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

(First External Review Draft)

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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

DISCLAIMER

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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

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[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.

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(cont'd)

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 27711

Dr. Jill S. Baron—U.S. Geological Survey, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins CO 80523-1499

Dr. Bernard J. Cosby, Jr.—Department of Environmental Sciences, University of Virginia, Charlottesville, VA 22904

Ms. Rebecca Daniels—National Center for Environmental Assessment (B243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Christine L. Goodale—Department of Ecology and Evolutionary Biology, Cornell University, Ithaca, NY 14853

Dr. Alan T. Herlihy—Department of Fisheries & Wildlife, Oregon State University, Corvallis, OR 97331

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

Dr. Alan J. Krupnick—Resources for the Future, 1616 P St NW, Washington, DC 20036-1400

Dr. Kathleen Fallon Lambert—Ecologic: Analysis and Communications, 39 Central Street, Suite 204, Woodstock, VT 05091

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

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

Dr. Todd C. McDonnell—E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339

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

Authors, Contributors, and Reviewers
(cont'd)

Authors
(cont'd)

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

Dr. Rich Scheffe—Office of Air Quality Planning and Standards (C304-02), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Juha Siikamaki—Resources for the Future, 1616 P St NW, Washington, DC 20036-1400

Dr. Timothy J. Sullivan—E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339

Dr. Helga Van Miegroet—Department of Wildland Resources, Department of Watershed Sciences, Utah State University, Logan, UT 84322-5230

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

Contributors

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

Dr. Tina Fan—EOHSI/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

Authors, Contributors, and Reviewers

(cont'd)

Reviewers

Mr. Greg Miller—Office of Policy, Economics, and Innovation (1809T), 1200 Pennsylvania Avenue, N. W., Washington, DC 20460

Dr. Brooke Hemming—National Center for Environmental Assessment (C604-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Brian Heninger—Office of Policy, Economics, and Innovation (1809T), 1200 Pennsylvania Avenue, N. W., Washington, DC 20460

Dr. Jason Lynch—Office of Air and Radiation, Office of Atmospheric Programs (6204J), Ariel Rios Building, 1200 Pennsylvania Avenue, N. W., Washington, DC 20460

Dr. Rick Scheffe—Office of Air and Radiation, Office of Air Quality Planning and Standards (C304-02), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Dale Evarts—Office of Air and Radiation, Office of Air Quality Planning and Standards (C504-04), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Bryan Hubbell—Office of Air and Radiation, Office of Air Quality Planning and Standards (C504-02), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Anne Rea—Office of Air and Radiation, Office of Air Quality Planning and Standards (C539-02), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Vicki Sandiford—Office of Air and Radiation, Office of Air Quality Planning and Standards (C504-06), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Randy Waite—Office of Air and Radiation, Office of Air Quality Planning and Standards (C504-04), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Robin Dennis—National Effects Research Laboratory (E243-01), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. John Walker—National Risk Management Research Laboratory (E305-02), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jana Compton—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, OR 97333-4902

Authors, Contributors, and Reviewers
(cont'd)

Reviewers
(cont'd)

Dr. William Hogsett—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, OR 97333-4902

Dr. Paul Ringold—National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, 200 S.W. 35th Street, Corvallis, OR 97333-4902

Dr. Dave A. Evans—Office of Policy, Economics, and Innovation (1809T), 1200 Pennsylvania Avenue, N. W., Washington, DC 20460

Ms. Lydia Wegman—Office of Air and Radiation, Office of Air Quality Planning and Standards (C504-02,) U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

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

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

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

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. 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. Jeffrey Herrick—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

Dr. Jeff Arnold—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

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

ABBREVIATIONS AND ACRONYMS

AIRMoN	Atmospheric Integrated Research Monitoring Network
Al	aluminum
ANC	acid neutralizing capacity
AOD	aerosol optical depth
APIMS	atmospheric pressure ionization mass spectrometer
AQCD	Air Quality Criteria Document
ARP	Acid Rain Program
As	arsenic
ASI	Acid Stress Index
asl	at sea level
ATLAS	Aggregated Timberland Assessment System
ATP	adenosine triphosphate
ATTILA	type of Lagrangian model
BC	black carbon
BMPs	best management practices
Br	bromine
Br^-	bromine ion
Br_2	molecular bromine
BrCl	bromine chloride
BrO	bromine oxide
C	carbon
Ca	calcium
CAA	Clean Air Act
CAAA	Amendments to the Clean Air Act
CalTech	1986 California Institute of Technology (study)
CAPMoN	Canadian Air and Precipitation Monitoring Network
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network
Cd	cadmium
CFCs	chlorinated fluorocarbons
CH_4	methane
$CH_3CH(O)OONO_2$	peroxyacetyl nitrate
CH_3CN	acetonitrile
$CH_3C(O)O$	peroxyacetyl radical
CH_2I_2	diiodomethane

CH_3-S-CH_3	dimethylsulfide, DMS
CH_3-S-H	methyl mercaptan
CH_3SO_3H	methanesulfonic acid
CH_3-S-S-CH_3	dimethyl disulfide
Cl	chorine
Cl^-	chorine ion
Cl_2	molecular chlorine
CLaMS	type of Lagrangian model
CIMS	chemical ionization mass spectroscopy
$ClNO_2$	nitryl chloride
CMAQ	Community Multiscale Air Quality modeling system
CMSA	consolidated metropolitan statistical area
CO	carbon monoxide
CO_2	carbon dioxide
CONUS	continental United States
CPUE	catch per unit effort
CS_2	carbon disulfide
CTM	chemical transport model
Cu	copper
DIC	dissolved inorganic carbon
DMS	dimethyl sulfide, CH_3-S-CH_3
DMSO	dimethylsulfoxide
DNDC	Denitrification-Decomposition (model)
DOC	dissolved organic carbon
EC	elemental carbon
EGUs	electrical generating units
ELD	Experimental Lake District
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
EPA	U.S. Environmental Protection Agency
ERP	Episodic Response Project
ESA	European Space Agency
EXT-RADM	Extended Regional Acid Deposition Model
Fe	iron
FDA	U.S. Food and Drug Adminstration
FEM	Federal Equivalent Method
FIA	Forest Inventory and Analysis (program)
FISH	Fish in Sensitive Habitats (project)

FLEXPART	type of Lagrangian model
FPD	flame photometric detection
FRM	Federal Reference Method
FTIR	Fourier Transform Infrared Spectroscopy
GAW	Global Atmospheric Watch (program)
GC-ECD	gas chromatography-electron capture detection
GFG	greenhouse gas
GWP	global warming potential
ha	hectare
HAPs	hazardous air pollutants
HCHO	formaldehyde
HCl	hydrochloric acid
HCN	hydrogen cyanide
HCs	hydrocarbons
HEADS	Harvard-EPA Annular Denuder System
HNO_2	nitrous acid
HNO_3	nitric acid
HNO_4	pernitric acid
H_2O_2	hydrogen peroxide
HOCl	hypochlorous acid
HOX	hypohalous acid
H_2S	hydrogen sulfide
H_2SO_4	sulfuric acid
$h\nu$	solar ultraviolet radiation
I	iodine
IADN	Integrated Atmospheric Monitoring Deposition Network
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
INO_3	iodine nitrate
IO	iodine oxide
IPCC	Intergovernmental Panel on Climate Change
IQR	interquartile range
ISA	Integrated Science Assessment
JPL	Jet Propulsion Laboratory
K	potassium
K_a	acid dissociation constant in M
K_H	Henry's Law constant in M atm^{-1}
K_w	ion product of water

LDH	lactic acid dehydrogenase
LIF	laser-induced fluorescence
LOD	limit of detection
LRTAP	Long Range Transport of Air Pollution
LTM	Long-Term Monitoring (project)
LWC	aerosol liquid water content
M	air molecule
MAGIC	Model of Acidification of Groundwater in Catchments (model)
MAX-DOAS	multiple axis differential optical absorption spectroscopy
MBL	marine boundary layer
MDN	Mercury Deposition Network
meq	milliequivalent
Mg	magnesium
MOBILE6	Highway Vehicle Emission Factor Model
MoO_x	molybdenum oxide
MPAN	peroxymethacryloyl nitrate; peroxy-methacrylic nitric anhydride
MSA	metropolitan statistical area
^{15}N	nitrogen-15 radionuclide
N	nitrogen
N, n	number of observations
N_2	molecular nitrogen
Na	sodium
NA, N/A, N.A.	not available
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAMS	National Air Monitoring Stations
NAPAP	National Acid Precipitation Assessment Program
NAPCA	National Air Pollution Control Association
NARSTO	program formerly known as North American Regional Strategy for Atmospheric Ozone
NAS	National Academy of Sciences
NASA	National Aeronautics and Space Administration
NATTS	National Air Toxics Trends (network)
NCore	National Core Monitoring Network
NEG/ECP	New England Governors and Eastern Canadian Premiers
NEI	National Emissions Inventory
NH_3	ammonia
NH_4^+	ammonium ion

NH_4NO_3	ammonium nitrate
NH_4HSO_4	ammonium bisulfate
$(NH_4)_2SO_4$	ammonium sulfate
NH_X	category label for NH_3 and NH_4^+
NILU	Norwegian Institute for Air Research
nitro-PAH	nitro-polycyclic aromatic hydrocarbon
NMOCs	nonmethane organic compounds
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	nitrite
NO_3	nitrate
NO_3^-	nitrate
N_2O	nitrous oxide
N_2O_5	dinitrogen pentoxide
NOAA	U.S. National Oceanic and Atmospheric Administration
NO_X	NO and NO_2
NO_Y	NO_x and NO_z; odd nitrogen species
NO_Z	all inorganic and organic reaction products of NO_x (i.e., HONO, HNO_3, HNO_4, organic nitrates, particulate nitrate, nitro-PAHs, etc.)
N_r	reactive nitrogen
nss	non-sea-salt
NSWS	National Surface Water Survey
O_2	molecular oxygen
O_3	ozone
OC	organic carbon
OCS	carbonyl sulfide
OH	hydroxyl radical
P, p	probability value
PAHs	polycyclic aromatic hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PAN	peroxyacetyl nitrate
PANs	peroxyacyl nitrates
Pb	lead
PBL	planetary boundary layer
PCBs	polychlorinated biphenyl compounds
PIRLA	Paleocological Investigation of Recent Lake Acidification (projects)
PM	particulate matter
PM_{10}	particulate matter with aerodynamic diameter ≤ 10 µm

$PM_{10-2.5}$	particulate matter with aerodynamic diameter between 10 and 2.5 µm
$PM_{2.5}$	particulate matter with aerodynamic diameter of ≤2.5 µm
PnET-BGC	Photosynthesis and EvapoTranspiration-BioGeoChemical (model)
pNH_4	particulate ammonium
pNO_3	particulate nitrate
$P(O_3)$	production of O_3
POPs	persistent organic pollutants
ppb	parts per billion
ppm	parts per million
PPN	peroxypropionyl nitrate
ppt	parts per trillion
PRB	policy relevant background
pSO_4	particulate sulfate
R	generic organic group attached to a molecule
r^2	correlation coefficient
RADM	Regional Acid Deposition Model
RANS	Reynolds Averaged Numerical Simulation
RNO_2	nitro compounds
RO_2	organic peroxyl
$RONO_2$	organic nitrate
RO_2NO_2	peroxy nitrate
S	sulfur
SAV	submerged aquatic vegetation
SCAQS	Southern California Air Quality Study
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
Se	selenium
SLAMS	State and Local Air Monitoring Stations
Si	silicon
SO	sulfur monoxide
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_4	sulfate
SO_4^{2-}	sulfate ion
S_2O	disulfur monoxide
SO_X	sulfur oxides
SPARROW	SPAtially Referenced Regressions on Watershed Attributes (model)
STE	stratospheric-tropospheric exchange

STN	Speciation Trends Network
SUM06	seasonal sum of all hourly average concentrations $\geq$ 0.06 ppm
τ	tau; atmospheric lifetime
T	time; duration of exposure
TAF	Tracking and Analysis Framework (model)
TAMM	Timber Assessment Market Model
TC	total carbon
Tg	teragram
TIME	Temporally Integrated Monitoring of Ecosystems
UNECE	United Nations Economic Commission for Europe
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey
UV	ultraviolet radiation
V_d	deposition rate
VOC	volatile organic compound
WATERS-N	Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen
WFPS	water-filled pore space
WMO	World Meteorological Organization
WSA	Wadeable Stream Assessment (survey)

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 qualities 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., N_2O or N_2) 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 (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), and ozone (O_3) are the primary greenhouse gases in the Earth's atmosphere. As well as CO_2, N_2O, and CH_4, the *Kyoto Protocol* deals with the greenhouse gases sulphur hexafluoride (SF_6), 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: $pH = -\log_{10}[H^+]$, where $[H^+]$ 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.

1. INTRODUCTION

This draft Integrated Science Assessment (ISA) presents a concise synthesis and evaluation of the most policy-relevant science. It forms the scientific foundation for the review of the secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for Oxides of Nitrogen (NO_X) and Sulfur Oxides (SO_X). All language in the Clean Air Act (CAA) referring to effects on welfare includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort/well-being. The scope of the joint NO_X and SO_X ISA is limited to welfare topics that do not duplicate those addressed by the forthcoming particulate matter (PM) science assessment. The welfare effects of visibility impairment and climate interactions associated with particulate NO_X and SO_X will be addressed within the secondary PM NAAQS review, as these processes occur via NO_X and SO_X residing in the particulate or aerosol phase and interact with other chemical components of PM. The effects of acidification and nitrogen-nutrient deposition on ecosystems are the main focus of this assessment; however, other welfare effects are discussed including SO_X interactions with mercury methylation, gas-phase effects on foliage, and N_2O as a greenhouse gas (GHG).

This draft ISA is intended to “accurately reflect the latest scientific knowledge expected from the presence of [a] pollutant in ambient air” (Clean Air Act, Section 108 (42U.S.C.7408)). Scientific research is incorporated from atmospheric sciences, exposure and deposition, biogeochemistry, hydrology, soil science, marine science, plant physiology, animal physiology, and ecology research on multiple scales (e.g., population, community, ecosystem, landscape levels). This document contains the key information and judgments formerly found in the Air Quality Criteria Documents (AQCDs) for NO_X and SO_X. Also, a series of supplemental Annexes to the draft ISA provide a more detailed discussion of the most pertinent scientific literature. The draft ISA and the Annexes thus serve to update and revise the last NO_X and SO_X AQCDs which were published in 1993 and 1982, respectively.

As discussed in the Draft Integrated Plan for the Review of the Secondary NAAQS for Nitrogen Dioxide (NO_2) and Sulfur Dioxide (SO_2) (U.S. Environmental Protection Agency, 2007a), a series of policy-relevant questions frames this review of the scientific evidence to provide a scientific basis for a decision on whether the current secondary NAAQS for NO_2

(0.053 parts per million [ppm], annual average) and the current secondary NAAQS for SO_2 (0.5 ppm, 3-h average) should be retained or revised. The scope of this draft ISA is to evaluate newly available scientific evidence to best inform consideration of these framing questions, including the following:

- What are the known or anticipated welfare effects influenced by ambient NO_X and SO_X, and for which effects is there sufficient information available to be useful as a basis for considering distinct secondary standard(s)?
- What is the nature and magnitude of ecosystem responses to NO_X and SO_X that are understood to have known or anticipated adverse effects and what is the variability associated with those responses (including ecosystem type, climatic conditions, environmental effects, and interactions with other environmental factors and pollutants)?
- To what extent do the current standards provide the requisite protection for the public welfare effects associated with NO_X and SO_X?
- Which biotic species are most vulnerable to the adverse effects of NO_X and SO_X air pollution? How is adversity defined?
- What ecosystems are most sensitive to NO_X and SO_X pollution?
- How does NO_X and SO_X pollution impact ecosystem services?
- What are the most appropriate spatial and temporal scales to evaluate impacts on ecosystems?
- What is the relationship between ecological vulnerability to NO_X and SO_X pollution and variations in current meteorology or gradients in climate?

1.1 BRIEF LEGISLATIVE BACKGROUND FOR NO_X AND SO_X: THE RATIONALE FOR A COMBINED REVIEW

1.1.2 Brief Legislative Background of NO_X

In 1971, the first AQCD for NO_X was issued by the National Air Pollution Control Association (NAPCA), one of the Environmental Protection Agency's (EPA's) predecessor agencies (U.S. Environmental Protection Agency, 1971). After reviewing the relevant science on the public health and welfare effects associated with oxides of nitrogen, EPA promulgated identical primary and secondary NAAQS for NO_2 on April 30, 1971. Under section 109 of the CAA, these standards were set at 0.053 ppm as an annual average (36 FR 8186).

In 1982, EPA published the NO_X AQCD (U.S. Environmental Protection Agency, 1982a), which updated the scientific criteria upon which the initial standards were based. On February 23, 1984, EPA proposed to retain these standards (49 FR 6866). After taking into account public comments, EPA published the final decision to retain these standards on June 19, 1985 (50 FR 25532).

In November 1991, EPA released an updated draft AQCD for Clean Air Scientific Advisory Committee (CASAC) and public review and comment (56 FR 59285). CASAC reviewed the document at a meeting held on July 1, 1993 and concluded in a closure letter to the Administrator that the document "provides a scientifically balanced and defensible summary of current knowledge of the effects of this pollutant and provides an adequate basis for EPA to make a decision as to the appropriate NAAQS for NO_2" (Wolff, 1993). The EPA also prepared a draft Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised AQCD and identified the critical elements to be considered in the review of the NO_2 NAAQS. In September 1995, EPA finalized the Staff Paper, "Review of the National Ambient Air Quality Standards for Nitrogen Dioxide: Assessment of Scientific and Technical Information," (U.S. Environmental Protection Agency, 1995a). The Administrator made a final determination that revisions to neither the primary nor the secondary NAAQS for NO_2 were appropriate at that time (61 FR 52852, October 8, 1996). The level for both the existing primary and secondary NAAQS for NO_2 remains 0.053 ppm (equivalent to 100 micrograms per cubic meter of air [$\mu g/m^3$]) in annual arithmetic average, calculated as the arithmetic mean of the 1-h NO_2 concentrations.

1.1.3 Brief Legislative Background of SO_X

Based on the 1970 SO_X AQCD (DHEW, 1970), EPA promulgated primary and secondary NAAQS for SO_2, under section 109 of the CAA on April 30, 1971 (36 FR 8186). The secondary standards included a standard at 0.02 ppm in an annual arithmetic mean and a 3-h average of 0.5 ppm, not to be exceeded more than once per year. These secondary standards were established solely on the basis of vegetation effects evidence. In 1973, revisions made to Chapter 5 "Effects of Sulfur Oxide in the Atmosphere on Vegetation" of the SO_X AQCD (U.S. Environmental Protection Agency, 1973), indicated that it could not properly be concluded that the reported vegetation injury resulted from the average SO_2 exposure over the growing season, rather than from short-term peak concentrations. EPA, therefore, proposed (38 FR 11355) and then finalized a revocation of the annual mean secondary standard (38 FR 25678).

In 1979, EPA announced that it was revising the SO_X AQCD concurrently with that for PM and would produce a combined PM-SO_X AQCD. Following its review of a draft revised criteria document in August 1980, CASAC concluded that acidic deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (1) emissions of relevant pollutants (e.g., SO_2 and NO_X); (2) formation of acidic wet and dry deposition products; and (3) effects on terrestrial and aquatic ecosystems. CASAC also noted that acidic deposition involves, at a minimum, several different criteria pollutants (i.e., SO_X, NO_X, and the fine particulate fraction of suspended particles). The Committee felt that any document on this subject should address both wet and dry deposition, as dry deposition was believed to account for at least one half of the total acid deposition problem.

For these reasons, CASAC recommended that a separate, comprehensive document on acidic deposition be prepared prior to any consideration of using the NAAQS as a regulatory mechanism for the control of acidic deposition. CASAC also suggested that a discussion of acidic deposition be included in the AQCDs for both NO_X and PM-SO_X. Following CASAC closure on the criteria document for SO_2 in December 1981, EPA's Office of Air Quality Planning and Standards (OAQPS) published a Staff Paper in November 1982 (U.S. Environmental Protection Agency, 1982b). The issue of acidic deposition was not, however, assessed directly in this Staff Paper; EPA followed CASAC guidance and subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (U.S. Environmental Protection Agency, 1984a,b), and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (U.S. Environmental Protection Agency, 1985). These documents, though they were not considered criteria documents and did not undergo CASAC review, represented the most comprehensive summary of relevant scientific information completed by the EPA at that point.

On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and secondary standards. This proposal regarding the secondary SO_2 NAAQS was due to the Administrators conclusions that (1) based upon the then-current scientific understanding of the acidic deposition problem, it would be premature and unwise to prescribe any regulatory control program at that time, and (2) when the fundamental scientific uncertainties had been reduced through ongoing research efforts, EPA would draft and support an appropriate set of control measures.

1.1.4 History of the Current Review

EPA's National Center for Environmental Assessment in Research Triangle Park, NC (NCEA-RTP) announced the official initiation of the current periodic review of air quality criteria for NO_X on December 9, 2005, and for SO_X on May 15, 2006. For each of these reviews, the Agency began by announcing in the Federal Register (70 FR 73236 and 71 FR 28023) the formal commencement of the review and a call for information. With these reviews underway, a workshop addressing the separate, joint review of just the secondary standards for these two pollutants was announced in the Federal Register on June 20, 2007 (72 FR 11960). The review of the NAAQS for NO_2 and SO_2 is under a court-ordered schedule, and that schedule includes a deadline for completion of the final ISA for the review of the secondary NAAQS for NO_2 and SO_2 by December 12, 2008.

In this draft ISA, EPA reviews the recent scientific evidence on the welfare effects resulting from the deposition of NO_X and SO_X and their transformation products to inform the review of the secondary NAAQS for these criteria pollutants. NO_X and SO_X are being considered jointly in this review due to the joint role they play in acidification and their similar effects on ecosystems.

1.2 DOCUMENT DEVELOPMENT

Papers are identified for inclusion in the publication base of the ISA in several ways. First, EPA staff reviews prepublication tables of contents for journals in which relevant papers may be published. Second, expert chapter authors are charged with independently identifying relevant literature. Finally, additional publications that may be pertinent are identified by both the public and CASAC during the external review process. The focus of this ISA is on literature published since the 1993 NO_X AQCD and the 1982 SO_X AQCD. Key findings and conclusions from the 1993 and 1982 reviews are discussed in conjunction with recent findings. Generally, only information that has undergone scientific peer review and been published (or accepted for publication) in the open literature is considered. The following sections briefly summarize criteria for selection of studies for this draft ISA.

Emphasis has been placed on studies that evaluate effects at realistic ambient levels and studies that consider NO_X and SO_X as components of a complex mixture of air pollutants. Studies conducted in any country that contribute significantly to the knowledge base have been considered for inclusion the assessment, but emphasis has been placed on findings from studies conducted in the United States and Canada where differences in emissions and the air pollutant mixture are important. In assessing the relative scientific quality of studies reviewed here and to assist in interpreting their findings, the following considerations were taken into account: (1) To what extent are the aerometric data/exposure metrics of adequate quality and sufficiently representative to serve as credible exposure indicators. (2) Were the study populations well defined and adequately selected so as to allow for meaningful comparisons between study groups. (3) Were the ecological assessment endpoints reliable and policy relevant. (4) Were the statistical analyses used appropriate and properly performed and interpreted. (5) Were likely important covariates (e.g., potential confounders or effect modifiers) adequately controlled or taken into account in the study design and statistical analyses. (6) Were the reported findings consistent, biologically plausible, and coherent in terms of consistency with other known facts.

These guidelines provide benchmarks for evaluating various studies and for focusing on the highest quality studies in assessing the body of environmental effects evidence. Detailed critical analysis of all NO_X and SO_X environmental effects studies, especially in relation to the above considerations, is beyond the scope of the ISA and its Annexes. Of most relevance for evaluation of studies is whether they provide useful qualitative or quantitative information on exposure effect or exposure response relationships for the environmental effects associated with current ambient air concentrations of NO_X and SO_X or deposition levels likely to be encountered in the United States.

1.3 ORGANIZATION OF THE DOCUMENT

This draft ISA includes five chapters. This introductory chapter (Chapter 1) presents background information on the purpose of the document and characterizes how policy-relevant scientific studies are identified and selected for inclusion in the ISA. Chapter 2 highlights key concepts or issues relevant to understanding the atmospheric chemistry. Chapter 3 evaluates emissions, atmospheric monitoring, deposition, and ecosystem exposure. Chapter 4 evaluates and integrates the information relevant to the review of the welfare effects of NO_X and SO_X. In this chapter, findings are organized into three categories: ecological impacts of acidification, ecological impacts of nitrogen nutrient pollution, and other effects. The third category addresses several minor effects of NO_X and SO_X on welfare, including gas phase foliar toxicity, materials and structures damage, and GHG emissions of N_2O. Finally, Chapter 5 articulates findings and conclusions.

In addition, a series of 10 supplemental Annexes provide additional details of the information discussed in the ISA. Annex 1 presents evidence related to the physical and chemical processes in the atmosphere, including both oxidized and reduced chemical species. In Annex 2, we present evidence related to emissions, air monitoring, and deposition processes of atmospherically derived NO_X and SO_X. Annex 3 presents the major ecosystem monitoring networks and models available for analysis of NO_X and SO_X effects on ecosystems. Annex 4 examines the effects of acidification on terrestrial and aquatic ecosystems, a process driven by the combined deposition of NO_X and SO_X. Annex 5 examines the non-acidification effects of NO_X on terrestrial and aquatic ecosystems and includes a broader discussion of the NO_X acting in combination with total reactive nitrogen. Annex 6 evaluates the non-acidification effects of S deposition, including interactions between SO_X deposition and mercury methylation in ecosystems. In Annex 7, a preliminary discussion of the interactions between climate variables and NO_X effects on the environment is presented. The concept and application of critical loads are presented in Annex 8. In Annex 9, we present the effects of NO_X and SO_X deposition on acid-driven erosion of man-made materials and structures. Finally, Annex 10 presents evidence on the valuation of environmental effects of NO_X and SO_X on ecosystems as one of a number of means of assessing whether an effect can be considered adverse.

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

This chapter presents fundamental and applied atmospheric sciences information relevant for assessing the ecological exposures (in Chapter 3) and effects (in Chapter 4) associated with nitrogen (N) and sulfur (S) oxides. The topics and organization here largely follow recommendations given in the National Research Council paradigm for integrating air pollutant research (National Research Council, 1998).

2.1 INTRODUCTION

As noted in Chapter 1, 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, 1996), 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

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[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.

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 strong mineral acids nitric acid (HNO_3) and sulfuric acid (H_2SO_4), respectively, thereby contributing to the acidity of cloud, fog, and rain water and ambient particles.

Ammonia (NH_3) is included in this ISA both because its oxidation can be a minor source of NO_X and because it is the precursor for ammonium ion (NH_4^+), which plays a key role in neutralizing acidity in ambient particles and in cloud, fog, and rain water. Excess NH_3 is also an actor in nitrification of aqueous and terrestrial ecosystems, participating alone and together with NO_X in the N cascade (Galloway et al., 2003). (NH_3 and NH_4^+ are conventionally grouped together under the category label NH_X.) Additionally, NH_3 is involved in the ternary nucleation of new particles and reacts with gas-phase HNO_3 to form ammonium nitrate (NH_4NO_3), a major constituent of ambient PM pollution in many areas of the continental United States (CONUS).

2.2 NITROGEN OXIDES IN THE TROPOSPHERE

2.2.1 Gas-Phase Chemistry

The generalized chemistry of reactive N compounds in the atmosphere is summarized in Figure 2.2-1 and described in greater detail below. NO_X is emitted by combustion sources mainly as NO though with ~5 to 10% NO_2. The major combustion sources of NO_X, shown schematically in Figure 2.2-1, are motor vehicles and electrical utilities, although stationary engines, off-road vehicles, and industrial facilities also emit NO_X. In addition to these emissions from fossil fuel combustion, biomass burning produces NO_X. And apart from these anthropogenic sources, there are also smaller natural sources, which include microbial activity in soils, lightning, and wildfires.

NO and NO_2 are often grouped together with the category label NO_X because they are emitted together and will rapidly interconvert as shown in the inner box in Figure 2.2-1. NO_2 reacts with various free radicals in the gas phase and on surfaces in multiphase processes to form the oxidation products shown in Figure 2.2-1. These products include inorganic species (shown

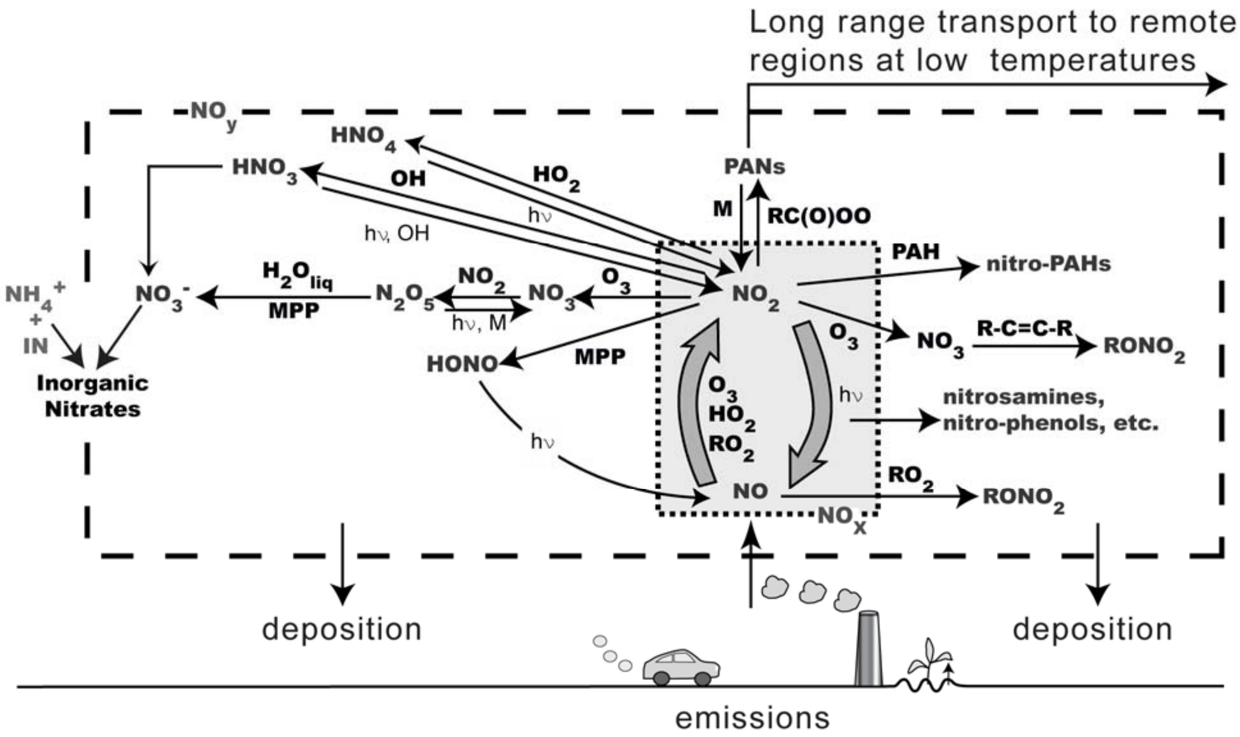


Figure 2.2-1. Schematic diagram of the cycle of reactive, oxidized nitrogen species in the atmosphere. IN refers to inorganic particulate species (e.g., Na^+,Ca^{++}), MPP to multiphase processes, h*ν* to a solar photon, and R to an organic radical. Particulate phase organic nitrates are also formed from the species on the right side of the figure.

on the left side of the outer box in Figure 2.2-1) and organic species (shown on the right side of the outer box in Figure 2.2-1). The oxidized N species in the outer box are often collectively termed NO_Z: thus, $NO_X + NO_Z = NO_Y$, or the total of all oxidized nitrogen. The time scale for reactions of NO_X to form products shown in the outer box of Figure 2.2-1 typically ranges from a few hours during summer days of high photon flux to roughly 24 h during winter hours with less heat and sunlight.

As shown in Figure 2.2-1, different sources emit NO_X at different altitudes with mobile sources nearer the Earth's surface and fixed point sources like power plants emitting from stacks 10s or 100s of meters above the surface. Because prevailing winds aloft are generally stronger than those at the surface, emissions from elevated point sources can be distributed over a wider area than those emitted at the surface; and because of the time required to mix emissions down to the surface, NO_X emissions from elevated sources will tend to be transformed to the more oxidized NO_Z products before they reach the surface at some distance from the source.

The concentrations ([ ]) and atmospheric lifetimes (τ) of inorganic and organic products from reactions of NO_X vary widely in space and time. Inorganic reaction products include nitrous acid (HNO_2), HNO_3, pernitric acid (HNO_4), and particulate nitrate (pNO_3). While a broad range of organic N compounds are emitted by combustion sources (e.g. nitrosamines and nitro-PAHs), they are also formed in the atmosphere from reactions of NO and NO_2. These include PAN and isoprene nitrates, other nitro-PAHs, and the more-recently identified nitrated quinones. By far the largest mass fractions of NO_Z products shown in the outer box of Figure 2.2-1 are in the form of PAN and HNO_3, although other $RONO_2$, e.g., isoprene nitrates and specific biogenic PANs can be important at locations nearer to biogenic sources (Horowitz et al., 2007; Singh et al., 2007).

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

Because O_3 changes are strongly nonlinear in the concentrations of its precursors VOC and NO_X, O_3 is unlike other secondarily formed atmospheric species whose rates of formation vary directly with their precursor emissions. At the low $[NO_X]$ usually found in environments ranging from remote continental areas to rural and suburban areas downwind of urban centers, the net $P(O_3)$ increases with increasing $[NO_X]$. At the high $[NO_X]$ found in downtown metropolitan areas and especially near busy streets and roadways and in power plant plumes, excess NO titrates O_3, and excess hydroxyl radicals (OH) combine with NO_2 removing them from the $P(O_3)$ chain. In this high $[NO_X]$ regime, NO_2 scavenges OH radicals that would otherwise oxidize VOCs to produce peroxy radicals (RO_2), which would in turn oxidize NO to NO_2. In the low $[NO_X]$ regime, oxidation of VOCs generates excess free radicals; hence, $P(O_3)$ varies more nearly monotonically with changes in $[NO_X]$ there. Between these two regimes lies a transition zone in which $P(O_3)$ and O_3 accumulation show only weak dependence on $[NO_X]$. Further explanation of these relationships appears in Annex 1.

The tropospheric chemical removal processes for NO_X include reaction of NO_2 with the OH radical as described above and hydrolysis of dinitrogen pentoxide (N_2O_5) in aqueous aerosol solutions, both producing HNO_3

$$OH + NO_2 \xrightarrow{M} HNO_3 \qquad (2.2\text{-}1)$$

$$N_2O_5 \xrightarrow{H_2O_{(l)}} HNO_3 \qquad (2.2\text{-}2)$$

The gas-phase reaction of OH with NO_2 in Reaction 2.2-1 is a major removal process for NO_X in the troposphere. The timescale for conversion of NO_X to HNO_3 in the planetary boundary layer (PBL) at 40° N latitude ranges from ~4 h in July to ~16 h in January; at 25° N latitude, the timescale is 4 to 5 h; and at 50º N latitude, from 4 to 20 h (Martin et al., 2003). Reaction 2.2-2 limits NO_X τ to a range of hours to days.

Gas-phase HNO_3 formed by Reaction 2.2-2 undergoes wet and dry deposition to the surface, and uptake by ambient aerosol particles. In addition, HNO_3 photolyzes and reacts with OH radicals

$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (2.2\text{-}3)$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O \qquad (2.2\text{-}4)$$

The HNO_3 τ with respect to these two reactions is long enough for HNO_3 to act as a minor reservoir species for NO_X during long-range pollutant transport, contributing in this way to $[NO_2]$ after photolysis returns NO_2 as in Reaction 2.2-3, and hence to $P(O_3)$ in areas remote from the source of the NO_X that formed the original HNO_3.

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

$$N_2O \rightarrow N_2 + O(^1D) \qquad (2.2\text{-}5)$$

driven by short wavelength UV present in the stratosphere. Although there are no tropospheric reactions to consider, N_2O is a greenhouse gas (GHG) with a global warming potential (GWP) on the conventional 100-year time horizon of ~296 – i.e., N_2O is nearly 300 times more effective for trapping heat in the atmosphere than carbon dioxide (CO_2) over a 100-year period (IPCC, 2001a); its sources and role in the total budget of U.S. GHG are described with the emissions sources of other nitrogen oxides in Chapter 3 and in Annexes 1 and 2.

Because N_2O has extremely low reactivity and hence a long τ in the troposphere, its radiative forcing climate effects in the stratosphere can be both direct and indirect. By comparison, the primary climate effects of NO and NO_2 are indirect and result from their role in promoting $P(O_3)$ in the troposphere and, to a lesser degree, lower stratosphere, where NO_X has positive radiative forcing effects. Additionally, NO_X emissions from high-altitude aircraft are also likely to decrease methane (CH_4) concentrations, thereby having a negative radiative forcing (IPCC, 1996). EPA does not compute GWPs for NO_X, SO_X, PM, or CO because there is no agreed method to estimate the contributions from these gases that are short-lived in the atmosphere, have strong spatial variability, or have only indirect effects on radiative forcing (IPCC, 1996).

A broad range of organic N compounds can be directly emitted by combustion sources or formed in the atmosphere from NO_X emissions. Oxidation of VOCs produces RO_2 as discussed in the O_3 AQCD (U.S. Environmental Protection Agency, 2006a). Reaction of RO_2 radicals with NO and NO_2 produces $RONO_2$ and peroxynitrates (RO_2NO_2)

$$RO_2 + NO \xrightarrow{M} RONO_2 \tag{2.2-6}$$

$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2 \tag{2.2-7}$$

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

Other $RONO_2$ may react further, depending on the functionality of the R group, but will typically not return NO_2 and so are viewed as a permanent sink for NO_X. The magnitude of this sink is usually small compared to that of HNO_3 formation, but the formation of C5H8 nitrates may be a significant sink for NO_X in the United States in summer (Liang et al., 1998).

The RO_2NO_2 produced by Reaction 2.2-7 are unstable, with τ on the order of a few minutes, owing to thermal decomposition back to the original reactants. Thus, they, too, are ineffective NO_X transport vehicles or sinks.

2.2.2 Heterogeneous-Phase Chemistry

In the polluted marine boundary layer (MBL) at night, the heterogeneous reaction

$$N_2O_5 + Cl^- \rightarrow ClNO_2 + NO_3^- \tag{2.2-8}$$

can also be important (Finlayson-Pitts et al., 1989; Behnke et al., 1997; Erickson et al., 1999). Diatomic bromine (Br_2), bromium chloride (BrCl), diatomic chloride (Cl_2), and nitryl chloride ($ClNO_2$) volatilize and photolyze in sunlight to produce atomic Br and Cl. The acidification of sea salt aerosol via incorporation of HNO_3 and other acids leads to the volatilization of hydrochloric acid (HCl) (Erickson et al., 1999)

$$HNO_3 + Cl^- \rightarrow HCl + NO_3^- \tag{2.2-9}$$

and the corresponding shift in phase partitioning can accelerate the deposition flux to the surface of total NO_3 (Russell et al., 2003; Fischer et al., 2006). However, Pryor and Sorensen (2000) have shown that the dominant phase form of NO_3 deposition is a complex function of wind speed.

In polluted coastal regions where HCl from Reaction 2.2-9 often exceeds 1 part per billion (ppb), significant additional atomic Cl^- is produced via

$$HCl + OH \rightarrow Cl + H_2O \tag{2.2-10}$$

(Singh and Kasting, 1988; Keene et al., 2007). The Br and Cl atoms so produced then catalytically destroy O_3 via

$$X + O_3 \rightarrow XO + O_2 \tag{2.2-11}$$

$$XO + HO_2 \rightarrow HOX + O_2 \tag{2.2-12}$$

$$HOX + h\nu \rightarrow OH + X \tag{2.2-13}$$

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

$$XO + NO_2 \rightarrow XNO_3 \tag{2.2-14}$$

and the subsequent reaction of XNO_3 with sea salt and sulfate aerosols via

$$XNO_3 + H_2O \rightarrow HOX + H^+ + NO_3^- \tag{2.2-15}$$

$$XNO_3 + Y^- \rightarrow XY + NO_3^- \tag{2.2-16}$$

(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 2.2-16 on sea salt while Reaction 2.2-15 is more significant for particulate SO_4^{2-} (pSO_4). Product NO_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 autocatalyic 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 diatonic 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 provide substrates for multiphase reactions that sustain the catalytic I-IO cycle. The iodine oxide (IO) radical has been measured by long-path and/or multi-axis differential optical absorption spectroscopy (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 part per trillion (ppt) with maxima up to 7 ppt (e.g., Allan et al., 2000; Pikelnaya et al., 2005). 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 2.2-11 through 2.2-16 accelerates the conversion of NO_X to pNO_3. The reaction $IO + NO \rightarrow I + NO_2$ also influences NO_X cycling.

