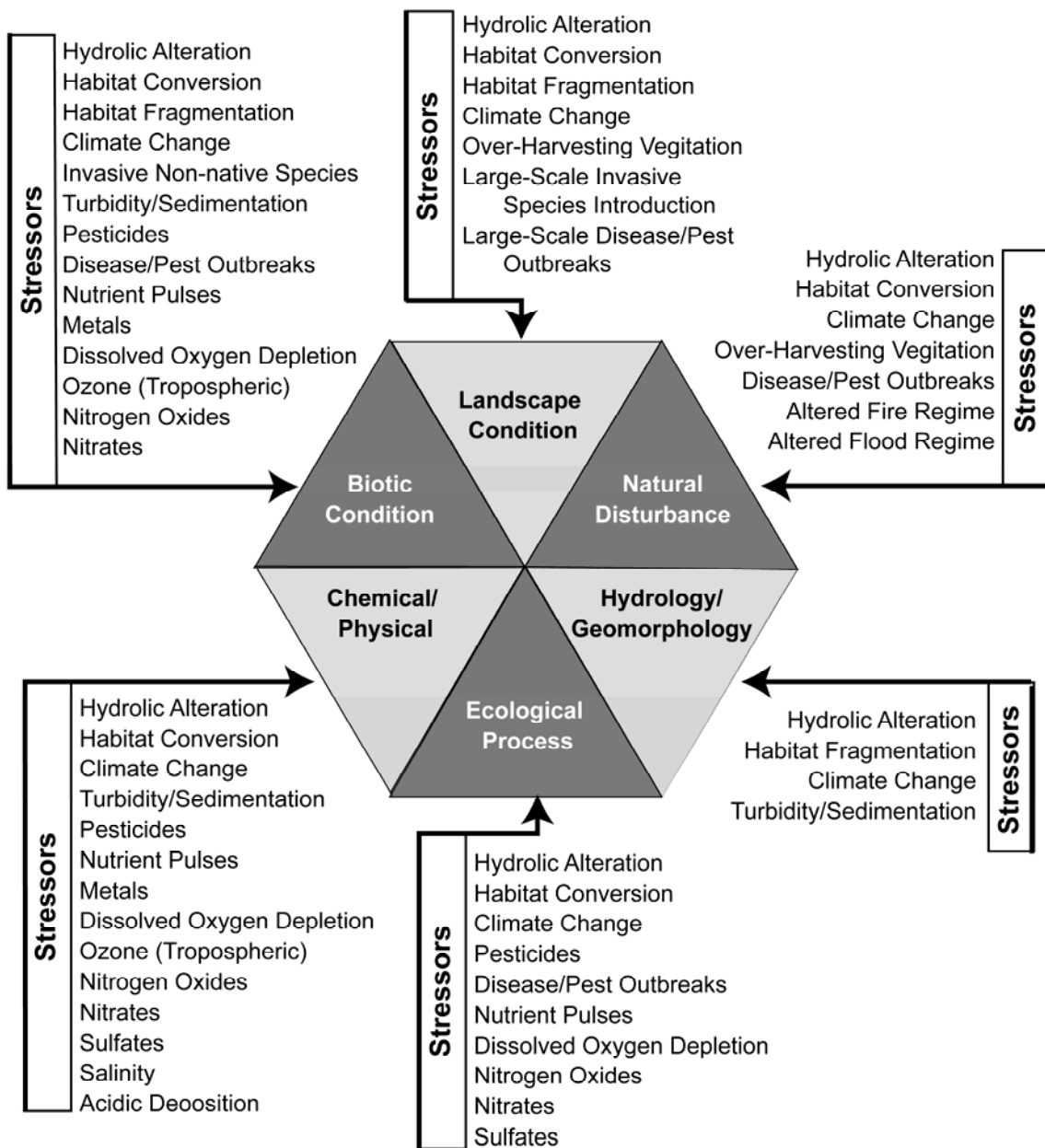


Figure AX5.6-1. Sample stressors and the essential ecological attributes they affect.

Source: Young and Sanzone (2002).

- 1 Of concern in this annex are relationships between NO_x atmospheric deposition, derived
- 2 from anthropogenic sources, and one or more of the EEAs. The ranges of likely changes in

1 ecosystem patterns and processes associated with changes in deposition are discussed in the
2 subsections that follow.

3 The following discussion assesses and characterizes the overall condition or integrity of
4 ecosystems within the United States that are affected by the deposition of atmospheric N and its
5 role as a nutrient. The six EEAs – landscape condition, biotic condition, chemical/physical
6 characteristics, ecological processes, hydrology/geomorphology, and natural disturbance regimes
7 (Table AX5.6-1) – provide a hierarchical framework for assessing ecosystem status.

8 Characteristics related to structure, composition, or functioning of ecological systems may be
9 determined by the use of endpoints or ecological indicators of condition that are measureable and
10 significant either ecologically or to society (Harwell et al., 1999).

11 The relationships among the EEAs are complex because all are interrelated. Changes in
12 one EEA may affect, directly or indirectly, every other EEA. Ecological processes create and
13 maintain environmental patterns. The patterns affect how the processes are expressed (Young
14 and Sanzone, 2002). Changes in patterns or processes can result in changes in the status and
15 functioning of an ecosystem.

16 Changes in the biodiversity, composition, and structure of ecosystems relate directly to
17 functional integrity. Changes in biodiversity are of particular significance in altering ecosystem
18 function. The energy obtained by plants (producers) from sunlight during photosynthesis and the
19 chemical nutrients taken up by those plants from the soil and the atmosphere are transferred to
20 other species (consumers) within the ecosystem through food webs. The movement of chemical
21 nutrients through an ecosystem is cyclic, as the nutrients are used or stored and eventually
22 returned to the soil by microorganisms and fungi (decomposers). Energy is transferred among
23 organisms through the food webs and eventually is dissipated into the environment as heat. The
24 flows of energy and cycling of nutrients provide the interconnectedness among the elements of
25 the ecosystem and transform the community from a random collection of numerous species into
26 an integrated whole.

27 Human existence and welfare on this planet depend on life-support services provided by
28 the interaction of the EEAs. Both ecosystem structure and function play essential roles in
29 providing goods and services (Table AX5.6-2) (Daily, 1997). Ecosystem processes provide
30 diverse benefits including absorption and breakdown of pollutants, cycling of nutrients, binding
31 of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of

1 radiation balance and climate, and fixation of solar energy (Westman, 1977; Daily, 1997; World
2 Resources Institute, 2000). These ecological benefits, in turn, provide economic benefits and
3 values to society (Costanza et al., 1997; Pimentel et al., 1997). Goods such as food crops,
4 timber, livestock, fish, and drinking water have market value. The values of ecosystem services
5 such as flood-control, wildlife habitat, cycling of nutrients, and removal of air pollutants are
6 more difficult to measure (Goulder and Kennedy, 1997). See discussion in Annex 10.

7 Biodiversity is an important consideration at all levels of biological organization,
8 including species, individuals, populations, and ecosystems. Human-induced changes in biotic
9 diversity and alterations in the structure and functioning of ecosystems are the two most dramatic
10 ecological trends of the past century (Vitousek et al., 1997b; U.S. Environmental Protection
11 Agency, 2004). The deposition of nutrient N from the atmosphere has the potential to alter
12 ecosystem structure and function by altering nutrient cycling and changing biodiversity. It is
13 important to understand how ecosystems respond to stress to determine the extent to which
14 anthropogenic stresses, including N deposition, affect ecosystem services and products (Table
15 AX5.6-2).

16 Particular concern has developed within the past decade regarding the consequences of
17 decreasing biological diversity (Hooper and Vitousek, 1997; Chapin et al., 1998; Ayensu et al.,
18 1999; Wall, 1999; Tilman, 2000). Human activities that decrease biodiversity also alter the
19 complexity and stability of ecosystems, and change ecological processes. In response,
20 ecosystem structure, composition and function can be affected (Figure AX5.6-2) (Pimm, 1984;
21 Tilman and Downing, 1994; Tilman, 1996; Chapin et al., 1998; Levlin, 1998; Peterson et al.,
22 1998; Daily and Ehrlich, 1999; Wall, 1999).

23

24 **AX5.6.2 Interactions with Land Use and Disturbance**

25 Scientific understanding of N cycling in forested watersheds is complicated by ecosystem
26 response to climatic variation, human land use, and various kinds of landscape disturbance,
27 including insect infestation, wind storm, fire, and disease (Aber and Driscoll, 1997; Goodale
28 et al., 2000; Mitchell et al., 2006). Nitrogen dynamics in watersheds of mixed land use (i.e.,
29 agriculture, urban, forest) are even more complicated. It is clear that disturbances have major
30 impacts on nutrient enrichment from N deposition, and that these effects can be long-lasting.

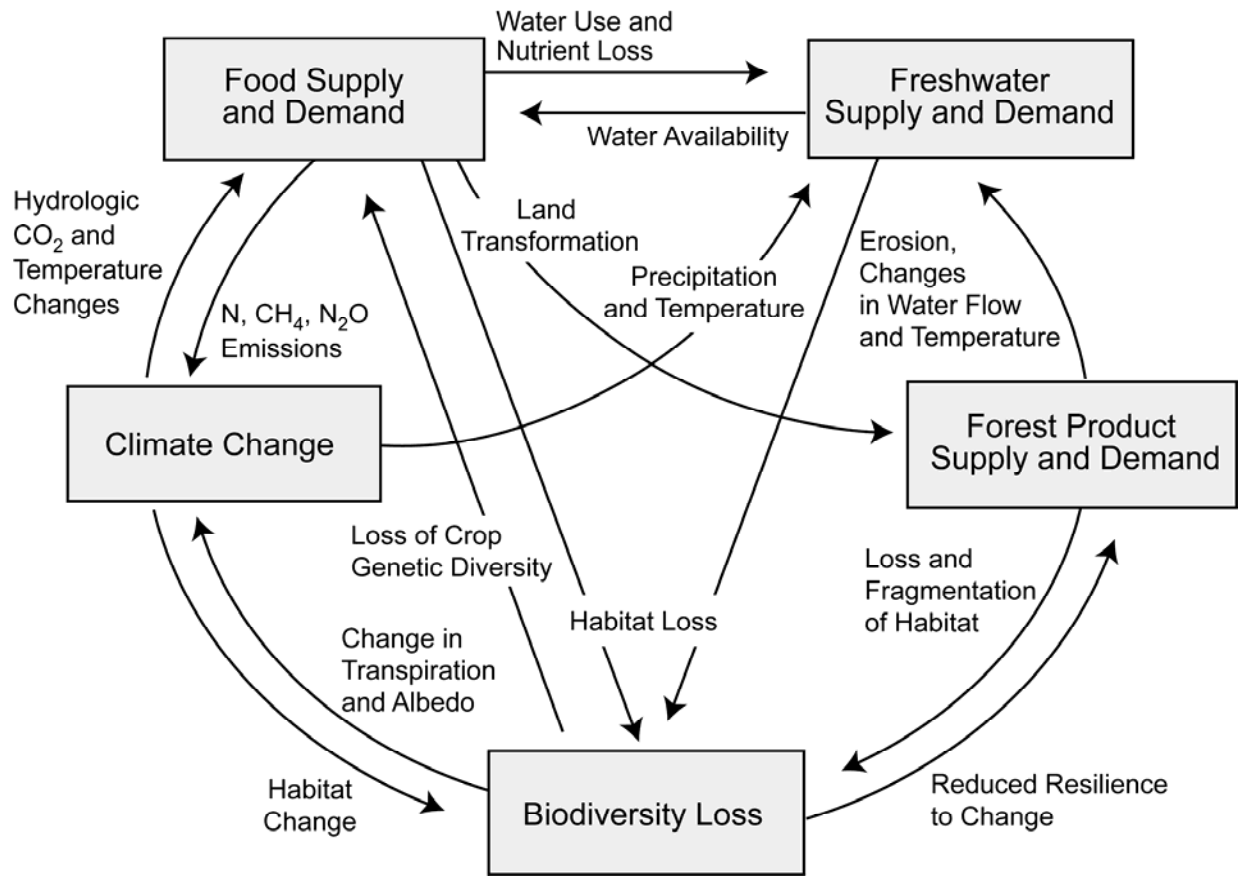


Figure AX5.6-2. Linkages among various ecosystem goods and services (food, water, biodiversity, forest products) and other driving forces (climate change).

Source: Modified from Ayensu et al. (1999).

1 Nevertheless, the scientific community is only in the early stages of learning how to quantify
 2 these interactions.

3 Changes in land use can affect nutrient heterogeneity in the mineral soil of forest stands.
 4 For example, Fraterrigo et al. (2005) found that patterns of variance in soil C, N, and Ca²⁺
 5 concentration increased with the extent of intensive past land use in western North Carolina.
 6 Land use might alter the local patchiness of soil nutrients by decoupling interactions among
 7 microclimate, topography, vegetation, and soil biota. In particular, mechanical soil mixing and
 8 maintenance of agricultural monocultures can homogenize soils in cultivated systems (Robertson
 9 et al., 1993; Paz-Gonzalez and Taboada, 2000). Such effects may be important if the land use is

1 changed to forest. Similarly, changes in species composition can alter the spatial distribution of
2 nutrients in litter inputs (Dijkstra and Smits, 2002; Fraterrigo et al., 2005).

3 In the northeastern United States, concentrations of N in streams of upland forested
4 watersheds tend to be considerably lower than in streams draining watersheds with other land
5 uses. In a comparison of small watersheds in eastern New York, concentrations of N were
6 highest and most variable in a stream draining a watershed where the predominant land use was
7 row crop production. Total dissolved N concentration in streams in sewered suburban and urban
8 watersheds were somewhat lower and less variable than in streams draining the agricultural
9 watershed. Streams in urban and suburban watersheds may also experience high episodic N
10 loading caused by combined sewer overflows (Driscoll et al., 2003c).

11 12 **AX5.6.2.1 Timber Harvest and Fire**

13 Timber harvest contributes to nutrient removal from the ecosystem via biomass export
14 and acceleration of leaching losses (Bormann et al., 1968; Mann et al., 1988). In particular,
15 logging contributes to loss of N and Ca^{2+} from the soil (Tritton et al., 1987; Latty et al., 2004).
16 The extent of nutrient loss is determined, at least in part, by the intensity of the logging and
17 whether or not it is accompanied by fire (Latty et al., 2004). The species composition of the
18 regrowth vegetation also has important effects on nutrient cycling. Fire is sometimes followed
19 by establishment of N-fixing vegetation that provide substantial sources of N_r (Johnson, 1995;
20 Johnson et al., 2004). Tree species also vary dramatically in their N cycling properties,
21 especially in their influence on litter mass and quality (Finzi et al., 1998; Ferrari, 1999; Ollinger
22 et al., 2002). Thus, over time, the extent of effect of logging and fire on nutrient cycling can
23 increase, depending largely on shifts in tree species composition and the degree to which C and
24 N pools are altered in the mineral soil and the forest floor.

25 Dissolved N exports have been clearly shown to increase substantially after major
26 watershed disturbance, often reaching peak concentrations in streamwater within 1 to 3 years of
27 disturbance, and then returning to background concentrations after about 5 to 10 years (Likens
28 et al., 1978; Bormann and Likens, 1979; Eshleman et al., 2000). Such transient NO_3^- leakage
29 has been shown to occur subsequent to both logging (Martin et al., 1984; Dahlgren and Driscoll,
30 1994; Yeakley et al., 2003) and insect infestation (Eshleman et al., 1998, 2004).

1 The extent to which timber harvesting influences leaching of NO_3^- and base cations from
2 soils to drainage waters depends on changes in primary productivity, nutrient uptake by plants
3 and microorganisms within the terrestrial ecosystem, and hydrological pathways for transferring
4 nutrients to drainage water (Hazlett et al., 2007). Because of the variety of responses and
5 interactions of environmental and forest litter and soil conditions, it is difficult to generalize
6 about the influence of harvesting on N cycling (Grenon et al., 2004; Hazlett et al., 2007).

7 We do know, however, that land use history constitutes a major influence on N leaching
8 from forested watersheds that receive moderate to high levels of atmospheric N deposition
9 (Pardo et al., 1995; Aber and Driscoll, 1997; Goodale et al., 2000; Lovett et al., 2000). The
10 severity of effect and length of the recovery period probably vary according to the nature of the
11 past disturbance. Extensive past logging appears to have considerable and long-lasting effects on
12 nutrient cycling (Goodale and Aber, 2001; Fisk et al., 2002). Latty et al. (2004) compared soil
13 nutrient pools and N cycling among three forest stands in the Adirondack Mountains: old
14 growth, selectively logged, and selectively logged and then burned. The logging and fire had
15 occurred about 100 years previously. Results suggested that even relatively light logging, plus
16 burning, may influence the extent of subsequent N limitation over time scales of decades to
17 centuries (Latty et al., 2004). Models of forest ecosystem response to disturbance incorporate
18 such long-lasting effects of land use on C and N storage, cycling, and release (Aber et al., 1997).

19 Chen and Driscoll (2004) simulated the response of five forested watersheds in the
20 Adirondack and Catskill regions of New York to changes in atmospheric deposition and land
21 disturbance. Simulation results suggested that forest harvesting caused increased leaching of
22 base cations and NO_3^- from the watersheds. These changes also affected model projections of
23 future pH and acid neutralizing capacity (ANC) of lake water. Model results suggested that
24 lakewater pH and ANC were lower in response to forest cutting as compared with undisturbed
25 conditions.

26 Nitrification rates at old growth sites in the White Mountains of New Hampshire ($63 \pm$
27 4.3 kg N/ha/yr) were approximately double those at previously burned (34 ± 4.4 kg N/ha/yr) and
28 previously logged (29 ± 4.7 kg N/ha/yr) sites (Goodale and Aber, 2001). Fire and logging
29 disturbances had occurred about 100 years previously on these study sites. Nitrification
30 increased as forest floor C:N ratio decreased, resulting in higher NO_3^- concentrations in

1 streamwater. These results suggest that forest disturbance can have long-lasting effects on N
2 cycling and the potential for N saturation.

3 Thus, disturbance can affect N cycling and the response of forest ecosystems to N
4 deposition. In addition, it also appears that vegetative changes stimulated by N deposition may
5 affect the frequency and severity of disturbance. Excess N_r deposition is thought to be impacting
6 essential ecological attributes associated with terrestrial ecosystems and how they respond to
7 disturbance. Effects of N_r deposition influence habitat suitability, genetic diversity, community
8 dynamics and composition, nutrient status, energy and nutrient cycling, and frequency and
9 intensity of natural fire disturbance regimes. For example, several lines of evidence suggest that
10 N_r deposition may be contributing to greater fuel loads and thus altering the fire cycle in a
11 variety of ecosystem types (Fenn et al., 2003a). Invasive grasses, which can be favored by high
12 N deposition, promote a rapid fire cycle in many locations (D'Antonio and Vitousek, 1992). The
13 increased productivity of flammable understory grasses increases the spread of fire and has been
14 hypothesized as one mechanism for the recent conversion of CSS to grassland in California
15 (Minnich and Dezzani, 1998).

16 High grass biomass has also been associated with increased fire frequency in the Mohave
17 Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). This effect is most
18 pronounced at higher elevation, probably because the increased precipitation at higher elevation
19 contributes to greater grass productivity. Increased N supply at lower elevation in arid lands can
20 only increase productivity to the point at which moisture limitation prevents additional growth.
21 Fire was relatively rare in the Mojave desert until the past two decades, but now fire occurs
22 frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

23

24 **AX5.6.2.2 Insect Infestation and Disease**

25 Insect infestation and plant disease can alter the effects of nutrient enrichment, via
26 atmospheric N deposition, on forest ecosystems. Such disturbances alter the pool of N_r in the
27 forest floor, with short-term impacts on NO_3^- and base cation leaching. Positive influences of N
28 deposition on root and seed biomass of an annual plant, common ragweed, were suppressed by
29 herbivory, which increased with higher available plant shoot N (Throop, 2005).

30 Eshleman et al. (2004) applied a regional lithology-based unit N export response function
31 model to simulate NO_3^- export to streams in the Chesapeake Bay watershed. The model

1 considered the geographic distribution of bedrock classes and the timing and extent of
2 defoliation by gypsy moth (*Lymantria dispar*) larvae. Modeling results suggested that the
3 regional annual NO_3^- -N export increased during the year following peak insect defoliation by
4 about 1500%, from an initial rate of 0.1 kg N/ha/yr to nearly 1.5 kg N/ha/yr.

5 Between the mid-1980s and the early 1990s, the southward expanding range of the gypsy
6 moth traversed Shenandoah National Park, VA (Webb, 1999). Some areas of the park were
7 heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more
8 than 90% defoliated in both 1991 and 1992. The gypsy moth population in White Oak Run then
9 collapsed due to pathogen outbreak. This insect infestation of the forest ecosystem resulted in
10 substantial impacts on streamwater chemistry. The most notable effects of the defoliation on
11 park streams were dramatic increases in the concentration and export of N and base cations in
12 streamwater. Figure AX5.6-3 shows the increase in NO_3^- export that occurred in White Oak
13 Run. Following defoliation, NO_3^- export increased to previously unobserved levels and
14 remained high for over 6 years before returning to predefoliation levels. The very low baseline
15 levels of NO_3^- export in park streams were consistent with expectations for N-limited,
16 regenerating forests (e.g., Aber et al., 1989; Stoddard, 1994). Release of NO_3^- to surface waters
17 following defoliation was likewise consistent with previous observations of increased N export
18 due to forest disturbance (e.g., Likens et al., 1970; Swank, 1988). The exact mechanisms have
19 not been determined, but it is evident that the repeated consumption and processing of foliage by
20 the gypsy moth larva disrupted the ordinarily tight cycling of N in the forests within this park.

21 The elevated concentrations of NO_3^- following defoliation did not appear to contribute to
22 baseflow acidification in White Oak Run. This was due to a concurrent increase in
23 concentrations of base cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation
24 concentrations also increased during high-runoff conditions, although the increase in base cations
25 did not fully compensate for the episodic increase in NO_3^- . As a consequence, episodic
26 acidification became more frequent and more extreme (Webb et al., 1995).

27 Large trees in old growth forests may resorb less N from foliage than do younger trees on
28 previously logged or burned sites (cf. Killingbeck, 1996). This process would be expected to
29 contribute to an alleviation of N limitation on plant processes in old-growth forests (Latty et al.,
30 2004). This effect might also extend to herbivores, which are often N-limited (Mattson, 1980).
31 Latty et al. (2004) attributed the high severity of beech bark disease in old growth forests to such

Change in Annual Streamwater Nitrate Flux Following Watershed Defoliation

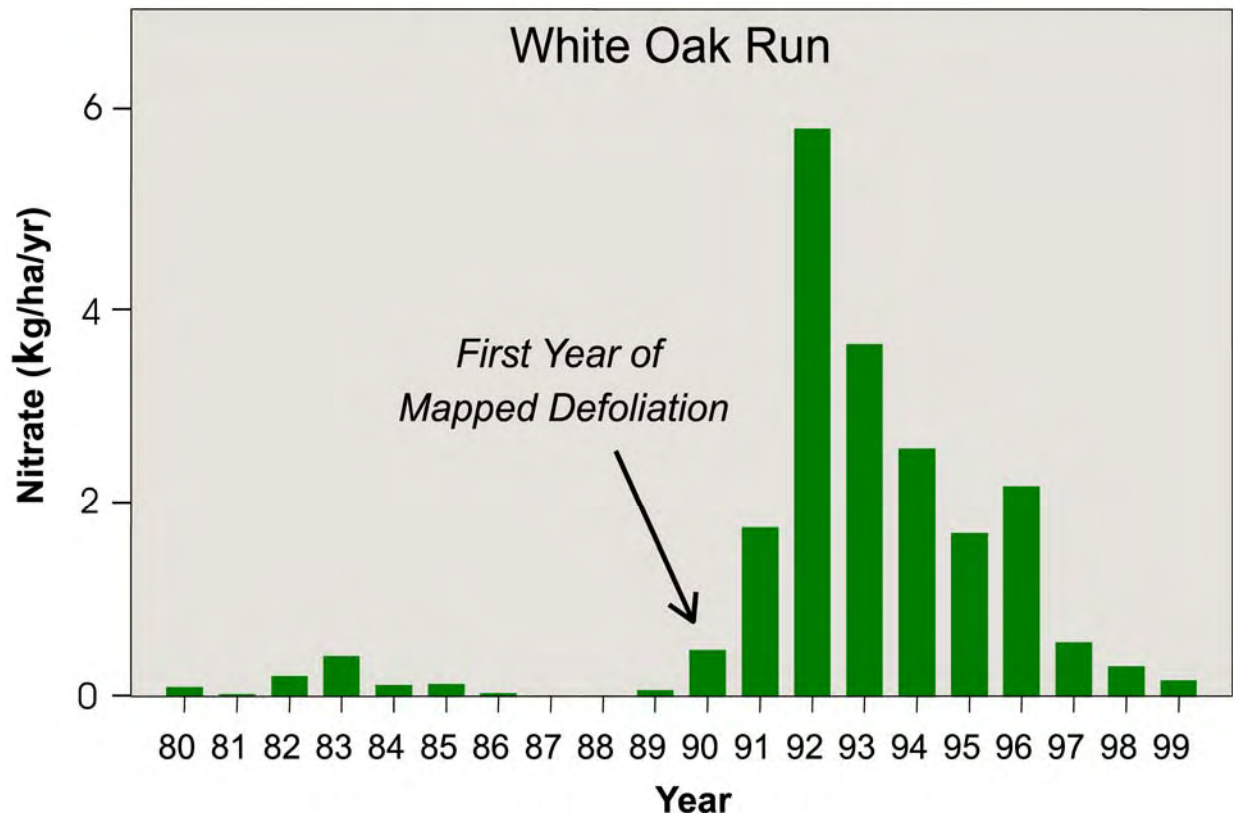


Figure AX5.6-3. Effect of watershed defoliation by the gypsy moth caterpillar on NO_3^- flux in streamwater. White Oak Run was heavily defoliated for three consecutive years. The watershed area defoliated was 46.5% in 1990, 92.9% in 1991, and 90.4% in 1992. In 1993, the gypsy moth population collapsed and there was no further defoliation.

Source: Sullivan et al. (2003).

1 a mechanism. Beech bark disease is caused by an introduced scale insect (*Cryptococcus*
 2 *fagisuga*), which has high N requirements (Wargo, 1988; Houston, 1994). The N-rich foliage in
 3 the old growth forest may improve insect fitness, contributing to a higher rate of infestation in
 4 the old growth stands (Latty et al., 2004).

5 6 AX5.6.2.3 Urbanization

7 Perhaps the most noteworthy impact of urban land use on processes of nutrient
 8 enrichment from N deposition concerns the transport of N_r to N-limited estuarine and near-

1 coastal waters. In agricultural, and especially in forested areas, it is generally expected that most
2 atmospherically deposited N is taken up by terrestrial vegetation. Relatively little of the
3 deposited N is available for transport to downstream receiving waters. This is not the case for
4 urban land use. Due to the relatively large impervious surface area in the urban landscape
5 (buildings, roads, parking lots, etc.), a higher percentage of precipitation is routed directly to
6 surface waters, with less opportunity for vegetative uptake of deposited N. Therefore,
7 atmospheric N deposition contributes proportionately more NO_3^- to surface waters in urban
8 settings than it does with other land uses. Because many large urban areas are both located close
9 to the coastline and expected to receive relatively high NO_x deposition, they can constitute
10 sizeable sources of N_r contribution to estuarine and marine waters.

11 12 **AX5.6.2.4 Agriculture**

13 Agricultural ecosystems are not sensitive to levels of N deposition typically found in the
14 United States. Rather, such ecosystems often act as net sources of NH_3 emissions rather than as
15 sinks (Grünhage et al., 1992; Krupa, 2003). Atmospheric N deposition can contribute a
16 quantitatively important component of the N_r requirements of pastures and croplands. In such
17 settings, atmospheric N deposition provides an additional chronic source of N fertilizer. This
18 may be viewed as a beneficial outcome. Nevertheless, some of the N that is atmospherically
19 deposited on agricultural land may eventually leach to drainage waters and contribute to
20 eutrophication, especially in estuarine and near-coastal marine environments. Industrial
21 livestock operations also contribute substantial amounts of NH_y to the atmosphere, some of
22 which is deposited on coastal waters.

23 Agriculture also experiences indirect effects of NO_x emissions through the formation of
24 ground-level O_3 . Such effects are not considered in this review.

25 26 **AX5.6.2.5 Other Disturbances**

27 In some ecosystems, chronic additions of atmospherically derived N may have had
28 irreversible consequences that involved interactions with invasive, non-native plants. For
29 example, California has many plant species that occur in shrub, forb, and grasslands that receive
30 high N deposition. There are up to 200 sensitive plant species in southern California CSS
31 communities alone (Skinner and Pavlik, 1994). About 25 plant species are thought to be extinct
32 in California, most of them forbs that occurred in sites that have experienced conversion to

1 annual grassland (U.S. Environmental Protection Agency, 2005). As CSS vegetation continues
2 to convert to grassland dominated by invasive species, loss of additional rare plant species may
3 occur. Invasive plant species are often identified as a major threat to rare native plant species.
4 However, the occurrence of invasive species may combine with other stress factors, including N
5 deposition, to promote increased productivity of invasive species at the expense of native
6 species.

7 As sensitive vegetation is lost, wildlife species that depend on these plants can also be
8 adversely affected. There are several threatened or endangered wildlife species listed by the U.S.
9 Fish and Wildlife Service, including the desert tortoise (*Gopherus agassizii*) and checkerspot
10 butterfly that are native to plant communities in California thought to be sensitive to atmospheric
11 N input. A native to the San Francisco Bay area, the bay checkerspot butterfly has declined in
12 association with invasion of exotic grasses that replaced the native forbs on which the butterfly
13 depends. In particular, the larval stage of the butterfly is dependent on *Plantago erecta*, which is
14 increasingly being outcompeted by exotic grasses (U.S. Environmental Protection Agency,
15 2005).

16 Decline in the population of the desert tortoise may be due to a number of co-occurring
17 stresses, including grazing, habitat destruction, drought, disease, and a declining food base. In
18 the desert shrub inter-spaces, sites where native forbs once flourished, invasive grasses now
19 dominate, reducing the nutritional quality of foods available to the tortoise (Nagy et al., 1998;
20 Fenn et al., 2003a). Nitrogen deposition contributes to the productivity and density of grasses at
21 the expense of native forbs (Brooks, 2003).

22

23 **AX5.6.2.6 Multiple Stress Response**

24 Ecosystems are often subjected to multiple stressors, of which nutrient enrichment from
25 atmospheric deposition of N is only one. Additional stressors are also important, including O₃
26 exposure, climatic variation, natural and human disturbance, the occurrence of invasive non-
27 native plants, native and non-native insect pests, and disease. Atmospheric N deposition
28 interacts with these other stressors to affect ecosystem patterns and processes in ways that we are
29 only beginning to understand.

30 For example, terrestrial ecosystems at many locations are subjected to high N deposition
31 and high exposure to O₃. This is especially true in portions of southern California and the
32 Appalachian Mountains. Mixed conifer forests in the San Bernardino and San Gabriel

1 mountains in southern California are exposed to high levels of atmospheric O₃ and receive
2 atmospheric N deposition in the range of about 5 to over 30 kg/ha/yr (Takemoto et al., 2001).
3 Spatial variability in N deposition is high due to the patchy characteristics of these forests and
4 associated canopy effects on dry deposition processes. The forest ecosystems have reached N-
5 saturation, as evidenced by high NO₃⁻ concentrations in stream water. However, evaluation of N
6 effects on vegetation is complicated by the concurrent effects of O₃, which has damaged
7 sensitive plant species, especially ponderosa and Jeffrey pine. Bytnerowicz (2002) summarized
8 N/O₃ interactions and consequent effects.

9 Peak diurnal concentrations of atmospheric O₃ and NO₂ co-occur at Tanbork Flat in the
10 San Bernardino Mountains (Bytnerowicz et al., 1987). They can have counteracting effects, with
11 O₃ reducing growth and N deposition enhancing growth of pine trees (Gulke and Balduman,
12 1999).

13 Jeffrey and ponderosa pine are the most sensitive western coniferous tree species to
14 injury from O₃ pollution (Miller et al., 1983; Duriscoe and Stolte, 1989). In some areas of the
15 western Sierra Nevada Mountains, O₃ concentrations have been high enough to cause visible
16 foliar injury to these species and reduced needle retention (Bytnerowicz, 2002). Reduced radial
17 growth has also been observed (Peterson et al., 1987, 1991). In the San Bernardino Mountains,
18 trees of these species that exhibit severe foliar injury from O₃ do not show growth reductions
19 (Arbaugh et al., 1999), and this has been attributed to the fertilizing effects of high N deposition
20 (Takemoto et al., 2001; Bytnerowicz, 2002). This may be an example of counteracting effects
21 from O₃ and N air pollution. It is also possible that N deposition in the western Sierra Nevada
22 Mountains may increase growth of pines, especially on nutritionally poor granitic soils
23 (Takemoto et al., 2001).

24
25

26 **AX5.7 ECOLOGICAL INDICATORS OF NUTRIENT ENRICHMENT**

27

28 **AX5.7.1 Chemical Indicators of Nutrient Enrichment**

29

30 **AX5.7.1.1 Soil Carbon-to-Nitrogen Ratio**

31 The N and C cycles are tightly coupled in forest soils. Nitrification and NO₃⁻ leaching
32 rates are generally low on sites having soil C:N ratios above about 22 to 25 (Lovett et al., 2002;

1 Ross et al., 2004). The C:N ratio of the forest floor can be changed by N deposition over time,
2 although it is difficult to detect a change over time against background spatial heterogeneity. For
3 example, in a compilation of soil C:N and nitrification data from 250 plots from across the
4 Northeast, Aber et al. (2003) found statistically significant but weak correlations between either
5 soil C:N or nitrification and annual N deposition rate. However, across plots, nitrification
6 increased sharply as C:N ratio (by mass) decreased below about 22. If root growth and
7 mycorrhizal formation are impaired by high N input, the forest floor vegetation may be affected.
8 The forest floor C:N ratio has been used as an indicator of ecosystem N status in mature
9 coniferous forests. For example, NO_3^- leaching has been correlated with forest floor C:N.

10 Ollinger et al. (2002) used observed field relationships between soil C:N ratio and canopy
11 lignin:N ratio and high spectral resolution remote sensing data to predict spatial patterns in C:N
12 across the White Mountains of New Hampshire. Remote-sensed data were obtained from
13 NASA's Airborne Visible and Infrared Imaging Spectrometer (AVIRIS) instrument.

14 Preliminary regional estimates of soil C:N ratio suggested that 63% of the land area in the region
15 had C:N below 22, which was suggested as a critical threshold for the onset of nitrification.
16 Below C:N = 22, Ollinger et al. (2002) found increasing, but variable, rates of nitrification.

17 Denitrification has been studied in riparian zone ecosystems (Lowrance, 1992; Pinay
18 et al., 1993, 2000; Watts and Seitzinger, 2001; Hefting et al., 2003) and seems to be related to C
19 availability. Riparian soils that are both rich in organic matter and anaerobic generally have high
20 denitrification potential. Where riparian soils are aerobic, however, nitrification, rather than
21 denitrification, can be the dominant process that produces N_2O (Stevens et al., 1997).

22

23 **AX5.7.1.2 Surface Water Nitrate Concentration**

24 One important result of excess N loading is an increase in the concentration of NO_3^- in
25 surface water. The concentration of NO_3^- in surface water can serve as a chemical indicator of N
26 input in excess of ecosystem requirements, and also has relevance with respect to acidification
27 and eutrophication effects on surface water. EPA is in the process of attempting to set nutrient
28 criteria for total N and P concentrations in lakes (U.S. Environmental Protection Agency,
29 2000b), streams, and rivers (U.S. Environmental Protection Agency, 2000a) in the United States.
30 Different nutrient criteria are being developed for each of 14 different nutrient ecoregions
31 throughout the country. Nutrient ecoregions are based on aggregations of level III Omernik

1 ecoregions. Draft nutrient guidelines are available on the web
2 (<http://www.epa.gov/waterscience/criteria/nutrient/ecoregions/sumtable.pdf>).

3
4 **AX5.7.1.3 Surface Water Clarity**

5 An important outcome of nutrient enrichment of aquatic ecosystems is the resulting
6 increase in phytoplankton biomass and NPP. One water measurement that serves as an index of
7 these changes in productivity is water clarity. Under conditions of high algal abundance, clarity
8 decreases. However, clarity is also influenced by the concentration of suspended solids, which
9 can increase substantially in response to erosional processes. Thus, change in water clarity can
10 reflect the results of N nutrient enrichment from N deposition, but clarity can also be changed by
11 increased erosion, which often occurs in response to rainfall or snowmelt events, especially
12 where watershed soils have been disturbed.

13
14 **AX5.7.1.4 Surface Water Chlorophyll *a* Concentration**

15 The most common indicator of change in algal productivity is the concentration of
16 chlorophyll *a*. Chlorophyll *a* concentration is generally more directly tied to algal productivity
17 than is water clarity. Chlorophyll *a* can be measured in the water column or in the surface
18 sediments. For estuary waters, an increase in the concentration of chlorophyll *a* is the most
19 unambiguous indicator of the early stages of eutrophication.

20
21 **AX5.7.1.5 Dissolved Oxygen Concentration**

22 Excessive growth of phytoplankton can cause a decrease in dissolved oxygen (DO) in
23 water. This occurs because microbial populations increase dramatically as large quantities of
24 dead phytoplankton decay on the sediment surface of fresh or marine waters. Microbial
25 respiration can lead to hypoxia, mortality of fish and other aquatic biota, and a variety of odor
26 and aesthetic problems. However, the amount of N contributed to aquatic ecosystems by
27 atmospheric deposition in the United States is not sufficiently high to cause these extreme
28 effects. Nevertheless, atmospheric deposition of N can contribute to such effects of excess N,
29 especially in estuaries and coastal marine ecosystems that receive high inputs of non-atmospheric
30 N.

1 **AX5.7.1.6 Trophic Status Indices**

2 Nutritional responses of aquatic ecosystems to atmospheric N deposition are heavily
3 dependent on surface water P concentrations. Thus, chemical ratios of N to P can be very useful
4 in evaluating eutrophication potential. A series of papers, described below, has been published
5 exploring nutrient limitations and offering indices that describe the trophic state of freshwaters.
6 Valuable insights have been gained from several indices, including total N to total P (TN:TP),
7 dissolved inorganic N to total P (DIN:TP), dissolved inorganic N to total dissolved P
8 (DIN:TDP), dissolved inorganic N to soluble reactive P (DIN:SRP), and dissolved inorganic N
9 to the ratio of chlorophyll *a* to total P (DIN/[chl *a*:TP]). While there are publications that
10 compare the effectiveness of some of these indices, it appears that different indices are useful for
11 different purposes; we make no attempt to favor one over another.

12 Algal growth was reported to be limited at DIN:TP values between 5 and 20 (Schindler,
13 1980; Grimm and Fisher, 1986; Morris and Lewis, 1988; Downing and McCauley, 1992;
14 Bergström and Jansson, 2006). When DIN:TP ratios are greater than reference values, growth
15 stimulation, N and P colimitation, or P limitation commonly occurs (Sickman et al., 2003b).
16 In a Swedish lake survey, N-limitation occurred in lakes where the DIN:TP ratio was less than 7
17 (concentrations < 33 µM N/L). Co-limitation of both N and P were found in lakes with DIN:TP
18 ratio between 8 and 10, and P-limitation at DIN:TP values greater than 10. This corresponds
19 roughly to N concentrations of 45 to 80 µM N/L for co-limited lakes, and concentrations
20 > 80 µM N/L for P-limited lakes (Bergström et al., 2005). Other thresholds for N-limitation
21 were reported in the literature to occur at DIN:SRP ratios < 4 (Lohman and Prisco, 1992) and
22 < 10 (Wold and Hershey, 1999).

23 Bergström et al. (2005) reported a new index, (DIN/[chl *a*:TP]) to indicate the
24 eutrophication of lakes from N deposition. The choice of DIN/[chl *a*:TP] was based on whole
25 lake experiments in Sweden (Jansson et al., 2001) and permits the assessment of a possible
26 eutrophication effect of N deposition independent of differences in P input between lakes in
27 different regions. These researchers found that the mean chl *a*:TP ratios increased more than
28 three times from low N to high N deposition areas, indicating that N deposition contributed to
29 eutrophication.

1 **AX5.7.2 Biological Indicators of Nutrient Enrichment**

3 **AX5.7.2.1 Phytoplankton**

4 The occurrence of two diatom species: *Asterionella formosa* and *Fragilaria crotonensis*,
5 has been linked experimentally, paleolimnologically, and in surveys to increased N availability,
6 including low levels of N from atmospheric deposition. These may not be the only algal species
7 to respond, but data are lacking on other possible indicators.

9 **AX5.7.2.2 Plant Species Composition and Richness**

10 Both vascular plants (especially herbaceous and shrub species) and lichens can serve as
11 indicators for nutrient enrichment effects from N deposition. Indicator endpoints could include
12 the occurrence and abundance of nitrophilous species and of native species that are most easily
13 displaced by the more invasive nitrophilous species.

14 Alternatively, taxonomic richness could be used to indicate effects of N enrichment on
15 biota. Changes in vascular plant indicators would be most likely to occur in sensitive terrestrial
16 (i.e., alpine, meadow, arid land) and transitional (i.e., bog, nutrient-poor fen) ecosystems.
17 Changes in lichen indicators could involve sensitive macrolichens in forested and non-forested
18 ecosystems. For example, Jovan and McCune (2005) constructed a model based on non-metric
19 multidimensional scaling ordination to analyze lichen species distribution from 98 FIA plots in
20 the greater Central Valley of California. The model used epiphytic macrolichen community data
21 to reflect air quality and climate in forested areas. Some species respond negatively to NO_x and
22 SO_x deposition (McCune, 1988; Gauslaa, 1995; van Haluwyn and van Herk, 2002). Other
23 species respond positively to NH_y deposition (de Bakker, 1989; van Dobben and de Bakker,
24 1996; van Herk, 1999, 2001; Jovan and McCune, 2005). Similarly, Jovan and McCune (2006)
25 developed a model of NH₃ exposure to epiphytic macrolichens in the Sierra Nevada region.
26 They found that lichens provide a relatively inexpensive tool for estimating fine-scale
27 distributions of NH₃ exposure to terrestrial ecosystems. Because NH₃ has a high deposition
28 velocity (Asman and van Jaarsveld, 1992), dry deposition of reduced N exhibits high spatial
29 variability. Monitoring of species composition of epiphytic lichen communities can therefore
30 help quantify spatially variable eutrophication risk to forest health in the Sierra Nevada region
31 (Jovan and McCune, 2006).

1 **AX5.7.2.3 Foliar Nitrogen Concentration**

2 The concentration of N in plant foliage, especially in forest trees, can provide an indicator
3 of nutrient enrichment (McNeil et al., in press). This indicator may be especially relevant
4 because there is a potential to acquire regional-scale data on foliar N through remote sensing
5 techniques. This allows rapid assessment of N status across large land areas. The plant tissue N
6 content of some plant species varies in proportion to N inputs (Baddeley et al., 1994; Hyvarinen
7 and Crittenden, 1998; Pitcairn et al., 2003). Similarly, species typical of nutrient-poor
8 environments tend to accumulate the amino acid arginine in plant tissue (van Dijk and Roelofs,
9 1988), and arginine concentration therefore varies in proportion to N inputs. Foliar N and foliar
10 arginine concentrations both provide good indices of N deposition effects. This was
11 demonstrated by Pitcairn et al. (2003) for three moss species in a mixed woodland downwind of
12 an intensive livestock farm in Scotland. Total tissue N and arginine concentrations were closely
13 correlated with both atmospheric NH₃ concentration and estimated N deposition ($r^2 > 0.97$ and
14 > 0.78 , respectively) (Pitcairn et al., 2003). Plant tissue N content, in turn, can affect the extent
15 of insect infestation. Nitrogen-rich foliage is frequently more palatable to insects than N-poor
16 foliage.

17
18

19 **AX5.8 SUMMARY**

20 Substantial progress has been made in the scientific understanding of nutrient enrichment
21 effects from atmospheric N deposition since preparation of the last AQCD for NO_x. Incremental
22 knowledge gains have occurred in research areas such as ecological stoichiometry,
23 characterization of ecosystem sensitivity, N versus P limitation in freshwater ecosystems,
24 quantification of denitrification, and use of stable isotopes to improve understanding of nutrient
25 cycling. Nutrient enrichment effects of N deposition are now known to be widespread and to
26 occur in a variety of highly sensitive ecosystems, even at relatively low levels of N deposition
27 (less than 5 kg N/ha/yr).

28 Atmospheric inputs of N can alleviate deficiencies and increase growth of some plants at
29 the expense of others. Thus, N deposition can alter competitive relationships among plant
30 species and therefore alter species composition and diversity. These kinds of species shifts and
31 ecosystem changes can occur even if the ecosystem does not exhibit signs of N saturation.

1 Nitrogen deposition could be increasing growth of forest trees slightly in some regions,
2 especially in portions of the eastern United States where O₃ levels and drought occurrence are
3 low. Such enhanced growth generally occurs mainly above ground level. This can cause
4 changes in the shoot-to-root ratio, which can be detrimental to the plant because of decreased
5 resistance to environmental stresses such as drought. Data are not sufficient with which to
6 quantify any increase in forest growth that may have occurred in response to N deposition, partly
7 because trees have been exposed to multiple stresses simultaneously. Reduced tree growth and
8 increased tree mortality have occurred in localized areas that have experienced depletion of
9 soil Ca²⁺ and increased Al in soil solution.

10 Increased N availability from N deposition has caused some herbaceous and understory
11 plant species to flourish at the expense of other species. Some native species have been replaced
12 at some locations by other (often non-native) opportunistic species (especially certain grass
13 species). The extent and magnitude of these changes in the United States are not known.
14 Ecosystems that are most sensitive to such changes are those that have evolved under naturally
15 low nutrient supplies. These include, in particular, alpine vegetation, nutrient-poor wetlands,
16 arid and semi-arid lands, and perhaps grassland communities.

17 Some wetland ecosystems, especially ombrotrophic bogs and nutrient-poor fens, receive
18 most of their nutrient inputs from atmospheric deposition. These wetlands have been shown in
19 Europe to experience changes in plant species composition in response to high levels of
20 atmospheric N deposition. Such ecosystems tend to occur in the United States in areas that
21 receive much lower levels of N deposition than do the affected wetlands in Europe. It is not
22 clear to what extent such effects occur under ambient N deposition levels in the United States.
23 The risk of species composition change is important, in part because wetland ecosystems often
24 contain a relatively large number of rare plant species.

25 Estuaries and near-coastal marine waters tend to be sensitive to nutrient enrichment from
26 N inputs, and many such waters in the United States have experienced moderate to severe
27 eutrophication. There is a scientific consensus that N-driven eutrophication of shallow estuaries
28 has increased over the past several decades and the degradation of coastal ecosystems is now a
29 widespread occurrence. Atmospheric N deposition constitutes one source of N input to estuaries
30 that have experienced eutrophication. Effects include O₂ depletion, excessive growth of algae,
31 fish kills, and damage to aquatic organisms at many trophic levels. Atmospheric N deposition

1 contributes to these damages. The relative contribution of atmospheric N sources, compared
2 with non-atmospheric sources, to estuarine and marine waters is poorly known. It is clear,
3 however, that the atmospheric contribution is usually, but not always, a small percentage of the
4 overall human-caused N input.

5 Fresh waters can be sensitive to nutrient enrichment effects from N deposition. In
6 general, sensitive waters tend to be those that are highly oligotrophic; these are most commonly
7 found at high elevation in remote areas, especially in the western United States. Such lakes and
8 streams are sometimes N-limited, and atmospheric N deposition can cause or contribute to
9 eutrophication. Primary productivity in N-limited freshwaters can be increased with the addition
10 of even very low concentrations of N. Eutrophication increases algal biomass, alters algal
11 species assemblages, and may affect food webs.

12 Increases in algal biomass have been associated with changes in algal assemblages that
13 favor certain species over others. Changes in diatom species occurrence are documented or
14 inferred in some high-elevation western lakes at relatively low levels of atmospheric N
15 deposition (<2 kg N/ha/yr). A widespread increase in the relative abundance of *Asterionella*
16 *formosa* and *Fragilaria crotonensis* has occurred in some oligotrophic lakes. These changes
17 have been documented from both lake sediments and limnological surveys, and are likely caused
18 at least in part by atmospheric N deposition.

19 Increased growth of silicate-utilizing diatoms as a result of NO_3^- - and PO_4^- -induced
20 eutrophication, and subsequent removal of fixed biogenic Si via sedimentation has brought about
21 changes in the ratios of nutrient elements Si, N, and P. In turn, such changes can cause shifts
22 from diatoms to non-siliceous phytoplankton in large rivers and coastal marine regions. Such
23 changes are expected to affect other levels of the food web.

24 Atmospheric deposition of N_r adds a critical element (N) to terrestrial, transitional, and
25 aquatic environments. In many ecosystems, this element is growth limiting to algae and plants at
26 the base of the food web. Therefore, even relatively small additions of N in atmospheric
27 deposition can alter the biotic make-up of sensitive ecosystems and key ecosystem processes. It
28 is often difficult to quantify such responses because nutrient enrichment effects from N addition
29 interact with the cycling of other elements and with the influence of climatic variability and both
30 natural and human-caused disturbances. For some high-elevation ecosystems, nutrient

- 1 enrichment effects seem to occur at much lower levels of N deposition than do acidification
- 2 effects.

TABLE AX5.3-1. CONTRIBUTION OF FENS TO SUPPORT OF PLANT SPECIES DIVERSITY IN SELECTED STATES

	Number of Vascular Species Found in Fens (# Native)	Percent of State Vascular Flora Found in Fens (% Native)	Non-Vascular Species Found in Fens	Number of Uncommon & Rare Species Found in Fens	Percent of State Uncommon & Rare Species Found in Fens	Percent of State Area in Fens
Colorado	~500	~14		20	3.3	0.08–0.15
Idaho	327		20	35	12.0	
Iowa	320 (307)	18 (17.2)		134	12.0	0.01
Montana	174		60	40		0.0015
New Hampshire	340	17.2	91	52	13.7	0.078
Calcareous fens						0.0058
Open fens						0.0726
New Jersey				96	13.5	0.00733
Calcareous fens	245			60		0.0073
Acidic seeps	169		13	36		0.00003
New York	440 (397)	13.8 (19.0)	77	55	7.0	0.07
North Carolina				77	11.0	0.0023

Source: Bedford and Godwin (2003).

TABLE AX5.5-1. PRINCIPAL AIR QUALITY INDICATOR LICHEN SPECIES IN OREGON AND WASHINGTON

Group	Sub-Group	Indicator Species
Clean Air	Regional distribution	<i>Bryoria capillaris, Lobaria oregana, Sphaerophorus globosus, Usnea filipendula, Usnea scabrata</i>
	Sub-regional distribution	<i>Ahtiana pallidula, Alectoria sarmentosa, Bryoria fuscescens, Hypogymnia enteromorpha, Nephroma bellum, Nodobryoria oregana</i>
Polluted Air	Regional nitrophytes	<i>Candelaria concolor, Physcia adscendens, Xanthoria polycarpa</i>

* Includes only species with highest indicator value, used by Geiser and Neitlich (2007) to define air quality zones.

Source: Geiser and Neitlich (2007).

**TABLE AX5.5-2. ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION DESCRIBED FOR STUDY SITES
IN THE WESTERN UNITED STATES**

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
<u>Effects in Aquatic Systems</u>				
Elevated NO ₃ ⁻ in runoff; most severe in southern California and in chaparral catchments in the southwestern Sierra Nevada	Transverse ranges of southern California; low-elevation catchments in the Sierra Nevada; high-elevation catchments in the Colorado Front Range	Well-documented response	It is unclear how widespread this phenomenon is outside the ecosystems listed, because there is little information from low-elevation systems in the Sierra Nevada and elsewhere.	Williams et al. (1996), Fenn and Poth (1999), Fenn et al. (2003b)
N enrichment and shifts in diatom communities in alpine lakes	Colorado Front Range; Lake Tahoe (California/Nevada border)	Documented for two lakes east of the Continental Divide and Lake Tahoe	These effects seem likely in other N-enriched lakes but have not been investigated.	Baron et al. (2000), Wolfe et al. (2001), Goldman (1988)
Reduced lake water clarity and increased algal growth	Lake Tahoe (California/Nevada border); high-elevation lakes throughout central and southern Sierra Nevada	Well-documented response; N and P deposition believed to be important factors	Lake Tahoe is an unusual case because of its renowned lake clarity; extent of occurrence elsewhere in northern Sierra Nevada is unknown.	Jassby et al. (1994), Sickman et al. (2003a)
Increased NO ₃ ⁻ concentrations in high-elevation lakes	Several regions, mainly downwind of urban centers	Fairly well established from lake surveys, but more data needed for improved definition of frequency and severity	Evidence suggests that urban plumes and agricultural emissions affect lake NO ₃ ⁻ levels. There is also evidence of impacts on low-elevation lakes.	Figure 2; Sickman et al. (2002)

TABLE AX5.5-2 (cont'd). ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION DESCRIBED FOR STUDY SITES IN THE WESTERN UNITED STATES

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
<u>Effects in Terrestrial Systems</u>				
N enrichment of soil and plants	Forests and chaparral ecosystems in the Transverse Ranges of southern California and in the southwest Sierra Nevada; coastal sage scrub in southern California; incipient responses reported for forests in the Colorado Front Range	Well-established response	Nitrogen enrichment seems likely in other areas of emissions sources because of the expectation of high atmospheric inputs (e.g., deposition data for the Phoenix, Arizona, region in Fenn et al. (2003a))	Fenn et al. (1996), Fenn and Poth (1999), Padgett and Allen (1999), Baron et al. (2000), Rueth and Baron (2002), Fenn et al. (2003b)
Increased fluxes of nitrogenous trace gases from soil	Forests and chaparral in southern California; alpine soils in the Colorado Front Range	Documented response in southern California chaparral and forests; experimentally shown in Colorado with N additions	This is a likely response from soils receiving chronic N deposition inputs.	Neff et al. (1994), Fenn et al. (1996)
Decreased diversity of mycorrhizal communities	White spruce in Kenai Peninsula, Alaska; coastal sage scrub and chaparral in southern California	Documented response	This is a likely response from soils and plants receiving chronic N deposition inputs, but it has not been studied elsewhere.	Egerton-Warburton and Allen (2000), Egerton-Warburton et al. (2001), Lilleskov et al. (2002)
Alpine plant community changes	Colorado Front Range	Supported by long-term monitoring data and manipulative experiments; moderate level of uncertainty	It is not known if this effect occurs elsewhere in alpine plant communities in the West.	Bowman and Steltzer (1998), Bowman (2000)

TABLE AX5.5-2 (cont'd). ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION DESCRIBED FOR STUDY SITES IN THE WESTERN UNITED STATES

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
Effects in Terrestrial Systems (cont'd)				
Enhanced growth of invasive species	Costal sage scrub, southern California; San Francisco Bay area	N deposition, fertilization studies, and plant community data supportive, but moderate uncertainty remains	It is not known if this effect occurs elsewhere, but it is expected that nitrophilous species will be selected for if N accumulates in soil.	Weiss (1999), Allen et al. (in press)
Lichen community changes	Parts of the Pacific Northwest; many areas in California; north and central Colorado	Well-established response; a highly sensitive air pollution indicator	Because of the sensitivity of many lichen species, it is likely that this effect occurs elsewhere.	Nash and Sigal (1999)
Deleterious effects on threatened and endangered species	San Francisco Bay area; southern California	Supportive evidence, but high degree of uncertainty about the precise role of N deposition	There is a high likelihood of effects in some habitats where N accumulates in soils	Weiss (1999), Brooks (2003)
Altered fire cycle	Coastal sage scrub in southern California	Hypothesis based on observations, fertilization studies, and N deposition and N cycling data; high level of uncertainty	Because it has not been studied elsewhere, it is uncertain whether this effect occurs in other areas.	Allen et al. (in press)
Altered forest C cycling and fuel accumulation	San Bernardino Mountains	Documented response	It is uncertain whether this effect occurs in other areas.	Grulke and Balduman (1999)
Physiological perturbation of overstory species	San Bernardino Mountains	Documented response	This effect has not been widely studied but is expected for sensitive plant species exposed to O ₃ and adapted to N limitation but growing in N-enriched soils.	Grulke et al. (1998), Grulke and Balduman (1999), Takemoto et al. (2001)

TABLE AX5.5-2 (cont'd). ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION DESCRIBED FOR STUDY SITES IN THE WESTERN UNITED STATES

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
Effects in Terrestrial Systems (cont'd)				
Forest expansion into grasslands	Great Plains of western Canada	Supportive evidence found, but high degree of uncertainty as to the role of N deposition	It is not know whether this effect occurs in other areas.	Köchy and Wilson (2001)
N emissions as a major contributor to regional haze problem	National forests and parks throughout California, the Pacific Northwest, and some sites in the Interior West	Well-established effect; contribution from nitrogenous pollutants has been quantified	This is known to occur in areas far removed from emissions sources because of long-range transport.	Fenn et al. (2003c), IMPROVE data (4 March 2003; http://vista.circa.colostate.edu/improve)
NO _x emissions as precursors for phytotoxic levels of O ₃ , leading to O ₃ injury to sensitive plant species	Southern California; Sierra Nevada	Well-established effect	Significant O ₃ injury to vegetation has not been reported from other sites downwind of urban centers but cannot be ruled out as urban regions expand.	Miller and McBride (1999), Carroll et al. (2003)

C, carbon; N, nitrogen; NO₃⁻, nitrate; NO_x, nitrogen oxides; O₃, ozone; P, phosphorus.