The studies described above considered 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; Hollwedel et al., 2004). The primary source of reactive halogens in these regions is thought to be due to activation along the lines of Reactions 2.2-8 through 2.2-10. High concentrations of bromium oxide (BrO) have also been measured in volcanic plumes (Bobrowski et al., 2003; Gerlach, 2004). Although very little is known about it, the substantial emissions of inorganic halogens during biomass burning (Lobert et al., 1999; Keene et al., 2006) and in association with crustal dust (Keene et al., 1999; Sander et al., 2003) may also support active halogen-radical chemistry and related transformations involving NO_X downwind of sources. Recent aircraft and satellite observations confirm that BrO is present in the free troposphere at levels sufficient to influence photochemistry significantly (see, e.g., von Glasow et al., 2004).

2.3 SULFUR OXIDES IN THE TROPOSPHERE

2.3.1 General Sulfur Chemistry

The four known monomeric sulfur oxides are SO, SO_2, SO_3, and S_2O. SO is formed by photolysis of SO_2 at wavelengths <220 nm and so is found only in the middle and upper stratosphere (Pinto et al., 1989). SO_3 can be emitted from the stacks of power plants and industrial facilities; however, it reacts rapidly with H_2O to form H_2SO_4 in the stack or immediately after release to the atmosphere. Of the four species, only SO_2 is present at concentrations significant for atmospheric chemistry and ecological exposures.

SO_2 can be oxidized either in the gas phase through OH attack, or, owing to its high solubility, in the aqueous phase in cloud droplets; this aqueous-phase oxidation dominates

$P(SO_4^{2-})$ at a ratio of ~80% (Warneck, 1999). Gas-phase oxidation of SO_2 proceeds through the reaction

$$SO_2 + OH + M \rightarrow HSO_3 + M \tag{2.3-1}$$

followed by

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{2.3-2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2.3-3}$$

But because H_2SO_4 is highly soluble, it will be removed rapidly by transfer to the aqueous phase of aerosol particles and cloud droplets; see the discussion in Section 2.4 below. Other pathways for SO_2 oxidation, such as reaction with HO_2 or NO_3^- have very low rate constants (JPL, 2003) and so are insignificant on urban and regional scales.

SO_2 is chiefly an emitted or "primary" pollutant, though it is also produced by photochemical oxidation of reduced S compounds like dimethyl sulfide (DMS; CH_3-S-CH_3), hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (OCS), methyl mercaptan (CH_3-S-H), and dimethyl disulfide (DMDS; CH_3-S-S-CH_3). All of these compounds are largely biogenic in origin, and the sources are discussed in Chapter 3. Excepting OCS, which is lost mainly by photolysis with a τ of ~6 months, these species are lost mainly through attack by OH and NO_3^-.

Because tropospheric OCS is relatively long-lived, it can be transported up into the stratosphere. Crutzen (1976) proposed that its oxidation serves as the major source of SO_4^{2-} in the stratospheric aerosol layer, sometimes called the "Junge layer" (Junge et al., 1961), during periods when volcanic plumes do not reach the stratosphere. By contrast, Myhre et al. (2004) proposed that SO_2 transported upwards from the troposphere is the most likely source since the up-flux of OCS is too small to sustain the observed SO_4^{2-} loadings in the Junge layer. Moreover, in situ measurements of the isotopic composition of S do not match those of OCS (Leung et al., 2002). Reaction with NO_3 at night is the most likely major loss process for DMS and CH_3-S-H.

Mechanisms of the oxidation of DMS are still incompletely understood. Excess SO_4^{2-} in marine aerosol is related mainly to production of SO_2 from oxidation of DMS. Initial attack by NO_3^- and OH involves H^+ abstraction, with a smaller branch leading to OH addition to the S atom; the yield from this latter branch varies inversely with temperature and is the major pathway at temperatures <285 K (Ravish Ankara et al., 1997). The adduct formed may then either decompose to form methane sulfuric acid (MSA), or undergo further reactions in the main pathway to yield DMS (Barnes et al., 1994). Following H+ atom abstraction from DMS, the main reaction products include MSA and SO_2. The ratio of MSA to SO_2 is strongly temperature-dependent, varying from ~0.1 in tropical waters to ~0.4 in Antarctic waters (Seinfeld and Pandis, 1998). Transformations among atmospheric S compounds are summarized in Figure 2.3-1, where S(IV) represents $SO_2{\cdot}H_2O$, HSO_3^-, and SO_3^{2-}, and S(VI) represents gas-phase SO_3 and H_2SO_4 or aqueous-phase HSO_4^- and SO_4^{2-}.

2.3.2 Heterogeneous-Phase Production and Loss Processes

Chemical transformations involving inorganic halogenated compounds effect changes in the multiphase cycling of sulfur oxides in ways analogous to their effects on NO_X. Oxidation of DMS by BrO produces dimethylsulfoxide (DMSO; $(CH_3)_2SO$) (Barnes et al., 1991; Toumi, 1994), and oxidation by atomic Cl leads to formation of SO_2 (Keene et al., 1996). DMSO and SO_2 are precursors for methanesulfonic acid (CH_3SO_3H) and H_2SO_4. In the MBL, virtually all H_2SO_4 and CH_3SO_3H vapor condenses onto existing aerosols or cloud droplets that subsequently evaporate, contributing to aerosol growth and acidification. Unlike CH_3SO_3H, H_2SO_4 also has the potential to produce new particles (Korhonen et al., 1999; Kumala et al., 2000); in marine air masses, these are thought to be present mainly in the free troposphere. Saiz-Lopez et al. (2004) estimated that observed levels of BrO at Mace Head would oxidize $(CH_3)_2S$ ~6 times faster than OH and thereby substantially increase production rates of H_2SO_4 and other condensable S species in the MBL.

SO_2 is also scavenged by deliquesced aerosols and oxidized to H_2SO_4 in the aqueous phase by several strongly pH-dependent pathways (Chameides and Stelson, 1992; Vogt et al., 1996; Keene et al., 1998). Model calculations indicate that oxidation of S(IV) by O_3 dominates in fresh, alkaline sea salt aerosols, whereas oxidation by hypohalous acids (primarily HOCl) dominates in moderately acidic solutions. Additional non-sea salt (nss) pSO_4 is generated by SO_2 oxidation in cloud droplets (Clegg and Toumi, 1998). Ion-balance calculations indicate that most nss pSO_4 in short-lived sea salt size fractions (on the order of 2 to 48 h) accumulates in

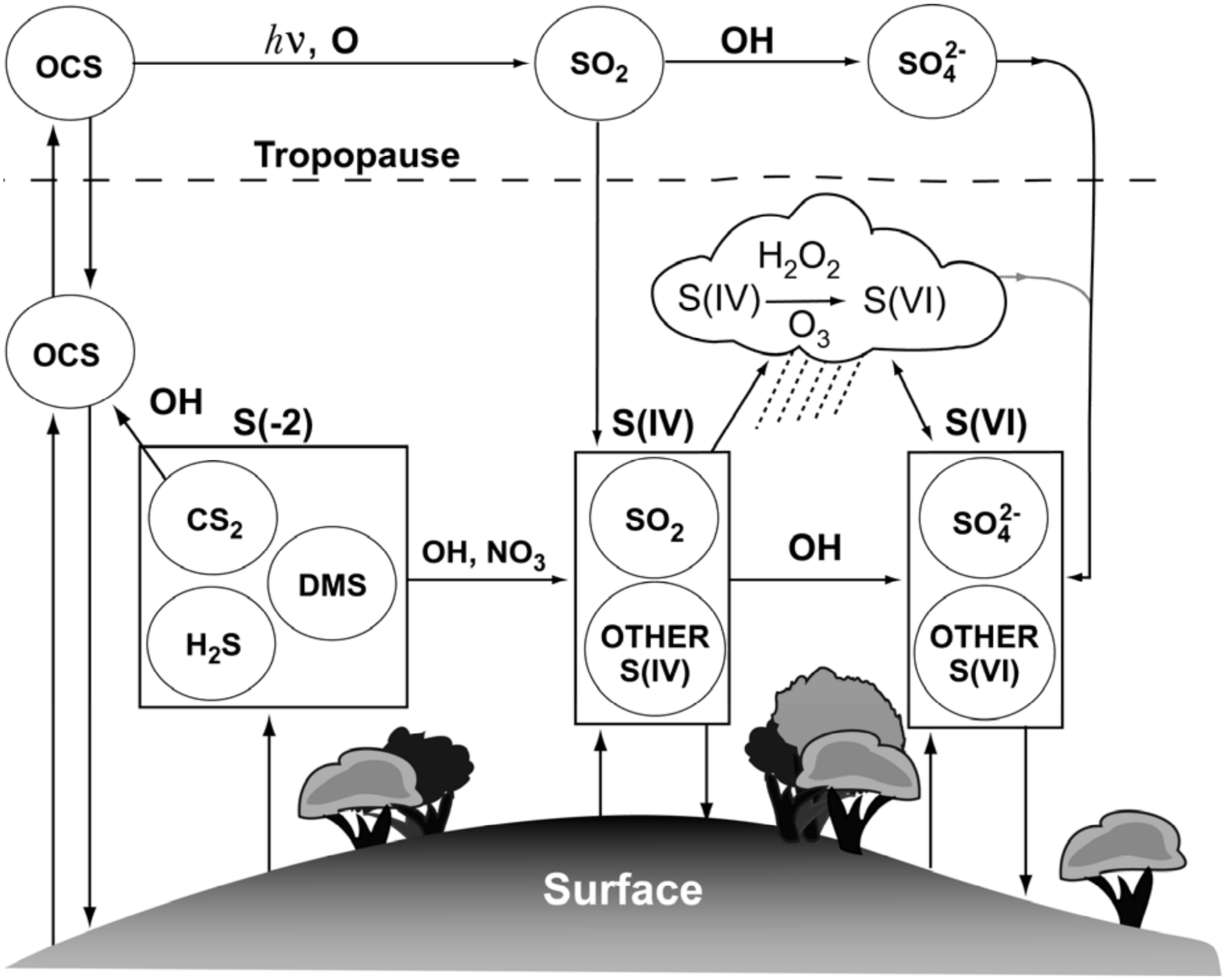


Figure 2.3-1. Transformations of sulfur compounds in the atmosphere.

Source: Adapted from Berresheim (1995).

acidic aerosol solutions and/or in acidic aerosols processed through clouds (see, e.g., Keene et al., 2004).

The production, cycling, and associated radiative effects of S-containing aerosols in marine and coastal air are regulated in part by chemical transformations involving inorganic halogens as described above; see Glasow et al., 2002b. These transformations include: dry-deposition fluxes of nss pSO_4 in marine air dominated by sea salt size fractions (Huebert et al., 1996; Turekian, 2001); HCl phase partitioning that regulates sea salt pH and associated pH-dependent pathways for S(IV) oxidation (Keene et al., 2002; Pszenny et al., 2004); and potentially important oxidative reactions with reactive halogens for DMS and S(IV). However, the absolute magnitudes and relative importance of these S cycling processes in the MBL are poorly known.

Iodine chemistry has been linked to ultrafine particle bursts at Mace Head (O'Dowd et al., 1999, 2002). Observed bursts coincide with the elevated concentrations of IO and are characterized by particle concentrations increasing from background levels to up to 300,000 cm^{-3} on a time scale of seconds to minutes. This newly identified source of marine aerosol would provide additional aerosol surface area for condensation of SO_X and thereby presumably diminish the potential for nucleation pathways involving H_2SO_4. However, a subsequent investigation in polluted air along the New England, USA, coast found no correlation between periods of nanoparticle growth and corresponding concentrations of I oxides (Russell et al., 2006). Thus, the potential importance of I chemistry in aerosol nucleation and its associated influence on S cycling remain highly uncertain.

2.4 AQUEOUS-PHASE FORMATION OF SULFATES AND NITRATES

The chief species capable of oxidizing S(IV) to S(VI) in cloud water are O_3, hydrogen peroxide (H_2O_2) and organic peroxides, OH radicals, and ions of the transition metals such as iron (Fe) and copper (Cu) that can catalyze oxidation by molecular oxygen (O_2).

The basic mechanism of aqueous-phase SO_2 oxidation has long been known and is found in numerous texts (see, e.g., Seinfeld and Pandis, 1998; Jacob, 2000; and Jacobson, 2002): dissolution of SO_2

$$SO_{2(g)} \Leftrightarrow SO_{2(aq)} \qquad (2.4\text{-}1)$$

followed by formation and dissociation of H_2SO_3

$$SO_{2(aq)} + H_2O_{(aq)} \Leftrightarrow H_2SO_3 \Leftrightarrow H^+ + HSO_3^- \Leftrightarrow 2H^+ + SO_3^{2-} \qquad (2.4\text{-}2)$$

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

$$HSO_3^- + H_2O_2 + H^+ \Leftrightarrow SO_4^{2-} + H_2O + 2H^+ \qquad (2.4\text{-}3)$$

because SO_3^{2-} is much less abundant than HSO_3^-.

These major pathways for aqueous-phase oxidation of S(IV) to S(VI) as a function of pH are shown in Figure 2.4-1. For pH up to ~5.3, H_2O_2 is the dominant oxidant; above 5.3, O_3 and Fe(III) dominate. Marine aerosols are expected to have higher pH; however, in marine aerosols the Cl-catalyzed oxidation of S(IV) may be the more significant process (Zhang and Millero, 1991; Hoppel and Caffrey, 2005).

Because NH_4^+ is so effective in controlling acidity, where it is present it affects the rate of oxidation of S(IV) to S(VI) and the rate of dissolution of SO_2 into particles and cloud droplets.

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

2.4.1 Heterogeneous Processes and NH_3

The phase partitioning of NH_3 with deliquesced aerosol solutions is controlled primarily by the thermodynamic properties of the system expressed as

$$NH_{3(g)} \overset{K_H}{\leftrightarrow} [NH_{3(aq)}] \overset{K_b}{\leftrightarrow} [NH_4{}^+] + K_W/[H^+] \tag{2.4-4}$$

where K_H and K_b are the temperature-dependent Henry's Law and dissociation constants for NH_3, 62 M atm^{-1} and 1.8×10^{-5} M, respectively; and K_w is the ion product of water, 1.0×10^{-14} M (Chameides, 1984). Reaction 2.4-4 shows that for any $[NH_X]$ in the system, increasing aqueous concentrations of particulate H^+ will shift the partitioning of NH_3 towards the condensed phase. Consequently, under the more-polluted conditions characterized by higher concentrations of acidic pSO_4, the ratios of gas-phase NH_3 to pNH_4 decrease (Smith et al., 2007). Thus, in marine air, where aerosol acidity varies substantially as a function of particle size, NH_3 partitions preferentially to the more acidic sub-μm size fractions (e.g., Keene et al., 2004; Smith et al., 2007).

Because the V_d of gas-phase NH_3 to the surface is substantially greater than that for the sub-μm size fraction of pSO_4 with which most pNH_4 is associated, dry-deposition fluxes of total NH_3 are dominated by the gas-phase fraction (Russell et al., 2003; Smith et al., 2007). Consequently, this partitioning with highly acidic pSO_4 effectively increases the τ of total NH_3

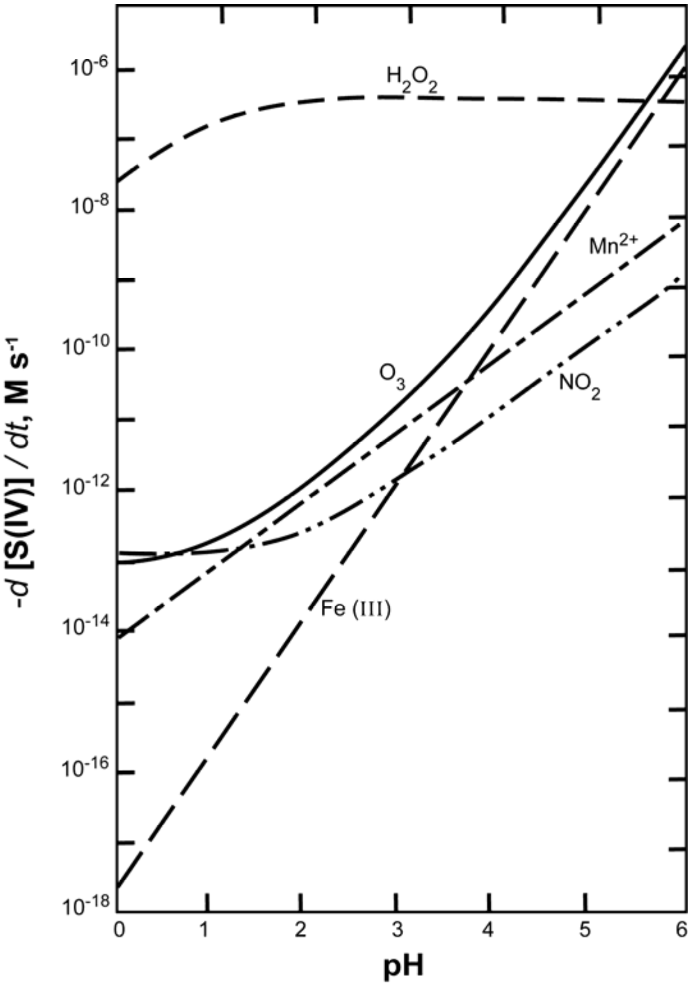


Figure 2.4-1. Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) is shown as a function of pH. Conditions assumed are: $[SO_{2(g)}]$ = 5 ppb; $[NO_{2(g)}]$ = 1 ppb; $[H_2O_{2(g)}]$ = 1 ppb; $[O_{3(g)}]$ = 50 ppb; $[Fe(III)_{(aq)}]$ = 0.3 µM; $[Mn(II)_{(aq)}]$ = 0.3 µM.

Source: Seinfeld and Pandis (1998).

against dry deposition loss. This shift has important consequences for NH_3 cycling and potential ecological effects as described below.

In coastal New England during summer, for example, air transported from rural eastern Canada contains relatively low concentrations of nss pSO_4 and total NH_3 (Smith et al., 2007). Under these conditions, the roughly equal partitioning of total NH_3 between gas and aerosol phases sustains dry-deposition fluxes of total NH_3 to coastal ocean waters with a median value of 10.7 µmol m^{-2} day^{-1}. By contrast, heavily polluted air transported from the industrialized midwestern United States contains nss [SO_4^{2-}] and total [NH_3] that are approximately a factor of 3 greater than those in clean air, based on median values. Under polluted conditions, >85% of total NH_3 partitions to the highly acidic pSO_4; consequently, the median dry-deposition flux of total NH_3 is 30% lower than that under the cleaner flow regime. The relatively larger τ of total NH_3 against dry deposition under more polluted conditions implies that, on average, total NH_3 would accumulate to higher atmospheric concentrations under these conditions and hence be subject to atmospheric transport over longer distances. Consequently, the importance of NH_X removal via wet deposition would also increase. Given the inherently sporadic character of precipitation, greater heterogeneity in NH_3 deposition fields and in any potential responses by sensitive ecosystems downwind of major S emission regions could be expected.

2.5 ATMOSPHERIC TRANSPORT OF NO_X AND SO_X

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

Because NO and NO_2 are only slightly soluble, they can be transported over longer distances in the gas phase than can more soluble species like SO_2 which are depleted by deposition to moist surfaces or taken up more readily on aqueous surfaces of particles. During transport, NO and NO_2 can be transformed into the longer-lived reservoir species HNO_3 and the PANs as described above. These species can then contribute to local NO_X concentrations and deposition in remote areas as it is now well established that PAN decomposition provides a major source of NO_2 in the remote troposphere (Staudt et al., 2003). The decomposition of PAN in subsiding air masses from Asia over the eastern Pacific may also make an important contribution to enhanced O_3 and NO_X concentrations in the United States (Kotchenruther et al., 2001; Hudman et al., 2004). Further details about mechanisms for transporting NO_X and SO_X are described Annex 1.

2.6 SAMPLING AND ANALYSIS FOR NO_X AND SO_X

2.6.1 NO_X Measurement Methods and Associated Issues

Separate sections in Annexes 1 and 2 on field-deployed measurement techniques focus on current methods and promising new technologies so no attempt is made here to cover the extensive development of these methods or of methods no longer in widespread use. Rather, the descriptions in this chapter concern chiefly the Federal Reference Methods and Federal Equivalent Methods (FRM and FEM, respectively). More detailed discussions of the FRM, FEM, and other, newer methods including issues about their field use is found in U.S. Environmental Protection Agency (1993a, 1996), McClenny (2000), Parrish and Fehsenfeld (2000), and Clemitshaw (2004).

2.6.1.1 NO and NO_2

NO is routinely measured using the principle of gas-phase chemiluminescence induced by the reaction of NO with O_3 at low pressure. However, Cardelino and Chameides (2000) reported that measured [NO] during the afternoon was frequently at or below the operational limit of detection (LOD), ~1 ppb, of the regulatory NO_X instruments even in large metropolitan regions such as Washington, DC, Houston, TX, and New York, NY, where [NO_X] from mobile sources would be high. The FRM for NO_2 also makes use of this NO detection technique using a prerequisite step to reduce NO_2 to NO on the surface of a molybdenum oxide (MoO_X) substrate heated to ~340 °C. Because the FRM monitor cannot detect NO_2 directly, the [NO_2] is determined as the difference between the sample passed over the heated MoO_X substrate (the nitrogen oxides total) and the sample not so reduced (the NO alone). However, reduction of NO_2 to NO on the MoO_X substrate is not specific for NO_2; hence, chemiluminescence monitors are all subject to unknown and varying interferants in the sample from other oxidized N compounds, i.e., species of NO_Z; see the outer box elements in Figure 2.2-1 above.

Interference by NO_Z compounds has long been known (Fehsenfeld et al., 1987; Rodgers and Davis, 1989; U.S. Environmental Protection Agency, 1993a, 2006; Crosley, 1996; Nunnermacker et al., 1998; Parrish and Fehsenfeld, 2000; McClenny et al., 2002; Dunlea et al., 2007). The sensitivity of the MoO_X instrument to interference from multiple NO_Z compounds is highly variable and dependent in part on instrument inlet design, on the temperature of the reducing substrate, and on the interactions of species with MoO_X. Because of losses on inlet surfaces and differences in the efficiency of reduction of NO_Z compounds on the heated MoO_X substrate, NO_X as reported from these instruments cannot be considered as a universal surrogate for NO_Y. However, in settings close to relatively high-concentration fresh emissions like those in urban areas during rush hour, most of the NO_Y is present as NO_X. Additional details on this interference and descriptions of methods other than chemilumenescence are given in Annex 1.

2.6.2 Total and Speciated NO_Y

Gold-catalyzed CO or H_2 reduction or conversion on heated MoO_X have been used to reduce total NO_Y to NO before detection by chemiluminescence (Fehsenfeld et al., 1987; Crosley, 1996). Both techniques offer generally reliable measurements, with response times on the order of 60 s and a linear dynamic range demonstrated in field intercomparisons from ~10 ppt to 10s of ppb. Under some conditions, hydrogen cyanide (HCN), NH_3, alkyl nitrates (RNO_2), and acetonitrile (CH_3CN) can be converted to NO; but at normal concentrations and humidity, these are minor interferants. Thermal decomposition followed by laser-induced fluorescence (LIF) has also been used for NO_Y detection, and this is described in more detail in Annex 1. In field comparisons, instruments based on these two principles generally showed good agreement (Day et al., 2002) with experimental uncertainty estimated to be on the order of 15 to 30%.

2.6.2.1 HNO_3

Accurate measurement of HNO_3 has presented a long-standing analytical challenge. In this regard, it is useful to consider the major factors that control HNO_3 partitioning between the gas and deliquesced-particulate phases in ambient air

$$HNO_{3(g)} \overset{K_H}{\leftrightarrow} [HNO_{3(aq)}] \overset{K_a}{\leftrightarrow} [H^+]+[NO_3^-] \qquad (2.6\text{-}1)$$

where K_H is the Henry's Law constant in M atm^{-1} and K_a is the acid dissociation constant in M. Thus, the primary controls on HNO_3 phase partitioning are its thermodynamic properties (K_H, K_a, and associated temperature corrections), aerosol liquid water content (LWC), solution pH, and kinetics. Aerosol LWC and pH are controlled by the relative mix of acids and bases in the system, the hygroscopic properties of condensed compounds, and meteorological conditions, chiefly RH, temperature, and pressure.

In the presence of chemically distinct aerosols of varying acidities (e.g., super-µm, predominantly sea salt; and sub-µm, predominantly pSO_4), HNO_3 should partition preferentially to the less-acidic particles, and observations are consistent with this (e.g., Huebert et al., 1996; Keene and Savoie, 1998; Keene et al., 2002). The kinetics of this phase partitioning are controlled by atmospheric concentrations of HNO_3 vapor and pNO_3, and the size distribution and τ of the particles against deposition. Sub-µm diameter aerosols typically equilibrate with the gas phase in seconds to minutes while super-µm aerosols require hours to a day or more see, e.g., Meng and Seinfeld (1996) and Erickson et al. (1999). Consequently, smaller aerosol size fractions are typically close to thermodynamic equilibrium with respect to HNO_3, whereas larger size fractions, for which τ against deposition range from hours to a few days, are often undersaturated (e.g., Erickson et al., 1999; Keene and Savioe, 1998).

Methods used widely for measuring HNO_3 include standard filterpacks configured with nylon or alkaline-impregnated filters (see, e.g., Goldan et al., 1983; Bardwell et al., 1990), annular denuders like EPA method IP-9, and standard mist chambers (see Talbot et al., 1990). Samples from these instruments are typically analyzed by ion chromatography. Intercomparisons of these measurement techniques by Hering et al. (1988), Tanner et al. (1989), and Talbot et al. (1990) reported differences on the order of a factor of 2 or more. In part, this variance is due to nonsystematic sampling error. When chemically distinct aerosols with different pHs, for example, sea salt and pSO_4, mix together on a bulk filter, the acidity of the bulk mixture will be greater than that of the less-acidic aerosols with which most of the NO_3^- is associated. This change in pH may cause the bulk mix to be supersaturated with respect to HNO_3 leading to volatilization and, thus, to a positive measurement bias in HNO_3 sampled downstream. Alternatively, when undersaturated super-µm size fractions like sea salt accumulate on a bulk filter and chemically interact over time with HNO_3 in the sample air stream, scavenging may lead to a negative bias in the HNO_3 sampled downstream. Because the magnitude of both effects will vary as functions of the overall composition and thermodynamic state of the multiphase systems, the combined influence can cause net positive or net negative measurement bias in data with unknown frequencies. Pressure drops across particle filters can also lead to artifact volatilization and associated positive bias in [HNO_3] measured downstream.

Recently, sensitive HNO_3 measurements based on the principle of chemical ionization mass spectroscopy (CIMS) have been reported; see, e.g., Huey et al. (1998), Mauldin et al. (1998), Furutani and Akimoto (2002), and Neuman et al. (2002). The CIMS relies on selective formation of ions such as $SiF_5^-{\cdot}HNO_3$ or $HSO_4^-{\cdot}HNO_3$ followed by detection via mass spectroscopy. Two CIMS techniques and a filter pack technique were intercompared in Boulder, CO (Fehsenfeld et al., 1998). Results indicated agreement to within 15% between the two CIMS instruments and between the CIMS and filterpack methods under relatively clean conditions with HNO_3 mixing ratios between 50 and 400 ppt. In more polluted air, the filterpack technique generally yielded higher values than the CIMS, suggesting that interactions between chemically distinct particles on bulk filters is a more important source of bias in polluted continental air. Differences were also greater at lower temperature when pNO_3 corresponded to relatively greater fractions of total NO_3.

A recent large field intercomparison of different techniques for HNO_3 measurement was conducted in Tampa, FL in 2003 (Arnold et al., 2007) using the annular denuder + filter pack time-integrated method and three semi-continuous techniques: two different implementations of the $NO_Y - NO_Y$* denuder difference technique (Joseph and Spicer, 1978); the parallel plate wet diffusion scrubber + online ion chromatography method (Boring et al., 2002); and the CIMS (Huey et al., 1998). Results for 10 min aggregates computed from the various higher sampling frequencies of each semi-continuous instrument showed good agreement ($R^2 > 0.7$) for afternoon periods of highest production and accumulation of HNO_3. Further, agreement was within ±30% even at [HNO_3] < 0.30 ppb, although the 12-h and 24-h time-integrated denuder + filterpack measurements were substantially in error. This study also confirmed the importance of sample inlet height for HNO_3 monitoring through comparison to previous field work at this and other sites where inlet height ranged from 1.5 to 10 m, producing systematic discrepancies in measured [HNO_3] of more than a factor of 2 correlated with height . The correlation of this concentration discrepancy with inlet height is governed by HNO_3's very fast V_d, which is essentially at the limit of aerodynamic resistance.

2.6.2.2 Other Nitrates

Methods for sampling and analysis of $RONO_2$ in the atmosphere have been reviewed by Parrish and Fehsenfeld (2000). PAN, PPN, and MPAN are typically measured using a gas chromatograph followed by electron capture detectors (GC-ECD) (see, e.g., Gaffney et al., 1998), although other techniques such as Fourrier Transform InfraRed (FTIR) analysis can also be used. Field measurements made using GC-ECD have reported a total uncertainty of ±5 ppt + 15% (Roberts et al., 1998).

In the two most extensive networks in the United States, the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Speciation Trends Network (STN) – see additional description of these networks in Chapter 3 and Annex 2 – pNO_3 in the ≤ 2.5 µm ($PM_{2.5}$) size fraction is typically collected on nylon filters downstream of annular denuders coated with a basic solution to remove acidic gases such as HNO_3, HNO_2, and H_2SO_4. Filter extracts are then analyzed by ion chromatography (IC) for NO_3^-, SO_4^{2-}, and Cl^-. NO_2^- ions are also measured by this technique but their concentrations are almost always below operation LODs. However, both networks measure NO_3^- only in the $PM_{2.5}$ fraction. Because of interactions with more highly acidic components on filter surfaces, there can be volatilization of NO_3^- in PM_{10} samples. These effects are minimized if separate aerosol size fractions are collected; i.e., by separating the more acidic $PM_{2.5}$ and the more alkaline $PM_{10-2.5}$ as is done in a dichotomous sampler or multistage impactor.

2.6.2.3 Remote Sensing of Tropospheric NO_2 Columns

The paucity of in situ NO_2 measurements motivates development of new techniques to infer surface $[NO_2]$ from satellite measurements of tropospheric total column $[NO_2]$. These total column $[NO_2]$ have been shown to have a strong correlation with in situ $[NO_2]$ when evaluated in northern Italy (Ordonez et al., 2006). Table 2.6-1 contains an overview of the three satellite instruments used to retrieve total column $[NO_2]$ from measurements of solar backscatter.

Figure 2.6-1 shows total column $[NO_2]$ retrieved from the Scanning Imagining Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument on the European ENVISAT satellite. Pronounced $[NO_2]$ enhancements are evident in Figure 2.6-1 over major urban and industrial emission centers. The high degree of spatial heterogeneity over the southwestern United States provides empirical evidence that most of the total column $[NO_2]$ is

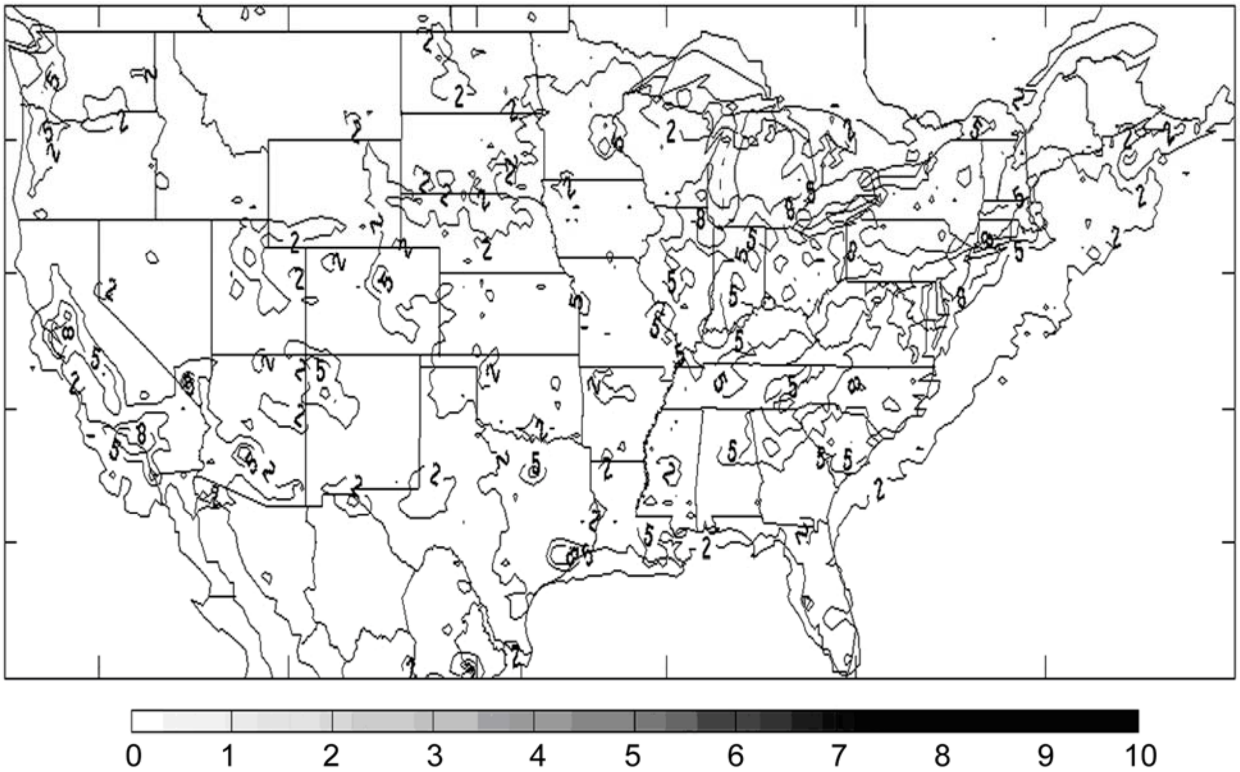


Figure 2.6-1. Tropospheric total column [NO_2] (molecules NO_2 cm^{-2}) retrieved from the SCIAMACHY satellite instrument for 2004-2005.

Source: Martin et al. (2006).

concentrated in the lower troposphere. These total column [NO_2] are more sensitive to NO_X in the lower troposphere than in the upper troposphere (Martin et al., 2002) because the NO_2/NO ratio is lower by a factor of 25 aloft relative to the surface, a difference driven by the temperature dependence of the NO + O_3 reaction. Martin et al. (2004a) integrated in situ airborne measurements of NO_2 and found that during summer the lower mixed layer contains 75% of the total column [NO_2] over Houston and Nashville. However, it should be noted that while certainly useful, the satellite measurements are very sensitive to surface albedo and aerosol loading and have considerable restrictions on timing and location.

2.6.3 SO_X Measurement Methods and Associated Issues

Currently, ambient SO_2 is measured using instruments based on pulsed UV fluorescence. The UV fluorescence monitoring method for atmospheric SO_2 was developed to improve upon the flame photometric detection (FPD) method, which in turn had displaced the pararosaniline wet chemical method. Although the pararosaniline method remains the EPA FRM for atmospheric SO_2, it is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as FEMs by EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity and sensitivity, and the need for consumable hydrogen gas for the FPD method.

The LOD for a non-trace-level SO_2 analyzer is 10 ppb (CFR, 2006). However, most commercial analyzers report operational detection limits of ~3 ppb. This concentration is very near the current ambient annual average [SO_2] of ~4 ppb; see the fuller description of concentrations and variations in Chapter 3. The EPA-sponsored National Core Monitoring Network (NCore) is intended to operate newer, trace-level SO_2 instruments to increase the accuracy and precision of measurements at the much lower ambient levels currently encountered in most of the United States.

2.6.3.1 Sources of Interference

The most common interferants for the UV fluorescence method for SO_2 are other gases that fluoresce like SO_2. Luke (1997) reported the positive artifacts of a modified pulsed fluorescence detector generated by the coexistence of NO, CS_2, and a number of highly fluorescent aromatic hydrocarbons such as benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, *m*-ethyltoluene, ethylbenzene, and 1,2,4-trimethylbenzene. Consequently, any such hydrocarbons in the sample in the optical chamber can act as a positive interferant. To remove this source of interference, high-sensitivity SO_2 analyzers like those to be used in the NCore network have hydrocarbon scrubbers to remove these compounds from the sample stream before the sample air enters the optical chamber.

Nonradiative deactivation (quenching) of excited SO_2 molecules can occur from collisions with common molecules in air, including N_2, O_2, and H_2O. During collisional quenching, the excited SO_2 molecule transfers energy, kinetically allowing the SO_2 molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO_2 fluorescence and, hence, an underestimation of [SO_2]. Of particular concern is the variable water vapor content of air. Luke (1997) reported that the response of the detector could be reduced by ~7 and 15% at water vapor mixing ratios of 1 and 1.5 mole percent, respectively.

Other techniques for SO_2 and other issues in their field deployment are described in Annex 1.

2.6.4 Sampling and Analysis for SO_4^{2-}, NO_3^-, and NH_4^+

SO_4^{2-}, NO_3^-, and NH_4^+ are commonly present in $PM_{2.5}$. The common techniques for sampling for these compounds uses air drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems generally have two critical flow-rate components for the capture of fine particulate: (1) the flow of air through the sampler must be at a flow rate that ensures the 2.5 µm size cut; and (2) the flow rate must be optimized to capture the desired amount of particulate loading with respect to the analytical method LODs.

When using the technique described above to collect pSO_4, pNO_3, and pNH_4, sampling artifacts can occur principally for two reasons similar to those described for HNO_3 above: (1) positive sampling artifacts for all three species due to chemical reactions on the filter face; and (2) negative sampling artifacts for NO_3 and NH_4^+ due to decomposition and evaporation after capture on the filter.

2.6.4.1 Denuder + Filter-Based Techniques

The STN and IMPROVE networks implement this general technique with somewhat different instruments and protocols. Current STN samplers include three filters: (1) Teflon for equilibrated mass and elemental analysis including elemental S; (2) a HNO_3-denuded nylon filter for ion analysis including NO_3^- and SO_4^{2-}; and (3) a quartz-fiber filter for elemental and organic carbon (EC and OC, respectively), analyzed using the thermal-optical reflectance (TOR) method. The IMPROVE sampler, which collects two 24-h samples each week, simultaneously collects one sample of particulate matter ≤ 10 µm (PM_{10}) on a Teflon filter, and three samples of $PM_{2.5}$ on Teflon, nylon, and quartz filters as STN does. In each network, total mass concentrations of $PM_{2.5}$ are determined gravimetrically from the $PM_{2.5}$ Teflon filter samples, which are also used to determine concentrations of selected individual elements. The STN and IMPROVE networks represent a major advance in the measurement of pNO_3, because the combination of a denuder coated with either sodium carbonate (Na_2CO_3) or magnesium oxide (MgO) to remove HNO_3 vapor and a nylon filter to adsorb HNO_3 vapor volatilizing from the collected NH_4NO_3 particles overcomes the loss of NO_3^- from Teflon filters.

In a side-by-side comparison of two of the chief aerosol monitoring techniques, $PM_{2.5}$ mass and major contributing species were well correlated among the different methods with $r > 0.8$ (Hains et al., 2007). Agreement was good for total mass, SO_4^{2-}, OC, total carbon (TC), and NH_4^+, while NO_3^- and black carbon (BC) showed less-good fits. Based on reported uncertainties, however, even daily concentrations of $PM_{2.5}$ mass and major contributing species were often significantly different at the 95% confidence level. The STN methods reported generally higher values of $PM_{2.5}$ total mass and of individual species than did the IMPROVE-like ones. Since these differences can only be partially accounted for by known random errors, the authors concluded that the current uncertainty estimates used in the STN network may underestimate the actual uncertainty.

2.6.4.1.1 Sampling Artifacts

The reaction of SO_2 and other acid gases with basic sites on glass fiber filters or with basic coarse particles on the filter leads to the formation of nonvolatile pSO_4, pNO_3, and Cl salts. These positive artifacts lead to the overestimates of the concentrations of PM total mass and SO_4^{2-} and likely NO_3^- as well. These problems were largely overcome by changing to quartz fiber or Teflon filters and by the separate collection of the $PM_{2.5}$ fraction. However, the possible reaction of acidic gases with basic coarse particles remains a possibility, especially with PM_{10} and $PM_{10-2.5}$ measurements. These positive artifacts could be effectively eliminated by removing acidic gases in the sampling line with denuders coated with NaCl or Na_2CO_3.

Positive sampling artifacts also occur during measurement of pNH_4. The reaction of NH_3 with acidic particles, as for example

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{2.6-2}$$

either during sampling or during transportation, storage, and equilibration could lead to an overestimation of pNH_4 concentrations. Techniques have been developed to overcome this problem, including using a denuder coated with hyrofluoric, citric, or phosphoric acid to remove NH_3 during sampling and to protect the collected PM from NH_3 (Suh et al., 1992, 1994; Brauer et al., 1991; Koutrakis et al., 1988a,b; Keck and Wittmaack, 2006; Possanzini et al., 1999; Winberry et al., 1999). Positive artifacts for pNH_4 can also develop during sample handling due to contamination. NH_3 emitted directly from human sweat, breath, and tobacco smoking will react with acidic aerosols on the filter to form $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3 if the filter is improperly handled (Sutton et al., 2000).

Although pSO_4 is relatively stable on a Teflon filter, it is now well known that volatilization losses of pNO_3 occur during sampling. For pNO_3, the effect on the accuracy of atmospheric measurements from these volatilization losses is more significant for $PM_{2.5}$ than for PM_{10}. The FRM for $PM_{2.5}$ will likely suffer a loss of pNO_3 similar to that experienced with other simple filter collection systems described above. Sampling artifacts resulting from the loss of pNO_3 species represents a significant problem in areas such as southern California that experience high total NO_3 loadings. Hering and Cass (1999) discussed errors in $PM_{2.5}$ mass measurements owing to the volatilization of pNO_3 using data from two field measurement campaigns conducted in southern California: (1) the Southern California Air Quality Study (SCAQS) (Lawson, 1990); and (2) the 1986 California Institute of Technology (CalTech) study (Solomon et al., 1992). In both studies, side-by-side sampling of $PM_{2.5}$ was conducted with one sampler collecting particles directly onto a Teflon filter, and a second using an MgO-coated denuder (Appel et al., 1981) to remove gaseous HNO_3, followed by a nylon filter to absorb the evaporating HNO_3. In both studies, the $PM_{2.5}$ mass lost from NH_4NO_3 volatilization represented a significant fraction of the total $PM_{2.5}$ mass, and these losses were greater during summer than fall: 17% (summer) versus 9% (fall) during SCAQS, and 21% (summer) versus 13% (fall) during CalTech. With regard to percentage loss of pNO_3, as contrasted to percentage loss of mass discussed above, Hering and Cass (1999) found that the amount of pNO_3 remaining on the Teflon filter samples was, on average, 28% less than that on the HNO_3-denuded nylon filters.

Diffusion denuder samplers, developed primarily to measure particle strong acidity (Koutrakis et al., 1988b, 1992), also can be used to study NO_3^- volatilization. Measurements were made with two versions of the Harvard-EPA Annular Denuder System (HEADS) for which HNO_3 vapor was removed by a Na_2CO_3-coated denuder and the remaining pNO_3 was reported either as the sum of nonvolatile NO_3 collected on a Teflon filter and volatized NO_3^- collected on a Na_2CO_3-coated filter downstream of the Teflon filter (full HEADS), or on a Nylon filter downstream of the Teflon filter (Nylon HEADS). The full HEADS consistently underestimated the total pNO_3 by approximately 20% compared to the Nylon HEADS.

This comparison technique was then used to measure loss of pNO_3 from Teflon filters in seven U.S. cities (Babich et al., 2000). Babich et al. (2000) found significant NO_3^- losses in

Riverside, CA, Philadelphia, PA, and Boston, MA, but not in Bakersfield, CA, Chicago, IL, Dallas, TX, or Phoenix, AZ, where measurements were made only during winter.

Negative sampling artifacts due to decomposition and volatilization are also significant for pNH_4. Ammonium particles are very sensitive to environmental factors such as temperature, relative humidity, acidity of aerosols, as well as to filter type (Spurny, 1999; Keck and Wittmaack, 2005). Any change in these parameters during the sampling period influences the position of the equilibrium between the particle and gas phases. Keck and Wittmaack (2005) observed that at temperatures below 0 °C, acetate-nitrate, quartz fiber, and Teflon filters could properly collect pNH_4, NH_3, and Cl; but at temperatures > 0 °C, the salts were lost from quartz fiber and Teflon filters, more so at higher temperatures and with no significant difference between quartz fiber and Teflon filters. The salts were lost completely from denuded quartz fiber filters at temperatures above ~20 °C, and from non-undenuded quartz fiber and Teflon filters at temperatures above ~25 °C. It is anticipated that current sampling techniques underestimate [pNH_4] due to volatilization, but fine particle mass contains many acidic compounds, and, as consequence, a fraction of volatilized NH_4^+ in the form of NH_3 can be retained on the Teflon filter by reactions with them. Therefore, it is reasonable to assume that the magnitude of pNH_4 loss, while uncertain because of these positive and negative effects, will be somewhat less than that for total pNO_3 loss. Techniques have been applied to pNH_4 sampling to correct its concentrations due to evaporation using a backup filter coated with hydrofluoric acids, citric acid, or phosphorous acids to absorb the evaporated NH_4 as NH_3; total [NH_4] then is the sum of the pNH_4 collected on the Teflon filter and [NH_3] collected on the backup filter.

2.7 SUMMARY

2.7.1 Significant Chemical Species

NO_X is the category label for oxides of nitrogen that includes a range of chemical species, chief among which are NO, NO_2, HNO_3, and PAN in the gas phase, and particulate nitrate pNO_3 in the particulate phase. Some of these species are directly emitted; others are formed as secondary products from the emitted species.

SO_X is the category label for oxides of sulfur including SO, SO_2, SO_3, and S_2O, though only SO_2 is present in concentrations relevant for atmospheric chemistry and ecological exposures.

Aqueous oxidation dominates production of SO_4^{2-} from SO_2; gas-phase oxidation is responsible for only ~20% of the SO_4^{2-} total. By contrast, there is little aqueous-phase oxidation of NO_2 to NO_3^- owing to its low solubility.

NH_3 and NH_4^+ (the category label is NH_X) play significant roles in controlling SO_2 oxidation by neutralizing acidity on particles and in cloud, fog, and rain water, and in determining the range and extent of N deposition both in themselves as reduced N and through combining to form NH_4NO_3.

Oxidation of NH_3 is a minor source of total NO_X.

Excess NH_3 is an actor alone and with NO_X in the N cascade leading to nitrification in aquatic and terrestrial ecosystems.

N_2O is a constituent oxide of nitrogen having effectively no chemical or ecological effects in the troposphere, thus giving it an atmospheric lifetime of ~114 yr. N_2O is also a GHG with a GWP on the standard 100-year basis of ~296 times that of CO_2.

Sea salt and other natural and anthropogenic particles provide surfaces for conversion of gas-phase N species to the particle phase, which can substantially alter the areal extent and magnitude of N deposition to the environment.

2.7.2 Field Sampling and Analysis

Techniques for routine regulatory monitoring of gas-phase NO_X and SO_2 are adequate but have important limitations. Routine NO_2 measurements by chemiluminescence (the FRM) are contaminated by unknown and varying concentrations of NO_Z. SO_2 measurements by the FRM in the standard regulatory network are now mostly at or below the instrument's operating LOD (~4 ppb), producing irresolvable uncertainty in these data.

Routine field sampling techniques for NH_3 are at present limited to integrated values over periods from several days to one week because higher frequency semi-continuous methods are not yet sufficiently robust to deploy widely.

Routine sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are also subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the measurement.

Despite the aforementioned limitations, for the purposes of identifying and quantifying the atmospheric concentrations and deposition totals causing ecological effects, these measurement techniques and sampling frequencies are fully adequate. Nevertheless, the coverage of the networks is very thin over large expanses of the interior United States.

TABLE 2.6-1. SATELLITE INSTRUMENTS USED TO RETRIEVE TROPOSPHERIC NO_2 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.

3. ECOLOGICAL EXPOSURES TO OXIDES OF NITROGEN AND SULFUR, AND TO AMMONIA AND AMMONIUM

Estimated annual emissions of nitrogen oxides (NO_X), sulfur oxides (SO_X), and ammonia (NH_3) for 2002 (U.S. Environmental Protection Agency, 2006a) are given in Annex Table AX2-1; methods for estimating these emissions, quality assurance procedures, and examples of calculated emissions are given in U.S. Environmental Protection Agency (EPA) (1999a). Recent discussions of uncertainties in current emissions inventories and strategies for improving them are found in NARSTO (2005). This section provides brief summaries of information on sources and sinks of some relevant NO_X and SO_X species and NH_3 and ammonium (NH_4^+). (The category label for NH_3 and NH_4^+ is NH_X.) Chemical and physical processes that transport, transform, and deposit these species to ecological receptors are described here both as observed and as represented in numerical chemical-transport models (CTMs). Last, model estimates of the Policy-relevant Background (PRB) NO_X and SO_X concentrations ([NO_X] and [SO_X], respectively) are presented.

3.1 NO_X EMISSIONS

3.1.1 Anthropogenic Sources of NO and NO_2

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

Emissions of NO_X from combustion are derived from both fuel and atmospheric N. Combustion zone temperatures greater than about 1300 K are required to fix atmospheric N_2

$$N_2 + O_2 \rightarrow 2NO \qquad (3.1\text{-}1)$$

Below this temperature NO can be formed from fuel N by

$$C_aH_cN_d + O_2 \rightarrow xCO_2 + yH_2O + zNO \tag{3.1-2}$$

Sawyer et al. (2000) have reviewed the factors associated with NO_X emissions by mobile sources. Both Reactions 3.1-1 and 3.1-2 have temperature dependencies and vary with concentrations of hydroxyl radical (OH), hydroperoxy radical (HO_2), and molecular oxygen (O_2).

3.1.2 Biogenic Sources of NO and NO_2

3.1.2.1 Soils

The pathways for nitrification and denitrification include two gas-phase intermediates, nitric oxide (NO) and nitrous oxide (N_2O) that can evolve from soil microbes before reaching the reaction endpoint, N_2. NO from soil metabolism is the dominant, but not exclusive, source of atmospheric NO_X from the biosphere. As noted below, present understanding of NO_2 exchange with vegetation suggests that there should be emission of NO_2 from foliage when ambient concentrations are less than the compensation point of ~1 part per billion (ppb). However, Lerdau et al. (2000) have pointed out that the global distribution of NO_X is not consistent with the large source that would be expected in remote forests if NO_2 emission were important when atmospheric concentrations were below that compensation point.

Temperature, soil moisture, and $[O_2]$ control the rates of reaction and, more importantly, the partitioning between NO and N_2O. In flooded soils where oxygen levels are low, N_2O is typically the dominant soil N gas; as soils dry, allowing more O_2 to diffuse, NO emissions increase. N metabolism in soil is strongly dependent on the substrate concentrations. Where N is limiting, it is efficiently retained and little gaseous N is released. Where N is in excess of demand, gaseous N emissions increase by microbial transformation. As a consequence, soil NO emissions are highest in fertilized agriculture and tropical soils (Davidson and Kingerlee, 1997; Williams et al., 1992). When soil microbes transform N, the gas-phase N is vented from the ecosystem; for some systems this alleviates ecological problems associated with N excess (see Chapter 4.3).

The three gas-phase products, NO, N_2O, N_2, have different chemical reactivities in different regions of the atmosphere. NO is a key precursor for formation of ozone (O_3) in the troposphere. Although N_2 is not reactive in the troposphere, N_2O is a greenhouse gas (GHG) with a significant global warming potential (GWP) from its direct radiative forcing and from its role in production and destruction of O_3 in the stratosphere. Additional details on these reactivities are given in Chapter 2 and in Annex 1.

Emission rates of NO from cultivated soils depend chiefly on fertilization levels and soil temperature. Production of NO from agriculture results from both the oxidation of NH_3 emitted by livestock and from soils after fertilization with ammonium nitrate (NH_4NO_3) and other exogenous sources of N. Estimates of these biogenic N emissions are less certain than those for anthropogenic sources. On a global scale, the contribution of soil emissions to the NO_X budget is on the order of 10% (van Aardenne et al., 2001; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998). On finer, more regional scales, however, NO_X emissions from fertilized fields can demonstrate wide variation around this value.

Local contributions to soil [NO] can be much greater than the global average, particularly in summer and especially where corn is grown extensively. Approximately 60% of total NO_X emitted by soils in the United States occurs in the central corn-growing region. The total mass and the chemical form of N (whether reduced or oxidized) applied to soils, the vegetative cover, temperature, soil moisture, and the agricultural practices such as tillage all influence the amount of fertilizer N released as NO. Williams et al. (1992) estimated that contributions to NO budgets from soils in Illinois are ~26% of the total NO emissions from industrial and commercial processes in that state.

3.1.2.2 Biomass Burning

During biomass burning, N is derived mainly from fuel N and not from atmospheric N_2 since temperatures required to fix atmospheric N_2 are likely to be found only in the flaming crowns of the most intense boreal forest fires. N in plants is present mostly as amino (NH_2) groups in amino acids. During combustion, N is released in many unidentified forms, presumably as N_2, with very little remaining in the fuel ash. Emissions of NO_X are ~0.2 to 0.3% relative to total biomass burned (e.g., Andreae, 1991; Radke et al., 1991). Apart from N_2, the most abundant species in biomass burning plumes is NO, emissions of which account for ~10 to 20% of the fuel N loadings (Lobert et al., 1991); other N-containing species such as NO_2, nitriles, and NH_3 together account for a similar amount. Westerling et al. (2006) have noted that the substantially increased frequency and intensity of wildfires in the western U.S. since 1970 will make emissions from this section increasingly important.

3.1.2.3 Lightning

Annual global production of NO by lightning is the most uncertain source of reactive N. In the last decade, literature values of the global average production rate range from 2 to 20 Tg N per year. However, most recent estimates are in the range of 3 to 8 Tg N per year. Estimates of the [NO] produced per flash have been made from theoretical considerations (e.g., Price et al., 1997); laboratory (e.g., Wang et al., 1998) and field experiments (e.g., Stith et al., 1999; Huntrieser et al., 2002); and through a combination of cloud-resolving model simulations, observed lightning flash rates, and measurements of [NO] in cloud anvils (e.g., DeCaria et al., 2000, 2005; Ott et al., 2007). The last method was used by Pickering et al. (1998), to show that only ~5 to 20% of the total [NO] produced by lightning in a given storm exists in the planetary boundary layer (PBL) at the end of a thunderstorm, thereby reducing its importance as an emissions source on regional or smaller scales.

3.1.3 Anthropogenic and Biogenic Sources of N_2O

N_2O, a gas-phase oxide of nitrogen with an atmospheric lifetime (τ) of ~114 years, is a small contributor to the total U.S. GHG budget, accounting for 6.5% of total GHG (on a Tg carbon dioxide (CO_2) equivalents basis) in 2005 (U.S. Environmental Protection Agency, 2007b). CO_2, for comparison, accounted for 83.9% in the same year and methane (CH_4) for 7.4% (U.S. Environmental Protection Agency, 2007b). Together with N_2O, these are the three largest GHG emissions components in the United States. Although the atmospheric [N_2O] has increased globally by ~18% to its current value of ~315 ppb owing to Western industrialization since 1750 (IPCC, 2001a; Hofmann, 2004), there is considerable interannual variation in N_2O emissions and this remains largely unexplained (IPCC, 2001b). N_2O emissions in the United States, for example, decreased by 2.8% or 13.4 Tg CO_2 equivalents over the years 1990-2005 (U.S. Environmental Protection Agency, 2007b).

N_2O is produced by biological processes occurring in the soil and water as described above and by a variety of anthropogenic activities in the agricultural, energy, industrial, and waste management sectors. The chief anthropogenic activities producing N_2O in the United States are agricultural soil management, fuel combustion in motor vehicles, manure management, production of adipic acid (nylon) and nitric acid (HNO_3), wastewater treatment, and stationary fuel combustion. N_2O emissions from these anthropogenic activities in the United States were 468.7 Tg CO_2 equivalent in 2005 (U.S. Environmental Protection Agency, 2007b).

In 2005, N_2O emissions from mobile sources were 38.0 Tg CO_2 equivalents, or ~8% of the U.S. N_2O emissions total (U.S. Environmental Protection Agency, 2007). From 1990 to 2005, N_2O emissions from mobile sources decreased by 13%; however, emissions increased by 10% in the period 1990-1998 due to control technologies that reduced on-road vehicle NO_X emissions at the expense of increasing N_2O emissions. Since 1998, newer controls have led to a steady decline in N_2O from mobile sources.

Biogenic production of N_2O stimulated through soil management accounted for >75% of total U.S. N_2O emissions in 2005 (U.S. Environmental Protection Agency, 2007b). N_2O emissions from this source have shown no significant long-term trend because the biogenic emitters are highly sensitive to the [N] applied to soils, which has been largely constant over this time period (U.S. Environmental Protection Agency, 2007b).

Biogenic N_2O emissions are predominately the result of incomplete bacterial denitrification and nitrification processes that occur in soils, sediments, and water. Denitrification is a reduction process performed by particular groups of heterotrophic bacteria having the ability to use nitrate (NO_3^-) as an electron acceptor during anaerobic respiration, thereby converting NO_3^- in soils and water to gas-phase N forms (Firestone and Davidson, 1989). At low [O_2], these microbial communities may use NO_3^-, nitrite (NO_2^-), or N_2O as alternative electron acceptors to O_2, with molecular N_2 as the final product in this reaction sequence (Davidson and Schimel, 1995).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (3.1\text{-}3)$$

There remains uncertainty about the conditions favoring the various products of the NO_3^- transformations. Groups of aerobic bacteria use most NH_4^+ in soils as an energy source in which it is oxidized to nitrogen dioxide (NO_2) and then to NO_3^-. Oxidized N products of nitrification may undergo denitrification and thus feed the production of N_2O. Some bacteria are shown to be nitrifiers and denitrifiers depending on environmental conditions.

Emissions of NO and N_2O can be increased by agricultural practices and activities, including use of synthetic and organic fertilizers, production of N-fixing crops, cultivation of soils with high organic content, and the application of livestock manure to croplands and pasture.

All of these practices directly add N to soils, of which a portion may then be converted to N_2O on the pathway to full conversion to N_2 as in Reaction 3.1-3. Indirect additions of N to soils can also result in N_2O emissions from agricultural and non-agricultural systems. Indirect additions include processes by which atmospheric NO_X is deposited directly to a region, or N from applied fertilizer or manure volatilizes into NH_3 and NO_X, and then is ultimately re-deposited onto the soil in the form of NH_4NO_3, HNO_3, and NO_X (U.S. Environmental Protection Agency, 2006a).

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

3.2 SO_X EMISSIONS

Emissions of sulfur dioxide ((SO_2), the chief component of SO_X; see the full description in Chapter 2) are due mainly to the combustion of fossil fuels by electrical utilities and other industries; transportation-related sources make only a very minor contribution (see Annex Table AX2-1). As a result, most SO_2 emissions originate from elevated point sources. Since S is a volatile component of fuels, it is released almost quantitatively during combustion; thus, emissions can be calculated on the basis of the S content of fuels to greater accuracy than they can be for other pollutants such as NO_X or primary particulate matter (PM), for example.

SO_2 data collected from the State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) networks show that the decline in SO_2 emissions following controls placed on electric generating utilities in the previous 15 years has improved air quality. There has not been a single monitored exceedance of the SO_2 annual ambient air quality standard in the United States since 2000, according to the EPA Acid Rain Program (ARP) 2005 Progress Report (U.S. Environmental Protection Agency, 2006b). EPA's trends data (www.epa.gov/airtrends) reveal that the national composite average SO_2 annual mean ambient concentration decreased by ~48% from 1990 to 2005, with the largest single-year reduction coming in 1994-1995, the ARP's first operating year (U.S. Environmental Protection Agency, 2006b). Figure 3.2-1 depicts data for SO_2 emissions in the continental United States (CONUS) in these years that reflect this reduction using individual state-level totals.

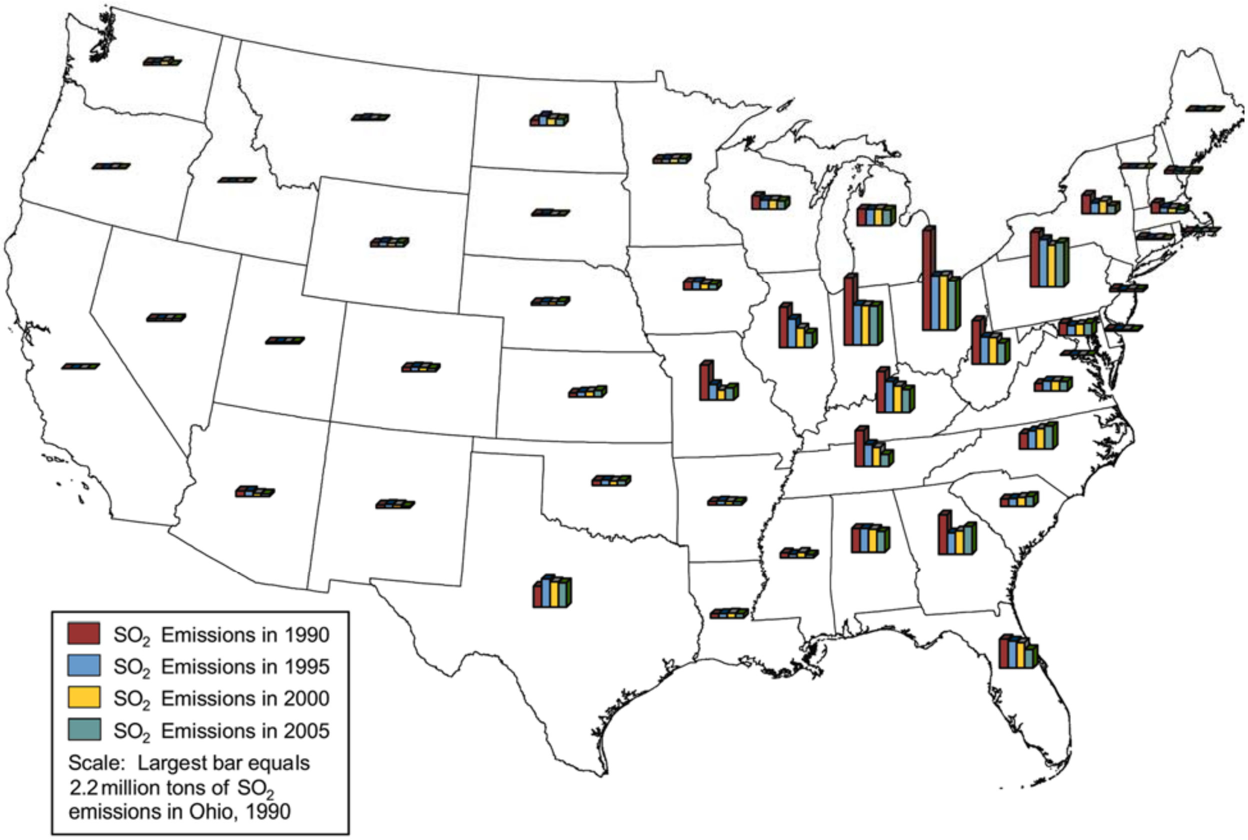


Figure 3.2-1. State-level SO_2 emissions, 1990-2005.

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

These trends in emissions data are consistent with the trends in the observed ambient concentrations from the Clean Air Status and Trends Network (CASTNET). Following implementation of the Phase I controls on ARP sources between 1995 and 2000, significant reductions in $[SO_2]$ and ambient sulfate concentrations ($[SO_4^{2-}]$) were observed at CASTNET sites throughout the eastern United States.

Figure 3.2-2 depicts for the CONUS the magnitude and spatial distribution of SO_2 emissions in 2006 from sources in the ARP. This depiction shows clearly the continuing over-representation of SO_2 sources in the United States east of the Mississippi River as compared to west of it, an over-representation that is strongest in the central Ohio River Valley.

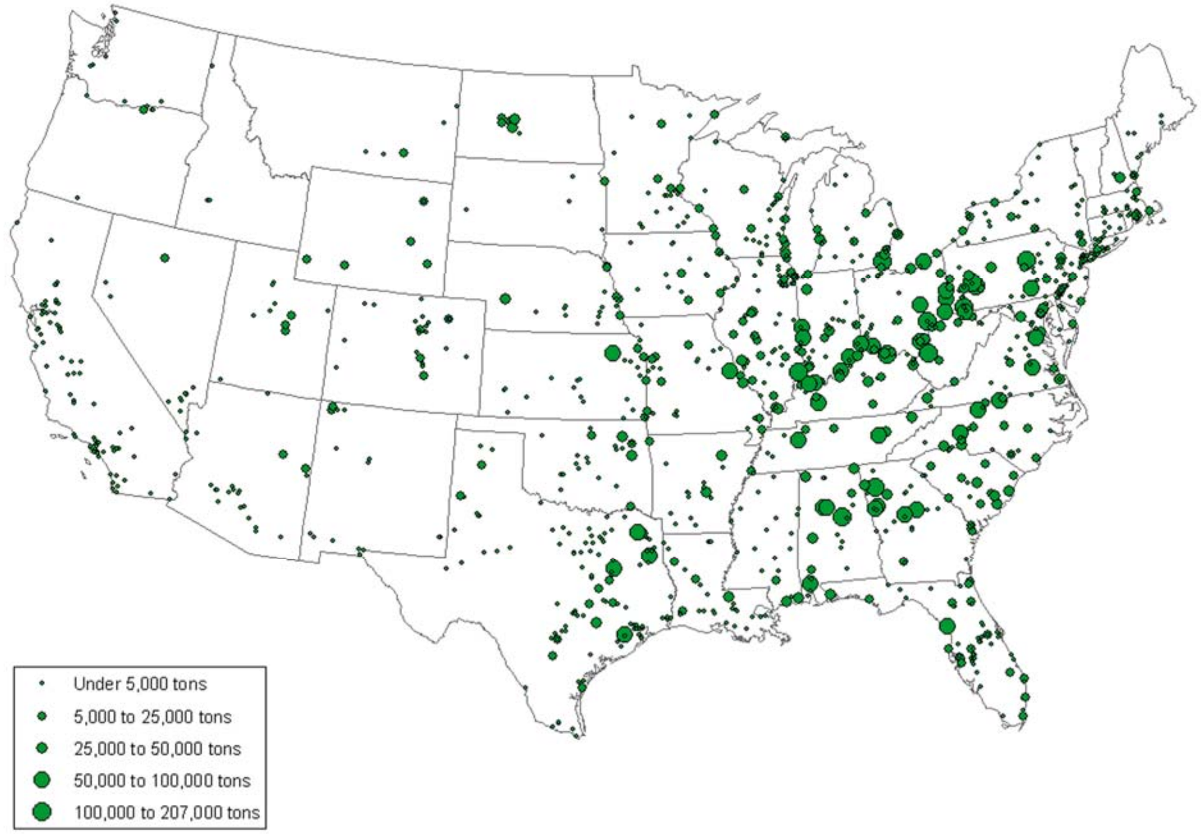


Figure 3.2-2. Annual SO_2 emissions in 2006 for acid rain program cooperating facilities.

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

The major natural sources of SO_2 are volcanoes, biomass burning, and dimethylsulfide (DMS) oxidation over the oceans. SO_2 constitutes a relatively minor fraction (0.005% by volume) of volcanic emissions (Holland, 1978), but the ratio of hydrogen sulfide (H_2S) to SO_2 is highly variable in volcanic gases. Volcanic sources of SO_2 in the United States are limited to the Pacific Northwest, Alaska, and Hawaii.

Emissions of SO_2 from burning vegetation are generally in the range of 1 to 2% of the biomass burned (e.g., Levine et al., 1999). S is bound in amino acids in vegetation and this organically bound S is released during combustion. However, unlike N, approximately one-half of the [S] initially present in vegetation is found in the ash (Delmas, 1982). Gas-phase emissions are mainly in the form of SO_2 with much smaller amounts of H_2S and carbonyl sulfide (OCS). The ratio of gas-phase N to S emissions is ~14, very close to the ratio in plant tissue (Andreae, 1991). The ratio of reduced N and S species such as NH_3 and H_2S to their more oxidized forms, such as NO and SO_2, increases as fire conditions go from the flaming to the smoldering phases of combustion because emissions of reduced species are favored by lower temperatures and reduced O_2 availability.

Emissions of reduced S species are associated typically with marine organisms living either in pelagic or coastal zones and with anaerobic bacteria in marshes and estuaries. Emissions of DMS from marine plankton represent the largest single source of reduced S species to the atmosphere (e.g., Berresheim et al., 1995). Other sources such as wetlands and terrestrial plants and soils probably account for less than 5% of the DMS global flux, with most of this coming from wetlands. The coastal and wetland sources of DMS have a dormant period in fall and winter from senescence of plant growth. Marshes die back in fall and winter, so DMS emissions from them are lower, and reduced light levels in winter at mid-to-high latitudes reduce phytoplankton growth also tending to reduce DMS emissions. Transport of SO_2 from regions of biomass burning seems to be limited by heterogeneous losses that accompany convective processes that ventilate the surface layer and the lower boundary layer (Thornton et al., 1996).

However, it should be noted that reduced S species are also produced anthropogenically. For example, DMS is used in petroleum refining and in petrochemical production processes to control the formation of coke and carbon monoxide (CO), and in steel mills to control dusting, and is used in a range of organic syntheses and as a flavoring component of foods.

3.3 NH_3 EMISSIONS

Anthropogenic emissions of NH_3 show a strikingly different pattern from those of NO_X or SO_2. Three-way catalysts used in motor vehicles emit small amounts of NH_3 as a byproduct during the reduction of NO_X. Stationary combustion sources make only a small contribution to emissions of NH_3 because their efficient combustion favors NO_X formation, and NH_3 from combustion is produced largely by inefficient, low-temperature fuel combustion. For these reasons, most emissions of NH_3 arise from fertilized soils and from livestock.

The initial step in the oxidation of atmospheric NH_3 to NO is reaction with OH radicals. However, the τ of NH_3 from this pathway is sufficiently long (1 to 2 months at typical OH values of 1 to 2×10^6 cm^{-3}) so that it is a small sink compared to the uptake of NH_3 by cloud droplets and aerosols and loss to dry deposition. Thus, gas-phase oxidation of NH_3 makes a very small contribution as a source of NO. Holland et al. (2005) estimated wet and dry deposition of NH_X, based on measurements over the CONUS, and found that emissions of NH_3 in the 1999 National Emissions Inventory (NEI) were underestimated by approximately a factor of 2 or 3. Possible reasons for this error include under-representation of deposition monitoring sites in populated areas and the neglect of offshore transport in the NEI estimate. The use of fixed deposition velocities (V_d) that do not reflect local conditions at the time of measurement introduces additional uncertainty into estimates of dry deposition to which NH_3 is particularly sensitive.

3.4 EVALUATING EMISSIONS INVENTORIES

Comparisons of emissions model predictions with observations have been performed in a number of environments. Studies using ratios of [CO] to [NO_X] and nonmethane organic compounds ([NMOC]) to [NO_X] carried out in the early 1990s in tunnels and ambient air (summarized in Air Quality Criteria for Carbon Monoxide (U.S. Environmental Protection Agency, 2000)) indicated that emissions of CO and NMOC were systematically underestimated in emissions inventories.

Results from some more recent emissions evaluation studies have been mixed, with some studies showing agreement to within ±50% (Trainer et al., 2000; Parrish et al., 1998; Parrish and Fehsenfeld, 2000; U.S. Environmental Protection Agency, 2000). However, Pokharel et al. (2002) employed remotely sensed emissions from on-road vehicles and fuel use data to estimate emissions in Denver, and their calculations indicate a continual decrease in CO, hydrocarbon (HC), and NO emissions from mobile sources over the 6-year study period, 1996 through 2001. Inventories based on the ambient data were 30 to 70% lower for CO, 40% higher for HC, and 40 to 80% lower for NO than those predicted by the MOBILE6 on-road mobile source emissions model.

Measurements at two urban areas in the United States confirmed the decrease in CO emissions (Parrish et al., 2002). That study also indicated that the ratio of CO to NO_X emissions decreased by almost a factor of 3 over 12 years. EPA NEI emissions estimates indicated a much smaller decrease in this ratio, suggesting that NO_X emissions from mobile sources may be either underestimated and/or increasing.

3.5 ECOLOGICAL SINKS

Several reactive N species are deposited to vegetation, among them, HNO_3, NO_2, peroxyacyl nitrates (PAN and its higher analogs), and other organic nitrates ($RONO_2$).

3.5.1 HNO_3

Field observations based on concentration gradients of HNO_3 and using eddy covariance techniques demonstrate rapid deposition that approaches the aerodynamic limit (as constrained by atmospheric turbulence) in the Wesely (1989) formulation based on analogy to resistance. Surface resistance to HNO_3 uptake by vegetation is negligible. Deposition rates are independent of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the leaf cuticle as well as leaf surfaces. The HNO_3 V_d typically exceeds 1 cm s^{-1} and exhibits a diel pattern controlled by turbulence characteristics of midday maxima and lower values at night in the more-stable boundary layer.

3.5.2 NO_2

NO_2 interaction with vegetation is more complex than that for HNO_3 in part because very fast measurements of NO_2 flux are confounded by the rapid interconversion of NO, NO_2, and O_3 (Gao et al., 1991). Application of ^{15}N-labeled NO_2 demonstrates that NO_2 is absorbed and metabolized by foliage (Siegwolf et al., 2001; Mocker et al., 1998; Segschneider et al., 1995; Weber et al., 1995). Exposure to NO_2 induces activation of nitrate reductase (Weber et al., 1995, 1998), a necessary enzyme for assimilating oxidized N. Understanding of NO_2 interactions with foliage is largely based on leaf cuvette and growth chamber studies which expose foliage or whole plants to controlled [NO_2] and measure the fraction of NO_2 removed from the chamber air. A key finding is that the fit of NO_2 flux to [NO_2], has a non-0 intercept, implying a compensation point or internal concentration. In studies at very low [NO_2], emission from foliage is observed (Teklemariam and Sparks, 2006). Evidence for a compensation point is not solely based on the fitted intercept. The NO_2 uptake rate to foliage is clearly related to stomatal conductance. Internal resistance is variable, and may be associated with concentrations of reactive species such as ascorbate in the plant tissue that react with NO_2 (Teklemariam and Sparks, 2006). Foliar NO_2 emissions show some dependence on N content (Teklemariam and Sparks, 2006). Internal NO_2 appears to derive from plant N metabolism.

Two approaches to modeling NO_2 uptake by vegetation are the resistance-in-series analogy which considers flux (F) as the product of concentration (C) and V_d, related to the sum of aerodynamic, boundary layer, and internal resistances (R_a, R_b, and R_c, respectively); positive fluxes are from atmosphere to foliage

$$F = CV_d \tag{3.5-1}$$

$$V_d = (R_a + R_b + R_c)^{-1} \tag{3.5-2}$$

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

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

$$J = g_s(C_a - C_i) \tag{3.5-3}$$

This model implicitly associates the compensation point with a finite internal concentration. Typically observed compensation points are ~1 ppb; values of internal $[NO_2]$ are consistent with metabolic pathways that include NO_X. In this formulation, the uptake will be linear with $[NO_2]$, which is typically measured in foliar chamber studies.

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

$$J = g_s(C_a - C_i) = J_s(UV) \tag{3.5-4}$$

3.5.3 PAN

PAN is phytotoxic and absorbed at the leaf. Observations based on inference from concentration gradients and rates of loss at night (Shepson et al., 1992; Schrmipf et al., 1996) and from leaf chamber studies (Teklemariam and Sparks, 2004) have indicated that uptake of PAN is slower than that of O_3; however, recent work in coniferous canopies with direct eddy covariance PAN flux measurements indicated a V_d more similar to that of O_3. Uptake of PAN is under stomatal control, has non-0 deposition at night, and is influenced by leaf wetness (Turnipseed et al., 2006). On the other hand, flux measurements determined by gradient methods over a grass surface showed a V_d closer to 0.1 cm s^{-1}, with uncertainty on the order of a factor of 10 (Doskey et al., 2004). Whether the discrepancies are methodological or indicate intrinsic differences between different vegetation is unknown. Uptake of PAN is smaller than its thermal decomposition in all cases.

3.5.4 Other $RONO_2$

The biosphere also interacts with NO_X through HC emissions and their subsequent reactions to form multi-functional $RONO_2$. Formation of the hydroxyalkyl nitrates occurs after OH attack on VOCs. In one sense, this mechanism is simply an alternate pathway for OH to react with NO_X to form a rapidly depositing species. If VOC were not present, OH would be available to react with NO_2 when it is present to form HNO_3.

Isoprene nitrates are an important class of $RONO_2$. Isoprene reacts with OH to form a radical that adds NO_2 to form the hydroxyalkyl nitrate. The combination of hydroxyl and nitrate functional group makes these compounds especially soluble with low vapor pressures, so they likely deposit rapidly (Shepson et al., 1996; Treves et al., 2000). Many other unsaturated HCs react by analogous routes. Observations at Harvard Forest show a substantial fraction of the total of all gas-phase forms of oxidized N (category label is NO_Y) not accounted for by NO, NO_2 and PAN, which is attributed to the $RONO_2$ (Horii et al., 2006; Munger et al., 1998). Furthermore, the total NO_Y flux exceeds the sum of HNO_3, NO_X, and PAN, which implies that the $RONO_2$ are a substantial fraction of the total N deposition. Other observations showing evidence of hydoxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

3.5.5 HNO_2

HNO_2 formation on vegetative surfaces at night has long been observed based on measurements of positive gradients (Harrison and Kitto, 1994). Surface reactions of NO_2 enhanced by moisture were proposed to explain these results. Production was evident at sites with high ambient NO_2; at low concentration, uptake of HNO_2 exceeded the source. Daytime observations of HNO_2 when rapid photolysis is expected to deplete ambient concentrations to very low levels implies a substantial source of photo-induced HNO_2 formation at a variety of forested sites where measurements have been made. Estimated source strengths are 200 to 1800 parts per trillion (ppt) h^{-1} in the surface layer (Zhou et al., 2002a, 2003), which is ~20 times faster than all nighttime sources.

3.6 MONITORING NETWORKS

This section provides an inventory of current environmental observation systems focused mostly on routine ambient air quality networks with emphasis on N and S species; this description also includes PM because of its significant role in N and S deposition; see Chapter 2 for more details.

Observational systems supporting air quality and related assessments include routine regulatory networks, routine deposition monitoring networks, intensive field studies, remote sensing systems, sondes, aircraft campaigns, satellites, and focused, fixed-site special purpose networks. Major networks currently operating are emphasized here; discussion of other networks discontinued or intended for a specific operating period is provided in Annex 2. The focus here is on operating North American air quality networks with limited coverage of European and international efforts except as relevant to North American assessments.

3.6.1 Routine Regulatory Air Monitoring Networks in North America

3.6.1.1 Gas- and Particle-Phase Networks and Sites

Routine ambient air and deposition monitoring networks in North America provide more than 3000 fixed platforms measuring numerous gaseous species and aerosol properties; see Annex Table AX2.5-1 for a listing. Many of these long-standing network systems were initialized after the 1970 Clean Air Act (CAA), subsequent CAA amendments, National Ambient

Air Quality Standards (NAAQS) reviews and National Academy of Sciences (NAS) recommendations resulting in periodic step enhancements to these routine networks. Examples include CASTNET and the National Atmospheric Deposition Program (NADP) addressing acidification; the Photochemical Assessment Monitoring Stations (PAMS) in response to persistent O_3 pollution and to monitor O_3 precursors including NO_X; and the particulate matter ≤2.5 µm ($PM_{2.5}$) network to monitor aerosol- and solid-phase pollutants that can act in concert with NO_X and SO_X. Annex Table AX2.5-1 lists the networks, sponsoring agencies, site densities, dates of operation, locations, and measurement parameters.

The relatively wide geographic distribution and persistence of exceedances of the O_3 and PM NAAQS (see Figure 3.6-1) have led to these pollutants dominating the national monitoring networks. These sites remain relevant for characterizing ambient concentrations and deposition of NO_X and SO_X because those species are often measured at the same locations and because of the role of NO_X in the formation and destruction of O_3, and because of PM's role in NO_X and SO_X deposition. Additional details about the homogeneous- and heterogeneous-phase atmospheric chemistry of NO_X and SO_X are given in Chapter 2 and in Annex 1.