Note: Summary includes the degree of uncertainty regarding the role of N deposition in each effect and the likelihood that these effects may occur elsewhere in the West.

TABLE AX5.5-3. SUMMARY OF PUBLISHED EFFECTS OF N ENRICHMENT ON AQUATIC BIOTA IN FRESHWATER ECOSYSTEMS

Species	Common Name	Life Stage	N Concentration (mg NO ₃ -N/L)	Observed Effects	Reference
Algae					
<u>Phytoplankton</u>					
<i>Asterionella formosa</i>	diatoms		0.252 mg/L	stimulated growth	Saros et al. (2005)
<i>Asterionella formosa</i>	diatoms		6.4 umol/L	stimulated growth	McKnight et al. (1990)
Multiple species	diatoms		1.06 mg/L	(low ambient N-deposition):increase in chlorophyll- <i>a</i> content and growth rate; no cell density effect	Lafrancois et al. (2004)
<i>Asterionella formosa</i>	diatoms		5.7×10^{-4} (>0.041 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
<i>Fragilaria crotonensis</i>	diatoms		0.252 mg/L	stimulated growth	Saros et al. (2005)
Multiple species	diatoms		1.06 mg/L	(low ambient N deposition):increase in chlorophyll- <i>a</i> content and growth rate; no cell density effect	Lafrancois et al. (2004)
<i>Fragilaria crotonensis</i>	diatoms		3.5×10^{-4} (>0.028 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
<i>Fragilaria crotonensis</i>	diatoms		8.4×10^{-6} (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
<i>Staurosirella pinnata</i>	diatoms		8.4×10^{-6} (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
<i>Tetracyclus glans</i>	benthic diatoms		1.7×10^{-4} (>0.012 uM) (low light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Multiple species	phytoplankton assemblages		3.0 uM	N saturation value for maximum diversity in WY low N lakes	Interlandi et al. (1999)
not identified	phytoplankton assemblages		0.5 mg/L	NO ₃ stimulated growth seasonally, while tributary periphyton communities were P limited	Stanley et al. (1990)
not identified	phytoplankton assemblages		0.3 uM	NH ₄ additions more effective at stimulating growth than NO ₃	Levine and Whalen (2001)
not identified	phytoplankton assemblages		100 ug/L	stimulated NO ₃ uptake	Axler and Reuter (1996)

TABLE AX5.5-3 (cont'd). SUMMARY OF PUBLISHED EFFECTS OF N ENRICHMENT ON AQUATIC BIOTA IN FRESHWATER ECOSYSTEMS

Species	Common Name	Life Stage	N Concentration (mg NO ₃ -N/L)	Observed Effects	Reference
Algae (cont'd)					
<u>Phytoplankton (cont'd)</u>					
Multiple species	crysophytes		1.21 mg/L	(elevated ambient N deposition): no response to NO ₃ additions; increased chlorophyll- <i>a</i> and cell density when NO ₃ combined with acid and P	Lafrancois et al. (2004)
Multiple species	epilimnetic algae		0.012 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)
Multiple species	hypolimnetic algae		0.050 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)
<u>Periphyton</u>					
	attached benthic algae		0.5 M NaNO ₃ in 2% agar	biomass increased in response to N and N&P additions during period of seasonal N-limitation (July-August)	Smith and Lee (2006)
	attached benthic algae		2.5 M	NO ₃ stimulated stream algal growth during seasonal N-limitation	Bushong and Bachmann (1989)
not identified	attached benthic algae		0.5 M NaNO ₃ in 3% agar	NO ₃ alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Wold and Hershey (1999)
not identified	attached benthic algae		0.5 M NaNO ₃ in 3% agar	NO ₃ alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Allen and Hershey (1996)
not identified	attached benthic algae		0.036 mg/L	stimulated NO ₃ uptake	Axler and Reuter (1996)
not identified	attached benthic algae		0.5 M NaNO ₃ in 2% agar	no growth response	Higley et al. (2001)
not identified	epilithic		~700 ug NO ₃ -N	suppressed N ₂ -fixation	Reuter et al. (1985)

TABLE AX5.5-3 (cont'd). SUMMARY OF PUBLISHED EFFECTS OF N ENRICHMENT ON AQUATIC BIOTA IN FRESHWATER ECOSYSTEMS

Species	Common Name	Life Stage	N Concentration (mg NO ₃ -N/L)	Observed Effects	Reference
Algae (cont'd)					
<u>Periphyton (cont'd)</u>					
not identified	attached benthic algae		0.16 mg/L	increased summer growth rate (measured at half the maximum growth rate)	Reuter et al. (1985)
not identified	attached benthic algae		0.32 mg/L	increased winter growth rate (measured at half the maximum growth rate)	Reuter et al. (1986)
not identified	sublittoral epilithic algae		0.259 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	eulittoral epilithic algae		0.126 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	epipellic algae		0.713 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
<u>Cyanobacteria</u>					
<i>Anabaena circinalis</i>	N fixing cyanobacteria		0.5 M NaNO ₃ in 2% agar	decreased abundance	Higley et al. (2001)
<i>Microcystis sp.</i>	non-N-fixing cyanobacteria		0.28 mg/L	increased growth rate; increased microcystin and anatoxin-a concentrations	Gobler et al. (2007)
Invertebrates					
<i>Hydropsyche occidentalis</i>	caddis fly	early instaar	1.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	2.2 (SC)	mortality	Camargo and Ward (1995)
<i>Cheumatopsyche pettiti</i>	caddis fly	early instaar	2.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	3.5 (SC)	mortality	Camargo and Ward (1995)
<i>Echinogammarus echinosetosus</i>	amphipod	adult	2.8 (120-h LC _{0.01})	mortality	Camargo et al. (2005)
<i>Eulimnogammarus toletanus</i>	amphipod	adult	4.4 (120-h LC _{0.01})	mortality	Camargo et al. (2005)

TABLE AX5.5-3 (cont'd). SUMMARY OF PUBLISHED EFFECTS OF N ENRICHMENT ON AQUATIC BIOTA IN FRESHWATER ECOSYSTEMS

Species	Common Name	Life Stage	N Concentration (mg NO ₃ -N/L)	Observed Effects	Reference
Invertebrates (cont'd)					
<i>Ceriodaphnia dubia</i>	water flea/cladoceran	adult	7.1-56.5 (7-d NOEC)	decreased reproductive ability; fewer neonates produced per female	Scott and Crunkilton (2000)
<i>Daphnia pulex</i>	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO ₃	Lafrancois et al. (2004)
<i>Daphnia schoedleri</i>	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO ₃	Lafrancois et al. (2004)
Vertebrates					
<u>Amphibians</u>					
<i>Rana temporaria</i>	common frog	larvae	5 (70-d NOEC)	delayed development, lower growth rate and body mass at metamorphosis	Johansson et al. (2001)
<i>Rana sylvatica</i>	wood frog	fertilized eggs	9 (NOAEL)	no effect of NO ₃ on survivorship	Laposata and Dunson (1998)
<i>Ambystoma jeffersonianum</i>	Jefferson's salamander	fertilized eggs	9 (NOAEL)	no effect of NO ₃ on survivorship	Laposata and Dunson (1998)
<i>Ambystoma maculatum</i>	spotted salamander	fertilized eggs	9 (NOAEL)	no effect of NO ₃ on survivorship	Laposata and Dunson (1998)
<i>Ambystoma gracile</i>	northwestern salamander	larvae	5-20	no effect of NO ₃ on survivorship	Romansic et al. (2006)
<i>Rana aurora</i>	red-legged frog	larvae	5-20	no effect of NO ₃ on survivorship; NO ₃ decreased susceptibility to Saprolegnia mold	Romansic et al. (2006)
<i>Hyla regilla</i>	Pacific tree frog	larvae	5-20	no effect of NO ₃ on survivorship	Romansic et al. (2006)
<i>Pseudacris triseriata</i>	striped chorus frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
<i>Rana pipiens</i>	northern leopard frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
<i>Bufo americanus</i>	American toad	fertilized eggs	9.0 (NOAEL)	no effect of NO ₃ on survivorship	Laposata and Dunson (1998)

TABLE AX5.5-3 (cont'd). SUMMARY OF PUBLISHED EFFECTS OF N ENRICHMENT ON AQUATIC BIOTA IN FRESHWATER ECOSYSTEMS

Species	Common Name	Life Stage	N Concentration (mg NO ₃ -N/L)	Observed Effects	Reference
Vertebrates (cont'd)					
<u>Fish</u>					
<i>Oncorhynchus mykiss</i> (anadromous)	steelhead	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Oncorhynchus mykiss</i> (nonanadromous)	rainbow trout	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Oncorhynchus mykiss</i> (nonanadromous)	rainbow trout	fry	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Oncorhynchus tshawytscha</i>	chinook salmon	fry	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Salmo clarki</i>	cutthroat trout (Lahontan)	eggs	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Salmo clarki</i>	cutthroat trout (Lahontan)	fry	4.5 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
<i>Coregonus clupeaformis</i>	lake whitefish	embryo	6.25 (~120-d NOEC)	hatching and developmental delays	McGurk et al. (2006)
Miscellaneous					
<i>Saprolegnia spp.</i>	pathogenic water mold		5-20 mg NO ₃ /L	decreased ability to infect and kill the larvae of the red-legged frog, <i>Rana aurora</i>	Romansic et al. (2006)

NOEC = No-observed-effect concentration; NOAEL = No-observed-adverse-effect level; SC = Safe concentration

**TABLE AX5.5-4. ESTIMATED PERCENT OF TOTAL N LOAD TO
DELAWARE BAY AND HUDSON RIVER/RARITAN BAY CONTRIBUTED
BY ATMOSPHERIC DEPOSITION**

Study	Percent of Nitrogen Load Contributed by Atmospheric Deposition	
	Delaware Bay	Hudson River/Raritan Bay
Paerl (1985)	44	--
Hinga et al. (1991)	--	33
Scudlark and Church (1993)	15	--
Paerl (1995)	--	68
Jaworski et al. (1997)	44	68
Alexander et al. (2001)	22	26
Castro et al. (2001)	--	10
Stacey et al. (2001)		
Land-based	16	10
Sparrow model	25	27
Castro and Driscoll (2002)	20	17
Castro et al. (2003)	23	18

TABLE AX5.6-1. ESSENTIAL ECOLOGICAL ATTRIBUTES AND REPORTING CATEGORIES

Landscape Condition	Ecological Processes
Extent of Ecological System/Habitat Types	Energy Flow
Landscape Composition	Primary Production
Landscape Pattern and Structure	Net Ecosystem Production
	Growth Efficiency
Biotic Condition	Material Flow
Ecosystems and Communities	Organic Carbon Cycling
Community Extent	Nitrogen and Phosphorus Cycling
Community Composition	Other Nutrient Cycling
Trophic Structure	
Community Dynamics	Hydrology and Geomorphology
Physical Structure	Surface and Groundwater flows
Species and Populations	Pattern of Surface flows
Population Size	Hydrodynamics
Genetic Diversity	Pattern of Groundwater flows
Population Structure	Salinity Patterns
Population Dynamics	Water Storage
Habitat Suitability	Dynamic Structural Characteristics
Organism Condition	Channel/Shoreline Morphology, Complexity
Physiological Status	Extent/Distribution of Connected Floodplain
Symptoms of Disease or Trauma	Aquatic Physical Habitat Complexity
Signs of Disease	Sediment and Material Transport
	Sediment Supply/Movement
Chemical and Physical Characteristics (Water, Air, Soil, and Sediment)	Particle Size Distribution Patterns
Nutrient Concentrations	Other Material Flux
Nitrogen	
Phosphorus	Natural Disturbance Regimes
Other Nutrients	Frequency
Trace Inorganic and Organic Chemicals	Intensity
Metals	Extent
Other Trace Elements	Duration
Organic Compounds	
Other Chemical Parameters	
pH	
Dissolved Oxygen	
Salinity	
Organic Matter	
Other	
Physical Parameters	

Source: Young and Sanzone (2002).

TABLE AX5.6-2. PRIMARY GOODS AND SERVICES PROVIDED BY ECOSYSTEMS

Ecosystem	Goods	Services
Agroecosystems	Food crops Fiber crops Crop genetic resources	<ul style="list-style-type: none"> • Maintain limited watershed functions (infiltration, flow control, and partial soil protection) • Provide habitat for birds, pollinators, and soil organisms important to agriculture • Sequester atmospheric carbon • Provide employment
Coastal Ecosystems	Fish and shellfish Fishmeat (animal feed) Seaweeds (for food and industrial use) Salt Genetic resources	<ul style="list-style-type: none"> • Moderate storm impacts (mangroves, barrier islands) • Provide wildlife (marine and terrestrial) (habitat and breeding areas/hatcheries/nurseries) • Maintain biodiversity • Dilute and treat wastes • Provide harbors and transportations routes • Provide human and wildlife habitat • Provide employment • Contribute aesthetic beauty and provide recreations
Forest Ecosystems	Timber Fuelwood Drinking and irrigation water Fodder Nontimber products (vines, bamboos, leaves, etc.) Food (honey, mushrooms, fruit, and other edible plants; game) Genetic resources	<ul style="list-style-type: none"> • Remove air pollutants, emit oxygen • Cycle nutrients • Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization) • Maintain biodiversity • Sequester atmospheric carbon • Moderate weather extremes and impacts • Generate soil • Provide employment • Provide human and wildlife habitat • Contribute aesthetic beauty and provide recreation
Freshwater	Drinking and irrigation water Fish Hydroelectricity Genetic resources	<ul style="list-style-type: none"> • Buffer water flow (control timing and volume) • Dilute and carry away wastes • Cycle nutrients • Maintain biodiversity • Provide aquatic habitat • Provide transportation corridor • Provide employment • Contribute aesthetic beauty and provide recreation
Grassland Ecosystems	Livestock (food, game, hides, and fiber) Drinking and irrigation water Genetic resources	<ul style="list-style-type: none"> • Maintain array of watershed functions (infiltration, purification, flow control, and soil stabilization) • Cycle nutrients • Remove air pollutants and emit oxygen • Maintain biodiversity • Generate soil • Sequester Atmospheric carbon • Provide human and wildlife habitat • Provide employment • Contribute aesthetic beauty and provide recreation

Source: World Resources Institute (2000).

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AX6. NON-ACIDIFICATION EFFECTS FROM SULFUR

A number of environmental effects are associated with sulfur (S) deposition and related exposure to high atmospheric concentrations of sulfur dioxide (SO₂). These include soil and water acidification, which are addressed in Annex 4, but also a number of non-acidification effects. Some of these are addressed in other Annexes. For example, atmospheric SO₂ concentrations and associated S deposition can accelerate corrosion of concrete and limestone (see Annex 9) used in buildings, art, and monuments that are part of the cultural heritage of the United States (U.S. Environmental Protection Agency, 1982).

This Annex addresses non-acidification effects of S deposition that are related to nutrient enrichment, toxicity, and secondary effects on the cycling and bioavailability of mercury (Hg), a highly neurotoxic contaminant. High concentrations of SO₂ can harm vegetation by causing foliar injury, decreased plant growth, and elimination of sensitive plant species, although atmospheric concentrations of SO₂ are seldom high enough to cause these effects on vegetation at ambient air pollution levels in the United States. However, the biogeochemical cycling of S is closely linked with the cycling of other important elements, including carbon (C), nitrogen (N), phosphorus (P), aluminum (Al), and mercury (Hg). S deposition can thus affect availability of other nutrients, and contaminant toxicity. In particular, current research suggests that S deposition intervenes in the cycling of Hg in transitional and aquatic ecosystems by stimulating the growth of sulfate (SO₄²⁻)-reducing bacteria (SRB), which are associated with Hg methylation, a key process in increasing the bioavailability of Hg.

AX6.1 EFFECTS ON BIOGEOCHEMICAL PATHWAYS AND CYCLES

AX6.1.1 Cycling and Storage of Sulfur

AX6.1.1.1 Terrestrial Ecosystems

Considerable effort was devoted in the 1980s to the computation of S budgets for watersheds and forest plots, with the objective of evaluating S retention and release. These budgets were subject to complications from fluxes that could not be measured directly, such as dry deposition and weathering, but they generally indicated net S retention at sites south of the

1 line of glaciation — a result attributed to net adsorption of SO_4^{2-} (Rochelle et al., 1987;
2 Cappellato et al., 1998). During the 1990s, little or no decrease in SO_4^{2-} concentration occurred
3 in streams in the Ridge and Blue Ridge physiographic provinces, despite regional decreases in
4 atmospheric deposition of S (Webb et al., 2004), and no evidence of S addition from mine
5 drainage. This lack of response in stream chemistry has been generally attributed to a shift in S
6 equilibrium between the adsorbed and solution phases under conditions of decreased
7 atmospheric inputs of SO_4^{2-} . This interpretation is supported by a decrease in concentrations of
8 adsorbed SO_4^{2-} from 1982 to 1990 in a Piedmont soil in South Carolina that received decreasing
9 levels of S deposition during this period (Markewitz et al., 1998). This same soil also
10 experienced an increase in adsorbed SO_4^{2-} from 1962 to 1972 (Markewitz et al., 1998). The
11 only published S budget more recent than 1992 for an unglaciated site in the United States
12 (Castro and Morgan, 2000) also suggested a net release of SO_4^{2-} . This upland Maryland
13 watershed released 1.6 times more SO_4^{2-} than measured in throughfall in 1996-97.

14 Numerous S budgets were compiled in the 1980s for glaciated sites, and results generally
15 indicated that inputs approximately equaled outputs on an annual basis (Rochelle and Church,
16 1987). The observation of little or no S retention at glaciated sites was attributed to relatively
17 low SO_4^{2-} adsorption capacity in soils. Balanced S budgets in glaciated regions implied that
18 decreases in atmospheric deposition of S would lead directly to decreases in SO_4^{2-} leaching. The
19 strong correlation between recent decreases in both atmospheric S deposition and SO_4^{2-}
20 concentrations in surface waters is widely recognized to be a result of this direct linkage
21 (Stoddard et al., 2003). Nevertheless, considerable evidence also indicates that S inputs in
22 glaciated ecosystems do not behave conservatively, but instead are cycled in part through
23 microbial and plant biomass (David et al., 1987; Alewell and Gehre, 1999; Likens et al., 2002).
24 As a result, large quantities of S are stored in organic forms within the soil. David et al. (1987)
25 found that annual S deposition (wet plus dry) at a site in the central Adirondack region of New
26 York was about 1% of the organic S pool in the soil. Houle et al. (2001) estimated that annual S
27 deposition at 11 sites in North America ranged from 1% to 13% of the organic S pool in soil.

28 The S cycle in forest ecosystems can be represented as a series of input, uptake, and
29 output terms (Figure AX6.1-1). Some of the fluxes illustrated in this schematic drawing can be
30 measured in the field, including wet deposition, litterfall, and throughfall. Other fluxes must be
31 calculated or estimated, which involves considerable uncertainty (Johnson and Mitchell, 1998).

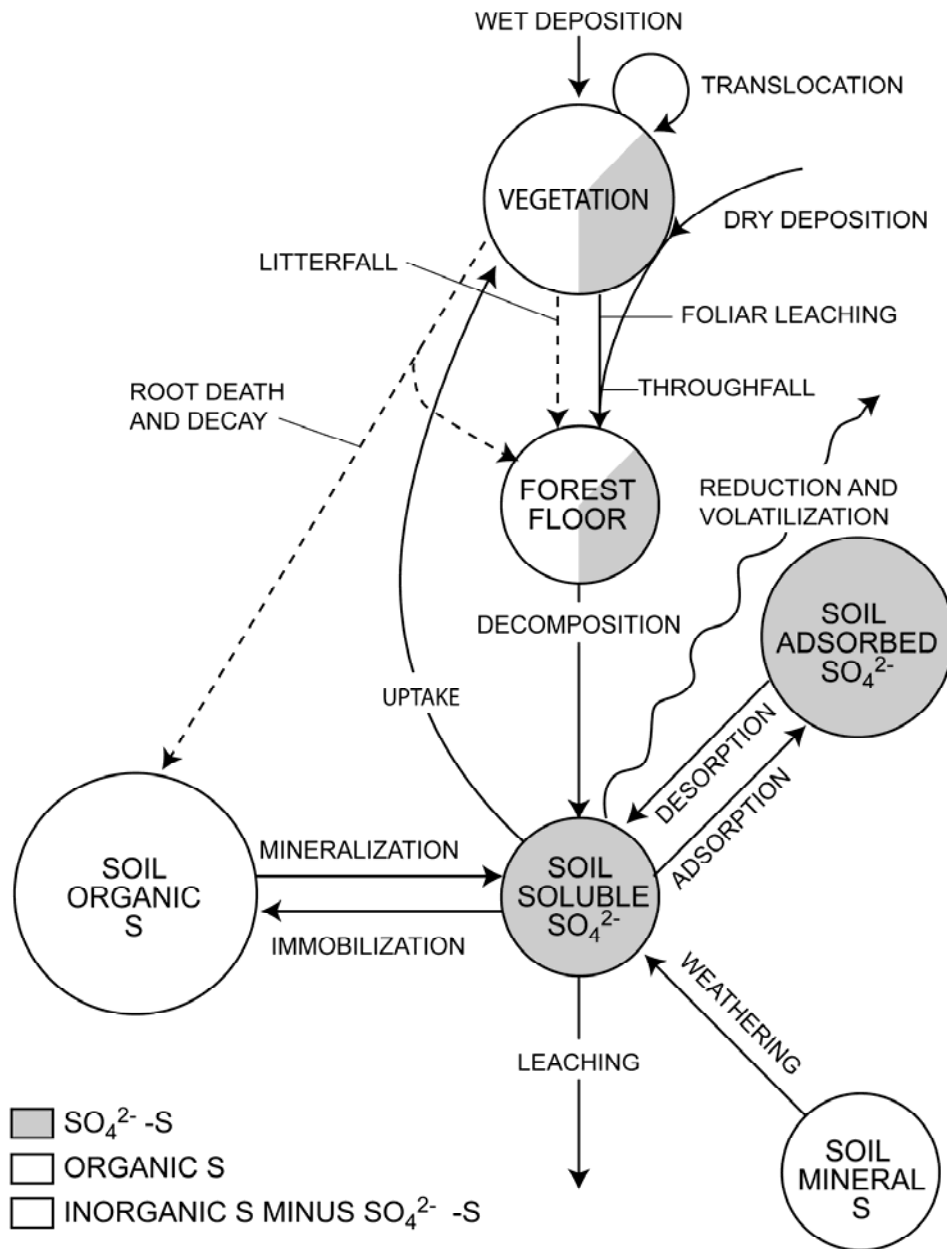


Figure AX6.1-1. Representation of the S cycle in forest ecosystems.

Source: Johnson (1984).

- 1 Perhaps the most important uncertainty concerns the amount of dry deposition, which can be
- 2 substantial (Lindberg et al., 1990).

1 Atmospheric deposition is an important part of the S cycle, including in areas that are not
2 exposed to appreciable air pollution levels. In fact, although agricultural S and geologic S
3 (especially associated with mining activities) can be locally important or dominant, atmospheric
4 S inputs may constitute the major source of S input to many terrestrial ecosystems (Probert and
5 Asmosir, 1983; Johnson and Mitchell, 1998).

6 Much of the organic S stored in soil is in C-bonded forms that are relatively unreactive,
7 but can be oxidized by bacteria or mineralized to SO_4^{2-} under oxic conditions, which are
8 typically found in moderately well drained to well drained soils (Johnson and Mitchell, 1998).
9 Carbon-bonded S in forest soils can be found in a variety of organic S compounds, including
10 amino acids, sulfolipids, and sulfonic acids. Carbon-bonded S can also be found in humic
11 material in the form of aliphatic and aromatic structures (Likens et al., 2002). Furthermore,
12 strong correlations have been shown between levels of atmospheric deposition of S and
13 concentrations of S in soil (Driscoll et al., 2001; Novák et al., 2005). Long-term increases in
14 concentrations of total S in soils that are at least partially attributable to increases in organic S
15 have also been documented (Knights et al., 2000; Lapenis et al., 2004), although the study of
16 Houle et al. (2001) did not find a relation between these factors. A Swedish “clean roof” study
17 also provides some insight into the role of organic S in possibly delaying chemical recovery from
18 acidification due to S deposition (Mörth et al., 2005). After 9 years of application of pre-
19 industrial levels of S deposition, the amount of SO_4^{2-} in runoff still exceeded inputs by 30%.
20 Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

21 Thus, research on the effects of atmospheric S deposition on soils has indicated
22 pronounced changes in soils from sustained SO_4^{2-} leaching, and accumulation of S through
23 physical/chemical adsorption and biological assimilation. The recent evidence of net loss of
24 S from soils at a number of sites is likely a response to decreased atmospheric inputs. The
25 gradual loss of previously accumulated S contributes to continued SO_4^{2-} leaching. Uncertainties
26 in estimates of ecosystem fluxes such as weathering and dry deposition, and complications in
27 discerning the effects of desorption from mineralization make it difficult to predict when
28 S outputs will no longer exceed inputs as levels of S deposition continue to decline. Research
29 based on experimental reduction of S inputs suggests that this process will occur on a decadal
30 time scale (Martinson et al., 2005; Mörth et al., 2005). The long-term role of C-bonded S adds
31 further uncertainty because enhancement of S mineralization by a warming climate could also

1 affect S retention and release (Knights et al., 2000; Driscoll et al., 2001). This process can be
2 microbially catalyzed, and bacteria are generally more active at higher temperature.

3
4 **AX6.1.1.2 Transitional Ecosystems**

5 Transitional ecosystems exert important controls on watershed S budgets, especially in
6 watersheds that contain extensive wetland development. Sulfur storage in wetland soils provides
7 an important buffering system that restricts chronic SO_4^{2-} leaching to surface waters.
8 Input-output studies of bogs in Massachusetts (Hemond, 1980), Ontario (Urban and Bayley,
9 1986), and Minnesota (Urban and Eisenreich, 1988) suggested more than 50% retention of
10 atmospheric S inputs. However, oxidation of S that was previously stored in wetland soils can
11 provide an important episodic source of SO_4^{2-} to downstream surface waters. (See discussion in
12 Section AX6.1.2.2.) Thus, the presence of wetlands in a watershed can either temporarily
13 increase or decrease the flux of SO_4^{2-} to surface waters, and these differences are largely
14 determined by changes in hydrology and redox conditions in wetland soils. Overall, wetlands act
15 as sinks for S because of microbial SO_4^{2-} reduction and sequestering of reduced S as sulfide
16 minerals and organic S.

17 Changes in S flux that are controlled by processes in transitional ecosystems can have
18 important effects on surface water chemistry. For example, reduction of SO_4^{2-} in sediments by
19 assimilatory and dissimilatory processes is an important source of acid neutralizing capacity
20 (ANC) to lakes having long hydraulic residence time, and a likely source also to beaver ponds
21 and wetlands. In-lake ANC production is mostly due to S retention from microbial SO_4^{2-}
22 reduction (Schindler, 1986; Brezonik et al., 1987; Turner et al., 1991). It is unlikely, however,
23 that the changes in S flux caused by wetlands and ponds in a watershed would be large enough to
24 have any direct non-acidification effects on biota. More likely, the major non-acidification
25 effects of wetland influence on S cycling relate to changes in Hg methylation in wetland soils.
26 This is discussed in Section AX6.3. Other changes can also occur, including enhanced release of
27 N and P from wetland soils.

28 Some of the organic S in wetlands can be converted to reduced S gasses, including
29 dimethylsulfide and hydrogen sulfide (under acidic conditions), and released to the atmosphere.
30 Up to 30% of the atmospheric deposition of S in remote areas may be derived from release of

1 reduced S gasses from wetlands (Nriagu et al., 1987). Thus, wetland processes can have
2 important effects on local atmospheric S deposition and trace gas emissions.

3 4 **AX6.1.1.3 Aquatic Ecosystems**

5 In aquatic ecosystems that are sensitive to acidification from atmospheric S deposition,
6 SO_4^{2-} is generally highly mobile within the ecosystem. Acid-sensitive streams tend to be
7 relatively fast-flowing, high-gradient, low-order streams that exhibit high SO_4^{2-} mobility. Acid
8 sensitive lakes tend to be relatively small, headwater lakes with short hydraulic residence times
9 (weeks to months). In such streams and lakes, most of the SO_4^{2-} contributed by inflowing
10 ground and surface waters is directly flushed through the ecosystem and emerges as outflow.

11 However, larger streams, streams that flow through series of ponds (i.e., beaver ponds) or
12 lakes, and especially larger lakes, tend to have longer hydraulic residence, and provide
13 opportunity for microbial S reduction in sediments. This S reduction can have important effects
14 on the concentration of SO_4^{2-} in drainage water, and results in the generation of ANC. The
15 importance of sediment reactions to the acid-base chemistry of surface water depends mainly on
16 the flux rate of material across the sediment-water interface and the amount of time that water
17 remains in contact with the sediment (Kelly et al., 1987; Baker and Brezonik, 1988; Turner et al.,
18 1991). In some lakes having long water residence times, about half of the input SO_4^{2-} is retained
19 in lake sediments (Kelly et al., 1987; Baker and Brezonik, 1988).

20 Sulfur is an essential nutrient for algae and planktonic bacteria. Nevertheless,
21 S concentration in most lakes is well above the limiting concentration for algal productivity, and
22 therefore biotic S uptake in the water column is not a quantitatively important part of the S cycle
23 in acid-sensitive lakes (Turner et al., 1991).

24 25 **AX6.1.2 Export of Sulfur**

26 27 **AX6.1.2.1 Terrestrial Ecosystems**

28 In order for atmospherically deposited S to exert influence on drainage water, with the
29 range of associated environmental effects that can occur, it must be exported as SO_4^{2-} from the
30 soil. If the incoming S in atmospheric deposition is retained in the vegetation or soil
31 compartments, it will not be available to affect soil water or surface water downstream within the
32 watershed. In areas of S deposition, almost all deposited S moves into the soil and can then be

1 exported from the terrestrial ecosystem or adsorbed on soil. In most parts of the United States,
2 most deposited S is exported in drainage water. In much of the southeastern United States,
3 however, S adsorption on soil substantially limits S export (See discussion in Annex 4).

4 5 **AX6.1.2.2 Transitional Ecosystems**

6 When saturated, wetland soils act as sinks for incoming S via SO_4^{2-} reduction. Sulfide is
7 produced through this process and sequestered in anoxic wetland sediments (Mitsch and
8 Gosselink, 2000). However, it has been observed that wetlands can act as sources of SO_4^{2-} to
9 downstream drainage waters during storm events that follow prolonged periods of drought
10 (Dillon and LaZerte, 1992; Devito and Hill, 1999; Eimers and Dillon, 2002; Jeffries et al., 2002;
11 Laudon et al., 2004; Mitchell et al., 2006). The mechanism has been described as follows.
12 Sulfate is produced through oxidative processes in wetland sediments when they are exposed to
13 atmospheric oxygen as the water table falls during periods of drought. This newly formed SO_4^{2-}
14 is mobile, and therefore can be flushed from the wetland into streams or lakes when the water
15 table rises as more typical hydrologic conditions resume. This flush of SO_4^{2-} can result in
16 episodic acidification of downstream surface waters (Laudon et al., 2004) and potentially
17 prolong the chemical recovery of surface water ANC as S deposition declines (Aherne et al.,
18 2006).

19 Much of the supporting research on this topic has been performed within the boreal
20 watersheds of Ontario, Canada (Dillon and LaZerte, 1992; Devito and Hill, 1997; Jeffries et al.,
21 2002; Aherne et al., 2004; Laudon et al., 2004). A Sphagnum-conifer wetland within the Plastic
22 Lake watershed in Ontario was determined to be a source of SO_4^{2-} to downstream drainage
23 waters after extended periods of summertime drought (Dillon and LaZerte, 1992). Comparisons
24 of stream water chemistry were made between the wetland inlet and the wetland outlet, which
25 drains a watershed consisting entirely of upland soils. The results showed little difference
26 between SO_4^{2-} concentrations in the wetland inlet and outlet during typical hydrologic
27 conditions. However, SO_4^{2-} concentrations in the outlet increased by up to a factor of five
28 during storm events that followed extended periods of drought. This occurred during 4 separate
29 years.

30 The majority of the study watersheds in the Plastic Lake region of Ontario, Canada have
31 consistently exported more SO_4^{2-} than was atmospherically deposited on an annual basis over an

1 18-year period (Eimers and Dillon, 2002). This observation suggests either the existence of an
2 internal watershed SO_4^{2-} source, or an underestimation of S deposition. It is possible that dry
3 deposition is underestimated (Likens et al., 1990; Edwards et al., 1999), but a variety of potential
4 watershed sources of additional S have also been proposed in areas that are sensitive to
5 atmospheric S deposition, including:

- 6 • weathering of S-containing minerals (Baron et al., 1995)
- 7 • desorption of SO_4^{2-} previously adsorbed to soils when S deposition was higher
8 (Driscoll et al., 1995; Mitchell et al., 1996)
- 9 • mineralization of S previously incorporated into organic matter (Driscoll et al., 1998)
- 10 • drought-related oxidation and release of S stored in wetlands and riparian soils
11 (Dillon and LaZerte, 1992; Dillon et al., 1997)

12 Underestimation of dry deposition was not considered to be a significant issue for the
13 Canadian study watersheds (Eimers and Dillon, 2002). Furthermore, mineral weathering is not
14 considered a significant source of SO_4^{2-} in that region, due to the low S content of the bedrock
15 (Neary et al., 1987). Reoxidation and mobilization of S stored in wetland sediments was
16 considered the most likely explanation for the observed higher SO_4^{2-} outputs for those
17 watersheds that contain a significant proportion of wetland. Other mechanisms, including
18 increased soil SO_4^{2-} desorption and/or increased S mineralization in response to decreased
19 S deposition inputs, may explain the SO_4^{2-} input/output imbalance observed in watersheds
20 containing little or no wetland area (Alewell and Gehre, 1999; Eimers and Dillon, 2002). Jeffries
21 et al. (1995, 2002) determined that within the Turkey Lakes watershed in western Ontario
22 wetland, reoxidation and SO_4^{2-} remobilization mechanism can delay lake acidification recovery
23 by as much as 6 years.

24 Wetland S transformations have been incorporated into state-of-the-science modeling to
25 better describe climate-induced acidification effects on lake water chemistry (Aherne et al.,
26 2004, 2006). A wetland component to the MAGIC model was developed and tested for its
27 ability to predict observed stream water SO_4^{2-} fluxes from the Plastic Lake watershed (Aherne
28 et al., 2004). This model was then used to investigate acidification recovery under two different
29 climate scenarios: (1) an “average climate” scenario consisting of long-term (most recent
30 20 years) monthly precipitation and runoff and (2) a “variable climate” scenario that included
31 sequential repetition of the measured monthly precipitation and runoff for the preceding

1 20 years. The average climate scenario did not include any significant drought periods, whereas
2 the variable climate scenario included several periods of summer drought.

3 Model results under the average climate scenario suggested that chemical recovery of
4 lake water would occur, with ANC reaching 40 µeq/L by 2020 and 50 µeq/L by 2080. However,
5 the variable climate scenario projected that recovery would be greatly reduced. ANC recovery
6 by 2080 was estimated to only reach 2.6 µeq/L. The authors acknowledged that reiterating the
7 past 20 years of climate under the variable climate scenario was somewhat arbitrary.
8 Nevertheless, results suggested that climate effects on the cycling of S can modify chemical
9 recovery of lake water from acidification in watersheds that are wetland-influenced.

10

11 **AX6.1.2.3 Aquatic Ecosystems**

12 Export of S from surface waters is controlled primarily by retention in sediments by
13 microbial SO_4^{2-} reduction. In-stream and in-lake biological demand for S is generally a very
14 small component of the S input levels in areas affected by atmospheric S deposition. Sulfur
15 reduction can be an important process regulating S export from aquatic ecosystems, mainly in
16 waters that exhibit long hydraulic retention. Sulfur reduction in lake and pond sediments can
17 also be closely associated with Hg methylation. Therefore, the dynamics of S storage and export
18 can influence the bioavailability of Hg to fish, piscivorous wildlife, and humans who consume
19 large quantities of fish.

20

21

22 **AX6.2 ROLE OF SULFUR IN METHYLATION OF MERCURY**

23 A key step in the entrance of Hg into the food chain is methylation, which converts
24 inorganic Hg to organic compounds of Hg that are highly bioavailable, and can accumulate in
25 fish tissue. Methylation rates are influenced by oxygen content, temperature, pH, and the
26 concentration of organic acids in solution (Nagase et al., 1984; Xun et al., 1987; Winfrey and
27 Rudd, 1990; U.S. Environmental Protection Agency, 1997). In 1996, the U.S. Environmental
28 Protection Agency's (EPA) Science Advisory Board concluded that "there is a large degree of
29 scientific uncertainty and variability among water bodies concerning the processes that methylate
30 Hg" (U.S. Environmental Protection Agency, 1997).

31 Although Hg concentration in fish is linked to low pH, the role of acidic deposition,
32 which is partly responsible for the low pH in some lakes and streams, is unclear. Experimental

1 observations have shown that when SO_4^{2-} is added to wetlands or lakes, SO_4^{2-} reduction is
2 enhanced, leading to increased methylation and methylmercury (MeHg) export, at least up to a
3 point (Branfireun et al., 1999; Benoit et al., 2003; Watras et al., 2006).

4 Many studies have shown an association between low lake water pH and high Hg
5 concentrations in fish (Grieb et al., 1990; Suns and Hitchin, 1990; Driscoll et al., 1994; Kamman
6 et al., 2004). Conversely, Hrabik and Watras (2002) found that decreases in fish Hg
7 concentration in an experimentally de-acidified lake basin exceeded those in the reference lake
8 basin by a factor of two over a 6-year period of experimental de-acidification. On the other
9 hand, in a study of over 600 randomly selected streams and rivers throughout the western United
10 States, Peterson et al. (2007) found little relationship between fish tissue Hg concentrations and
11 surface water pH, SO_4^{2-} , or dissolved organic carbon (DOC). They attributed the lack of a
12 chemical relationship to the fact that low pH (<7) and high DOC systems were rare in the West.
13 The major factors controlling fish tissue Hg concentrations in western streams and rivers were
14 fish size (bigger fish > smaller fish) and feeding group (piscivores >> non-piscivores), not water
15 chemistry. Highest MeHg concentrations are found in large piscivorous fish.

16 17 **AX6.2.1 Conditions Conducive to Mercury Methylation**

18 Mercury in fish muscle tissue occurs mainly as MeHg (Bloom, 1992; Harris et al., 2003).
19 Mercury methylation is largely attributed to SRB, which are commonly found in anoxic wetland
20 and lake bottom sediments (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Gilmour
21 et al., 1992). Under increased S load, the number and activity of SRB increase. The
22 mechanisms for Hg methylation, as mediated by SRB, have been discussed by Choi et al. (1994),
23 Ekstrom et al. (2003), and Ekstrom and Morel (2004). Abiotic mechanisms responsible for Hg
24 methylation also exist (Weber, 1993; Hintelmann and Evans, 1997; Siciliano et al., 2005), but
25 have not been shown to be important.

26 Wetland environments, including peatlands, have been shown to be significant areas of
27 MeHg production and sources of export to downstream receiving waters (St. Louis et al., 1994).
28 Experimental wetland studies have found that SO_4^{2-} addition can increase SRB activity and
29 cause increased MeHg production (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason
30 et al., 2006). For example, SO_4^{2-} additions of both 2.8 kg/ha and 28 kg/ha to a poor fen peatland
31 in Ontario, Canada showed enhanced pore water MeHg production (Branfireun et al., 1999).

1 Gilmour et al. (1992) investigated MeHg production within anoxic sediments of a
2 reservoir located in central Massachusetts. Elevated MeHg production with SO_4^{2-} addition was
3 measured in both experimental laboratory slurries (Figure AX6.2-1; Gilmour et al., 1992) and
4 intact sediment cores. The background SO_4^{2-} concentration in the experimental sediment
5 slurries was 60 $\mu\text{eq/L}$. Sulfate additions of 0, 100, 200, and 400 $\mu\text{eq/L}$ were applied to these
6 samples in the presence of 50 mg/L of Hg as HgCl_2 . The rate of production and the final
7 concentration of MeHg increased in proportion to the initial SO_4^{2-} concentration. Furthermore,
8 SO_4^{2-} concentrations decreased during the experiment (Figure AX6.3-1; Gilmour et al., 1992),
9 suggesting that SO_4^{2-} reduction had occurred. Methylmercury production within isolated lake
10 bottom sediment cores was also enhanced across a gradient of SO_4^{2-} addition (3 to 1040 μmol
11 sodium sulfate [Na_2SO_4]; Figure AX6.2-2). Sediment MeHg production was most enhanced
12 when SO_4^{2-} concentration was above about 60 $\mu\text{eq/L}$, with increased production from a pre-
13 treatment background MeHg concentration of 0.26 ng/g to approximately 7.0 to 8.5 ng/g. These
14 results suggest maximum MeHg production at SO_4^{2-} concentrations between about 200 and
15 400 $\mu\text{eq/L}$, although optimal conditions for methylation are likely to vary with other factors that
16 influence SO_4^{2-} reduction (i.e. redox potential, temperature, C availability, porosity) and the
17 bioavailability of Hg. At high SO_4^{2-} loading, the associated accumulation of sulfide may inhibit
18 Hg methylation. Sulfate concentrations in the range of these experiments (about 60 to
19 200 $\mu\text{eq/L}$) are often found in waters impacted by S deposition in the United States.

20 Evidence regarding the importance of SRB in regulating MeHg production was provided
21 by Gilmour et al. (1992) who showed that MeHg production was substantially reduced with
22 addition of a known SRB inhibitor (Na_2MoO_4). This is also in agreement with observations of
23 SRB mediated Hg methylation in salt marsh sediments (Compeau and Bartha, 1985). The work
24 of Gilmour et al. (1992) considered anoxic lake bottom sediments, rather than wetland
25 sediments. However, anoxia is also common in freshwater wetland sediments, where SO_4^{2-}
26 addition has also been observed to enhance Hg methylation (Branfireun et al., 1999; Harmon
27 et al., 2004; Jeremiason et al., 2006).

28 Wetland MeHg production has been measured at rates 26 to 79 times higher than
29 in upland areas of a Canadian boreal forest (wetland: 1.84 to 5.55 mg/ha/yr; upland:
30 0.07 mg/ha/yr; St. Louis et al., 1994). Watersheds containing 14.0% to 16.3% wetland yielded
31 5 to 14 times more MeHg than upland catchments that lacked wetlands (St. Louis et al., 1994).

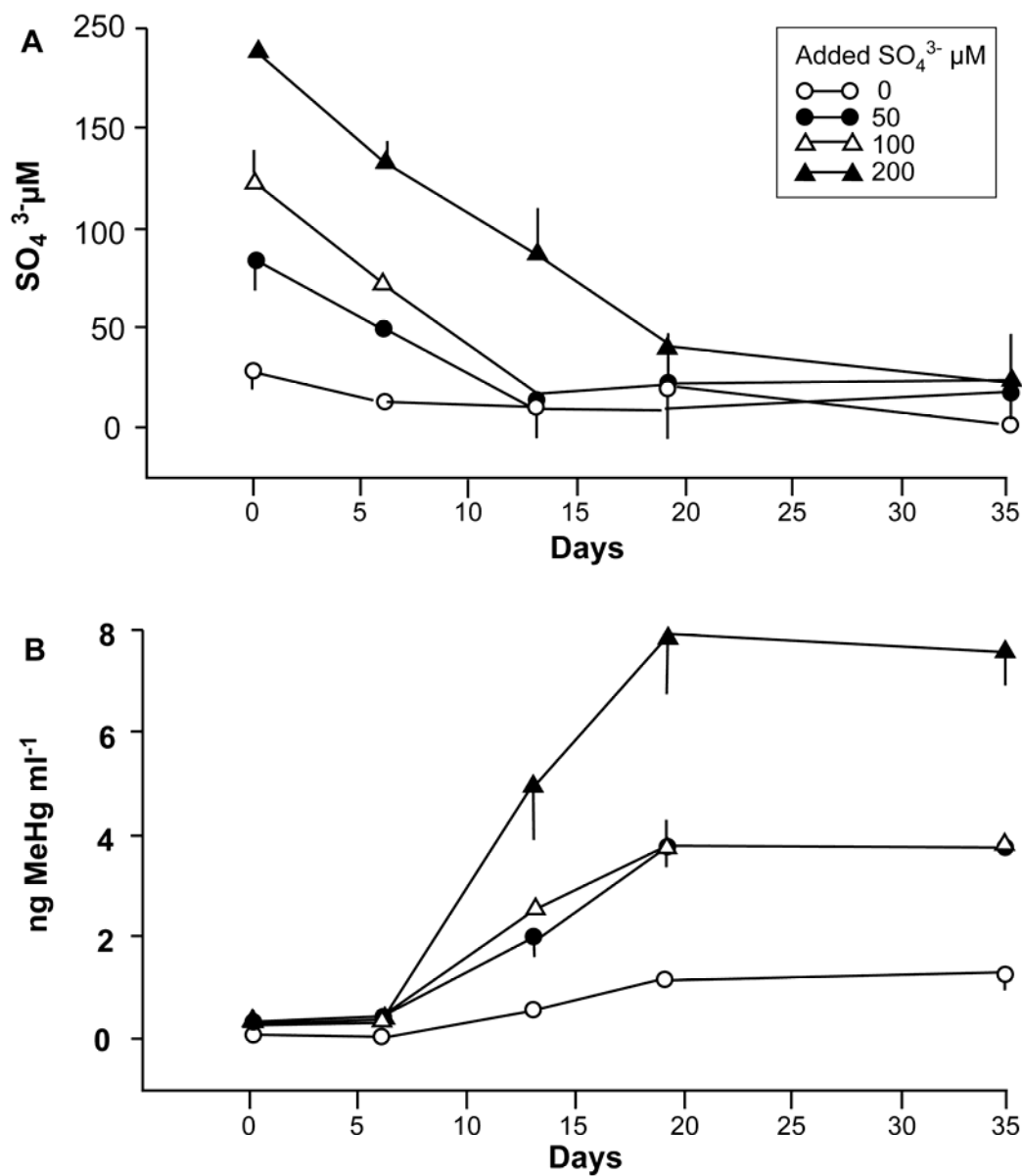


Figure AX6.2-1. (A) Sulfate and (B) methylmercury (MeHg) concentrations as a function of time in sediment slurries made from Quabbin Reservoir littoral sediments. Each delta point represents the average value from three separate incubations and the associated standard error.

Source: Gilmour et al. (1992).

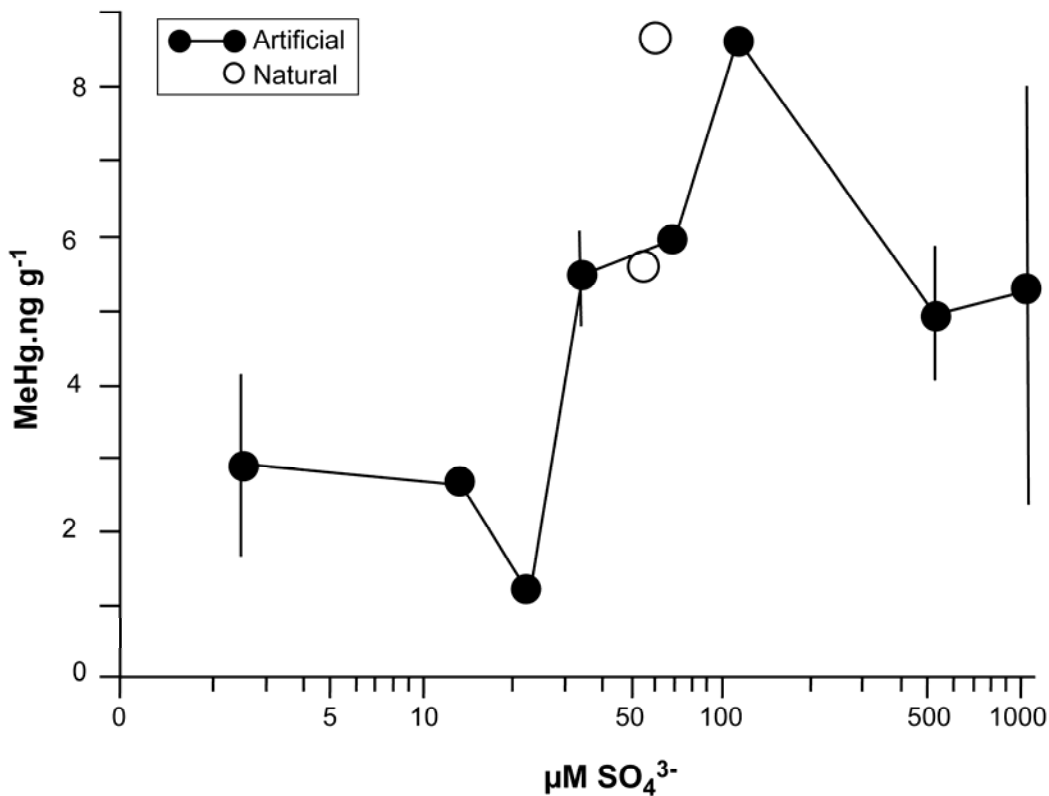


Figure AX6.2-2. Methylmercury produced in sediment cores incubated two weeks under artificial lake water containing 3-1040 μM Na_2SO_4 . Error bars represent standard error between two replicate cores. Data from cores incubated under natural water are shown individually. The average MeHg concentration in unamended Purgee sediments sampled in July was 0.26 ± 0.01 ng/g ($n = 2$).

- 1 In the same region, St. Louis et al. (1996) found that all watersheds were net sinks for total Hg
- 2 and that watersheds containing wetlands regularly exported MeHg (St. Louis et al., 1996).
- 3 However, MeHg export from these watersheds was not directly proportional to percent
- 4 wetland coverage, indicating that other variables are also involved in the major processes that
- 5 regulate MeHg production and export. In particular, the level of atmospheric Hg deposition
- 6 and the acid-base chemistry of drainage water may be important.

1 Branfireun et al. (1996) measured highest peat and pore water MeHg concentrations in
2 wetland areas that exhibited characteristics of a poor fen environment (i.e. interaction with
3 ground water). Poor fen environments did not occur in the riverine and valley bottom wetlands
4 found in the study area. The absence of these wetland types within the riverine and valley
5 bottom areas was suggested as the reason for lower MeHg production as compared to the basin
6 wetland (St. Louis et al., 1996). They also observed that MeHg export corresponded with water
7 yield. High water yield resulted in high MeHg export. It was determined that the proportion of
8 upland to wetland land area within a watershed was not the only control on MeHg export, but
9 wetland type and annual water yield also played important roles (St. Louis et al., 1996).

10 11 **AX6.2.2 Characterization and Distribution of Ecosystems Where Mercury** 12 **Methylation is Most Likely to Occur**

13 Mercury methylation occurs in anoxic sediments that contain a sufficient C source to
14 support SRB activity along with an adequate supply of SO_4^{2-} for SRB-mediated SO_4^{2-} reduction.
15 These conditions are found in lake and pond bottom sediments (Gilmour et al., 1992), freshwater
16 wetland sediments (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006), and
17 salt marsh sediments (Compeau and Bartha, 1985). Anoxic conditions can also be found in the
18 hypolimnion of some lakes. Mercury must also be present and bioavailable to SRB for
19 methylation (Benoit et al., 1999). Microbial SO_4^{2-} reduction can further enhance the reducing
20 conditions in sediments and bottom waters via the production of sulfide. These systems can be
21 found throughout the United States.

22 Several studies have shown a strong negative correlation between surface water pH and
23 Hg concentration in fish tissue, but the mechanisms responsible for this linkage are not clear.
24 Mercury concentrations in fish have also been shown to be less strongly correlated with a variety
25 of other variables, including dissolved inorganic C, calcium (Ca^{2+}), magnesium (Mg^{2+}), DOC,
26 sodium (Na^+), lake area, and watershed area (U.S. Environmental Protection Agency, 1997).

27 Driscoll et al. (2007) developed indicators of Hg sensitivity using two stratified, random-
28 probability surveys of northeastern lakes combined with the survey data sets of Chen et al.
29 (2005). This analysis showed that lakes with Hg levels above the EPA criterion of 0.3 $\mu\text{g/g}$ in
30 yellow perch had significantly higher DOC, and lower pH, ANC, and total P than lakes with fish
31 Hg concentrations below 0.3 $\mu\text{g/g}$ (Driscoll et al., 2007). Based on the probability surveys they
32 further report that 20% of lakes in the region had total P concentrations above 30 $\mu\text{g/L}$ and

1 yellow perch Hg concentrations below 0.3 µg/g. In the remaining 80% of lakes, 75% had yellow
2 perch Hg concentrations exceeding 0.3 µg/g when surface water DOC levels exceeded 4.0 mg
3 C/L, a pH of less than 6.0, or an ANC of less than 100 µeq/L.

4 Most Hg in the water column of fresh waters is bound to organic matter, either to DOC or
5 to suspended particulate matter. Therefore, total Hg and MeHg concentrations are often
6 positively correlated with DOC in lake waters (Mierle and Ingram, 1991; Driscoll et al., 1994;
7 U.S. Environmental Protection Agency, 1997). DOC, in turn, has an important influence on pH.
8 Thus, several interrelated factors also seem to be related to Hg contamination. For example,
9 Driscoll et al. (1995) found one or more yellow perch exceeding the 0.5 µg/g action level in
10 14 of 16 Adirondack study lakes despite wide ranges in pH (to above 7) and ANC (to above
11 200 (Mierle, 1990) µeq/L).

12 Driscoll et al. (1994) concluded that the dominant factor regulating the concentration and
13 availability of both total Hg and MeHg in Adirondack lakes is DOC. They found increased fish
14 Hg concentrations with increasing DOC up to DOC concentrations of about 8 mg/L, followed by
15 lower concentrations in the highly dystrophic Rock Pond (DOC = 26 mg/L). They hypothesized
16 that DOC may bind with MeHg at very high DOC concentration, limiting the bioavailability of
17 the Hg.

18 In addition, calculations made by Driscoll et al. (1995) with the Mercury Cycling Model
19 suggested that increases in DOC result in increasing concentrations of Hg in biota but decreases
20 in the bioconcentration factor of Hg in fish tissue. Because the transport of Hg to Adirondack
21 lakes appeared to be linked to DOC production from wetlands within the watersheds of the study
22 lakes, Driscoll et al. (1995) concluded that DOC is important in regulating Hg concentrations in
23 the lakes, and ultimately the supply to fish.

24 Several researchers have suggested that the export of Hg from terrestrial watersheds to
25 lakes may be controlled in large part by the nature of watershed soils and the movement of
26 naturally occurring organic acids (Mierle, 1990; Meili, 1991; Mierle and Ingram, 1991;
27 Engstrom et al., 1994). This suggestion is based partly on the fact that dissolved organic matter
28 strongly complexes (binds with) Hg, and partly on the observed positive correlation between Hg
29 accumulation in lake sediments and the ratio of watershed area to lake area in relatively
30 undisturbed watersheds ($r^2 = 0.91$) ($r^2 = 0.91$; Engstrom et al., 1994). Engstrom et al. (1994)
31 concluded that Hg export from the terrestrial watershed to lake water may be explained by

1 factors regulating the export of fulvic and humic matter and by watershed area. They based this
2 conclusion on the close correlation between Hg concentration and humic matter in surface
3 waters, the observation that peak concentrations of both Hg and dissolved organic matter tend to
4 occur during periods of high runoff, and the experimental determination that Hg transport occurs
5 primarily in upper soil horizons.

6 In a recent study of biological Hg hotspots in the northeastern United States and
7 southeastern Canada, Evers et al. (2007) analyzed more than 7,300 observations of Hg levels in
8 seven species in three major taxonomic groups to quantify the spatial heterogeneity in tissue Hg
9 concentrations. Using published effect thresholds for Hg tissue concentrations, they identified
10 five known and nine possible biological Hg hotspots. They reported that two of the biological
11 hotspots, located in the Adirondack Mountains of New York and south-central Nova Scotia,
12 occur in areas with relatively low to moderate atmospheric Hg deposition and high landscape
13 sensitivity, as determined by the abundant forest and wetland cover as well as the acidic surface
14 water conditions (Evers et al., 2007).

15 16 17 **AX6.3 NON-ACIDIFICATION BIOLOGICAL EFFECTS OF EXCESS** 18 **SULFUR DEPOSITION**

19 20 **AX6.3.1 Effects on Wildlife and Humans**

21 A variety of biological effects can result from S deposition, in addition to the
22 acidification effects discussed in Annex 4. In particular, the enhanced methylation (and
23 consequent enhanced bioavailability) of Hg that occurs in response to S addition can have
24 adverse effects on fish and on species that consume large quantities of fish. Methylmercury is a
25 potent neurotoxin to piscivorous species (Scheuhammer et al., 2007), and bioaccumulates at
26 higher trophic levels. Piscivorous birds generally have higher tissue Hg concentrations than non-
27 piscivorous birds (Boening, 2000). Enhanced bioavailability of Hg poses a public health risk to
28 people who consume fish.