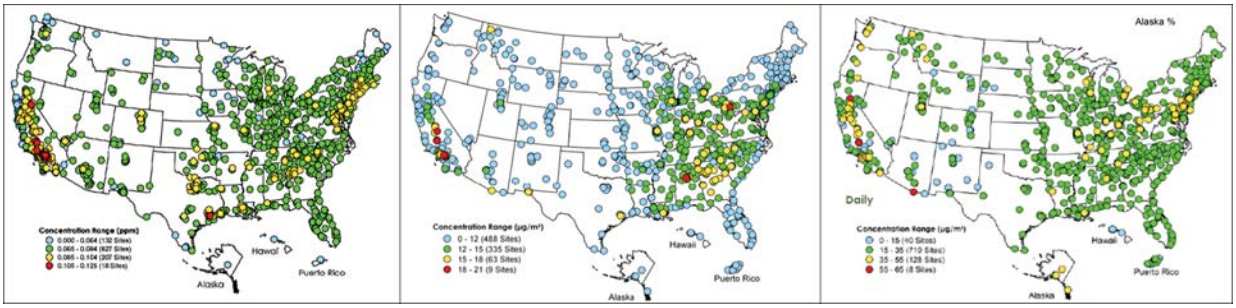


Figure 3.6-1. 2006 air quality summaries for O_3, annual average $PM_{2.5}$, and daily $PM_{2.5}$. Yellow and red sites indicate values exceeding NAAQS levels.

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

Networks with more direct relevance to ecological effects include the Interagency Monitoring of Protected Visual Environments (IMPROVE) network with more than 100 sites in U.S. National Parks and other remote locations; see Figure 3.6-2. The IMPROVE network is intended primarily to assess visibility impairment but has provided a reliable long-term record

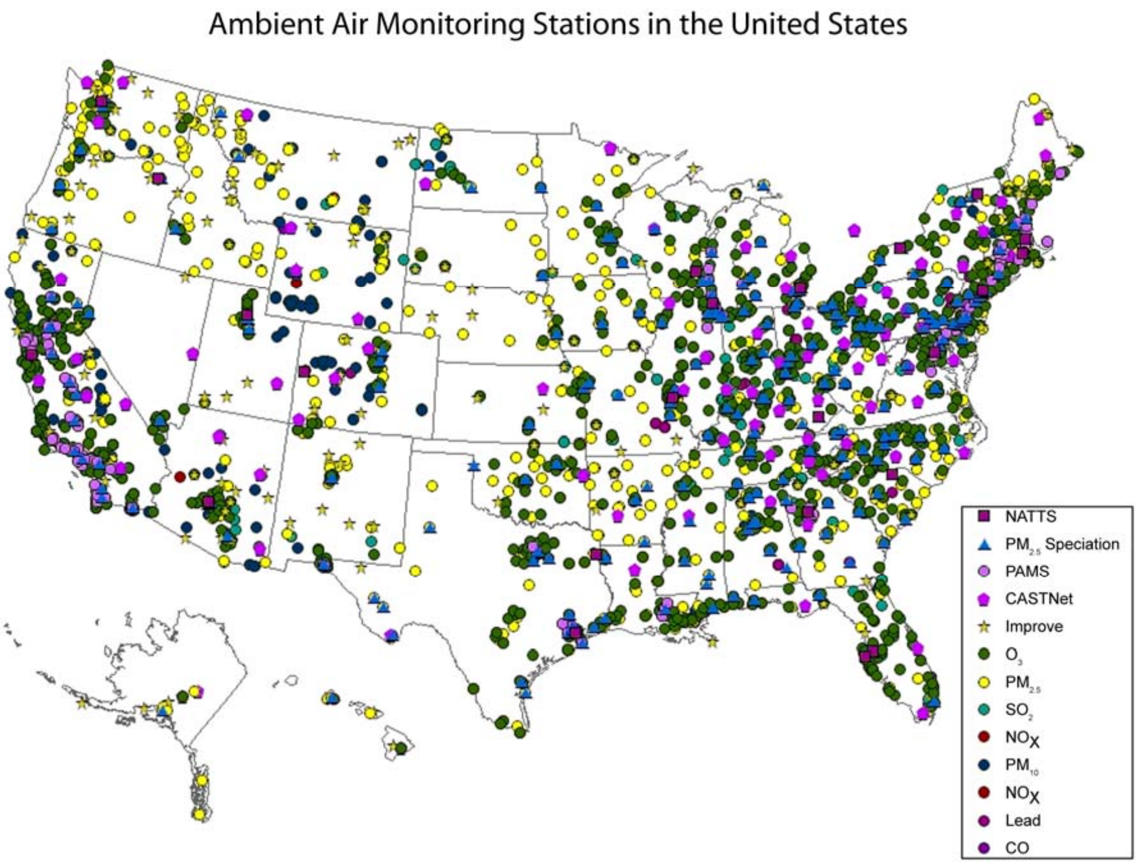


Figure 3.6-2. Aggregate map of the majority routine U.S. monitoring stations.

of PM mass and major speciation components; in addition, data from IMPROVE has been useful for testing data from the EPA Speciation Trends Network (STN) (see Figure 3.6-2), which has provided an urban complement to characterize aerosol composition; see Figure 3.6-3 and the additional details in Annex 2.

The CASTNET also shown in Figure 3.6-2 was established in the early 1990s to track changes in the dry deposition of major inorganic ions and gas-phase precursors associated with the CAA Title 4 reductions in S and N, which were designed to address surface water acidification in eastern North America.

Additional, minor networks identified in Figure 3.6-2 include those of the state and local air agencies deployed since the mid-1980s measuring a variety of aerosol-phase, solid-phase, metallic, and gas-phase hazardous air pollutants (HAPs) at ~200 locations; and a modest National Air Toxics Trends (NATTS) network of 23 sites.

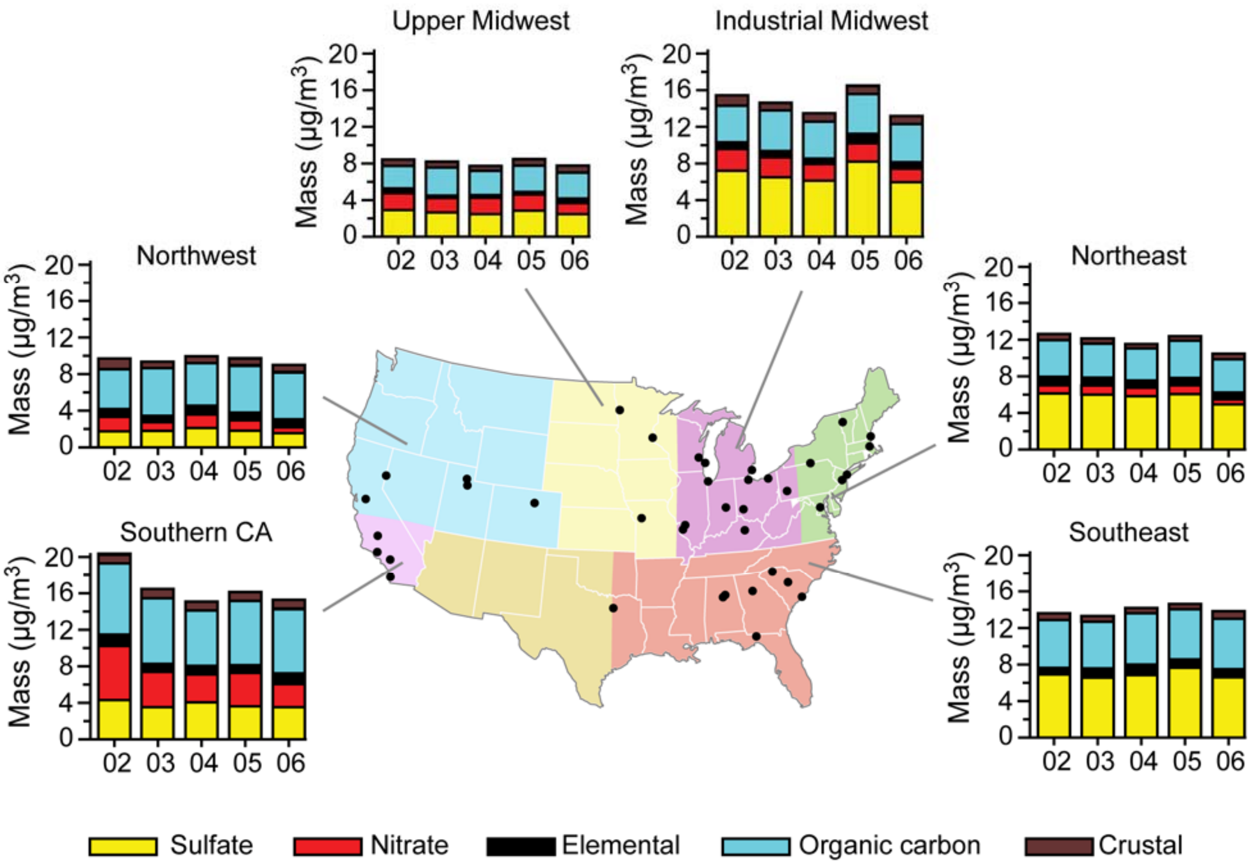


Figure 3.6-3. Regional chemical composition of $PM_{2.5}$ aerosols based on urban speciation sites and averaged over the entire 2006 sampling period.

Source: http://www.epa.gov/air/airtrends/index.html.

A new multipollutant monitoring network, the National Core Monitoring Network (NCore), was incorporated in the 2006 revisions to the PM standards (http://www.epa.gov/air/airtrends/index.html). When fully implemented in 2009, NCore will provide a minimum of 75 "Level 2" sites (see Figure 3.6-4) in most major urban areas and in the important transportation corridors and at background locations.

Nearly 1500 sites were established in the years from 1997 to 2001 to determine $PM_{2.5}$ mass gravimetrically. The network has evolved to add more than 500 continuous $PM_{2.5}$ monitors, with a reduction of the 24-h gravimetric samplers to fewer than 1000 sites; see Figure 3.6-5. While this expansion of continuous $PM_{2.5}$ sites adds spatial coverage of data with a high temporal resolution, the mix of instrument types and protocols can compromise data

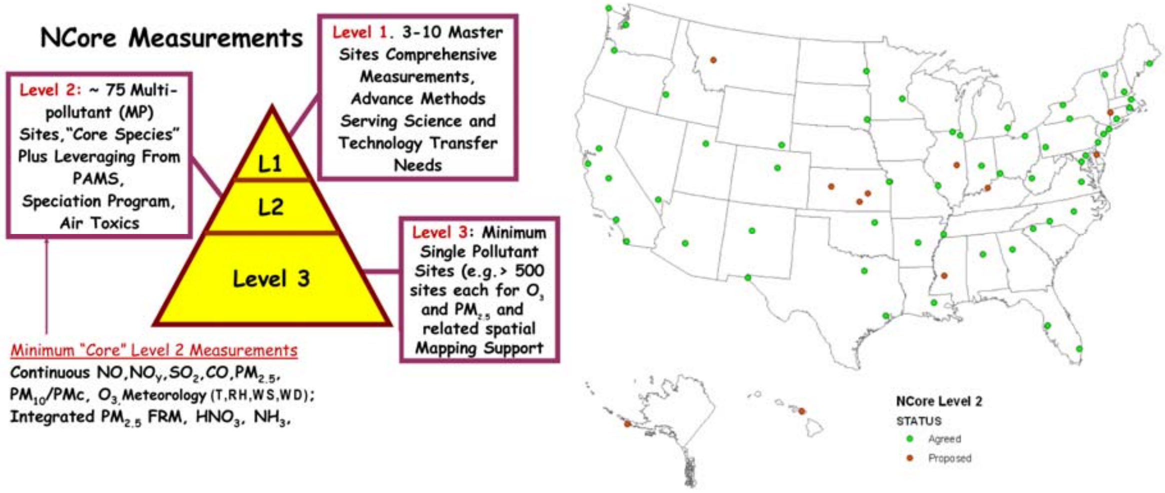


Figure 3.6-4. Planned 3-tiered NCore design (left) and proposed site locations for Level 2 multiple pollutant sites.

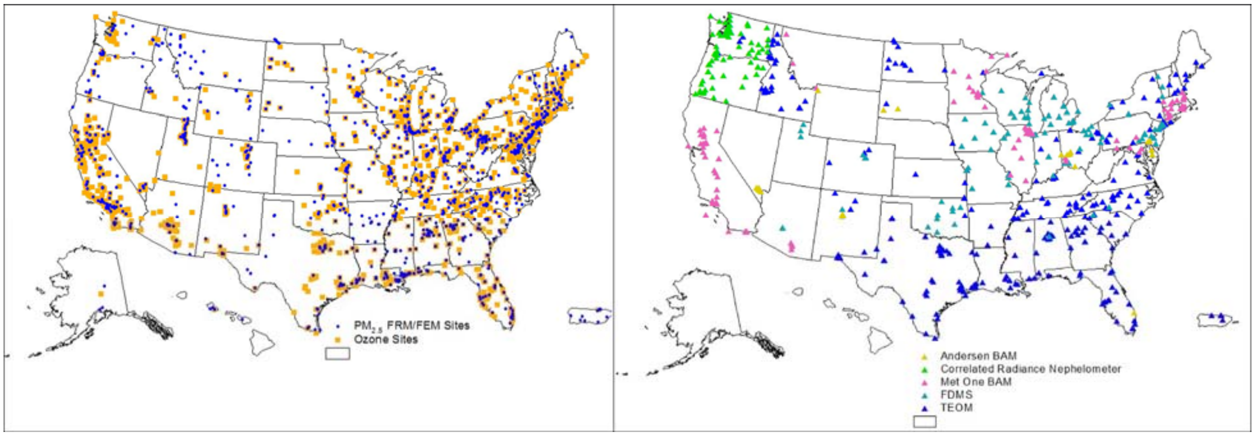


Figure 3.6-5. Maps illustrating breadth of $PM_{2.5}$ FRM and FEM and O_3 networks (left); and $PM_{2.5}$ continuous samplers (right).

comparison across sites and geographic areas with different operational characteristics. In recognition of potential geographic differences, EPA has developed monitoring policy (U.S. Environmental Protection Agency, 2006b) for regionally approved methods to lead to equivalency status (Federal Equivalent Method, (FEM)) from the Federal Reference Method (FRM) for the continuous $PM_{2.5}$ samplers and compliance applications.

The IMPROVE network has provided a nearly 20-year record of the chief components (SO_4^{2-}, NO_3^-, organic and elemental carbon fractions (OC and EC, respectively) and trace metals) of $PM_{2.5}$ aerosols mostly in pristine areas of the United States in and around National Parks. More than 300 additional speciation sites were added between 2000 and 2002 in urban areas of the United States to assist assessment efforts related to the $PM_{2.5}$ NAAQS. This total cross-network coverage (see Figure 3.6-6) is now a widely used resource across disciplines from exposure and epidemiology and atmospheric sciences over spatial scales of interest ranging from long-range hemispheric transport to near-source analysis.

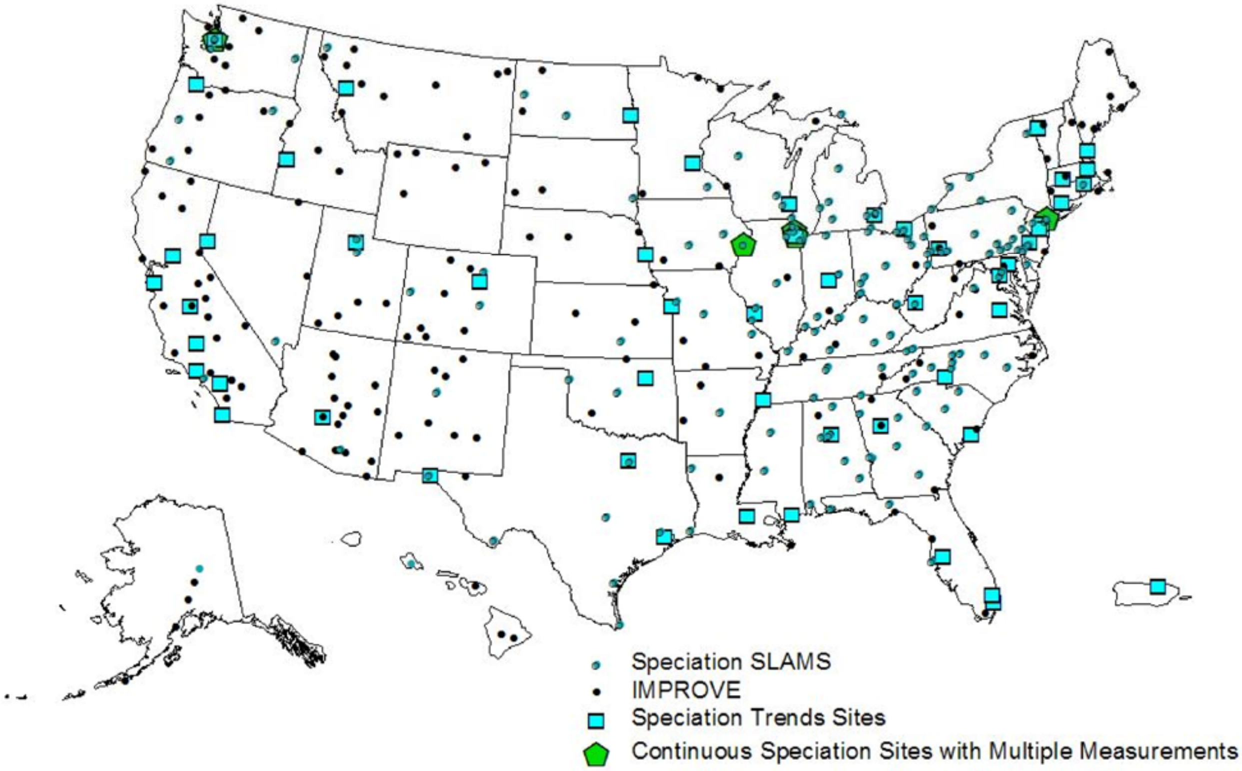


Figure 3.6-6. Locations of chemical speciation sites delineated by program type.

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

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

3.6.1.2 Precipitation-based Networks and Sites

Precipitation chemistry is the primary link between atmospheric and terrestrial and aquatic systems. The NADP (http://nadp.sws.uiuc.edu/) oversees a network of more than 250 sites (see Figure 3.6-7) where most of the major ions key to aquatic chemistry addressing acidification and eutrophication effects are measured. The NADP includes the Mercury Deposition Network (MDN) of ~90 sites and 7 Atmospheric Integrated Research Monitoring Network (AIRMoN) sites providing greater temporal resolution.

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

3.6.3 Intensive Field Campaigns

Intensive field campaigns of relatively short duration supplement these routine longer-term monitoring networks by enhancing spatial, temporal, and compositional distribution of atmospheric species to better elucidate physical and chemical processes relevant to the fate, transport, and removal of secondarily formed gases and aerosols. Typically, these campaigns

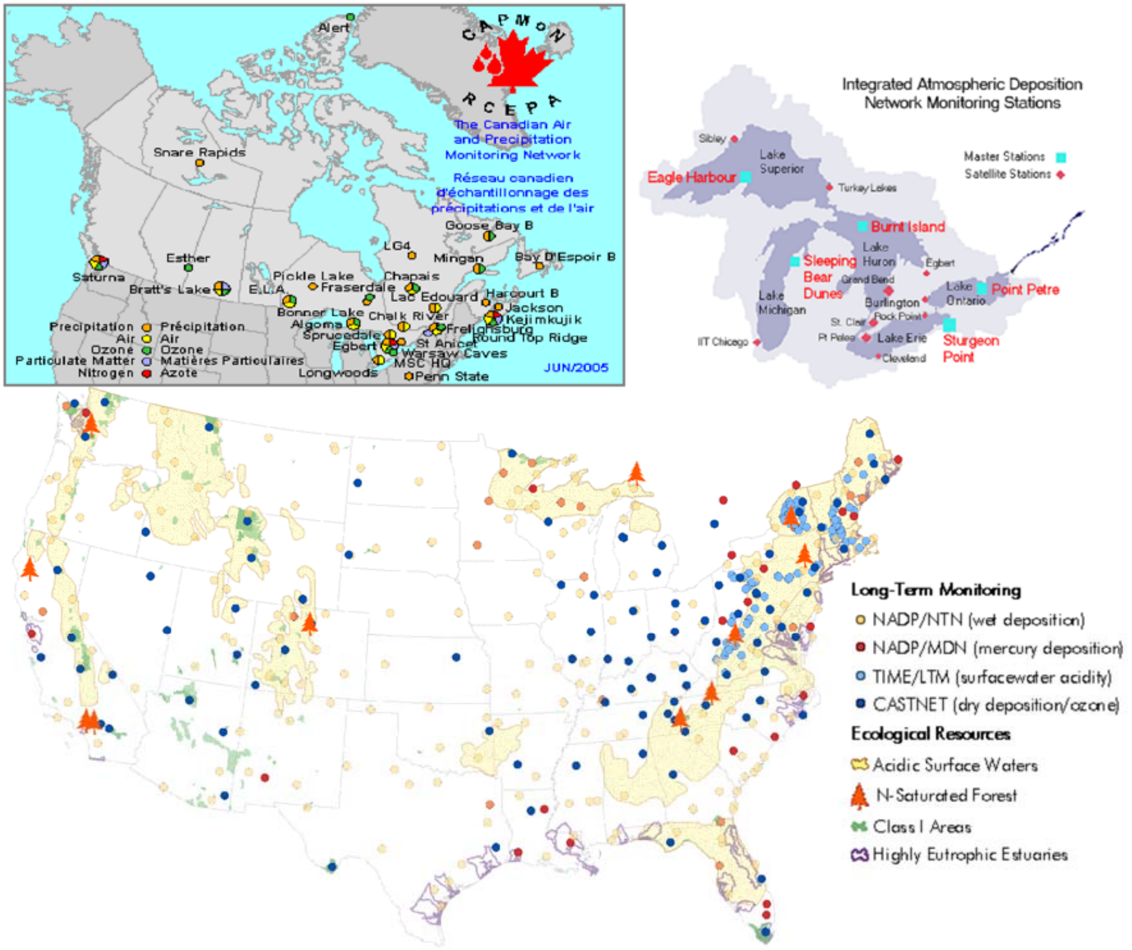


Figure 3.6-7. Routinely operating North American precipitation and surface water networks: Upper left, Canadian Air and Precipitation Monitoring Network (CAPMoN); upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); bottom, National Atmospheric Deposition Monitoring Program (NADP) with TIME/LTM surface chemistry sites.

use some combination of aircraft studies, high time-resolved instrumentation, and advanced in-situ and laboratory analytical methods, all complementing routine ground-based measurements. More description of recent campaigns and their measurements is included in Annex 2.

3.6.4 Satellite–Based Air Quality Observing Systems

An extensive array of satellite-based systems (see Annex Tables AX2.5-2 and AX2.5-3) with the capability of measuring species in the total atmospheric column has been established by the United States and European satellite programs lead by the National Aeronautic and Space

Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) in the United States and the European Space Agency (ESA). A suite of satellites including Aqua, Aura, CALIPSO, OCO, Glory, as well as NOAA-17, NOAA-18, and NPOESS, have either been launched since roughly 2000 or have near-term proposed launch dates. Collectively, the remote sensing techniques for measuring total atmospheric columns and/or profiles exist for aerosol optical depth (AOD), O_3, carbon monoxide (CO), formaldehyde (HCHO), carbon dioxide (CO_2), CH_4, SO_2, NO_2, and chlorinated fluorocarbons (CFCs) among other pollutants, and for such atmospheric parameters as temperature and total H_2O content. Satellites with a near-polar orbit can make two passes each day over a given location. When taken together, a group of six satellites (Aqua, Aura, CALIPSO, OCO, as well as CloudSat and PARASOL; category label is "A-Train") is being configured to fly in a formation that crosses the equator a few minutes apart at around 1330 local time to give a comprehensive picture of Earth's weather, climate, and atmospheric conditions.

Satellite imagery offers the potential to cover broad spatial areas; however, an understanding of the spatial, temporal and measurement limitations of satellite data is necessary to determine how these systems complement ground-based networks and can support air quality assessments. Extensive details on individual satellite data streams and coverage is included in Annex 2.

3.6.5 Monitoring Networks in Europe

Extensive air monitoring networks have also been implemented in Europe, many served by centralized organization structures linked to international efforts like the Convention on Long Range Transport of Air Pollution ((LRTAP); http://www.unece.org/env/lrtap/) and the underlying technical assessment body, the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). The Global Atmospheric Watch program ((GAW); http://www.wmo.int) under the World Meteorological Organization (WMO) provides quality assurance guidelines and data to an important body of air quality measurements relevant to assessing intercontinental pollution transport and climate forcing phenomena. The Norwegian Institute for Air Research ((NILU), http://www.nilu.no), maintains a database for many of the European based networks. Annex Table AX2.5-5 includes combined contributions from several European countries ranging from a few sites to tens of sites in a country, some with data records extending more than 30 years. Measurements for a variety of air pollutants are addressed including O_3, metals, persistent organic pollutants (POPs), PM, VOCs, and acidifying and eutrophying N and S compounds.

3.7 AMBIENT CONCENTRATIONS

3.7.1 NO_X and NO_Y

Figure 3.7-1 shows ambient [NO_2] measured at all monitoring sites located within Metropolitan Statistical Areas (MSAs) in the United States from 2003 through 2005. Mean [NO_2] are ~15 ppb for averaging periods ranging from a day to a year, with an interquartile range (IQR) of 10 to 15 ppb. However, the average daily maximum 1-h [NO_2] are ~30 ppb, roughly a factor of 2 greater than the 24-h averages. The single highest maximum 1-h concentration of ~200 ppb in this period (measured at one monitor in southern California) was more than a factor of 10 greater than the mean 1-h or 24-h concentrations.

Data for concentrations of other oxidized N species in urban areas in the United States are sparse. The most comprehensive set of data was obtained for HNO_3, for example, as part of the Children's Health Study for which gas-phase HNO_3 was measured at 12 sites in Southern California from 1994 through 2001 (Alcorn and Lurmann, 2004). Levels ranged from <1 ppb to >10 ppb. In general, the highest [HNO_3] and the highest ratio of [HNO_3]-to-[NO_2] were found downwind of central Los Angeles in the San Bernardino Valley during summer, as one would expect for this more-oxidized N product.

Measurements of HNO_2 in urban areas are still very limited; however, data from Stutz et al. (2004) indicate that [HNO_2] are <1 ppb even under heavily polluted conditions, with the highest levels at night and just after dawn and lowest values in the afternoon because of rapid photolysis; see the fuller descriptions in Chapter 2. Several field studies such as Hayden et al. (2003) in rural Quebec, Williams et al. (1987) near Boulder, CO, and Singh et al. (2007) in aircraft flights over eastern North America have also found much higher levels of HNO_3 and of other, further oxidized N compounds in relatively unpolluted rural air.

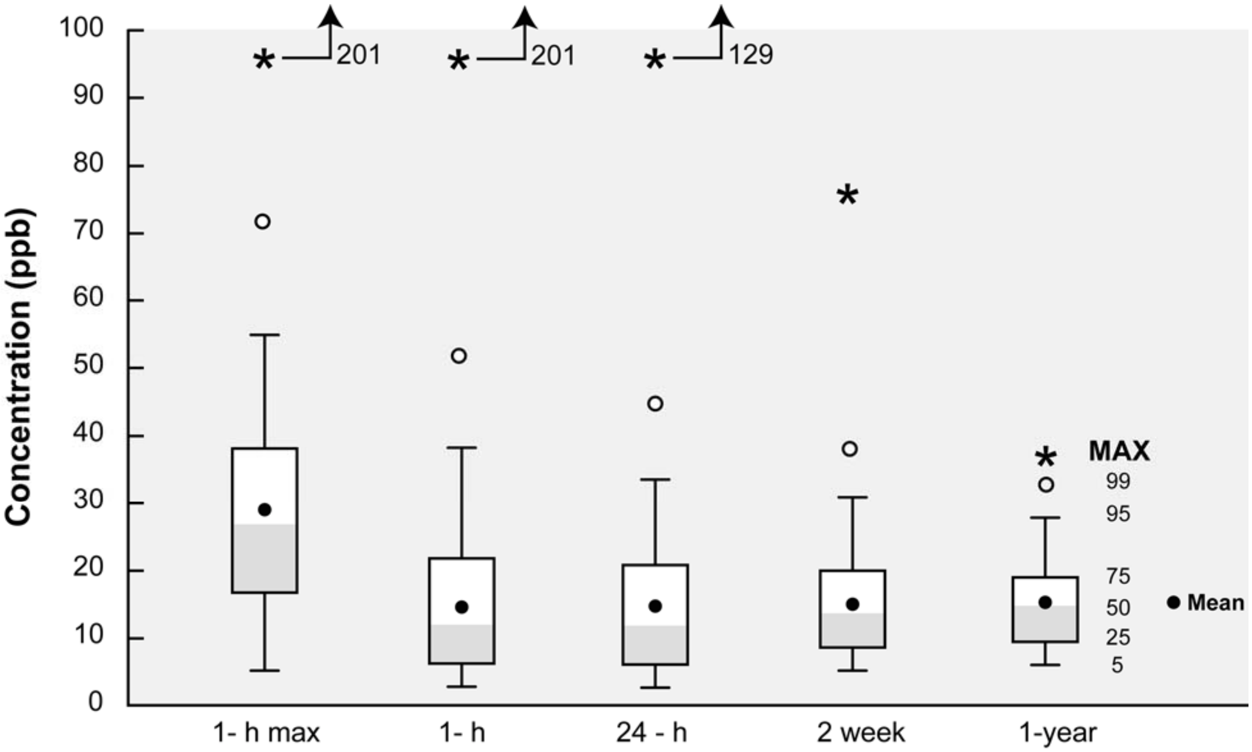


Figure 3.7-1. Ambient concentrations of NO_2 measured at all monitoring sites located within Metropolitan Statistical Areas in the United States from 2003 through 2005.

Calculations with EPA's Community Multiscale Air Quality (CMAQ) modeling system for the Mid-Atlantic region in a domain from Virginia to southern New Jersey showed that the highest [HNO_3] and [$RONO_2$] occur during mid-afternoon, consistent with their formation by photochemical processes also producing O_3. Model simulations of an O_3 episode in July 2002 made for the Maryland State O_3 Implementation Plan (SIP) showed episode averages of the ratio of the further-oxidized N species like HNO_3 to NO_2 ranging from 0.26 to 3.6 in rural Virginia, with the highest ratios in rural areas and lowest ratios in urban centers nearer the sources of fresh NO_X emissions.

3.7.2 SO_X

The mean annual [SO_2] and [SO_4^{2-}] from CASTNET's long-term monitoring sites can be compared using two 3-year periods (1989 through 1991, and 2003 through 2005) shown in Figure 3.7-2 for SO_2, and Figure 3.7-3 for SO_4^{2-}.

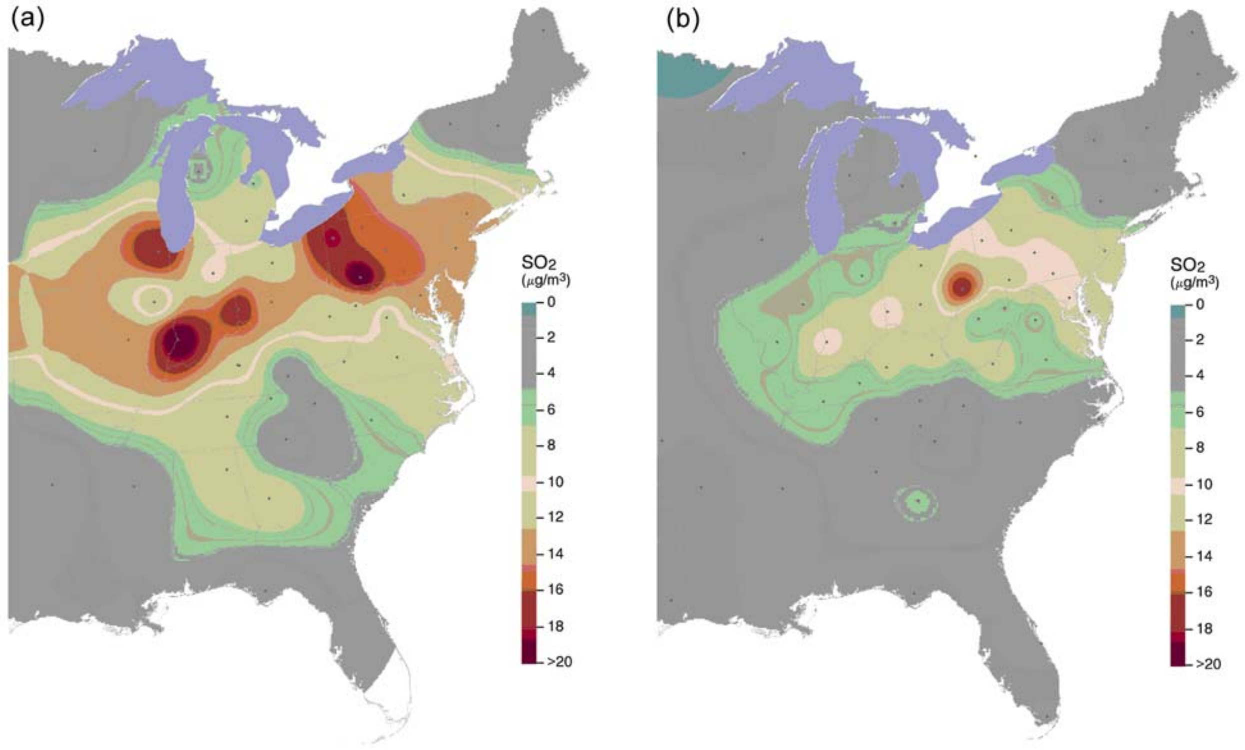


Figure 3.7-2. Annual mean ambient SO_2 concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

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

Source: U.S. Environmental Protection Agency, CASTNET (www.epa.gov/castnet/).

From 1989 through 1991, that is, in the years prior to implementation of the ARP Phase I controls on S emissions, the highest ambient mean [SO_2] and [SO_4^{2-}] were observed in western Pennsylvania and along the Ohio River Valley: >20 µg m^{-3} (~8 ppb) SO_2 and >15 µg m^{-3} SO_4^{2-}. As with SO_2, in the years since the ARP controls were enacted, both the magnitude of [SO_4^{2-}] and their areal extent have been significantly reduced, with the largest decreases again coming along the Ohio River Valley.

SO_2 concentrations have been falling throughout all regions of the United States as demonstrated by the CASTNET data depicted in Figure 3.7-2. In and around most individual CMSAs, the trends are also toward lower [SO_2]. Many annual and even 1-h mean concentrations for the years 2003 through 2005 were consistently at or below the operating LOD of ~3 ppb for the standard SO_2 monitor deployed in the networks, while the aggregate mean value over all

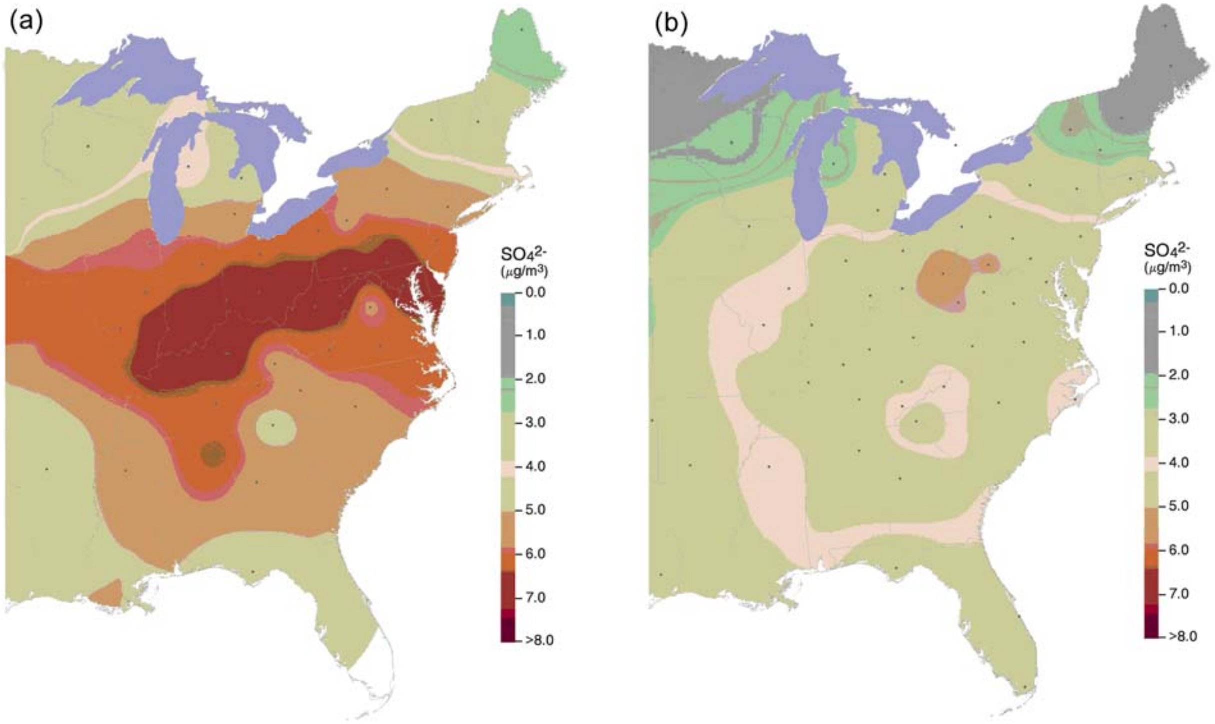


Figure 3.7-3. Annual mean ambient SO_4^{2-} Concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

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

Source: U.S. Environmental Protection Agency, CASTNET (www.epa.gov/castnet/).

3 years and all sites in and around the CMSAs was just above the LOD at ~4 ppb, and identical to the 1-h and 24-h means; see Annex 2 for fuller descriptions.

Figure 3.7-4 shows the composite diel variation in hourly [SO_2] from all monitors reporting data to the Air Quality System (AQS) database. (The AQS contains measurements of air pollutant concentrations in the 50 states, plus the District of Columbia, Puerto Rico, and the Virgin Islands for the six criteria air pollutants (SO_2, NO_2, PM, CO, Pb, O_3) and some hazardous air pollutants.) As can be seen from Figure 3.7-4, concentrations beneath the 95th percentile level are indistinguishable from each other, but are typically in the range of a few ppb. However, the peaks in the distribution at any hour of the day can be a factor of 10 or more higher than values in the bulk of the distribution. Overall, there is some indication that the highest values are reached either at midday or during the middle of the night. Daytime peaks could result from

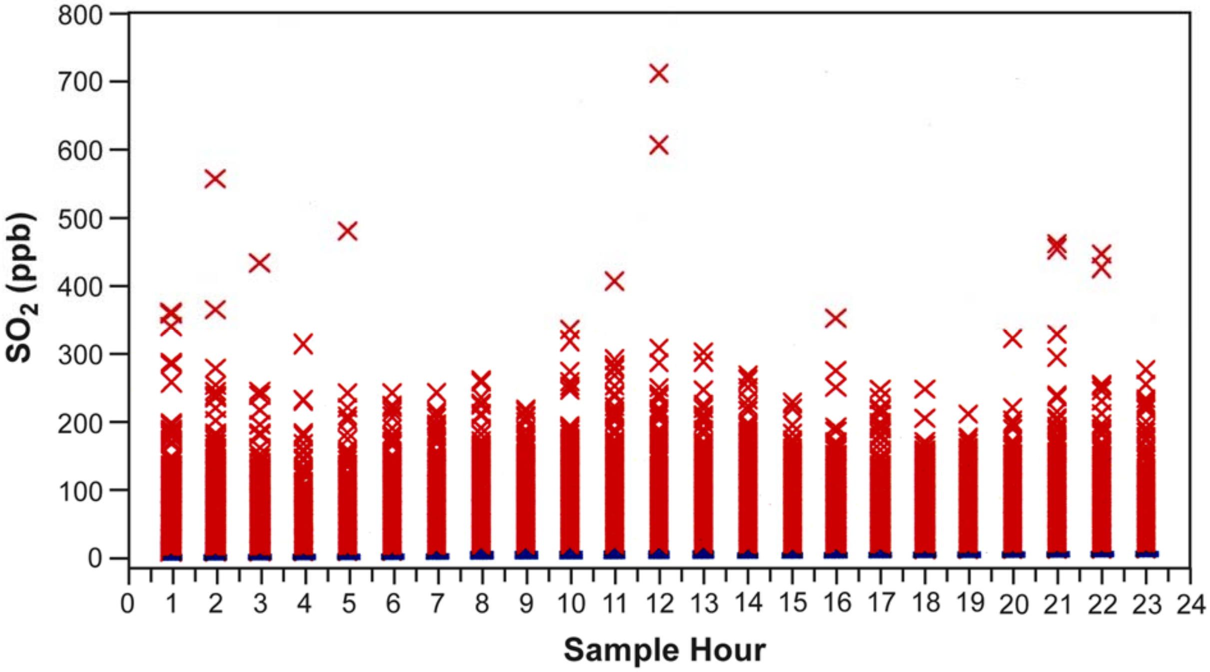


Figure 3.7-4. Boxplot of hourly SO_2 concentrations across all cities in focus.

down-mixing of air aloft due to convective activity since SO_2 is emitted mainly by elevated sources. Nighttime peaks are more likely due to trapping of local emissions beneath a shallow stable nocturnal boundary layer.