29 A range of effects has been demonstrated, including behavioral, reproductive,
30 neurochemical, and hormonal effects (Scheuhammer et al., 2007). Exposure of fish and wildlife
31 to Hg occurs primarily through diet. Top predatory, especially piscivorous, animals feeding on
32 aquatic food chains are at greatest risk for Hg accumulation and toxicity (Scheuhammer et al.,

1 2007). Wildlife living in inland lake habitats tend to accumulate higher tissue concentrations of
2 Hg than those living in coastal habitats (Frederick et al., 2002; Evers et al., 2005).

3 Methylmercury exposure can affect growth, reproductive ability, morphological
4 characteristics, and feeding efficiency in fish. Friedman et al. (1996) investigated the effects of
5 low-level (0.137 µg Hg/g) and high-level (0.987 µg Hg/g) dietary Hg concentrations (as MeHg)
6 on hatchery juvenile walleye (*Stizostedion vitreum*). These experimental Hg exposures were
7 chosen to reflect dietary Hg concentrations commonly encountered in North American lakes and
8 streams. Results showed impaired fish growth and impaired gonad development in males.

9 Fjeld et al. (1998) exposed grayling (*Thymallus thymallus*) embryos to varying
10 concentrations of methylmercury (0.16, 0.8, 4.0, and 20 µg Hg/L) during their first 10 days of
11 development. This exposure resulted in body tissue MeHg concentrations of 0.09, 0.27, 0.63,
12 and 3.80 µg Hg/g respectively. Morphological deformities were observed in fish exposed to the
13 highest level of MeHg. Samson and Shenker (2000) also observed morphological disturbance in
14 zebrafish (*Danio rerio*) at embryonic methylmercury exposure levels of 20 and 30 µg
15 CH₃HgCl/L. Other fish such as mummichog (*Fundulus heteroclitus*) and rainbow trout
16 (*Oncorhynchus mykiss*) have also been observed to have teratogenic effects such as cyclopia, tail
17 flexures, cardiac malformations, jaw deformities, twinning, and axial coiling from embryonic
18 MeHg exposure (Samson and Shenker, 2000).

19 Fish survival and subsequent population status can be jeopardized as a result of exposure
20 to MeHg. Fathead minnows (*Pimephales promelas*) showed impaired feeding efficiency after
21 exposure to both 6.79 and 13.57 µg HgCl₂/L (Grippio and Heath, 2003). Reduced feeding
22 efficiency and competitive ability was also observed in grayling exposed to 0.8 to 20 µg Hg/L as
23 embryos (Fjeld et al., 1998).

24 Sulfur deposition is most likely to result in enhanced Hg methylation in regions that
25 receive relatively high levels of atmospheric Hg and S deposition and that exhibit characteristics
26 conducive to methylation. These include low alkalinity and low pH surface waters, with large
27 upstream or adjoining wetlands (Scheuhammer and Blancher, 1994; Wiener et al., 2003; Chen
28 et al., 2005; Scheuhammer et al., 2007). Such sensitive ecosystems are prevalent in portions of
29 the northeastern United States and southeastern Canada. Studies of Hg concentration in feathers,
30 blood, and eggs of the common loon (*Gavia immer*) indicate decreasing concentrations from
31 west to east in this region (Evers et al., 1998, 2003). This pattern is in general agreement with

1 patterns of deposition of both Hg and S. Available data suggest that numerous wild populations
2 of fish, birds, and mammals experience MeHg exposures that are high enough to cause
3 substantial reproductive, behavioral or health impairment. Reproduction is the component of
4 response that appears to be most affected (Scheuhammer et al., 2007).

6 **AX6.3.2 Effects on Plants**

7 Sulfur is a major component of plant proteins and, as such, is an essential plant nutrient.
8 Sulfur plays a critical role in agriculture, and is an essential component of fertilizers used to
9 increase food production (Ceccotti and Messick, 1997). It is particularly important for plants
10 growing in S-deficient soil (Hogan et al., 1998). The most important source of S to vegetation is
11 SO_4^{2-} , which is taken up from the soil by plant roots (Marschner, 1995). There are few field
12 demonstrations of foliar SO_4^{2-} uptake (Krupa and Legge, 1986, 1998; U.S. Environmental
13 Protection Agency, 2004). Rather, SO_4^{2-} in throughfall is often enriched above levels in
14 precipitation. The relative importance of the contribution of foliar leachate versus prior dry-
15 deposited SO_4^{2-} particles to this enrichment is difficult to quantify (Cape et al., 1992). The
16 major factor controlling the movement of S from the soil into vegetation is the rate of release
17 through microbial decomposition of S from organic to inorganic forms (May et al., 1972; U.S.
18 Environmental Protection Agency, 1982, 1993; Marschner, 1995). Current levels of S deposition
19 throughout much of the United States exceed the capacity of most plant communities to
20 immobilize the deposited S (Johnson, 1984; Lindberg, 1992).

21 With the discovery of S deficiencies in some unpolluted regions (Kelly and Lambert,
22 1972; Humphreys et al., 1975; Turner et al., 1977; Schnug, 1997) and excesses associated with
23 acidic deposition in other regions (Shriner and Henderson, 1978; Meiwes and Khanna, 1981;
24 Johnson et al., 1982a), interest in S nutrition and cycling in forests has heightened (U.S.
25 Environmental Protection Agency, 2004). General reviews of S cycling in forests were written
26 by Turner and Lambert (1980), Johnson (1984), Mitchell et al. (1992a,b), and Hogan et al.
27 (1998). The influence of atmospheric deposition on the S cycle was summarized by Johnson and
28 Mitchell (1998).

29 A certain level of foliar SO_4^{2-} is necessary for adequate plant S nutrition (Johnson and
30 Mitchell, 1998; Marschner, 1995), and S deficiency has been shown to occur at foliar SO_4^{2-}
31 levels below 80 $\mu\text{g/g}$ (Turner and Lambert, 1980). Nevertheless, the annual increment of S in

1 vegetation is usually small compared to atmospheric deposition and leaching fluxes. Plants
2 require similar levels of S and P, but S is generally available in much higher concentrations in
3 soil. Storage of S in vegetation is of minor significance in the retention or loss of S in most
4 forests (Mitchell et al., 1992a,b; Johnson and Mitchell, 1998).

5 The availability of S to plants is limited by its solubility in water. Sulfur deficiency in
6 forest soil is rare, but has been reported in remote areas that receive very low levels of
7 atmospheric S deposition and that have inherently low S levels in soil (Turner et al., 1977, 1991).
8 In such cases, atmospheric S deposition might be taken up by vegetation, with little SO_4^{2-}
9 leaching. Within areas of the United States influenced by acidic deposition, this is not expected
10 to be a common phenomenon. To some extent, plant uptake of S is determined by the
11 availability of N. This is because most S in plant tissue is in protein form, with a specific S:N
12 ratio (Turner et al., 1977, 1991; Johnson et al., 1982b).

13 Sulfur deposition can also have direct effects on plants via nutrient enrichment pathways.
14 Sulfur is an essential nutrient for protein synthesis in plants. Adequate S supply for sustaining
15 plant health is 0.01% to 0.05% in soils (Nriagu, 1978). Sulfate is the dominant form of
16 bioavailable S in soils. Plants can also utilize volatile S compounds such as SO_2 in the
17 atmosphere to fulfill nutrient requirements (Rennenberg, 1984). This S is directly available for
18 diffusive uptake through the leaf surface to support plant growth (Jager and Klein, 1980), and
19 can also become bioavailable in the soil for plant root uptake (Moss, 1978). However, excess
20 S inputs via atmospheric deposition can be toxic to plants and result in delayed flowering,
21 reduced growth, and mortality (Smith, 1981; Rennenberg, 1984; Roelofs, 1991; Smolders and
22 Roelofs, 1996). Plants that have exhibited reduced growth due to S toxicity have also been
23 observed to have reduced molybdenum (Mo) uptake and increased copper (Cu), manganese
24 (Mn), and zinc (Zn) uptake (Gupta and Munro, 1969; Gupta and Mehla, 1980). The threshold
25 level of S toxicity is variable among species (Mudd and Kozlowski, 1975).

26 Koch et al. (1990) found that hypoxia and high levels of sulfide (>1 mM) limited wetland
27 plant growth by inhibiting nutrient uptake. Sulfide toxicity to plants (e.g., *Carex* spp. *Juncus*
28 *acutiflorus*, *Galium palustre*, *Gramineae*) has also been observed in wetland mesocosm
29 experimentally enriched with SO_4^{2-} (Lamers et al., 1998). Biomass regrowth was significantly
30 reduced for these species for both 2 and 4 mmol/L SO_4^{2-} treatments (Lamers et al., 1998).
31 Van der Welle (2007) also showed that increased SO_4^{2-} loading had negative effects on aquatic

1 macrophytes (*Stratiotes aloides* and *Elodea nuttallii*), via sulfide toxicity. Though *S. aloides* was
2 native to the study region (The Netherlands) of Van der Welle et al. (2007), it is considered a
3 noxious invasive plant in the United States. However, *E. nuttallii* is native to the United States,
4 widely distributed across 33 states, and is considered threatened in Kentucky and a species of
5 concern in Tennessee (<http://plants.usda.gov/>, accessed 3/15/07). Negative impacts from
6 elevated rates of atmospherically deposited SO_4^{2-} on this species could be of concern. It is
7 important to note, however, that the SO_4^{2-} concentrations reported in these studies were much
8 higher than would generally be expected to occur in regions of the United States exposed to
9 elevated atmospheric S deposition.

10 Iron (Fe) concentrations can influence the level of sulfide toxicity in wetland sediments
11 (Smolders et al., 2001; Lamers et al., 2002). Free sulfide produced through SO_4^{2-} reduction is
12 able to bind with Fe, forming insoluble Fe sulfide (FeS). If sufficient Fe is present, this
13 complexation can reduce or eliminate sulfide toxicity to plants by removing the free sulfide from
14 solution. Van der Welle et al. (2007) confirmed the role of Fe in buffering against sulfide
15 toxicity to plants by observing no toxic effects when sufficient Fe was available to precipitate
16 free sulfide.

17 However, the formation of FeS can disrupt, or compete with, Fe phosphate (FePO_4)
18 complexation, resulting in P release and potential undesirable eutrophication effects on
19 downstream receiving waters (Caraco et al., 1989; Smolders et al., 2003). Iron(III)(hydr)oxides
20 and iron(III) phosphates are reduced in anaerobic soils and highly insoluble FeS is formed,
21 increasing phosphate (PO_4^{3-}) mobility and bioavailability in surface waters (Smolders et al.,
22 2006). This process has been termed ‘internal eutrophication’ since P is mobilized from within
23 the system and is not contributed from an external source (Roelofs, 1991). Increased nutrient
24 availability via SO_4^{2-} -induced P release from wetland sediments can result in changes in aquatic
25 vegetation community composition. Rooted aquatic macrophytes can be out-competed by non-
26 rooting floating species and filamentous algae (Smolders et al., 2003). If Fe is available in high
27 enough concentrations, it can prevent P release from saturated soils with high S loading by
28 providing adequate Fe to bind with sulfide without releasing P (Van Der Welle et al., 2007).

29 The observation that NO_3^- addition decreases P release in wetland enclosures provides
30 further indication that S-induced P release is related to redox conditions and microbial dynamics
31 in the soil profile (Lucassen et al., 2004). Sufficiently high NO_3^- concentrations can prevent

1 SO_4^{2-} reduction, and subsequent interruption of Fe-P binding, by maintaining redox status above
2 that suitable for SO_4^{2-} reduction (Lucassen et al., 2004). In the absence of a sufficient supply of
3 NO_3^- to act as a redox buffer, SO_4^{2-} will undergo reduction and potentially trigger the internal
4 eutrophication mechanism described above (Lucassen et al., 2004). It is important to note that
5 the majority of research on the topic of internal eutrophication of has occurred in Dutch
6 peatlands that have historically experienced much larger N loading than those in the United
7 States, making it difficult to extrapolate these findings to U.S. systems.

8

9 **AX6.3.3 Effects on Methane-Producing Microbes**

10 Increased atmospheric S deposition and its impacts on microbial community structure can
11 also affect methane (CH_4) emissions from saturated soils. Early investigation into the effects of
12 elevated pore water SO_4^{2-} concentrations on CH_4 emissions from wetland soils involved of the
13 application of a single large dose of SO_4^{2-} (Fowler et al., 1995). Methane production was
14 observed to be suppressed (40% less than the control) three weeks after the addition of SO_4^{2-} .
15 This was followed by a 4-week recovery period, after which CH_4 production had returned to pre-
16 treatment levels. These results led to the hypothesis that large single dose SO_4^{2-} addition, as
17 applied by Fowler (1995), only stimulate SRB activity for a short time. Fowler concluded that
18 studies that more closely approximated long-term SO_4^{2-} loading, as with atmospheric S
19 deposition, were necessary. Dise and Verry (2001) and Gauci et al. (2002) showed that smaller
20 and more numerous SO_4^{2-} additions sustained CH_4 emission suppression in wetland soils. These
21 studies more closely approximated SO_4^{2-} enrichment associated with acidic deposition. These
22 results provided support to the hypothesis that continuous elevated SO_4^{2-} deposition, as
23 encountered in areas affected by acidic deposition, contributes to sustained suppression of CH_4
24 emissions from wetland soils.

25 Gauci et al. (2004) considered both methods of SO_4^{2-} addition (a single large dose versus
26 numerous small doses) in the same experiment. Rates of SO_4^{2-} addition ranged between 15 and
27 100 kg S/ha/yr to wetland soils previously exposed to 4 kg S/ha/yr of atmospheric S deposition.
28 They observed that CH_4 emissions from these wetland soils were almost equally suppressed
29 under each treatment, and that each treatment experienced the same CH_4 emission “recovery” as
30 found in the single-dose Fowler et al. (1995) study. The two main conclusions from Gauci et al.
31 (2004) were that 15 kg S/ha/yr is either at or above the rate of S deposition required to achieve

1 maximum CH₄ emission suppression, and that a single large dose of S has similar effects on CH₄
2 emission suppression as do numerous smaller doses. The authors observed that CH₄ emissions
3 from treated soils recovered to those observed from untreated soils during the period of plant
4 senescence. This led to the hypothesis that SRB will out-compete CH₄ producing bacteria under
5 conditions of elevated S deposition and during vigorous plant growth when available C substrate
6 is limited, but that root exudates and root degradation during the period of plant senescence
7 provides adequate substrate to sustain both methanogenic and SRB bacteria populations.
8 Although the suppression of CH₄ emissions can fluctuate based upon plant growth cycles,
9 elevated S deposition is considered to shift microbial community structure in favor of SRB over
10 methanogenic bacteria, reducing annual CH₄ emissions from saturated soils (Granberg et al.,
11 2001). However, climate change simulations suggest that increased soil temperature may
12 override the suppressive effect that elevated S deposition has on CH₄ emissions (Granberg et al.,
13 2001; Gauci et al., 2004).

14
15

16 **AX6.4 SUMMARY**

17 The most important non-acidification effects of S deposition in areas of the United States
18 that receive high levels of S deposition derive from the influence of S supply on Hg methylation.
19 The extent of methylation governs the bioavailability of Hg to biota. High concentrations of
20 MeHg in fish can constitute an important health concern for people who consume large
21 quantities of fish and can affect the health and reproduction of piscivorous wildlife, including the
22 common loon, bald eagle (*Haliaeetus leucocephalus*), and river otter (*Lutra canadensis*).
23 Mercury methylation occurs mostly in wetland soils and bottom sediments of lakes and ponds.
24 Sulfur deposition to these ecosystems can enhance S reduction and Hg methylation processes.
25 Although S can also be directly toxic to terrestrial vegetation, levels of S in ambient air pollution
26 and levels of S deposition commonly found in the United States are generally not high enough to
27 cause substantial direct adverse effects on plants.

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1 **AX7. MODIFYING EFFECTS OF CLIMATE FACTORS**
2 **ON ECOSYSTEM RESPONSES TO**
3 **NITROGEN DEPOSITION**

4
5
6 **AX7.1 INTRODUCTION**

7 Climate is a key factor influencing ecological processes. Simply defined, climate is the
8 “average weather.” More rigorously defined, climate is a statistical description of quantities that
9 include Earth’s surface variables such as temperature, precipitation, and wind over a period of
10 time ranging from months to thousands or millions of years (IPCC, 2007a). As discussed in
11 detail in the recent report from the Intergovernmental Panel on Climate Change (IPCC, 2007b),
12 the anthropogenic input of greenhouse gases (GHGs) into the atmosphere is currently forcing
13 global climate change by trapping infrared radiation. This annex assesses how climate,
14 specifically temperature and precipitation, influences ecosystem responses to nitrogen (N)
15 deposition, and supports information presented in the Integrated Science Assessment (ISA)
16 chapters 1, 2, and 4. It is important to note that the research reviewed here is limited to
17 ecosystem effects and does not address how climate influences the atmospheric production,
18 transport, and deposition of NO_x, nor does this annex attempt to conduct an independent
19 assessment of anthropogenic climate change. As noted above, such an evaluation has been
20 recently published by the IPCC (2007b).

21
22
23 **AX7.2 ECOSYSTEM RESPONSES**

24 This section focuses on the relationship between climate factors and several selected
25 topics: (1) the response of biogenic nitrous oxide (N₂O) production to N deposition, (2) effects
26 on N export from large watersheds in the northeastern United States, and (3) interactions
27 between climate and N deposition effects on terrestrial carbon (C) cycling. These brief
28 discussions provide illustrative examples of the influence of climate on N-related effects. In
29 addition, the climate factors discussed here are primarily temperature and precipitation, as these
30 are the factors most commonly evaluated in the ecological literature.

1 **AX7.2.1 Effects of Nitrogen Deposition, Temperature, and Precipitation on** 2 **Biogenic N₂O Production in Terrestrial Ecosystems**

3 This section addresses the effects of temperature and precipitation on ecosystem
4 microbial processes that cause N₂O efflux from ecosystems to the atmosphere, also called
5 biogenic emissions. It is important to understand these interactions because N₂O is a GHG with
6 an atmospheric lifetime of approximately 114 years. N₂O is about 310 times more effective in
7 trapping heat in the atmosphere than CO₂ over a 100-year period (Forster et al., 2007). Global
8 average atmospheric concentrations of N₂O have increased approximately 16% over the last
9 250 years and the rate of increase has been 0.25% per year during the last two decades. There
10 has been significant multiyear variance in the observed growth of N₂O concentrations; the
11 reasons for these trends are not yet fully understood (IPCC, 2001).

12 N₂O emissions from anthropogenic activities in the United States were 468.6 Tg CO₂
13 equivalent yr⁻¹ in 2005 (U.S. Environmental Protection Agency, 2007). These emissions are the
14 result of combustion, industrial practices, and stimulation of biogenic sources (see Annex 2).
15 Biogenic N₂O emissions account for >76% of U.S. emissions and are produced through the
16 microbial processes of denitrification and nitrification in soils (see discussion below).
17 Biogenic N₂O emissions can be increased by agricultural activities, including the use of
18 synthetic and organic fertilizers, production of N-fixing crops, cultivation of high organic content
19 soils, and the application of livestock manure to croplands and pasture. N₂O emissions from
20 agricultural and nonagricultural systems may also be increased by N deposition from the air,
21 such as that originating from NO_x and NH_x (U.S. Environmental Protection Agency, 2007).

22 Biogenic N₂O emission predominately results from incomplete bacterial denitrification
23 and nitrification processes that occur in soil, sediment, and water (Figure AX7.2-1 summarizes
24 these processes). Denitrification is a reduction process performed by particular groups of
25 heterotrophic bacteria that have the ability to use nitrate (NO₃⁻) as an electron acceptor during
26 anaerobic respiration, thereby converting NO₃⁻ in soils and water to gaseous forms (Firestone
27 and Davidson, 1989). At low oxygen (O₂) concentrations, these microbial communities may
28 use nitrate (NO₃⁻), nitrite (NO₂⁻), or N₂O as alternative electron acceptors to O₂, with
29 molecular N₂ as the final product, given by the following reaction sequence: NO₃⁻ → NO₂⁻ →
30 NO → N₂O → N₂ (Davidson and Schimel, 1995). Uncertainty remains about the conditions
31 favoring the various products of the NO₃⁻ transformations. Groups of aerobic bacteria use

Denitrification: $\text{NO}_3^- \rightarrow \text{N}_2$ (gas) (N_2O intermediate product of incomplete reaction)

- General conditions that increase denitrification:
 - Low O_2
 - Flooded, anoxic soils
 - Well-drained soils with low O diffusion
 - Rainfall because O diffuses slower in wet soils
- Controls on ratios of gases are poorly understood but include
 - Soil pH
 - Relative abundance of NO_3^- and oxygen as oxidants and C as reductant
 - Acetylene may block the conversion of N_2O to N_2
 - When NO_3^- is abundant relative to C more N_2O is produced
 - Occurs in almost all types of ecosystems
 - Terrestrial
 - Freshwater
 - Coastal
 - Some oceanic ecosystems

Nitrification: oxidization of $\text{NH}_4^+ \rightarrow \text{NO}_3^-$

- Conditions that increase nitrification:
 - Higher O_2
 - C/N ratio (stimulated below ratio of 25)
 - Higher temperatures (77-86 °F)
- Causes acidity in soils

Figure AX7.2-1. Summary of denitrification and nitrification.

1 ammonium (NH_4^+) in soils as an energy source in which NH_4^+ is oxidized to NO_2^- and then
2 NO_3^- . Oxidized N products of nitrification may undergo denitrification and thus feed the
3 production of N_2O . Some bacteria are known to be nitrifiers and denitrifiers, depending on the
4 environmental conditions.

5

6 **AX7.2.1.1 NO_x Effects on Biogenic N_2O Emissions from Terrestrial Ecosystems**

7

8 ***Terrestrial Ecosystems***

9

10 Human activities can significantly enhance the natural processes that lead to N_2O
11 formation. Numerous studies show that N_2O emissions from soils increase with N additions
12 (Brumme and Beese, 1992; Matson et al., 1992; Klemmedtsson et al., 1997; Papen et al., 2001).
13 Regions with elevated atmospheric N deposition due to anthropogenic activity also show
14 increased N_2O emissions (Butterbach-Bahl et al., 1998, 2002). For example, Ambus and
Robertson (2006) investigated study sites located in southwest Michigan consisting of old

1 growth deciduous forest (40 to 60 years old), coniferous forest, and grassland ecosystems that
2 they stimulated by introducing an additional 1 to 3 g N m⁻² yr⁻¹ (0.84 g N m⁻² yr⁻¹ ambient).
3 They compared the field results to a second experiment conducted in a laboratory setting that
4 simulated the field conditions. The results indicated no change in N₂O emissions for the conifer
5 forest and grassland ecosystems. The deciduous forest that was studied showed increased N
6 mineralization, suggesting the system was approaching N saturation. The additional laboratory
7 study showed a significant and positive relationship between N deposition and N₂O efflux with
8 N additions up to 10 g m⁻² in both coniferous and deciduous forests (Ambus and Robertson,
9 2006). Investigation of N₂O emissions from a 145-year-old European beech stand in Stollig,
10 Germany, that compared ambient N deposition (35 kg N ha⁻¹ yr⁻¹) to elevated N deposition
11 (145 kg N ha⁻¹ yr⁻¹) indicated that elevated N deposition stimulated annual N₂O emissions
12 (5.6 to 7.8 kg N ha⁻¹ yr⁻¹, respectively) (Brumme and Beese, 1992). Investigation of sites with
13 similar species composition and climate across Europe yet differing rates of wet N deposition
14 (measured as NH₄⁺) showed a significant and positive correlation between increasing N
15 deposition and increasing N₂O flux ($f(x) = 4.7 + 1.4x$, $r^2 = 0.38$, $p < 0.001$) (Butterbach-Bahl
16 et al., 1998).

17 Other studies have shown that N deposition causes ecosystems to switch from a sink to a
18 source of biogenic N₂O. For example, a study of a mixed spruce, fir, and pine stand (85 to
19 125 years old) in Germany showed that the ecosystem was a sink in 7 out of 9 sampling dates
20 under ambient N deposition (10 kg N ha⁻¹ yr⁻¹). However, the ecosystem functioned as a source
21 6 out of 9 sampling dates under elevated N deposition (150 kg N ha⁻¹ yr⁻¹). This switch in
22 ecosystem function from sink to source was attributed to a stimulation of nitrification rather than
23 denitrification (Papen et al., 2001).

24 25 ***Soil Moisture and Rainfall***

26 Soil moisture and rainfall are connected because soil moisture will increase in response to
27 a rainfall event. Soil moisture plays an important role in affecting N₂O production. A study of
28 mixed spruce, pine, and birch forest in Sweden (100 years old) compared N₂O efflux from well
29 and poorly drained soil moisture conditions. The results indicated poorly drained soils produced
30 1/3 more N₂O (118 g N₂O-N ha⁻¹ yr⁻¹). When N deposition was increased from ambient (12 kg

1 N ha⁻¹ yr⁻¹) to elevated (42 kg N ha⁻¹ yr⁻¹), N₂O emissions increased by a factor of more than 2
2 (254 kg N ha⁻¹ yr⁻¹) (Klemedtsson et al., 1997).

3 Rainfall events are important in controlling N₂O produced via denitrification. Rainfall
4 inhibits oxygen diffusion into the soil, creating an anoxic condition, which increases rates of
5 denitrification. A study of a spruce forest under ambient and elevated N deposition (20 and
6 30 kg N ha⁻¹ yr⁻¹, respectively) revealed that through most of the study period N₂O emission was
7 equivalent between the ambient and elevated plots (Mohn et al., 2000). However, after rainfall
8 events, the maximum rate of N₂O emission was much higher for the elevated N plots, especially
9 when rainfall caused low soil redox potential (an indicator of anoxic conditions).

10 Pore space in soils is another characteristic that is related to rainfall and soil moisture.
11 When water occupies pore space, the amount of oxygen available to microbes decreases.
12 Optimum conditions for N₂O production are 60 to 80% water-filled pore space (WFPS), however
13 further increasing WFPS causes N₂ to be the main product of denitrification and N₂O emissions
14 go down (Davidson 1991).

15

16 ***Modeling Ecosystem Response under Temperature and Precipitation Variations***

17 The PnET-N-DNDC (Photosynthesis-Evapotranspiration coupled with the
18 Denitrification-Decomposition model) model is designed to simulate and predict soil carbon and
19 N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N₂O and NO
20 from forest soils. The model couples the PnET (Photosynthesis-EvapoTranspiration) model, the
21 DNDC (Denitrification-Decomposition) model, and a nitrogen module described in Li et al.
22 (1992, 1996, 2000), Li (2000), and Stange et al. (2000). The capacity of this model to simulate
23 N trace gas emissions from forest soils was tested by comparing model results with results from
24 field measurements at 19 different field sites across Europe and 1 site in the United States (Kesik
25 et al., 2005). Denitrification is described in the model as a series of sequential reductions driven
26 by microorganisms using N oxides as electron acceptors under anaerobic conditions. NO and
27 N₂O are intermediates of denitrification and, therefore, are tightly controlled by the kinetics of
28 each step in the sequential reactions.

29 The effects of temperature and precipitation change on forest soil NO and N₂O emissions
30 in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006). Climate over the period
31 of 1991 to 2000, characterized by a mean annual temperature (MAT) of 7.4 °C, is used as a

1 baseline from which to compare how increasing temperature to a MAT of 9.8 °C affects other
2 climatic factors and NO and N₂O emissions. The model parameters are summarized in Table
3 AX7.2-1 and the results are summarized in AX7.2-2. In areas with light texture soils (below
4 15%), decreasing precipitation and increasing temperature resulted in decreased soil moisture
5 values, in turn, soil aeration increased and N₂O production by denitrification decreased. Under
6 these same environmental conditions, NO production by nitrification increased.

7 8 **AX7.2.2 Interactions between Nitrogen Export from Large Watersheds in** 9 **the Northeast and Climate Factors**

10 Large inputs of N cause eutrophication in coastal marine ecosystems, resulting in lower
11 biodiversity, hypoxic and anoxic conditions, harmful algal blooms, degradation of sea grass
12 beds, and alterations in ecologic food webs that reduce fish and shellfish production (NRC, 2000;
13 see discussion in Annex 5). Eutrophication is now considered the biggest pollution problem in
14 the coastal waters of the United States (Howarth et al., 2000; NRC, 2000). The EPA Coastal
15 Condition Report (U.S. Environmental Protection Agency, 2001) lists eutrophication as one of
16 the greatest threats to the health of the nation's estuaries. Eutrophication has severely degraded
17 approximately 40% of the estuarine area in the United States (Bricker et al., 1999; U.S.
18 Environmental Protection Agency, 2007). The flux of nitrogen in large rivers in North America
19 and Europe is well explained as a function of the net anthropogenic inputs of nitrogen to the
20 landscape, with on average 20 to 25% of these inputs exported in rivers and 75 to 80% of the
21 nitrogen retained or denitrified in the landscape (Howarth et al., 1996, 2002; Boyer et al., 2002).

22 Recently Howarth et al. (2006) addressed how climate affects the amount of N
23 discharged through rivers by examining 16 watersheds from Maine to Virginia during the time
24 interval of 1988 to 1993. Watershed areas upriver of U.S. Geological Survey (USGS)
25 monitoring stations were used for this analysis and generally did not include heavily urbanized
26 coastal cities (e.g., Boston, New York, Philadelphia, Baltimore). Net anthropogenic nitrogen
27 inputs (NANI) were determined for each watershed by calculating the sum of fertilizer use,
28 nitrogen fixation in agro-ecosystems, the net import of nitrogen in human food and animal feed
29 and the atmospheric deposition of oxidized nitrogen (NO_y). It is important to note that the
30 deposition of ammonia (NH₃) and NH₄⁺ is not considered an input in this approach, as the
31 majority deposited in a watershed is assumed to have originated from emissions within the same
32 watershed. The 16 watersheds range in size from 475 km² (Charles River basin) to over

1 70,000 km² (Susquehanna). Nitrogen inputs from anthropogenic sources ranged from 310 to
2 1760 N km⁻² yr⁻¹ (see Table AX7.2-3). Inputs of NO_y ranged from 360 to 890 kg N km⁻² yr⁻¹
3 and constituted 16 to 70% of the anthropogenic N input with an average input of 34%. Results
4 from Howarth et al. (1996) in which analysis included urbanized areas in the northeastern United
5 States are also listed in Table AX7.2-3 for comparison and illustrate the important contribution
6 made by urban areas to NO_y load in ecosystems. Analysis using their reported data indicated the
7 contribution of NO_y decreases as total anthropogenic N increased (Figure AX7.2-2). Riverine
8 exports of anthropogenic N from the watersheds were calculated to be 26% of input, an amount
9 that is consistent with previous findings (Howarth 1996, 2002b; Boyer 2002) and equates to 145
10 to 1372 kg N km⁻² yr⁻¹.

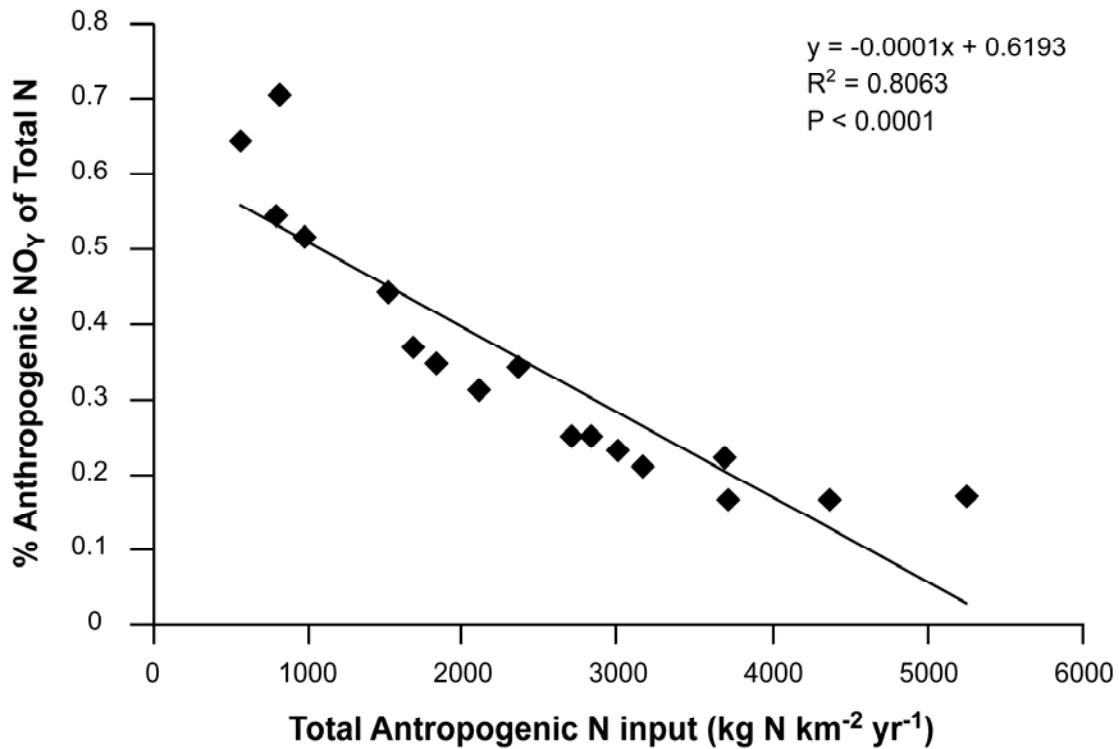


Figure AX7.2-2. Inverse relationship between total anthropogenic N and NO_y fraction of total anthropogenic N.

Source: Calculated from data presented in Howarth et al. (2006).

1 After establishing the baseline N exports from the rivers, the influence of climate factors
2 on anthropogenic N export was calculated (Howarth et al., 2006). Export was well correlated
3 with both precipitation ($R^2 = 0.53$; $p = 0.0015$) and discharge ($R^2 = 0.48$; $p = 0.003$). These
4 factors were also correlated to each other. The results indicate that watersheds with greater
5 precipitation generally have higher discharge and thus result in greater export of
6 anthropogenic N.

7 Interacting-term linear regressions were the best parameterized relationship for the effects
8 of climate on riverine N flux. The equations that best fit the data accounted for high levels of
9 variance ($R^2 = 0.87$ to 0.90) and calculated precipitation and rivine discharge (Q) as a linear and
10 exponential function, the latter suggesting N-saturation conditions at the highest levels of flux
11 where N exported from the landscape may increase disproportionately to nitrogen loading
12 (relationships for calculated riverine discharge shown in Figure AX7.2-3, those for precipitation
13 are not shown).

14 Among the climate parameters tested, precipitation and discharge were more significant
15 than temperature. Therefore, the authors suggested that within the MAT range they studied (~ 4
16 to 12°C), precipitation was the most dominant climate effect, causing less denitrification in
17 watersheds that experienced greater precipitation and discharge. They noted that was likely due
18 to faster flushing of water through riparian wetlands and low-order streams, diminishing the
19 chance of denitrification.

20 The relationships between anthropogenic N export and climate factors that were
21 parameterized by the interacting-term models were then used to estimate how variations in
22 climate affect riverine nitrogen fluxes. The climate scenario that was used is based on
23 precipitation and riverine discharge under climate warming and was modeled by the Canadian
24 Climate Center and the Hadley Center (Najjar et al., 2000). The Susquehanna River basin was
25 selected for this analysis, because the scenario of precipitation does not exceed the range
26 recorded for the 16 watersheds used to parameterize the applied equations. The authors noted
27 this second criteria is critical, because their data suggested that when precipitation is less than
28 800 mm yr^{-1} or greater than 1300 mm yr^{-1} the effects on N export are undoubtedly not linear.
29 Mean increases of precipitation and discharge of +4% and +2% for 2030 and +15% and +11%
30 for 2095 are calculated. These future scenarios applied to the models result in mean increases in
31 N export based on precipitation and discharge of +3% and +17% for 2003 and +16% and 65%

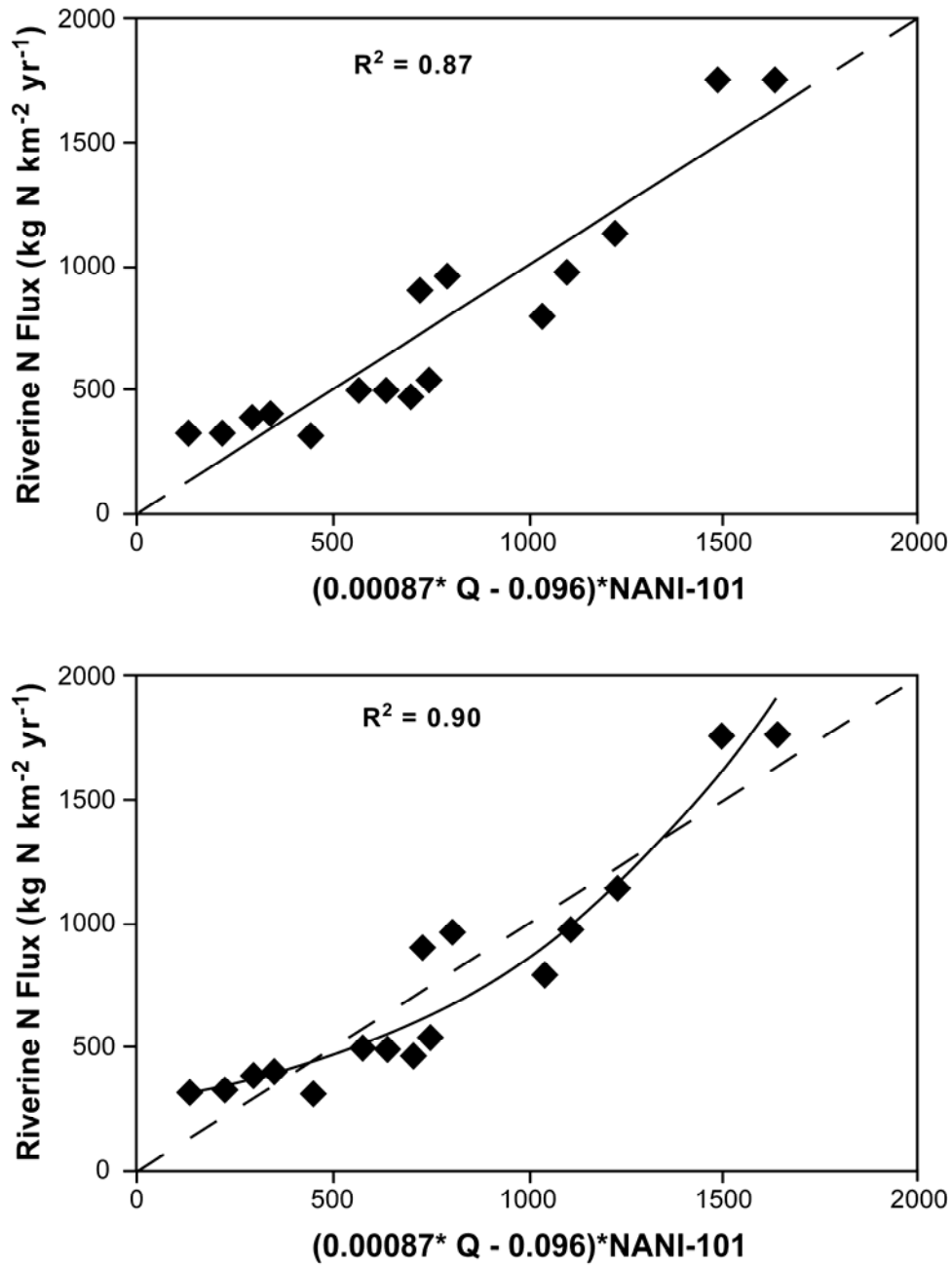


Figure AX7.2-3. Graphs from Howarth et al. (2006) show the (a) linear relationship between calculated riverine discharge and N flux and (b) exponential relationship between calculated riverine discharge and N flux. The latter relationship suggesting N saturation of ecosystems.

Source: Howarth et al. (2006).

1 for 2095. These estimates did not consider that increased precipitation may result in increased N
2 deposition.

3
4 **AX7.2.3 Interactions between Terrestrial Carbon Cycling, Nitrogen**
5 **Deposition, and Climate Factors**

6 The following section discusses the mechanisms by which atmospheric N deposition
7 alters C cycling in terrestrial ecosystems, and how climate affects this relationship. C cycling is
8 a complex process that can be quantified into ecosystem C budgets on the basis of net ecosystem
9 productivity (NEP), defined as gross primary productivity (GPP) after subtracting the ecosystem
10 respiration (vegetative + heterotrophic respiration). Factors that may increase terrestrial CO₂
11 sinks on a regional scale are increased net primary productivity (NPP), and decreased respiration
12 of CO₂ from leaf or soil processes. These two mechanisms may be altered by atmospheric
13 deposition of N and factors associated with climate warming (Myneni et al., 1997; Melillo et al.,
14 2002). The discussion begins with the topic of above- and below-ground processes, and then the
15 scale of ecological processes increases to whole-forest patterns.

16
17 **AX7.2.3.1 Above-Ground Ecosystem Processes**

18
19 ***Plant Biomass and Productivity***

20 There is substantial evidence that N additions to plants cause increased leaf-level
21 photosynthetic rates. However, the potential for N deposition to cause ecosystem C biomass to
22 increase is limited for numerous reasons. First, trees only take up a small portion of N
23 deposition. A recent study using labeled ¹⁵N to trace the path of N amendments through
24 temperate forests indicates recoveries were highest in organic soil, ranging from 34 to 83%.
25 Mineral soil (0 to 20 cm in depth) was the second largest sink, with tracer recoveries ranging
26 from 15 to 34% of additions. Tree biomass (e.g., foliage, woody tissue, and fine roots)
27 accumulated 7 to 16% of tracer additions (Nadelhoffer et al., 2004). Nitrogen may be
28 immobilized in the soil, leached out before biologic assimilation, or, upon the addition of N,
29 some other factor may become limiting to growth (e.g., water or other nutrients). Only a small
30 portion of added N is taken up by vegetation, thus only a small portion of N contributes to C
31 capture by trees. Even though only a portion of N deposition is incorporated into vegetation, the
32 general result is an increase in leaves, wood, and root biomass (Nilsson and Wiklund, 1995).

1 However, N addition may also increase tree mortality, as illustrated by Harvard Forest Long-
2 Term Ecological Research (LTER) where 15 years of high N additions ($15 \text{ kg N m}^{-2} \text{ yr}^{-1}$) were
3 added to the forest floor and caused N saturation, characterized by high N-leaching rates and
4 increased tree mortality (Magill et al., 2004). As previously stated, the potential for elevated N
5 deposition to increase C sinks in woody biomass is limited, and the extent of the limitation is a
6 matter of ongoing debate (Jenkinson et al., 1999; Nadelhoffer et al., 1999, 2004; Sievering,
7 1999).

8

9 **AX7.2.3.2 Below-Ground Ecosystem Processes**

10 Soils contain the largest near-surface reservoir of terrestrial C; therefore, understanding
11 the factors that control soil C storage and turnover is essential for understanding the C cycle and
12 sequestration. There remains considerable uncertainty in the potential response of soil C to
13 increases in reactive N additions (Neff et al., 2002); however some of the general trends are
14 discussed below.

15

16 ***Root Biomass***

17 More than 50% of C captured annually by plants may be allocated below ground
18 (Kubiske and Godbold, 2001). Estimations from temperate forests of central Europe reveal that
19 the contribution of C from roots to the total below-ground C pool is about 42% but can vary
20 widely across ecosystems and latitudes, with typical averages ranging between 4 to 20%
21 (Brunner and Godbold, 2007). The relationship between N deposition and root production has
22 been the subject of debate. Nadelhoffer (2000) argues it is likely that N deposition functions to
23 decrease forest fine-root biomass but to stimulate fine-root turnover and production. However,
24 very high levels of N ($>100 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) decreased root life span of *Pinus ponderosa*
25 (Johnson et al., 2000).

26

27 ***Litter Fall, Decomposition, and Soil Respiration***

28 Above-ground biomass which falls to the forest floor is called litter fall and is usually the
29 dominant source of soil organic C. Once in the soil, the C is assimilated, leached, or respired. If
30 the soil stores more C than it emits, it is considered a C sink. Understanding the impact of
31 additional N on the soil C cycled is important to understanding the C sink strength of soils. The
32 N input to ecosystem by leaf litter is referred to as organic N and is not available for uptake by

1 vegetation. Nitrogen mineralization is the transformation via decomposition of organic N to
2 inorganic N, the latter of which is available for plant uptake. Decomposition is often facilitated
3 by heterotrophic bacteria and mycorrhizae. The quantity of litter has been shown to increase
4 with elevated N deposition (Schulze et al., 2000), with the result of increased microbial
5 metabolism in soil.

6 A 10-year experiment that investigated decomposition in 21 sites from 7 biomes found
7 net N release from leaf litter is predominantly driven by the initial N concentration and mass
8 regardless of climate, edaphic conditions, or biota (Parton et al., 2007). It is well demonstrated
9 that N availability alters the ratio of C:N in leaf tissue. In turn, lower C:N in leaf litter has been
10 shown to cause faster rates of decomposition (Melillo et al., 1982). A recent meta-analysis by
11 Knorr et al. (2005) indicated that, as expected, litter decomposition was stimulated by additional
12 N deposition, however only at sites with low ambient N deposition ($<5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$).
13 Additional N deposition reduced decomposition at sites with moderate levels of N deposition (5
14 to $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$).

15 Under higher decomposition rates, N is expected to be bound in leaf organic matter for
16 shorter periods and lead to lower N retention by the soil. De Vries (2006) confirmed this
17 relationship by analyzing data from 34 forest sites in Europe. The results showed N retention
18 was above 90% at soil C:N ratios of >30 to 35 (high C:N ratio) and retention was below 10% at
19 C:N ratios of <20 . This relationship occurred when N throughfall was considered the source of
20 N input and N output refers to nitrate only. Nitrogen retention was not tightly coupled to C:N
21 ratios when N deposition was the input and N leaching the output; however, the authors noted
22 the majority of sites in their analysis were characterized by low N input and low C:N (e.g., boreal
23 forests) that may exhibit higher N retention than other forests.

24 An investigation by Neff et al. (2002) of long-term effects (10 years) of N deposition
25 ($10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) in a dry meadow ecosystem indicated that nitrogen additions significantly
26 accelerated decomposition of soil C fractions with decadal turnover times while further
27 stabilizing soil C compounds in mineral-associated fractions with multi-decadal to century
28 lifetimes. Despite these changes in the dynamics of different soil pools, no significant changes
29 in bulk soil C were observed, highlighting a limitation of the single-pool approach for
30 investigating soil C responses to changing environmental conditions (Neff et al., 2002). The
31 authors noted that it remains to be seen if the effects that were caused by relatively high,

1 decadal-term fertilizer additions are similar to those which would arise from lower, longer-term
2 additions of nitrogen to natural ecosystems from atmospheric deposition.

3 Soil respiration is the dominant source by which plant-assimilated C is returned to the
4 atmosphere via CO₂. Changes in the magnitude of soil CO₂ efflux due to changes in
5 environmental conditions will likely influence the global atmospheric CO₂ budget (Schlesinger
6 and Andrews, 2000). Roots and heterotrophic bacteria are the two main sources of respiratory
7 CO₂ in the soil. The effects of N addition on soil respiration are mixed, including reductions at
8 high levels of N (Lu, 1998), no effect (Vose et al., 1995), and increases (Griffin et al., 1997;
9 Mikan et al., 2000) have been observed. In long-term experiments, both increases and decreases
10 of soil respiration have been observed in response to N additions. At the Harvard Forest LTER
11 Site Chronic Nitrogen Amendment Study, N additions to a red pine and mixed deciduous stand
12 resulted in initial increase in soil respiration. However, continued N additions over a decade
13 caused a 40% decrease in soil respiration that was attributed mostly to a decrease in microbial
14 respiration (Bowden et al., 2004).

15 16 **AX7.2.3.3 Interactions between Climate and Above- and Below-Ground Processes**

17 The following section is a brief discussion of climate effects on above- and below-ground
18 ecological processes that contribute to C cycling.

19 20 ***Above Ground***

21 22 ***Plant Biomass and Productivity***

23 As a single factor, temperature typically increases leaf-level photosynthetic and
24 respiration rates. In a review of 20 temperate and boreal forests, Magnani et al. (2007) noted that
25 ecosystem respiration and gross primary productivity increased with increasing temperature. In
26 contrast, a study of above-ground NPP in the Great Plains indicated that plant productivity
27 declined with increasing temperatures (Epstein et al. 2002). Piao et al. (2008) showed how
28 increasing temperatures were altering the phasing of seasonal cycles of CO₂ in the atmosphere
29 (the time when a region becomes a source or a sink of C) in 10 sites north of the 20 degree
30 northern latitude. Seasonal cycles of atmospheric CO₂ are caused primarily by the terrestrial
31 biosphere moving from being a net source of C in the atmosphere (mainly in the winter) to

1 becoming a net sink (mainly in the summer), where net C uptake or release is determined by the
2 balance between photosynthesis and respiration.

3
4 ***Below Ground***

5 A study of Great Plains ecosystems indicated that precipitation contributed more than
6 either temperature or soil texture to decomposition rates, explaining 30% of the variability
7 (Epstein et al., 2002). Decomposition rates increased with more precipitation and with
8 decreasing soil clay content, while temperature explained 8% of the regional variability. The
9 response of decomposition to temperature is probably constrained by moisture in this
10 water-limited region. Therefore, changes in decomposition rates resulting from temperature
11 dynamics are likely to be minimal unless they are accompanied by sufficient changes in
12 precipitation (Epstein et al., 2002). Based on a study of four Canadian forests, litter
13 decomposition was related to MAT and precipitation. The authors predicted decomposition rates
14 to increase by 4 to 7% following an increase in temperature and precipitation estimated from
15 future climate change scenarios (Moore et al., 1999). Lastly, as soils warm in response to
16 climate change, nutrient mineralization from soil organic matter is expected to increase,
17 especially in Arctic ecosystems (Hobbie, 1996).

18
19 **AX7.2.3.4 Climate Interactions with Ecosystem C Budgets**

20 A recent analysis of >100 young and mature forest stands from around the world
21 indicated that annual values of CO₂ exchange varied from approximately -100 to 250 g C m⁻²
22 yr⁻¹ for boreal forests and 250 to 700 g C m⁻² yr⁻¹ for temperate forests (Malhi et al., 1999). Net
23 ecosystem exchange (NEE) was positive when the forest was a sink taking up CO₂. Townsend
24 et al. (1996) and Holland et al. (1997) modeled the impact of NO_y and NH_x deposition on
25 ecosystem C budgets by combining estimates of emissions with three dimensional transport
26 models. They used spatially explicit estimates of N inputs and climate data as drivers for a
27 process-based biogeochemical model to simulate ecosystem C dynamics globally. Their
28 simulations predicted that CO₂-C uptake due to NO_y deposition on land surfaces ranged from 0.3
29 to 1.4 Pg C uptake yr⁻¹ (Townsend et al., 1996; Holland et al., 1997; Holland and Lamarque,
30 1997). The model allowed for variations in the degree of ecosystem nitrogen retention. The
31 highest C uptake was calculated when trees were assumed to uptake 80% of nitrogen inputs, a
32 likely overestimation (see section AX7.2.3.1).

1 The role that nitrogen deposition plays in determining sink strengths of forests for CO₂-C
2 depends on where N inputs to forest ultimately reside. If the majority of it is allocated to woody
3 tissues with high C:N ratios (200 to 500) and long turnover times, then the effects on nitrogen
4 deposition to C uptake are large. However, if nitrogen inputs are sequestered mainly in soils
5 with low C:N ratios (10 to 30), exported as nitrate in drainage water, or as N gas to the
6 atmosphere, then C storage is minor. The results of ¹⁵N-tracer studies on six European and three
7 American forests indicate that trees are not the primary sinks for nitrogen deposition
8 (Nadelhoffer et al., 1999): the mean uptake in wood was 3% of total N deposition. Typical
9 losses due to drainage were <10%; however, these losses were observed to reach as high as 33%.
10 The largest sink was in the soil (forest floor and mineral soil). Using these values for
11 calculation, they estimated that N deposition accounts for 0.25 Pg C uptake yr⁻¹ (Nadelhoffer
12 et al., 1999).

13 Modeling techniques that demonstrate the relationship between N deposition and the C
14 budget in forest ecosystems incorporate parameters of above- and below-ground processes based
15 on field measurements from a range of forested sites within a region, often with different species
16 compositions. The parameters incorporated into models by Nadelhoffer et al. (1999) and
17 De Vries et al. (2006) are:

- 18 1. N uptake of deposition by trees (5 to 10% of deposition),
- 19 2. N retention of deposition in soil (70 to 100%),
- 20 3. C:N ratio in wood (400 to 500), and
- 21 4. C:N ratio in soil (25 to 30).

22 De Vries et al. (2006) calculated the C sequestration due to additional N input of 2.8 kg ha⁻¹yr⁻¹
23 (from 1960 to 2000) across Europe using data from 121 monitoring stations to parameterize their
24 model. Their results indicated that additional N led to a 5.3% increase in tree C sequestration
25 (11 kg C kg N⁻¹) and 29% (15 kg C kg N⁻¹) increase in soil C sequestration. Total ecosystem C
26 sequestration increases by 10% (25 kg C kg N⁻¹). Geographic variation of C sequestration
27 across Europe indicates lower values for trees in colder-climate and water-stressed environments,
28 in both cases due to lower growth rates. The pattern of C sequestration in soils increases with
29 increasing N deposition.

1 Magnani et al. (2007) measured both C stock and C fluxes at five representative forest
2 chronosequences throughout Europe. The results indicated that age accounts for 92% of the total
3 variability in C sequestration (i.e., NEP) for the five ecosystems measured. In a second analysis,
4 using a recently published map of N fluxes across western Europe and North America (Holland
5 et al., 2005), a tight relationship between long-term net ecosystem productivity and estimated
6 1990 wet N deposition (up to $9.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) was discovered (Arrhenius function, $R^2 = 0.97$)
7 (Magnani et al., 2007). The authors concluded that the net C sequestration by many temperate
8 forests appeared to be determined by the additional input of N induced by human activities.

9 10 ***Tundra***

11 Mack et al. (2004) examined C and N pools in a long-term fertilization experiment at the
12 arctic Long-Term Ecological Research site near Toolik Lake, AK. Fertilized plots in moist
13 acidic tundra received 10 g N and $5 \text{ g N m}^{-2} \text{ yr}^{-1}$ from 1981 to 2000. This is approximately 5 to
14 8 times the annual soil N uptake requirement for above-ground production in the ecosystem.
15 Two decades of fertilization shifted community composition from graminoid tundra dominated
16 by the tussock-forming sedge, *Eriophorum vaginatum*, to shrub tundra dominated by *Betula*
17 *nana* (Shaver et al., 2001). Consequently, this greatly increased above-ground NPP, but had a
18 larger effect on decomposition than on plant production, resulting in a net loss of almost $2,000 \text{ g}$
19 C m^{-2} from this ecosystem over 20 yr ($p < 0.04$). Carbon storage increased above ground
20 because of the accumulation of woody shrub biomass and litter, but this was offset by a larger
21 decrease of C in below-ground pools due to a pronounced decrease in the C contained in deep
22 organic (>5 cm depth) and upper mineral soil layers. This study clearly showed that increased
23 nutrient availability enhanced decomposition of below-ground C pools in deep soil layers more
24 than it increased primary production, leading to a substantial net loss of C from this ecosystem.

25 Mack et al. (2004) demonstrated how N deposition can cause C loss from Tundra
26 ecosystems. The key process responsible for the C loss was identified as increased deep soil C
27 decomposition in response to increased nutrient availability. The authors noted that increasing
28 temperatures may amplify these effects and further stimulate C losses from high-latitude
29 systems. As temperature rises, the amount of N released due to a 3 to 7 °C increase in MAT is
30 likely to range in magnitude from 7 to $9.4 \text{ g N m}^{-2} \text{ yr}^{-1}$, respectively (Mack et al., 2004). This
31 will cause species shifts in the vegetation community from tussock to increased shrub abundance

1 and lead to decreased ecosystem C storage. Finally, the decreased soil moisture and increased
2 depth of thaw with temperatures rise are predicted to have a positive effect on decomposition
3 (Shaver, 2001), releasing more CO₂.

4 Previously, it was thought that warmer soils should stimulate decomposition and increase
5 nutrient availability, which, in turn, would stimulate plant production more than decomposition,
6 consequently increasing ecosystem C storage. However, Mack (2004) showed the opposite
7 response to increased nutrient availability. Decomposition was stimulated more than plant
8 production, leading to a net loss of C from the ecosystem. Furthermore, the system had no
9 capacity for net retention of increased N inputs. These results indicate that a new conceptual
10 model for the response of tundra to climate warming is required, one in which decomposition is
11 more sensitive than production to changes in nutrient availability and the ecosystem is
12 susceptible to N loss.

15 **AX7.3 SUMMARY**

16 In this chapter, the effects of temperature and/or precipitation on three ecosystem
17 responses to N deposition are discussed, these include: (1) N deposition effects on N₂O efflux
18 from forests, (2) the relationship between N deposition and riverine N efflux in the northeastern
19 United States, and (3) N deposition effects on the forest and tundra C cycle. In most cases, the
20 information presented here is more detailed than that which is presented in ISA Chapters 2 and 4.

21 In general, regions with elevated atmospheric N deposition due to anthropogenic activity
22 show increased N₂O emissions. The effects of N deposition on N₂O emissions are amplified by
23 low oxygen conditions in soils, these conditions are often caused by high soil moisture content
24 and the related characteristic of water-filled pore space in the soil. Poorly drained soils are
25 shown to produce up to 1/3 more N₂O than well-drained soils. The PnET-N-DNDC
26 (Photosynthesis-EvapoTranspiration-Denitrification-Decomposition) model is designed to
27 simulate and predict soil carbon and nitrogen biogeochemistry in temperate forest ecosystems
28 and to simulate the emissions of N₂O and NO from forest soils. Using this model, a comparison
29 of N₂O emissions for regions in Europe with MATs of 7.4 °C and 9.8 °C showed that
30 temperature effects on soil moisture drive N₂O emissions.

31 The flux of nitrogen in large rivers in North America and Europe is well explained as a
32 function of the net anthropogenic inputs of nitrogen to the landscape, on average 20 to 25% of

1 these inputs are exported in rivers and 75 to 80% of the nitrogen is retained or denitrified in the
2 landscape. Recently, the effect of climate on the amount of N discharged through rivers was
3 examined in 16 watersheds from Maine to Virginia during the time interval of 1988 to 1993.
4 The results indicated that watersheds with greater precipitation generally have higher discharge
5 and thus results in greater export of anthropogenic N. Among the climate parameters tested,
6 precipitation had a greater effect on N export than temperature.

7 There is substantial evidence that N additions to plants cause increased leaf-level
8 photosynthetic rates. However, the potential for N deposition to cause forest ecosystem C
9 biomass to increase is limited, because trees only take up a small portion of N deposition. The
10 role that nitrogen deposition plays in determining sink strengths of forests for C depends on
11 where N inputs to forest ultimately reside. If the majority of it is allocated to woody tissues with
12 high C:N ratios (200 to 500) and long turnover times, then the effects of nitrogen deposition to C
13 uptake are large. However, if nitrogen inputs are sequestered mainly in soils with low C:N ratios
14 (10 to 30), exported as nitrate in drainage water, or N gas to the atmosphere, then C storage is
15 minor. The results of ¹⁵N-tracer studies on six European and three American forests indicate that
16 trees are not the primary sinks for nitrogen deposition; the mean uptake in wood was 3% of total
17 N deposition. Typical losses due to drainage were <10%; however, these losses were observed
18 to reach 33%. The largest sink was in the soil (forest floor and mineral soil). Using these values
19 for calculation, they estimated that N deposition accounts for 0.25 Pg C uptake yr⁻¹.

20 In tundra, N addition causes C loss from the ecosystem. Two decades of experimental
21 fertilization shifted community composition from graminoid tundra dominated by the tussock-
22 forming sedge, *Eriophorum vaginatum*, to shrub tundra dominated by *Betula nana*.
23 Consequently, this greatly increased above-ground NPP but had a larger effect on decomposition
24 than on plant production, resulting in a net loss of almost 2,000 g C m⁻² from this ecosystem
25 over 20 years. Carbon storage increased above ground because of the accumulation of woody
26 shrub biomass and litter, but this was offset by a larger decrease of C in below-ground pools due
27 to a pronounced decrease in the C contained in deep organic (>5 cm depth) and upper mineral
28 soil layers. This study clearly showed that increased nutrient availability enhanced
29 decomposition of below-ground C pools in deep soil layers more than it increased primary
30 production, leading to a substantial net loss of C from this ecosystem. As temperature rises, the
31 amount of N released due to a 3 to 7 °C increase in MAT is likely to range in magnitude from 7

1 to 9.4 g N m⁻² yr⁻¹, respectively. This will cause species shifts in the vegetation community
 2 from tussock to increased shrub abundance and lead to decreased ecosystem C storage. Finally,
 3 the decreased soil moisture and increased depth of thaw that are associated with temperatures
 4 rise are predicted to have a positive effect on decomposition, releasing more CO₂.

TABLE AX7.2-1. PARAMETERS INCLUDED IN THE PnET-N-DNDC MODEL AS MODELED FOR EUROPEAN FOREST

Forest Properties	Soil Properties	Daily Climate Input Parameters	Tree Species/Genera
Forest type	Texture	Precipitation	Pine
Age	Clay content	Min and max air temps	Spruce
Above and below ground biomass	pH	Inorganic [N] in precip	Hemlock
Plant physiology parameters	Soil organic Carbon content		Fir
	Stone content		Oak
	Humus type		Birch
			Beech
			Slash Pine
			Larch
			Cypress
		Evergreen Oak	

Source: Kesik (2006).

**TABLE AX7.2-2. EXPERIMENTS ADDRESSING THE COMBINED EFFECTS
OF CHANGING TEMP AND PRECIPITATION ON BIOGENIC NO AND
N₂O EMISSION**

		Climate Variation
Mean annual surface temp	7.4 °C	9.8 °C
Winter and spring temp		Show highest increase Winter: +1.8 °C Spring: +2.2 °C
Summer and fall temp		Summer: +1.7 °C Fall: +1.5 °C
Mean annual precip		Unchanged, however regional and seasonal shifts occur
Regional changes		Mediterranean, W. Coast of France, and W. Coast of Scotland up to 30% increase All other regions except parts of Norway and Finland 0-20% decrease
Seasonal changes		NS Slightly higher values for winter. Mediterranean up to 80% decrease in summer precipitation
PnET-N-DNDC		6% decline in N ₂ O emissions in the future due to a shift in N ₂ O/N ₂ ratio driven by enhanced denitrification
Annual soil moisture		NS
Seasonal soil moisture		+22% in spring -2.4% in summer and -1.6 in fall
Annual mean biogenic N ₂ O emissions	0.53 kg N ₂ O-N ha ⁻¹ yr ⁻¹	0.50 kg N ₂ O-N ha ⁻¹ yr ⁻¹
Annual mean biogenic NO emissions	0.52 kg N ₂ O-N ha ⁻¹ yr ⁻¹	0.58 kg N ₂ O-N ha ⁻¹ yr ⁻¹

TABLE AX7.2-3. AVERAGE ANNUAL NITROGEN INPUTS FROM ANTHROPOGENIC SOURCES TO THE 16 MAJOR WATERSHEDS OF THE NORTHEASTERN UNITED STATES FOR 1988 TO 1993 (kg N km⁻² year⁻¹)

	NO_y Deposition	N Fertilizer Use	Agricultural N Fixation	Net N Import in Foods and Feeds	Total Net Anthropogenic N Inputs (NANI)
Penobscot	360	90	70	40	560
Kennebec	430	50	160	150	790
Androscoggin	500	80	150	240	970
Saco	570	40	100	100	810
Merrimack	610	150	210	710	1680
Charles	670	200	190	2090	3150
Blackstone	710	310	310	1500	2830
Connecticut	630	270	360	570	1830
Hudson	660	200	370	270	1500
Mohawk	710	410	1240	620	2980
Delaware	810	530	680	350	2370
Schuylkill	890	1210	1230	1950	5280
Susquehanna	820	620	1150	1100	3690
Potomac	710	1020	1170	1450	4350
Rappahannock	620	1030	1440	610	3700
James	650	360	700	400	2110
Area-weighted mean	680	560	740	740	2720
Northeastern U.S. mean Howarth et al. (1996)	1200	600	750	1000	3550

Source: Howarth et al. (2006).

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AX8. CRITICAL LOADS

AX8.1 INTRODUCTION

AX8.1.1 Background

Critical loads and critical levels are used to express how much deposition of an atmospheric pollutant (a “load”) or how large a concentration of an airborne pollutant (a “level”) can be tolerated by natural or man-made systems without significant harm or change occurring in those systems (see section AX8.2.1). The critical load and critical level approaches to quantifying the effects of pollutants attempt to estimate the atmospheric deposition load or concentration that would be likely to cause environmental harm. They are founded on ecological effects and extensively informed by toxicological results. The expectation is that environmental harm can be avoided by keeping pollution levels or loads below these critical values. This approach is commonly used to estimate loads or levels of pollution required to protect lakes, streams, or forest soils from environmental harm. The basic principles are, however, transferable to any sensitive receptor. Since the present evaluation deals primarily with the effects of atmospheric deposition of S and N compounds, this chapter focuses on critical loads more than critical levels.

Most critical load studies in North America have been undertaken in Canada. The critical load concept has been used in Canada to design emission reduction programs (RMCC, 1990; Jeffries and Lam, 1993). Modeling of critical loads for the 1997 Canadian Acid Rain Assessment (Jeffries, 1997) was conducted for six regional clusters of lakes, four in eastern Canada, one in Alberta, but also the Adirondack Mountains in New York. More recently, critical loads have been determined and mapped for waters (Hindar et al., 2001; Henriksen et al., 2002; Aherne et al., 2004; Dupont et al., 2005; Watmough et al., 2005) and forest soils (Arp et al., 1996; Moayeri et al., 2001; Watmough and Dillon, 2003; Ouimet et al., 2006), for a number of regions in eastern Canada. There have also been a number of regional critical loads studies (cf. Henriksen and Dillon, 2001; Ouimet et al., 2006) focused on acid-sensitive lakes on the Canadian pre-Cambrian shield. Much of this work is summarized and presented, along with steady state critical load maps for eastern Canada, in the 2004 Canadian Acid Deposition Science Assessment (Jeffries et al., 2005).

1 At the regional, cross-border level, critical loads in northeastern North America have
2 been addressed by a joint United States-Canadian cooperative. The Conference of New England
3 Governors and Eastern Canadian Premiers (NEG/ECP) has undertaken a program with the
4 objective to “estimate sustainable acidic deposition rates and exceedances for upland forests
5 representative of the New England States and the Eastern Canadian Provinces,...” (NEG/ECP
6 Forest Mapping Group, 2001). The Forest Mapping Working Group within the NEG/ECP
7 conducts regional assessments of the sensitivity of northeastern North American forests to
8 current and projected S and N emissions levels. The group is charged with identifying specific
9 forested areas most sensitive to continued S and N deposition and estimating deposition rates
10 required to maintain forest health and productivity at large spatial scales (cf. Miller, 2006). The
11 NEG/ECP has also provided estimates of critical loads for surface waters in northeastern North
12 America (cf. Dupont et al., 2005).

13 Aside from the NEG/ECP studies, the use of critical loads to assess S and N deposition
14 effects in the United States has not been as geographically extensive as elsewhere in North
15 America or Europe. Most critical loads studies in the United States have focused on smaller sub-
16 regional areas or individual sites. Critical loads studies for forests in the United States have been
17 centered in the northeast and have usually used a catchment-based approach (cf. Pardo and
18 Driscoll, 1993, 1996; Aber et al., 2003; Driscoll et al., 2003). Critical load studies for surface
19 waters have been more extensive along the eastern seaboard. Critical loads have been estimated
20 for lakes in the Northeast (cf. Driscoll et al., 2001; Pembroke, 2004) and for streams in the Mid-
21 Atlantic States and central Appalachians (cf. Sverdrup et al., 1992; Sullivan et al., 2004). In the
22 western United States there have been a few studies of critical loads for acidification of surface
23 waters (cf. Sullivan et al., 2004). The primary concern in the West, however, has been the
24 critical load of N deposition affecting both terrestrial and aquatic resources through
25 eutrophication and/or through N enrichment and its impact on community structure (cf. Baron
26 et al., 1994, 2000; Williams and Tonnessen, 2000; Fenn et al., 2003; Nydick et al., 2003, 2004a;
27 Wolfe et al., 2003; Burns, 2004; Stevens et al., 2004; Baron, 2006; Bowman et al., 2006).

28 The critical load approach has been used extensively in Europe for organizing
29 information about effects, and for specifying emissions reductions that would be required to
30 protect ecosystems and other sensitive receptors from the harmful effects of atmospheric sulfur
31 (S) and nitrogen (N) deposition. Outside of North America and Europe, there is an increasing

1 use of critical loads for assessment purposes, and to inform policy development. Examples
2 include studies in Siberia (Bashkin et al., 1995), Thailand (Milindalekha et al., 2001), and South
3 Africa (Van Tienhoven et al., 1995). In China, several studies have been carried out to study the
4 sensitivity of surface waters to acidification and the critical loads of acid deposition (Duan et al.,
5 2000a; Li et al., 2000; Ye et al., 2002; Hao et al., 2001), and to calculate the critical loads of S
6 and N acidity for soils at both the local and regional scales (Zhao and Seip, 1991; Xie et al.,
7 1995; Duan et al., 2000b, 2001).

8

9 **AX8.1.3 The Critical Load Process**

10 The process of estimating critical loads is not a purely scientific enterprise. Management
11 or policy input to the process is needed to insure that the appropriate science is included and the
12 appropriate questions are addressed. The critical load process integrates knowledge of a
13 multitude of physical, chemical and biological mechanisms affected by ambient air quality, and
14 presents the current scientific understanding in a format that is most useful for assessing current
15 or future management practices and policy decisions regarding air quality, or the resources
16 affected. The critical loads process provides decision-making insight based on both scientific
17 evidence, and policy priorities.

18 The close coupling of science and policy in the critical loads process can potentially be
19 confusing. In the development of critical load estimates, it is important to identify those
20 elements that are essentially scientific in nature as opposed to those elements that are driven by
21 management or policy priorities. The scientific elements include tasks such as: relating ambient
22 air quality to pollutant deposition, quantifying the relationships between pollutant deposition and
23 resource responses, identifying the resources at risk to adverse effects, understanding the
24 temporal and spatial responses of resources to pollutant deposition, and more. The policy-
25 dependent elements include tasks such as: identifying the environmental resources to be
26 protected, establishing appropriate criteria for different land use areas (e.g., Class I areas,
27 national parks, wildlife refuges), defining significant harm to protected resources, and more.
28 When all elements are integrated, it is apparent that the critical load process provides a
29 framework for alternate ways of examining and understanding the cascade of effects from
30 ambient air quality to resource effects, described in the preceding four annexes. Changing
31 scientific assumptions or understanding may result in different critical load estimates for the

1 same resources. Changing policy or management assumptions or priorities may also result in
2 different critical load estimates.

3 There is, therefore, no single “definitive” critical load for a natural resource. Critical load
4 estimates are explicitly linked to policy, but their reliability is conditioned on the soundness of
5 the underlying science. As elements of the critical load process change, the critical load
6 estimates will change to reflect both the current state-of-knowledge and policy priorities.
7 Changes in scientific understanding may include: new dose-response relationships, better
8 resource maps and inventories, larger survey datasets, continuing time series monitoring,
9 improved numerical models, etc. Changes in the policy elements may include: new definitions
10 of harm, new mandates for resource protection, focus on new pollutants, or inclusion of
11 perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

12 The critical load process is thus an iterative process — as science changes, the content is
13 updated; as policy needs change, the content is re-directed. Being iterative, the process allows
14 incremental improvement in understanding resource responses to ambient air quality. Individual
15 elements of the process can be replaced as needed to reflect new science or policy. Continuing
16 to update the process may reduce uncertainty and risk, as new data or techniques allow
17 refinement of existing pieces. The piecewise nature of the process provides adaptability as new
18 policy concerns arise, such as new pollutants or mandates. As the critical load process advances,
19 a “library” of critical load estimates will result. Examining and comparing these accumulated
20 results, and their underlying scientific and policy bases, may produce a “weight of evidence”
21 consensus, even if any single estimate entails substantial uncertainty.

22

23 **AX8.1.4 Organization of the Annex**

24 This annex is intended as a review of the current state of critical loads science. It is not
25 the intention to address questions of management or policy other than to point out where these
26 activities influence the critical loads process. The material in section AX8.2 presents necessary
27 definitions and describes the conceptual framework for a critical load analysis. This framework
28 identifies those elements that are primarily scientific in nature and those elements that require
29 policy input. The framework also describes the steps that are taken in deriving a critical load
30 estimate for a given resource. It is not an objective of this annex to provide details of all critical
31 loads studies that have been implemented in the United States or elsewhere. The conceptual

1 framework, however, provides a generalized summary of the steps most critical loads studies
2 have followed. Section AX8.3 discusses the time frame of responses for implementation of a
3 critical load. Time frames of resource response are often ignored, or assumed implicitly, in
4 defining a critical load analysis. The time required to implement the policy and technology to
5 achieve a critical load can also affect the responses of the resources at risk. The time frames of
6 response are important for selecting the data and models used to estimate critical loads. Section
7 AX8.4 discusses the disturbances, receptors, and indicators commonly addressed in critical loads
8 analyses. The acidification effects of S and N, and the eutrophication effects of N, as they affect
9 various components of the receptor ecosystems are discussed in context of critical load
10 estimation. Much of the literature relevant to this topic is discussed in more detail in other
11 annexes to this report (see Annexes 4 and 5 in particular). Section AX8.4 is intended to present
12 specific examples of the use of those data in critical load analyses. Summary tables of the
13 thresholds of effects for various receptors and indicators are presented. Section AX8.5
14 summarizes the tools (models and modeling approaches) commonly used in calculating critical
15 loads. The annex concludes in Section AX8.6 with a summary of the current agreement on
16 critical loads uses in the United States that was a product of the Multi-Agency Workshop on
17 Critical Loads held in 2006. The workshop produced a series of recommendations for current
18 and future activities related to critical loads analyses in the United States.

19
20

21 **AX8.2 DEFINITIONS AND CONCEPTUAL APPROACH**

22

23 **AX8.2.1 Critical Load Definitions**

24 Critical loads and critical levels are used to express how much deposition of an
25 atmospheric pollutant (a “load”) or how large a concentration of an airborne pollutant (a “level”) can be tolerated by natural or man-made systems without significant harm or change occurring in
26 those systems. The generally accepted definition of a critical load or a critical level of
27 atmospheric pollutants emerged from a pair of international workshops held in the late 1980s
28 (Nilsson, 1986; Nilsson and Grennfelt, 1988). The workshop participants defined a critical load
29 or a critical level as:
30

1 “a quantitative estimate of an exposure to one or more pollutants below which
2 significant harmful effects on specified sensitive elements of the environment do
3 not occur according to present knowledge.”

4 This evaluation deals primarily with the effects of atmospheric deposition of S and N
5 compounds. This annex, therefore, will deal exclusively with the concept of critical loads of S
6 and N compounds from atmospheric deposition. Critical levels of pollutant concentration will
7 not be addressed. As discussed in previous annexes, the deposition of both S and N has
8 acidifying effects on receptors (Annex 4), and the deposition of oxidized and/or reduced N
9 compounds can produce eutrophication or nutrient-enrichment effects in receptors (Annex 5).
10 The following material, therefore, will focus on critical loads of S and N for acidification effects,
11 and on critical loads of N for nutrient effects.

12 In addition to the generic definition of a critical load/level presented above, the
13 participants in the second international workshop (the Skokloster Workshop) (Nilsson and
14 Grennfelt, 1988) developed a number of specific definitions related to known atmospheric
15 pollutants. Two of those definitions are relevant to this annex.

16 Recognizing that both S and N compounds contribute to the acidity of deposition, the
17 workshop participants developed a definition for critical loads of S and N for acidification of an
18 ecosystem:

19 “the highest deposition of acidifying compounds that will not cause chemical
20 changes leading to long-term harmful effects on ecosystem structure and
21 function according to present knowledge”

22 Recognizing that N in both oxidized ($\text{NO}_Y = \text{NO} + \text{NO}_2 + \text{NO}_2 + \text{NO}_3^-$) and reduced
23 ($\text{NH}_X = \text{NH}_3 + \text{NH}_4^+$) forms in deposition may influence the eutrophication and nutrient balances
24 of ecosystems, the workshop participants defined the critical load of N for nutrient effects in an
25 ecosystem as:

26 “the highest deposition of nitrogen as NH_X and/or NO_Y below which harmful
27 effects in ecosystem structure and function do not occur according to present
28 knowledge.”

29 All three definitions can be applied to different receptors in a number of different
30 environments (e.g., terrestrial ecosystems, transitional ecosystems, aquatic ecosystems,
31 groundwater, agricultural crops, etc.). A sensitive element can constitute a part of, or the whole
32 of, an ecosystem. Harmful effects can occur to individual organisms, to populations, or to entire

1 communities within an ecosystem. Harmful effects can also be defined at the level of the
2 ecosystem itself as changes in ecosystem processes, structure, and/or function.

3 While the concepts expressed in these definitions of critical loads and levels are easily
4 understood and intuitively satisfying, the application of the critical load concept requires careful
5 consideration and definition of a number of terms and procedures. It is apparent that there can be
6 many different critical load values for a given atmospheric pollutant depending on the receptor or
7 sensitive element(s) being considered. There can also be multiple different atmospheric
8 pollutants that can produce the same harmful effects in a given receptor. Therefore, the critical
9 load of a given pollutant can potentially be dependent on the deposition and/or atmospheric
10 concentration of other pollutant species. Finally, the same atmospheric pollutant can produce a
11 variety of different disturbances in a sensitive ecosystem that might occur at different pollutant
12 loads. For example, N deposition produces both nutrient and acidification effects and the critical
13 load of N for each type of disturbance may be different.

14 Therefore, in order to derive a quantitative estimate of the critical load of an atmospheric
15 pollutant, a number of factors must be identified and defined (Figure AX8.2-1). These include
16 disturbance type, receptor, sensitive elements, and definition of what constitutes significant
17 harm. In addition, a numerical relationship between pollutant deposition and the identified
18 receptor response must be formulated, generally based on either an empirical dose-response
19 relationship or a steady state or dynamic numerical model simulation. The next section outlines
20 the steps (decisions) that must be taken to implement this process.

21 **AX8.2.2 Critical Load Analysis Procedures**

22 The development of a quantitative critical load estimate requires a number of steps. In
23 this discussion, Figure AX8.2-1 is used to illustrate the procedure. The figure is simplified to
24 facilitate general discussion and does not represent the full complexity of the choices that must
25 be made, or the scientific understanding underlying those choices.

26 There are eight general steps that must be taken to define the basic critical load question
27 in any analysis.

- 28 1. Identify the ecosystem disturbance of concern (acidification, eutrophication, etc.).
29 Not all disturbances will occur in all regions or at all sites, and the degree of
30 disturbance may vary across landscape areas within a given region or site.
31

- 1 6. Determine the critical chemical limits for the chemical indicators at which the
2 harmful responses to the biological indicators occur (e.g., pH < 5, base saturation <
3 5%, Al concentrations >100 µg/L, etc.). Critical limits may be thresholds for
4 indicator responses such as presence/absence, or may take on a continuous range of
5 values for continuous indicator responses such as productivity or species richness.
6 Critical limits may vary regionally or locally depending on factors such as
7 temperature, existence of refugia, or compensatory factors (e.g., high calcium
8 concentration mitigates the toxicity of Al to fish and plant roots).
- 9 7. Identify the atmospheric pollutants that control (affect) the pertinent chemical
10 indicators (deposition of SO₄, NO₃, NH₄, HNO₃, etc.). Multiple pollutants can affect
11 the same chemical variable. The relative importance of each pollutant in producing a
12 given chemical response can vary spatially and temporally.
- 13 8. Determine the critical pollutant loads (kg/ha/yr total deposition of S or NO₃⁻N, etc.)
14 at which the chemical indicators reach their critical limits. Critical pollutant loads
15 usually include both wet and dry forms of pollutant deposition. The critical pollutant
16 load may vary regionally within a receptor or locally within a site (as factors such as
17 elevation or soil depth vary) and may vary temporally at the same location (as
18 accumulated deposition alters chemical responses).

19 The definition of the critical load problem for a region or individual site generally
20 requires that we work down the table from top to bottom (Figure AX8.2-1). What is the
21 disturbance? What receptors are affected? What indicator organisms are, or were previously
22 present and observable? What chemical indicators are changing and can be measured? What
23 atmospheric pollutant is driving the changes in the chemical indicators?

24 The derivation of a quantitative estimate of a critical load generally requires that we work
25 from the bottom of the table back towards the top, as indicated by the arrows in Figure AX8.2-1.
26 What is the maximum load of a pollutant that will cause a shift in the chemical indicator to its
27 critical limit such that a critical indicator response occurs, or does not occur? From this point of
28 view, it can be seen that steps 8 and 6 require the development of dose-response functions for the
29 components of the ecosystem being considered (arrows in Figure AX8.2-1). Step 8 describes the
30 response of the chemical indicator as a function of the pollutant load, and Step 6 describes the
31 responses of the biological indicator as a function of the chemical variable. As discussed in later
32 sections, these response functions can be derived using empirical (e.g., statistical) or process-
33 based (e.g., mechanistic) models that are either time-invariant (static or steady state) or time-
34 variable (dynamic).

35 Each step in the development of the critical load, as summarized in Figure AX8.2-1, can
36 be classified as either a predominantly scientific task or as a task benefiting from, or perhaps

1 requiring, collaboration and input from scientists, decision-makers, and other interested parties.
2 For instance, tasks 1, 2, and 3 can be viewed as predominantly scientific tasks that can be
3 completed by asking questions of fact. At task 4, however, questions of what defines
4 “significant harm” entail subjective elements that cannot be determined by scientific techniques
5 alone. In anticipation of the ultimate use of the critical load definition to set policy or establish
6 management strategies, it is appropriate that political, socioeconomic, or perhaps ethical
7 considerations be brought to bear in defining “significant harm”. To define “harm” is to imply a
8 corrective action, the cost of which will have to be borne by someone. Having reached
9 agreement on task 4, however, tasks 5, 6, 7, and 8 are again predominantly scientific in nature,
10 requiring determination of the causal links, represented as response functions or models, leading
11 from the loading of the pollutant to the defined “significant harm”.

12 This procedure will almost certainly result in calculation of multiple critical load values
13 for a given pollutant and analysis location. The multiple solutions derive from the nested
14 sequence of disturbances, receptors, and biological indicators that must be considered for a given
15 pollutant. Multiple critical load values may also arise from an inability to agree on a single
16 definition of “significant harm” at step 4. Finally, there is the inescapable heterogeneity of all
17 natural environments. Consider soils for instance. The high spatial variability of soils almost
18 guarantees that for any reasonably sized soil-based “receptor” that might be defined in a critical
19 load analysis, there will be a continuum of critical load values for any indicator chosen. The
20 range of this continuum of values may be narrow enough to be ignored, but in any critical load
21 analysis there is nevertheless an a priori expectation of multiple values, or of a range of values.

22 The existence of multiple estimates of critical loads for a given pollutant and receptor
23 should present no real problem. Examination of the range of critical loads derived may be
24 deemed useful in subsequent discussions of the analysis, and in the decision-making steps that
25 may follow critical load calculation. For instance, the lowest critical load of all those derived
26 may be adopted as “the” critical load, as is often done in Europe. This however, is a policy
27 choice. The scientific task is the derivation of the multiple values using best available
28 information.

1 **AX8.2.3 Target Load Definition**

2 As seen in the previous section, it is expected that a potentially large number of critical
3 load values may be objectively determined for a given atmospheric pollutant and a given
4 receptor. Like the definition of “significant harm”, the choice of which critical load value to use
5 for management or decision-making is subjective, and should be driven by socioeconomic,
6 political, and ethical considerations. The target load concept was developed to address these
7 issues. Target loads are deposition loads of a given pollutant, based on critical load estimates for
8 the pollutant, which incorporate policy and/or management decisions about the amount of
9 pollutant deposition, and therefore the amount of resource damage that is deemed acceptable.
10 Target loads can be set at, above, or below the various critical loads. If the target load is set
11 **above** some of the estimated critical loads, one accepts the inevitability that some of the
12 ecosystem components, generally the most sensitive, will be adversely affected. If the target
13 load is set **below** all of the estimated critical loads, a safety margin has been established to
14 account for uncertainty inherent in the process.

15 Given the spatial heterogeneity of natural systems, target loads might also be used to
16 provide some measure of “cumulative resource protection”. As discussed above, there typically
17 exists a range of critical loads for a particular “significant harm” in a particular receptor.
18 Selecting a target load within the range will provide protection for the fraction of the receptor
19 with critical loads above the chosen target load, whereas that fraction with critical loads below
20 the chosen target load will be expected to suffer some harm at that deposition level. In this way,
21 it is possible to use the target load to define protection for some cumulative proportion of the
22 receptor (i.e., a target load for protection of 95% of the resource from “significant harm”).

23 While most of the steps involved in estimating critical loads depend on sound, objective
24 scientific analysis, the selection of target loads is almost entirely a subjective judgment. The
25 selection of target loads must begin with reliable estimates of critical loads to set the constraints,
26 and define the expected consequences of the target load choices. Nevertheless, the final
27 decisions of which indicators are the key indicators, how much cumulative resource should be
28 protected, how much sooner or later resource protection will be implemented, cannot be
29 answered scientifically. Political, socioeconomic, and ethical considerations will form the basis
30 of the final target load selections. Frequently, the legal mandates for various public lands would
31 have a determinant influence on the selection of target loads. For instance, Federal Class I areas

1 may be held to one standard of harm because of mandates to protect “natural condition”, whereas
2 Federal mixed-use lands may be held to a different standard of harm, and cropland to yet another
3 standard of harm.

4 It is also important to note that scientific understanding, modeling approaches, and the
5 data used to estimate critical loads are continually improving. Furthermore, the political,
6 economic, and social environments surrounding selection of target loads are also constantly
7 shifting. Therefore, the analysis and estimation of critical and target loads must be an iterative
8 process.

9
10

11 **AX8.3 TIME FRAME OF RESPONSE**

12 The critical load definitions and procedures discussed in the previous section do not
13 explicitly consider the time frame of ecosystem response. When is “significant harm” expected?
14 How long will it be before existing harm is reversed? When should critical loads be
15 implemented? How long should a critical load be maintained? The use of critical and target
16 loads in resource management always has some time frame of expected response, and some
17 context of management priorities. For instance, it may be that a target load well below the
18 critical load would hasten the recovery of a receptor with existing harm. Or, it may be that a
19 receptor that has not yet been damaged can sustain a target load above the critical load for some
20 finite period before incurring “significant harm”. Such time frames can be very long (many
21 decades or centuries).

22 The time frame of response between implementation of a critical load and the
23 corresponding changes in biological or chemical indicators is a potentially important factor in
24 establishing critical load analysis procedures and in selecting the final target load. Analyses can
25 be designed to provide estimates of either “steady state critical loads” or “dynamic critical loads”
26 depending on the perceived, or mandated, importance of the time frame of response and the
27 types of models (transfer functions) used.

28 Steady state critical loads analyses provide estimates of the long-term sustainable
29 deposition of a pollutant that will not cause “significant harm” to a receptor. This is the relevant
30 information needed for any receptor to provide protection from damage by the pollutant in
31 perpetuity as the receptor comes into equilibrium with the pollutant critical load (the implicit
32 purpose of steady state analyses). However, no information is given concerning the time to

1 achieve the equilibrium or what may happen to the receptor along the path to equilibrium.
2 Estimated steady state critical loads for receptors that are currently damaged provide no
3 information concerning when the desired long-term sustainable protection will occur and the
4 existing “significant harm” will be mitigated. There exists the possibility that receptors with no
5 current damage could suffer “significant harm” while waiting for implementation of the critical
6 load. The possible occurrence, timing, and duration of such “interim periods of harm” are not
7 the subject of steady state analyses.

8 Dynamic critical loads analyses provide estimates of a specifically scheduled deposition
9 load of a pollutant that will not result in “significant harm” to a receptor at a specified time. This
10 is the relevant information needed for any receptor to provide protection from damage by the
11 pollutant within a specified time frame (the explicit purpose of dynamic analyses). However,
12 care should be taken in interpreting the results of dynamic analyses to ensure that “significant
13 harm” to the receptor does not occur after the specific timetable has been completed. Many
14 receptors can tolerate higher loads of a pollutant for a few decades (a common length of
15 specified schedules for dynamic analyses) than can be sustained over longer periods. The use of
16 dynamic critical load estimates in such cases may provide protection from harm during a time
17 frame of immediate interest, but ultimately fail to provide long-term protection, unless these
18 issues are considered.

19

20 **AX8.3.1 Steady State Critical Loads**

21 If the time frame of response is not important, for instance, if the target load is to provide
22 long-term sustainable protection and the immediacy of the responses is not relevant, the use of
23 static or steady state models (response functions) is justified in the critical load analysis
24 procedure. Using steady state models to estimate critical loads and compare the estimated
25 critical load to current or future deposition, only two cases can be distinguished: (1) current or
26 future deposition is below the critical load, or (2) current or future deposition exceeds the critical
27 load. In the first case, no problem is apparent, and no target load is deemed necessary, unless
28 increases in deposition are anticipated. In the second case, there is by definition an increased
29 risk of “significant harm” to the receptor and selection of a target load for resource protection is
30 indicated.

1 The lack of explicit consideration of time in a steady state critical load analysis can lead
2 to assumptions that are frequently not warranted. The critical load derived in a steady state
3 analysis is an estimate of the long-term, constant deposition that a receptor can tolerate with no
4 significant harm after it has equilibrated with the critical load deposition. However, biological
5 and geochemical processes that affect a receptor may delay the attainment of equilibrium (steady
6 state condition) for years, decades, or even centuries. By definition, steady state critical loads do
7 not provide any information on these time scales. As a result, it is often assumed that reducing
8 deposition to, or below the steady state critical load value will immediately eliminate or mitigate
9 “significant harm”. That is, it is assumed that the chemical indicator affected by the atmospheric
10 pollutant immediately attains a non-critical value upon implementation of the critical load, and
11 that there is immediate biological recovery as well. As discussed in the next section, these
12 assumptions may not be valid.

13

14 **AX8.3.2 Dynamic Critical Loads**

15 The time frame of receptor response is important if the establishment of target loads is
16 tied to defined schedules of deposition change or receptor responses. The use of time-dependent
17 or dynamic model response functions will be necessary if the critical load analysis considers the
18 response time frame. In the cascade of events that occur from changed deposition of an
19 atmospheric pollutant to development of responses of key biological indicators, there are many
20 processes in natural systems that are time and/or resource dependent and therefore can introduce
21 delays in the response pattern. In the decision-making process leading to the adoption of target
22 loads, there are likewise considerations of when deposition changes can be initiated and
23 completed and when biological indicator responses are desired. With dynamic models, either
24 empirical or process-based, a wide range of estimated critical loads can be derived for
25 comparison with current or future deposition depending on the temporal constraints imposed on
26 the critical load analysis. Temporal constraints that can be imposed on a given critical load
27 analysis are determined by: (1) the receptor responses—the characteristic time scales and
28 inherent lags of the receptor being analyzed (a function of hydrobiogeochemical processes in the
29 receptor), and (2) the deposition schedules—the years designated for beginning and completing
30 the changes in deposition and for evaluating the indicator responses (a function of political,
31 socioeconomic, and management constraints).

1 AX8.3.2.1 Receptor Responses

2 The general conceptual model of the linkages among pollutant deposition and the
3 responses of chemical and biological indicators can be characterized as a series of delays. In the
4 causal chain from deposition of pollutant to damage to key biological indicators there are two
5 major links that can give rise to delays. First, hydrological and biogeochemical processes in
6 catchments can delay the responses of chemical indicators. Second, biological processes and
7 population dynamics can further delay the response of biological indicators. The pattern of
8 chemical and biological indicator responses can be represented conceptually (Figure AX8.3-1)
9 (adapted from Jenkins et al., 2003; Posch et al., 2003). Five stages in the conceptual pattern can
10 be distinguished (Figure AX8.3-1):

11 *Stage 1:* Pollutant deposition is below the critical load for either the critical chemical
12 limit or the critical biological response, and there is no “significant harm” to the receptor.
13 As long as deposition stays below the critical load, this is the ‘ideal’ situation.

14 *Stage 2:* Pollutant deposition rises above the critical load, but chemical and biological
15 indicators still do not violate their respective criteria because there is a delay. No damage
16 is likely to occur at this stage, despite the exceedance of the critical load. The time
17 between the first exceedance of the CL and first violation of the biological criterion (first
18 occurrence of “significant harm”) is called the Damage Delay Time ($DDT = t_3 - t_1$).

19 *Stage 3:* Pollutant deposition is above the critical load and both the chemical and
20 biological criteria are violated. Measures to reduce emissions are taken to avoid further
21 harm to the receptor and pollutant deposition begins to decrease.

22 *Stage 4:* Pollutant deposition has been reduced to a level below the critical load, but the
23 chemical and biological criteria are still violated, and thus “recovery” has not yet
24 occurred. The time between the first non-exceedance of the critical load and the
25 subsequent non-violation of both criteria can be called the Recovery Delay Time
26 ($RDT = t_6 - t_4$).

27 *Stage 5:* This stage is similar to Stage 1. Pollutant deposition has been reduced to a level
28 below the critical load and neither the chemical nor biological criteria are violated. Only
29 at this stage can the receptor be considered to have recovered to an undamaged level.

30 Stages 2 and 4 can be further subdivided into two sub-stages each: chemical damage and
31 recovery delay times ($DDT_c = t_2 - t_1$ and $RDT_c = t_5 - t_4$; dark grey in Figure AX8.3-1) and
32 (additional) biological damage and recovery delay times ($DDT_b = t_3 - t_2$ and $RDT_b = t_6 - t_5$; light
33 grey). Given opportunities for “confounding effects” (i.e., mechanisms not related to acidic
34 deposition but affecting biological indicators, such as forest pest infestation or climate change)
35 occurring during the “delay periods”, it is clear that unambiguous short-term patterns of recovery

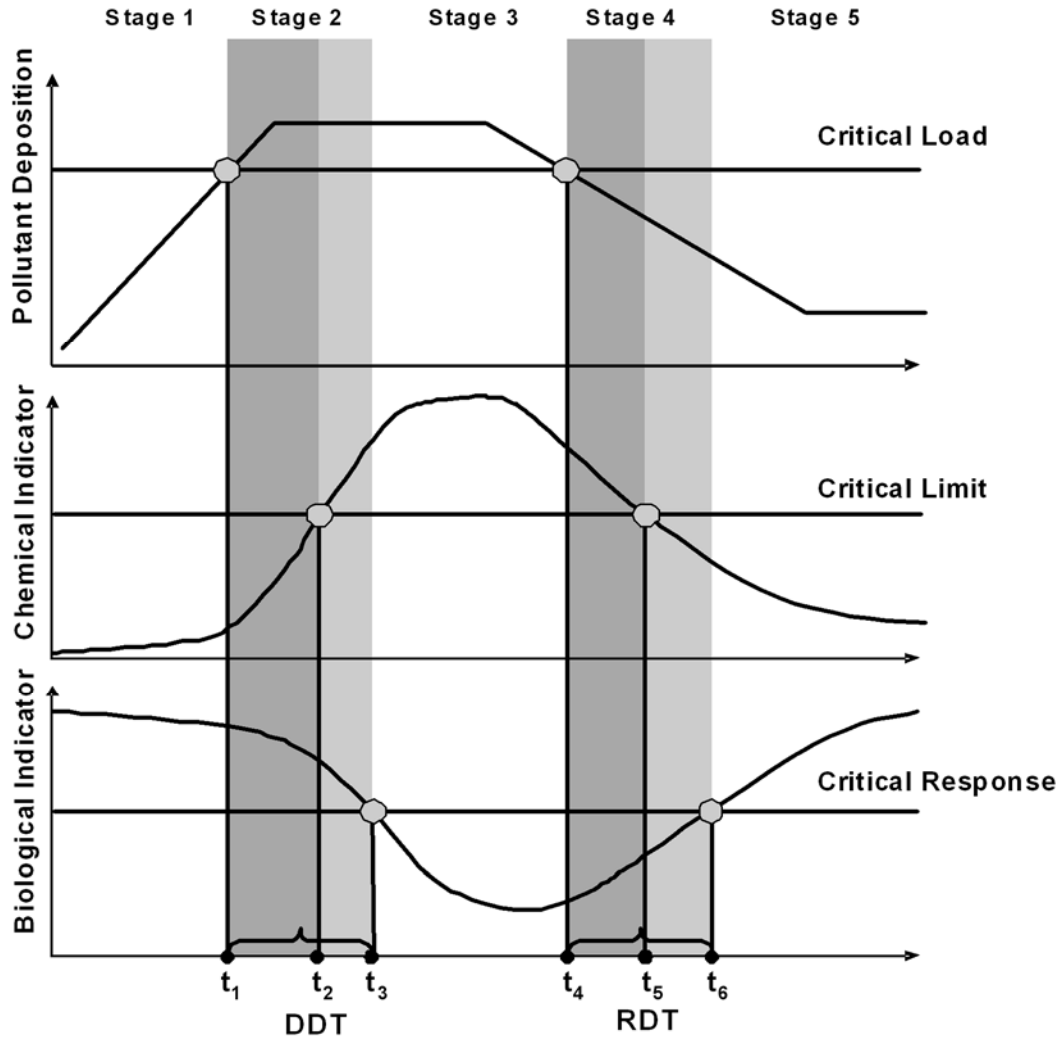


Figure AX8.3-1. Conceptual patterns of pollutant deposition effects on a chemical indicator and a corresponding biological indicator during increasing and decreasing deposition. Critical limits and responses for the chemical and biological indicators are indicated as horizontal lines, along with the critical load of deposition that produces these levels. The delays between the exceedance of the critical load (t_1), the violation of the critical chemical limit (t_2), and the crossing of the critical biological response (t_3) are indicated in grey shades, highlighting the Damage Delay Time (DDT). Similar delays in chemical and biological recovery during deposition reductions (t_4 , t_5 , and t_6) define the Recovery Delay Time (RDT) of the system.

1 of biological indicators are unlikely to be observed, even in the presence of rather large declines
2 in pollutant deposition. This has important implications for recovery expectations.

3 4 **AX8.3.2.2 Deposition Schedules**

5 Dynamic critical loads, by definition, must explicitly account for the receptor time scales
6 and lags described above. Therefore, the process of estimating dynamic critical load values for a
7 given pollutant must be based on a planned or assumed deposition schedule for changing the
8 pollutant deposition and for assessing the receptor responses. Three different time periods are
9 specified, as illustrated in Figure AX8.3-2. [The nomenclature used here for the three years
10 specified in the deposition schedule conforms to that used in European “dynamic target loads
11 analyses” (Posch et al., 2003)].

12 The first time period is the protocol year when deposition changes moving toward the
13 critical load are begun. It will be the case that voluntary or mandated changes in deposition will
14 require a number of years to get underway once a critical load has been calculated or target load
15 has been selected. These delays in moving toward the critical load will affect the dynamic
16 responses of the chemical and biological indicators and, therefore, must be included in the
17 dynamic modeling of receptor response. Before the protocol year, it must be assumed that
18 pollutant deposition will be continuing along the pattern of recent or historical deposition change
19 or along the pattern dictated by future deposition scenarios already planned and assumed to take
20 effect.

21 The second time period is the implementation year when deposition changes are complete
22 and pollutant deposition has reached the desired critical or target load. It is likely that a number
23 of years will elapse between the time changes in deposition toward the critical load are initiated,
24 and the time when they are completed. During this transition period, pollutant deposition
25 continues at a rate higher, or lower, than the critical load. The effects of these years of
26 deposition inputs above or below the critical load value will affect the dynamic responses of the
27 chemical and biological indicators, and must also be included in the dynamic modeling of
28 receptor response. It is assumed in dynamic critical loads analyses that the pollutant deposition
29 to the receptor remains constant at the critical load for all years after the implementation year.

30 The final time period is the target year when the biological indicators are evaluated.
31 Recognizing that there are inherent lags in receptor responses following changes in pollutant
32 deposition, it a number of years will frequently be allowed to elapse after the implementation

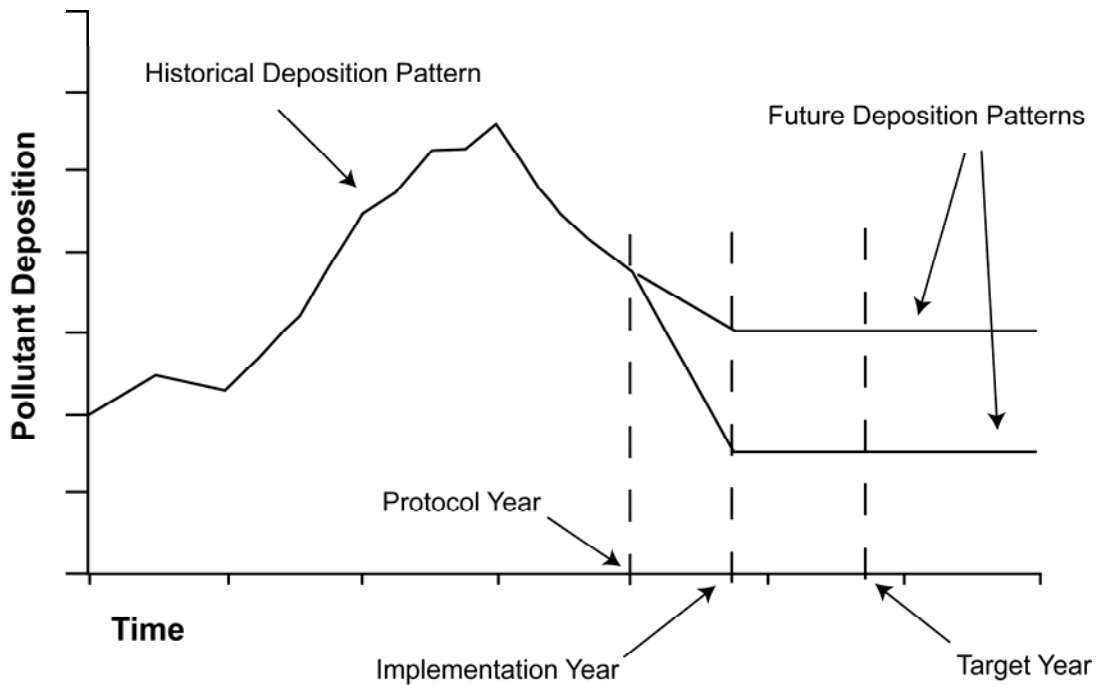


Figure AX8.3-2. Pollutant deposition patterns for defining the temporal parameters of dynamic critical loads analyses. The deposition schedule requires that three years be specified: (1) the year in which changes in pollutant deposition are begun, called the protocol year; (2) the year in which changes in pollutant deposition are completed, called the implementation year; and (3) the year in which the chemical or biological response indicator is evaluated, called the target year.

1 year before the receptor responses are assessed. It must also be recognized that receptor
 2 responses will continue to change over time. Thus, selection of the target year will affect
 3 attainment of the critical limit.

4 The deposition schedule for a dynamic critical load analysis can be driven by a number of
 5 considerations, and can be organized from protocol year to target year or vice versa. The
 6 selection of the protocol and implementation years is often a matter of political will and
 7 economic possibility. Large-scale pollution abatement programs take time to negotiate. Costs or
 8 engineering difficulties may delay the start of the abatement program and affect the length of
 9 time it takes to complete the program once it is begun. Once these constraints have been
 10 established, it is then possible to select a reasonable target year for evaluation of the receptor
 11 responses. Alternately, resource management mandates might require that “significant harm” to

1 receptor indicators be mitigated or eliminated by a certain time. This establishes the target year
2 for the dynamic analysis and the protocol and implementation years must be selected to allow
3 time for any lags in the receptor responses to occur.

4 Clearly, there is tension between the two approaches when developing a deposition
5 schedule. It is possible, for instance, to defer the protocol and implementation years so far into
6 the future that extensive “significant harm” occurs to the receptor indicators in the intervening
7 years. If that damage is especially severe, the critical load, when the target year is finally
8 reached, may not be achievable. Similarly, if a receptor is currently suffering harm, it is possible
9 to choose a target year for receptor response too close to the present day to allow time for the
10 receptor to recover, even if the pollutant deposition was reduced to zero immediately.

11 Both of these hypothetical scenarios raise important points about dynamic critical load
12 estimates. Because time is explicitly incorporated, there are certain dynamic critical loads
13 questions that have no answer. Commonly called “you can’t get there from here” problems,
14 these deposition schedules choose protocol, implementation, or target years that are inconsistent
15 with the time scales of receptor response. For example, setting a target year 5 years in the future
16 for achievement of no “significant harm” in a receptor that is currently badly damaged, and has a
17 history of high pollutant loading, may be asking the impossible. Critical load estimates derived
18 in this case would require having set the pollutant deposition to zero some years in the past. In
19 other words, the state of no significant harm cannot be reached within the specified five years
20 regardless of how deposition is changed within that five-year period (“you can’t get there from
21 here”). This problem is moot for steady state critical loads. Steady state critical loads analyses
22 will always provide some sensible estimate (zero or finite) of long-term sustainable pollutant
23 deposition for every receptor because time is not a factor. Dynamic critical loads analyses, on
24 the other hand, may frequently provide non-quantitative results, but these results nonetheless
25 convey useful information concerning the current status of the receptor and point out the
26 necessity to continue the analysis with modified assumptions or expectations in order to develop
27 realistic and achievable target load values.

28 29 **AX8.3.2.3 Long-Term Implications**

30 The explicit inclusion of time in critical loads estimation provides useful information for
31 managers or policymakers when deciding when and how much to alter pollutant emissions and
32 deposition, but the dynamic approach leads to implicit assumptions that must be recognized.

1 Focus on the near-term aspects of receptor responses (the years included in the deposition
2 schedule) can be misleading. The implicit assumption is that having attained the desired
3 biological or chemical response in the target year, nothing more will happen, or at least that
4 further changes in the receptor, if they do occur, will not produce “significant harm”. Available
5 dynamic model critical load estimates suggest that this is not always true, and the long-term
6 implications of dynamic critical load estimates should be examined carefully.

7 The dynamic critical loads procedure assumes that pollutant deposition remains constant
8 at the critical load from the implementation year until the target year, and the assessment of
9 receptor response. Model simulations can be continued, assuming deposition at the constant
10 critical load value, for a number of years after the specified target year to ensure that lags in the
11 receptor response will not result in “significant harm” appearing at some later date, even though
12 it was not present in the target year. Some receptors have chemical or biological lags that are
13 many decades long, or longer. Critical loads analyses based on deposition schedules that cover
14 only 20 to 30 years can produce the unwanted result of estimating a dynamic critical load that
15 avoids “significant harm” to the receptor in the target year, only to have the receptor suffer
16 damage some years later.

17 It is important to determine which receptor responses and which deposition schedules
18 might lead to such an unwanted result. There are some general guidelines concerning this
19 potential problem. For any receptor for which there is currently no “significant harm”, the
20 estimated critical load provided by the dynamic approach will be one that brings the biological or
21 chemical indicators to the threshold of harm without crossing it (the definition of the critical
22 load). However, this dynamic critical load has then put the biological or chemical indicator on a
23 trajectory away from its currently good status and toward the threshold of harm. In most cases,
24 the trajectory toward harm will continue past the target year and “significant harm” will occur in
25 these receptors some time after the target year.

26 On the other hand, in any receptor for which there currently is “significant harm”, the
27 estimated critical load provided by the dynamic approach will be one that brings the biological
28 and chemical indicators to the threshold of harm and crosses it, just to return to a state of no
29 harm. This dynamic critical load puts the biological or chemical indicator on a trajectory away
30 from harm and towards good status. In most cases, it is likely that the upward trajectory will

1 continue past the target year and significant further recovery will occur in these receptors after
2 the target year.

3 These are, however, merely generalizations. Depending on the geochemical and
4 biological process affecting a receptor, there exist possibilities that upward trajectories could
5 become downward trajectories sometime after the target year and vice versa. The most
6 straightforward procedure is to run the model(s) used in the dynamic critical loads analyses for a
7 sufficiently long time after the target year so that any reasonable chance of delayed damage to
8 the receptor or delayed recovery is either discovered or discounted.

9

10 **AX8.3.3 Steady State and Dynamic Critical Loads – Complementary** 11 **Information**

12 There is no “correct” choice to be made between steady state and dynamic critical loads
13 analyses. Both provide estimates of pollutant loads that are intended to avoid “significant harm”
14 to a receptor. Both are valid scientific expressions of the receptor’s sensitivity to the pollutant.
15 They differ primarily in the time scales implicit in their use. Steady state analyses provide
16 critical load estimates for long-term sustainable protection, but ignore questions of near-term
17 recovery and avoidance of interim harm. Dynamic analyses provide critical load estimates that
18 can be used to examine short-term or long-term options for recovery of damaged systems and
19 avoidance of interim harm, but may ignore the ultimate long-term sustainability of the estimated
20 deposition, which may evolve over centuries. Clearly, the two approaches provide
21 complementary information.

22 The complementary nature of the two critical loads approaches can be exploited in the
23 selection of a target load estimate for a receptor. Selecting the lower of the two critical load
24 estimates for the receptor (steady state or dynamic) should result in facilitation of recovery, or
25 avoidance of harm, in the short-term, as well as long-term sustainability once the receptor has
26 reached equilibrium with the selected target load. Multiple lines of evidence reflecting multiple
27 critical load values can provide important information that collectively provides the foundation
28 for management decision-making.

29 The procedures, data requirements, and computational resources needed for each of the
30 two critical loads approaches may differ significantly depending on the models (response
31 functions) adopted for the analyses. Differences in the approaches may also depend on the
32 disturbance, receptor, or indicator being evaluated. The next two sections discuss the

1 disturbances, receptors, and indicators relevant to deposition of S and N, and the models used for
2 calculation of critical load estimates by each approach.

3 4 5 **AX8.4 DISTURBANCES, RECEPTORS, INDICATORS, AND** 6 **THRESHOLDS**

7 Atmospheric deposition of S and N causes two general types of disturbance.

8 Acidification effects are primarily associated with deposition of S, but at some locations
9 deposited N can also contribute to acidification if it is not assimilated in the nutrient cycles of the
10 receptor ecosystem. See discussion in Annex 4. Nutrient N effects can be caused by the
11 deposition of both oxidized and reduced N compounds and are mediated by the nutrient cycles of
12 the receptors. See discussion in Annex 5.

13 Disturbances have occurred in all three major receptor categories: aquatic, terrestrial, and
14 transitional ecosystems. Generally, the effects of acidification have been most severe in aquatic
15 ecosystems, though acidification of forest soils has also occurred in the United States. Nutrient
16 effects of N have likely been most severe in terrestrial and transitional ecosystems, with aquatic
17 eutrophication effects limited mostly to coastal and estuarine waters and some, mostly high-
18 elevation, N-limited lakes.

19 For some of these disturbances and receptors, the affected chemical and biological
20 indicators can be readily identified and thresholds of harm can be quantified, as in the case of
21 acidification effects in aquatic ecosystems. For other disturbances and receptors, however, the
22 indicator responses and thresholds are less well understood and may only be identifiable in
23 qualitative or semi-quantitative manner, as for N nutrient effects in terrestrial ecosystems.

24 25 **AX8.4.1 Acidification Effects of Sulfur and Nitrogen**

26 The link between the deposition of oxides of S and N and reduced N from the atmosphere
27 and the subsequent acidification of soils and surface waters is well established and understood.

28 The impact of the acidification-related changes in soil and surface water chemistry on associated
29 biota is also sufficiently understood, such that chemical indicators can be specified for soils and
30 surface waters for the protection of both aquatic and terrestrial organisms. The following
31 discussion presents examples of aquatic and terrestrial receptors that are susceptible to

1 acidification by S and N, the indicators that are known to be adversely affected, and their
2 thresholds of harm.

3 4 **AX8.4.1.1 Aquatic Ecosystems**

5 6 **AX8.4.1.1.1 Responses of Chemical Indicators**

7 Atmospheric deposition of S and N generally causes increased concentrations of SO_4^{2-} in
8 surface waters and can, in some cases, cause increased concentrations of NO_3^- . An increase in
9 the concentration of either of these strong acid anions will generally result in a number of
10 additional changes in water chemistry. These can include increased concentration of base
11 cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), decreased ANC, increased concentration of hydrogen ion (H^+ ;
12 decreased pH), and increased concentration of dissolved inorganic aluminum (Al_i) (Sullivan,
13 2000).

14 Increased leaching of base cations along with SO_4^{2-} or NO_3^- can lead to base cation
15 depletion in base-poor watershed soils. With soil depletion, base cation concentrations in
16 drainage waters decrease, sometimes to levels that are well below those found prior to the
17 initiation of acidic deposition. Increased concentrations of H^+ and Al in surface water, which
18 can be toxic to fish and other aquatic biota, occur only in response to relatively high fluxes of
19 SO_4^{2-} or NO_3^- through watershed soils; sufficient to cause surface water ANC to decrease to less
20 than about 50 to 100 $\mu\text{eq/L}$. At higher ANC values, contributions of SO_4^{2-} or NO_3^- are mainly
21 balanced by increasing base cation concentrations in runoff and some decrease in ANC.