To be sure, the maximum 1-h concentration observed at some sites in and around some CMSAs did still exceed the mean by a large margin, with maximum 1-h values of >600 ppb. However, the 50th percentile maximum value outside CMSAs, 5 ppb, was only slightly greater than the 1-h, 24-h, and annual mean values of 4 ppb. The 50th percentile maximum value inside CMSAs, 7 ppb, was 75% greater than these longer-term averages, reflecting heterogeneity in source strength and monitor location. In addition, even with 1-h maximum values of >600 ppb, the maximum annualized mean value for all CMSAs was still <16 ppb, and, hence, below the current annual primary SO_2 NAAQS.

3.8 NITROGEN AND SULFUR DEPOSITION ACROSS THE LANDSCAPE

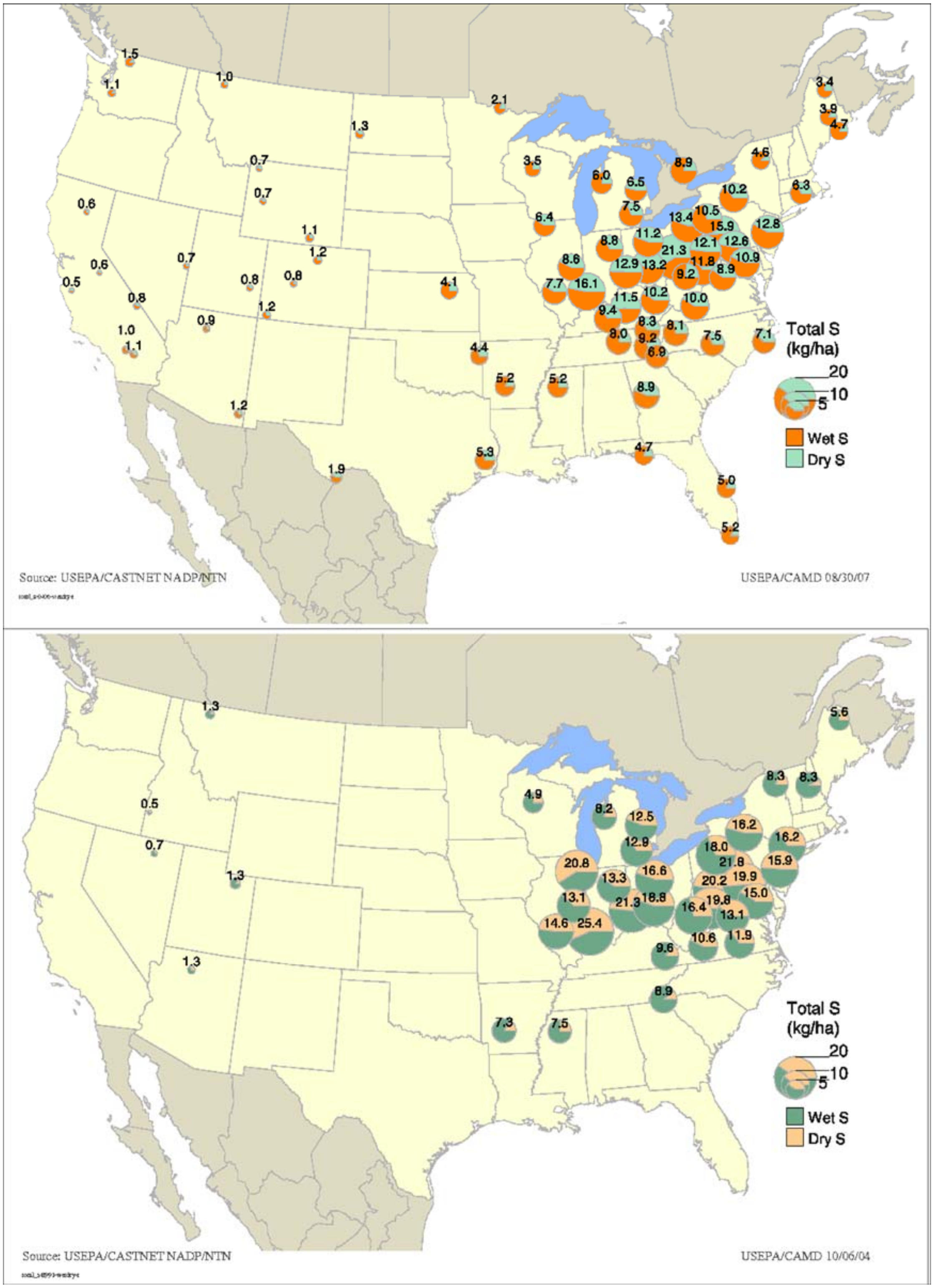
Emissions of SO_X and NO_X have decreased substantially in the last 35 years (see Annex Table AX2-1). From 1970 until 2005, NO_X emissions were down from 26.9 million tons per year (Mt yr^{-1}) to 19 Mt yr^{-1} and SO_2 emissions were down from 31.2 to 15 Mt yr^{-1}. These decreases in emissions have led to correlative decreases in N and S atmospheric deposition across the landscape.

Deposition maps were developed by CASTNET to show the composition of total deposition for N and S (See Figures 3.8-1 through 3.8-4). The maps are labeled with estimated total deposition at each site and a pie chart showing the relative proportion of wet and dry deposition or the chemical components of the deposition at the site. Wet deposition is estimated from the interpolated concentration as measured by NADP multiplied by the measured rainfall at the site. Dry deposition is estimated from the measured ambient air concentrations of the chemical multiplied by the V_d obtained from an inferential model of linked resistances; see the CASTNET quality control plans for more information on methods. It is important to recognize that NH_3 is not included in these total N estimates because it is not at present measured in these networks, even though it is a major component of total N in some areas.

Data in this section are presented to show deposition across the landscape; finer-scale data and maps of sensitive and vulnerable regions and ecosystems are presented in other sections and with discussion of effects in Chapter 4. Data presented in the maps and charts represent 3-year averages. For example, “89-91” is the average total deposition of 1989, 1990, and 1991 for a given site. Only sites having valid total deposition for at least two of the three years are shown, and in some instances, sites only met this criterion for one of the two reporting periods. Because of differences like these, direct site-by-site comparisons are not possible everywhere. However, the maps here do provide useful information on trends in deposition and the spatial extent of N and S deposition.

3.8.1 Nitrogen

For the 3-year period 2004 to 2006, mean N deposition was greatest in the Ohio River basin, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg ha^{-1} yr^{-1}, respectively. N deposition is lower in other parts of the East, including the Southeast and in northern New England. In the central United States, Kansas and Oklahoma reported the



Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 08/30/07

Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 10/06/04

Figure 3.8-1. Total average yearly wet and dry sulfur deposition for 2004-2006 (top) and 1989-1991 (bottom).

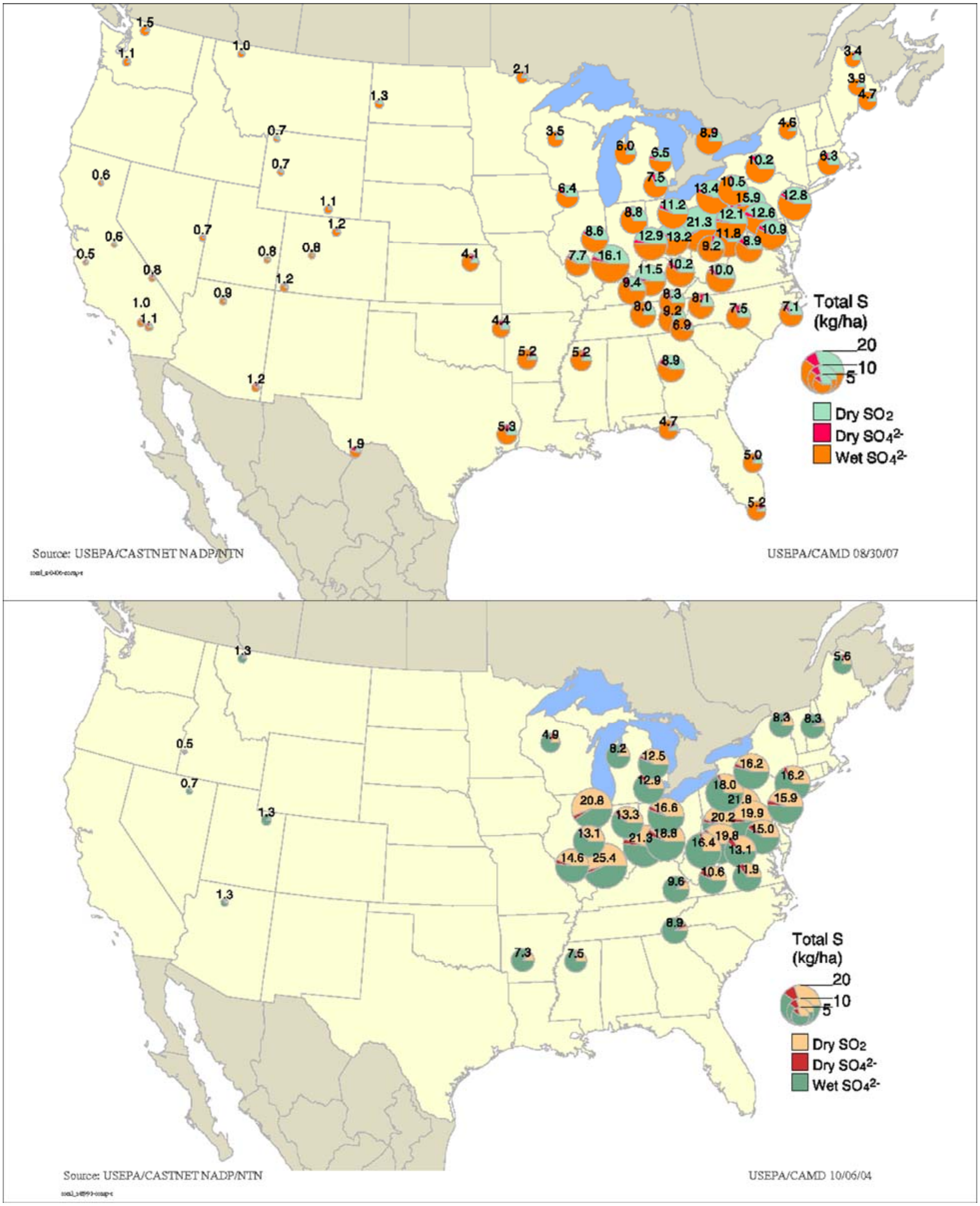


Figure 3.8-2. Total average yearly sulfur deposition by species for 2004-2006 (top) and 1989-1991 (bottom).

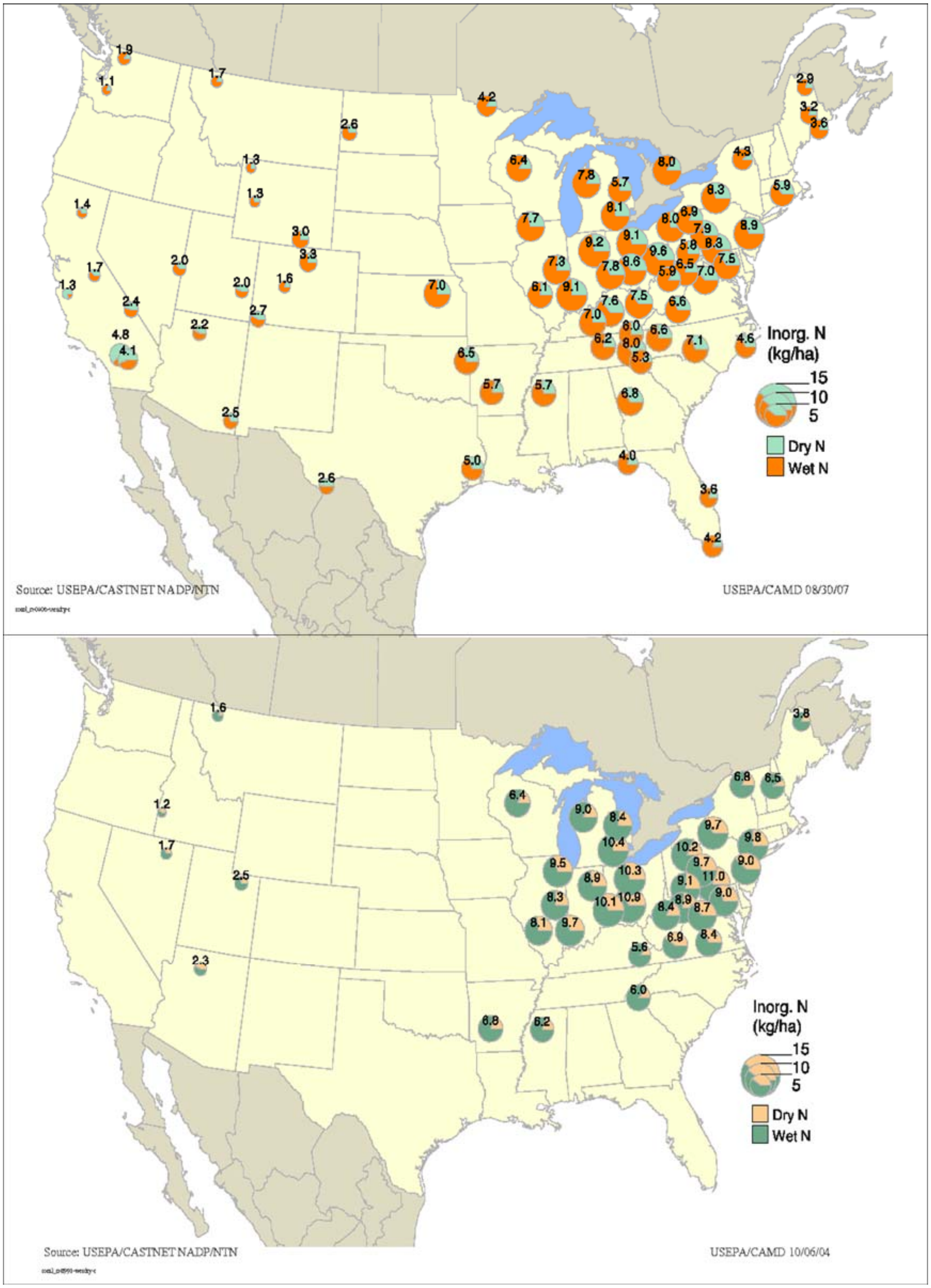


Figure 3.8-3. Total average yearly wet and dry inorganic nitrogen deposition for 2004-2006 (top) and 1989-1991 (bottom).

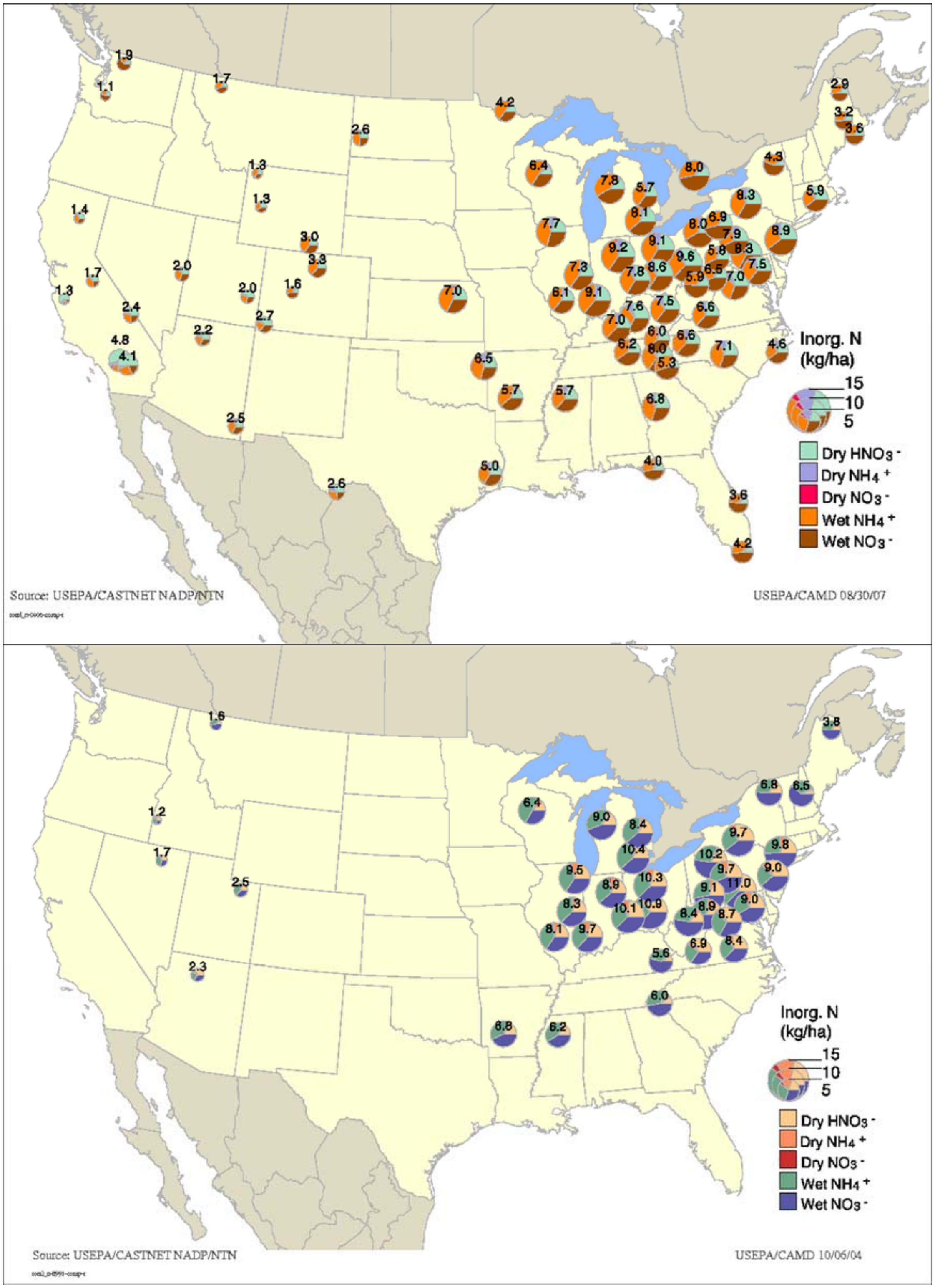


Figure 3.8-4. **Total average yearly inorganic nitrogen deposition by species for 2004-2006 (top) and 1989-1991 (bottom).**

highest deposition, 7.0 and 6.5 kg ha^{-1} yr^{-1}, respectively. Like S, N deposition is generally much lower in the western United States, where it is highest in urban areas in Southern California and in Denver, CO: 4.8 and 3.3 kg ha^{-1} yr^{-1}, respectively. It should be noted, however, that large portions of the United States west of the Mississippi River are poorly covered by the current deposition monitoring networks as these maps make clear. Hence, the actual degree of heterogeneity in the West is largely unknown.

Because NO_X emissions decreased by ~25% between 1990 and 2005, recent N deposition is lower compared with average deposition for the years 1989 to 1991. For 1989 to 1991, several recording stations in the Ohio River basin reported average annual deposition rates in excess of 10 kg ha^{-1} yr^{-1}. Data are lacking, however, for much of the central and western United States and little can be said for changes between the two reporting periods in these areas for the reasons given above. The greatest mass of N deposition primarily occurred as wet NO_3^- and NH_4^+, followed in importance by dry HNO_3, dry NH_4^+, and dry NO_3^-. Although most deposition for both reporting periods occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

3.8.2 Sulfur

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

Station-by-station comparisons between averaging periods are difficult because some stations do not have sufficient data to report a mean for the sampling period. There are, however, clear regional decreases in S deposition across the country. S deposition for the years 1989 through 1991 (the earliest 3-year reporting period available) is almost uniformly greater than for the years 2004 through 2006. Deposition since the period 1989 through 1991 has declined throughout the Ohio River basin from a pervious high of 25.4 kg ha^{-1} yr^{-1}; and in New

England and the Mid-Atlantic states, deposition is consistent with the ~48% decrease in SO_2 emissions nationwide between 1990 and 2005. Very little coverage for the western and central United States was available for the 1989 through 2001 reporting period, but sites with data show a similar decrease. For both the 1989 through 1991 and 2004 through 2006 reporting periods, S was primarily deposited as wet SO_4^{2-}, followed by a smaller proportion of dry SO_2, and a much smaller proportion of deposition as dry SO_4^{2-}.

3.9 EXAMPLE NO_2 AND HNO_3 FLUX DATA FROM HARVARD FOREST

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

An intensive study in 2000 used a Tunable Diode Laser Absorption Spectrometer (TDLAS) to measure [NO_2] and [HNO_3]. The TDLAS has an inherently fast response, and for species such as NO_2 and HNO_3 with well-characterized spectra it provides an absolute and specific measurement. Absolute concentrations of HNO_3 were measured, and the flux inferred based on the dry deposition inferential method that uses momentum flux measurements to compute a V_d and derive an inferred flux along the suggestions of Wesely and Hicks (1977) and Hicks et al. (1987); see the descriptions around Equations 3.5-1 and 3.5-2 above. Direct eddy covariance calculations for HNO_3 were not possible because the atmospheric variations were attenuated by interaction with the inlet walls despite very short residence time and use of fluorinated silane coatings to make the inlet walls more hydrophobic. NO response was adequate to allow both concentration and eddy covariance flux determination. Simultaneously, NO and NO_Y eddy covariance fluxes were determined with two separate O_3 chemiluminescence detectors, one equipped with a H_2-Au catalyst at the inlet to convert all reactive N compounds to NO. (A full description of this technique appears in Chapter 2.) Additionally, the measurements included concentration gradients for NO, NO_2, and O_3 over several annual cycles to examine their vertical profiles in the forest canopy.

Overall, the results show typical [NO_2] of 1 ppb under clean-air conditions and mean concentrations up to 3 ppb at night and 1 ppb during daytime for polluted conditions. Net positive fluxes (emission) of NO_2 were evident in the daytime and negative fluxes (deposition) were observed at night as Figure 3.9-1 shows. NO fluxes were negative during the daytime and near 0 at night.

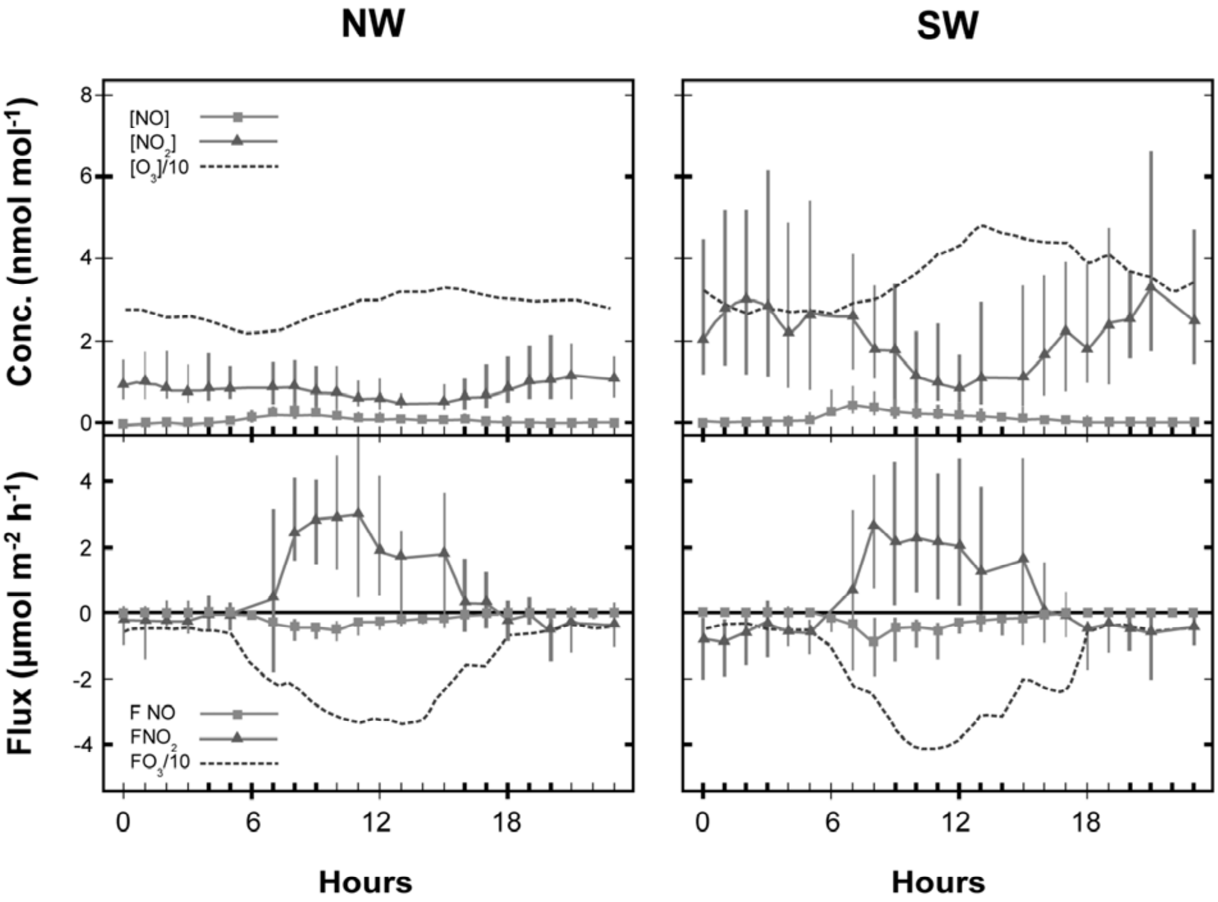


Figure 3.9-1. Diel cycles of median concentrations (upper panels) and fluxes (lower panels) for the Northwest clean sector, left panels) and Southwest (polluted sector, right panels) wind sectors at Harvard Forest, April-November, 2000, for NO, NO_2, and O_3/10. NO and O_3 were sampled at a height of 29 m, and NO_2 at 22 m. Vertical bars indicate 25th and 27th quartiles for NO and NO_2 measurements. NO_2 concentration and nighttime deposition are enhanced under southwesterly conditions, as are O_3 and the morning NO maximum.

Source: Horii et al. (2004).

In part, the opposite NO and NO_2 fluxes are simply consequences of variable NO and NO_2 distributions responding to vertical gradients in light intensity and [O_3], which resulted in no net NO_X flux (Gao et al., 1993). In the Harvard Forest situation, the NO and NO_2

measurements were not at the same height above the canopy, and the resulting differences come at least in part from the gradient in flux magnitude between the two inlets; see Figure 3.9-2. At night, when [NO] are near 0 owing to titration by ambient O_3, there is no flux of NO to offset NO_2 fluxes. Nighttime data consistently show NO_2 deposition as seen in Figure 3.8-3, and these increase with increasing [NO_2]. Concentrations > 10 ppb were rare at this site, but the few high [NO_2] suggest a nonlinear dependence on concentration. The data fit a model with V_d of −0.08 plus an enhancement term that is second order in [NO_2]. The second-order term implies that NO_2 deposition rates to vegetation in polluted urban sites would be considerably larger than what was observed at this rural site.

After accounting for the time of the NO-NO_2 null cycle during the measurement sampling period, the net NO_X flux can be derived. Overall, there was a net deposition of NO_X during the night and essentially 0 flux in the day with large variability in the magnitude and sign of individual flux observations. For the periods with [NO_2] > 2 ppb, deposition was always observed. These canopy-scale field observations are consistent with a finite compensation point for NO_2 in the canopy that offsets foliar uptake or even reverses it when concentrations are especially low. At concentrations above the compensation point, NO_X is absorbed by the canopy. Examination of concentration profiles corroborates the flux measurements as shown in Figure 3.9-4. During daytime low [NO_X] conditions, there is a local maximum in the concentration profile near the top of the canopy where O_3 has a local minimum, consistent with foliar emission or light-dependent production of NO_X in the upper canopy. Depletion is evident for both NO_X and O_3 near the forest floor. Air reaching the ground has passed through the canopy where uptake is efficient and the vertical exchange rates near the ground are slow. At night, the profiles generally decrease with decreasing height above the ground, leaving only the uptake process. At higher concentrations, daytime [NO_X] are nearly constant through the canopy; no emission is evident from the sunlit leaves.

Figure 3.9-5 compares observed fluxes of all the sampled species described here. The measured NO_X and estimated PAN fluxes are small relative to the observed total NO_Y flux. In clean air, HNO_3 accounts for nearly all the NO_Y flux and the sum of all measured species is roughly equal to [NO_Y]. However, under polluted conditions, unmeasured species can be up to 25% of total [NO_Y], and HNO_3 fluxes cannot account for all of the observed NO_Y flux. Likely

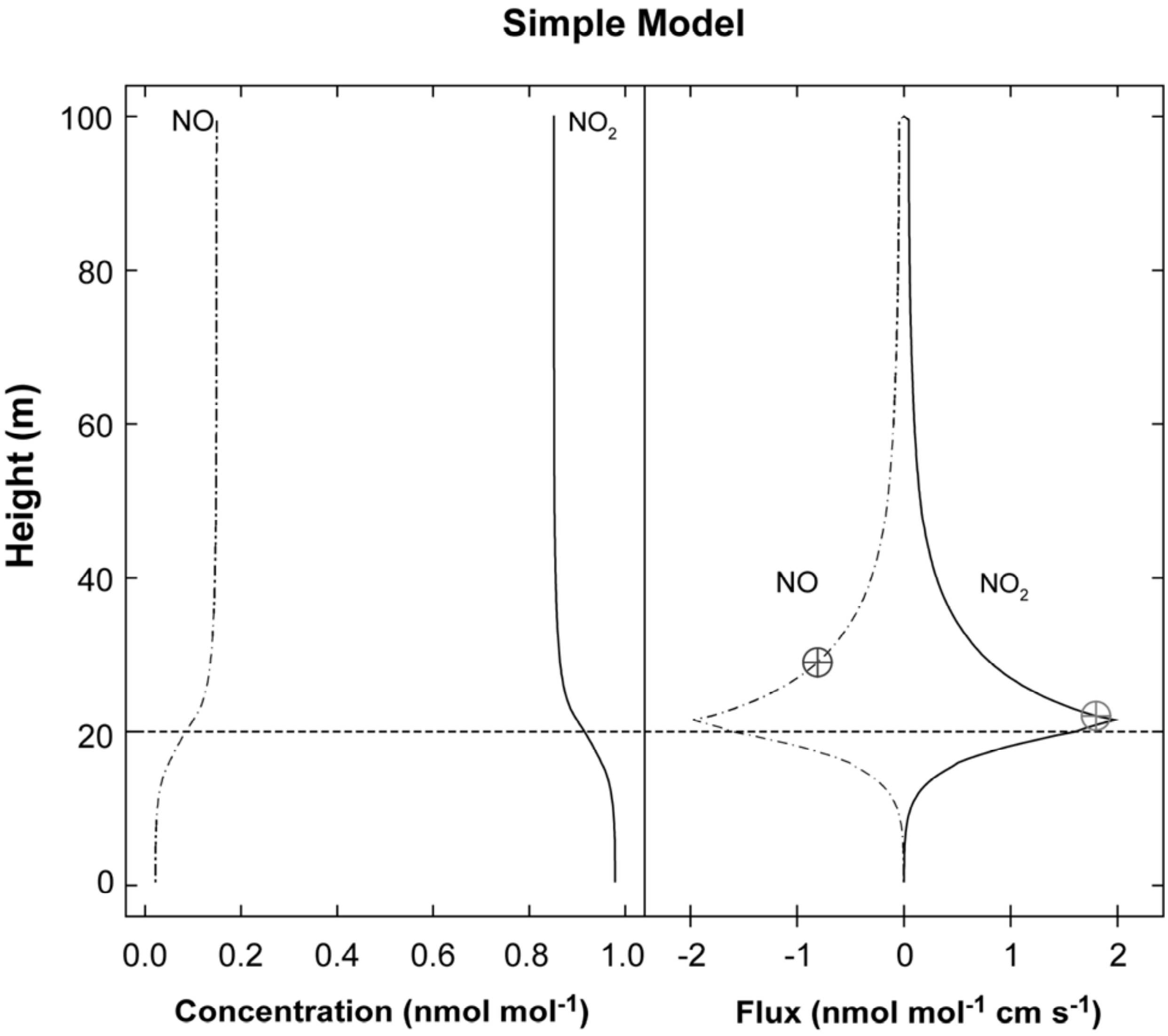


Figure 3.9-2. Simple NO_X photochemical canopy model outputs. Left panel, concentrations of NO (dashed) and NO_2 (solid); right, fluxes of NO (dashed) and NO_2 (solid). Symbols indicate measurement heights for NO (29m) and NO_2 (22m) at Harvard Forest. The model solves the continuity equation for NO 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 is normalized to 1ppb. t1 = 70s in this example. Due to the measurement height difference, observed upward NO_2 flux due to photochemical cycling alone should be substantially larger than observed downward NO flux attributable to the same process.

Source: Horii (2002).

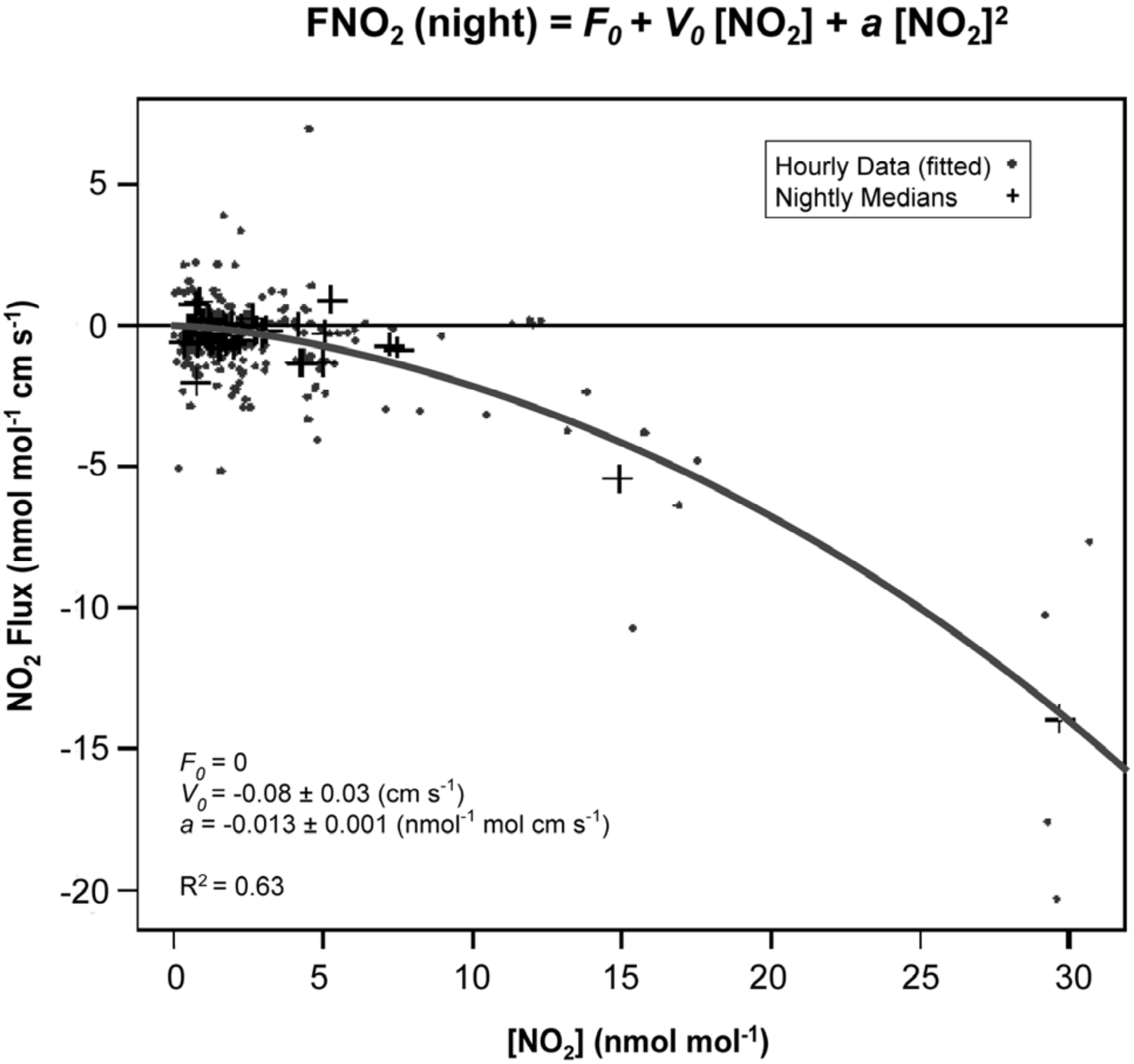


Figure 3.9-3. Hourly (dots) and median nightly (pluses) NO_2 flux vs. concentration, with results of least-squares fit on the hourly data (curve). The flux is expressed in units of concentration times velocity (nmol mol^{-1} cm s^{-1}) in order to simplify the interpretation of the coefficients in the 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).

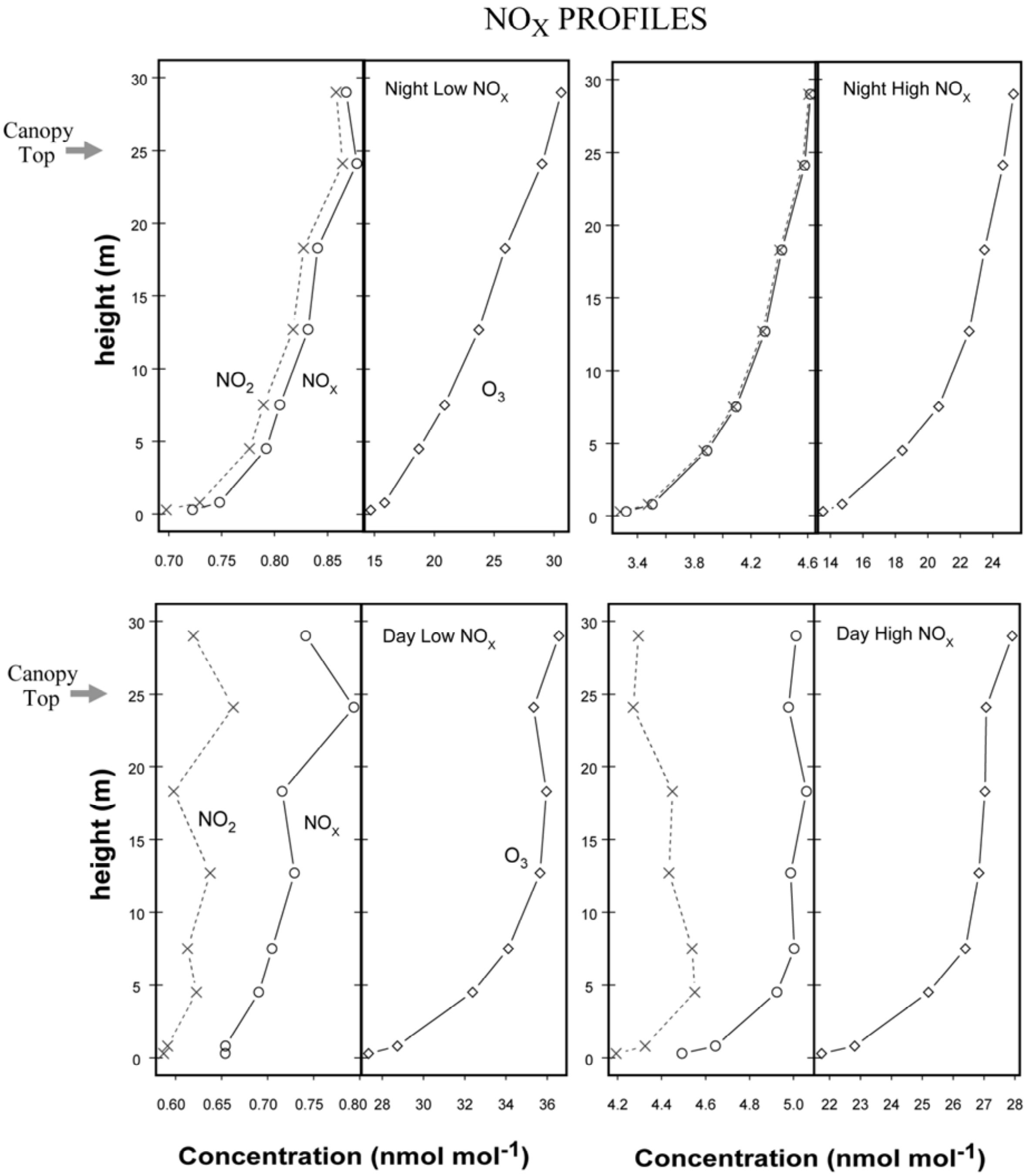


Figure 3.9-4. Averaged profiles at Harvard Forest give some evidence of some NO_2 input near the canopy top from light-mediated ambient reactions, or emission from open stomates.