22 23 **AX8.4.1.1.2 Chemical Thresholds for Change in Biological Indicators**

24 Surface water pH has probably received the most attention with respect to effects on fish.
25 The pH range of 5.5 to 6.0 is associated with loss of sensitive fish species such as the blacknose
26 dace (*Rhinichthys atratulus*) (Baker and Christensen, 1991; Dennis and Bulger, 1995), and pH
27 near 5.0 is associated with loss of more tolerant fish species such as the brook trout (*Salvelinus*
28 *fontinalis*) (MacAvoy and Bulger, 1995). Another factor that affects fish populations is the
29 presence of elevated Al concentrations. As summarized by Baker et al. (1991), the toxicity of Al
30 fractions differs. Aluminum that is complexed with dissolved organics is relatively nontoxic;
31 waters with high organic content generally contain little toxic Al. The inorganic Al (Al_i) fraction

1 is generally regarded as the toxic component, with concentrations as low as 2 μM associated
2 with adverse biological effects.

3 Dissolved Ca^{2+} has the effect of mitigating the physiological responses of fish to acidity
4 (low pH) and dissolved Al_i (Baker et al., 1991). Depletion of Ca^{2+} from watershed soils reduces
5 the availability of Ca^{2+} both for neutralization of acidity by exchange in soil, and for mitigation
6 of surface water toxicity.

7 ANC criteria have been used extensively for evaluation of potential acidification effects
8 on aquatic ecosystems in the context of critical loads. The utility of these criteria lies in the
9 association between ANC and the surface water constituents that directly contribute to or
10 ameliorate acidity-related stress on aquatic biota. ANC is often the preferred criterion because it
11 exhibits a linear response, is not subject to measurement instability (as is pH) from dissolved
12 CO_2 , and is readily modeled using both steady state and dynamic modeling approaches. Bulger
13 et al. (2000) developed ANC thresholds for brook trout response to acidification in forested
14 headwater catchments in western Virginia, showing that brook trout populations become
15 impaired below ANC values of 20 $\mu\text{eq/L}$, and are extirpated when ANC approaches 0 $\mu\text{eq/L}$.
16 Bulger et al. (2000) point out that because the brook trout is comparatively acid tolerant, adverse
17 effects on other fish species may be expected to occur at relatively higher ANC values.
18 Empirical relationships between ANC and fish population status have been developed for brown
19 trout (*Salmo trutta* L.) and other species in Norway (Lien et al., 1992, 1996; Bulger et al., 1993).
20 For brown trout in Norwegian lakes the probability of damage is < 10% if ANC > 20 $\mu\text{eq/L}$ and
21 is 50% if ANC < 0 $\mu\text{eq/L}$. For the more sensitive species Atlantic salmon (*Salmo salar* L.), the
22 ANC critical limit is 30 $\mu\text{eq/L}$.

23 ANC criteria have also been used to evaluate the species richness of aquatic fish
24 communities. Cosby et al. (2006) showed that the number of species of fish in headwater
25 streams in the central Appalachians begins to decline in the ANC range from 50-100 $\mu\text{eq/L}$, and
26 is much reduced in the range 0-50 $\mu\text{eq/L}$. Sullivan et al. (2006) have also shown that the number
27 of fish species in Adirondack lakes declines sharply in the range of ANC 0-100 $\mu\text{eq/L}$. These
28 studies indicate that the threshold of harm for fish communities may occur at higher ANC values
29 than that for the individual fish species that have been studied to date.

30 An acidification index for macro-invertebrates in Norway developed by Raddum and
31 Fjellheim (1984) has been successfully applied in other regions in Europe (Raddum and

1 Skjelkvåle, 2001). For sites included in the ICP Waters database, the ANC limit suggested for
2 protection of macroinvertebrates is 50 µeq/L in central Europe, 30 µeq/L in the central Alps, and
3 20 µeq/L in the British Isles and Scandinavia (Skjelkvåle et al., 2000). Cosby et al. (2006)
4 demonstrated that both the diversity and evenness of benthic macroinvertebrate communities in
5 central Appalachian streams begins to decline at ANC below 100 µeq/L of ANC and are sharply
6 reduced at ANC below 50 µeq/L. Sullivan et al. (2006) examined zooplankton populations in
7 Adirondack lakes and concluded that lakewater ANC explained nearly half of the variation in
8 total zooplankton and crustacean taxonomic richness, and somewhat less of the variation in large
9 cladoceran and rotifer taxonomic richness. For all groups, the richness declined significantly
10 with lakewater ANC for lakes with ANC of 200 µeq/L or less. There was no apparent threshold
11 in the observed decline.

12 In general, most aquatic organisms show a graded response to ANC (or pH) rather than a
13 step change, and thus response curves can be fitted using logistic regression. In this way,
14 appropriate chemical targets can be defined to protect or establish a required biological status.
15 For example, logistic regression that describe the occurrence of the diatom *Achnanthes*
16 *minutissima*, the macroinvertebrate *Baetis rhodani*; non-impooverished macroinvertebrate
17 assemblages, the number of mayfly species, and the density of trout/salmonid populations in
18 relation to surface water chemistry, especially ANC, have been constructed from surveys
19 undertaken in England, Scotland and Wales (Juggins et al., 1995), and elsewhere in Europe
20 (Skjelkvåle et al., 2003).

21 The discussion above briefly reviews some of the more widely known and cited studies
22 that have published chemical thresholds for aquatic biological effects. Additional examples are
23 cited in Annex Table AX8.4-1. The text and tables are not exhaustive but are intended to
24 provide a broad perspective on the types of receptors, indicators, and thresholds that have been
25 studied and published (more detail may be found in Annex 4). In order to use these chemical
26 thresholds to estimate critical loads of S and N, it will necessary to relate the responses of the
27 chemical variables (Ca, ANC, pH, Al, etc.) in the aquatic receptors to the deposition of S and N.
28 This is usually accomplished using acidification models (see Section AX8.5).

29 30 **AX8.4.1.2 Terrestrial Ecosystems**

31

1 **AX8.4.1.2.1 Responses of Chemical Indicators**

2 Calcium and other base cations are major components of surface water acid-base
3 chemistry, and are also important nutrients that are taken up through plant roots in dissolved
4 form. Base cations are typically found in abundance in rocks and soils, but a large fraction of the
5 base cation stores are bound in mineral structures and are unavailable to plants. The pool of
6 dissolved base cations resides in the soil as cations that are adsorbed to negatively charged
7 exchange sites. They can become desorbed in exchange for H^+ or Al^{n+} , and are thus termed
8 exchangeable cations. The process of weathering gradually breaks down rocks and minerals,
9 returning their stored base cations to the soil in dissolved form and thereby contributing to the
10 pool of adsorbed base cations. Base cation reserves are gradually leached from the soils in
11 drainage water, but are constantly being re-supplied through weathering.

12 An increase in the concentration of SO_4^{2-} or other strong-acid anions in soil water will be
13 balanced by an equivalent increase in the concentration of cations. Depending upon the
14 availability of exchangeable base cations in the soil (primarily Ca^{2+} , Mg^{2+} , and K^+ ions), the
15 cations associated with increasing concentrations of strong-acid anions in soil water can be either
16 acidic or basic. The export of acidic cations (primarily H^+ and Al^{n+} ions) may contribute directly
17 to loss of ANC, or soil water acidification. Although the export of base cations serves to reduce
18 direct soil water and surface water acidification, it may also contribute to depletion of the base
19 cation supply in the soil. As the base-cation supply is depleted, the soil becomes more acidic and
20 an increasing proportion of the cation supply that is released from soils to soil water and surface
21 water consists of H^+ and Al^{n+} ions (Reuss and Johnson, 1986).

22 The supply of base cations to watershed soils can be external or internal. External
23 sources include atmospheric deposition. The primary internal sources of base cations in most
24 watersheds are weathering and soil exchange. Internal watershed sources are the main sources of
25 base cations in most upland drainage waters of the eastern United States (Baker, 1991). By
26 comparison with exchange reactions, weathering occurs at relatively slow and constant rates
27 (Turner et al., 1991; Munson and Gherini, 1991). Thus, the main source of cations for acid
28 neutralization in most watersheds is the accumulated supply of exchangeable base cations in the
29 soil. However, the size of this supply, and thus the degree to which soil and surface water
30 acidification occurs, is ultimately determined in large part by the weathering of base cations in
31 watershed bedrock.

1 There is a general tendency for trees to accumulate Ca^{2+} , and this can cause Ca^{2+}
2 depletion and soil acidification. Such effects can be exacerbated by both tree harvesting and
3 acidic deposition (Johnson et al., 1988). Several studies have suggested impending Ca^{2+}
4 depletion with intensive harvesting (Johnson et al., 1988; Federer et al., 1989; Johnson and Todd,
5 1990).

6 Sulfur retention in watershed soils delays or reduces the potential for soil and surface
7 water acidification in response to S deposition. This is particularly the case in the southeastern
8 United States, where watersheds commonly retain more than 50% of deposited S (Rochelle and
9 Church, 1987; Turner et al., 1991), largely due to S adsorption on watershed soils. However,
10 such S adsorption is capacity-limited, and as the adsorption capacity of soils becomes
11 diminished, SO_4^{2-} concentration in soil waters and surface waters can increase, contributing to
12 further acidification (Munson and Gherini, 1991; Church et al., 1992).

13 14 **AX8.4.1.2.2 Chemical Thresholds for Change in Biological Indicators**

15 There are three changes in chemical indicators resulting from acidification of soils in
16 terrestrial ecosystems that are known to have direct impacts on terrestrial plants. They are
17 increased acidity (Driscoll et al., 2001), release of Al from soil to soil water, lakes, and streams
18 (Cronan and Schofield, 1990; Cronan and Grigal, 1995; Driscoll and Postek, 1995), and
19 depletion of base cations, which is of increasing concern (Federer et al., 1989; Driscoll et al.,
20 2001). Without an adequate supply of base cations, trees are susceptible both to toxicity from Al
21 in acidic environments, and to nutritional deficiency. Consequences of base cation depletion
22 include reduced cold tolerance and increased winter injury (DeHayes et al., 1999; Schaberg
23 et al., 2000), crown dieback (Wilmot et al., 1995), increased susceptibility to pest and disease
24 (McLaughlin and Wimmer, 1999), reduced growth and increased mortality (Schaberg et al.,
25 2002), reduced regeneration and species composition changes. Base cation depletion from
26 acidification can be exacerbated by land management practices (cf. Adams et al., 2000).

27 Changes in these chemical indicators have contributed to the decline of red spruce and
28 sugar maple trees, and perhaps other species, that has been observed in the eastern United States
29 during the past four decades. Symptoms of tree decline include poor condition of the canopy,
30 reduced growth, and unusually high levels of mortality.

1 Red Spruce. Since the 1960s, more than half of large canopy trees in the Adirondack
2 Mountains of New York and the Green Mountains of Vermont, and approximately one quarter of
3 large canopy trees in the White Mountains of New Hampshire, have died (Craig and Friedland,
4 1991). Significant growth declines and winter injury to red spruce have been observed
5 throughout its range (DeHayes et al., 1999). Red spruce decline occurs by both direct and
6 indirect effects of acidic deposition. Direct effects include the leaching of calcium from leaves
7 and needles of trees (DeHayes et al., 1999), whereas indirect effects refer to acidification of the
8 underlying soil chemistry (Shortle and Smith, 1988; Cronan and Grigal, 1995). Similar impacts
9 have been observed within the Appalachian Mountain region (Sullivan et al., 2003).

10 Sugar Maple. The decline of sugar maple has been studied in the eastern United States
11 since the 1950s. Extensive mortality among sugar maples appears to have resulted from
12 deficiencies of nutrient cations, coupled with other stresses such as insect defoliation or drought
13 (Drohan et al., 1999; Horsley et al., 2000). The probability of decreased vigor of the sugar maple
14 canopy or incidence of tree death increased on sites where the supply of calcium and magnesium
15 to soil and foliage were lowest and stress from insect defoliation and drought was high (Horsley
16 et al., 2000).

17 The examples presented above illustrate that adverse acidification effects on terrestrial
18 plants and animals arise from increases in soil acidity and decreases in the availability of base
19 cations in the soil. The chemical indicators most frequently used to measure these changes are
20 soil pH, soil Al and Ca concentrations, soil base saturation, and the ratio of base cations to Al or
21 Ca to Al in soil solution. However, specification of thresholds of harm for these chemical
22 variables is difficult due to the spatial heterogeneity of soils and terrestrial communities. Unlike
23 surface water ANC or pH, the values of these soil chemical indicators, and their thresholds of
24 harm, are highly site specific and difficult to extrapolate across different receptors. Thus, while
25 the receptors and indicators are readily identifiable, the chemical thresholds needed for
26 estimating critical loads are poorly documented.

27 The discussion above briefly reviews some of the more widely known and cited studies
28 that have published chemical thresholds for aquatic biological effects. Additional examples are
29 cited in Table AX8.4-1. The text and tables are not exhaustive but are intended to provide a
30 broad perspective on the types of receptors, indicators, and thresholds that have been studied and
31 published (more detail may be found in Annex 4).

1 **AX8.4.2 Nutrient Effects of Nitrogen**

2 The deposition of either oxidized or reduced N can cause a number of ecosystem
3 disturbances that can be broadly collected under the heading “nutrient effects of N”. Nitrogen is
4 an essential nutrient for both aquatic and terrestrial organisms, and is the growth-limiting nutrient
5 in many ecosystems. For each ecosystem, there is an input level of N which will increase
6 ecosystem productivity without causing significant changes in species distribution or abundance.
7 Above that input level, adverse effects can occur in both aquatic and terrestrial ecosystem
8 compartments (cf. Stoddard, 1994; Aber et al., 1998, 2003; Gundersen et al., 1998; Bowman
9 et al., 2006). In general, ecosystems that are most sensitive to nutrient enrichment from
10 atmospheric N deposition are those that have evolved in nutrient-poor environments. Such
11 ecosystems often contain species that are prone to being replaced by opportunistic nitrophyllic
12 species when the supply of N is increased. Particularly sensitive ecosystems include alpine and
13 other grassland ecosystems, arid lands, and alpine and other oligotrophic lakes.

14 In Europe the effect of N deposition is now considered as the most relevant effect of air
15 pollution on plant diversity (de Vries et al., 2003). During the past two decades, the general
16 attention has shifted from effects of S deposition and acidification towards effects of N
17 deposition, eutrophication, and climate change. Evidence suggests that increasing N availability
18 often causes overall declines in plant species diversity. Since the recognition of nitrogen
19 deposition as one of the main drivers behind the general loss of biodiversity in Europe, a number
20 of expert workshops have taken place in order to reach agreement among specialists regarding
21 the impacts of nitrogen on various ecosystems and related critical loads (Nilsson and Grennfelt,
22 1988; Bobbink et al., 1992, 1996; Hornung et al., 1995; Achermann and Bobbink, 2003).

23 24 **AX8.4.2.1 Nutrient Effects on Aquatic Ecosystems**

25 If NO_3^- leaches into stream or lakewater as a result of increased N deposition, the result
26 can be either eutrophication, or acidification. If N is limiting for aquatic primary production, the
27 added NO_3^- can result in increased algal productivity, which can cause disruption of aquatic
28 community dynamics. If N is not limiting, then the added NO_3^- will remain in solution. If the
29 added NO_3^- is not balanced by an increase in base cation concentration, acidification of water
30 will occur.

1 Nitrate concentrations in most upland surface waters in the eastern United States are
2 commonly low due to demand for N as a nutrient, especially in regenerating forests (Aber et al.,
3 1989, 1998; Johnson and Lindberg, 1992). The deposition and fate of S in watersheds has
4 accordingly received most of the attention in regional-scale assessments of acidic-deposition
5 effects on aquatic ecosystems in the east (e.g., NAPAP, 1991; Church et al., 1992; Sullivan et al.,
6 2002). However, there have been a number of recent studies demonstrating that N deposition
7 can alter the chemistry of high elevation lakes in the western United States (e.g., Clow and
8 Sueker, 2000; Clow et al., 2003; Campbell et al., 2004), and contribute to eutrophication of
9 alpine lakes (e.g., Interlandi and Kilham, 1998; Campbell et al., 2000; Fenn et al., 2003;
10 Lafrancois et al., 2003, 2004; Baron, 2006).

11 The aquatic biota most likely to show eutrophication effects from N deposition are the
12 phytoplankton and zooplankton. Such effects are most likely to occur in fresh waters that
13 historically received very low levels of nutrient inputs. Studies have shown an increase in lake
14 phytoplankton biomass with increasing N deposition in the Snowy Mountain range in Wyoming
15 (Lafrancois et al., 2003). Community shifts in phytoplankton were observed in the Snowy
16 Mountains, with chrysophytes favored in lakes having lower N and cyanophytes and
17 chlorophytes favored in lakes having higher N (Lafrancois et al., 2003). Sediment cores from
18 lakes in the Colorado Front Range showed increasing representation of mesotrophic diatoms in
19 recent times, as compared with pre-development conditions (Wolfe et al., 2001, 2003). Saros
20 et al. showed changes in the diatom community structure of lakes in the Beartooth Mountains.

21 In a review covering the Rocky Mountains of Colorado and Wyoming, Burns (2004)
22 concluded that the effects of atmospheric N deposition on aquatic ecosystems in the region were
23 uncertain and that a widespread shift from N to P limitation had not been clearly demonstrated.
24 Burns (2004) stated that recent studies did suggest a change in diatom species dominance in the
25 1950s, but widespread species changes across lakes in the region and the role of N deposition in
26 these changes needed confirmation.

27 Little is known about the possible effects of N deposition on fish production in nutrient-
28 sensitive aquatic ecosystems because many of the lakes in sensitive, high-elevation, oligotrophic
29 regions are, or historically were, fishless or have a history of fish stocking. Adverse effects on
30 fish in Rocky Mountain lakes and streams due to nutrient enrichment from N deposition are
31 probably minimal (Burns, 2004).

1 Annex 5 provides a detailed review of the nutrient effects of N deposition on aquatic
2 receptors. That review demonstrates that most thresholds for nutrient N effects in aquatic
3 receptors in the western United States are usually expressed in terms of N deposition fluxes
4 (instead of using chemical indicators in the water body as is done for acidification effect
5 thresholds). Some examples of these thresholds are cited in Table AX8.4-2.

6 7 **AX8.4.2.2 Nutrient Effects on Terrestrial Ecosystems**

8 The N cycle is extremely complex and controlled by many factors besides atmospheric
9 emissions and deposition. Also, N inputs that may be beneficial to some species or ecosystems
10 may be harmful to others. Nitrogen inputs to terrestrial ecosystems are typically derived from
11 the atmosphere, either through natural N-fixation, or from atmospheric deposition. However, the
12 pool of available N used by plants and microbes can originate either from an external
13 (atmospheric) source, or an internal source, via decomposition and mineralization of stored
14 organic N. The amount of inorganic N released through mineralization is affected by the size
15 and quality of the soil N pool (Aber et al., 1998), which in turn can be affected by disturbance
16 and land use.

17 Increased atmospheric deposition of N to terrestrial ecosystems does not necessarily
18 cause adverse environmental impacts. In many areas, added N is taken up by terrestrial biota and
19 the most significant effect seems to be an increase in plant productivity (Kauppi et al., 1992).
20 However, under certain circumstances, atmospherically deposited N can exceed the capacity of
21 terrestrial ecosystems to take up N. In some areas terrestrial ecosystems have become N-
22 saturated and high levels of N deposition have caused elevated levels of NO_3^- in drainage waters
23 (Aber et al., 1989, 1991; Stoddard, 1994). This enhanced leaching of NO_3^- causes depletion of
24 Ca^{2+} and other base cations from forest soils and can cause acidification of soils and drainage
25 waters in areas of base-poor soils (Reuss and Johnson, 1986).

26 As increasing amounts of pollutant N become available in the terrestrial system, plants
27 and soils suffer from an excessive supply or 'eutrophication'. In plants, exposure to increased N
28 concentrations has direct effects on growth, and form, and has the potential to increase foliar N
29 content and alter N metabolism, including winter hardiness Increased N also alters soil chemistry
30 and N cycling, affects mycorrhizae, and modifies soil microbial dynamics (Takemoto et al.,
31 2001). Furthermore, litter decomposition rates are higher in areas with highest N deposition,

1 presumably because of lower C:N ratios in the forest-floor litter (Fenn and Dunn, 1989; Fenn
2 et al., 1998). The ultimate consequence of an excessive N supply to nutrient-poor communities
3 is a shift in the composition of the community such that N-sensitive plants are lost, often through
4 competition with species that more effectively utilized added N, and an overall reduction is seen
5 in biodiversity. This is supported by both empirical and theoretical evidence (Galloway et al.,
6 2003).

7 Some arid and semi-arid ecosystems in the United States are believed to be highly
8 sensitive to nutrient enrichment effects from atmospheric N deposition. For instance, the coastal
9 sage scrub community in California has been declining in land area and in shrub density over
10 about the past 60 years and is being replaced in many areas by Mediterranean annual grasses.
11 Increased N availability has been implicated in this shift. The biogeochemistry and N-dynamics
12 of high elevation spruce forests near the continental divide in Colorado have been shown to be
13 related to gradients in N deposition (Rueth and Baron, 2001, 2002). Increased soil N has been
14 implicated in the dominance of alien annual plants in the Mojave Desert (Brooks, 2003).

15 The mechanisms through which N causes these changes are many, owing to the different
16 N pollutant forms deposited, the contrasting plant receptors and the diverse range of processes in
17 which N is involved. The potential effects of nutrient N in terrestrial systems can be summarized
18 as (CEH, 2003; Rowe et al., 2005):

- 19 • Direct toxic effects of N pollutants on above ground parts of plants resulting in poor
20 growth and performance;
- 21 • Accumulation of N compounds in soil and subsequent increase in their availability to
22 plants causing change in plant community composition;
- 23 • Increased susceptibility of plants to secondary stress and disturbance factors such as
24 frost, drought, pathogens, and herbivores;
- 25 • Increased leaching of N from soils into waters with consequences for stream water
26 chemistry and aquatic biota;
- 27 • Acidification of soils leading to nutrient imbalance and changes in plant community
28 composition.

29 Annex 5 provides a detailed review of the nutrient effects of N deposition on many types
30 of terrestrial ecosystems (grasslands, deserts, forests, wetlands, etc.). The brief discussion above
31 is intended to indicate the breadth of receptors, indicators, and response patterns associated with

1 the effects of N as a nutrient in terrestrial systems. As with aquatic receptors, most thresholds
2 for nutrient N effects in terrestrial receptors are usually expressed in terms of N deposition
3 fluxes. Some examples of these thresholds are cited in Table AX8.4-2. As with aquatic
4 receptors, the effects and thresholds reported may be local and unique for some receptors, but
5 widespread and robust for others.

6 7 **AX8.4.2.3 Nutrient Effects in Europe – A Comparison**

8 Effects of nitrogen deposition are now recognized in nearly all oligotrophic natural
9 ecosystems in Europe; these include aquatic habitats, forests, grasslands (including tundra and
10 Mediterranean grasslands), oligotrophic wetlands (mire, bog, and fen), heathland, and coastal
11 and marine habitats (Achermann and Bobbink, 2003). An overview of major effects on plant
12 species diversity, including impacts on mosses, lichens, and mycorrhizae, for major terrestrial
13 ecosystems in Europe (grasslands, heathland, coastal habitats, wetlands, and forests) is presented
14 in Table AX8.4-3, based on an overview of those effects and critical loads in Bobbink et al.
15 (2003). These European empirical critical loads are presented in Table AX8.4-2 for comparison
16 with values estimated in the United States.

17 18 19 **AX8.5 CALCULATION OF CRITICAL LOADS**

20 The derivation of quantitative estimates of critical loads requires the development of
21 dose-response functions (models) for the components of the ecosystem being considered.
22 Models are needed to describe two different classes of dose-response function (Figure AX8.2-1).
23 Geochemical models describe the changes in the chemical indicators that occur as functions of
24 changes in the pollutant loads. Biological response models describe the changes in the biological
25 indicators as functions of changes in the chemical variables.

26 Models for either class of dose-response function can be developed using two general
27 approaches. Empirical models are based on direct observations of indicator response to pollutant
28 deposition. They are usually developed using statistical techniques and generally do not contain
29 a mechanistic pathway linking pollutant deposition to indicator response. Process-based models
30 are based on conceptual representations of chemical and biological mechanisms, and use
31 mathematical equations to express the inter-relationships among system components. Whereas
32 process-based models frequently also use observations of receptor responses to pollutant

1 deposition for calibration and validation, they are fundamentally different from empirical models
2 in that mechanistic pathways from pollutant deposition to indicator response are explicitly
3 included in the model structures. In general, the geochemical models used to link S and N
4 deposition to chemical indicator response are mostly process-based, whereas biological
5 responses to acidification by S and N are mostly modeled using empirical approaches. Finally,
6 both geochemical models and biological response models, whether developed using either
7 empirical or process-based approaches, can be further classified as static or dynamic depending
8 on whether or not time is included among variables.

9 10 **AX8.5.1 Empirical Models**

11 Empirical models can be constructed relating either chemical or biological indicators to
12 pollutant deposition. The empirical models currently in use for calculating critical loads employ
13 steady state approaches. This is not a necessary constraint, however, because even with no
14 knowledge of the underlying mechanisms, there exist many statistical techniques for relating the
15 time-series of outputs and inputs of ecosystems. The reason empirical critical loads models are
16 usually based on a steady state approach is primarily because time-series data of long enough
17 duration to parameterize dynamic empirical models are not generally available. In general,
18 empirical models require less complex datasets, are more straightforward to implement, and are
19 easier to understand than process-based models. For some receptors, the lack of conceptual
20 understanding of the mechanisms of indicator response to pollutant deposition renders the use of
21 process-based models problematic, and the use of empirical models is then the only viable
22 critical load analysis approach.

23 **AX8.5.1.1 Acidification Effects of Sulfur and Nitrogen**

24 Empirical models of critical loads for acidity assign critical loads to soils on the basis of
25 soil mineralogy and chemistry (UNECE, 2004). For example, at the Critical Loads Workshop at
26 Skokloster (Nilsson and Grennfelt, 1988) soil forming materials were divided into five classes on
27 the basis of the dominant weatherable minerals. A critical load range, rather than a single value,
28 was assigned to each of these classes according to the amount of acidity that could be neutralized
29 by the base cations produced by mineral weathering. The classification of soil materials
30 developed at Skokloster used a relatively small range of primary silicate minerals and

1 carbonates. A larger range of minerals was classified by Sverdrup and Warfvinge (1988) and
2 Sverdrup et al. (1990) for use in the PROFILE model (Warfvinge and Sverdrup, 1992).

3 4 **AX8.5.1.2 Nutrient Effects of Nitrogen**

5 Empirical models of critical loads for nutrient N have been developed in Europe within
6 LRTAP to set critical loads for atmospheric N deposition (e.g., UNECE, 2004). Empirical
7 critical loads of N for natural and semi-natural terrestrial ecosystems and wetland ecosystems
8 were first presented in a background document for the 1992 workshop on critical loads held
9 under the UNECE LRTAP Convention at Lökeberg, Sweden (Bobbink et al., 1992). A number
10 of European expert workshops have taken place in order to reach agreement among specialists
11 regarding the impacts of N for various ecosystems and related critical loads (Nilsson and
12 Grennfelt, 1988; Bobbink et al., 1992, 1996; Hornung et al., 1995; Achermann and Bobbink,
13 2003). Empirical relationships have also recently been developed in the United States,
14 particularly for western ecosystems (e.g., Baron et al., 1994, 2000; Williams and Tonnessen,
15 2000; Fenn et al., 2003; Burns, 2004; Nydick et al., 2004b).

16 17 **AX8.5.2 Process-Based Models**

18 A number of process-based models are currently in use for calculating critical loads using
19 both steady state and dynamic approaches. Developing a process-based modeling approach that
20 includes all appropriate chemical and biological indicators is a complex task. Some process
21 models incorporate both geochemical and biological response mechanisms in one program. An
22 alternate approach is to chain individual process-based models, for example taking the output of
23 a geochemical model and passing it as input to a biological-response model. In either approach,
24 the level of process complexity varies a great deal among the various available models. The
25 choice of a particular process-based modeling approach to be used in a critical load analysis
26 (dynamic or steady state, all-in-one or chained, etc.) will depend on the scope of the analysis, the
27 quality and quantity of available data, and the availability of resources (time and money) for the
28 analysis. The following is a brief overview of some of the process-based biogeochemical models
29 that are commonly used to calculate critical loads.

1 **AX8.5.2.1 Steady State Models**

2 The Simple Mass Balance (SMB) model is the standard model for calculating critical
3 loads for terrestrial ecosystems under the LRTAP Convention (Sverdrup et al., 1990; Sverdrup
4 and De Vries, 1994). The SMB model is a single-layer model. There also exist multi-layer
5 steady state models for calculating critical loads in terrestrial ecosystems. Examples are the
6 MACAL model (De Vries 1988) and the widely used PROFILE model (Warfvinge and
7 Sverdrup, 1992), which has at its core a model for calculating weathering rates from total
8 mineral analyses.

9 The Steady State Water Chemistry (SSWC) model (Sverdrup et al., 1990; Henriksen
10 et al., 1992; Henriksen and Posch, 2001) calculates critical loads of acidity for surface waters,
11 based on the principle that acid loads should not exceed the balance of non-marine, non-
12 anthropogenic base cation sources and sinks in a catchment, minus a buffer to protect selected
13 biota from being damaged.

14 The First-order Acidity Balance (FAB) model for calculating critical loads for surface
15 waters takes into account sources and sinks within the lake and its terrestrial catchment. The
16 original version of the FAB model was developed and applied to Finland, Norway, and Sweden
17 by Henriksen et al. (1992) and Posch et al. (1997). A modified version was first reported in
18 Hindar et al. (2000, 2001) and is described in more detail by Henriksen and Posch (2001).

19

20 **AX8.5.2.2 Dynamic Models**

21 MAGIC is a lumped-parameter model of intermediate complexity, developed to predict
22 the long-term effects of acidic deposition on surface water chemistry (Cosby et al., 1985a,b,
23 2001). The model simulates soil solution chemistry and surface water chemistry to predict the
24 monthly and annual average concentrations of the major ions in these waters. MAGIC consists
25 of: (1) a sub-model in which the concentrations of major ions are assumed to be governed by
26 simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation-
27 speciation of Al, and dissolution-speciation of inorganic carbon (C) and (2) a mass balance sub-
28 model in which the flux of major ions to and from the soil is assumed to be controlled by
29 atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff.
30 At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the
31 fluxes to and from this pool change over time owing to changes in atmospheric deposition, the
32 chemical equilibria between soil and soil solution shift to give changes in surface water

1 chemistry. The degree and rate of change of surface water acidity thus depend both on flux
2 factors and the inherent characteristics of the affected soils. MAGIC is described in more detail
3 in Annex 3.

4 PnET-BGC is an integrated dynamic biogeochemical model that simulates chemical
5 transformations of vegetation, soil, and drainage water. It was formulated by adding the sub-
6 model BGC (biogeochemistry) to PnET-CN, a model of C, water, and N balances (Aber and
7 Federer, 1992; Aber and Driscoll, 1997; Aber et al., 1997), in order to expand the model to
8 include vegetation and organic matter interactions of major elements (i.e., Ca^{2+} , Mg^{2+} , K^+ , Na^+ ,
9 Si , S , P , Al^{3+} , Cl^- , F^-), abiotic soil processes, solution speciation, and surface water processes
10 (Gbondo-Tugbawa et al., 2001). The model was initially developed for, and applied to, the
11 northern hardwood forest ecosystem. It was tested extensively at the Hubbard Brook
12 Experimental Forest, New Hampshire, including a detailed sensitivity analysis of parameter
13 values. The model has subsequently been applied to intensively-studied watersheds in the
14 Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen
15 and Driscoll, 2005b) and northern New England (Chen and Driscoll, 2005a,c). See additional
16 description in Annex 3.

17 Simulation Model for Acidification's Regional Trends (SMART2) is a soil acidification
18 and nutrient cycling model and is an extension of the dynamic soil acidification model SMART
19 (Kros et al., 1995). The original model was a relatively simple simulation of the response of soil
20 and soil water quality to atmospheric inputs. Improvements in SMART2 include processes of
21 canopy interactions, litter fall, root decay, mineralization, and root uptake of nutrients. SMART2
22 has been used primarily in European critical loads studies.

23 The Soil Acidification in Forest Ecosystems model (SAFE) was developed at the
24 University of Lund in Sweden (Warfvinge et al., 1993; Alveteg and Sverdrup, 2002). The main
25 differences between the SAFE and MAGIC models are: (a) weathering of base cations is not
26 calibrated for SAFE, but it is modeled with the PROFILE sub-model, using soil mineralogy as
27 input (Warfvinge and Sverdrup, 1992); (b) SAFE is oriented to soil profiles in which water is
28 assumed to move vertically through several soil layers, (c) cation exchange between Al, H, and
29 (divalent) base cations is modeled in SAFE with Gapon exchange reactions rather than Gaines-
30 Thomas reactions, and the exchange between the soil matrix and soil solution is diffusion-
31 limited. The standard version of SAFE does not include S adsorption although a version, in

1 which S adsorption is dependent on SO_4^{2-} concentration and pH of soil solution, has recently
2 been developed (Martinson et al., 2003).

3 ForSAFE is a mechanistic model that simulates N and C cycling and soil chemistry.
4 Climatic drivers within the model include temperature, precipitation, radiation, and deposition.
5 ForSAFE combines three established models (SAFE, PnET-CN, and DECOMP). SAFE
6 simulates soil chemistry (e.g., chemical weathering, cation exchange, leaching, and solution
7 equilibrium reactions). PnET-CN (Aber et al., 1997) is used to predict forest growth within
8 ForSAFE, through the simulation of C fixation, litterfall, and C and nutrient allocation.
9 DECOMP (Walse et al., 1998) is a dynamic, multi-layered process-oriented decomposition
10 model that incorporates the influences of temperature, moisture, pH, and Al. Very Simple
11 Dynamic soil acidification model (VSD) only includes a few key processes, such as cation
12 exchange and N immobilisation, and a mass balance for cations and N (Posch et al., 2003). VSD
13 does not consider seasonal variations, as the time step in the model is one year. The VSD model
14 is based on mass balance equations that describe soil input-output fluxes and equations
15 describing the rate-limited (e.g., uptake and silicate weathering) and equilibrium (e.g., cation
16 exchange) soil processes. Soil solution chemistry is based solely on the net element input from
17 the atmosphere (i.e., deposition minus net uptake minus net immobilization) and geochemical
18 interactions in the soil (i.e., CO_2 equilibria, weathering of carbonates and silicates, and cation
19 exchange). VSD simulates a single soil layer with a constant density and a fixed depth. The
20 concentration of the soil water leaving the compartment is assumed to be equal to the annual
21 precipitation excess.

22
23

24 **AX8.6 USE OF CRITICAL LOADS IN THE UNITED STATES –** 25 **CURRENT STATUS**

26 At the Multi-Agency Critical Loads Workshop for Sulfur and Nitrogen Deposition
27 Effects on Freshwater and Terrestrial Ecosystems, convened by the EPA, the U.S. Forest Service
28 (USFS), the National Park Service (NPS), and the U.S. Geological Survey (USGS) in May 2006,
29 approximately 75 scientists, conservation representatives, and state and federal agency officials
30 gathered to share information, discuss scientific advances, and develop a broad federal strategy
31 for advancing critical loads in the United States (U.S. Environmental Protection Agency, 2006).
32 The conclusions and recommendations of that workshop are presented below. These conclusions

1 and recommendations represent the current understanding of critical loads as scientific tool and
2 policy instrument in the United States.

3 The conclusions and recommendations below were reached by the Federal Agencies
4 sponsoring the workshop. It is worth noting that some state agencies have pursued the use of
5 critical loads independently in order to link science and policy in addressing the management of
6 natural resources. For instance, in the State of Colorado, critical loads for N deposition that were
7 developed for Rocky Mountain National Park (Baron, 2006) are being used to develop goals for
8 N emissions reductions by the State of Colorado, EPA, and NPS. (See “Nitrogen Deposition
9 Reduction Plan” at <http://www.cdphe.state.co.us/ap/rmnp.html>)

10

11 **AX8.6.1 Current Recommendations on Critical Loads Uses in the United** 12 **States**

13 The participants in the Multi-Agency Critical Loads Workshop developed a set of
14 findings and recommendations to help advance critical loads usage in the United States. The
15 “areas of agreement” published in the workshop report (U.S. Environmental Protection Agency,
16 2006) included the following:

- 17 • A critical load is defined as: a quantitative estimate of the exposure to one or more
18 pollutants below which significant harmful effects on specific sensitive elements of
19 the environment do not occur according to present knowledge (Nilsson and Grennfelt,
20 1988).
- 21 • Despite reductions in S and N emissions in the United States, deposition rates still
22 exceed preindustrial levels and acidification and eutrophication effects remain
23 widespread.
- 24 • Critical loads can be used to better understand impacts of atmospheric deposition,
25 assess the effectiveness of emissions programs, and guide natural resource
26 management.
- 27 • The development of critical loads is a process that is subject to continued
28 development and improvement as knowledge advances.
- 29 • Adequate information exists to move forward with the development and limited
30 application of critical loads in some regions and ecosystems in the United States.

- 1 • An intensive research and monitoring agenda should be pursued to support the
2 development and refinement of critical loads in the United States.
- 3 • Critical loads should be based on a matrix of biological and chemical indicators for
4 aquatic and terrestrial ecosystems that account for acidification, N saturation, and
5 eutrophication effects and are relevant to the geographic area or ecosystem of
6 concern.
- 7 • Adequate information exists to establish harmful effect thresholds for some indicators
8 based on specific protection and recovery objectives defined by policymakers and
9 managers.
- 10 • Dynamic models provide the most accurate site-specific information and account for
11 time-dependent processes, but are generally too data intensive to be applied across
12 large geographic areas at present. Simple mass balance models can be applied to
13 current conditions in large geographic areas, but in some instances do not adequately
14 highlight some sensitive areas because they tend to average conditions across the
15 landscape. Hybrid approaches that link observational datasets with dynamic and
16 steady state models represent a useful approach for regionalizing site-specific
17 information.

18 **AX8.6.2 Questions and Limitations Regarding Critical Loads Uses in the** 19 **United States** 20

21 The participants in the Multi-Agency Critical Loads Workshop also developed a set of
22 “Questions Needing Further Discussion” (U.S. Environmental Protection Agency, 2006):

- 23 • What are the appropriate applications of critical load estimates to policy and
24 management issues given current knowledge? For applications where buy-in to an
25 incremental process does not exist, greater investment in critical loads methods may
26 be needed before this application can be pursued.
- 27 • How strong is the relationship between specific indicators, thresholds, and biological
28 responses?
- 29 • What are the suitable interpretations and uses of existing databases for the
30 development of national simple mass balance critical load models?

1 **AX8.6.3 Critical Loads Research and Monitoring Needs**

2 Finally, the participants in the Multi-Agency Critical Loads Workshop presented a list of
3 “Critical Loads Research and Monitoring Needs” (U.S. Environmental Protection Agency,
4 2006), which are summarized below.

5 6 **AX8.6.3.1 Emissions and Deposition**

- 7 • Update N and S emissions inventories on a state-by-state basis back to the 1900s to
8 correspond with methods used in current emissions inventories.
- 9 • Develop ammonia emissions inventory.
- 10 • Improve dry deposition estimates for S and N.
- 11 • Improve total S and N deposition estimates.
- 12 • Measure gaseous ammonia concentrations.
- 13 • Add ammonia deposition measurements to current networks.
- 14 • Improve estimates of total deposition in complex terrain.
- 15 • Develop N and S deposition maps for North America.

16 17 **AX8.6.3.2 Soils**

- 18 • Improve spatial coverage and representativeness of soil chemistry databases,
19 particularly in sensitive terrain.
- 20 • Increase soil monitoring.
- 21 • Improve estimates of mineral weathering rates.
- 22 • Develop soil archiving and well characterized reference samples to promote cross-
23 laboratory comparisons.
- 24 • Expand research on the nature and size of soil nutrient pools.
- 25 • Conduct research on threshold values of soil quality for biologic responses.
- 26 • Determine N supply rates in different soil types.
- 27 • Investigate N soil accumulation rates in arid lands and implications for critical loads.

28 29 **AX8.6.3.3 Surface Waters**

- 30 • Incorporate TIME and LTM surface water monitoring programs into a larger network
31 with better geographic coverage (e.g., the West and Southeast).

- 1 • Improve spatial coverage and representativeness of surface water chemistry
2 databases, particularly in sensitive and complex terrain.
- 3 • Integrate fixed-site monitoring with regional probability monitoring design.
- 4 • Continue to monitor major drivers of acidity.
- 5 • Build critical loads considerations (e.g., validation, improvement, regionalization)
6 into monitoring from the start by combining chemistry, hydrology, deposition and
7 biology, and integrating site-specific models and measurements into regional
8 contexts.
- 9 • Expand research to understand what is driving dissolved organic carbon (DOC)
10 changes in the East.
- 11 • Analyze the impact of groundwater transport on recovery times.

12 13 **AX8.6.3.4 Biological Effects**

- 14 • Develop better understanding of the link between chemical indicators and biological
15 response (e.g., quantify the minimum N level at which plankton communities shift).
- 16 • Conduct additional research on the sequential impacts of N and relationship between
17 N deposition and ecosystem impacts.
- 18 • Integrate critical load estimates with biodiversity and climate change interactions.
- 19 • Undertake more research on biological change and “harmful effects” to help establish
20 appropriate critical loads thresholds (e.g., in arid lands, what level of productivity of
21 exotic invasive species will cause the reduction versus the extinction of native
22 species?).
- 23 • Collect sediment cores from lakes that vary in rates of N deposition to track changes
24 in diatom assemblages.

25 26 **AX8.6.3.5 Critical Loads Models**

- 27 • Improve representation of N dynamics in models.
- 28 • Expand models to include ammonia.
- 29 • Improve explicit consideration of changing base cations and DOC.
- 30 • Conduct ground-truthing of forest sensitivity and other models.

- 1 • Integrate water flowpaths into nutrient cycling models since lateral and vertically
- 2 upward flowpaths are common.
- 3 • Understand and quantify uncertainties in models.
- 4 • Conduct site level model comparisons of dynamic and simple mass balance models.
- 5 • Integrate observational databases with steady state and dynamic models.
- 6 • Incorporate capacity to understand and evaluate climate change interactions.

TABLE AX8.4-1. EXAMPLE THRESHOLDS FOR EFFECTS OF ACIDIFICATION BY S AND N DEPOSITION ON INDICATORS IN AQUATIC AND TERRESTRIAL RECEPTORS (SEE TEXT FOR ADDITIONAL EXAMPLES)

Indicator	Threshold	Biological Response	Citation
Fish (trout)	pH < 5.0-5.2	Episodic acidification threshold in Appalachian streams	Baker et al. (1996)
Fish (trout)	Al > 100-200 µg/L	Episodic acidification threshold in Appalachian streams	Baker et al. (1996)
Fish (52 species)	pH < 6.0 (equiv to ~30 µeq/L ANC)	pH threshold for presence of fish in streams	Driscoll et al. (2003)
Fish (eggs of native western cutthroat trout)	pH 5.0	Mortality of native western trout eggs	Woodward et al. (1989)
Fish (eggs of native western cutthroat trout)	pH 6.0 or less	Reduced growth and survival of cutthroat trout alevins and swim-up larvae in lab studies	Woodward et al. (1989)
Fish (brook trout)	ANC 20-50, ANC 0-20, ANC < 0	Brook trout response to ANC in western Virginia	Bulger et al. (2000)
Soils	BC/AL ratio <1	Harmful effect on tree growth or vitality in Europe	Sverdrup and Warfvinge (1993)
Soils	Ca/Al ratio <1	General thresholds for toxicity to trees	Cronan and Grigal (1995)

TABLE AX8.4-2. EXAMPLE THRESHOLDS FOR NUTRIENT EFFECTS OF N DEPOSITION ON INDICATORS FOR AQUATIC AND TERRESTRIAL RECEPTORS (SEE TEXT FOR ADDITIONAL EXAMPLES)

Indicator	Threshold	Biological Response	Citation
Amphibians	2.5 mg/L NO ₃ -N in water	Laboratory threshold for amphibian sub-lethal effects	Rouse et al. (1999)
Amphibians	0.5 mg/L NO ₂ -N, ~2.5 mg NO ₃ -N in water	Laboratory threshold for amphibian (LC50) effects	Marco and Blaustein (1999)
Freshwater invertebrates	2 mg/L NO ₃ -N in water	Sub-lethal effects	Camargo et al. (2005)
Algae	1 mg/L N in water	Changes in algal community structure in western lakes	Nydick et al. (2004b)
Diatoms	1.5 kgN/ha/yr wet deposition	Species shifts from nitrogen-limited to nitrophilic types	Baron (2006); Saros et al. (2003)
Soil N saturation	7 kgN/ha/yr deposition	NO ₃ leaching in NE U.S.	Driscoll et al. (2003)
Soil N saturation	6.3 kgN/ha/yr deposition	NO ₃ leaching in NE U.S. at base of watershed	Aber et al. (2003)
Soil N saturation	10 kgN/ha/yr deposition	NO ₃ leaching in NE U.S. as whole watershed avg.	Aber et al. (2003)
Soil N saturation	Soil C:N ratio <30	NO ₃ leaching in European coniferous forests	Kristensen et al. (2004)
Plant N enrichment	Foliar N <13 mg N/g	NO ₃ leaching in European coniferous forests	Kristensen et al. (2004)
Soils	Soil C:N ratio <29	Increased mineralization in western U.S.	Rueth and Baron (2002)
Soils	Soil C:N ratio 22	Increased N nitrification (microbial activity)	Aber et al. (2003)
Lichens	0.04-0.08 mg N/l wet deposition	Threshold for community changes toward nitrophilous lichen species in Pacific NW	Geiser and Neitlich (2007)
Alpine grasses and forbs	4 kg N/ha/yr total deposition	Increased grass species and biomass	Bowman et al. (2006)

TABLE AX8.4-3. BIOLOGICAL INDICATORS FOR THE EFFECTS OF ELEVATED N DEPOSITION AND RELATED EMPIRICAL CRITICAL LOADS FOR MAJOR ECOSYSTEM TYPES (ACCORDING TO THE EUNIS CLASSIFICATION) OCCURRING IN EUROPE

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
<i>Grasslands and tall forb habitats (E)</i>		
Sub-atlantic semi-dry calcareous grassland	Increased mineralization, nitrification and N leaching; increased tall grasses; decreased diversity	15-25
Non-mediterranean dry acid and neutral closed grassland	Increase in nitrophilous graminoids, decline of typical species	10-20
Inland dune grasslands	Decrease in lichens, increase in biomass, accelerated succession	10-20
Low and medium elevation hay meadows	Increased tall grasses, decreased diversity	20-30
Mountain hay meadows	Increase in nitrophilous graminoids, changes in diversity	10-20
Moist and wet oligotrophic grasslands	Increase in tall graminoids, decreased diversity, decrease in bryophytes	10-25
Alpine and subalpine meadows	Increase in nitrophilous graminoids, changes in diversity	10-15
Moss and lichen dominated mountain summits	Effects on bryophytes and lichens	5-10
<i>Heathland habitats (F)</i>		
Northern wet heaths	Decreased heather dominance, transition heather to grass, decline in lichens and mosses	10-20
Dry heaths	Transition heather to grass, decline in lichens	10-20
Arctic, alpine, and subalpine scrub habitats	Decline in lichens, mosses, and evergreen shrubs	5-15

TABLE AX8.4-3 (cont'd). BIOLOGICAL INDICATORS FOR THE EFFECTS OF ELEVATED N DEPOSITION AND RELATED EMPIRICAL CRITICAL LOADS FOR MAJOR ECOSYSTEM TYPES (ACCORDING TO THE EUNIS CLASSIFICATION) OCCURRING IN EUROPE

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
<i>Coastal habitat (B)</i>		
Shifting coastal dunes	Increased biomass, increased N leaching	10-20
Coastal stable dune grasslands	Increase in tall grasses, decreased prostrate plants, increased N leaching	10-20
Coastal dune heaths	Increase in plant production, increased N leaching, accelerated succession	10-20
Moist to wet dune slacks	Increase in biomass and tall graminoids	10-25
<i>Mire, bog, and fen habitats (D)</i>		
Raised and blanket bogs	Changed species composition, N saturation of Spagnum	5-10
Poor fens	Increased sedges and vascular plant, negative effects on mosses	10-20
Rich fens	Increase in tall graminoids, decreased diversity, decrease of characteristic mosses	15-35
Mountain rich fens	Increase in vascular plants, decrease in bryophytes	15-25
<i>Forest habitats (G)</i>		
Mycorrhizae	Reduced sporocarp production, reduced below ground species composition	10-20
Ground vegetation	Changed species composition, increased nitrophilous species; increased susceptibility to parasites (insects, fungi, virus)	10-15
Lichens and algae	Increase in algae; decrease in lichens	10-15

Source: Adapted from Achermann and Bobbink (2003).

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AX9. EFFECTS OF NO_Y, NH_X, AND SO_X ON MAN-MADE STRUCTURES AND MATERIALS

AX9.1 INTRODUCTION

The purpose of this chapter is to summarize the research published since the most recent Air Quality Criteria Documents (AQCDs) on materials and structures damage caused by: (1) nitric oxide (NO), nitrogen dioxide (NO₂), and their combination (NO + NO₂ = NO_X); the organic and inorganic reaction products of NO_X (denoted as NO_Z); and the combination of NO_X and NO_Z (NO_X + NO_Z = NO_Y), (2) the effects of ammonia and ammonium (NH_X), and of (3) sulfur oxides (SO_X). Materials and structures exposed to the environment are subject to damage from exposure to sunlight, moisture, salt, windblown dust, and cycles of temperature and humidity, whether or not air pollutants are present. However NO_Y, NH_X, and SO_X air pollutants may cause such damage to be greater or occur more rapidly than with natural environmental factors alone. Damage to materials and structures may be physical, potentially affecting the durability or maintenance needs of a material or structure, or may be purely aesthetic, affecting only the outward appearance of the material or structure. In the case of historical buildings, monuments, or artifacts, aesthetic damage may be a relevant concern.

Note that very extensive work related to materials damage from acidic deposition related to sulfur (S) and nitrogen (N) was conducted in the 1980s as part of the National Acid Precipitation Assessment Program (NAPAP). The results of that work are well known to U.S. Environmental Protection Agency (EPA) and so are not discussed here, but can be found in the relevant NAPAP final report (NAPAP, 1991). For the N oxides, the most recent AQCD was published in 1993 (U.S. Environmental Protection Agency, 1993), and that for sulfur dioxide (SO₂) was published in 1982 (U.S. Environmental Protection Agency, 1982). However, NO_Y/NH_X/SO_X species are important components of atmospheric particulate matter (PM), and as a result material and structural effects of NO_Y, NH_X, and particularly SO_X were also addressed in the 2004 AQCD for atmospheric PM (U.S. Environmental Protection Agency, 2004). In compiling information for this chapter on NO_Y/NH_X/SO_X effects, the information presented in the 1993 AQCD for Oxides of Nitrogen (U.S. Environmental Protection Agency, 1993) and the 2004 PM AQCD (U.S. Environmental Protection Agency, 2004) was updated by literature

1 searches reaching back to approximately 1992. This update was based on peer-reviewed
2 literature, with a focus on studies that were conducted in the United States, that evaluated effects
3 at realistic ambient air pollutant levels, and that treated $\text{NO}_Y/\text{NH}_X/\text{SO}_X$ as components of a
4 complex mixture of air pollutants. These latter two factors result in an emphasis on studies done
5 with exposures to ambient atmospheric pollution, rather than exposures at high levels, e.g., in
6 test chambers. The studies cited in this chapter were selected from those found in a broad
7 literature search based on criteria that they (1) address damage caused by exposure to
8 atmospheric contaminants, (2) focus on S and N containing species, (3) provide a clear link
9 between pollutant concentrations and damage, and (4) give complete information on methods
10 and data analysis used.

11 Broadly speaking, the pace of research on NO_Y , NH_X , and SO_X materials effects has
12 slowed considerably since the publication of the previous AQCDs. In particular, although the
13 literature searches conducted for this update emphasized studies conducted in the United States,
14 the great majority of the relevant publications found originated in Europe or Asia. The relative
15 scarcity of recent U.S. studies on structural and materials damage from $\text{NO}_Y/\text{NH}_X/\text{SO}_X$ may be a
16 natural fall-off in research in this area, following the extensive efforts that were summarized in
17 the previous AQCDs and in the NAPAP report. Certainly the greater number and age of
18 aesthetically valuable buildings and archeological sites in Europe and Asia, relative to the United
19 States, may be a driving force for current research in those geographic areas. In this chapter,
20 each discussion of the effects of $\text{NO}_Y/\text{NH}_X/\text{SO}_X$ on a material type begins with a brief summary
21 of the state of knowledge as represented in the previous AQCDs, and then continues with a
22 description of recent research on that type of material.

23
24

25 **AX9.2 ENVIRONMENTAL EXPOSURES OF MATERIALS**

26

27 **AX9.2.1 Mechanisms of Materials Damage**

28 As noted in the introduction to this chapter, materials damage may occur by natural
29 physical processes without the involvement of $\text{NO}_Y/\text{NH}_X/\text{SO}_X$ air pollutants. When those
30 pollutants are involved, the destructive processes may be chemical, physical, or even biological.
31 Chemical processes include direct reactions with gaseous pollutants such as NO_2 , SO_2 , or nitric
32 acid (HNO_3), reaction with electrolytes (proton (H^+), ammonium (NH_4^+), nitrate (NO_3^-), sulfate

1 (SO₄⁻), etc.) in water on material surfaces, and reactions with chemicals in deposited particulate
2 matter. An example of a physical process is the deterioration of stone that occurs when gypsum
3 (CaSO₄·2H₂O) forms from reaction of SO₂ with the calcium carbonate (CaCO₃) in the stone.
4 The gypsum thus formed occupies a larger volume than the original stone, causing the surface to
5 deteriorate. Biological degradation can occur when deposited pollutants are oxidized to acids by
6 fungi or bacteria.

7 A key factor affecting damage to certain materials, primarily metals and stone, is the
8 frequency and duration of wetting of the surface. Liquid water on materials surfaces can
9 dissolve deposited pollutants, producing reactive electrolyte solutions, and can serve as a
10 reaction medium in which S and N oxides are converted to more damaging acids. Pollutants
11 deposited on surfaces may contain or form hygroscopic salts, which enhance the formation of
12 liquid water and thereby increase materials damage. As Dubowski et al. (2004) have shown, the
13 deposition of HNO₃ onto surfaces can increase the extent of wetting of surfaces, and promote the
14 damaging effects of both HNO₃ and other pollutants.

15

16 **AX9.2.2 Deposition Processes**

17 Air pollutants come into contact with surfaces through both dry and wet depositional
18 processes. Dry deposition occurs in the absence of precipitation and is governed by factors such
19 as atmospheric turbulence, the chemical and physical properties of the pollutant (e.g., water
20 solubility and reactivity for gases; size, density, and shape for particles), and surface properties
21 (e.g., reactivity, roughness, moisture level, and pH). The deposition rate of a pollutant is
22 proportional to the atmospheric concentration of that pollutant. Dry deposition of gases depends
23 primarily on the water solubility of the gas, the moisture level on the surface, and the pH of the
24 electrolyte formed on the surface of a material. Nitric acid and ammonia are deposited very
25 efficiently to most surfaces regardless of the surface properties of the material. Particle size
26 plays an important role in determining the rate of deposition of particles to a surface. For very
27 small particles, Brownian diffusion is the dominant deposition mechanism. For larger particles,
28 inertial impaction and gravitational settling are important deposition processes. Particles
29 between 0.05 and 2 μm, which include most atmospheric particles containing NO₃⁻, SO₄⁻, and
30 NH₄⁺, may have long atmospheric lifetimes in the absence of moisture.

1 Wet deposition occurs when gas or particle species come into contact with moisture (as
2 rain, fog, snow, or ice). Atmospheric species can be dissolved into moisture and then deposited
3 as the moisture falls to the ground. Solubility and the chemical reactions of the dissolved species
4 determine the degree of wet deposition. For acid gases, high dissolution is observed due to the
5 dissociation of the dissolved species in water. Wet deposition of pollutants occurs at a faster rate
6 than dry deposition, but is only an important mechanism when moisture is present.

7 **AX9.2.3 Chemical Interactions of Nitrogen and Sulfur Oxide Species**

9 Nitrogen and sulfur oxide species are subject to many atmospheric reactions in both the
10 gaseous and particulate phase. Emissions of S and N oxides are primarily in the form of gas
11 phase SO_2 and NO_x . In the atmosphere, these species can be oxidized by reaction with other
12 atmospheric species to gas and particle phase product species. On the surface of materials, the
13 oxides are generally oxidized to their acid forms (nitrous acid (HNO_2), HNO_3 , sulfurous acid
14 (H_2SO_3), and sulfuric acid (H_2SO_4)), which then dissociate to form nitrite, nitrate, sulfite, and
15 sulfate ions. These acids are the primary species responsible for damage to materials by S and N
16 pollutants. Ammonia, the primary gaseous basic compound in the atmosphere, can partly or
17 completely neutralize these acids in particulate matter or in the aqueous phase, forming NH_4^+
18 ions.

19 On the surfaces of materials, N and S species can react to form a variety of degradation
20 products. On metals and stone, the possible degradation products include nitrite, nitrate, sulfite,
21 and sulfate species as well as minerals that incorporate nitrate or sulfate into a more complex
22 composition. These degradation products may be more or less reactive to further degradation
23 than the original material. Degradation products that are more reactive, or those that are soluble
24 in water, do not have long lifetimes on a material surface. They undergo further chemical
25 reactions and are transformed to other species, or they are washed off the surface by
26 precipitation. Products which are less reactive and less soluble in water than the original
27 material may form a protective layer on the surface of the material which inhibits or prevents
28 further damage from atmospheric pollutants. Products that are more reactive or water-soluble
29 than the original material are readily removed, exposing the surface to more damage. The
30 protectiveness of the products formed depends on the complex mixture of species present and the
31 physical/chemical properties of the material.

1 Synergistic effects, which influence the rate of degradation of materials, are possible in
2 atmospheres containing a complex mixture of pollutants. NO_x may enhance the oxidation of
3 sulfite to sulfate and lead to faster rates of corrosion. The deposition velocity of SO₂ and NO_x
4 may be influenced by the presence of HNO₃ deposited to the surface due to the increased degree
5 of surface wetting.

6 7 **AX9.2.4 Materials Damage Experimental Techniques**

8 The NO_y/NH_x/SO_x air pollutants are comprised of numerous distinct chemical species,
9 which may exist in the gaseous and/or particulate phases in the atmosphere, as well as in
10 dissolved form in atmospheric precipitation and in condensed water on surfaces. In order to test
11 the damaging effects of NO_y/NH_x/SO_x species on man-made materials, it is often necessary to
12 simplify the system by testing under controlled laboratory conditions, typically with a very
13 limited set of pollutants in a test chamber. Such tests generally use pollutant concentrations that
14 are greatly elevated relative to ambient atmospheric levels, and may also use exaggerated
15 temperature, humidity, or wetting, to accelerate the development of materials damage so that it
16 can be detected. Chamber tests may not accurately mimic the mass transfer of pollutants in the
17 atmosphere, and efforts in such tests to isolate the effects of one pollutant from the complex
18 mixture present in the atmosphere are unrealistic. As a result, chamber tests may provide
19 valuable information on potential effects and mechanisms involving ambient air pollutants, but
20 cannot accurately predict the corrosion rates or effects of such pollutants in real situations.

21 Exposing materials of interest to the ambient atmosphere for extended time periods can
22 provide a realistic look at the effects of air pollutants on materials. However, such ambient
23 exposure tests are limited by the occurrence of natural (i.e., non-air pollutant) materials damage,
24 and by the complexity of the NO_y/NH_x/SO_x system. While it is relatively easy to determine
25 which materials suffer more or less damage during equivalent exposures to ambient air pollution,
26 it is extremely difficult to determine which air pollutants are responsible for the observed
27 damage. This is due to the co-occurrence of all air pollutants simultaneously, complexities in
28 accurately measuring the suite of NO_y/NH_x/SO_x species, and interconversions among species
29 (e.g., SO) and SO₄⁻, NO_x and HNO₃) related to contact with materials or with moisture. The
30 amount of time that surfaces are wet is a key factor in the extent of materials damage, and this
31 factor may be difficult to determine in ambient exposures, because the presence of air pollutants

1 themselves may enhance surface wetness on the microscale beyond that expected based on
2 meteorological conditions (Dubowski et al., 2004). Ambient exposure tests lead to retrospective
3 analyses, in which meteorological and air pollutant data, surface analyses, and measurements of
4 chemical and physical properties are evaluated statistically to estimate the impacts of air
5 pollutants on the exposed materials.

6 7 8 **AX9.3 EFFECTS ON DYES AND TEXTILES**

9 10 **AX9.3.1 Fading of Dyes**

11 The fading of dyes by N oxides has long been recognized, and dye manufacturers have
12 worked to produce products less susceptible to this effect, through both improved dye chemicals
13 and the use of inhibitors in dye formulations to minimize fading. Fading has been observed with
14 both red and blue dyes, both on natural fibers (e.g., cotton, silk, wool) and on synthetics (e.g.,
15 nylon, rayon, polyester). The fading effect of NO₂ is generally reported to be greater than that of
16 NO on various dyes with various fabrics. In exposures of dyed fabrics to ambient air, test
17 samples must be shielded from sunlight, to avoid the substantial fading of dyes that results from
18 sunlight exposure. Under such conditions, NO₂ and ozone (O₃) are often found to be about
19 equally important in the fading of dyed fabrics.

20 21 **AX9.3.2 Degradation of Textile Fibers**

22 Nitrogen oxides can degrade a variety of synthetic fibers, with the greatest effects seen
23 with nylon. With NO₂, the damage to nylon occurs due to breaking of the polymer chain (i.e.,
24 chain-scissioning). Similar weakening of nylon has been observed in tests with elevated
25 concentrations of HNO₃. A synergistic effect was observed between mechanical stress and NO_x
26 in the degradation of oriented nylon-6 fibers (Smith and DeVries, 1993).

27 28 29 **AX9.4 EFFECTS ON PLASTICS AND ELASTOMERS**

30 The group of materials called plastics includes a wide variety of polymeric materials such
31 as polyethylene, polypropylene, polystyrene, polyurethanes, acrylic polymers, phenolics, and
32 fluorocarbon polymers, among others. Plastic materials may include other components such as
33 hardeners or plasticizers, and fillers that may impart properties such as physical strength.

1 Elastomers are polymers that can stretch to at least their twice their normal dimensions and then
2 return to their original dimensions when the stress is removed. Examples of elastomers include
3 various rubber formulations and neoprene. Plastics and elastomers can be damaged by NO₂,
4 SO₂, and O₃, as well as by UV radiation in sunlight, and some studies have been designed to
5 separate the effects of these factors.

6 Chamber studies at relatively high pollutant concentrations with sunlight or UV light
7 have generally shown greater damage than from the pollutants alone. NO₂ is damaging to a
8 variety of polymers and elastomers, causing either chain-scissioning or cross-linking (formation
9 of additional bonds between polymer chains) depending on the polymer. Polypropylene is
10 reported to be damaged more severely by SO₂ than by NO₂. Elastomers are damaged more
11 severely than plastics. In tests where light and NO₂ have been present simultaneously, much of
12 the damage observed in chamber tests has been attributed to O₃, produced by the interactions of
13 the pollutants and UV light, rather than to NO₂ alone. In studies in which the same pollutant
14 concentrations are present both with and without light, the greater damage observed in samples
15 exposed to the light is often attributed to the light itself, when in fact chemical processes initiated
16 by light (such as the formation of O₃) undoubtedly also play a part.

17 Cellulose nitrate can break down through hydrolytic, thermal, and photochemical
18 reactions. Addition of plasticizer to cellulose nitrate slows the degradation substantially. NO₂ is
19 of particular interest with regard to cellulose nitrate because it is not only capable of causing
20 damage, but is also produced as a result of damage to the material (Shashoua, 2006). NO₂ is
21 formed when N-O bonds connecting cellulose rings are broken. The NO₂ formed will then
22 further degrade cellulose nitrate, thus the degradation is an autocatalytic process.

23
24

25 **AX9.5 EFFECTS ON METALS**

26 Metals are considered to be the materials most subject to damage from the
27 NO_y/NH_x/SO_x air pollutants, and have been the subject of a great deal of research. The nature
28 and concentration of the pollutant, its rate of deposition, and especially the duration of wetting of
29 the surface are key factors in the corrosion of metals. Numerous studies have indicated corrosion
30 rates of metal surfaces on the order of 1 to several micrometers per year (µm/yr) under real or
31 simulated atmospheric conditions.

1 Table AX9.5-1 summarizes the materials tested, exposure conditions, and findings of
2 recent studies related to the effects of NO_Y/NH_X/SO_X air pollutants on metals. The studies listed
3 in Table AX9.5-1 are discussed where applicable in the following sections.

4 **AX9.5.1 Role of NO_Y, NH_X, and SO_X in the Corrosion Process**

6 In the atmosphere the NO_Y/NH_X/SO_X pollutants occur together, along with other
7 pollutants such as O₃ or chloride salts. While wetting of metals surfaces is the single greatest
8 factor promoting corrosion, an important observation is the enhanced damage that occurs due to
9 interactions among this mixture of pollutants. It must be noted that in many studies the various
10 NO_Y/NH_X/SO_X species have not been adequately separated or quantified, and this may be the
11 cause of conflicting observations from some studies. However, some generalizations can be
12 made. Sulfur and chloride pollutants are generally more important at causing metals corrosion
13 than N pollutants, however NO_X (or NO_Y) and SO₂ together have been shown to be more
14 damaging than SO₂ alone. The combination of NO₂ and SO₂ has been shown to result in a
15 synergistic effect where the total damage from the mixture is greater than the additive damage
16 from the two pollutants separately (Svensson and Johansson, 1993a). This effect may be due to
17 enhanced wetting of the surfaces caused by NO_Y pollutants, resulting in corrosion at lower
18 relative humidities than would otherwise be the case. This enhancement has been attributed to
19 the formation of hygroscopic nitrate salts, but may also be caused directly by the deposition of
20 gaseous HNO₃ onto the surface (Dubowski et al., 2004). The corrosion effect of HNO₃ on zinc,
21 copper, and steel is larger than that of SO₂ alone or a mixture of SO₂ and NO₂ (Samie et al.,
22 2007).

23 Although deposition of NO_Y/NH_X/SO_X species in particulate matter can soil metal
24 surfaces, such deposition does not directly result in substantial metals damage. However, under
25 wet conditions these soluble species form an electrolytic solution that can cause corrosion.
26 Corrosion of steel and zinc has been found to depend on the surface electrolyte irrespective of
27 the presence of particles (Askey et al., 1993).

28 Temperature has been found to have a complex effect on metals corrosion. Lower
29 temperatures tend to increase surface wetness, but decrease the diffusivity of gaseous pollutants,
30 and may reduce the rates of some reactions that convert SO₂ and NO_X to sulfuric and nitric acids.
31 Thus, the effect of temperature changes on long-term corrosion rates can be hard to predict.

1 **AX9.5.2 Effect on Economically Important Metals**

2 Steel is the most common and economically important structural metal, and is often used
3 in galvanized form (i.e., with a protective coating of zinc). SO₂ is generally reported to be more
4 corrosive than NO_x, however for well-protected steel the effects of ambient air pollutants are
5 usually a small increment on top of the natural weathering process. The N pollutants can have an
6 enhancing effect on the corrosion caused by the S pollutants. This is attributed to the increased
7 wetting that can result from the presence of hygroscopic NO₃ salts. Relative humidity has been
8 shown to be very important in the corrosion of steels by SO₂ with much slower corrosion rates
9 observed when the relative humidity is below 70% (Dehri et al., 1994). The presence of SO₂ has
10 been shown to reduce the corrosion pitting of iron induced by sodium chloride (NaCl) but there
11 may be an overall synergistic effect among SO₂, NO₂, and NaCl (Weissenrieder et al., 2004).
12 Steel corrosion rates have been shown to decrease over time (Almeida et al., 2000) (Damian and
13 Fako, 2000) approaching steady state rates after approximately 4000 days (Damian and Fako,
14 2000).

15 Zinc corrosion has been shown to be inversely dependent on temperature (Svensson and
16 Johansson, 1996). Corrosion products formed on zinc in polluted environments are less water
17 soluble, and therefore more protective against further corrosion, than corrosion products formed
18 in clean environments (Vilche et al., 1995). The combination of SO₂ and NO₂ showed
19 synergistic (i.e., greater than simply additive) corrosive effects on zinc (Svensson and Johansson,
20 1993a). SO₂ slowed the NaCl-induced corrosion of zinc while NO₂ accelerated that corrosion
21 (Svensson and Johansson, 1993b).

22 Aluminum is naturally protected from corrosion by a formation of a durable surface film,
23 but some effects of the NO_y/NH_x/SO_x pollutants have been observed. Minimal damage is
24 caused to aluminum by NO_x. The mixture of SO₂ and NO_x is variously said to be either more or
25 less corrosive to aluminum than SO₂ alone. The deposition rate of SO₂ to aluminum was shown
26 to increase in the presence of O₃, but no effect on SO₂ deposition rate was found for NO₂
27 (Blucher et al., 2005). Interaction between SO₂ and NaCl results in an increased corrosion rate
28 but decreased pitting of aluminum compared to NaCl alone (Blucher et al., 2005). Oesch and
29 Faller (1997) found that SO₂ is more corrosive to aluminum than NO₂ and that there is no
30 difference in aluminum corrosion rate when exposed to NO or clean air.

1 Mixture of NO_x and SO₂ are more corrosive to copper than either pollutant alone.
2 When hydrogen sulfide (H₂S) and O₃ were also evaluated for damage to copper, they also were
3 found to be more damaging to copper than NO_x. The corrosion rate of copper exposed to SO₂ or
4 NO₂ has been shown to slow over time (Oesch and Faller, 1997; Leuenberger-Minger et al.,
5 2002). The corrosion rate of copper in the presence of NO₂ is greater than in clean air. In the
6 first 24 h of exposure to NO₂, an acidic electrolyte is formed on the surface that dissolves copper
7 oxides and results in an increased corrosion rate (Dante and Kelly, 1993). Synergistic effects
8 have been seen between SO₂ and O₃ (strong) and NO₂ (weak) (Aastrup et al., 2000). High
9 corrosion rates were observed for field exposures of copper at sites with a combination of SO₂
10 and O₃. After four years of exposure, 90% of the corrosion products formed on copper remained
11 on the surface (Leuenberger-Minger et al., 2002). The copper hydroxy sulfates brochantite and
12 antlerite are stable copper corrosion products formed in the presence of SO₂, O₃, and NO₂
13 (Strandberg, 1998).

14 Nickel is also damaged more severely by SO₂ or chloride salts than by NO_x. Nickel
15 samples deployed at urban, industrial, and rural sites showed that corrosion rates increase with
16 SO₂ concentrations. Soluble hydrated nickel sulfates were the main corrosion products and are
17 easily removed from the surface by rainfall events, thereby exposing the underlying surface
18 (Jouen et al., 2004).

19 Kim et al. (2004) conducted a study of the effects of ambient SO₂ and NO₂ on steel,
20 bronze, copper, and marble at sites in China, Korea, and Japan. Both sheltered and unsheltered
21 samples were exposed with the corrosion rates of the unsheltered samples higher in all cases.
22 The corrosion rate of steel was the highest, followed by marble, bronze, and copper. Higher
23 corrosion rates (especially for unsheltered samples) were found to be correlated with high SO₂
24 concentrations.

25

26 **AX9.5.3 Effects on Electronics**

27 The increasingly wide penetration of electronic devices into daily life offers greater
28 opportunities for environmental damage to sensitive components. The hardware of
29 communication systems may be exposed to pollutants in outdoor air, and the ubiquitous cell
30 phones may be exposed in both indoor and outdoor environments. Sulfur and N oxides have
31 been shown to corrode the metallic contacts in electronic equipment, which are often made of

1 copper or brass coated with a precious metal such as gold, palladium, or nickel. Such materials
2 are corroded more by NO₂ than by SO₂, but a mixture of these two pollutants is more corrosive
3 than either alone. The combination of SO₂ and H₂S is also less damaging than either NO₂ alone
4 or a combination of NO₂ and these pollutants. NO₂ is also moderately corrosive to solder in
5 electronic components.

6
7

8 **AX9.6 EFFECTS ON PAINTS**

9 Painted surfaces are extremely common as a means of preventing damage to other
10 materials, and may be categorized as architectural coatings (e.g., house paint), product coatings
11 (e.g., automobile finishes), and special-purpose coatings (e.g., bridge paint). Environmental
12 damage to painted surfaces is expected, and periodic repainting is normal, but any factor that
13 causes more rapid degradation or discoloration of paints will require more frequent repainting
14 and thus result in higher costs. Paint formulations may differ widely for different applications,
15 so the extent of air pollution damage in a given application cannot necessarily be predicted from
16 published information. Previous work at elevated pollutant concentrations has shown that oil-
17 based house paint is readily damaged by SO₂ and moisture, and is more subject to damage by
18 SO₂ than by NO₂. Sample weights increased with increasing NO₂, but it is not clear if this
19 indicates direct reaction of NO₂ or an enhancement of the effects of SO₂ and moisture by NO₂.
20 The effect of SO₂ may be due to reaction with CaCO₃ and zinc oxide (ZnO) present in the paint.
21 Tests with various paints showed that NO_x becomes incorporated into the paint surface upon
22 long exposure, apparently by reaction with polymers that make up the cured paint. In other tests
23 HNO₃ was found to produce substantially more damage to paints containing both low and high
24 levels of carbonate (CO₃⁻) than did an equal mixing ratio of NO₂.

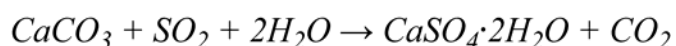
25 Grosjean et al. (1994) studied the fading of colorants on cellulose paper. Twelve
26 colorants were exposed to various atmospheres including purified air, NO₂, SO₂, and a mixture
27 of oxidants (O₃, NO₂, and peroxyacetyl nitrate (PAN)). Not all colorants were tested in each
28 atmosphere. The mixture of oxidants resulted in the largest color change for each tested
29 colorant. Only one colorant was exposed to SO₂, NO₂, and the mixture. For that colorant, the
30 color change induced by the mixture of oxidants was approximately three times the color change
31 with NO₂ alone; the color change with SO₂ was approximately 70% of the color change with
32 NO₂. An increase in relative humidity results in increased fading of colorants (Grosjean et al.,

1 1993, 1994). Of 35 colorants exposed to a mixture of O₃, NO₂, and PAN, nine exhibited
2 substantial color changes and three exhibited moderate color changes (Grosjean et al., 1993).

3 Paint samples were exposed to UV light, NO_x, SO₂, and a combination of the treatments
4 by Colombini et al. (2002). The exposure conditions were chosen to produce accelerated aging
5 of paint samples. Non-pigmented paints were chosen to isolate degradation of the paint binder
6 from synergistic effects with pigments. Exposure to the combination of treatments resulted in
7 increased cross-linking in the paint binder as well as formation of organic acids. An examination
8 of paint samples taken from naturally aged paintings confirmed the presence of organic acids as
9 degradation products.

10 11 12 **AX9.7 EFFECTS ON STONE AND CONCRETE**

13 The effects of NO_y/NH_x/SO_x air pollutants on stone and concrete are undoubtedly the
14 most widely studied because of their impact on historic buildings, monuments, and archeological
15 treasures. Table AX9.7-1 summarizes studies of the effects of NO_y/NH_x/SO_x on stone,
16 concrete, and mortars. Calcareous stone (i.e., that consisting of CaCO₃, such as marble,
17 limestone, and cement) is most susceptible to damage. Mortar used in stone construction is often
18 more porous than calcareous stone, and therefore more subject to damage. The damage to such
19 materials is attributed primarily to the effect of SO₂ in forming gypsum (CaSO₄·2H₂O):



21 The gypsum thus formed occupies a larger volume than the original carbonate, so the stone
22 surface becomes pitted and damaged. Gypsum is also more soluble than the carbonate, so it can
23 be removed by precipitation, exposing the surface to further reaction and damage. As a result,
24 dry deposition of SO₂ to the stone surface between rain events is important, as it causes
25 continued damage. The reaction of SO₂ with calcareous stone is more energetically favorable
26 than the reaction of N oxides, and thus SO₂ is the primary cause of damage to stone, however the
27 combination of SO₂ and NO_x is more damaging than SO₂ alone. This effect may be due to
28 enhanced wetting of the stone, to oxidation of SO₂ by the N oxides, or to formation of calcium
29 nitrate (Ca(NO₃)₂), which is much more soluble than CaCO₃ and is easily washed off the stone
30 surface by precipitation. Removal of the nitrate salts in this way may result in underestimation

1 of the role of N oxides in stone damage when surface layers are analyzed for chemical
2 composition.

3 Concrete is more susceptible to damage from N oxides than are the calcareous stones,
4 because concrete contains calcium hydroxide ($\text{Ca}(\text{OH})_2$), which can react to form calcium nitrate
5 ($\text{Ca}(\text{NO}_3)_2$). This product is soluble and can be washed out of the concrete, weakening the
6 material.

7 Deposition of particulate matter onto stone primarily results in soiling of the stone, due to
8 the elemental carbon and organic compound content of the deposited particles. The orientation
9 of the surfaces and size of the particles affect deposition: vertical surfaces are more affected by
10 deposition of fine particles, whereas horizontal surfaces are more affected by large particles. The
11 fine particles carry the bulk of the carbon and organic material. Metal oxides present in
12 deposited particles may enhance the reaction of SO_2 to form gypsum.

13 Gypsum crusts form more readily in rain-sheltered environments than on rain-washed
14 stone surfaces (Zappia et al., 1998). The presence of fog water has been shown to increase the
15 rate of gypsum formation on surfaces sheltered from rain washing (Del Monte and Rossi, 1997).
16 Gypsum crust formation has been shown to proceed at a faster rate when the stone surface is
17 sprinkled with fly-ash particles. In addition, fly-ash (or other carbonaceous particles) can
18 become entrained in the gypsum matrix and affixed to the stone surface. Normally, gypsum
19 crusts are gray in color, but when carbon containing particles are entrained, they become black
20 (Ausset et al., 1999). While gypsum crusts are composed primarily of sulfates, they have been
21 found to contain nitrate compounds as well (Marinoni et al., 2003; Martinez-Arkarazo et al.,
22 2007). The inclusion of nitrates in gypsum crusts suggests that N oxides, as well as SO_2 , play a
23 role in the degradation of stone exposed to the atmosphere. The presence of particulate matter,
24 in addition to SO_2 , has been shown to increase gypsum formation by 20% (Boke et al., 1999).
25 Ambient SO_2 concentrations alone are not adequate to predict the degree of damage to stone
26 samples (Torfs and van Grieken, 1996).

27 Dolomite has been shown to be less sensitive to sulfation than calcite (Lan et al., 2005).
28 Corrosion of marble due to S species has been found to be of the same order of magnitude as that
29 caused by N species. Damage is caused not by the gas phase oxides (SO_2 , NO_2 , NO) but by acid
30 (H_2SO_4 , HNO_3) and salt (SO_4^- , NO_3^-) species present in the electrolyte which forms on the
31 marble surface (Sikiotis and Kirkitsos, 1995). The rate of marble surface recession by rain

1 washing is faster than the rate of gypsum crust formation due to dry deposition of S and N
2 containing pollutants. Marble is damaged by rain washing through two mechanisms, dissolution
3 of the gypsum crust and dissolution of the underlying marble. The gypsum crust is more soluble
4 in water than marble and is rapidly dissolved in rain. The naturally occurring acidity in
5 rainwater from the dissolution of carbon dioxide (CO₂) is an important mechanism by which
6 stone samples are degraded, but additional acidity from the dissolution of SO₂ and NO₂ in
7 rainwater does not greatly increase the solubility of marble in rainwater (Yerrapragada et al.,
8 1996).

9 While gypsum is the primary degradation product found on stone, mortar, and concrete
10 samples, other damage products do occur. Sulfite species have been found on mortars as
11 intermediate damage products. On mortars, a secondary damage mechanism exists in which
12 gypsum reacts with calcium aluminum hydrates present in the mortar to produce ettringite
13 (3CaO·Al₂O₃·3CaSO₄·32H₂O). Ettringite is an insoluble sulfate that may cause damage by
14 expansion and lead to cracking of mortars (Sabbioni et al., 2001, 2002).

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17 **AX9.8 EFFECTS OF NITROGEN OXIDES ON PAPER AND** 18 **ARCHIVAL MATERIALS**

19 The cellulose fibers that make up paper are reactive with NO₂ and other NO_Y species, and
20 storage condition standards have been set regarding acceptable levels of NO_X for archives,
21 libraries, and museums. Exposure of archival materials to NO_Y species in such facilities can
22 arise from normal outdoor or indoor sources, but also from generation of such NO_Y species from
23 the materials themselves. Specifically, stored materials that include cellulose nitrate, e.g., in the
24 form of photographic film, adhesives, or recording media, can slowly decompose to release NO_X
25 and product species such as HNO₃. These emissions can degrade archival materials, and even be
26 a safety hazard if allowed to accumulate. In terms of outdoor air pollutants, it is likely that
27 HNO₃ is a key reactant in the degradation of paper archives. The rapid deposition velocity of
28 HNO₃ and the numerous surfaces in archival facilities provide opportunity for attack by HNO₃,
29 and probably result in the effects of HNO₃ being underestimated, relative to those of NO_X, based
30 on indoor air measurements. Artists' pigments can also be damaged by extended exposure to
31 ambient atmospheric NO₂.

1 The effects of SO₂ and O₃ on paper were studied by Johansson and Lennholm (2000).
2 The deposition rate of SO₂ to fresh paper was found to decrease rapidly with time and
3 approached steady state after ten hours. The deposition rate of SO₂ to fresh paper in the presence
4 of O₃ was found to be elevated compared to SO₂ alone. The deposition rates to aged paper were
5 much lower and there was no effect on the SO₂ deposition rate observed in the presence of O₃.
6 The decrease in deposition rate with time is thought to be due to protonation of all available
7 carboxylate ions to carboxylic acid.

8 Pigments in works of art can be degraded or discolored by atmospheric pollutants. H₂S
9 has been shown to react with both copper and lead pigments, but only lead white has been seen
10 to darken over time (Smith and Clark, 2002). A synergistic effect has been detected between
11 NO₂ and both benzene and toluene resulting in an increased rate of attack on pigment oxides
12 (Agelakopoulou et al., 2007). Deposition of S to the surface of paintings, either as SO₂ or
13 ammonium sulfate ((NH₄)₂SO₄) particles, can damage, varnish, or cause discoloring of paint
14 (Gysels et al., 2004). Paint models subjected to accelerated aging in SO₂ (10 ppm) and NO_x (10
15 ppm) as well as UV radiation for 15 days exhibited a variety of damage markers. Both nitrate
16 and sulfate damage mechanisms were observed with sulfation sometimes masking other
17 processes (Arbizzani et al., 2004).

18
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20 **AX9.9 COSTS OF MATERIALS DAMAGE FROM NO_y, NH_x, 21 AND SO_x**

22 Materials exposed to the ambient atmosphere are degraded and damaged through a
23 number of mechanisms. Damage associated with air pollutants result in effects such as
24 decreased usable lifetime, increased maintenance frequency, and loss of aesthetic appeal. It is
25 difficult to separate the costs associated with air pollutants from costs associated with other
26 damage mechanisms. Some estimates of cost have been based on empirically derived dose-
27 response functions for specific materials. Other estimates have been developed using inspection
28 of actual materials damage and maintenance guidelines for the materials (Cowell and Apsimon,
29 1996). Estimation of costs over large geographic areas is subject to considerable uncertainty due
30 to unknown distribution of materials at risk and spatial variations in pollutant concentrations. A
31 cost estimate for material cost savings from SO₂ emission reductions in Europe was performed
32 by Cowell and Apsimon (1996). In this study, the cost savings of theoretical future emission

1 reductions across Europe was modeled using cost data extrapolated from a study conducted in
2 three Norwegian cities. Total theoretical SO₂ reductions of 15,904 kilotons per year resulted in
3 modeled annual cost savings of \$9,504 million total for Europe (Cowell and Apsimon, 1996;
4 Apsimon and Cowell, 1996).

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7 **AX9.10 SUMMARY**

8 Many types of materials, including metals, electronics, plastics, paints, stone, and paper
9 may be damaged by atmospheric NO_y/NH_x/SO_x species. Damage occurs due to dry and/or wet
10 deposition of the pollutants onto the surface of a material and subsequent formation of an
11 electrolytic solution in water present on the surface. At low relative humidity, when little water
12 is present on surfaces, damage rates have been observed to be much lower, and in some cases, no
13 damage has been observed. Both SO₂ and NO₂ have been implicated in damage processes for
14 different materials. In general, damage to materials by SO₂ is greater than by NO₂. Little work
15 has been conducted to investigate the effects of NO on material damage. What work has been
16 conducted shows no damage, or very minor damage for NO containing environments compared
17 to clean air. Synergistic effects between SO₂ and NO₂ lead to increased damage rates for the
18 gases in combination. Other species such as O₃, NaCl, organics, or particulate matter have also
19 been shown to have synergistic effects with SO₂ and NO₂. The corrosive effects of nitric acid
20 have been found to be stronger than effects of other NO_y/NH_x/SO_x species. Costs associated
21 with damage to materials by atmospheric pollutants are difficult to estimate because of the many
22 sources of uncertainty in the estimation process. For heavily polluted environments, the cost
23 savings due to decreased rates of material degradation could offset a significant portion of the
24 costs to reduce emissions. In general, for polluted environments, reductions in SO₂ or HNO₃
25 concentrations will reduce damage rates more than reductions in NO₂, NO, or NH₃. In areas
26 with low SO₂ concentrations, reductions in NO₂, O₃, or particulate matter concentrations may
27 reduce damage rates.

TABLE AX9.5-1. STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x EFFECTS ON METALS

Materials	Exposure Conditions	Findings	Source
Zinc Mild Steel	Samples were exposed to fly-ash in clean air and in air with SO ₂ and/or HCl (presentation rates of 27×10^{-6} and 4.7×10^{-6} mg/cm ² s, respectively). A synthetic acid rain solution was used to model wet deposition.	Corrosion was found to depend on the surface electrolyte irrespective of the presence of particles. Inert particles were found to increase corrosion rates in relatively unpolluted atmospheres. With higher pollution levels, species leached from particulate matter contribute to the conductance of the surface electrolyte and thus increase the corrosion rate.	Askey et al. (1993)
Copper	Copper samples were exposed to 264 ppb NO ₂ in a laboratory setting. Exposures were limited to 72 h to study the initial corrosion behavior.	The corrosion rate of copper in the presence of NO ₂ was much greater than in clean air. The surface electrolyte was found to contain predominantly nitrate with only trace levels of nitrite. After 24 h, the electrolyte had become sufficiently acidic to dissolve the copper oxide layer. Once the copper oxide was dissolved, corrosion proceeded at a significantly faster rate.	Dante and Kelly (1993)
Zinc	Zinc samples were exposed to SO ₂ (0.78 ppm) and/or NO ₂ (1.06 ppm) for 420 h. Some samples were treated with NaCl prior to exposure.	SO ₂ slowed the corrosion of zinc with moderate to high surface concentrations of NaCl due to the formation of sodium zinc hydroxychloride sulfate. Nitrogen dioxide (which, alone, is unreactive toward zinc) accelerated the corrosion of zinc in the presence of small amounts of NaCl.	Svensson and Johansson (1993b)
Galvanized Iron Zinc	Samples were exposed to SO ₂ or NH ₃ in the laboratory. Air was supplied at 5 cm ³ /s and the pollutant gases at 3 cm ³ /s. The concentrations of the gases were very high to accelerate the tests.	Corrosion rates in SO ₂ were found to be largely dependent on relative humidity. No such humidity dependence was observed for corrosion induced by NH ₃ . Corrosion rates in both gases decreased sharply with time (approaching steady state values after 30 h).	Dehri et al. (1994)

TABLE AX9.5-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x EFFECTS ON METALS

Materials	Exposure Conditions	Findings	Source
Aluminum Zinc	Samples were exposed to ambient air for 4 yrs at 6 sites. SO ₂ deposition rates ranged from 10 mg/m ² day to non-detectable levels across the sites. Time of wetness was also measured at each site.	Corrosion products that developed in rural environments were found to be easily removed from the surface and thus result in poor protectiveness. Corrosion products formed in more aggressive environments were found to be more protective against continuing corrosion.	Vilche et al. (1995)
Zinc	Samples were exposed at temperatures of 4, 14, 22, and 30 C with 95% relative humidity. SO ₂ was supplied at 500 (± 5) ppb and 107 (± 2) ppb.	SO ₂ induced corrosion was found to be inversely dependent on temperature. The maximum corrosion rate (at 107 ppb SO ₂) of 11 mg/cm ² d was observed at 4 C. The corrosion rate at 30 C was 6.8 mg/cm ² d.	Svensson and Johansson (1996)
Copper Zinc Aluminum	Samples were exposed in the laboratory to SO ₂ (1.5 ppb, 0.5 ppm, 10 ppm), NO ₂ (10 ppm), NO (10 ppm), or O ₃ (10 ppm).	NO was found to have no effect on the corrosion of copper, zinc, or aluminum. Copper in the presence of SO ₂ (10 ppm) and NO ₂ led to significant material loss initially with a slowing of the rate with increasing time. O ₃ was found to have the strongest influence on the corrosion of copper. Only very slight mass gains were observed for copper exposed to 0.5 ppm SO ₂ . A small effect on zinc was observed for NO ₂ with SO ₂ (10 ppm) resulting in the largest weight gain. SO ₂ at 0.5 ppm had a much larger effect on zinc than on copper. For aluminum, O ₃ had the largest effect followed by SO ₂ and NO ₂ .	Oesch and Faller (1997)

TABLE AX9.5-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x EFFECTS ON METALS

Materials	Exposure Conditions	Findings	Source
Copper	Powdered samples of copper patina compounds (tenorite, cuprite, brochantite, antlerite, and atacamite) were exposed to SO ₂ (476 ppb) alone or in combination with NO ₂ (450 ppb) or O ₃ (500 ppb). Some samples were pretreated with carbon.	Tenorite reacted rapidly with SO ₂ to form brochantite and other sulfate containing products. Cuprite reacted slowly with SO ₂ alone but addition of O ₃ formed antlerite and brochantite. NO ₂ did not produce the same effect. For samples with carbon on the surface, the oxidation reaction was greatly enhanced. Brochantite and antlerite were found to be stable in atmospheres with SO ₂ in combination with O ₃ or NO ₂ .	Strandberg (1998)
Copper	Samples were exposed to atmospheres containing approximately 200 ppb of SO ₂ , SO ₂ and O ₃ , or SO ₂ and NO ₂ . O ₃ and NO ₂ were introduced at different times in the exposure scenarios.	Copper sulfite and cuprous oxide formed on copper surfaces exposed to SO ₂ . With O ₃ present, an increased rate of mass gain was measured, and copper sulfite was converted to copper sulfate. NO ₂ increased the mass gain to a lesser extent than O ₃ and resulted in the formation of copper nitrate in addition to copper sulfate.	Aastrup et al. (2000)
Mild Steel	Steel samples were exposed to the atmosphere in 47 marine atmospheres with varying levels of chloride and SO ₂ . Atmospheres were separated for data analysis based on chloride and SO ₂ deposition rates.	Samples exposed at sites with moderate SO ₂ and chloride deposition rates formed compact, rounded corrosion structures. Samples at sites with high SO ₂ and moderate chloride exhibited cracking in the corrosion products. Samples at sites with high chloride and moderate SO ₂ exhibited the highest corrosion rates of the mixed atmospheres. The 1 site with high chloride and high SO ₂ exhibited a lower corrosion rate than expected.	Almeida et al. (2000)

TABLE AX9.5-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x EFFECTS ON METALS

Materials	Exposure Conditions	Findings	Source
Steel	Two types of steel were exposed to urban-industrial and rural atmospheres for 20 yrs. Avg SO ₂ concentrations were 90 and <10 µg/m ³ (34 and <4 ppb) for urban and rural environments, respectively.	The corrosion rates of the two grades of steel were similar with values of 0.1 and 0.08 mm/yr for the urban and rural environments, respectively. The initial rate of corrosion was significantly faster and steady state values were approached after 4000 days exposure. The similar corrosion rates measured for the samples were thought to be due to similar time of wetness at both sites.	Damian and Fako (2000)
Copper Zinc	Samples were exposed in the field at 8 sites. SO ₂ , NO ₂ , and O ₃ concentrations were monitored over a 4-yr exposure duration at each of the sites.	The highest corrosion losses for copper were observed at the site with the highest combination of SO ₂ and O ₃ . For zinc, the highest corrosion losses were observed at the site with the highest SO ₂ concentration. Both metals showed a decrease in corrosion rate with time. Runoff rates from copper were much smaller than from zinc. 90% of the corrosion products remained on the copper surface after 4 yrs; only 40% of the zinc corrosion products remained after 4 yrs.	Leuenberger-Minger et al. (2002)
Nickel	Nickel samples were exposed in the field at 3 sites (urban, industrial, and rural) for 1 yr. Concentrations of NO (41.1, 9.7, and 2.9 µg/m ³) (33, 8, and 2 ppb), NO ₂ (50.1, 24.2, and 8.7 µg/m ³) (26, 13, and 5 ppb), SO ₂ (22.3, 29.0, and 12.2 µg/m ³) (8, 11, and 5 ppb), and O ₃ (25.8, 47.1, and 60.1 µg/m ³) (13, 24, and 30 ppb) were measured at the urban, industrial, and rural sites, respectively.	Mass loss rates of 320, 570, and 200 µg/cm ² y were determined for urban, industrial, and rural environments, respectively. Mass loss was found to increase with increasing SO ₂ concentration. Soluble corrosion products were formed on the surface and then removed by rainfall events. Hydrated nickel sulfates were the main corrosion products formed on the nickel surface.	Jouen et al. (2004)

TABLE AX9.5-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x EFFECTS ON METALS

Materials	Exposure Conditions	Findings	Source
Iron	Samples were exposed to humidified air in the laboratory. Samples were exposed to clean air, SO ₂ (200 ppb), SO ₂ and NO ₂ (each 200 ppb), or SO ₂ and O ₃ (each 200 ppb). The same exposure conditions were used for iron samples with NaCl deposited on the surface.	No corrosion products were detected on samples exposed to humidified air alone. The addition of SO ₂ alone was not enough to initiate a change in corrosion behavior of the samples. When an oxidant (NO ₂ or O ₃) was added to the humidified air/SO ₂ system, a significant increase in corrosion rate was observed. SO ₂ was found to inhibit the NaCl induced corrosion of iron, but the combination of SO ₂ and NO ₂ was found to accelerate NaCl induced corrosion.	Weissenrieder et al. (2004)
Aluminum	Aluminum samples were exposed to SO ₂ (96 ppb) either alone or in the presence of other pollutants (NaCl, NO ₂ , or O ₃).	SO ₂ alone resulted in the loss of metallic luster. 50% of the surface had developed corrosion products after 672 h. Samples exposed to NaCl alone showed significantly larger mass gain than samples exposed to only SO ₂ . The combination of SO ₂ and NaCl resulted in the largest mass gain (fastest corrosion rate). While the rate of mass gain was highest with a combination of SO ₂ and NaCl, the pitting observed in the presence of NaCl alone was significantly reduced. O ₃ was found to slightly increase the deposition rate of SO ₂ , no effect on SO ₂ deposition rate was observed for NO ₂ .	Blucher et al. (2005)
Copper Zinc Steel	Samples were exposed to HNO ₃ (50-180 ppb) in a laboratory exposure chamber. Tests were conducted at 65% and 85% relative humidity.	The corrosion effects of HNO ₃ on carbon steel were larger than on zinc or copper. The corrosion effect of HNO ₃ was found to be larger than corrosion from SO ₂ alone or a mixture of SO ₂ with O ₃ or NO ₂ . No increase in corrosion was observed at 85% relative humidity compared to 65% relative humidity.	Samie et al. (2007)

TABLE AX9.7-1. STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x ON STONE

Materials	Exposure Conditions	Comments	Source
Marble	Laboratory exposure to HNO ₃ ranging from 54 to 4174 µg/m ³ (21 to 1603 ppb). Field exposures were conducted in several stages in Greece. Avg concentrations for field exposures were 1.41 µg/m ³ (0.5 ppb) HNO ₃ , 2.39 µg/m ³ (3 ppb) NH ₃ , 4.84 µg/m ³ NO ₃ ⁻ , 14.61 µg/m ³ SO ₄ ²⁻ , and 5.01 µg/m ³ NH ₄ ⁺ .	Marble was found to be a very good sink for HNO ₃ . The extent of corrosion by sulfates and nitrates were found to be of the same order of magnitude. Corrosion was found to be caused by acid and salt species (HNO ₃ , H ₂ SO ₄ , etc.) on the surface rather than the oxides (SO ₂ , NO _x).	Sikiotis and Kirkitsos (1995)
Limestone	Samples of differing thickness were exposed in the field and runoff water collected for 5 mos. The avg SO ₂ concentration was 60 µg/m ³ (23 ppb).	Damage functions were developed to try to determine the ionic sulfate content in runoff water from the ambient SO ₂ concentration. It was determined that the ambient SO ₂ concentration alone does not determine the sulfate concentration in runoff water.	Torfs and van Grieken (1996)
Marble	Laboratory exposure to 10 ppm of SO ₂ and NO ₂ . Field exposure to either dry deposition or dry and wet deposition in Louisville, Kentucky. Avg concentrations of 10 ppb SO ₂ and 25 ppb NO ₂ for field exposures.	Gypsum crust thickness of 1.9 µm for rain sheltered samples after 1 yr of exposure. SO ₂ was found to be the dominant factor in crust formation. Surface recession due to rain washing was 14.5 µm/yr and due to dissolution of the gypsum crust as well as dissolution of the original marble.	Yerrapragada et al. (1996)

TABLE AX9.7-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x ON STONE

Materials	Exposure Conditions	Comments	Source
Marble Brick	Samples exposed in the field for 8 days with multiple fog episodes. Over 3 measurement campaigns, the mean pollutant concentrations were 17.2 µg/m ³ (7 ppb) SO ₂ , 265 µg/m ³ (139 ppb as NO ₂) NO _x , and 131 µg/m ³ suspended particles.	For all samples, gypsum was the only stable mineral formed following exposure to fog water in a polluted environment. Exposure to fog water may be a significant cause of corrosion for materials sheltered from rainwater, but is of lesser importance if a material is exposed to rain.	Del Monte and Rossi (1997)
Marble Limestone Mortars	Samples were exposed to urban environments in both sheltered and unsheltered configurations. Pollutant concentrations were not reported.	Sulfation was the primary damage mechanism and was more intense on mortars than on stones due to higher porosity. Higher concentrations of degradation products were found on samples sheltered from rain than on samples exposed to rain.	Zappia et al. (1998)
Jaumont limestone	Samples were exposed to 340 µg/m ³ (125 ppb) SO ₂ and 98 µg/m ³ (50 ppb) NO ₂ in the laboratory. Samples were either exposed naked or sprinkled with fly-ash particles. Field exposure was conducted for 1 yr with samples sheltered from rainwater. Avg SO ₂ concentration during the field exposure was 107 µg/m ³ (40 ppb).	Sulfation (gypsum formation) was found to proceed with greater intensity for samples sprinkled with fly-ash than for naked samples. The growth of gypsum crystals fixed the fly-ash to the surface of the limestone. Fly-ash was found to be an important factor in crust formation by facilitating gypsum crystal formation. Fly-ash particles also darken gypsum crusts from gray to black.	Ausset et al. (1999)

TABLE AX9.7-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x ON STONE

Materials	Exposure Conditions	Comments	Source
Calcium carbonate	Powdered calcium carbonate was exposed to 10 ppm SO ₂ and 90% relative humidity for 124 days.	Reaction between calcium carbonate and SO ₂ was found to take place in a liquid film on the calcium carbonate surface. The presence of several different types of airborne particles was found to increase the extent of sulfation by 20%. The SO ₂ concentration used is unrealistic for ambient conditions.	Boke et al. (1999)
Mortars	A wide range of mortar and plaster samples were collected from sites throughout Europe. Pollutant concentrations over the life of the buildings were not reported.	Sulfation was the primary damage mechanism observed. Sulfite was found as an intermediate damage product in the sulfation process. Ettringite was also found as a secondary damage product due to a reaction between gypsum and calcium aluminum hydrates.	Sabbioni et al. (2001)
Mortars	Plaster and mortar samples were collected from buildings in the Old Venice Arsenal. Pollutant concentrations over the life of the building were not reported.	Gypsum was found to be the primary damage product on all of the mortars sampled. A secondary damage mechanism was found where gypsum reacts with calcium aluminum hydrates to form ettringite, an insoluble sulfate. The presence of sulfur in the damage products indicates SO ₂ as the most aggressive atmospheric pollutant toward mortars.	Sabbioni et al. (2002)

TABLE AX9.7-1 (cont'd). STUDIES ON CORROSIVE EFFECTS OF NO_y/NH₃/SO_x ON STONE

Materials	Exposure Conditions	Comments	Source
Concrete	Samples were collected from the interior of a tunnel in Italy. The tunnel formerly held a railway and currently houses a road with heavy automobile traffic. SO ₂ levels have declined from 350 µg/m ³ (132 ppb) in 1970 to ~10 µg/m ³ (4 ppb) in 2002. NO _x concentrations have remained relatively constant around 100 µg/m ³ (52 ppb as NO ₂) over the same time period.	The urban mixture of pollutants (SO ₂ , NO _x , CO ₂ , and particles) results in formation of dendritic crusts on concrete. Nitrates were found to be present in the largely gypsum crusts. Soot particles were found embedded in the crusts as well. Low quality starting materials provide a more porous media that is more susceptible to degradation by atmospheric pollutants. The degradation of concrete is more similar to that of sandstone than of limestone.	Marinoni et al. (2003)
Marble	Samples exposed to atmosphere and sheltered from rain at 4 sites. SO ₂ concentrations ranged from ~2 to 20 ppb across the sites.	Sulfation was the primary damage mechanism observed. Marble containing dolomite was less sensitive to SO ₂ than calcite marble. For relative humidity greater than 72%, humidity was an important factor in determining the sulfation rate.	Lan et al. (2005)
Limestone Sandstone	Samples were collected from 3 facades of a historical building in Spain. Samples were collected from the surface as well as 5 mm below the surface to determine degradation and original compositions, respectively. Pollutant concentrations over the life of the building were not reported.	The main decay products on the surface were found to be nitrate compounds. Samples with black crusts on the surface were found to have predominantly gypsum and soot, but nitrate compounds were identified in the crusts as well. Sandstone samples were much more damaged than limestone samples due to their higher porosity.	Martinez-Arkarazo et al. (2007)

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1 **AX10. VALUATION OF THE ENVIRONMENTAL**
2 **EFFECTS OF NITROGEN AND SULFUR**
3 **(NON-MATERIALS)**
4
5

6 **AX10.1 INTRODUCTION**

7 The monetary valuation of ecological effects associated with Oxides of Nitrogen (NO_x)
8 and Oxides of Sulfur (SO_x) emissions starts with natural science endpoints. These may be things
9 that people value directly, such as loss of a particular species, or some remote effect on a
10 resource that is not clearly understood by the general public or not valued by the public for itself,
11 such as forest soils. Of course, damage to forest soils will affect the terrestrial ecosystem in
12 ways that may be valuable to humans, such as tree growth, habitat, and even the aesthetics of the
13 forest. This annex is a review of the literature that estimates such values for various ecosystem
14 endpoints (as discussed in the Integrated Science Assessment [ISA]) or that provide values for
15 effects that can be reasonably inferred from what is provided.

16 The purpose of this annex is to provide an assessment of the economics literature on the
17 effects of NO_x and SO_x emissions on terrestrial, transitional, and aquatic ecosystems.

18
19 **AX10.1.1 Valuation in the Context of NO_x and SO_x**

20 Figure AX10.1-1 provides a schematic representation of how economic valuation is
21 derived from changes to NO_x and SO_x secondary standards. Starting at the upper left-hand side,
22 the NO_x and SO_x standards are set and emissions reductions occur to change the ambient
23 concentrations of NO_x and SO_x. Reading down from “Change in Ambient Concentrations,”
24 these reductions will lead to changes in a variety of ecological endpoints (as identified in the
25 ISA) in terrestrial, transitional, and aquatic ecosystems. The box below, “Change in Economic
26 Endpoints,” refers to physical endpoints that people care about, in which changes can be valued
27 (at least in principle) in monetary terms. Many times, these are referred to as ecosystem
28 services. In a few cases, such as agricultural crop growth and yield, ecological and economic
29 endpoints are nearly the same. Finally, at the bottom of this diagram is a box labeled “Valuation
30 Methods,” which notes alternative approaches for placing monetary values on these economic
31 endpoints. As endpoints are discussed in detail in the ISA, this annex focuses solely on
32 valuation.

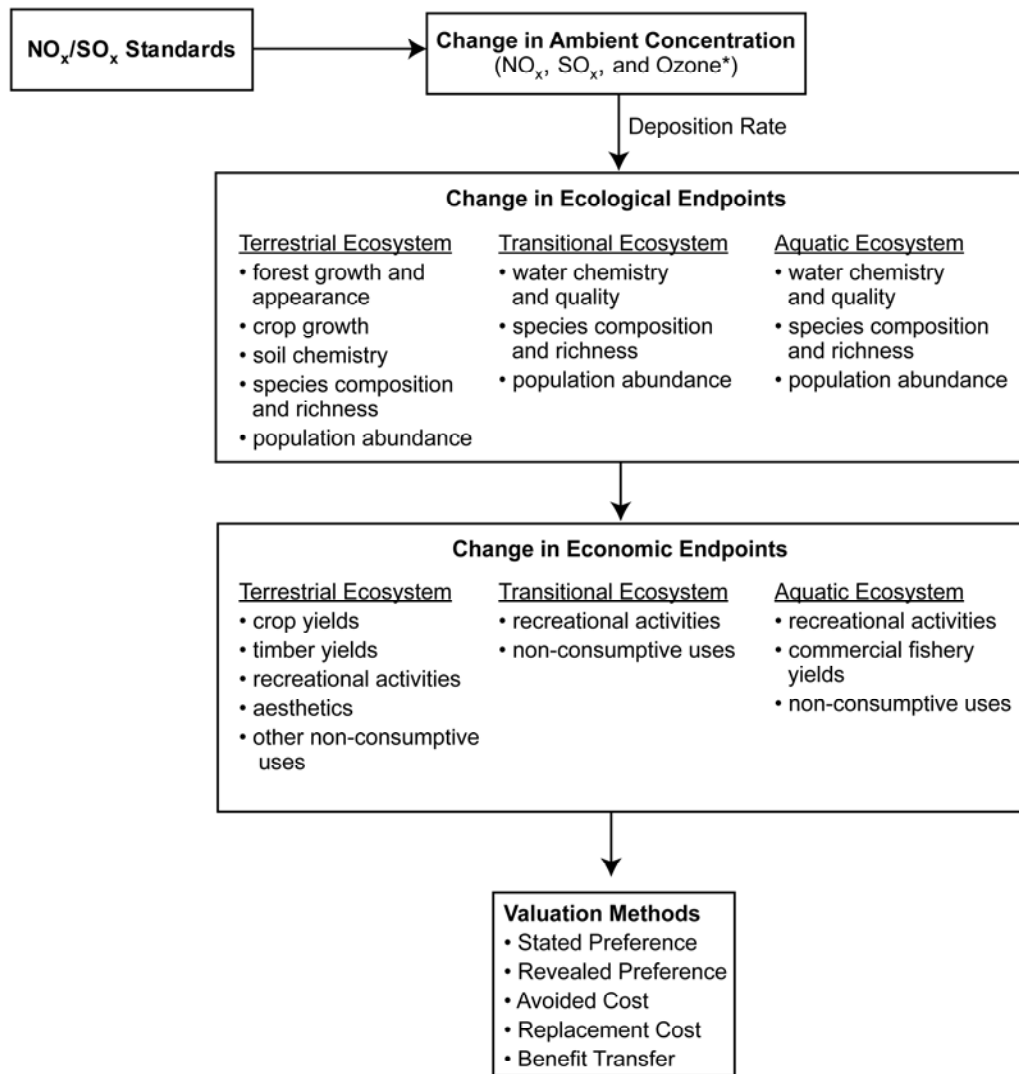


Figure AX10.1-1. Illustration chart of the assessment.

1 **AX10.1.2 Ecosystem Services**

2 Broadly defined, ecosystem services are the benefits that people obtain from ecosystems
 3 (Millennium Ecosystem Assessment, 2003). In the Millennium Ecosystem Assessment (MA),
 4 ecosystem services are classified into provisioning, regulating, supporting, and cultural services.
 5 Provisioning services denote the products people obtain from ecosystems; regulating services are
 6 associated with the ecosystem functions that regulate climate, nutrient cycle, water filtration, and
 7 so forth; supporting services are ecosystem functions, such as primary productivity and
 8 production of oxygen, that support the provision of ecosystem services; and cultural services are

1 the non-material benefits ecosystems provide to people through spiritual enrichment, cognitive
2 development, reflection, recreation, and aesthetic experiences.

3 Ecosystems are productive systems in which various biological and physical factors, as
4 well as their interactions, serve various functions in the production of ecosystem services.
5 However, economic valuation of the environment has focused mostly on the contributions of
6 individual goods and services to human well-being. Alternately, ecosystem services valuation is
7 based on the various benefits generated by the ecosystem (Polasky et al., 2005). In this case,
8 benefits include both marketed and non-marketed services, and their valuation considers the
9 environment as a natural capital asset that generates returns on investment in ecosystem
10 protection and management.

11 For example, wetlands constitute a form of natural capital. They serve as flood barriers,
12 soaking up excess water and slowing and preventing floodwaters from spreading uncontrollably.
13 Wetlands help replenish groundwater and improve both ground and surface water quality by
14 slowing down the flow of water, and absorbing and filtering out sediments and contaminants.
15 They also provide spawning habitat for fish, supporting the regeneration of fisheries. In
16 addition, wetlands provide habitat for many wildlife species and support commercial and sport
17 fishing, as well as hunting and other forms of recreation.

18 Though different functions and processes of ecosystems, such as water filtration, may be
19 economically important, they need to be viewed as inputs of or mechanisms for the production of
20 economically valuable services, such as drinking water, timber, or recreational benefits. The end
21 products, not the elements of the production process, ultimately generate economic well-being.
22 Along these lines, Boyd and Banzhaf (2007) advocate defining ecosystem services as
23 “components of nature, directly enjoyed, consumed, or used to yield human well-being.” In
24 other words, ecosystem services are the end products of nature to which ecosystems contribute as
25 intermediate inputs or production technologies. Though this distinction may at first seem
26 unimportant, it is crucial for the accurate valuation of ecosystem services. Regarding the
27 incorporation of ecosystem services into the measurements of national income and the value of
28 goods and services produced in an economy, such as gross domestic product (GDP) accounts,
29 Boyd and Banzhaf (2007) note that:

30 If intermediate and final goods are not distinguished, the value of intermediate goods is
31 double-counted because the value of intermediate goods is embodied in the value of final goods.

1 For example, clean drinking water, which is consumed directly by a household, is dependent on a
2 range of intermediate ecological goods, but these intermediate goods should not be counted in an
3 ecosystem service welfare account. Also important is that ecosystem services are attributed only
4 the incremental value they contribute to the production of valuable end products. Using the
5 above example, the value of ecosystem services associated with drinking water denotes the
6 marginal contribution of ecosystems in the production of drinking water, not the full value of the
7 final product.

8 Given the complexity and variety of ecosystems and their services, their valuation poses
9 several challenges. According to the National Academy of Sciences' Committee on the
10 Valuation of Ecosystem Services, the importance of ecosystem functions and services is often
11 taken for granted and overlooked in environmental decisionmaking. Moreover, the key
12 challenge in the valuation of ecosystem services lies in the difficult integration of economic
13 valuation and ecological production theory. This is no straightforward task, because many
14 ecosystem goods and services are not quantifiable using available methods, and the application
15 of economic valuation methods may be subject to judgment, uncertainty, and bias (Heal et al.,
16 2005).

17 A study by Costanza et al. (1997), seeking to determine the value of global ecosystem
18 services, exemplifies the problems and pitfalls in the valuation of ecosystem services. Deriving
19 and summing value estimates from the existing literature for a wide range of ecosystem attributes
20 and services, this study suggested that the total value of global ecosystem services likely ranges
21 from \$16 to \$54 trillion annually, or roughly one to three times global GDP. The study has been
22 influential and widely quoted and used, especially among scientists and environmentalists.
23 Economists consider it fundamentally problematic both conceptually and methodologically,
24 preferring to focus on the value of changes to ecosystem services, which is relevant for policy, or
25 what is termed the marginal value of ecosystem services. More profoundly, the entire concept of
26 the value of global ecosystem services is problematic; without the global ecosystem we would all
27 perish. The estimate of the value of global ecosystem services by Costanza et al. (1997) has
28 therefore been characterized as a "serious underestimate of infinity" (cf. Toman, 1998; Smith,
29 2007).

1 **AX10.1.3 Use of the Valuation Literature to Define Adversity**

2 A secondary standard, as defined in Section 109(b)(2) of the Clean Air Act, must
3 “specify a level of air quality the attainment and maintenance of which, in the judgment of the
4 Administrator, based on such criteria, is required to protect the public welfare from any known
5 or anticipated adverse effects associated with the presence of [the] pollutant in the ambient air.”
6 One way to quantify adverse effects is through monetary valuation.

7 Adversity is difficult to quantify and measure, and there are several challenges to using a
8 monetary valuation approach. A major effect that is geographically extensive might be
9 considered to be more adverse than a more severe effect limited to one geographic location.
10 Another problem is aggregation. Any change in pollution may have multiple effects (i.e. effects
11 on many types of ecosystem services) leading to difficulty in aggregating in a consistent way.