Source: Horii et al. (2004).

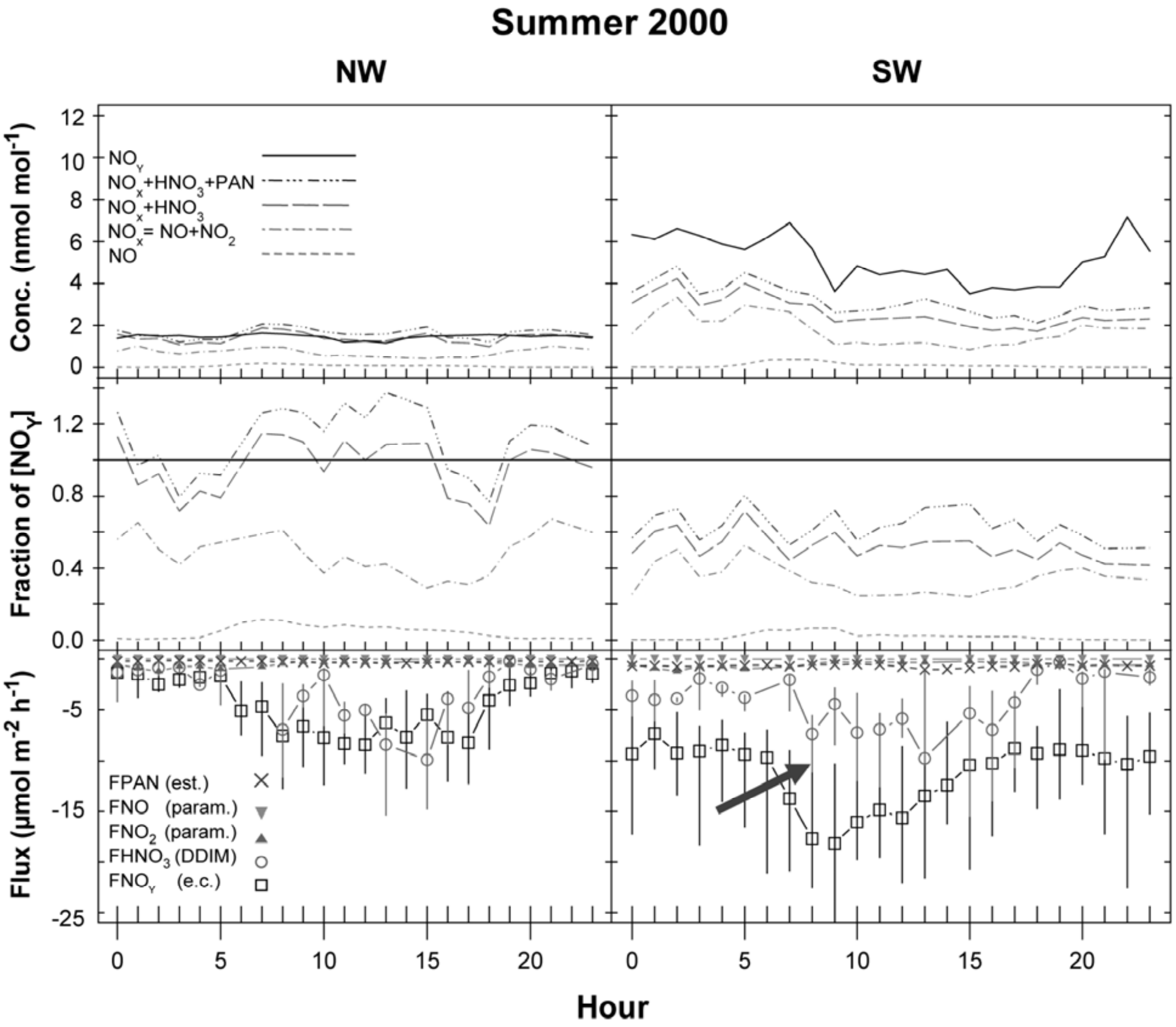


Figure 3.9-5. **Summer (June-August) 2000 median concentrations (upper panels), fractions of NO_Y (middle panels), and fluxes (lower panels) of NO_Y and component species separated by wind direction (Northwest on the left and Southwest on the right). Vertical lines in the flux panels show 25th and 75th quartiles of $F(NO_Y)$ and $F(HNO_3)$; negative fluxes represent deposition; $F(NO_X)$ is derived from eddy covariance F(NO) and $F(NO_2)$ measurements (corrected for photochemical cycling), $F(HNO_3)$ is inferred, and $F(NO_Y)$ 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 $F(NO_Y)$ under Southwesterly flows are in the form of reactive nitrogen species whose fluxes are not measured or estimated here.**

Source: Horii et al. (2006).

these unmeasured NO_Y species are hydroxyalkyl nitrates and similar compounds and are rapidly deposited.

Although NO_2 uptake may be important to the plant, because it is an input directly to the interior of foliage that can be used immediately in plant metabolism, it is evidently not a significant part of overall N deposition to rural sites.

The deposition of HNO_3 and multifunctional $RONO_2$ are the largest elements of the N dry deposition budget. Two key areas of remaining uncertainty are the production of HNO_2 over vegetation and the role of the very reactive biogenic VOCs. HNO_2 is important both because its photolysis is a source of OH radicals and because its formation may represent an unrecognized mechanism to regenerate photochemically active NO_X from NO_X that had been considered terminally removed from the atmosphere.

3.10 METHODS TO COMPUTE NO_X AND SO_X CONCENTRATIONS AND CHEMISTRY

Atmospheric chemical transport models (CTMs) are the major tools used to calculate the relations among O_3, other oxidants and their precursors, the transport and transformation of air toxics, the production of secondary organic aerosols, the evolution of the particle size distribution, and the production and deposition of pollutants affecting ecosystems. CTMs are driven by emissions inventories for primary species such as the precursors for O_3 and PM and by meteorological fields produced by other numerical prediction models. Meteorological quantities such as winds and temperatures are taken from operational analyses, reanalyses, or circulation models. In most cases, these are off-line analyses, i.e., they are not modified by radiatively active species such as O_3 and particles generated by the model.

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

3.10.1 CTMs

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

Global-scale CTMs are used to address issues associated with climate change and stratospheric O_3 depletion, and to provide boundary conditions for the regional-scale models. The CTMs include simplified mathematical descriptions of atmospheric transport, the transfer of solar radiation through the atmosphere, chemical reactions, and removal to the surface by turbulent motions and precipitation for pollutants emitted into the model domain. The upper boundaries of the CTMs extend anywhere from the top of the mixed layer to the mesopause at ~80 km in order to obtain more realistic boundary conditions for problems involving stratospheric dynamics.

There are two major formulations of CTMs in current use. In the first approach, grid-based, or Eulerian, air quality models, the domain to be modeled is subdivided into a three-dimensional array of grid cells. Spatial derivatives in the species continuity equations are cast in finite-difference or, less often, in finite-element form, and a system of equations for the concentrations of all the chemical species in the model are solved numerically in each grid. Time-dependent continuity or mass conservation equations are solved for each species including terms for transport, chemical production and destruction, and emissions and deposition (if relevant) in each cell. Chemical processes are simulated with ordinary differential equations, and transport processes are simulated with partial differential equations. More details are available in Annex 2.

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

3.10.1.1 Regional-Scale CTMs

Most major modeling efforts within EPA use CMAQ (Byun and Ching, 1999; Byun and Schere, 2006). A number of other modeling platforms using Lagrangian and Eulerian frameworks were reviewed in the 1996 Air Quality Criteria Document (AQCD) for O_3 (U.S. Environmental Protection Agency, 1997), and in Russell and Dennis (2000). The capabilities of a number of CTMs designed to study local- and regional-scale air pollution problems were also summarized by Russell and Dennis (2000). Recent evaluations of CMAQ performance are given in Arnold et al. (2003), Eder and Yu (2005), Appel et al. (2005), and Fuentes and Raftery (2005). More details are available in Annex 2.

3.10.1.2 Global-Scale CTMs

The importance of the global transport of pollutant precursors and secondary products and their contribution to regional pollutant levels in the United States is now apparent. There are at present ~25 3-dimensional global models developed to address problems in tropospheric physics and chemistry. These models resolve synoptic meteorology, O_3-NO_X-CO-HC photochemistry, have parameterizations for wet and dry deposition, and parameterize sub-grid scale vertical mixing processes like convection. Global models have proved useful for testing and advancing scientific understanding beyond what is possible with observations alone. For example, they can calculate quantities of interest that cannot be measured directly, such as the export of pollution from one continent to the global atmosphere or the response of the atmosphere to future perturbations to anthropogenic emissions. Additional details are available in Annex 2.

3.10.2 Computed Deposition with CTMs

Both wet deposition and dry deposition are important removal processes for pollutants on urban and regional scales and so are included in CTMs. The general approach used in most models is the resistance-in-series method described above and represented in Equations 3.5-1 and 3.5-2. This approach works for a range of substances, although it is inappropriate for species with substantial re-emissions from the surface or for species where deposition to the surface depends on concentrations at the surface itself. The approach is also modified somewhat for aerosols in that the terms R_b and R_c are replaced with a surface V_d to account for gravitational settling.

Wesley and Hicks (2000) listed several shortcomings of the then-current knowledge of dry deposition. Among those shortcomings were difficulties in representing dry deposition over varying terrain where horizontal advection plays a significant role in determining the magnitude of R_a and difficulties in adequately determining V_d for extremely stable conditions such as those occurring at night; see the discussion by Mahrt, 1998, for example. Under optimal conditions, when a model is exercised over a relatively small area where dry deposition measurements have been made, models still generally showed uncertainties on the order of ±30% (see e.g., Massman et al., 1994; Brook et al., 1996; Padro, 1996). Wesely and Hicks concluded (2000) that an important result of those comparisons was that the level of sophistication of most dry deposition models was relatively low, and that deposition estimates, therefore, must rely heavily on empirical data. Still larger uncertainties exist when the surface features in the built environment are not well known or when the surface comprises a patchwork of different surface types, as is common in the eastern United States.

Both wet and dry deposition are highly parameterized in global CTMs. While all current models implement resistance schemes for dry deposition, the V_d generated from different models can vary highly across terrains (Stevenson et al., 2006). The accuracy of wet deposition in global CTMs is tied to spatial and temporal distribution of model precipitation and the treatment of chemical scavenging. Dentener et al. (2006b) compared wet deposition across 23 models with available measurements around the globe. Figures 3.10-1 and 3.10-2 extract results of a comparison of the 23-model mean versus observations over the eastern United States for pNO_3 and pSO_4 deposition, respectively. The mean model results are strongly correlated with the observations ($r > 0.8$), and usually capture the magnitude of wet deposition to within a factor

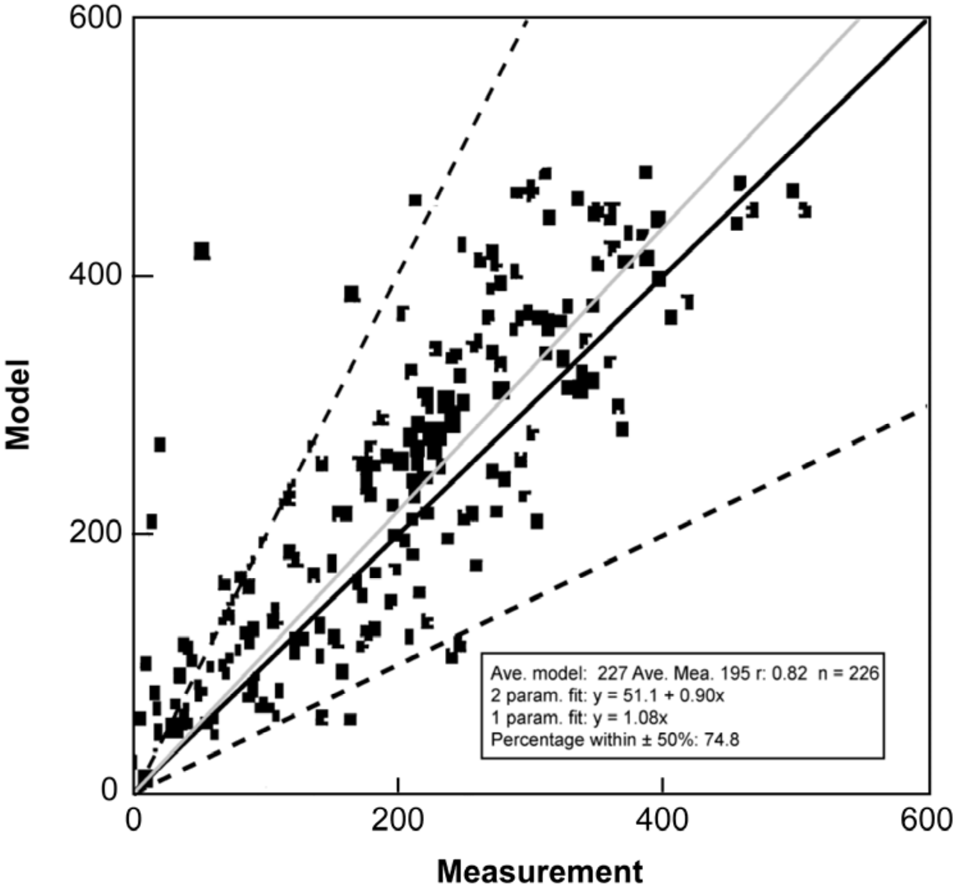


Figure 3.10-1. Scatter plot of total nitrate (HNO_3 plus aerosol nitrate) wet deposition ($mg(N)m^{-2}yr^{-1}$) of the mean model versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through 0.

Source: Dentener et al. (2006b).

of 2 over the eastern United States. Dentener et al. (2006b) conclude that 60 to 70% of the participating models capture the measurements to within 50% in regions with quality controlled observations. This study then identified world regions receiving >1000 mg N m^{-2} yr^{-1}, which they defined as the critical load, and found that 20% of non-crop, natural vegetation in the United States is exposed to N deposition in excess of that amount (Dentener et al., 2006b).

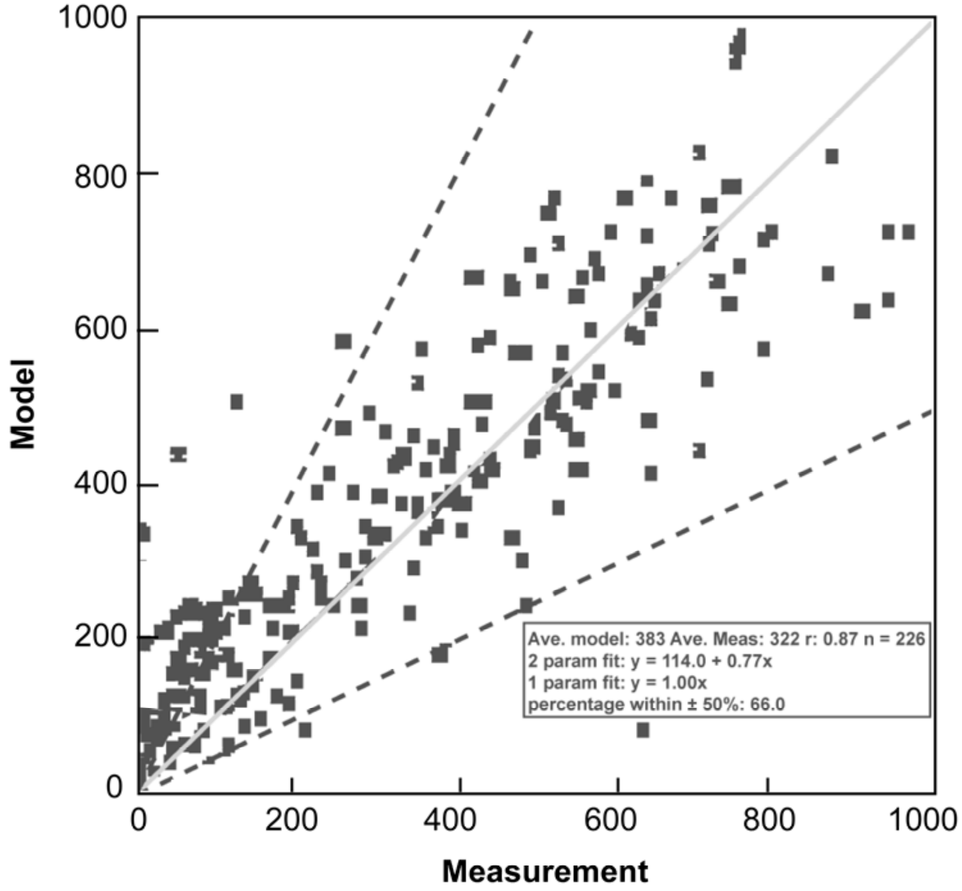


Figure 3.10-2. Same as Figure 3.10-1 but for sulfate wet deposition (mg(S)m^{-2}yr^{-1}).

Source: Dentener et al. (2006b).

3.10.3 CTM Evaluation

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

Discrepancies between model predictions and observations can be used to delineate gaps in the current understanding of atmospheric chemistry and to spur improvements in parameterizations of atmospheric chemical and physical processes. Model evaluation does not merely involve a straightforward comparison between model predictions and the concentration field of the pollutant of interest. Such comparisons may not be meaningful because it is difficult to determine if agreement between model predictions and observations truly represents an accurate treatment of physical and chemical processes in the CTM or the effects of compensating errors in complex model routines. Ideally, each of the model components (e.g., emissions inventories, chemical mechanism, meteorological driver) should be evaluated individually, although this is rarely done in practice. More details are available in Annex 2.

The evaluation of urban- and regional-scale models is also limited by the availability of data. Measured [NO] and some speciated [VOC] are available through the EPA AQS, but questions have been raised about the accuracy of some of those measurements; see the fuller descriptions of measurement techniques relevant for NO_X and SO_X in Chapter 2. Evaluation of urban- and regional-scale models against measurements has generally relied on results from a limited number of field studies in the United States. Short-term, research-grade measurements for species relevant to O_3 formation, including VOCs, NO_X, PANs, HNO_3, and hydrogen peroxide (H_2O_2) are also sometimes available during focused campaigns at selected rural and remote sites. See the descriptions in Daum et al. (1990 and 1996); Martin et al. (1997); Young et al. (1997); Thompson et al. (2000); Hoell et al. (1997 and 1999); Fehsenfeld et al. (1996a); Emmons et al. (2000); Hess (2001); and Carroll et al. (2001) for examples. The equivalent measurements are available for some polluted rural sites in the eastern United States, but only for a few urban locations as described in Meagher et al. (1998); Hübler et al. (1998); Kleinman et al. (2000 and 2001); and Fast et al. (2002). Extensive measurements have also been made in Vancouver (Steyn et al., 1997) and in several European cities (Staffelbach et al., 1997; Prévôt et al., 1997, Dommen et al., 1999; Geyer et al., 2001; Thielman et al., 2001; Martilli et al., 2002; Vautard et al., 2002).

3.11 COMPUTING ATMOSPHERIC DEPOSITION TO SPECIFIC LOCATIONS

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

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

Direct and indirect deposition to watersheds depend on air pollutant concentrations in the airshed above the watershed. The shape and extent of the airshed is quite different from that of the watershed. In a watershed, everything that falls in its area, by definition, flows into a single body of water. An airshed, by contrast, is a theoretical concept that defines the source area containing the emissions contributing a given level, often 75%, to the deposition in a particular watershed or to a given waterbody. Hence, airsheds are modeled domains containing the sources estimated to contribute a given level of deposition from each pollutant of concern. The principal NO_X airsheds and corresponding watersheds for several regions in the eastern United States are shown in Figure 3.11-1.

N inputs have been studied in several east and Gulf Coast estuaries owing to concerns about eutrophication there. N from atmospheric deposition in these locations is estimated to be 10 to 40% of the total input of N to many of these estuaries, and could be higher for some. Estimates of total N loadings to estuaries or to other large-scale elements in the landscape are then computed using measurements of wet and dry N deposition where these are available

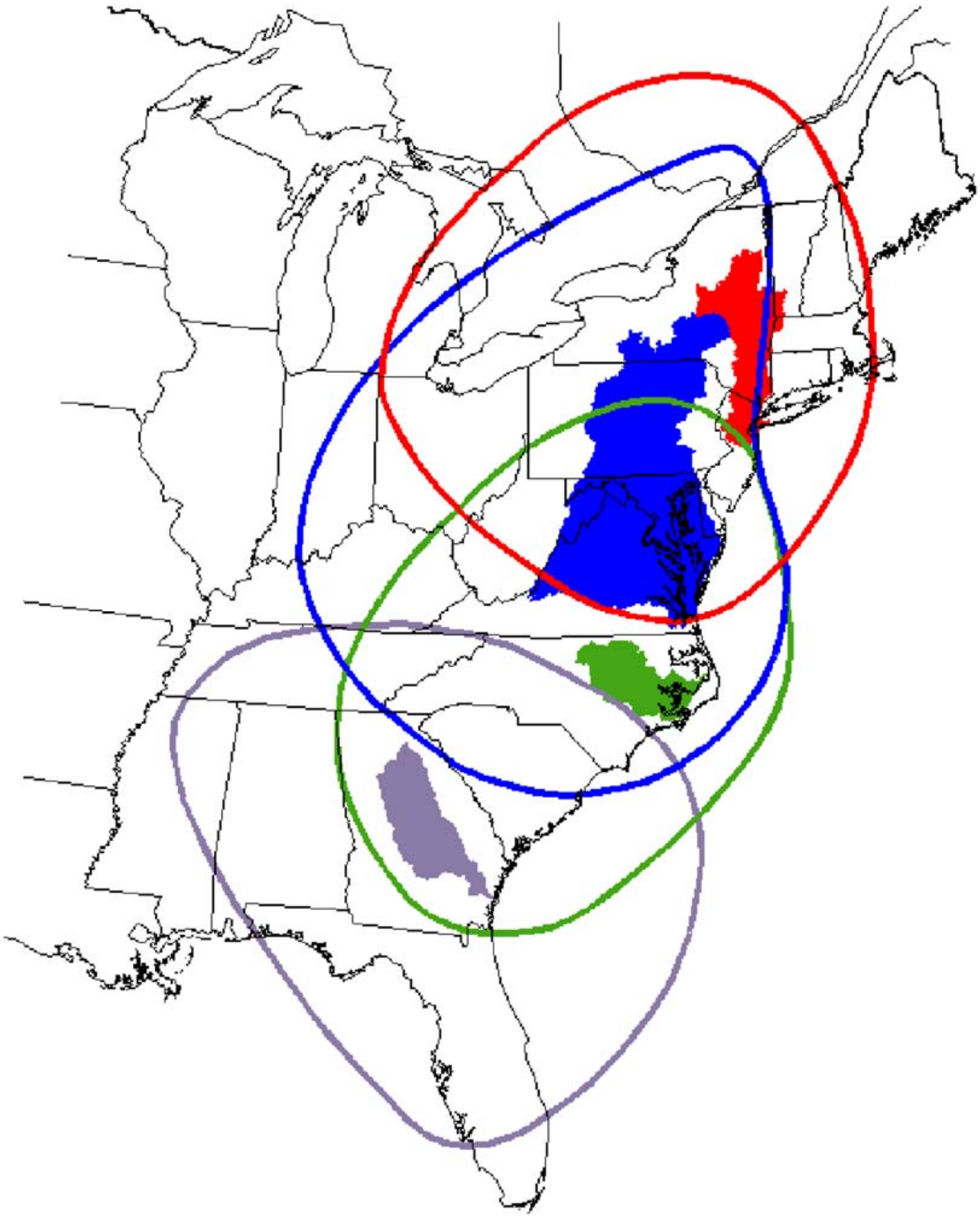


Figure 3.11-1. **Principal airsheds and watersheds for oxides of nitrogen for these estuaries: Hudson/Raritan Bay; Chesapeake Bay; Pamlico Sound; and Altamaha Sound (listed from North to South). Airshed extents developed by R. Dennis, NOAA-ARL.**

and interpolated with or without a set of air quality model predictions such as the Extended Regional Acid Deposition Model (Ext-RADM) (Mathur and Dennis, 2000; Dennis, 1997; Dennis et al., 1990).

Table 3.11-1 lists several waterbodies for which atmospheric N inputs have been computed and ratioed to total N loads. The contribution from the atmosphere ranges from a low of 2-8% for the Guadalupe Estuary in South Texas to highs of ~38% in the New York Bight and the Albemarle-Pamlico Sound in North Carolina.

Chemically, N deposited from the atmosphere directly or indirectly can be present as an oxide or in reduced form as NH_3 and NH_4^+ or as dissolved or particulate organic N; see the listing in Table 3.11-2 for a division of these and an approximate ranking of source strengths. NO and NO_2, chiefly from fossil fuel combustion, dominate total N pollution in the United States at ~50 to 75% of the total; see the descriptions of this chemistry in Chapter 2 and of sources just above here.

Confined animal feeding operations and other intensified agricultural production methods have resulted in greatly increased volumes of animal wastes, of which 30 to 70% may be emitted as NH_3 (Whitall and Paerl, 2001). The increase in reduced N deposition in the United States measured as increased NH_4^+ deposition correlates well with the local and regional increases in this agricultural intensity (Whitall and Paerl, 2001). Moreover, the increases in NH_4^+ deposition in the United States track the effects in Europe where animal operations have dominated agricultural production for much of the previous 100 years and where NH_4^+ is the dominant form of N deposited from the atmosphere (Holland et al., 1999). Tables 3.11-3 and 3.11-4 list several important watersheds and their respective oxidized (Table 3.11-3) and reduced (Table 3.11-4) airsheds. Airsheds for oxidized N tend to be larger than those for reduced N owing to differences in the transport and deposition of NO_X and NH_X described briefly above and in more detail in Chapter 2 and in Annexes 1 and 2.

Considerable uncertainty attaches to estimates of the third form of atmospherically derived N, organic N, in part because convenient methods for measurement and analysis are not widely available; see Table 3.11-2. Intensive studies at individual sites have shown, however, that for the North Carolina coast, for example, 30% of rain water N and deposition consisted of organic N, 20-30% of which was then available to primary producers on time scales of hours to days (Peierls and Paerl, 1997).

3.12 PRB CONCENTRATIONS OF NO_X AND SO_X

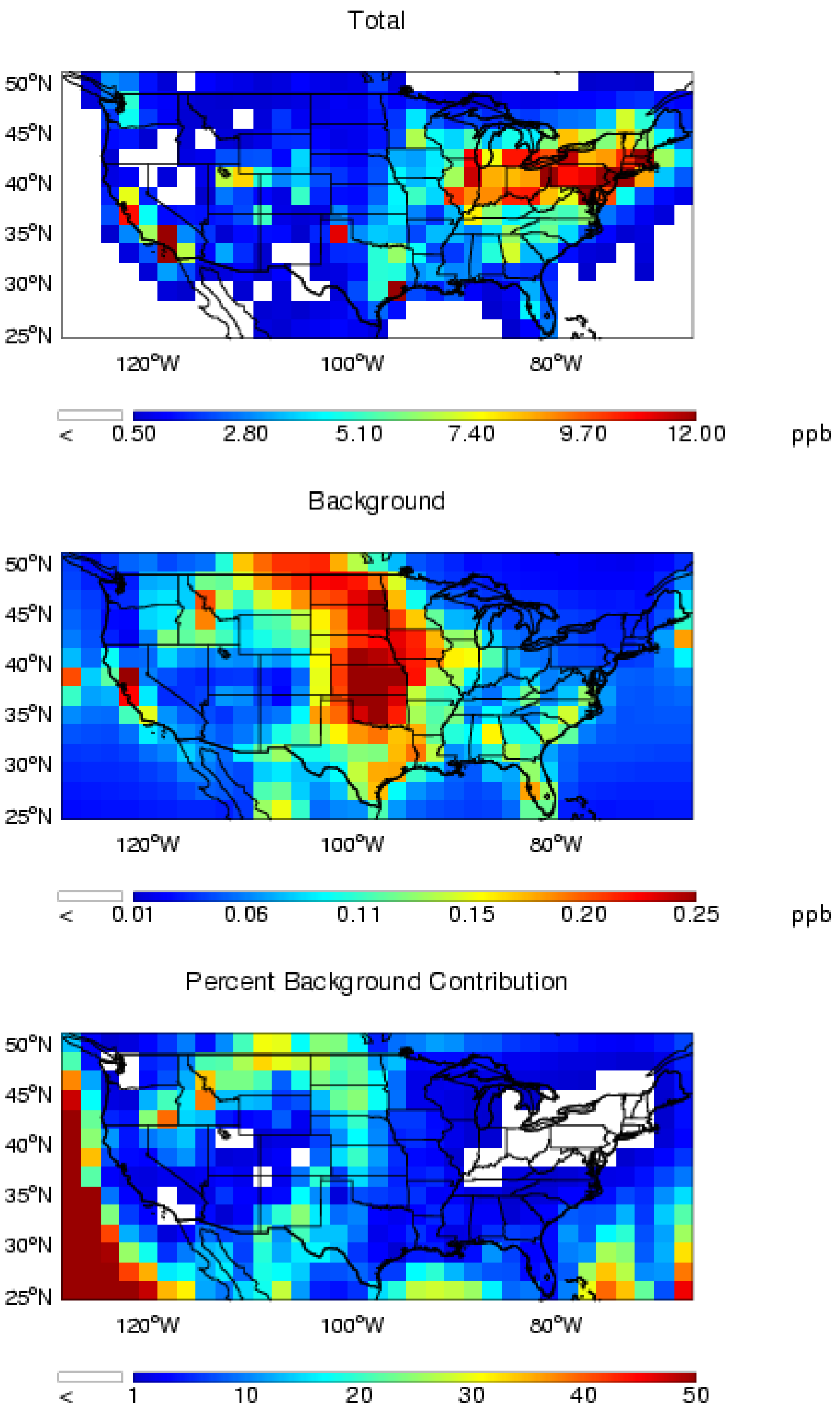
Background concentrations of NO_X and SO_X used for purposes of informing decisions about NAAQS are referred to as PRB concentrations. PRB concentrations are those concentrations that would occur in the United States in the absence of anthropogenic emissions in continental North America (defined here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

Background levels so defined facilitate separation of pollution levels that can be controlled by U.S. regulations (or through international agreements with neighboring countries) from levels that are generally uncontrollable by the United States. EPA assesses risks to human health and environmental effects from NO_2 and SO_2 levels in excess of these PRB concentrations.

The MOZART-2 global model of tropospheric chemistry (Horowitz et al., 2003) is used to diagnose the PRB contribution to [NO_X] and [SO_X] and to total (wet plus dry) deposition. The model setup for the present-day simulation has been published in a series of papers from a recent model intercomparison (Dentener et al., 2006a,b; Shindell et al., 2006; Stevenson et al., 2006; van Noije et al., 2006).

First, the role of PRB in contributing to [NO_2] and [SO_2] in surface air is considered. Figure 3.12-1 shows the annual mean [NO_2] in surface air in the base case simulation (top panel) and from the PRB simulation (middle panel), along with the percentage contribution of the background to the total base case [NO_2] (bottom panel). Maximum concentrations in the base case simulation occur along the Ohio River Valley and in the Los Angeles basin just as they do in reported measurements; see the section on emissions and concentrations above. While present-day concentrations are often >5 ppb, PRB is <300 ppt over most of the CONUS and <100 ppt in the eastern United States. The distribution of PRB (middle panel of Figure 3.12-1) largely reflects the distribution of soil NO emissions, with some local enhancements due to biomass burning such as is seen in western Montana. In the northeastern United States, where present-day [NO_2] are highest, PRB contributes <1% to the total concentrations.

The spatial pattern of present-day [SO_2] over the CONUS is similar to that of NO_2, with highest concentrations of >5 ppb along the Ohio River valley; see the upper panel Figure 3.12-2.


Total

Background

Percent Background Contribution

Figure 3.12-1. Annual mean concentrations of NO_2 (ppbv) 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.

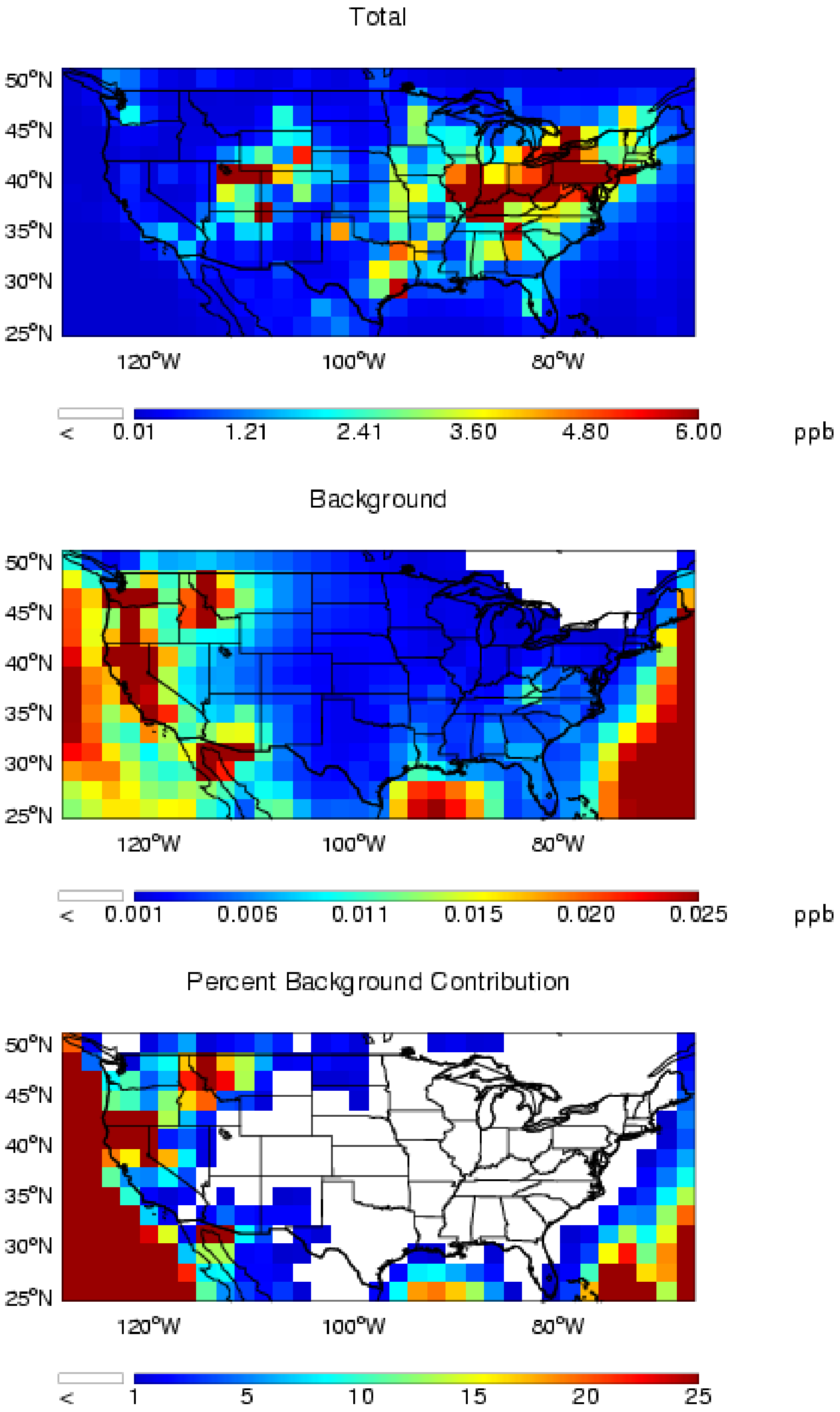


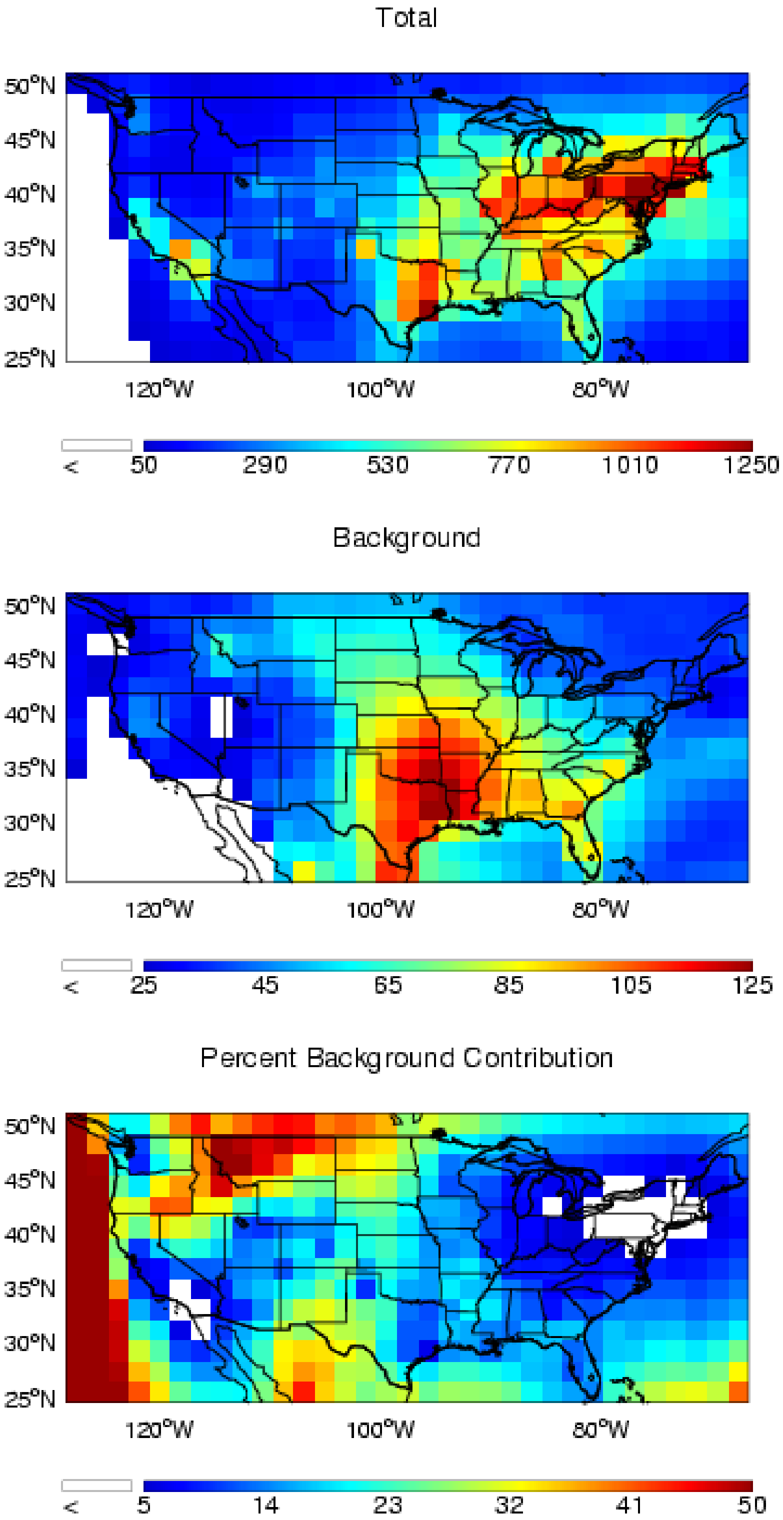
Figure 3.12-2. Same as Figure 3.12-1 but for SO_2 concentrations.

Background [SO_2] are orders of magnitude smaller, <10 ppt over much of the CONUS as shown in the middle panel of Figure 3.12-2. Maximum PRB [SO_2] are 30 ppt. In the Northwest where there are geothermal sources of SO_2, the contribution of PRB to total SO_2 is 70 to 80%. However, excepting this, PRB contributes <1% to present-day [SO_2] in surface air as shown in the bottom panel Figure 3.12-2.

The spatial pattern of NO_Y (defined in the model as HNO_3 + NH_4NO_3 + NO_X + HO_2NO_2 + $RONO_2$) in wet and dry deposition is shown in Figure 3.12-3. Figure 3.12-3 (upper panel) shows that highest values are found in the eastern United States in and downwind of the Ohio River Valley. The pattern of N deposition in the PRB simulation shown in the Figure 3.12-3 middle panel, however, shows maximum deposition centered over Texas and in the Gulf Coast region, reflecting a combination of N emissions from lightning in the Gulf region, biomass burning in the Southeast, and from microbial activity in soils with maxima in central Texas and Oklahoma. The bottom panel of Figure 3.12-3 shows that the PRB contribution to N deposition is <20% over the eastern United States, and typically <50% in the western United States where NO_Y deposition is already lower at 25 to 50 mg N m^{-2} yr^{-1}.

Present-day deposition of SO_2 and pSO_4 is largest in the Ohio River Valley, due to coal-burning power plants in that region, while background deposition is typically at least an order of magnitude smaller; see Figure 3.12-4. Over the eastern United States, the background contribution to SO_X deposition is <10%, and it is even smaller, <1%, where present-day SO_X deposition is highest. The contribution of PRB to S deposition is highest in the western United States at >20% because of the geothermal sources of SO_2 and oxidation of DMS in the surface of the eastern Pacific.

Figure 3.12-5 shows results from MOZART-2 discussed above as compared with those from another tropospheric chemistry model, GEOS-Chem (Bey et al., 2001), which was previously used to diagnose PRB [O_3] (Fiore et al., 2003; U.S. Environmental Protection Agency, 2006a). In both models, the surface PRB [NO_X] tend to mirror the distribution of soil NO emissions, which are highest in the Midwest. The NO emissions in GEOS-Chem are greater than those in MOZART-2 by nearly a factor of 2 reflecting different assumptions regarding the contribution to soil NO emissions largely through fertilizer, since GEOS-Chem total soil NO emissions are actually higher than MOZART-2 at 0.07 versus 0.11 Tg N over the United States



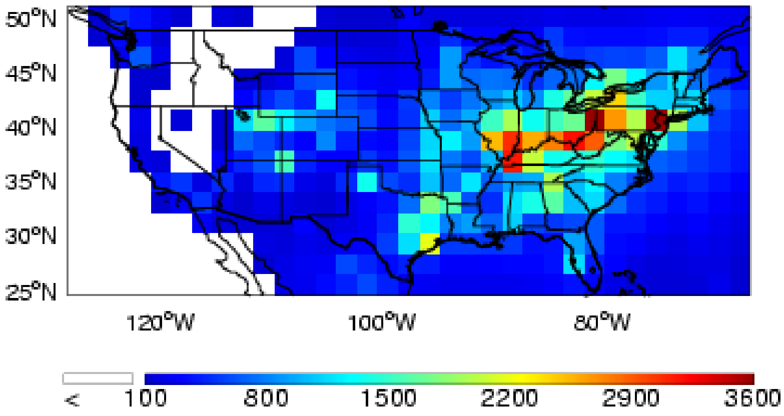
Total

Background

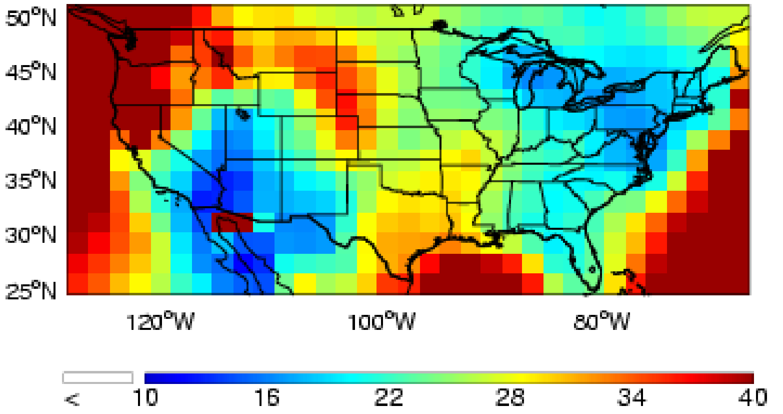
Percent Background Contribution

Figure 3.12-3. Same as for Figure 3.12-1 but for wet and dry deposition of HNO_3, NH_4NO_3, NO_X, HO_2NO_2, and organic nitrates (mg N $m^{-2}y^{-1}$).

Total



Background



Percent Background Contribution

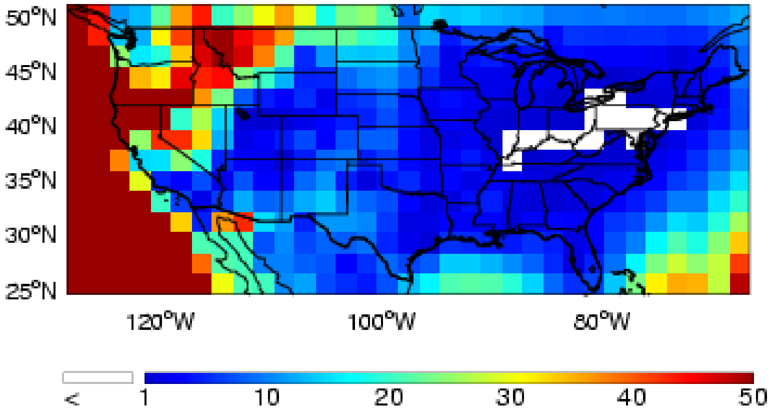


Figure 3.12-4. Same as Figure 3.12-1 but for SO_X deposition (SO_2 + pSO_4) (mg S $m^{-2}y^{-1}$).

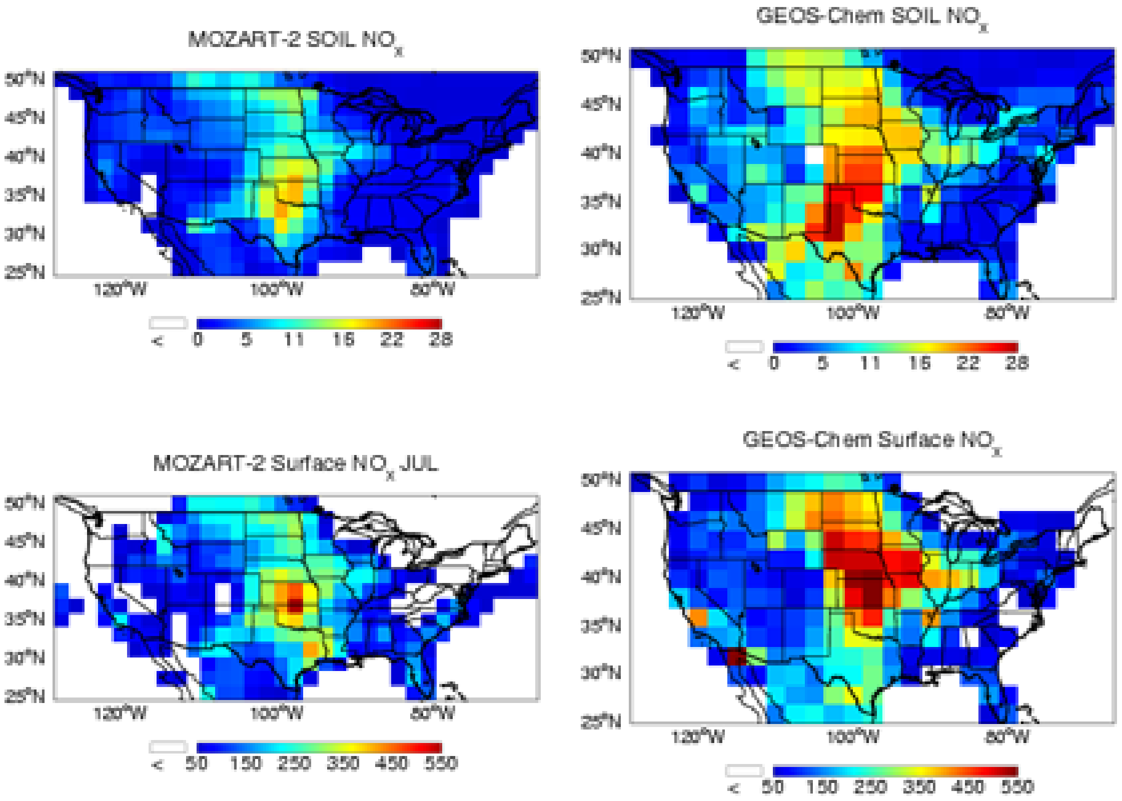


Figure 3.12-5. July mean soil NO emissions (upper panels; 1 × 10^9 molecules cm^{-2} s^{-1}) and surface PRB NO_X concentrations (lower panels; pptv) over the United States from MOZART-2 (left) and GEOS-Chem (right) model simulations in which anthropogenic O_3 precursor emissions were set to zero in North America.

in July. Even with the larger PRB soil NO emissions, however, surface [NO_X] in GEOS-Chem are typically <500 ppt.

It is also instructive to consider measurements of SO_2 at relatively remote monitoring sites, i.e., ones located in sparsely populated areas not subject to obvious local sources of pollution. Berresheim et al. (1993) used a type of atmospheric pressure ionization mass spectrometer (APIMS) at Cheeka Peak, WA (48.30N, 124.62W, 480 m asl), in April 1991 during a field study for DMS oxidation products: [SO_2] there ranged from 20 to 40 ppt. Thornton et al. (2002) have also used an APIMS with an isotopically labeled internal standard to determine background [SO_2] and found 25 to 40 ppt in northwestern Nebraska in October 1999 at 150 m above ground using the NCAR C-130. These values are comparable to remote central south Pacific convective boundary layer [SO_2] (Thornton et al., 1999).

Volcanic sources of SO_2 in the United States are limited to the Pacific Northwest, Alaska, and Hawaii. Since 1980 the Mt. St. Helens volcano in Washington Cascade Range (46.20 N, 122.18 W, summit 2549 m asl) has been a variable source of SO_2. Its major effects came in the explosive eruptions of 1980, which primarily affected the northern part of the mountainous west of the United States. The Augustine volcano near the mouth of the Cook Inlet in southwestern Alaska (59.363 N, 153.43 W, summit 1252 m asl) has had SO_2 emissions of varying extents since its last major eruptions in 1986. Volcanoes in the Kamchatka peninsula of the eastern region of Siberian Russia do not especially affect surface concentrations in northwestern North America. The most serious effects in the United States from volcanic SO_2 occurs on the island of Hawaii. Nearly continuous venting of SO_2 from Mauna Loa and Kilauea produce SO_2 in such large amounts that >100 km downwind of the island, [SO_2] can be >30 ppb (Thornton and Bandy, 1993). Depending on wind direction, the Kona region of the Hawaiian west coast has had significant effects from SO_2 and pSO_4 for the past decade. Indeed, [SO_2] in Volcanoes National Park, HI were in excess of the 3-h and the 24-h NAAQS in the 2004 to 2005 reporting period.

In summary, the PRB contribution to NO_X and SO_X over the CONUS is very small, except for SO_2 in areas with volcanic activity.

3.13 SUMMARY

3.13.1 Emissions and Atmospheric Concentrations of NO_X and SO_X

Combustion chemistry at stationary sources, such as electrical utilities and industrial sites, contributes roughly one-half of the total anthropogenic NO_X emissions; mobile source emissions make up most of the rest.

Ambient annual [NO_X] have decreased ~35% in the period 1990–2005.

Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils.

NO and N_2O can be emitted from soils as intermediate products from denitrification, either naturally; or as stimulated by addition of N containing fertilizers to crops and other soil management practices.

N_2O is a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2-equivalent basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this number.

PRB [NO_2] are <300 ppt over most of the CONUS and <100 ppt in the eastern United States on an annual average basis. The 24-h ambient [NO_2] in CMSAs where most monitors are located were, on average, <20 ppb with a 99%ile value <50 ppb for the years 2003–2005. Annual-average [NO_2] over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.

Energy production at electrical generating units (EGUs) accounts for nearly all SO_X emissions in the United States; very little SO_X is emitted by transportation-related and other sources.

Ambient annual [SO_X] has decreased ~50% in the period 1990–2005.

Annual-average policy-relevant background [SO_2] are <10 ppt over most of the CONUS, or <1% of observed [SO_2] everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.

NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices.

3.13.2 Deposition of Nitrogen and Sulfur

Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the United States and comprises ~50 to 75% of the total N atmospheric deposition.

Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes that are high in N, of which 30% to 70% may be emitted as NH_3. This increase in NH_3 emissions, and consequent increase in NH_4^+ deposition, correlates well with the local and regional increases in agricultural intensity.

For the period 2004–2006, the routine monitoring networks report the mean N deposition in the United States was greatest in the Ohio River valley, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg ha^{-1} yr^{-1}, respectively. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central United States, Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg ha^{-1} yr^{-1}, respectively. Deposition primarily occurred as wet NO_3 and NH_4, followed by dry HNO_3, dry NH_4, and dry NO_3. Although deposition in most areas of the United States occurred in wet form, there were some exceptions, including parts of California where N deposition was primarily dry. Data are very sparse for the central United States between the 100th meridian and the Mississippi River; but, where available, N deposition values there are lower than most of the eastern United States, ranging from 4.1 to 5.3 kg ha^{-1} yr^{-1}.

For the period 2004–2006, mean S deposition in the United States was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg ha^{-1} yr^{-1}, in the Ohio River valley where most recording stations reported three-year averages >10 kg ha^{-1} yr^{-1}. Numerous other stations in the East reported S deposition >5 kg ha^{-1} yr^{-1}. Total S deposition in the United States west of the 100th meridian is relatively low, with all recording stations reporting less than 2 kg ha^{-1} yr^{-1} and many reporting less than 1.0 kg ha^{-1} yr^{-1}. S was primarily deposited as wet SO_4 followed by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry SO_4. However, these S data in the western United States, like those for N deposition, are very thinly spread over the landscape there.

N from atmospheric deposition is estimated to comprise 10 to 40% of the total input of N to many coastal estuaries, and could be higher for some. Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape, are then computed using measurements of wet and dry N deposition where these are available, and then interpolated with or without a set of air quality model predictions.

Atmospheric inputs of reactive N directly to the surface of coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of external N loadings to these systems: 11, 5.6, and 5.6 kg N ha^{-1} yr^{-1} for the northeast Atlantic coast of the United States, the southeast Atlantic coast of the United States, and the eastern Gulf of Mexico, respectively.

Atmospheric N loads to great waters and estuaries in the United States are estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the Catherines-Sapelo estuary (Castro et al., 2003) at the highest end.

At Chesapeake Bay, where N and S deposition and ecological effects have been extensively studied, total atmospheric deposition of atmospheric NO_3 is estimated to contribute from 20 to 30% of total N and 14% of the NH_4 loadings to the Bay.

TABLE 3.11-1. 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 3.11-2. 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_2O (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 3.11-3. 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 3.11-4. CHARACTERISTICS OF PRINCIPAL AIRSHEDS FOR REDUCED-NITROGEN DEPOSITION

Watershed	Principal Red-N Airshed Area (km^2)	Red-N Area as % of OX-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH_3 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.

4. EFFECTS OF ACIDIFICATION AND NITROGEN ENRICHMENT ON ECOSYSTEMS AND OTHER WELFARE EFFECTS

This chapter is organized into four sections. The introduction (Section 4.1) frames several important concepts in this assessment including basic principles of ecology, a definition of ecosystem service categories and challenges with defining adversity. Section 4.2 presents a discussion of acidification. Section 4.3 addresses nitrogen (N) enrichment. Lastly, in Section 4.4, other welfare effects are presented, including interactions between sulfur (S) deposition and mercury (Hg) methylation, gas phase injury to vegetation, nitrous oxide (N_2O) as a greenhouse gas (GHG) and drinking water quality.

4.1 INTRODUCTION TO ECOLOGICAL CONCEPTS

4.1.1 Ecosystem Scale, Function, and Structure

To address the effects of oxides of nitrogen and sulfur (NO_X and SO_X, respectively) on ecosystems, this Integrated Science Assessment (ISA) presents information collected at multiple scales of inquiry, ranging from individual physiology of a given species to population, community, and ecosystem-level investigations. For the purpose of this assessment, *ecosystem* is defined as a functional entity consisting of interaction groups of living organisms and their abiotic (chemical and physical) environment. 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.

Ecosystems have both structure and function. Structure refers to the species richness, abundance, and community composition that ultimately relate to ecosystem biodiversity. Competition among species and their tolerance to environmental stresses are key elements of survivorship. When environmental conditions shift, e.g., by the presence of anthropogenic air pollution, these competitive relationships may change and tolerance to stress may be exceeded. Function refers to the suite of processes and interactions among the ecosystem components and their environment that involve nutrient and energy flow. The plant processes of photosynthesis, nutrient uptake, respiration, translocation carbon (C) allocation, and biosynthesis are directly related to functions of energy flow and nutrient recycling. The energy accumulated and stored by vegetation (via photosynthetic C capture) is available to other organisms. Energy moves from one organism to another through the food chain in one direction, until it is ultimately released as heat. Nutrients and water can be recycled. Air pollution alters the function of ecosystems when nutrient cycle or the energy flow is altered.

4.1.2 Ecosystem Services

Ecosystem structure and function may be translated into ecosystem services. Ecosystem services identify the varied and numerous ways that ecosystems are important to human welfare. Ecosystems provide many goods and services that are of vital importance for the functioning of the biosphere, and provide the basis for the delivery of tangible benefits to human society. Hassan et al. (2005) define these to include supporting, provisioning, regulating, and cultural services.

> i. Supporting services are necessary for the production of all other ecosystem services. Some examples include biomass production, production of atmospheric oxygen, soil formation and retention, nutrient cycling, water cycling, and provisioning of habitat. Biodiversity is a supporting service that is increasingly recognized to sustain many of the goods and services that humans enjoy from ecosystems. These provide a basis for three higher-level categories of services.
>
> ii. Provisioning services, such as products (cf. Gitay et al., 2001), i.e., food (including game, roots, seeds, nuts and other fruit, spices, fodder), fiber (including wood, textiles), and medicinal and cosmetic products (including aromatic plants, pigments).
>
> iii. Regulating services, which are of paramount importance for human society such as (a) C sequestration, (b) climate and water regulation, (c) protection from natural hazards such as floods, avalanches, or rock-fall, (d) water and air purification, and (e) disease and pest regulation.
>
> iv. Cultural services, which satisfy human spiritual and aesthetic appreciation of ecosystems and their components.

4.1.3 Quantifying Adverse Effects of Anthropogenic Pollution

Quantifying adverse effects of pollution to ecosystems has been a challenge to the secondary National Ambient Air Quality Standards (NAAQS) process from the onset (Tingey et al., 1990). The following section discusses critical loads as a conceptual approach for quantifying adversity. A second approach for quantifying adversity is valuation, this method is discussed in more detail in Annex 10.

4.1.3.1 Critical Loads

Critical loads are used to express the amount of deposition of an atmospheric pollutant (a "load") that can be tolerated by natural or man-made systems without significant harm or change occurring in those systems. The generally accepted definition of a critical load of atmospheric pollutant deposition emerged from a pair of international workshops held in the late 1980s (Nilsson, 1986; Nilsson and Grennfelt, 1988). The workshop participants defined a critical load as:

> "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."

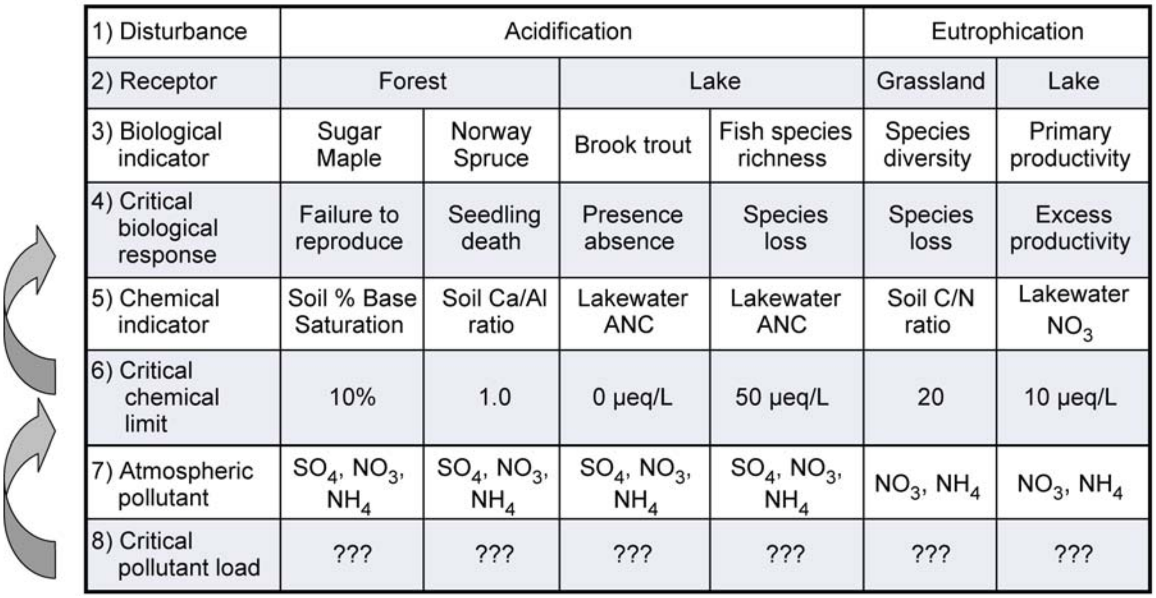
In North America, critical loads studies have been undertaken in Canada, partly to support efforts to design emission reduction programs (RMCC, 1990; Jeffries and Lam, 1993). Critical loads modeling was included in the 1997 Canadian Acid Rain Assessment (Jeffries, 1997) for several regions in eastern Canada. More recently, critical loads have been determined and mapped for waters and forest soils for a number of regions in eastern Canada and acid-sensitive lakes on the Canadian pre-Cambrian shield.

The Conference of New England Governors and Eastern Canadian Premiers (NEG/ECP) has undertaken a program to "estimate sustainable acidic deposition rates and exceedences for upland forests representative of the New England States and the Eastern Canadian Provinces…" (NEG/ECP Forest Mapping Group, 2001). The Forest Mapping Working Group within the NEG/ECP conducts regional assessments of the sensitivity of northeastern North American forests to current and projected S and N emissions levels. The NEG/ECP have also provided estimates of critical loads for surface waters in northeastern North America (cf. Dupont et al., 2005).

Aside from the NEG/ECP studies and the national mapping effort of McNulty et al. (2007), most critical loads studies on N and S in the United States have focused on smaller sub-regional areas or individual sites. Critical loads studies for forests in the United States have been centered in the Northeast and have usually used a catchment-based approach (cf. Pardo and

Driscoll, 1996; Aber et al., 2003; Driscoll et al., 2003a). Critical load studies for surface waters have been more extensive throughout the Eastern region. Critical loads have been estimated for lakes in the Northeast (cf. Driscoll et al., 2001b; Pembrook, 2004) and for streams in the Mid-Atlantic States and central Appalachians (Sverdrup et al., 1992; Sullivan et al., 2004a). In the western United States, there have been a few studies of critical loads for acidification of surface waters (cf. Sullivan et al., 2005). The primary concern in the West, however, has been for the critical load of N deposition affecting both terrestrial and aquatic resources through eutrophication and/or N enrichment affecting community structure (cf. Baron et al., 1994, 2000; Williams and Tonnessen, 2000; Fenn et al., 2003a; Burns, 2004; Nydick et al., 2004a).

The development of a quantitative critical load estimate requires a number of steps (Figure 4.1-1). Eight general steps must be taken to define the basic critical load question in any analysis.



1) Disturbance	Acidification				Eutrophication	
2) Receptor	Forest		Lake		Grassland	Lake
3) Biological indicator	Sugar Maple	Norway Spruce	Brook trout	Fish species richness	Species diversity	Primary productivity
4) Critical biological response	Failure to reproduce	Seedling death	Presence absence	Species loss	Species loss	Excess productivity
5) Chemical indicator	Soil % Base Saturation	Soil Ca/Al ratio	Lakewater ANC	Lakewater ANC	Soil C/N ratio	Lakewater NO_3
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	NO_3, NH_4	NO_3, NH_4
8) Critical pollutant load	???	???	???	???	???	???

Figure 4.1-1. An example of the matrix of information that must be considered in the definition and calculation of critical loads (see discussion in text). Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits could be used.

1. Identify the *ecosystem disturbance* that is occurring (e.g., acidification, eutrophication). Not all disturbances will occur in all regions or at all sites, and the degree of disturbance may vary across landscape areas within a given region or site.

2. Identify the *landscape receptors* subjected to the disturbance (e.g., forests, surface waters, crops). Receptor sensitivity may vary locally and/or regionally, and the hierarchy of which receptors are most sensitive to what kind of disturbance may vary as well.

3. Identify the *biological indicators* within each receptor that are affected by atmospheric deposition (i.e., individual organism, species, population, or community characteristics). Indicators will vary geographically and perhaps locally within a given receptor type.

4. Establish the *critical biological responses* that define "significant harm" to the biological indicators (e.g., presence/absence, loss of condition, reduced productivity, species shifts). Significant harm may be defined differently for biological indicators that are already at risk from other stressors, or for indicators that are perceived as "more valued."

5. Identify the *chemical indicators* or variables that produce or are otherwise associated with the harmful responses of the biological indicators (e.g., streamwater pH, lake aluminum (Al) concentration, soil base saturation). In some cases, the use of relatively easily measured chemical indicators (e.g., surface water pH or acid neutralizing capacity [ANC]) may be used as a surrogate for chemical indicators that are more difficult to measure (e.g., Al concentration).

6. Determine the *critical chemical limits* for the chemical indicators at which the harmful responses to the biological indicators occur (e.g., $\mathrm{pH} < 5$, base saturation $<5\%$, inorganic Al concentration greater than 2 μM). Critical limits may be thresholds for indicator responses such as presence/absence, or may take on a continuous range of values for continuous indicator responses such as productivity or species richness. Critical limits may vary regionally or locally depending on factors such as temperature, existence of refugia, or compensatory factors (e.g., high calcium (Ca) concentration mitigates the toxicity of Al to fish and plant roots).

7. Identify the *atmospheric pollutants* that control (affect) the pertinent chemical indicators (e.g., deposition of sulfate [SO_4^+], nitrate [NO_3^-], ammonium [NH_4^+], nitric acid [HNO_3]). Multiple pollutants can affect the same chemical variable. The relative importance of each pollutant in producing a given chemical response can vary spatially and temporally.

8. Determine the *critical pollutant loads* (e.g., kg ha^{-1} yr^{-1} total deposition of S or nitrate-N) at which the chemical indicators reach their critical limits. Critical pollutant loads usually include both wet and dry forms of pollutant deposition. The critical pollutant load may vary regionally within a receptor or locally within a site (as factors such as elevation or soil depth vary) and may vary temporally at the same location (as accumulated deposition alters chemical responses).

The development of the critical load approach for a region or an individual site generally requires that we work down the table from top to bottom (Figure 4.1-1). What is the disturbance? What receptors are affected? What indicator organisms are (or previously were) present and observable? What chemical indicators are changing and can be measured? What atmospheric pollutant is driving the changes in the chemical indicators?

The derivation of a quantitative estimate of a critical load generally requires that we work from the bottom of the table back towards the top (as indicated by the arrows in Figure 4.1-1). What is the maximum load of a pollutant that will cause a shift in the chemical indicator to its critical limit such that a critical indicator response occurs (or does not occur)? From this point of view, it can be seen that steps 8 and 6 require the development of dose-response functions for the components of the ecosystem being considered (arrows in Figure 4.1-1). Step 8 describes the response of the chemical indicator as a function of the pollutant load, and step 6 describes the responses of the biological indicator as a function of the chemical variable.

There is, therefore, no single “definitive” critical load for a natural resource. Critical loads estimates are explicitly policy-linked and their reliability is conditioned on the soundness of the underlying science. As elements of the critical load process change, the critical loads estimates will change to reflect the current state-of-knowledge and policy priorities. Changes in scientific understanding may include, e.g., new dose-response relationships; better resource maps and inventories; larger survey datasets; continuing time-series monitoring; improved numerical models. Changes in the policy elements may include new definitions of harm; new mandates for resource protection; focus on new pollutants, and inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

This procedure will almost certainly result in calculation of multiple critical load values for a given pollutant and analysis location. The multiple solutions derive from the nested sequence of disturbances, receptors, and biological indicators that must be considered for a given pollutant. Multiple critical load values may also arise from an inability to agree on a single definition of “significant harm” at step 4. Calculation of critical loads for multiple definitions of “harm” may be deemed useful in subsequent discussions of the analysis and in the decision-making steps that may follow critical load calculation.

Finally, there is the inescapable heterogeneity of all natural environments. Consider soils, for instance. The high spatial variability of soils almost guarantees that for any reasonably sized soil-based “receptor” that might be defined in a critical load analysis, there will be a continuum of critical load values for any indicator chosen. The range of this continuum of values may be narrow enough to be ignored; nevertheless, there is an a priori expectation in any critical load analysis that multiple values (or a range of values) will result from the analysis. Given the policy requirements for establishing critical loads and the heterogeneity of ecosystem impacted by acidic deposition, we have not attempted to define critical loads for the United States in this ISA.

4.2 ECOLOGIC EFFECTS OF ACIDIFICATION

4.2.1 Effects on Major Biogeochemical Processes

Acidic deposition has altered major biogeochemical processes in the United States by increasing the S and N content of soils, accelerating SO_4^+ and NO_3^- leaching from soil to drainage water, depleting base cations (especially Ca and magnesium [Mg]) from soils, and increasing the mobility of Al. The extent of soil acidification is a critical factor that regulates virtually all acidification-related ecosystem effects from S and N deposition. Soil acidification occurs in response to both natural factors and acidic deposition. To best integrate the effects of acidic deposition, this assessment starts with a description of the effects on soils and major biogeochemical processes within ecosystems, then summarizes the chemical and biological effects on terrestrial, transitional, and aquatic ecosystems.

4.2.1.1 Soil Acidification

Soil acidification is the buildup of hydrogen cations (H^+), also called protons, in the soil. This happens when a proton donor is added to the soil. Soil acidification can be a natural process. However, the donor can also be a mineral acid, such as HNO_3 and sulfuric acid (H_2SO_4), the common components of acid rain that result from NO_X and SO_X air pollution. Decreases in soil pH attributable to acidic deposition have been documented in the United States. Effects in the eastern United States appear to have been limited mainly to the Northeast and portions of the Appalachian Mountains in both hardwood and coniferous forests. Soil acidification has also probably occurred in localized areas of mixed conifer forest and chaparral vegetation in, and near, the Los Angeles Basin, in response to locally high levels of atmospheric dry N deposition.

To evaluate soil acidification, the soil must be considered in terms of the surface organic layer (the primary rooting zone), of which the Oa horizon (or in some studies the O horizon, which combines the Oe and Oa horizons) is an important component (See Figure 4.2-1). In addition, the B horizon, which lies below the Oa horizon and is primarily comprised of mineral matter, must be considered.

Acidity deposited from the atmosphere can have a direct effect on soil pH. However, net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter. This process can decrease the pH of soil water in the Oa horizon well below the lowest pH values measured in acidic deposition (Krug et al., 1985; Lawrence et al., 1995). Oa-horizon soils under coniferous vegetation are strongly acidified by organic acids and are unlikely to have experienced a lowering of pH as a result of acidic deposition (Johnson and Fernandez, 1992; Lawrence et al., 1995). Soils influenced by the growth of hardwood species tend to be less acidic naturally and are, therefore, more susceptible to decreased pH in the Oa horizon from acidic deposition.

Several studies document declines in soil pH within the Oa/A horizons and the upper B horizon in sensitive regions of the United States over the past several decades (Johnson et al., 1994a,b; Drohan and Sharpe, 1997; Bailey et al., 2005). These declines have been attributed at least partly to acidic deposition (Bailey et al., 2005).

In summary, soil acidification is a natural process, which is often exacerbated by acidic deposition. Natural acidification is particularly pronounced in coniferous forests. Acidic deposition can contribute to soil acidification, with consequent effects on the availability of nutrient cations in soil and the chemistry of drainage water that flows from soil into streams and lakes.

4.2.1.2 Sulfur Accumulation and SO_4^+ Leaching

Most acidification-related consequences of atmospheric S and N oxide deposition in the United States are caused by SO_4^+ (Sullivan, 2000; Driscoll et al., 2001a). The mobility within the watershed of SO_4^+, derived from atmospheric S deposition, is the primary factor governing

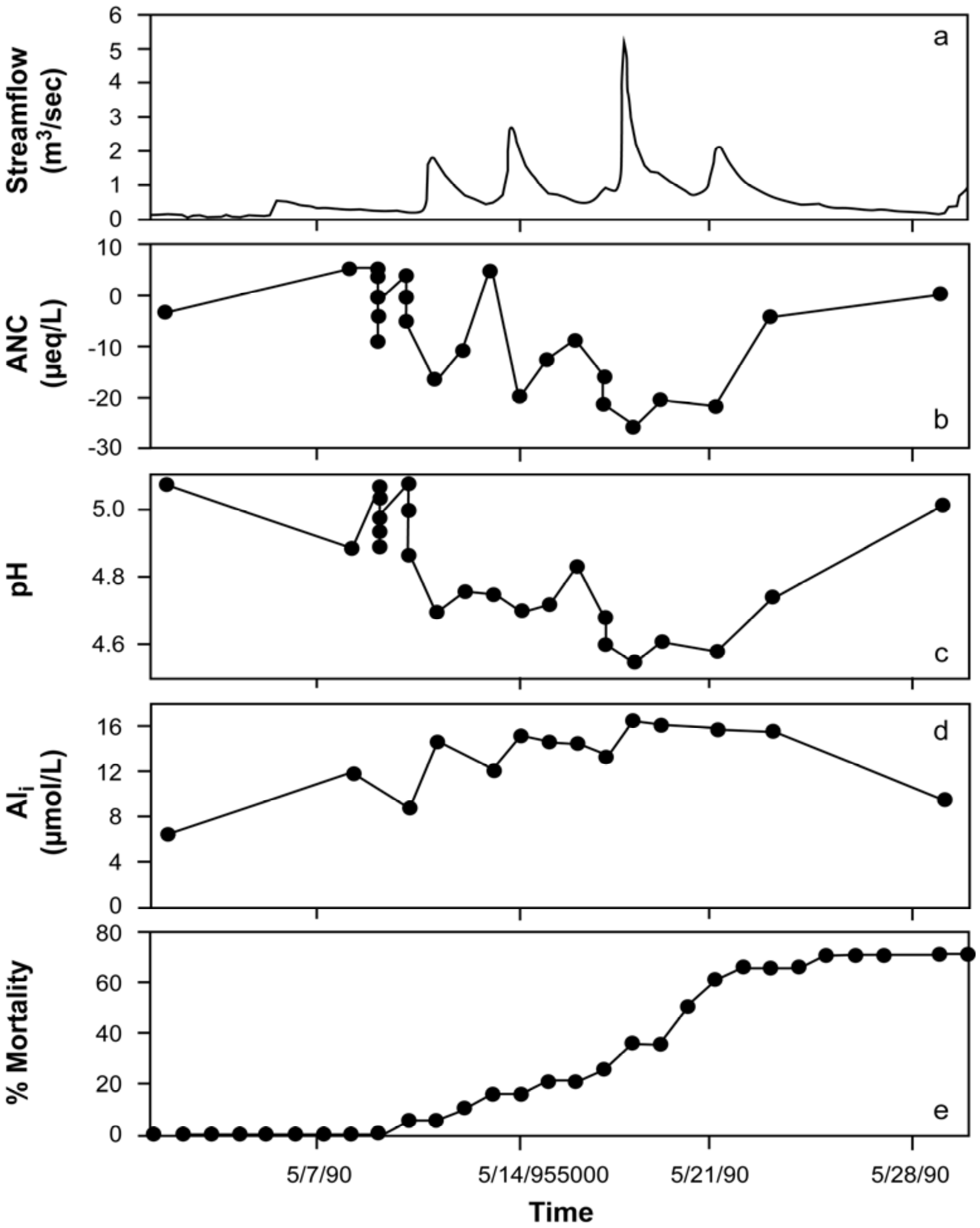


Figure 4.2-1. Diagram illustrates "ideal" soil horizons to which many soils conform. Each main horizon is denoted by a capital letter: O) Organic matter: Litter layer of plant residues in relatively undecomposed form. A) Surface soil: Layer of mineral soil with most organic matter accumulation and soil life. This layer is depleted of iron, clay, aluminum, organic compounds, and other soluble constituents. B) Subsoil: This layer accumulates iron, clay, aluminum and organic compounds. C) Substratum: Layer of unconsolidated soil parent material. This layer may accumulate the more soluble compounds that bypass the "B" horizon.

Source: Driscoll et al. (2001b).

most aspects of soil and water acidification at most of the locations in the United States that are affected by acidic deposition.

Upon deposition to the Earth's surface, S may be assimilated by vegetation or microbes, accumulate in the soil or act as a mobile ion and leach out of the soil. When a given area is affected by acidic deposition, S deposition levels are typically much higher than plant demand for S and consequently almost all deposited S moves into the soil where it may accumulate and is available for leaching as SO_4^+. SO_4^+ acts as a mobile ion at many locations in the United States that receive high levels of S deposition, notably the glaciated Northeast and Upper Midwest, where much of the deposited S leaches through soils into streams and lakes. SO_4^+ leaching leads to most of the ecological impacts from atmospheric S deposition because it is accompanied by leaching of other ions, and this contributes to acidification of soil, soil water, and surface water.

Over time, sustained SO_4^+ leaching and associated soil acidification contribute to pronounced changes in soils in some areas. When S moves from soils to surface waters in the form of SO_4^+, an equivalent amount of cations, or countercharge, is also transported. When the countercharge is provided by base cations, the base saturation of the soil is reduced as the acidity of the soil water is neutralized. However, this process acidifies the soil, thereby decreasing the soil's capacity to neutralize additional acidity deposited from the atmosphere and prevent acidification of soil water, and by connection, surface water. As the base cations become depleted, the countercharge provided by acidic cations (hydrogen and inorganic Al) increases, sometimes resulting in toxic conditions for plant roots and aquatic organisms.

In the United States, there are some regional trends of soil accumulation, retention, and leaching of S that are discussed below.

Southeast

Accumulation of atmospherically deposited S in soil has resulted from anion adsorption and incorporation of S into organic matter through biological assimilation. Such retention of S can temporarily reduce SO_4^+ leaching and cause a delay in ecosystem recovery in response to changes in S deposition, as accumulated S is slowly released from the soil into drainage water. S adsorption on soil is especially pronounced in the southeastern United States, where it is expected to cause further acidification of some streams in the foreseeable future, even under substantially reduced levels of S deposition (Sullivan et al., 2004a).

Northeast

In the Northeast, accumulation of atmospherically deposited S in the past was demonstrated by a positive relationship between wet deposition of SO_4^+ and concentrations of total S in the forest floor of 12 red spruce stands (Driscoll et al., 2001b). However, net loss of S from soils now appears to be occurring in a number of northeastern watersheds in response to decreased levels of atmospheric S deposition. Where leaching of previously stored S occurs, it delays soil and surface water chemical recovery from acidification (Driscoll et al., 2001a).

Uncertainties in estimates of ecosystem S fluxes, such as weathering and dry deposition, and complications in discerning the effects of S desorption from mineralization make it difficult to predict when S outputs in the northeastern United States will no longer exceed inputs. Recent research results, based on experimental reduction of S inputs, suggest that this process will occur on a decadal timescale (Martinson et al., 2005; Mörth et al., 2005). The long-term role of C-bonded S adds further uncertainty because enhancement of S mineralization by a warming climate could also affect S retention and release from soil (Knights et al., 2000; Driscoll et al., 2001b).

In summary, atmospheric S deposition alters soil chemistry through the following mechanisms: (1) sustained SO_4^+ leaching and associated changes in soil chemistry, and (2) accumulation of S in the soil through physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S from soils at a number of sites in the Northeast is a likely response to recent decreases in atmospheric S inputs (Driscoll et al., 2001a). The gradual loss of previously accumulated S is further contributing to continued SO_4^+ leaching and soil acidification.

4.2.1.3 Nitrogen Accumulation and NO_3^- Leaching

This scope of this section is the role of N deposition in the process of acidification. This assessment divides the effects of N deposition into the two broad categories of acidification and N nutrient enrichment effect. The latter is discussed in Section 4.3. N deposition may cause acidification of ecosystems via two mechanisms: (1) excess accumulation in soils followed by increased rates of nitrification by microbes and (2) change in base cation status of soils caused by NO_3^- leaching.

Nitrification and Accumulation

Atmospherically deposited N accumulates in soil through incorporation of N into organic matter. Accumulation is either documented or suggested to occur across large areas of the United States. Direct evidence for such accumulation has been found in the northeastern United States and in Colorado. Increased accumulation of N in soil is suggested, for example, by a positive correlation between atmospheric deposition levels and total N concentration in the Oa soil horizon at red spruce sites in New York, Vermont, New Hampshire, and Maine (Driscoll et al., 2001b). Evidence that atmospheric deposition has increased the availability of N in soil is also provided by the strong negative correlation between atmospheric deposition levels and the C:N ratio of the Oa soil horizon across the northeastern United States (Aber et al., 2003).

Nitrification is the microbial-mediated reduction of NH_4^+ to NO_3^- that produces acidity in the form of HNO_3. It is important to introduce the concept of N saturation to understand how the N accumulation and status of terrestrial ecosystems relates to elevated rates of nitrification. N saturation refers to the condition when N inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem. Excess N supply reduces competition between plants and heterotrophic microbes for NH_4^+ to the point that net nitrification occurs (Aber et al., 1998, 2003). The nitrification process is mediated by autotrophic bacteria that derive energy by reducing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils. This process often results in elevated NO_3^- concentration in soil waters and surface waters (Aber et al., 2003; Ross et al., 2004). Thus, data collected from streams and lakes can yield important information about processes that occur in the soil.