12 Monetary values on any service or resource degradation reflect human preferences about
13 what is a severe effect. Larger unit values correlate with more severe effects, other things equal.
14 Also, more extensive effects, will contribute to larger welfare loss (or gain). In addition, since
15 monetary units can be added, the aggregation issue can be addressed by “simply” summing the
16 welfare losses (or gains). Although this is not strictly true (e.g., values for improvements in
17 water quality and fish populations may not be additive), in principle the differences in how
18 people conceptualize ecosystem improvements can be captured in the way resource
19 improvements are valued in monetary terms.

20 Clearly, there are many practical problems associated with using monetary value as a way
21 of defining adversity. First, many resources and services have not been valued and efforts to
22 credibly transfer the results of valuation studies to other areas and resources have been minimal.
23 Second, studies addressing multiple effects are particularly difficult to transfer and few in
24 number. Finally, even with the first two problems addressed, a judgment would still need to be
25 made on whether the air quality standard was the contributing factor for eliminating adverse
26 (highly monetarily valued) effects.

27 28 **AX10.1.4 Methods for Selecting Literature for this Assessment**

29 Assessing the economics literature on the effects of NO_x and SO_x emissions on
30 terrestrial, transitional, and aquatic ecosystems requires identifying and reviewing relevant
31 studies addressing these effects. Multiple methods were used for this annex: searching existing

1 databases of this valuation literature; conducting systematic searches of the economics literature;
2 reviewing a large number of key articles, reports, authors, and journals; and identifying studies
3 based on the expertise and familiarity with the relevant literature of lead researchers.

4 Two existing databases on environmental valuation studies – the Environmental
5 Valuation Reference Inventory (EVRI) and the Beneficial Use Values Database (BUVD) – were
6 particularly useful for this assessment. The EVRI database, which includes nearly 1,900
7 valuation articles/studies on environmental and human health effects, was screened according to
8 criteria regarding the potential relevancy of geographical location (United States), types of
9 environmental goods and services valued (ecological functions, extractive uses, non-extractive
10 uses, passive uses); and environmental stressor. This resulted in over 200 articles/studies of
11 interest. BUVD is a relatively small database (131 articles/studies), so it was imported into the
12 literature review database in its entirety, with unrelated articles/studies later excluded on an
13 individual basis.

14 A large number of additional journals and literature databases were identified that publish
15 and cover research potentially relevant to this assessment. The selected peer-reviewed journals¹
16 and library databases² were then reviewed using search engines and a range of key words
17 developed to find studies addressing relevant ecological endpoints (aquatic, transitional,
18 terrestrial) and their economic values. The tables of contents of those journals that could not be
19 searched electronically were reviewed in hard copy and relevant articles were added to the
20 literature review database. These searches were augmented by reviews of the bibliographies of
21 the following EPA reports: *EPA Report to Congress: The Benefits and Costs of the Clean Air*
22 *Act 1990-2010* (November 1999); *Air Quality Criteria for Ozone and Related Photochemical*
23 *Oxidants* (February 2006); *Air Quality Criteria for Particulate Matter* (October 2004).

¹ *American Economic Review, American Journal of Agricultural Economics, Canadian Journal of Economics, Canadian Journal of Forestry, Contemporary Economic Policy, Ecological Economics, Environment and Development Economics, Environmental and Resource Economics, Environmental Science and Technology, Forest Science, Forestry Chronicle, Journal of Agricultural and Applied Economics, Journal of Applied Econometrics, Journal of Agricultural and Resource Economics, Journal of Agricultural Economics, Journal of Environmental Economics and Management, Journal of Forest Economics, Journal of Forestry, Journal of Political Economy, Journal of Risk and Uncertainty, Land Economics, Marine Resource Economics, Resource and Energy Economics, Review of Agricultural Economics, Review of Economics and Statistics, Water Resources Research.*

² AgEcon Search, Agricola, BioOne, CSA Illumina, EconLit, GeoRef, Google Scholar, SciSearch/Science Citation Index (Web of Science), SCOPUS, Sportfishing Values Database, SSRN.

1 The results from these searches were checked for duplicates and clearly irrelevant
2 studies, after which over 500 potentially relevant articles/studies were identified for initial
3 assessment. Relevancy of each study for this assessment was determined according to the
4 following key criteria.

- 5 • Does the study address an ecological endpoint sensitive to reductions in NO_x and
6 SO_x emissions?
- 7 • Does the study value quality changes in the ecological endpoint, which is actually or
8 potentially attributed to reductions in NO_x and SO_x emissions?
- 9 • Is the study peer-reviewed and preferably, published in an academic journal?

10 Very few, if any studies fully satisfy all above criteria. For this reason, studies that at least
11 partially satisfy these criteria were deemed potentially relevant for this project. Finally, reviews
12 and meta-analyses were included in the assessment whenever they were available and dealt with
13 potentially relevant ecological endpoints.

14 In the initial assessment, each record's potential relevancy to the assessment was rated on
15 a scale of 1 to 4, with 1 indicating that the record appears directly relevant to this assessment (the
16 study addresses quality change of an ecological endpoint, which is actually or potentially
17 attributable to NO_x/SO_x). Records rated 2 only partially satisfied the "relevancy criteria," but
18 were considered important to be referenced in this report. Records rated 3 were to be reviewed
19 more closely to determine their usefulness, and those rated 4 were found not relevant for the
20 purposes of this assessment. Because our goal in the initial assessment was to avoid missing
21 potentially relevant studies, we classified borderline cases to the lower number category.

22 All studies rated 1 through 3 were next reviewed using several attributes, including
23 ecological endpoints, valuation techniques, geographical area, use vs. non-use value category,
24 and other details of interest. Of those studies, about half addressed aquatic ecosystems (Figure
25 AX10.1-2). The reviewed studies addressed many different ecological endpoints, such as sport
26 fishing, commercial fisheries, aquatic recreation (e.g., swimming and boating), general water
27 quality, ecosystems services provided by aquatic ecosystems, and coral reefs (Figure AX10.1-3).
28 Nearly one third of the studies addressed terrestrial ecosystems (e.g., forestry/commercial timber,
29 outdoor recreation, and agriculture); the rest dealt with transitional ecosystems (e.g., ecosystems
30 services provided by wetlands and wetlands recreation).

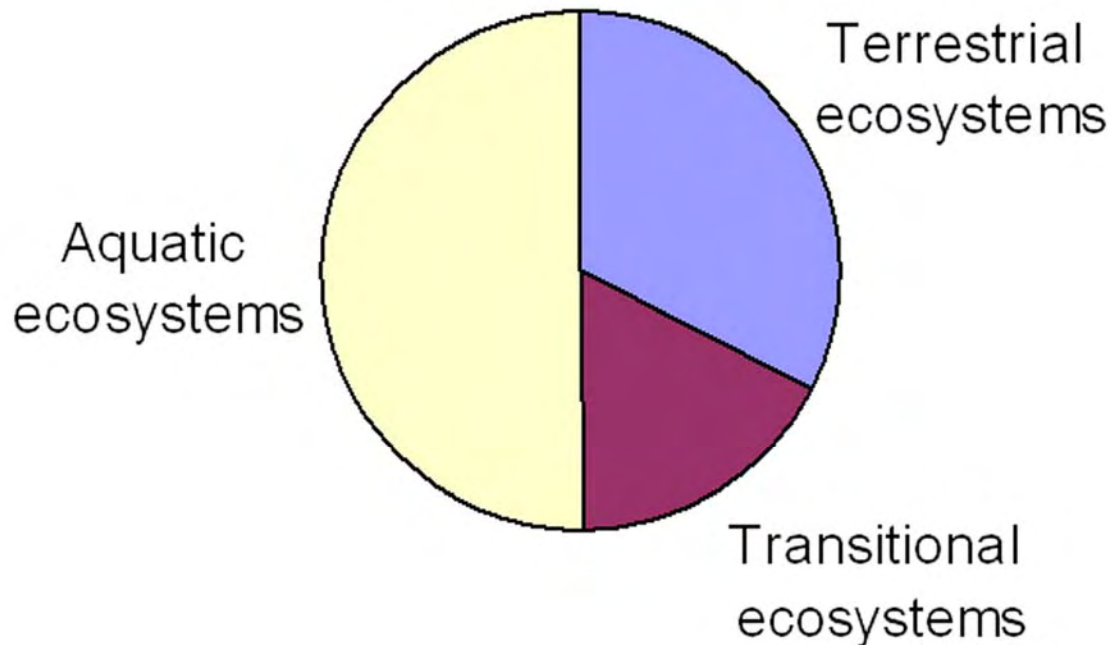


Figure AX10.1-2. Reviewed studies by ecosystem addressed.

1 **AX10.2 CONCEPTUAL FRAMEWORK**

2

3 **AX10.2.1 Taxonomy of Values for Environmental Goods and Services**

4

The economic value derived by society from these ecological goods and services can be categorized as either “use” or “non-use” values. Use values comprise values for those goods and services that can be used either directly or indirectly. Non-use values denote the characteristics of the ecological goods and services that are not used at all but still hold economic value. The schematic in Figure AX10.1-4 illustrates these divisions of values for environmental goods and services.

10

Direct use values are held for those goods and services which can be directly consumed or utilized by individuals or society. Some direct use goods, such as fish caught or timber cut are sold in markets and thus valued using market data. Other direct uses, such as recreational use of

12

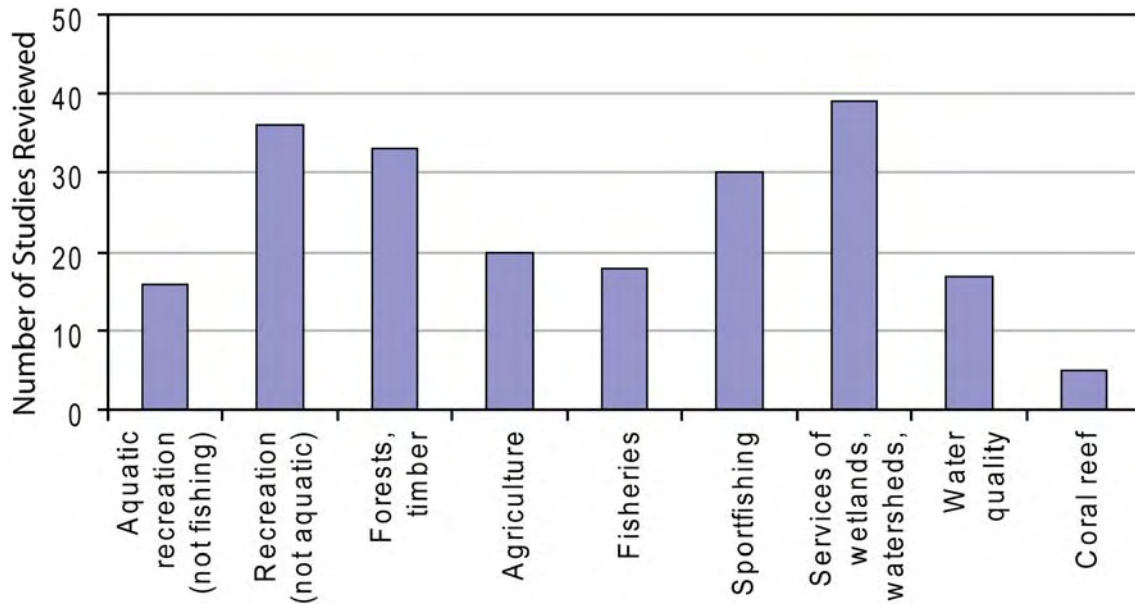


Figure AX10.1-3. Reviewed studies by ecological endpoint.

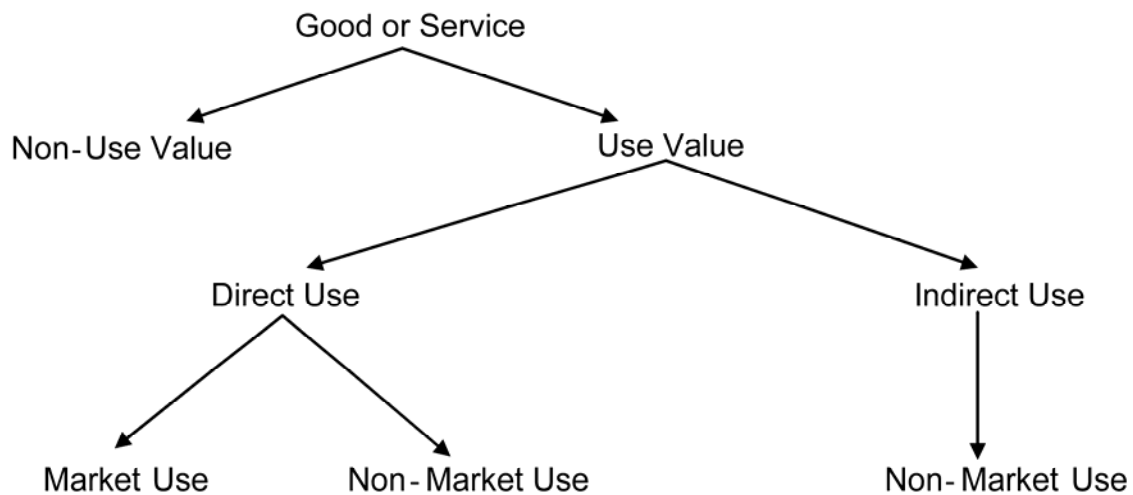


Figure AX10.1-4. Taxonomy of values for environmental goods and services.

Source: U.S. Environmental Protection Agency (2002).

- 1 ecosystems for fishing, hunting, and sightseeing, are usually not bought or sold through a market
- 2 and are therefore more difficult to value. Similarly, changes in their value are more difficult to

1 quantify. Thus, direct use can be subdivided into directly used market and non-market goods or
2 services.

3 Examples of direct, market uses of ecological goods and services include commercially
4 sold food sources (fish, crops, other animals); building materials (wood, stone); fuel sources
5 (wood, coal, oil); drinking water (groundwater, surface water); chemicals; and minerals
6 (U.S. Environmental Protection Agency, 2002). Examples of direct, non-market uses of
7 ecological goods and services include recreational fishing and hunting; beach use (sunbathing,
8 swimming, walking); boating; hiking; camping; wildlife watching; and sightseeing
9 (U.S. Environmental Protection Agency, 2002).

10 Indirect use values capture those ecological services that are not used directly but still
11 provide benefits of economic value to society. These services include flood control, storm water
12 treatment, ground water recharge, climate control, pollution mitigation, wave buffering, soil
13 generation, nutrient cycling, habitat value, and biodiversity (U.S. Environmental Protection
14 Agency, 2002).

15 Non-use values denote the characteristics of the ecological goods and services that are
16 not used at all but still hold economic value. These non-use values include what are known as
17 existence and bequest values—the value of simply knowing that certain ecosystems exist and of
18 ensuring that they continue to exist for future generations, respectively. These services are also
19 not traded in a market and quantifying their value is a challenge.

20 Importantly, empirical methods for addressing non-use value generally estimate the total
21 value of a resource. Distinguishing between the use and non-use values often is not possible, and
22 the valuation results including non-use values should therefore generally be considered total
23 valuation rather than non-use valuation studies. Examples of non-use values of ecological goods
24 and services include existence value, cultural/historical value, intrinsic value, bequest value, and
25 altruistic value (U.S. Environmental Protection Agency, 2002).

26 In this annex, the focus is on the potential incremental benefit that might be realized from
27 tightening the standards for SO_x or NO_x by a relatively small amount, rather than the total value
28 of the affected ecosystems. Therefore, the term “total value” in this annex generally denotes
29 total marginal benefits that contain both use and non-use values, not the total value of the entire
30 resource. This notation is consistent with the principles of economic valuation of the

1 environment, which generally focus on predicting damages or benefits from marginal changes in
2 environmental conditions.

3 4 **AX10.2.2 Welfare Economics**

5 Any environmental goods or services that somehow contribute to human well-being are
6 economically valuable. Their economic value reflects the capacity of the environment to satisfy
7 different human needs, which is related to the direct consumption of different goods and services
8 derived from the environment. It also includes different indirect, passive, and non-use values for
9 environmental goods and services, such as recreational benefits, enjoyment of natural landscape,
10 purity of air and water, and provision of habitat for species other than humans.

11 Economic valuation is rooted in the basic principle of consumer sovereignty. Rather than
12 judging whether an individual's choices are right or wrong, each person is considered able to
13 make rational choices that advance his or her well-being, given the possibilities available. The
14 principle of consumer sovereignty extends also to the valuation of environmental goods and
15 services. Even in the absence of markets for environmental benefits, each individual is
16 considered able to assess the importance of changes in environmental quality on personal well-
17 being or, as economists commonly refer to it, utility.

18 Consumer (CS) and producer surpluses (PS) are the basic monetary measures of well-
19 being (or welfare) in economics. They denote the "excess utility" consumers and producers
20 enjoy when consuming or producing specific goods or services after paying for them. Producer
21 surplus is measured by profit, the value of production after accounting for all costs. Consumer
22 surplus, which is a more subtle concept, can be thought of as the difference between the price
23 and the maximum value that an individual holds for a good or service. However, it generally is
24 not an exact measure of changes in welfare because CS does not fix the baseline level of utility,
25 thereby ignoring the income effects of a changing baseline

26 CS has two exact (Hicksian) measures: willingness-to-pay (WTP) and willingness-to-
27 accept (WTA). In the context of environmental valuation, WTP denotes an individual's
28 maximum willingness to pay for an environmental good or service. WTA, on the other hand,
29 stands for the minimum compensation an individual is willing to accept to forgo an
30 environmental good or service. Though WTP and WTA both are exact measures of CS, they
31 generally are not equal, meaning that the CS in general does not have a unique measure. WTP

1 and WTA for usual marketed goods and services are similar and within narrow bounds of
2 income effects (Willig, 1976). Similar findings can be expected with environmental goods and
3 services only when they have close substitutes (Hanemann, 1991; Shogren et al., 1994).

4 Since many environmental goods and services cannot be easily substituted, WTP and
5 WTA are expected to differ, sometimes substantially. In fact, the WTP-WTA divergence can
6 range from zero to infinity, depending on the substitutability of an environmental good and other
7 market or non-market goods (Hanley et al., 1997). Using WTA to measure welfare changes
8 might often be justified on the grounds of economic theory and property rights, but many studies
9 choose to estimate WTP for its practicality. In addition, WTP generally is lower than WTA and
10 therefore is conservative, providing another justification for using WTP for valuing the
11 environment. Finally, both WTP and WTA can be difficult to measure, and valuation studies
12 therefore sometimes estimate the ordinary CS. It approximates WTP and WTA and is between
13 these two exact measures of welfare. In the special case of no income effects, all different
14 measures of consumer welfare coincide.

15 Various methods have been developed to determine the value of different ecological
16 goods and services by estimating the change in social welfare or WTP for changes in the quantity
17 or quality of a given environmental resource (see Table AX10.2-1). Some valuation techniques
18 obtain WTP from observing people's actions (revealed preferences or RP) while others rely on
19 people's responses to hypothetical situations (stated preferences or SP). Yet another set of
20 valuation methods relies on other studies, either by transferring their estimates into another
21 context (benefits transfers) or by conducting statistical meta-analyses of earlier studies to
22 examine their systematic findings. See Section AX10.2.3 for details about these approaches.

23 As noted by Kramer et al. (2003), several forest protection valuation studies also
24 considered the sensitivity of contingent valuation estimates to various preference elicitation
25 methods, including dichotomous choice, payment card, and open-ended techniques. Haefele
26 et al. (1992) used payment card and dichotomous choice techniques in a contingent valuation
27 survey measuring the WTP of Southern Appalachian residents for protecting high-elevation
28 spruce-fir trees from exotic insects and air pollution. Estimates for mean WTP were \$20.86 per
29 year using a payment card method, and \$99.57 per year using a discrete choice method. Sample
30 sizes for each method were relatively small (232 and 236 respondents, respectively). Another
31 limitation concerns the wide span between the two valuation statistics, which despite a large

1 difference in the mean estimates showed no overlap of the 95% confidence intervals. Similar
2 studies have been performed by Loomis et al. (1996) and Kramer and Mercer (1997).

3 4 **AX10.2.3 Benefit Estimation Approaches**

5 Table AX10.2-1 introduces different valuation techniques and indicated which type of
6 value (direct use, indirect use, total value) each can be used to estimate. Studies addressing non-
7 use values are referred to in this annex as total valuation studies. This is because non-use
8 valuation methods in fact generally estimate the total value of a resource, including both its use
9 and non-use components.

10 Travel cost (including site choice models) and hedonic pricing methods are perhaps the
11 most regularly applied revealed preference (RP) methods for valuing the environment, whereas
12 contingent valuation and choice experiments are the most popular stated preference (SP)
13 methods. One of the key differences between the RP and SP methods is that RP methods can
14 only fully address direct and indirect use values, whereas SP methods are required for the
15 estimation of total values of environmental resources, including their non-use value component.

16 *Travel cost studies* predict use values for ecological resources, such as natural parks, by
17 examining individuals' travel expenditures to utilize that resource (most often at a park or some
18 other recreational site), including the opportunity cost of work time missed while traveling to and
19 utilizing the resource. Travel cost studies commonly use a random utility framework, which
20 infers individuals' WTP for an ecological resource (again usually a recreational site) by
21 observing their choice from among one or more alternatives. While the travel cost method uses
22 changes in the quality of one resource to ascertain its value, the random utility model uses
23 individuals' choices among various options of various qualities at various prices to do the same.

24 *Hedonic price studies* predict the value of ecological resources by examining their effect
25 on property values. Assuming that all the benefits from living in a specific location and house
26 are capitalized into the market value of the property, hedonic models estimate the independent
27 effects of different housing characteristics on housing prices. Controlling for all observable
28 housing and location characteristics, hedonic pricing models examine environmental values for,
29 for example, proximity to forests or particular watersheds by estimating the implicit incremental
30 price people are willing to pay for that proximity. Hedonic pricing relies on assumptions such as
31 efficiently functioning housing market and perfect information and mobility by individuals.

1 However, because WTP is not necessarily tied to ecosystem changes, this annex does not
2 consider property values as a method of valuation.

3 Other market or RP-based approaches to valuing changes in ecological goods and
4 services include the alternative/replacement cost method; avoidance expenditures/averting
5 behavior method; referendum method; user fee method; market price and market simulation
6 method; and a host of different variations of these and other valuation approaches. See, for
7 example, Freeman (2003) for the theory and applications of different methods for valuing
8 environmental quality.

9 The RP methods have the advantage of gleaned their value estimates from individuals'
10 real world actions. However, because they do not include the non-use value of ecological
11 resources, none of them capture total value. This problem has given rise to the development of a
12 variety of non-market valuation methods that use surveys to elicit preferences for public goods.
13 Because these methods are generally based on eliciting "stated" rather than "revealed"
14 preferences, they are broadly categorized as SP methods.

15 *The contingent valuation* method is the most common SP method. It involves developing
16 and administering surveys, in which respondents are presented with a scenario or a program with
17 specified environmental outcomes and costs. Each respondent is asked to indicate approval or
18 disapproval of the proposed environmental scenario and its monetary cost. Researchers vary the
19 proposed costs across different survey respondents and use their choices to estimate how much
20 people on average are willing to pay for different scenarios to improve the environment.
21 Because some of the respondents may use a public good also for direct enjoyment, say viewing
22 an endangered bird, the surveys actually capture total value for the improvements, rather than
23 just their non-use value.

24 *Choice experiment methods* (including contingent ranking, contingent choice, and
25 conjoint analysis) separate an environmental good into its constituent attributes, recombine those
26 attributes into different bundles, and elicit respondents' preferences for those bundles. Often a
27 monetary value can be assigned to those attributes and thus the process allows researchers to
28 determine WTP for the bundle and each attribute. Conjoint analysis usually is performed by
29 choosing the most preferred attribute bundle from a group (choice experiment, contingent
30 choice) or via ranking a series of attribute bundles (contingent ranking). Using conjoint analysis,
31 researchers may be able to simultaneously value various relevant goods or services that an

1 environmental resource provides. For example, improving a public body of water provides
2 improved recreational opportunities, drinking water, and support of aquatic ecosystems.

3 *Valuing the environment as a factor of production* monetizes the incremental benefits
4 from using the environment as an input to production. In other words, this method treats the
5 environment as a production input comparable to other raw materials and infrastructure, such as
6 land, capital, labor, and so forth. This method is appropriate for valuing environmental effects
7 that have direct value as a factor of production. Examples of such cases include the effects of
8 water quality on the productivity of commercial fisheries, or the impact of soil characteristics on
9 agricultural productivity. However, this method is limited to market goods and services and can
10 only address their role as part of the production process. This method does not address non-
11 market environmental goods and services or non-use values.

12 *Benefits transfer approaches* translate the entire estimated demand function from one
13 application to another. Sometimes the function is adjusted to meet the specific criteria of the
14 target site, and then new WTP value estimates are generated for the environmental good/service
15 at the new site using the demand function. Using the transferred demand function, both changes
16 in the level of use and the unit value benefits for the new site can be estimated (U.S.
17 Environmental Protection Agency, 2002). There are four general types of benefits transfer
18 technique: mean unit value transfer/ adjusted unit value transfer, benefit/demand function or
19 model transfer, meta-function transfer, and structural benefits transfer. The first three methods
20 dominate the literature (Smith et al., 2006).

21 *Mean unit value transfer/adjusted unit value transfer* entails taking the value of a specific
22 environmental good or service (such as recreational hunting), sometimes from a single study of
23 the same good and sometimes estimated by averaging a range of value estimates from various
24 primary studies, and transferring that value to the same good or service at a new site.

25 *Benefit/demand function or model transfer* is the translation of the entire estimated
26 demand function from one site to another. Sometimes the function is adjusted to meet the
27 specific criteria of the target site, and then new WTP value estimates are generated for the
28 environmental good/service at the new site using the demand function. Using the transferred
29 demand function, both changes in the level of use and the unit value benefits for the new site can
30 be estimated (U.S. Environmental Protection Agency, 2002). *Meta-function transfer* involves
31 the use of meta-regressions to combine the results of numerous valuation studies and allows

1 researchers to account for influencing factors, thus enabling them to create value estimates for
2 new policy sites. *Structural benefits transfer*, also known as preference calibration, requires
3 selection of a preference model which can describe individual choices over a set of market and
4 associated non-market goods to maximize utility when faced with budget constraints
5 (Rosenberger and Loomis, 2001; Smith et al., 2006).

6 *Meta-study review* provides a useful way of summarizing the literature on the valuation
7 of ecological endpoints from reductions in NO_x and SO_x, though there are few studies exactly
8 on this topic. But there are studies summarizing monetary valuation efforts for particular sets of
9 endpoints, such as the economic valuation of fresh water ecosystem services. Where such
10 studies are available, they are summarized in the appropriate section of this annex.

11 Even more valuable are *meta-analyses*, which perform statistical analyses of the results
12 of original studies. Such studies explain variation in monetary value estimated for various
13 endpoints using features of the original studies' methodologies as well as the characteristics of
14 the site being studied and other factors. Smith and Pattanayak (2002) defined meta-analysis as
15 the practice of using a collection of formal and informal statistical methods to synthesize the
16 results found in a well-defined class of empirical studies.

17 In general, the three uses of meta-analysis are: (1) synthesize or “take stock” of the
18 literature on a particular valuation topic; (2) test hypotheses with respect to the effects of
19 explanatory variables on the value construct of interest; and (3) use the estimated meta-analysis
20 model to predict estimates of the value construct across time and space (Bergstrom and Taylor,
21 2006). Bergstrom and Taylor (2006) provided a review of the techniques and theory behind the
22 use of meta-analysis for benefits transfer. They noted that to conduct a successful meta-analysis
23 for benefits transfer, it is important to be as comprehensive as possible in terms of the studies to
24 be included. Excluding a study would be equivalent to applying a zero weight to the information
25 in that study. The authors list some additional criteria to be considered when identifying studies
26 for inclusion in a meta-analysis, including controlling for the valuation method and estimated
27 welfare measure, as well as addressing the temporal and spatial scales of the valued commodity.

28 Extensive evaluation of the relative merits of, and issues with, different environmental
29 valuation methods is not within the scope of this annex. Vast amounts of research have been
30 conducted to develop and evaluate alternative environmental valuation methods. For example,

1 the Handbook of Environmental Economics recently dedicated an entire 1,100-page volume to
2 addressing methods for valuing environmental changes (Mäler and Vincent, 2005).

3 The validity of environmental valuation methods is sometimes questioned, in particular
4 that of SP methods. Because survey-based valuation methods are based on what people say
5 rather than what they do, there is a tendency to question the credibility of the results. For this
6 reason, nonmarket valuation researchers, following the lead of the National Oceanic and
7 Atmospheric Administration (NOAA) Expert Panel that reviewed the highly publicized studies
8 valuing damages from the Exxon Valdez oil spill, often build into their surveys a series of
9 validity tests, such as testing for the sensitivity of WTP to the scope of resource being valued
10 (Federal Register, 1993). Additionally, SP surveys are vulnerable to a variety of issues dealing
11 with the design and administration of surveys, as well as analyzing their data (e.g., Carson and
12 Hanemann, 2005).

13 Though examining actual choices lends credence to RP methods, they are not free of
14 problems. For example, hedonic pricing studies of housing markets rest on the assumptions that
15 the housing market is at equilibrium and that housing choices accurately reflect the attributes of
16 interest, such as air pollution or environmental amenities associated with the residential location.
17 Hedonic studies and other RP studies, such as recreation trip demand analysis, are also
18 susceptible to potential biases. These include the omission of important variables, which may
19 thwart the efforts to accurately value environmental quality.

20 A number of studies have compared SP analyses with RP analyses, such as hedonic
21 property value studies. Generally, these comparisons have suggested that when similar
22 environmental values are examined, RP methods generally yield somewhat higher value
23 estimates than SP methods. For example, Carson et al. (1996) reviewed over 80 studies which
24 included comparisons of SP and RP methods, and concluded that SP methods are on average
25 about 75% to 90% of corresponding RP values.

26 27 28 **AX10.3 VALUATION OF FORESTS AND TERRESTRIAL** 29 **ECOSYSTEMS**

30 31 **AX10.3.1 Use Values**

1 The impacts of NO_x and SO_x can occur over many different terrestrial ecosystems and
2 use-value efforts must look at each of these ecosystems individually. One serious threat to
3 agriculture from NO_x emissions comes from ambient ozone (O₃), which is a byproduct of
4 atmospheric reactions between Volatile Organic Compounds (VOCs) and NO_x. In commercial
5 forests, air pollution effects have not been addressed in economics beyond evaluating the
6 potential effects of O₃. Unlike in agriculture, the scientific understanding of O₃ effects on trees
7 is more limited and related mostly to visual injury to leaves in young saplings, an indicator that is
8 difficult to link to tree growth in mature forests. However, the valuation of O₃ has already been
9 evaluated in detail in the *Air Quality Criteria Document (AQCD) for Ozone* (U.S. Environmental
10 Protection Agency, 2006), and will not be covered in this annex or the ISA (see also Tables
11 AX10.3-1 and AX10.3-2).

12 Some studies have attempted to specifically measure use values associated with forest
13 quality, without regard to the factor that is altering forest quality. For example, an early study by
14 Leuschner and Young (1978a) considered the effects of crown density changes due to insect
15 infestation around 19 lakeside campgrounds in east Texas. A travel-cost model estimated the CS
16 losses from a 10% reduction in crown density to fall between 0.69% and 6.5%, depending on the
17 number of substitute recreation sites available. More studies that look at how forest quality
18 affects various uses are listed in Table AX10.3-3. Also, Table AX10.3-3 lists value estimates
19 from a meta-analysis but does not reflect the considerable variation of value estimates across
20 underlying studies.

21 22 **AX10.3.2 Non-Use Values**

23 Figure AX10.1-5 depicts the linkages between aesthetic welfare benefits and air
24 pollution. One such linkage that is shown is the visual quality of forests (Table AX10.3-4).
25 Changes in woodland appearances are monitored using scientific indicators of ecosystem change,
26 such as crown condition, mortality, foliar damage, vegetation structure, and plant diversity
27 (McLaughlin and Percy, 1999). However, in comparison to valuation of changes in commercial
28 timber, measuring the economic value of aesthetic changes in forests and natural ecosystems can
29 be more directly based on scientific information regarding the effects of pollution on forest
30 health. Although the scientific linkages between air pollution and visual forest quality include
31 large degrees of uncertainty, historic examples of air pollutant effects on forest aesthetics

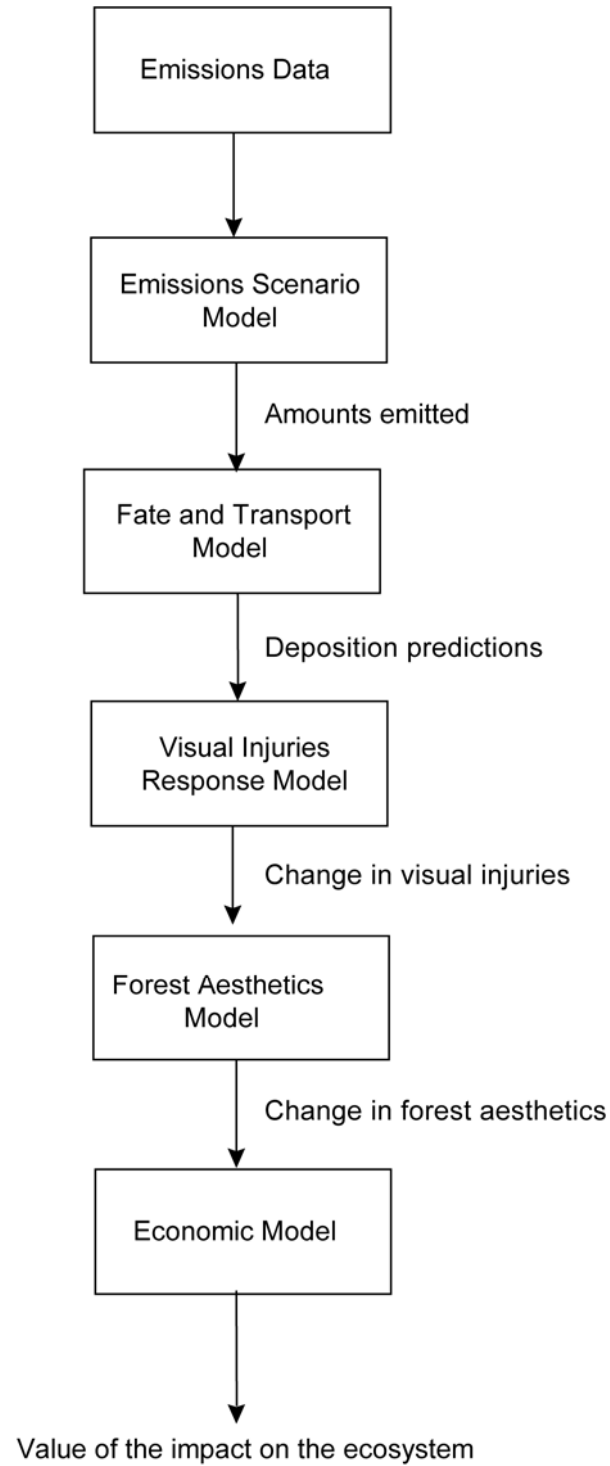
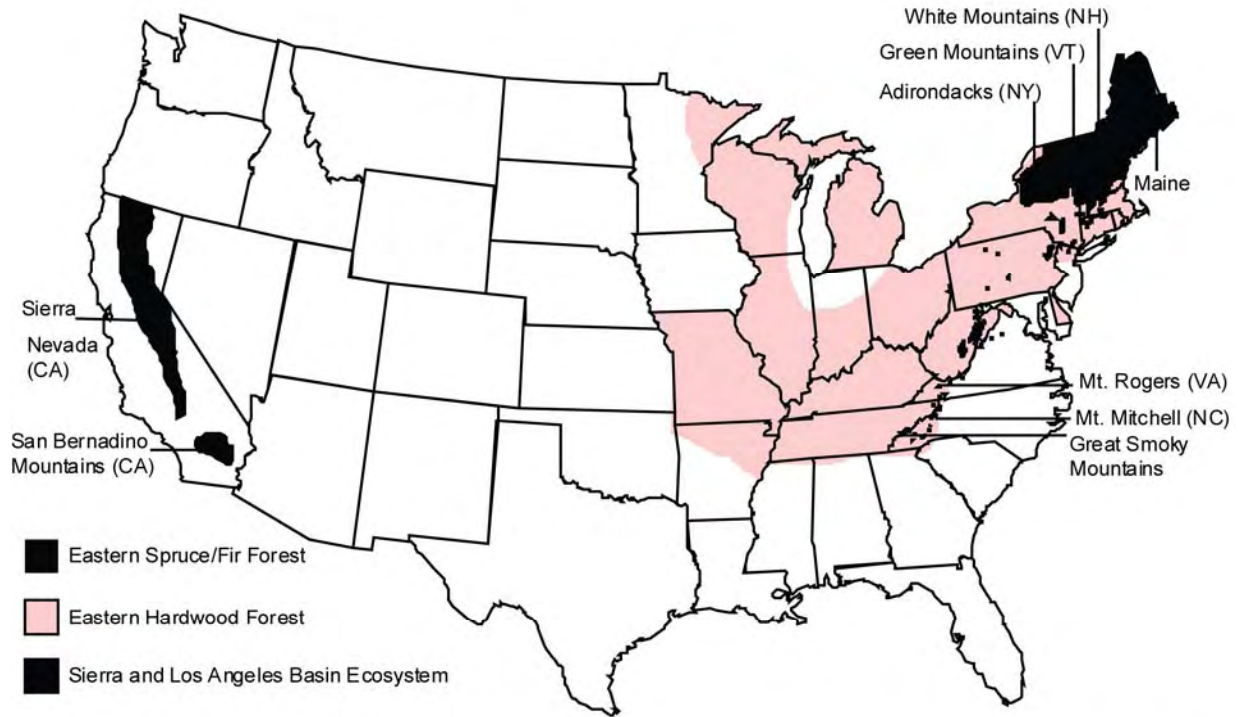


Figure AX10.1-5. Linkages from emissions to forest aesthetics.

Source: Exhibit 1 in IEc (1999a).

1 facilitate their empirical valuation. Figure AX10.1-6 shows the regions and species that have
2 been identified as historically affected by air pollutants.

U.S. Major Forest Types Affected by Air Pollution-Induced Visual Injuries



Note: Only areas affected by non-point source pollution are shown. Scientific certainty varies with location. Direct ozone-induced injuries also occur in several other locations not indicated. (e. g., Southern Forests, Berraug et al., 1995.)
Sources: NAPAP (1991); White and Cogbill (1992).

Figure AX10.1-6. Geographic distribution of forested areas historically affected by air pollution.

Source: Figure 2 in IEC (1999a).

3 When the aesthetic quality of forests is important to people, visible injuries to trees can
4 affect consumer welfare. Loss of or damage to foliage, changes in tree density, changes in
5 species composition, and changes in vegetation structure can all affect the enjoyment that people
6 derive from forests, and are therefore appropriate for economic assessment. Estimation of the

1 aesthetic value of forest condition uses RP or SP methods and often focuses on long-term
2 outcome stressors, rather than current intermediate situations. Nevertheless, there are few
3 scientific studies that relate changes in pollution concentrations to these endpoints, and that make
4 a direct linkage between science and economics. A memorandum by Industrial Economics, Inc.
5 (IEc) (1999b) produced for *Benefit-Cost Analysis of the Clean Air Act 1999*, provided a
6 comprehensive review of early forest aesthetics valuation literature. A recent literature review
7 by Kramer et al. (2003) also summarized several key studies described in this report. Table
8 AX10.3-5 lists and describes studies which have estimated monetary value for the types of non-
9 consumptive use and non-use values for forests and natural ecosystems which may be affected
10 by N and sulfur emissions.

11 12 **AX10.3.3 Total Values**

13 Several studies were reviewed by Kramer et al. (2003), and measured the total WTP of
14 the general public for forest aesthetics and attempted to separate contributions of use values and
15 non-use values. Most of these studies indicated that in the aggregate, non-use values (including
16 option, bequest, and existence value) were significantly greater than use values (recreation).

17 Walsh et al. (1990) employed a contingent valuation study using an iterative bidding
18 technique to estimate WTP of Colorado residents for protecting ponderosa pine (*Pinus*
19 *ponderosa*) forests from the mountain pine beetle (*Dendroctonus ponderosae*). Presented with
20 pictures of mid-level forest quality representing current conditions (100 to 125 live trees
21 measuring more than 6-inches in diameter per acre), respondents were asked their WTP to
22 prevent the lowest forest quality (0 to 50 trees per acre) and to attain the highest forest quality
23 (125 to 175 trees per acre). Overall mean WTP for changes in forest quality was estimated at
24 \$47 per household. In addition, respondents decomposed total value into four categories of value
25 (recreational use, option, existence, and bequest). Results showed that use values accounted for
26 27.4% of total value, and non-use values accounted for 72.6% of total value. The study was
27 limited by small sample size (200 respondents) and possible bias from framing the scenario as
28 “one of the most important issues facing Colorado residents.”

29 A study by Haeefele et al. (1992) that measured WTP to protect Southern Appalachian
30 spruce-fir forests, used a decomposition approach to determine dominate influences on total
31 values. The authors found that non-use values (bequest and existence values) overshadowed use

1 values as reasons to protect forests. Holmes and Kramer (1996) relied on results from Haefele
2 et al. (1992) to compare WTP between recreational forest users and members of the general
3 public. Mean household estimates for forest-users (\$36.22) were substantially larger than
4 estimates for nonusers (\$10.37).

5 Kramer et al. (2003) used a dichotomous-choice, contingent-valuation format to
6 determine WTP of Southern Appalachian residents for protecting spruce-fir forests from insects
7 and air pollution. The study measured incremental levels of forest protection using two
8 scenarios: the first increment occurred along road and trail corridors, a scenario that would
9 appeal to people valuing the ecosystem primarily for recreational use; the second level was for
10 the entire ecosystem, a scenario that would appeal to people valuing the continued existence of
11 the entire threatened ecosystem. Using randomly assigned values between \$2 and \$500 dollars,
12 respondents were asked if they would pay a certain tax amount for each scenario. Results
13 suggested that preferences for forest ecosystem protection created a well-behaved demand curve,
14 with incremental WTP increasing at a decreasing rate.

15 16 **AX10.3.4 National-Scale Valuation**

17 An EPA-contracted valuation study by IEc (1999b) developed a benefits-transfer model
18 using results from Holmes and Kramer (1996), Peterson et al. (1987), and Walsh et al. (1990) to
19 estimate national benefits from the 1990 Clean Air Act Amendments (CAAA). Calculations
20 applied WTP values from these previous studies across all households in the affected states.
21 (See Table AX10.3-6 for more information on the underlying original studies, and Table
22 AX10.3-7 for benefits transfer results.) Estimates for the total value of avoiding air pollution-
23 induced damage to forest aesthetics in the United States during the period 1990-2010 were found
24 to range from \$3 to \$17 billion. Due to limitations in the original studies and the simplicity of
25 the benefits-transfer model, the authors warned that the estimates should only be used to consider
26 the general magnitude of benefits to forest aesthetics (in the range of billions of dollars) rather
27 than as precise values.

28 29 **AX10.3.5 Valuation of Degrees of Injury**

30 A few studies—Hollenhorst et al. (1993), Ruddell et al. (1989), Hammitt et al. (1994),
31 Buhyoff et al. (1982)—measured general preferences for forest aesthetics without estimating
32 changes in welfare. Hollenhorst et al. (1993) considered the effect of tree mortality on perceived

1 forest aesthetics. On a 1 to 10 scale for visual and recreational appeal, 400 respondents ranked
2 pictures of 25 sites with tree mortality ranging from 6% to 98% from gypsy moth (*Lymantria*
3 *dispar*) damage. The results produced a hill-shaped function, whereby site appeal increased with
4 mortality at levels as high as 40% but then declined. The authors speculated that respondents
5 had a general distaste for tree mortality but valued light penetration to the forest understory,
6 which allows for the growth of wild flowers and lower-level vegetation.

7 Other studies confirmed this visual preference for light penetration, including Ruddell
8 et al. (1989) and Hammitt et al. (1994), who observed positive responses to forest edges and
9 open middle grounds without light-obstructing tree canopies. Buhyoff et al. (1982) tested how
10 awareness of environmental damages affects perception of aesthetic losses. The study compared
11 aesthetic rankings of photographs between a control group and a group that is informed about the
12 cause of forest damage prior to the ranking session. Results show a heightened level of
13 sensitivity to forest damage by the “informed” group of subjects.

14 Several other studies investigated the notion of aesthetic thresholds, or discontinuous
15 jumps in aesthetic preferences across small changes in visual injuries. Of particular interest to
16 early studies were thresholds at the lower limit of visual perceptibility.

17 Contingent valuation studies by Vaux et al. (1984) and Flowers et al. (1985) assessed
18 aesthetic preferences at recreational areas with fire damage and found that small differences in
19 site appearance can produce large changes in recreation preferences. This finding is generally
20 consistent with the results from two early studies by Buhyoff et al. (1979) and Buhyoff and
21 Wellman (1980), which asked respondents to rate various levels of insect damage. The authors
22 found that preferences seemed to be most affected by the presence or absence of insect damage,
23 as opposed to the degree of damage.

24 Crocker (1985) surveyed 100 recreationists for their WTP for recreational experiences at
25 forested sites with slight injury, moderate injury, or severe injury. Mean WTP estimates for the
26 environment with slight injury were three times higher than WTP for environments with
27 moderate and severe injury, suggesting that people are willing to pay a premium for recreational
28 access below the lower limit of perceptibility. As a group, respondents did not indicate a clear
29 preference ordering between the moderate and severe injury environments.

30 Holmes et al. (2006) use a hedonic method to predict the impact of forest damage due to
31 the hemlock woolly adelgid (*Adelges tsugae*), an invasive insect, on the value of residential

1 properties. Examining 3,379 residential property sales in New Jersey between 1992 and 2002,
2 the study analyzed how the appearance/health of the forest on the home's parcel and within
3 0.1, 0.5, and 1 km buffers around it affects the housing market. Controlling for other relevant
4 variables, the study estimated that hemlock health status had a statistically significant effect on
5 property values. The estimation results suggest, for example, that a 1-point increase (e.g., from
6 10% to 11%) in the percentage of healthy hemlocks (less than 25% foliar damage) of all forests
7 on the home's parcel was associated with a 0.66% sales price increase. Similar changes in the
8 hemlock forests and their health status in the home's near proximity are predicted to be
9 associated with yet larger increments in the sales price.

10 At least one study seems to provide evidence against the concept of thresholds at the
11 lower limit of perceptibility. A referendum-type contingent valuation survey by Jenkins et al.
12 (2002) used two sample populations to value a forest protection program. The initial forest
13 condition was described as "pristine" for one group and already "somewhat damaged" for
14 another group. The degree of forest damage incurred in the absence of a forest protection
15 program was the same for both sample groups. Regressions for the entire sample population
16 showed no statistically significant difference in WTP for forest protection between the two
17 groups.

18 Further analysis of Jenkins et al. (2002) suggested that aesthetic preferences and
19 thresholds differ between recreational groups. Comparisons among recreational groups revealed
20 that consumptive forest users (hunters and anglers) held values that were sensitive to change in
21 forest condition, while non-consumptive forest users (hikers and campers) held values that were
22 insensitive to the same amount of change. Overall, however, non-consumptive forest users
23 expressed higher values than consumptive forest users. Aesthetic thresholds also seem apparent
24 for recovering forests. Paquet and Belanger (1997) found that the aesthetic effects of clear
25 cutting were largely removed once re-growth reached a height of 4 m.

26 Finally, there is substantial literature related to the amenity value of urban/suburban
27 forests and open space. McConnell and Walls (2005) recently reviewed this literature,
28 evaluating more than 60 published articles that have attempted to estimate the value of different
29 types of open space. Two lines of research emerge in this literature: studies that estimate the
30 hedonic value of open space proximity to residential properties, and studies that use SP methods
31 to value preservation of open space. Unfortunately, neither line of research generally comprises

1 studies that provide information on the WTP for quality changes to open space that might be
2 caused by changes in NO_x and SO_x emissions. In most cases, the proximity or preservation of
3 open space or urban/suburban forest is valued without reference to the quality or even the type of
4 open space or forest. Although this literature demonstrates the value of the availability and
5 preservation of open space, its relevancy for the purposes of this assessment is at best limited.

6

7 **AX10.3.6 Limitations and Uncertainties**

8 Shortcomings in the air pollution terrestrial valuation literature have been well
9 documented in recent reviews (Adams and Horst, 2003; U.S. Environmental Protection Agency,
10 2006). In existing economics literature, the effects of O₃ on terrestrial endpoints overshadow
11 assessments of other effects of NO_x and SO_x pollution, such as acid deposition and N
12 fertilization. The latter effects have been well documented in the scientific literature, but the
13 lack of valuation studies related to them limits full assessments of terrestrial damages from NO_x
14 and SO_x pollution. Incomplete scientific understanding of the effects of air pollutants on
15 ecosystems and economic endpoints extends to many valuation studies. Even in the valuation of
16 O₃ effects, which have been relatively thoroughly studied, improvements in noneconomic input
17 data could play an important role in evaluating the magnitude of vegetation damages from O₃.

18 Economic models should incorporate more specific temporal (dynamic) and spatial data
19 regarding terrestrial effects of air pollution to reflect more realistic situations. For example, the
20 O₃ effects valuation literature analyzes air pollution effects across a period of time using only
21 two or three scenarios that represent large, static changes. In the real world, however, these
22 changes would occur gradually and incrementally. Future studies should try to consider more
23 dynamic models that can describe effects of marginal air quality changes. From a spatial
24 perspective, previous studies often assumed that producer responses are similar across large
25 geographic areas. However, regional factors may be important, suggesting a possible need for
26 finer-scale agricultural and forestry data that would allow models to consider micro-level
27 physical and economic factors (Adams and Horst, 2003).

28 With regards to the effects of air pollution on agricultural crops, most economics studies
29 date from the 1980s and many focus on O₃. Therefore, there is a general need for updated
30 valuation studies that consider agricultural damages from air pollution, especially with regards to
31 the roles played by NO_x and SO_x. Specific issues include the need to develop new exposure-

1 response functions for sensitive crops and the effects of air pollution on crop yields under actual
2 farm conditions.

3 Assessments of welfare losses in commercial forestry from air pollution are mainly
4 limited by scientific uncertainty regarding the extent of ecological damage. Restrained by the
5 large size and slow growth of trees, scientific research has primarily considered O₃ effects on
6 seedlings and has little transferability to mature trees.

7 Existing literature on valuation of changes in forest aesthetics has focused primarily on
8 historical cases of acute air pollution or insect infestation and may be overly simplistic.
9 Although these valuations are useful, no existing assessments have examined the effects of
10 reduced air pollution on forest aesthetics. Understanding the effects of marginal changes in air
11 pollution would require the collection of long-term high-quality data about forest health, as well
12 as improved causal linkages between air pollutants and visible injuries to trees. Scientific
13 advancements at this scale would require a sophisticated monitoring network operating over
14 several decades. Until the impacts of pollution on the foundational services of terrestrial
15 ecosystems are better understood, valuation assessments may be premature. Additionally, most
16 studies also fail to distinguish between marginal values of forest health and average values of
17 forest health, an oversight that may create bias in final estimates.

18 A major limitation of both non-economic and economic forest health assessments
19 concerns the limited extent of documented ecosystem-level changes. Most forest health surveys
20 focus on average forest conditions that allow for modeling of near-term trends in economic
21 value, but fail to detect fundamental changes in ecosystem processes that sustain natural capital
22 in the long run (McLaughlin and Percy, 1999). Quantifications of impacts on species effectively
23 conform to existing valuation methods; however, these effects may be overshadowed by long-
24 term or irreversible reductions in ecosystem structure and function (U.S. Environmental
25 Protection Agency, 1999). Assessing ecosystem-level changes presents new challenges to both
26 science and economics as they include a large degree of uncertainty in the scale and nature of
27 effects. In particular, economic assessments of ecosystem impacts may require regional- to
28 national-scale modeling of numerous ecosystem functions rather than analyses of specific service
29 flows that directly contribute to human welfare (U.S. Environmental Protection Agency, 1999).
30 In spite of these challenges, the relationship between air pollution and forest health has enormous
31 implications for policy development and should be addressed in future research.

1 More advanced methods to address uncertainty and irreversibility are essential to future
2 modeling of complex ecosystem-level impacts. Several alternative methods to address
3 ecological uncertainties are currently being developed and should play a central role in future
4 models (U.S. Environmental Protection Agency, 1999).

5 6 7 **AX10.4 VALUATION OF TRANSITIONAL ECOSYSTEMS**

8 The economic analysis of the benefits on wetlands (transitional ecosystems) from
9 reduced emissions are limited in this annex to three recent and comprehensive meta-analyses.
10 Brander et al. (2006) provided a comprehensive review and meta-analysis of the wetland
11 valuation literature. This study improved upon previous similar studies (Brouwer et al., 1999;
12 Woodward and Wui, 2001) by including tropical wetlands estimates from other valuation
13 methodologies, other wetland services, and estimates from more countries.

14 It is well known that wetlands serve a variety of potentially valuable ecological functions,
15 including flood and flow control, storm buffering, sediment retention, groundwater discharge,
16 and habitat for plant and animal species. Wetlands also contribute to climate stabilization,
17 carbon sequestration, and the overall quality of the natural environment. Brander et al. (2006)
18 (Table AX10.4-1) described these functions and their associated goods and services, as well as
19 their values as determined by common valuation methods.

20 21 **AX10.4.1 Use and Non-Use Values**

22 The Brander et al. (2006) meta-analysis included 191 different wetland valuation studies
23 from 25 different countries. Eighty of those studies, half of which were from North America,
24 provided useful empirical data for the meta-analysis. A total of 215 individual observations were
25 gleaned from those studies for use in meta-regressions. The study reviewed the literature,
26 discussed valuation techniques, calculated average wetland values using the results from the
27 combined data set, and then performed a meta-regression of the data to determine which
28 explanatory variables had the greatest effect on wetland value. Non-market use values of
29 wetlands, as well as non-use/existence values, were also included in the analysis. Because not all
30 of the studies generated WTP value estimates, wetland size and population statistics were used to
31 convert estimates from the diverse valuation methodologies to 1995 dollar values per hectare per
32 year, following the example of Woodward and Wui (2001), which is described below.

1 The results of the Brander et al. (2006) meta-analysis showed an average value for
2 wetlands of \$2800/ha/yr (1995 dollars), and median value of \$150/ha/yr. Individual values were
3 calculated by wetland type, the wetland service provided, contingent, and valuation method used.
4 The meta-regression also revealed that studies using the contingent valuation method
5 consistently returned the highest wetland values. It is noted that this may have been due to the
6 type of wetland values that this method was applied to, rather than something intrinsic to the
7 methodology.

8 To look at the value differences from a reduction specifically in N emissions, there is a
9 focus on Brander et al.'s (2006) analysis of wetland value changes that resulted from a small
10 change in water quality or some other ecosystem service. These results are valuable because
11 they may be related to changes in acid deposition as a result of changes in the concentrations of
12 NO_x or SO_x. In the meta-regression results of Brander et al. (2006), the only such ecosystem
13 service which was shown to have a statistically significant effect on wetland value was hunting.
14 Hunting had an unexpected negative influence on wetland value. Although not statistically
15 significant, water quality, habitat and nursery service (specifically support for commercial
16 fisheries and hunting), fishing, and biodiversity all had positive effects on wetland value. The
17 accuracy of the value transfer exercise in Brander et al. (2006) seems to be in line with other
18 similar efforts, with an average transfer error of 74%. Overall, the value transfer function from
19 Brander et al. (2006) produced higher-value transfer error for less valuable wetlands (and
20 systematically over-predicted their value) and lower value transfer error for more valuable
21 wetlands (and slightly under-predicted their value).

22 Woodward and Wui (2001) found 39 studies that contained sufficient data for inter-study
23 comparison, including peer-reviewed and gray literature. Similar to the approach of Brander
24 et al. (2006), Woodward and Wui (2001) assumed that a wetland's value is a function of its
25 ecological characteristics and socio-economic environment, and that there exists a true public
26 WTP at a given moment for a particular wetland. With these assumptions, they attributed
27 variability in wetland value to two principal sources: differing characteristics of the wetland and
28 error in the estimation of the true value (Woodward and Wui, 2001).

29 Brouwer et al. (1999) analyzed the WTP of 30 CV studies addressing ecosystem
30 functions of wetlands, providing a total of 103 estimates. The studies were mostly conducted in
31 the United States, but were not in any way comprehensive spatially. They ranged from

1 1981 to 1997 and covered a wide range of commodity definitions, including preserving wetlands
2 threatened by flooding, maintaining or improving current catch levels and fish populations,
3 saving the bald eagle (*Haliaeetus leucocephalus*), improving/maintaining habitat, water quality
4 ladder changes, preventing shellfish bed closures, increasing the number of protected rivers, and
5 explicitly preserving a measure of water quality. No attempt was made to standardize the degree
6 of change being valued. Instead, the authors attempted to address differences in the studies
7 through the use of dummy variables and some degree of sub-setting.

8 Based on all of the included studies, Brouwer et al. (1999) estimated that the average
9 WTP for the addressed ecosystem functions was about \$90 per household per year. These
10 studies covered types of wetlands (primarily fresh water systems), ecosystem functions (water
11 quality and biodiversity, and to a lesser extent water quantity and flood control), and wetlands
12 size. Cutting across types of systems, location, and function enhanced, the WTP for salt and
13 fresh water improvements was about the same. Within fresh water wetland systems, riverine
14 wetland improvements appeared to be more highly valued than palustrine wetland
15 improvements. Across ecosystem function, flood control was more highly valued than
16 biodiversity, water quality and water generation, in that order. Improvements to larger wetlands
17 appeared to be somewhat more highly valued than to improvements to smaller wetlands.
18 Improvements in use values averaged slightly more than \$100 per household per year, whereas
19 improvements in non-use values only showed values about half this size. Spatially, values were
20 higher in California, followed by Georgia and Louisiana.

21 The review of outdoor recreation valuation studies by Rosenberger and Loomis (2001)
22 included 13 studies and 59 value estimates associated with waterfowl hunting, a popular activity
23 in transitional ecosystems. On average, these studies estimated that the value of waterfowl
24 hunting is about \$32 per person per day (1996 dollars). However, different value estimates
25 ranged from about \$2 to over \$160 per person per day. In their meta-analysis, Rosenberger and
26 Loomis (2001) predicted a \$40 value per person for a day for waterfowl hunting (Table
27 AX10.3-1). These results demonstrate potential benefits from waterfowl hunting, but do not
28 address changes in the quality of transitional ecosystems that may possibly be associated with
29 reduced NO_x/SO_x emissions.

1 **AX10.4.2 Limitations and Uncertainties**

2 Meta-analyses of wetland value (and the underlying original studies) are not directly
3 useful because they do not measure changes in ecosystem services that would follow from some
4 tightening or loosening of the standard for NO_x or SO_x. Nevertheless, they have indirect use by
5 pointing out the importance of various methodologies, the overall values commonly assigned to
6 wetland improvement, and types of ecosystem services that might be affected by air pollutants.
7 For example, both Brander et al. (2006) and Woodward and Wui (2001) found that CV studies
8 generally yielded greater value per acre than travel cost studies. This is not surprising, as the
9 former would generally include non-use values. Furthermore, Woodward and Wui's (2001)
10 meta-analysis showed that the availability of bird hunting, bird watching, and amenity services
11 affect wetland value. For example, bird watching (which could be affected by bird populations
12 which, in turn, could be affected by nutrient enrichment) contributes more value to an ecosystem
13 than any of the other ecosystem services. This is mainly due to the popularity of bird watching
14 and the large numbers of people who engage in this recreational activity.

15 16 17 **AX10.5 VALUATION OF AQUATIC ECOSYSTEMS**

18 As discussed in the ISA and the preceding annexes, acidification and eutrophication are
19 the two main effects of NO_x and SO_x on aquatic ecosystems. In economic valuation of the
20 effects of NO_x and SO_x deposition on aquatic ecosystems, these effects are reflected partly in
21 the WTP for recreational fishing (with effects on the catch rate and fishing quality in a particular
22 aquatic ecosystem) and partly on aesthetic and non-use (and total) values. Valuation methods
23 used to assess the value of aquatic ecosystems include contingent valuation (CV) (open-ended,
24 discrete choice, etc.), choice experiments, hedonic-pricing valuation, travel cost (TC) (hedonic
25 travel cost and traditional travel cost), cost-effectiveness analysis, avoided-damage cost,
26 replacement cost, market analysis, and so forth. The CV method has gained popularity for total
27 (use plus non-use) value estimation, whereas the travel cost method plays an important role in
28 deriving use values. Currently, there is also a tendency to use stated and RP techniques together
29 for the valuation of recreational activities. Supplemental to the below discussions about
30 valuation of acidification and eutrophication on aquatic ecosystems, Table AX10.5-1 describes
31 different aquatic valuation studies according to the ecological effect examined (acidification,
32 eutrophication) and lists their relevant details.

1 An extensive literature review by Wilson and Carpenter (1999) provides an excellent
2 starting point to the valuation literature on aquatic ecosystems. This paper examined 30 studies
3 published between 1971 and 1997 that estimated the value of nonmarket ecosystem services
4 provided by fresh water bodies in the United States. Sixteen were SP studies, with the rest split
5 between travel cost and hedonic pricing approaches. The travel cost studies covered very
6 specific water bodies and stressors, such as a boatable to swimmable change in water quality for
7 13 recreation sites along the Monongahela River in Pennsylvania (Smith and Desvousges, 1986),
8 and a change in water quality measured by the Uttormark's Lake Condition Index for
9 recreational use of Pike Lake in Wisconsin (Bouwes and Schneider, 1979). Beyond spatial and
10 stressor differences, the studies differ in their units for expressing value. The Monongahela
11 River study used benefits per household, with the largest value expressed for a change from
12 boatable to swimmable (\$51). The Bouwes and Schneider (1979) study concluded that the total
13 (aggregate) annual mean CS was almost \$86,000.

14 There are several additional meta-analyses that describe methods of valuation for aquatic
15 ecosystems, but not specifically relating to effects caused by NO_x or SO_x. Van Houtven et al.
16 (2007) analyzed WTP for fresh water quality improvements, covering 131 valuation estimates
17 from 18 SP studies that used or could be transformed to use the water quality ladder (boatable,
18 fishable, swimmable) modified into a 10-point scale. The analysis started with 90 studies but
19 found that most were not sufficiently comparable for statistical analyses. The studies ranged
20 from 1977 to 2003 and covered rivers, lakes and estuaries.

21 A meta-analysis by Johnston et al. (2005) examined the value of fish catch based on a
22 total of 48 studies published in the United States and Canada between 1977 and 2001. The study
23 statistically examined WTP for fish relative to variations in resource, context, angler, and policy
24 attributes, as well as methodological attributes of the studies themselves. The attributes
25 examined included species targeted, geographic region, water body type, catch rate, angler
26 demographics, and fishing method. Among 391 WTP observations, 122 were estimated using
27 CV methods, 59 using TC methods and the remaining from discrete choice models.

28 Johnston et al. (2005) found that SP studies have generally resulted in lower WTP
29 estimates than RP studies, which is consistent with earlier multiple study reviews and meta-
30 analyses. Dichotomous choice CV also has produced lower WTP estimates than choice
31 experiment or conjoint surveys, compared to the default of open-ended surveys (including

1 payment cards and iterative bidding). However, these findings were not robust across all
2 regression model specifications. The study supported previous findings (Poe et al., 2000) that
3 WTP is systematically associated with variations in resource, context, and angler attributes. The
4 study also concluded that WTP per fish varies systematically across study methods, but the
5 variation due to methodology accounted for a relatively small proportion of total WTP variation.
6 Again, these results demonstrate the value of recreational fishing, but do not address changes in
7 water quality that may be associated with reduced NO_x/SO_x emissions.

8 9 **AX10.5.1 Acidification**

10 The Adirondack Park in New York is the best documented of all areas affected by acidic
11 deposition in the United States. Due to air pollution that largely originated from power plants
12 and other sources to the west and southwest of the park, many watersheds in the park have
13 experienced slow acidification of water and soil since the late 18th century. This park has been
14 the subject of numerous valuation studies in recent decades.

15 Morey and Shaw (1990) applied the travel cost model and estimated recreational fishing
16 values associated with water quality change resulting from acidic deposition in the Adirondack
17 Park area. The results showed that the aggregate expected conditional compensating variation
18 for a 50% increase in catch rate of two trout species at four sites was \$3,863 (1977 dollars;
19 \$13,175 in 2007 dollars), based on 607 survey respondents with an estimated standard deviation
20 of \$89 (\$304 in 2007 dollars).

21 A travel cost model was also applied by Mullen and Menz (1985) to link acidic
22 deposition and recreational fishing in the Adirondack Park. A net average economic value per
23 angler day was calculated to be \$20 (1976 dollars; \$73 in 2007 dollars) for lakes, ponds, and
24 streams in the Adirondacks, with an estimated total loss in net economic value of \$1.07 million
25 (1976 dollars; \$3.89 million in 2007 dollars) per year for a 5% reduction in fishable area. These
26 estimates excluded streams because limited knowledge existed to assess the effect of pH
27 fluctuations on aquatic life in streams. Shaw (1989) questioned the reliability of these results,
28 arguing that the demand equation was not compatible with economic theory and that aggregating
29 separate CS measures from different equations was inappropriate.

30 Englin et al. (1991) assessed the economic impact on recreational fishing in four upper
31 northeastern states resulting from acidic deposition control. Biological effects of acidification

1 were linked with hedonic travel cost and random utility models through the acid stress index
2 (ASI) and fish catch per unit effort (CPUE). The analysis was based on multiple data sources
3 and yielded positive social welfare for 2030 under a scenario of reducing by 50% the ambient
4 deposition in 1989. This level of decline in acidic deposition was expected to occur on the basis
5 of analyses conducted by the National Acid Precipitation Assessment Program (NAPAP).

6 Cameron and Englin (1997) measured welfare under an assumption that people are not
7 certain about participation in fishing. Based on WTP results from a survey and a random utility
8 model, surpluses were estimated for preventing a 20% loss in the availability of high-elevation
9 lakes for fishing in northeastern states.

10 Randall and Kriesel (1990) employed a SP method to value a National Pollution Control
11 Program, which led to improved air and water quality by 25% within 5 years. A nationwide
12 survey conducted in multiple modes found an estimated annual willingness to pay of \$694
13 (\$1,098 in 2007 dollars) per household. The researchers concluded that the estimated value was
14 lower than their multimarket hedonic estimates.

15 Banzhaf et al. (2006) conducted a CV survey, which was designed to estimate the total
16 value (use plus non-use values) of reducing acidification by liming the lakes and forests in the
17 Adirondack Park to a degree matching recent SO_x and NO_x reductions under emissions trading
18 programs. The mean WTP for improving 600 lakes “of concern,” and small increases in
19 populations of two bird species and one tree species was \$48 (2003 dollars; \$54 in 2007 dollars)
20 per year per New York household. The mean WTP for improving 900 lakes “of concern,” four
21 bird species and three tree species was \$54 (2003 dollars; \$61 in 2007 dollars) per year per New
22 York household.

23 Sequential implementation of several regulations, including in particular the CAA, has
24 substantially reduced acidic deposition, especially in the eastern part of the United States.

25 Burtraw et al. (1997) conducted a benefit-cost analysis for the NAPAP program. Besides
26 improving public health and visibility, emissions controls contributed to decreased lake
27 acidification which was projected to have economic benefit associated with improved
28 recreational fishing in the Adirondack Park. The ASI and CPUE approaches were used in the
29 Tracking and Analysis Framework (TAF) model to capture the response of three recreationally
30 fished species to water quality improvement in 33 statistically selected Adirondack lakes. The

1 per capita recreational fishing benefits in 2010 were estimated to be \$0.62 (1990 dollars; \$0.98 in
2 2007 dollars) annually per angler fishing in the Adirondack area.

3 4 **AX10.5.2 Eutrophication**

5 As is the case for acidification, the endpoints most studied in the valuation literature for
6 nutrient enrichment concern fishing and non-use (or total) values. Change in aquatic recreational
7 behavior is another endpoint for looking at valuation of such ecosystems, although it is difficult
8 to link those changes due to ambient NO_x or SO_x concentrations.

9 10 **AX10.5.2.1 Recreation**

11 Bockstael et al. (1989a) measured the benefits of improvements in water quality of the
12 Chesapeake Bay using travel cost and SP methods. A telephone survey with 959 respondents
13 revealed an aggregate WTP for water quality improvement from current level to a level
14 acceptable for swimming and/or other water activity of about \$91 million (1987 dollars;
15 \$166 million in 2007 dollars) for households in Maryland. Based on three other surveys, a travel
16 cost model yielded aggregate use values of about \$34.7, \$4.7, and \$1.4 million (\$63.1, \$8.6, and
17 \$2.6 million in 2007 dollars) for a 20% water quality improvement for beach use, boating, and
18 sport fishing, respectively.

19 Morgan and Owens (2001) simulated water quality change under a baseline (without
20 additional pollution control) and a scenario with pollution control in the Chesapeake Bay
21 watershed and then calculated aggregate benefits for beach use, boating, and striped bass sport
22 fishing by transferring the benefits from Bockstael et al. (1989a). Lower bound aggregate
23 benefits for beach use, boating, and sport fishing were \$288.8, \$6.7, and \$288.8 million
24 (1996 dollars; \$380.4, \$8.8, and \$380.4 million in 2007 dollars), respectively for a 60%
25 improvement in Chesapeake Bay water quality.

26 Lipton (2004) mailed out an open-ended contingent valuation survey to 2,510 randomly
27 selected Maryland boaters regarding willingness to pay for one unit improvement in the water
28 quality of the Chesapeake Bay. The boaters ranked their perception of water quality on a scale
29 of one to five. The median WTP for a one step improvement in water quality was \$17.50
30 (\$19.66 in 2007 dollars) per year and the mean was \$63 (\$71 in 2007 dollars), with 38% of
31 respondents expressing a zero WTP. It was found that the boaters who keep their boats in the
32 water would pay more than those who keep them on trailers. Individuals who ranked ambient

1 water quality lower and had more concern for the health effects from water quality degradation
2 would likely pay more for water quality improvement. The aggregated WTP for the Chesapeake
3 Bay boaters in Maryland was approximately \$7.3 million (\$8.2 million in 2007 dollars) per year
4 with a \$146 million (\$164 million in 2007 dollars) present value (a 5% discount rate).

5 Smith et al. (1991) estimated the recreational fishing value of Albemarle-Pamlico Estuary
6 in North Carolina using a hedonic travel cost model. The analysis was based on an intercept
7 survey with 1,012 interviews at 35 boat sites and 44 bank sites in 1981 and 1982. The estimated
8 benefit derived from the application of a conventional demand model to the boat site sample
9 ranged from \$1.49 to \$2.58 (1982 dollars; \$3.19 to \$5.53 in 2007 dollar), and for the bank site
10 sample ranged from \$0.65 to \$1.11 (\$1.39 to \$2.38 in 2007 dollars) for an increase in catch rate
11 of one fish per hour per person.

12 Four years later, Kaoru (1995) and Kaoru et al. (1995) used the information collected
13 from the same survey to estimate the recreation value from improvements in Albemarle and
14 Pamlico Sounds using a household production model and a random utility model. They linked
15 the effluent loading and quality of sport fishing with the fisherman's decision on site selection.
16 Instead of fish availability being estimated as the average number of fish caught per person per
17 hour for each entry point, Kaoru et al. (1995) used total catch per trip per person as their key
18 measure of fishing success. They included not only the estimated N loadings but also the effect
19 on biochemical oxygen demand as an influence on fishing quality. The results suggested that
20 depending on aggregation methods, CS ranged between \$7.05 and \$36.19 (\$9.56 and \$49.08 in
21 2007 dollars) for a 5% increase in total catch. The CS was \$1.27 to \$6.52 (\$1.72 to \$8.84 in
22 2007 dollars) for a 36% decrease in N loadings at all sites.

23 Whitehead et al. (2000) used a joint stated and RP model to estimate recreation value of
24 improvements to Albemarle and Pamlico Sounds in terms of CS per trip and per season. A
25 telephone survey was conducted in 1995 to learn how North Carolina residents would value
26 improvements of water quality resulting in a 60% increase in fish catch and a 25% increase in
27 open shellfish beds. The analysis was based on 765 completed responses. The CS per trip was
28 estimated at \$64 (1995 dollars; \$87 in 2007 dollars) for current quality and \$85 (\$115 in
29 2007 dollars) for improved quality and the CS per season was \$121 (\$164 in 2007 dollars) for
30 current and \$155 (\$210 in 2007 dollars) for improved quality.

1 The Catawba River in North and South Carolina is used for electric power generation,
2 recreation, drinking water, and wastewater assimilation. With population growth and land use
3 change, the health and vitality of the river system are declining as the river flows downstream.
4 Through a mail-phone survey of 1,085 residents randomly selected from 16 counties of Catawba
5 River Basin, Kramer and Eisen-Hecht (2002) presented a management plan designed to maintain
6 the water quality at the current level over time. The water quality in the entire watershed was
7 classified as good, fair or poor on maps to illustrate the distribution of the tributaries with
8 different water quality. The mean WTP was estimated to be \$139 (\$160 in 2007 dollars) for
9 protecting current water quality from deterioration.

10 A site choice model applied jointly with a trip frequency model was used by Needelman
11 and Kealy (1995) to assess the relative benefits of eliminating eutrophication, fecal bacteria, and
12 oil and grease in New Hampshire lakes. The site choices analysis was based on 53 individuals
13 and 1,021 trips, while the trip frequency model was based on a total of 519 individuals including
14 the responses for the site choices model. The mean seasonal benefits were valued at \$1.40
15 (\$1.90 in 2007 dollars) for eliminating eutrophication from all sources (\$1.33; \$1.80 in 2007
16 dollars) for eliminating nonpoint source pollution alone and \$0.09 (\$0.12 in 2007 dollars) for
17 eliminating point source pollution alone) with an aggregate seasonal benefit of \$1.16 million
18 (\$1.57 million in 2007 dollars), with \$1.11 million for nonpoint source and \$0.08 million for
19 point source pollution. However, the economic benefit estimates were exclusively for swimming
20 and day trips. The measures of water quality were not from the year of the survey (1989) but
21 from a range of years from 1976 to 1991.

22 The Tar-Pamlico River has experienced declining fish catches, disease in fish and
23 shellfish beds, algae blooms, and aquatic grass losses. More than half of the pollution impairing
24 one third of the river was estimated to come from agricultural nonpoint sources. Whitehead and
25 Groothuis (1992) proposed a management program in which farmers used best management
26 practices (BMPs) to significantly improve the water quality of the Tar-Pamlico River such that
27 recreational anglers would be able to catch twice as many fish per trip. A mail survey was sent
28 to 179 households in four counties in Tar-Pamlico River basin (with a 61% response rate). The
29 mean WTP for doubling fish catch was estimated at \$25 (\$38 in 2007 dollars), which was
30 bounded from above by a \$35 use value (\$53 in 2007 dollars) and from below by a \$21 (\$32 in
31 2007 dollars) non-use value. The benefits of water quality improvement in the study area were

1 aggregated at \$1.62 million (1991 dollars; \$2.46 million in 2007 dollars) each year. The
2 researchers believed that non-use value could account for as high as 84% of the estimate.
3 However, the study suffered from small sample size and relatively high non-response rate (11%)
4 to the WTP questionnaire.

5 Some portions of the coastal coral reefs in the Florida Keys are projected to disappear
6 within 10 to 25 years. In 2000, the U.S. government announced a long-term plan to save coral
7 reefs proposing that 20% of all coral reefs in American-controlled waters would become
8 ecological preserves by 2010. Park et al. (2002) investigated the WTP to preserve current water
9 quality and health of the coral reefs in the Florida Keys. Based on 460 responses to a CV survey
10 and 4,035 respondents to a travel cost survey (460 responses used in the analysis), the annual use
11 value was estimated at \$481 per person per snorkeling trip (\$553 in 2007 dollars). The mean
12 predicted WTP per trip from a Tobit model was \$735 (\$844 in 2007 dollars). Over 85% of the
13 predicted WTP value was within plus or minus \$50 (\$57 in 2007 dollars) of the total trip
14 expenses from the contingent valuation scenario.

15 16 **AX10.5.2.2 Commercial Fisheries**

17 As one of six background studies for the National Science and Technology Council
18 (NSTC), Diaz and Solow (1992) used a time series estimation approach to examine the effects
19 from hypoxia³ in the Gulf of Mexico. The study failed to confirm the relationship between the
20 annual occurrence of hypoxia and commercial fishery health, based on catch rate per unit effort
21 of three major species from the 1960s to 1990s. Although the benefit assessment did not detect
22 effects attributable to hypoxia, this does not necessarily mean that the economic effects would
23 not occur. NSTC (2000) identified alternatives for reducing the adverse effects of hypoxia and
24 examined the costs associated with reduction of N and P inputs. A net cost estimated by the U.S.
25 Mathematical Programming Model for Agriculture was about \$0.8 per kilogram (\$0.36 per
26 pound; \$0.96 per kilogram/\$0.36 per pound in 2007 dollars) for a 20% edge-of-field N loss
27 reduction on agricultural lands, whereas restoring 5 million acres of wetland would have a net

³ Hypoxia (DO depletion) is a phenomenon resulting from the overloading of nutrients (usually N or P) in water. Most fresh waters are P-limited, and therefore added N from atmospheric deposition does not have a substantial effect on productivity. In contrast, marine and estuarine waters tend to be N-limited, and are therefore expected to respond to additional N inputs by increasing algal productivity. Excessive production of algae can deplete the water of oxygen when those algae die and are decomposed by oxygen-consuming microorganisms. If the concentration of DO decreases to very low levels, fish, and other life forms can die.

1 cost of \$1.00 per kilogram (\$0.45 per pound) (\$1.2 per kilogram/\$0.54 per pound in 2007
2 dollars) of N removal.

3 The Neuse River in North Carolina is important to the commercial blue crab (*Callinectes*
4 *sapidus*) fishery in the eastern United States. It accounted for about a quarter of the blue crab
5 harvest from 1994 to 2002. Smith and Crowder (2005) simulated the progress of eutrophication
6 in the Neuse River using a series of ordinary differential equations, which linked changes in the
7 quantity of nutrients, algal growth, spatial population distribution of blue crab and its prey
8 species with fishing efforts. Results suggested that a 30% reduction in N loading in the Neuse
9 River watershed over a 50-year period would result in about a \$2.56 million (\$2.71 million in
10 2007 dollars) discounted present value generated in fishery rent (the difference between fishing
11 revenues and costs including fixed and opportunity cost).

12

13 **AX10.5.2.3 Water Clarity**

14 In addition to effects on fish populations, eutrophication reduces water clarity due to
15 excessive growth of algae. Boyle et al. (1999) studied the social welfare related to water clarity
16 of four lakes in Maine employing a two-stage hedonic demand model. Based on data from 1990
17 to 1995 on property sales for 25 lakes, tax records, mail survey, and water clarity data from the
18 Maine Department of Environmental Protection (DEP), the CS for water clarity improvement
19 from the average ambient level (3.78 m) to 5.15 m was estimated to be \$3,677, \$3,765, and
20 \$12,870 (\$4,562, \$4,671, and \$15,967 in 2007 dollars) for differently specified demand systems
21 (Cobb-Douglas, semilog, and linear demand models, respectively). Social welfare loss for
22 visibility deterioration from an average level to 2.41 m ranged from \$25,388 to \$46,750 (\$31,497
23 to \$57,989 in 2007 dollars). One of the interesting findings in the study was that the slope of the
24 Cobb-Douglas demand model increased to 3.0 m, a threshold used by the Maine Department of
25 Environmental Protection to indicate improved water quality and public preferences for it.

26 Poor et al. (2006) evaluated water quality in a small watershed of Maryland using a
27 hedonic property valuation model. The watershed is located in a peninsula surrounded by the
28 Potomac and Patuxent Rivers and the Chesapeake Bay. Due to nonpoint source pollution runoff,
29 water quality has deteriorated, which might have negative impacts on residential housing prices,
30 especially for those close to the river. To estimate the possible extent of the impact, total
31 suspended solids (TSS) and dissolved inorganic nitrogen (DIN) were averaged by year and
32 included in the model as indicators of ambient water quality. The estimates showed that a

1 marginal increase in TSS reduced average housing prices by \$1,086 (\$1,113 in 2007 dollars),
2 and a marginal increase in DIN decreased housing prices by \$17,642 (\$18,087 in 2007 dollars).

3 4 **AX10.5.2.4 Avoided Costs**

5 Based on a model projection, IEC (1999c) estimated the benefits of decreased N
6 deposition to the estuaries in the eastern United States using the avoided cost method. According
7 to their results, the annual avoided cost in 2010 would range from \$26 to \$102 million if 12.8
8 million pounds of N loading was reduced annually in Long Island Sound. An annual reduction
9 of 58 million pounds of N loading into Chesapeake Bay would avoid an annual cost of \$349 to
10 \$1,278 million. Uncertainty associated with model assumptions and the inappropriate use of
11 avoided cost estimates to value benefits or damages are two major sources of potential error in
12 generating such estimates. In addition, the avoided costs method generally does not measure
13 values conceptually accurately, and these values also are not linked to benefits from reduced
14 pollution.

15 16 **AX10.5.3 Limitations and Uncertainties**

17 Several general limitations apply to the valuation of water quality changes. First, the
18 definition of water quality is too ambiguous to quantify comparisons across studies. Second, the
19 degree of water quality improvement is not often clear. A common obstacle in any
20 environmental economic valuation is the availability of data. Problems stemming from lack of
21 data extend from biological data on the populations of target species to limitations of the
22 available economic data on the value of commercial and recreational fisheries to small samples
23 of survey respondents (Smith and Crowder, 2005).

24 The geographical focus of valuation studies is another limitation. The studies reviewed
25 here largely focused on the eastern part of the United States, represented by the Adirondacks,
26 Chesapeake Bay, and Albemarle and Pamlico Sounds. Several studies investigated the total
27 value of aquatic ecosystems and the majority of the studies calculated recreational values of
28 water quality improvement. Only a few studies addressed the economic value of commercial
29 fisheries. There is considerable uncertainty in the estimates of benefits as they vary significantly
30 even for studies in the same area, with similar changes in the commodity, and use of the same
31 valuation methodology.

1 Almost every study reviewed here mentioned the problem of uncertainties about the
2 natural science (Diaz and Solow, 1992; NSTC, 2000). For example, the processes involved in
3 the development of hypoxia are not fully known. There is also no clear connection between a
4 decrease in pollution level and an increase in catch rate (Bockstael et al., 1989b). Additionally,
5 uncertainty arises from the selection of parameter values (Smith and Crowder, 2005) and models
6 (Burtraw et al., 1997). Due to the uncertainty about water quality improvement in tributaries of
7 the Chesapeake Bay, the estimates provided by Morgan and Owens (2001) excluded benefits
8 from water recovery in the tributaries.

9 Study coverage also affects benefit estimates. For example, Morey and Shaw (1990)
10 only included those fishermen who could make day trips to one or more of the study sites,
11 fishermen with complete records, and fishermen whose distance to the farthest site was less than
12 200 miles. Morey and Shaw (1990) evaluated four sites and two kinds of trout in the
13 Adirondacks while Englin et al. (1991) valued only one trout species and lakes in four states.

14 Many studies relied on information from surveys, which may suffer from various biases.
15 For example, several studies reviewed here used intercept surveys, which are not necessarily
16 representative of the target population (Bockstael et al., 1989b; Smith et al., 1991). Double
17 counting of values may also introduce errors into value estimation. For example, people who are
18 boating may also go fishing (Bockstael et al., 1989b).

19 20 21 **AX10.6 SUMMARY**

22 Previous ecosystem valuations presented in AQCDs were very limited because they
23 considered only studies that could directly attribute monetary values to changes in emissions.
24 The assessment of the literature in this annex has a different approach: the voluminous literature
25 that values various ecosystem services affected by emissions is included, whether or not the
26 actual linkages all the way from emissions to those effects have been quantified. This approach
27 nevertheless necessitates that the natural science underpinnings be examined in the context of
28 preferences, that is, descriptions of damages (or benefits) from NO_x and SO_x emissions (or
29 reductions in those emissions) from the natural sciences that translate into things that the public
30 cares about. These include, for example, whether the water is boatable or swimmable, the
31 marketable yield associated with changes in a forest or a crop, and effects on aesthetics of
32 wetlands.

1 The physical endpoints and their corresponding valuation studies are divided into
2 different ecological and value endpoints applicable to terrestrial, transitional, and aquatic
3 ecosystems. There is significant valuation literature on the effects of O₃ on crops (and to a far
4 lesser degree on forest yield), but this topic is beyond of the scope of this assessment. Beyond
5 the O₃ effects, there is little quantification of the science describing the effects of pollution
6 related to NO_x and SO_x on ecosystems. Valuation studies are themselves classified into meta-
7 analyses and original studies, the latter into market studies (e.g., commercial fishing), RP studies
8 (e.g., those related to recreation behavior, property values, etc.), and SP studies (those that ask
9 people survey questions about their WTP for hypothetical ecosystem improvements).

10 For valuation of terrestrial effects, survey methods are most common. Supplemented by
11 travel cost approaches, this literature leads to a variety of estimates of WTP for improved forest
12 quality that could prove useful for estimating benefits of N and S reductions (provided a number
13 of linkages can be made), even though some of the endpoints valued are related to insect
14 damage. One meta-analysis is available that summarizes this valuation literature.

15 For wetland valuation, three meta-analyses are available that summarized the valuation
16 literature. This literature is problematic because it focuses on values per wetland acre rather than
17 WTP for changes in services provided by a wetland affected by deposition of N and S pollutants.
18 However, some of the available studies provide WTP for discreet ecosystem services, which is
19 helpful in matching these values to services affected by reductions in N and S deposition.
20 Nevertheless, because there is a very poor understanding of the scientific basis for linking NO_x
21 and SO_x emissions to ecosystem health endpoints, the ability to make the necessary linkages to
22 estimate benefits of pollution reductions is very limited.

23 The aquatic service valuation literature is the most voluminous of the three categories
24 reviewed. It contains many recreation value studies, a number of property value studies, some
25 total (use plus non-use) value studies, some studies on commercial fishery damages and several
26 good meta-analyses of primary valuation studies, which provide estimates of the WTP of
27 households for improvements in the aquatic ecosystem related to N and S changes. Again,
28 however, there is little focus on NO_x or SO_x as the cause of alterations to the aquatic ecosystem.

29 Overall, there is a robust literature valuing a variety of ecosystem services that could be
30 related to reductions in N and S emissions. Therein addition, issues affecting the credibility of
31 any individual study and even the studies grouped by technique, such studies can only be used

- 1 for general valuation purposes. The most important limitation is establishment of the linkages
- 2 between the physical, chemical, and biological effects of air pollutants on natural ecosystems and
- 3 changes in exposure to NO_x and SO_x .

TABLE AX10.2-1. COMMONLY ADOPTED ENVIRONMENTAL VALUATION METHODS BASED ON REVEALED OR STATE PREFERENCES

Methods	Description	Direct Use	Indirect Use	Total Value
Revealed Preference Methods	Observing individual choices and behavior to predict their preferences for environmental goods and services.			
• Avoided expenditure method	Predicting the cost of mitigating the effects of reduced environmental quality.	X	X	
• Derived demand functions	Estimate the value of environmental goods and services by deriving the demand functions of households or firms for them (e.g. water use)	X	X	
• Hedonic valuation method	Estimating an implicit price for the environmental quality attributes of marketable goods, such as housing.	X	X	
• Market analysis	Used for valuing market goods using data on prices and quantities of outputs and inputs. May use prices of close substitutes, methods of deriving shadow prices, or simulation of changes in market conditions.	X	X	
• Referenda	Examining voting results related to environmental resources to predict values for them.	X	X	
• Replacement cost	Measures expenditures incurred in replacing or restoring environmental good or service lost (e.g. water filtration). Provides accurate valuation only under strict assumptions usually not met.	X	X	
• Travel cost method	Values the environmental attributes of recreational sites by examining visitation frequency and cost differential incurred in reaching site with different attributes.	X	X	
• User fee	Examine user fees paid to gain access to an ecological resource such as a park to estimate the lower bound of society's value for that resource.	X	X	

TABLE AX10.2-1 (cont'd). COMMONLY ADOPTED ENVIRONMENTAL VALUATION METHODS BASED ON REVEALED OR STATE PREFERENCES

Methods	Description	Direct Use	Indirect Use	Total Value
Stated Preferences Approach	Directly surveying individuals to predict their preferences for environmental goods and services.			
• Choice experiments, conjoint analysis	Elicits individuals' choices from several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to contingent ranking).	X	X	X
• Contingent valuation	Elicits data on individuals' willingness to pay for environmental goods and services (hypothetical setting, limited by potential biases). Often implemented using a hypothetical referenda.	X	X	X
• Contingent ranking	Elicits data on the ranking of several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to choice experiments, conjoint analysis).	X	X	X

TABLE AX10.3-1. ECONOMIC EFFECTS OF OZONE AND OTHER POLLUTANTS ON AGRICULTURE, AS REPORTED IN THE 1996 OZONE CRITERIA DOCUMENT

Study	Region	Pollutant and Concentration	Model Features				Results (Annual 1980 U.S. Dollar)			
			Price Changes	Output Substitutions	Input Substitutions	Quality Changes	Crops	Consumer Benefits	Producer Benefits	Total Benefits (Costs)
Adams et al. (1986a) ^b	U.S.	Ozone, 25% reduction from 1980 level for each state ^c	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, barley	1160×10 ⁶	550×10 ⁶	1700×10 ⁶
Kopp et al. (1985) ^b	U.S.	Ozone, universal reduction from 53 ppb to 40 ppb ^a	Yes	Yes	Yes	No	Corn, soybeans, wheat, cotton	Not reported	Not reported	Not reported
Adams et al. (1986b)	U.S.	Acid deposition, 50% reduction in wet acidic deposition	Yes	Yes	Yes	No	Soybeans	172×10 ⁶	-30×10 ⁶	142×10 ⁶
Adams and Crocker (1989)	U.S.	Ozone, seasonal standard of 50 ppb with 95% compliance ^d ; Includes adjustments for 1985 Farm Bill	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, rice, hay, barley	905×10 ⁶	769×10 ⁶	1674×10 ⁶

^a Seven-h growing season geometric mean. Given a long-normal distribution of air pollution events, a 7-h seasonal ozone level of 40 ppb is approximately equal to an hourly standard of 80 ppb, not to be exceeded more than once a year (Heck et al., 1983).

^b Reported in 1986 criteria document.

^c Reported All studies except Garcia et al. use NCLAN data to generate yield changes due to ozone.

^d Seven- and twelve-h growing season geometric mean. Analysis includes both fixed rollbacks (e.g., 25% and seasonal standards (with variable compliance rates).

Source: Adams and Horst (2003).

TABLE AX10.3-2. ECONOMIC EFFECTS OF OZONE ON MARKETABLE BENEFITS FROM FORESTS

Study	Pollutant/Coverage	Response and Air Quality Data	Economic Model	Annual Damages or Benefits of Control
Callaway et al. (1986) ^a	All pollutants. Forest products (hardwood and softwood) in the eastern U.S.	Assumes three arbitrary growth reductions (10%, 15%, and 20%) for hardwood and softwood tree species.	Spatial equilibrium models of softwood and hardwood stumpage and forest products industries in the U.S.	\$340 to \$510 million; damage in 1984 dollars for assumed reductions in growth levels.
Crocker (1985)	Acid deposition. Forest products and forest ecosystem service flows for eastern U.S.	Assumes a 5% reduction in products due to acid deposition: assumes a pristine background pH of approximately 5.2.	Naive; assumed changes in output multiplied by avg value of those goods or services.	\$1.75 billion damage in 1978 dollars from current levels of acid deposition.
Crocker and Forster (1986)	Acid deposition. Forest products and forest ecosystem services for eastern Canada.	Assumes 5% reduction in forest productivity for all eastern Canadian forests receiving \$10 kg/ha/yr sulphate deposition.	Naive; assumed changes in output multiplied by avg value of goods or services.	\$1.5 billion damage in 1981 Canadian dollars from current levels of acid deposition.
Haynes and Adams (1992)	Air pollutants, including acid precipitation. Losses estimated for eastern U.S. softwoods.	None; paper demonstrates a methodology for assessing economic effects of yield (growth and inventory) reductions due to any course. Assumes losses from 6% to 21% for softwoods.	Econometric model of U.S. timber sector (TAMM).	Damages of \$1.5 to \$9.0 billion in 1988 dollars. ^b
Bentley and Horst (1998)	Ozone. All hardwoods and softwoods except western hardwoods.	Dose-response based on survey of experts scaled to partial attainment of secondary standard relative to the current primary standard. SUM06 exposure metric is based on a cumulative daytime exposure during the growing season.	Econometric model of U.S. timber sector (TAMM).	Benefits of \$14 million in 2010 (1990 dollars) for partial attainment of 0.08 ppb 3rd max secondary standard. This standard was considered during the standard development process.

Source: Adams and Horst (2003), exceptions:

^aWe used the updated version of Crocker et al. from 1986, while Adams and Horst cited a prior version, from 1985.

^bWe drew different numbers from the Crocker and Forster study than those reported by Adams and Horst.

Source: Table 2 in Bentley and Horst (1998).

TABLE AX10.3-3. FORECASTED AVG VALUES FOR SELECT ACTIVITIES, PER DAY PER PERSON IN 1996

Activity	Northeast	Southeast	Intermountain	Pacific Coast	Alaska	USA
Swimming	14	9	19	9	14	14
General recreation*	30	25	34	25	30	30
Fishing	37	32	41	32	37	37
Waterfowl hunting	40	35	44	34	40	39
Big game hunting	45	40	50	40	45	45

*The activity category includes camping, picnicking, sightseeing, hiking, small game hunting, wildlife viewing, and other general recreation. In the meta-analysis, values for these activity categories do not differ statistically significantly.

Source: from the meta-analysis benefit function by Rosenberger and Loomis (2001), Table 6.

TABLE AX10.3-4. TYPICAL IMPACTS OF SPECIFIC POLLUTANTS ON THE VISUAL QUALITY OF FORESTS

	Geographic Extent	Direct/Indirect Injuries	Major Types of Visual Injuries	Notes
Ozone	Area or regional effects	Direct injuries	Foliar injuries (e.g., pigmented stipple), increased needle/leaf abscission, premature senescence of leaves. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for ozone.	
		Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as insect attacks. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	
Acidic Deposition	Area or regional effects	Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as climatic factors. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	Acidic deposition can also cause direct foliar injuries. Acids are, however, more likely to indirectly affect the visual appearance of forest trees, unless exposure levels are very high.
Sulfur Dioxide	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Sulfur dioxide may also cause indirect injuries. Indirect injuries, however, are not well documented.
Hydrogen Fluoride	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Hydrogen fluoride may also cause indirect injuries. Indirect injuries, however, are not well documented.

Source: Exhibit 2 Industrial Economics (IEc) (1999a).

TABLE AX10.3-5. ECONOMIC VALUATION STUDIES RELATED TO FOREST AESTHETICS

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Crocker (1985)	CV (open ended)	Southern California	Evaluating visits to recreational sites with slight, moderate, and severe O ₃ induced damages to ponderosa and Jeffery pine stands.	Household WTP (per trip)	Slight damage: \$2.09 Moderate damage: \$0.66 Severe damage: \$0.74
Haefele et al. (1992)	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution	Household WTP (per yr)	PC: \$21 DC: \$100
Holmes and Kramer (1996) ^a	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution. Analysis compared forest users and non-users.	Household WTP (per yr)	Forest users: \$36 Non-users: \$10
Holmes et al. (2006)	Hedonic pricing	New Jersey	Evaluate the effects of hemlock forest health status on housing prices. Hemlock health status is potentially deprived by hemlock woolly adelgid; an exotic forest insect.	Housing price	Hemlock forest health status is positively associated with housing prices. For example, a 1-point increment in (e.g., from 10% to 11%) in the % of healthy hemlocks of all forests on the home parcel was associated with a 0.66% sales price increase. Similar changes in home's near proximity are associated with yet larger price increments.
IEc (1999b) ^b	Benefits transfer	National	Protect trees from various different types of damage (see description of source studies)	Welfare Loss (1990-2010)	\$3 to \$17 billion

TABLE AX10.3-5 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO FOREST AESTHETICS

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Jakus and Smith (1991)	CV (dichotomous choice)	Maryland and Pennsylvania	Protect private homeowner property and surrounding public lands from gypsy moth damages (reduce tree defoliation by 25%)	Household WTP (for entire program)	Private Property Prgm (only): \$254 to \$420 Private and Public Prgm: \$314 to \$527
Jenkins (2002)	CV (open ended)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout ecosystem	Household WTP (per yr)	\$153
Kramer et al. (2003)	CV (dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout the entire ecosystem	Household WTP (per yr)	Road side only: \$18 Entire ecosystem: \$28 Non-use: 87% of total value Use: 13% of total value
Kramer and Mercer (1997)	CV (payment card and dichotomous choice)	National (USA)	Protect 10% of tropical rainforests as national parks or forest reserves.	Household WTP (per yr)	PC: \$31 DC: \$21
Loomis et al. (1996)	CV (dichotomous choice, open ended)	Oregon	Protect old growth forests of Pacific Northwest from fires.	Household WTP (per yr)	DC: \$98 OE: \$33
Leuschner and Young (1978b)	TCM	Texas	Reduce crown density in recreational areas.	Consumer Surplus (losses)	-0.69 to -6.5% (depending on level of substitute sites)
Miller and Lindsey (1993)	CV (dichotomous choice)	New Hampshire	Protect private homeowner property from gypsy moth damages (reduce tree defoliation by various amounts)	Household WTP (per yr)	\$55 to \$86 (depending on level of reduction in tree defoliation)

TABLE AX10.3-5 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO FOREST AESTHETICS

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Peterson et al. (1987)	CV, hedonic property	Los Angeles area	Avoid O ₃ induced damages to trees in local national forests for recreationists (in greater LA area) and homeowners (with property bordering forest).	Household WTP (per yr) Consumer Welfare	Recreationist: \$43 Homeowner: \$131 \$31 to \$161 million
Treiman (2006)	CV (dichotomous choice)	Missouri	Improve residential tree care and maintenance in different sized cities.	Household WTP (per yr)	Urban areas: \$14 to \$16
Walsh et al. (1989)	TCM	Colorado Rockies	Reduce tree density in recreational areas.	Consumer Surplus (losses)	-8.5 to -23.2% (for reductions in tree density ranging between 10 to 30%)
Walsh et al. (1990)	CV (iterative bidding)	Colorado	Protect ponderosa pine forests from damages caused by the mountain pine beetle.	Household WTP (per yr)	\$47 Non-use: 73% of total value Use: 27% of total value

^aHolmes and Kramer study applies same results found in Haeefele et al. (1991).

^bBenefits transfer was based on results from Holmes and Kramer (1996), Peterson et al. (1987), Walsh et al. (1990).

TABLE AX10.3-6. SUMMARY OF THE MONETIZED ESTIMATES OF THE ANNUAL VALUE OF FOREST QUALITY CHANGES

Study	Aesthetic Change Valued	Value of Change per Household (Current Dollars)	Value of Change per Household (1990 Dollars) ⁱ	Total Value of Change for Region (Current Dollars)	Total Value of Change for Region (1990 Dollars) ⁱ
Peterson et al. (1987)	Ozone damage to San Bernardino and Angeles National Forests	\$6.31 - \$32.70 ⁱⁱ	\$7.26 - \$37.62	\$27 - \$140 million	\$31 - \$161million
Walsh et al. (1990)	Visual damage to Colorado's Front Range	\$47	\$61.68	\$55.7 million	\$73.09 million
Holmes and Kramer (1996)	Visual damage to spruce-fir forests in southern Appalachia	\$10.81 nonusers \$36.22 users	\$10.37 nonusers \$34.76 users	NA	NA

Source: Exhibit 4 Industrial Economics (IEc) (1999a).

TABLE AX10.3-7. ESTIMATED VALUE OF AVOIDING FOREST DAMAGE IN THE UNITED STATES

Affected System	States Included	Value per Household	Households ⁱ	Total Annual Value	Cumulative Value (1990-2010) ⁱⁱ
Sierra Nevada and Los Angeles Basin	CA	\$7.26 - \$37.62	10.4 million	\$75.5 million - \$391.2 million	\$1.02 billion - \$5.27 billion
Eastern Spruce Fir and Selected Eastern Hardwood	ME, VT, NH, MA, NY, PA, WV, TN, KY, NC, VA	\$7.26 - \$37.62	23.2 million	\$168 million - \$872.8 million	\$2.27 billion - \$11.75 billion

Source: Exhibit 5 Industrial Economics (IEc) (1999a).

TABLE AX10.4-1. ECOLOGICAL WETLAND FUNCTIONS, ECONOMIC GOODS AND SERVICES, TYPES OF VALUE, AND APPLICABLE VALUATION METHODS

Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Methods (s)^a
Flood and flow control	Flood protection	Indirect use	Replacement cost Market prices Opportunity cost
Storm buffering	Storm protection	Indirect use	Replacement cost Production function
Sediment retention	Storm protection	Indirect use	Replacement cost Production function
Groundwater recharge/discharge	Water supply	Indirect use	Production function, NFI Replacement cost
Maintenance/Nutrient retention	Improved water quality	Indirect use	CVM
	Waste disposal	Direct use	Replacement cost
Habitat and nursery for plant and animal species	Commercial fishing and hunting	Direct use	Market prices, NFI
	Recreational fishing and hunting	Direct use	TCM, CVM
	Harvesting of natural materials	Direct use	Market prices
	Energy resources	Direct use	Market prices
Biological diversity	Appreciation of species existence	Non-use	CVM
Micro-climate stabilization	Climate stabilization	Indirect use	Production function
Carbon sequestration	Reduced global warming	Indirect use	Replacement cost

TABLE AX10.4-1 (cont'd). ECOLOGICAL WETLAND FUNCTIONS, ECONOMIC GOODS AND SERVICES, TYPES OF VALUE, AND APPLICABLE VALUATION METHODS

Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Methods (s)^a
Natural environment	Amenity	Direct use	HP, CVM
	Recreational activities	Direct use	CVM, TCM
	Appreciation of uniqueness to culture/ heritage	Non-use	CVM

^a Acronyms refer to the contingent valuation method (CVM), hedonic pricing (HP), net factor income (NFI), and the travel cost method (TCM).

Source: Table 1, Brander et al. (2006).

Source: with modifications adapted from Barbier (1991); Barbier et al. (1997); Brouwer et al. (1999); and Woodward and Wui (2001).

TABLE AX10.5-1. ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Acidification	Banzhaf et al. (2006)	Injured lakes in Adirondacks, NY	CV	Fish, bird species, and tree species	WTP (total value)	1. The mean WTP for base version was \$48 per yr per household in New York State while the mean WTP for scope version was \$54 per yr per household in New York State (discounting rate =3%)	1. Base version: improvement in fish population of 600 lakes, small improvements in the populations of two bird and one tree species. 2. Scope version: improvement in fish population of 900 lakes, improvement in the population of four bird and three tree species.
	Bockstael et al. (1989a)	Chesapeake Bay, MA and DC	CV and TC	Fish	Aggregate benefit/consumer surplus (recreational value)	1. 20% water quality improvement resulting in aggregate benefits for beach use, boating, and sportfishing were about \$34.7, 4.7, and 1.4 millions. 2. aggregate WTP for water quality improvement from current to a level acceptable for water activity was about \$91 million (1987 dollars)	1. TNP, product of nitrogen and phosphorus, was included in the model. 2. WTP was aggregated for households in Maryland.
	Cameron and Englin (1997)	Northeast United States	CV and RUM	Trout fishing (uncertain about use)	Consumer surplus (recreational value, existence value)	1. For passive user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was \$218 for S model and \$215 for OP model. 2. For active user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was \$283 for S model and \$439 for OP-I model and \$436 for OP-D.	1. S model: Surplus interpretation of the WTP responses 2. OP model: Option price interpretation of the WTP responses. 3. I: complete independence between yr-to-yr decisions 4. D: complete dependence on previous decisions

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Acidification (cont'd)	Englin et al. (1991)	ME, NH, NY (excluding New York City) and VT	HTC and RUM	Catch per unit effort (number of fish caught in an h)	Consumer surplus (recreational value)	<ol style="list-style-type: none"> Under baseline scenario (1989), welfare loss was estimated at \$0.27 m (HTC) and \$1.75 (RUM) Under NAPAP scenario 1, welfare loss was occurred in 2010 at \$13.7 m (HTC) and \$1.2 m (RUM) but social welfare would gain in 2030 at \$3.5 m (HTC) and \$5.5 m (TCM) Under NAPAP scenario 4, welfare would gain in 2010 at \$3 m (HTC) and \$7.4 m (TCM) and also gain in 2030 at \$4.4 m (HTC) and \$9.7 m (TCM) 	<ol style="list-style-type: none"> Acidic stress index (ASI) measuring fish biological tolerance to acidity was included in the model. The benefits were valued in 1989 dollars Multiple datasets were used in the analysis. Only trout species fishing was included. The benefit estimates were aggregated for four states by accounting income increase and population change resulting from baby boom.
	Kaoru et al. (1995)	Albemarle and Pamlico Sounds, NC	CV and RUM	Fish	Consumer surplus (recreational value)	<ol style="list-style-type: none"> 35-site model: \$36.19 for 5% increase of total catch at all sites (full-wage) 35-site model: \$6.52 for 36% decrease in nitrogen loadings at all sites (full-wage) 	<ol style="list-style-type: none"> Estimated nitrogen loadings and biochemical oxygen demand, were used in household production models to measure fishing quality. The paper also estimated benefit based on opportunity cost at 1/3 wage for 23-site and 11-site models.
	Morey and Shaw (1990)	Four fishing sites in Adirondacks, NY	CV and TC	Brook and Lake Trout	Consumer surplus (conditional compensating variations) (recreational value)	<ol style="list-style-type: none"> \$475.87 for 5% increase in catch rates for trout (1977 dollars) \$2162.04 for 25% increase in catch rates for trout (1977 dollars) \$3862.94 for 50% increase in catch rates for trout (1977 dollars) 	<ol style="list-style-type: none"> Economic values were aggregate CCV for 607 survey respondents. Catch rate, as an indicator of acid deposition, was included as a variable in the model.

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Acidification (cont'd)	Morgan and Owens (2001)	Chesapeake Bay	Water quality model and Benefit transfer	Water quality	Aggregate benefit (recreational value)	<ol style="list-style-type: none"> Lower bound total benefit for beach use was \$288.8m from a 60% improvement in Chesapeake Bay water quality. Lower bound total benefit for trailered boating was \$6.7m from a 60% improvement in Chesapeake Bay water quality. Lower bound total benefit for striped bass sport fishing was \$288.8m from a 60% improvement in Chesapeake Bay water quality. 	<ol style="list-style-type: none"> The study also provided aggregate benefits at avg and high level for three recreational uses. Benefit transfer was based on the results in Bockstael et al. (1988).
	Mullen and Menz (1985)	Adirondack, NY	TC	Fish	Net economic value per angler day/ Consumer surplus (recreational value)	<ol style="list-style-type: none"> Net economic value per angler day was avgd at \$19.90 for entire waterbody including lakes, ponds, and streams. Total angler value was estimated \$31.3 million for entire water body. The loss in net economic value was estimated at \$1.07 million for lakes and ponds due to reduction in angler visitation. 	<ol style="list-style-type: none"> The values were in 1976 dollars. Total value was aggregated by number of trips.
	Randall and Kriesel (1990)	Nationwide, U.S.	CV	Water/air quality	WTP (total value)	<ol style="list-style-type: none"> The estimated annual willingness to pay was \$694.42 per household. 	<ol style="list-style-type: none"> The study valued a National Pollution Control Program, which improved air and water quality by 25 percent in 5 yrs.

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Acidification (cont'd)	Smith et al. (1991)	Albemarle and Pamlico Sounds, NC	HTC and demand function	Fish	Benefit/consumer surplus (recreational value)	<ol style="list-style-type: none"> 1. Conventional demand model: \$2.58 for boat, \$1.11 for bank fishing 2. Simple inverse demand model: \$0.79 for boat, \$0.62 for bank fishing 3. Detailed inverse demand model: \$0.88 for boat, \$0.79 for bank fishing 	<ol style="list-style-type: none"> 1. Benefit was calculated for an one-fish increase in catch rate per h per person 2. Catch rate was included in the model. 3. The paper also estimated benefit based on opportunity cost at 1/3 wage.
	Whitehead et al. (2000)	Albemarle and Pamlico Sounds, NC	CV and TCM	Fish catches and shellfish beds	Consumer surplus per season/ per trip (recreational value)	<ol style="list-style-type: none"> 1. The consumer surplus per trip is \$64 for current quality and \$85 for 60% increase in fish catch and 25% more open shellfish beds. 2. The consumer surplus per season is \$121 for current quality and \$155 for 60% increase in fish catch and 25% more open shellfish beds. 	<ol style="list-style-type: none"> 1. The consumer surplus per trip difference between two baseline and scenario was not significant at the 0.10 level while the consumer surplus per season difference between two situations was. 2. The studies also estimated annual aggregate consumer surplus per season for 41 counties within the watershed.
Eutrophication	Boyle et al. (1999)	Four lakes, ME	HTC (two stages, hedonic demand model)	Water clarity (visibility)	Consumer surplus (recreational value)	<ol style="list-style-type: none"> 1. The consumer surplus (+) for an avg visibility improvement from 3.78m to 5.15m was \$3,765 and \$3,677 for semi-log and Cobb-Douglas model. 2. The welfare losses (-) for an avg visibility decrease from 3.78m to 2.41m was \$25,388 and \$46,750 for semi-log and Cobb-Douglas model. 	<ol style="list-style-type: none"> 1. The welfare was also measured in linear demand model. However, the own price of water clarity is not significant.

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Eutrophication (cont'd)	Diaz and Solow (1992)	Gulf of Mexico	Time series	Brown shrimp, white shrimp, and Menhaden	Mean catch rate per unit effort	1. The study failed to quantify economic effects of hypoxia based on past data.	1. Hypoxia was measured in terms of area (zone) and index in the model to calculate correlation.
	Kramer and Eisen-Hecht (2002)	Catawba River, NC and SC	CV	Water quality	WTP (total value)	1. A mean willingness to pay was revealed at \$139 for maintaining current water quality over time.	1. Phone-mail-phone and mail-phone survey formats applied.
	Lipton (2004)	Chesapeake Bay, MA	CV	Water quality	WTP (use value)	1. The median WTP for a one scale improvement in water quality was \$17.50 per boater per yr and the mean was \$63, with 38% expressing a zero WTP.	1. The aggregate WTP for the Chesapeake Bay boaters in Maryland was about \$7.3 million per yr, total improvement gets a \$146 million present value.
	Needelman and Kealy (1995)	Lakes, NH	Site choice model and a trip frequency model	Water quality	Benefit (recreational value)	1. The mean seasonal benefits estimates were \$1.4 for eliminating eutrophication from all sources (\$1.33 for nonpoint source and \$0.09 for point source) and the aggregate seasonal benefits were estimated at \$1,163,000 for eliminating eutrophication from all sources (\$1,105,000 for nonpoint source and \$75,000 for point source).	1. The study also reported mean and aggregate seasonal benefits for eliminating bacteria, oil and grease, eutrophication problems, and all pollution from all sources. 2. The benefit estimates address exclusively swimming and day trips.

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Eutrophication (cont'd)	NSTC (2000)	Gulf of Mexico, Mississippi-Atchafalay River Basin	Cost effective, simulation model (US Mathematic Programming Model in Agriculture)	Fish, shrimp, and marine ecosystem	Social cost for reduction/restoration	1. For 20% edge-of-field nitrogen-loss reduction, the net cost was estimated at \$0.8/kg (\$0.36/pound), while restoring 5 million acres of wetland would have net cost of \$1.00/kg (\$0.45/pound).	1. The benefit to reduce nitrogen loadings to the Gulf was difficult to calculate because economic analysis failed to show direct effects on Gulf fisheries, which was a background study conducted by Diaz and Solow (1992).
	Park et al. (2002)	Florida Keys, FL	CV	Water quality and health of coral reefs	WTP per trip expenses (recreational value)	1. The annual avg use value was \$481.15 per person per snorkeling trip.	
	Poor et al. (2006)	St. Mary's River watershed, MA	HPVM	Ambient water quality	Avg housing price within the watershed (commercial value)	1. One unit (mg/L) increase in TSS resulted in a \$1,086 loss on avg housing prices within the watershed. 2. One unit increase in the dissolved inorganic N resulted in a \$17,642 loss on avg housing prices.	1. Total suspended solids and dissolved inorganic nitrogen included as indicators of ambient water quality.
	Smith and Crowder (2005)	Neuse river, NC	Bio-economic model	Blue crab	Fish rent (commercial value)	1. A 30% reduction in nitrogen loadings over a 50-yr time period increases present value rents by 2.56 million, total catch by 12.4 million pounds, and total trips by 91,000.	1. Discounting rate was 2.5%.

TABLE AX10.5-1 (cont'd). ECONOMIC VALUATION STUDIES RELATED TO ACIDIFICATION AND EUTROPHICATION IN AQUATIC ECOSYSTEMS

Ecological Effect	Study	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Eutrophication (cont'd)	Whitehead and Groothuis (1992)	Tar-Pamlico River, NC	CV	Catch rate	WTP (total value, use, and non-use value)	<p>1. The mean WTP resulting from a 61% response rate was estimated at \$25, which was bounded from above by a \$35 use value, and from below a \$21 nonuse value.</p> <p>2. The aggregate benefits from water quality improvement estimated at \$1.62 million each yr.</p>	<p>1. The study proposed a program in which farmers are required to use BMPs to improve the water quality of the Tar-Pamlico River so that anglers would catch twice as many fish per trip.</p> <p>2. A mail survey was sent to 179 households in four counties in Tar-Pamlico River basin.</p>
Various effects	Johnston et al. (2005)	U.S. and Canada	Meta-analysis	Catch rate	WTP (recreational use)	<p>1. WTP per fish over the sample ranged from \$.048 to \$612.79, with a mean of \$16.82</p>	<p>1. This study supports previous findings that WTP is systematically associated with resource, context, and angler attributes.</p>

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