Leaching

In many upland forested areas in the United States, a large fraction of the N received in atmospheric deposition is retained in soil. Nevertheless, elevated NO_3^- concentration in surface waters during the growing season is common and widespread in the United States. High concentrations of NO_3^- in lakes and streams, indicative of ecosystem N saturation in most natural systems, have been found at a variety of locations throughout the United States

(Stoddard, 1994; U.S. Environmental Protection Agency, 2004). In general, atmospheric deposition of 8 to 10 kg ha^{-1} yr^{-1} of N or more, results in NO_3^- leaching to surface waters in the eastern United States. Lower N deposition levels (less than 5 kg N ha^{-1} yr^{-1}) may lead to NO_3^- leaching in the mountainous West because of colder temperatures, shorter growing season, little soil development, extensive exposed bedrock, and rapid melting of large snowpacks (Baron et al., 1994; Williams et al., 1996a).

NO_3^- leaching usually contributes to the leaching of base cations from soils to surface waters. Although there is typically less NO_3^- than SO_4^+ leaching in most ecosystems in the United States, concentrations of NO_3^- in some streams are high enough to suggest a substantial role for NO_3^- in base cation loss from soil, particularly during periods of high soil-water NO_3^- flux during the nongrowing season (Van Miegroet et al., 1992; Cook et al., 1994).

The relationship between atmospheric N deposition and NO_3^- leaching from terrestrial ecosystems is often modified by land-use history, current land-use, and climate. The N retention capacity of soils is highly dependent on land-use history. For example, the removal of trees reduces the amount of N in the watershed and enhances the demand of vegetative regrowth for added N. This effect results in little or no NO_3^- leaching and can last for decades to more than a century (Goodale et al., 2000). NO_3^- leaching is also affected by current land use. In the northeastern United States, concentrations of N in streams of upland forested watersheds tend to be considerably lower than in streams draining watersheds with other land uses. Perhaps the most noteworthy affect of urban land use on processes of nutrient enrichment from N deposition concerns the transport of NO_3^- to N-limited estuarine and near-coastal waters. This topic is discussed in Section 4.3.2.2. In agricultural, and especially in forested areas it is generally expected that most atmospherically deposited N is taken up by terrestrial vegetation. This is usually not the case in urban landscapes, although it is sometimes possible. Due to the relatively large impervious surface area in the urban landscape (e.g., buildings, roads, parking lots), a higher percentage of precipitation is routed directly to surface waters, with little opportunity for vegetative uptake of deposited N.

Climatic factors also play an important role in determining the extent of NO_3^- leaching. In particular, temperature and moisture have large effects on N cycling and NO_3^- leaching. Murdoch et al. (1998) found that, for at least one site, annual mean NO_3^- concentrations in stream water were not related to annual wet N deposition, but rather were positively correlated with mean annual air temperature. This was likely due partly to the fact that microbial processes responsible for NO_3^- production are very sensitive to temperature. Fluctuations in microbial immobilization and mineralization in response to climatic variability affect NO_3^- losses to drainage waters.

Long-term data sets also suggest that climate may affect patterns of NO_3^- loss. Many of the original (sampled periodically since the early 1980s) long-term monitoring lakes in the Adirondack Mountains showed increased NO_3^- leaching from terrestrial ecosystems throughout the 1980s, which was followed by a decline during the 1990s. Decreasing stream NO_3^- concentrations during the 1990s was also observed in the Catskill Mountains and in New Hampshire. There was not a substantial change in N emissions or deposition in the Northeast region over that period. Climatic factors, increases in atmospheric carbon dioxide (CO_2), and interactions with increasing availability of dissolved organic carbon (OC) have been proposed as possible contributing factors for regional decreases in NO_3^- in drainage water during the 1990s, but the driver of this decadal scale pattern remains under investigation.

4.2.1.4 Base-Cation Leaching

Acidic deposition has been shown to be an important factor causing decreases in concentrations of exchangeable base cations in soil. Loss of base cations from soil is a natural process. Under natural conditions of low atmospheric deposition of S and N the limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching. Because inputs of S and N in acidic deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

Leaching of base cations from watershed soils to surface waters is a mechanism that (1) depletes essential plant nutrients from soil and (2) limits the extent of surface water acidification in response to acidic deposition. When SO_4^+ and NO_3^- leaching occur in equal magnitude to base cation leaching, the drainage water is not acidified. However, in the process of neutralizing the acidity of drainage water, base cation release from soil causes depletion of the base saturation of the soil. Once base cations in the soil become depleted, Al is mobilized from soil into drainage water, with potentially harmful consequences for sensitive terrestrial plants and aquatic organisms throughout the food web.

In the 1990s, data were published supporting the occurrence of base cation depletion from soils in the United States, although decreases in exchangeable Ca concentrations had earlier been identified in European soils through repeated sampling. Recent data reveal that decreases in concentrations of exchangeable base cations and base saturation in the Oa and B soil horizons have occurred over the past several decades in the eastern United States and most studies attribute this change to the effects of acidic deposition. For example, the most thorough soil re-sampling study in the United States was conducted in northwestern Pennsylvania by Bailey et al. (2005). This study showed that between 1967 and 1997 pronounced decreases, attributed largely to acidic deposition, were measured in exchangeable Ca and Mg concentrations in Oa/A horizons and throughout the B horizon. Similarly, Sullivan et al. (2006a,b) documented base saturation of B-horizon soils in the Adirondack Mountains between the mid-1980s and 2003. The depletion of base cations contributes to soil acidification and influences the ability of watershed soils to support acid-sensitive vegetation and to neutralize acidity in future acidic deposition.

Upslope decreases in exchangeable soil base cation concentrations were found to be positively correlated with higher S deposition in the Catskill Mountains (Lawrence et al., 1999). Furthermore, declines in surface water base cation concentrations have been attributed to decreases in soil exchangeable base cations in New Hampshire (Likens et al., 1996) and Norway (Kirchner and Lydersen, 1995). In summary, leaching of base cations associated with acidic deposition is occurring in sensitive regions in the United States. Base cation loss increases the sensitivity of the watershed to further acidic deposition. Watersheds that were capable of fully neutralizing a particular level of acidic deposition in the past may no longer be capable of fully neutralizing that level today or at some time in the future because of the cumulative effect of acidic deposition on soil base saturation. Where the availability of exchangeable base cations is limited, the leaching of potentially toxic inorganic Al into soil and surface waters can result.

4.2.1.5 Aluminum Leaching

If soil base saturation is 20 to 25%, or lower, acidic deposition can mobilize inorganic Al, which can lead to the leaching of this toxic form of Al into soil waters and surface waters (Reuss and Johnson, 1985). This is an extremely important effect of acidic deposition because inorganic Al is toxic to tree roots, fish, algae, and aquatic invertebrates (see Section 4.2.3). In fact, fish mortality in response to surface water acidification is usually attributable to Al toxicity. Increases in the concentration of exchangeable Al in soil over the past several decades have been documented at several locations in North America and Europe. Increased amounts of exchangeable inorganic Al in the mineral soil have been identified through repeated soil sampling over periods ranging from 17 years to 41 years (see discussion in Annex 4). In areas of Europe with very high acidic deposition levels, evidence of inorganic Al depletion in the mineral soil has also been found. Al depletion has not been documented in the United States.

Acidic deposition is an important cause of increased mobilization of inorganic Al from soils to streams and lakes. Acidic deposition introduces mineral acidity associated with anions that are more mobile than those from organic matter. If the release of base cations from the soil is insufficient to neutralize the inputs of sulfuric and HNO_3, then Al that had previously been deposited by normal soil development in the upper mineral soil is mobilized. Al may also be mobilized by organic acids. However, acidic deposition, mobilizes Al in inorganic forms, and in doing so increases the amount of exchangeable inorganic Al within the B horizon and results in transport of inorganic Al into soil waters and surface waters. Inorganic Al is minimally soluble at pH about 6.0. Solubility increases steeply at pH values below about 5.5. This distinction between organic and inorganic forms of Al is important because organic Al is not toxic, whereas inorganic Al is toxic to a variety of plants and aquatic organisms (Section 4.2.3.1.6).

Recovery of soil chemistry will require a decrease in exchangeable Al concentrations and Al leaching. It is unclear what level of Ca weathering, and for what length of time, would be required to decrease soil exchangeable Al concentrations to levels characteristic of unpolluted systems. Furthermore, in most cases it is unclear whether exchangeable Al concentrations are continuing to increase, remaining stable, or decreasing. Predictions of future trends in exchangeable Al concentrations remain uncertain because of our incomplete understanding of mechanisms through which mineral matter and organic matter interact to control dissolved Al concentrations. Possible changes in the dynamics of soil organic matter that could be expected from climate change add further uncertainty to predictions of future change in exchangeable Al concentrations in soils.

In summary, the natural downward movement and deposition of Al within the upper soil profile is altered by acidic deposition if the release of base cations is insufficient to buffer atmospheric inputs of acidity. Rather than be deposited as an alumino-organic complex, Al mobilized by acidic deposition tends to stay in solution in an inorganic form that can be transported out of the soil and into surface waters. Depletion of exchangeable base cations precedes the mobilization of inorganic Al. Therefore, as base cation concentrations in drainage water decrease, inorganic Al concentrations increase. Increases in concentrations of inorganic Al have been documented at several locations in base-cation depleted soils in the United States and Europe. In soils with base saturation values less than about 15 to 20%, the ratio of exchangeable Ca to Al is typically low in upper mineral soils (Lawrence et al., 2005).

4.2.1.6 Short-Term Changes in Surface Water Chemistry: Episodic Acidification

The status of surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less buffering of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits lower pH and ANC during episodes than during baseflow conditions.

One of the most significant impacts of acidic deposition on surface water chemistry is the short-term change in chemistry that is termed “episodic acidification.” While natural processes contribute to seasonal and short-term increases in the acidity of surface waters, research from several regions in the United States indicates that acidic deposition has substantially increased the magnitude, frequency, and biological impacts of episodic acidification events.

Many streams that exhibit chemistry during base flow (relatively stable flows that occur between storms) that is suitable for aquatic biota, are subject to occasional episodic acidification with adverse consequences. During such episodes, both stream flow and water chemistry can change markedly (Figure 4.2-2). Episodic acidification events can cause declines in pH and ANC, and most significantly, increases in inorganic Al concentrations in stream waters of the Northeast, Pennsylvania, and southern Appalachia. Episodic decreases in pH and ANC have been documented throughout the country.

The EPA’s Episodic Response Project (ERP) confirmed the chemical and biological effects of episodic pH and ANC depressions in lakes and streams in parts of the eastern United States. The ERP illustrated the processes of episodic acidification and the role played by SO_4^+ and especially NO_3^- attributable to atmospheric deposition in the episodic acidification of

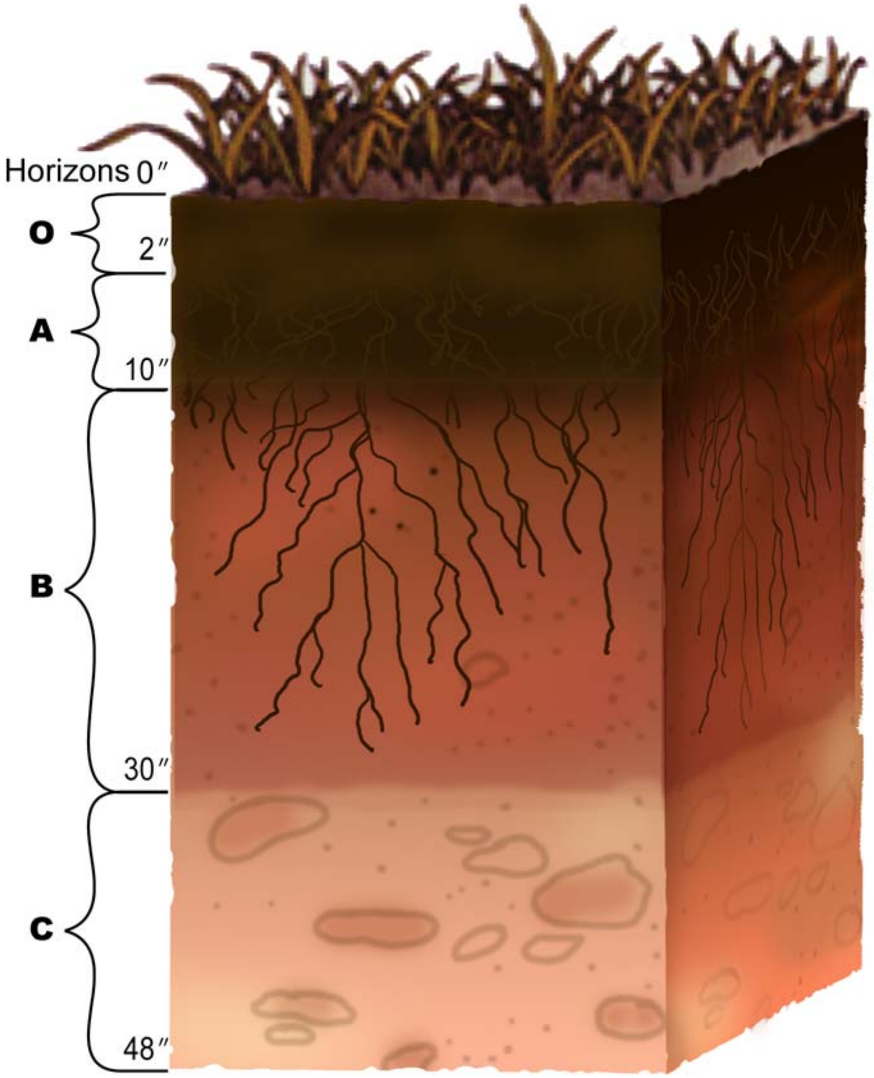


Figure 4.2-2. Results of an in situ bioassay during a period of episodic acidification in Buck Creek, Adirondack Mountains, in spring 1990: (a) discharge, (b) acid neutralizing capacity, (c) pH, (d) concentration of inorganic monomeric aluminum, and (e) cumulative percentage of mortality of brook trout over time.

Source: Driscoll et al. (2001b).

surface waters. The ERP also clearly showed that the episodic chemical response that has the greatest effect on aquatic biota is increased inorganic Al concentration (Wigington et al., 1996).

Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in inorganic Al in waters having low Ca concentration. Baker et al. (1990a) concluded that episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. The most thorough characterization of episodic variation in stream chemistry in the United States was conducted through the ERP, in which 13 low-order streams (watershed areas less than 24 km^2) in the Adirondack and Catskill regions of New York, and the Appalachian Plateau in Pennsylvania were monitored from 1988 to 1990 (Wigington et al., 1996). About 10% of the acid episodes involved decreases in ANC of up to 200 µeq/L, decreases in pH of up to one unit, and increases in concentrations of inorganic Al of up to 15 µM (Wigington et al., 1996). Results showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and inorganic Al concentration exceeded 3.7 µM, despite the relatively short duration of episodes (Baker et al., 1996).

Results from the ERP demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low flow, but low pH and high inorganic Al levels during high flow, had substantially lower numbers and biomass of brook trout than were found in nonacidic streams (Wigington et al., 1996).

In general, the most severe acidification of surface waters generally occurs during spring snowmelt (Charles, 1991) in many regions. Stoddard et al. (2003) found that, on average, spring ANC values in New England, the Adirondacks, and the Northern Appalachian Plateau were about 30 µeq/L lower than summer values during the period 1990 to 2000 (Figure 4.2-3). This implies that lakes and streams in these regions would need to recover to chronic ANC values above 30 µeq/L before they could be expected to not experience acidic episodes (Stoddard et al., 2003). However, the estimate of 30 µeq/L is certain to be low because the comparison was made with non-episodic sampling in spring, expressed as average spring ANC. Episodic ANC during spring would be expected to be lower than average ANC during spring.

The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt water and storm-flow water through the watershed. The routing of water as it flows through a watershed determines the degree of contact with acidifying orneutralizing materials and therefore influences (along with soils and bedrock characteristics) the amount of episodic acidification that occurs. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with deep versus

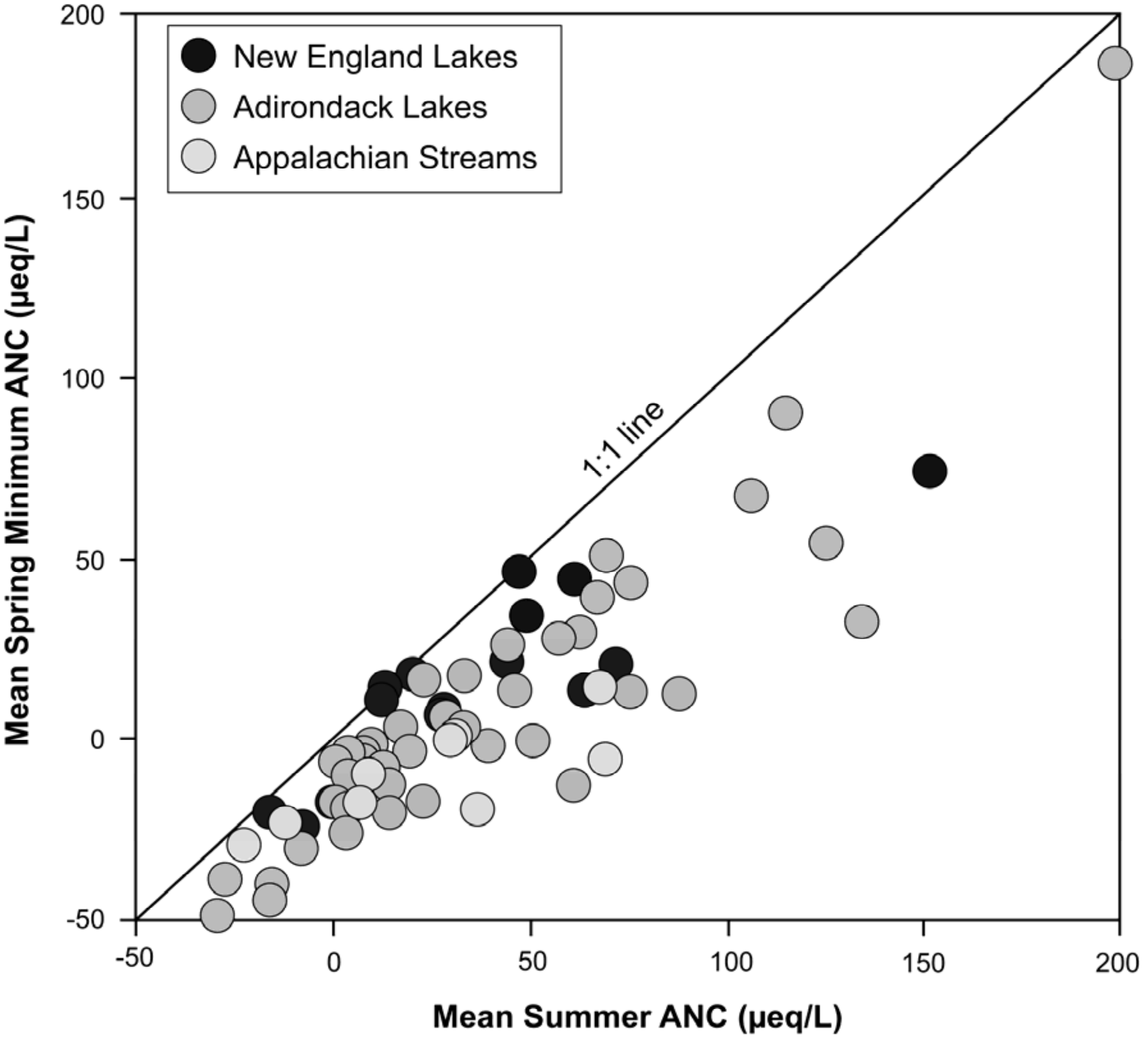


Figure 4.2-3. Relationship between mean summer ANC and the mean of minimum spring ANC values at long-term monitoring lake and stream sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

Source: Stoddard et al. (2003).

shallow soil horizons; the more subsurface contact, the higher the surface water ANC (Turner et al., 1991). This can be attributed in part to higher base saturation and (in some watersheds) greater SO_4^+ adsorption capacity in subsurface soils. It may also relate to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition and decay processes (Lynch and Corbett, 1989; Turner et al., 1991).

Streams having acidic episodes show significantly higher fish mortality and other aquatic community changes as compared with streams in which ANC remains above zero. Results from in situ bioassay studies from across the eastern United States show that acidic episodes (with associated low pH and elevated inorganic Al concentrations, and high streamwater discharge) induced rapid fish mortality under some conditions (Baker et al., 1996; Bulger et al., 1999; Driscoll et al., 2001b). For example, streams with suitable conditions during low flow, but moderate-to-severe episodic acidification during high flow, had higher fish mortality in bioassays, higher net downstream movement of brook trout during events, and lower brook trout abundance and biomass compared to streams that did not experience appreciable episodic acidification. These episodically impacted streams lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into refugia (areas with higher pH and lower inorganic Al) during episodes only partially mitigated the adverse effects of episodes (Baker et al., 1996).

Consideration of episodic acidification greatly increases the extent and degree of estimated impacts for acidic deposition on surface waters. In the Northeast, inclusion of episodically acidified water bodies in regional assessments substantially increases estimates of the extent of surface water acidification. For example, baseflow samples collected from 1991 to 1994 through the EPA Temporally Integrated Monitoring of Ecosystems (TIME) Program indicated that 10% of the 1,812 lakes larger than 1 ha surface area in the Adirondack region could be considered chronically acidic (ANC values less than 0 μeq/L), but that an additional 31% of these lakes had baseflow ANC values less than 50 μeq/L and were, therefore, estimated to be susceptible to episodic acidification (Driscoll et al., 2001b).

Lawrence (2002) estimated the extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km^2) using an index site at the base of the watershed that became episodically acidified at high flows. Upstream sites with a lower base flow ANC than the index site at the same date and time were found to have a high likelihood of becoming episodically acidified. Base flow sampling of 122 upstream sites indicated that approximately 16% of the total upstream reaches had chronic ANC less than 10 μeq/L, but that 66% of the stream reaches had episodic ANC less than 10 μeq/L.

In the Southeast, a recent study by Deviney et al. (2006) within Shenandoah National Park, Virginia used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the Shenandoah National Park catchments using catchment geology and topography to stratify watershed response patterns. On the basis of the models, they concluded that a large number of Shenandoah National Park streams had 6- to 168-h periods of low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically, on the basis of a 4-year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions that are classified with respect to brook trout response categories (Bulger et al., 1999) as indeterminate (ANC 20 to 50), episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous hours. Many catchments were predicted to have successive years of ANC values sufficiently low as to potentially extirpate some aquatic species (Deviney et al., 2006). The authors of the study reported that smaller catchments are more vulnerable to episodic acidification than larger catchments underlain by the same bedrock. Results from a study of six intensively monitored sites in the Park demonstrated a clear pattern of larger episodic ANC depressions in streams having higher median ANC than in streams with lower ANC. However, streams with low median ANC typically experienced decreases that resulted in minimum ANC values associated with toxicity to biota. These low ANC conditions were more likely to occur in streams underlain by siliclastic bedrock than in those with granitic or basaltic bedrock.

In the West, episodic acidification is an especially important issue for surface waters throughout high-elevation areas. Where soils are sparse, as in alpine regions, most snowpack N is flushed to surface waters early in the snowmelt period. Even though there is evidence through use of isotopic tracers that much of the N was cycled microbially, snowpack N has been reported to cause temporary acidification of alpine streams (Williams and Tonnessen, 2000; Campbell et al., 2002). Snowmelt-related temporary acidification of alpine lakes and streams and associated effects have been reported in the Rocky Mountains (Brooks et al., 1996; Williams et al., 1996a) and Sierra Nevada (Johannessen and Henriksen, 1978; Stoddard, 1995).

There have been no studies in the United States to determine if either the severity or frequency of episodic acidification has lessened in response to recent decreases in acidic deposition over the past three decades. In a study of two streams in Nova Scotia (Laudon et al., 2002), trends in ANC during four phases of storm hydrographs from 1983 to 1998 were not detected other than during the peak-flow phase of one stream (an increase of 0.87 µeq/L).

In summary, the vast majority of water chemistry data for acid-sensitive lakes and streams in the United States have been collected under low-flow conditions. It is well known, however, that water chemistry changes with season and with weather. Water chemistry is most stressful to aquatic biota (lowest pH and ANC; highest inorganic Al concentration) during high flow episodes that are associated with snowmelt and rainstorms. During such conditions, stream chemistry can be toxic to species that thrive under chemical conditions more typical of base flow. The EPA's ERP and other more localized studies have quantified the effects of episodes on fish. Episodes are driven by hydrological processes, but the acidification that occurs is largely a result of acidic deposition, especially in cases where inorganic Al has been mobilized. Consideration of such variability in water chemistry is critical for accurate assessment of the extent, magnitude, and biological effects of surface water acidification. The biological effects of changes in surface water chemistry are discussed in greater detail in Section 4.2.3.2.

4.2.2 Terrestrial Ecosystems

The changes in major biogeochemical processes and soil conditions described above contribute to a series of effects on terrestrial ecosystems. These changes are manifest in both chemical and biological effects that can include reduced soil base saturation, altered key element ratios, lowered plant productivity, reduced stress tolerance of sensitive plant species, and in some cases, increased mortality of canopy trees. Specific chemical indicators of change can be used to assess sensitivity to, and impacts from, acidic deposition. In the United States, terrestrial effects of acidification are best described for forested ecosystems, with supplemental information on other plant communities, including shrubs and lichens.

4.2.2.1 Chemical Effects

There are several chemical indicators that provide useful information about the acid-base status of soils. These include (1) soil base saturation, (2) Ca:Al ratio, and (3) C:N ratio (Table 4.2-1). Each chemical indicator provides insight into the degree to which the ecosystem has acidified and may be susceptible to associated biological effects. These chemical indicators may also be used to monitor the extent of acidification or recovery that occurs in forest ecosystems as deposition rates of S and N change. As such, several chemical indicators and possible impact thresholds have been developed and applied in conjunction with efforts to estimate critical loads. The critical load refers to a quantitative estimate of deposition below which significant harmful effects on the environment do not occur according to present knowledge (Nilsson and Grennfelt, 1988). The critical loads approach is discussed in more detail in Section 4.1.2

4.2.2.1.1 Soil Base Saturation

Soil base saturation expresses the concentration of exchangeable bases (Ca, Mg, potassium [K]), sodium [Na]) as a percent of the total cation exchange capacity (which includes exchangeable hydrogen ion and inorganic Al). In soils with a base saturation less than about 15 to 20%, exchange ion chemistry is dominated by Al (Reuss, 1983). Under this condition, responses to sulfuric and HNO_3 inputs largely involve the release and mobilization of inorganic Al through cation exchange. This is the form of Al that interferes with uptake of Ca by plant roots and is also toxic to many forms of aquatic biota.

The soil O horizon tends to have a much higher base saturation than the B horizon, despite having lower pH due to organic acidity. The base saturation of the B horizon is more sensitive than that of the O horizon to base cation depletion from leaching by SO_4^+ and NO_3^-, and is therefore particularly useful for assessing base status with regard to acidic deposition. Little direct work has been done to relate soil base saturation to forest health, but Cronan and Grigal (1995) determined that base saturation values below about 15% in the B horizon could lead to impacts from Al stress. Lawrence et al. (2005) also observed pronounced decreases in diameter growth of Norway spruce in northwestern Russia, where base saturation decreased from 30% to 20% in the upper 10 cm of the B horizon over a period of 37 years.

Base saturation values less than 10% predominate in the soil B horizon in the areas in the United States where soil and surface water acidification from acidic deposition have been most pronounced, including conifer and hardwood forests in the Adirondack Mountains (Sullivan et al., 2006a), red spruce forests throughout the Northeast (David and Lawrence, 1996), hardwood forests in the Allegheny Plateau (Bailey et al., 2004), and conifer and hardwood forests in the southern Appalachian Mountains (Sullivan et al., 2003). In a study of sugar maple decline throughout the Northeast, Bailey et al. (2004) found threshold relationships between base cation availability in the upper B soil horizon and sugar maple mortality at Ca saturation less than 2%, and Mg saturation less than 0.5% (Bailey et al., 2004). They concluded that base saturation varied as a function of topography, geologic parent material, and acidic deposition.

4.2.2.1.2 Aluminum Concentration in Soil Solution: Calcium to Aluminum Ratio

Al is toxic to tree roots. Plants affected by high Al concentration in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially Ca (Parker et al., 1989). Ca is well known as an ameliorant for Al toxicity to roots in soil solution, as well as to fish in a stream. However, because inorganic Al does not become mobilized until after soil Ca is depleted, elevated concentrations of inorganic Al tend to occur with low levels of Ca in surface waters. Mg, and to a lesser extent Na and K, have also been associated with reduced Al toxicity.

Dissolved Al concentrations in soil solution at spruce-fir study sites in the southern Appalachian Mountains frequently exceed 50 µM and sometimes exceed 100 µM (Johnson et al., 1991; Joslin and Wolfe, 1992; Eagar et al., 1996). All studies reviewed by Eagar et al. (1996) showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution. They surmised that the occurrence of periodic large pulses of NO_3^- in solution were important in determining Al chemistry in the soils of spruce-fir forests.

The negative effect of Al mobilization on uptake of Ca by tree roots was proposed by Shortle and Smith (1988), and substantial evidence of this relationship has accumulated over the past 2 decades through field studies (McLaughlin and Tjoelker, 1992; Schlegel et al., 1992; Minocha et al., 1997; Shortle et al., 1997; Kobe et al., 2002) and laboratory studies (Sverdrup and Warfvinge, 1993; see also review of Cronan and Grigal, 1995). Based on these studies, it is clear that high inorganic Al concentration in soil water can be toxic to plant roots. The toxic response is often related to the concentration of inorganic Al relative to the concentration of Ca, expressed as the molar ratio of Ca to inorganic Al in soil solution. As a result, considerable effort has been focused on determining a threshold value for the ratio of Ca to Al that could be used to identify soil conditions that put trees under physiological stress.

From an exhaustive literature review, Cronan and Grigal (1995) estimated that there was a 50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. They estimated that there was a 100% risk for adverse effects on growth at a molar ratio value below 0.2 in soil solution.

The information available to define levels of risk for the Ca:Al ratio is complicated by differences in natural soil conditions. As a result of these complications, the risk levels for the ratio defined in laboratory experiments have not necessarily been successfully applied to field conditions. For example, Johnson et al. (1994a,b) reported Ca:Al ratios above 1.0 through most of 4 years in the Oa and B horizons of a high-elevation red spruce stand experiencing high mortality. In the 3-year study of DeWitt et al. (2001), Al additions lowered molar Ca to inorganic Al ratios in soil solutions of a Norway spruce stand below 0.5, but the authors found no response other than reduced Mg concentrations in needles in the third year, which was a possible precursor to damage.

In summary, a molar ratio of Ca to Al in soil solution can be used as a general index that suggests an increasing probability of stress to forest ecosystems as the ratio decreases. The ratio value of 1.0 is proposed as a general damage threshold, but cannot be interpreted as a universally applicable threshold in all natural systems. Tree species vary widely in their sensitivity to Al stress (See Figure 4.2-4). In addition, Al concentrations in soil solution often exhibit pronounced spatial and temporal variability that is difficult to relate to root activity. Finally, the form of Al present in solution plays an important role in determining toxicity. For example, organically complexed Al, which predominates in upper, organic-rich soil horizons, is essentially nontoxic.

4.2.2.1.3 Soil Nitrogen: Calcium to Nitrogen Ratio

Mechanisms of retention and release of N in forest ecosystems are not fully understood, but the adverse effects of nitrification and associated acidification and cation leaching have been consistently shown to occur only in soils with a C:N ratio below about 20 to 25 (Aber et al., 2003; Ross et al., 2004). This observation makes the C:N ratio especially useful because N mineralization and nitrification rates cannot be measured directly under natural conditions. All available measurement approaches disturb the soil and often cause artificially high rates. Therefore, field measurement provides a relative index rather than a realistic quantitative rate (Ross et al., 2004). Approaches for measuring N mineralization and nitrification also are subject to high degrees of variability, both temporally (hourly to seasonal) and spatially (down to the sub meter level). Measurements of total OC and N however, are less variable in space and time and are therefore more straightforward to document than N mineralization and nitrification rates. Also, ratios of C to N in the forest floor are inversely related to acidic deposition levels, although the relation is stronger for hardwood stands than conifer stands (Aber et al., 2003). In sum, these factors make the C:N ratio a reliable and relatively straightforward measure for identifying forest ecosystems that may be experiencing soil acidification and base leaching as a result of N input and increased nitrification.

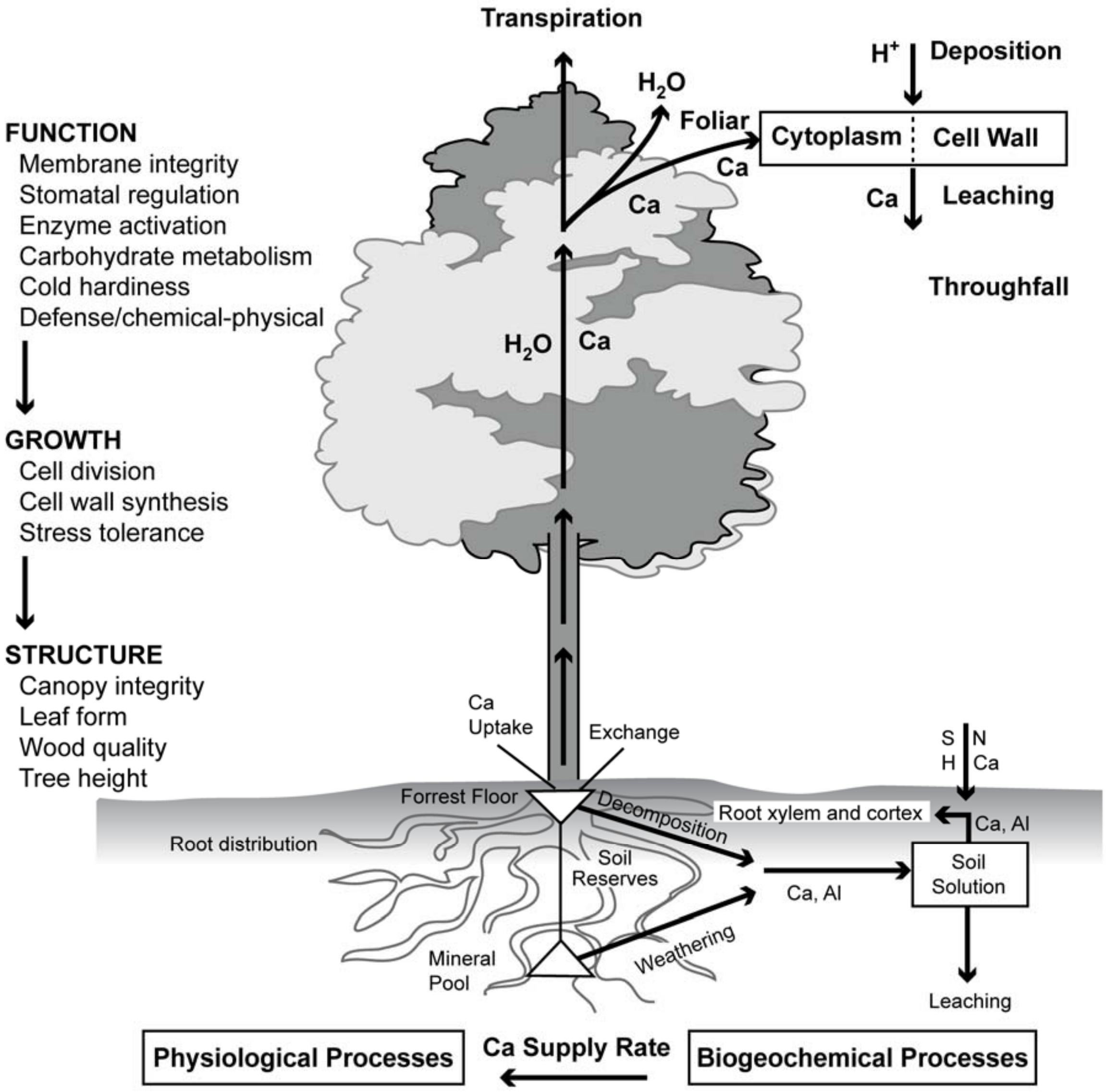


Figure 4.2-4. Diagram based on Fenn et al. (2006) shows indicators of forest physiological function, growth and structure that are lined to biogeochemical cycles through processes that control rates of Ca supply. Calcium effects plant physiological processes that influence growth rates and the capacity of plants to resist environmental stresses such as extremes of temperature, drought, insects, and diseases. Therefore, factors such as acidic deposition, which can deplete soil Ca or interfere with Ca uptake through mobilization of soil A1, is a concern for maintenance of forest health.

Source: Fenn, ME, Huntington TG, McLaughlin SB, Eagar C, Gomez A, Cook RB (2006) Status of soil acidification in North America. Journal of Forest Science (52):3-13.

4.2.2.2 Biological Effects

Acidic deposition can affect terrestrial ecosystems by direct impacts on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations (especially Ca) and water from the soil. Acidic deposition to acid-sensitive soils can cause soil acidification, increased mobilization of inorganic Al from soil to drainage water, and depletion of the pool of stored base cations in the soil. Effects on the soil and direct effects of acidic deposition on foliage can influence the response of plants to climatic stresses such as drought and cold temperature. They can also influence the sensitivity of plants to other stresses, including insect pests and disease.

The combined impacts of acidic deposition and other stressors on terrestrial vegetation are typically measured using indices such as percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback (Table 4.2-2). Each of these variables has a rating system used to quantify forest condition and relate the variables to foliar and soil nutrient concentrations.

The effects of acidic deposition on the health, vigor, and productivity of terrestrial ecosystems in the United States are best documented in spruce-fir and northern hardwood forests of the eastern United States. Some information is also available for individual species such as red spruce, sugar maple, and some species of lichen. In the western United States, the health of Ponderosa pine and Jeffrey pine has been affected by air pollution, but such effects have largely been attributed to ozone exposure, not acidic deposition.

4.2.2.2.1 Health, Vigor, and Reproduction of Tree Species in Forests

Both coniferous and deciduous forests throughout the eastern United States are experiencing gradual losses of base cation nutrients from the soil due to accelerated leaching from acidic deposition. This change in base cation nutrient availability may reduce the quality of forest nutrition over the long term. Evidence suggests that red spruce and sugar maple in some areas in the eastern United States have experienced declining health as a consequence of acidic deposition. Existing information regarding the effects of acidic deposition on these two forest tree species is summarized below and reference is made to specific health indicators where such information is available.

Red Spruce

Red spruce (*Picea rubens*) is a conifer that occurs mainly in the northeastern United States and at scattered high-elevation sites in the Appalachian Mountains (Figure 4.2-5). Red spruce dieback or decline has been observed across high elevation landscapes of both the northeastern and southeastern United States. At high elevations in the Adirondack and Green Mountains, more than 50% of the canopy red spruce trees died during the 1970s and 1980s. In the White Mountains, about 25% of the canopy spruce died during that same period. Dieback of red spruce has also been observed in mixed hardwood-conifer stands at relatively low elevations in the western Adirondack Mountains, an area that receives high inputs of acidic deposition (Shortle et al., 1997). Acidic deposition has been implicated as a causal factor (DeHayes et al., 1999). The frequency of freezing injury to red spruce needles has increased over the past 40 years, a period that coincided with increased emissions of S and N oxides and increased acidic deposition (DeHayes et al., 1999).

From the 1940s to 1970s, red spruce growth also declined in the southeastern United States, as emissions of both nitrogen oxides and sulfur dioxide (SO_2) increased to maxima of about 25 and 30 million tons/yr, respectively. The growth decline started earlier at higher elevations (around the 1940s and 1950s) and was steeper, while the growth decline developed at lower elevation sites 20 years later. After the 1980s, red spruce growth increased substantially at both the higher- and lower-elevation sites, corresponding to a decrease in SO_2 emissions in the United States (to about 20 million tons/yr by 2000), while nitrogen oxide emissions held fairly steady (at about 25 million tons/yr). Annual emissions of S plus nitrogen oxides explained about 43% of the variability in red spruce tree ring growth between 1940 and 1998. Climatic variability accounted for about 8% of the growth variation for that period. At low elevation, changes in radial growth could be explained by climatic variables only, and there was no correlation with national S plus nitrogen oxide emissions trends. Recent reductions in S oxide emissions may have changed growth trajectories (Webster et al., 2004).

The observed dieback in red spruce has been linked, in part, to reduced cold tolerance of red spruce needles, caused by acidic deposition. Results of controlled exposure studies showed that acidic mist or cloud water reduced the cold tolerance of current-year red spruce needles by

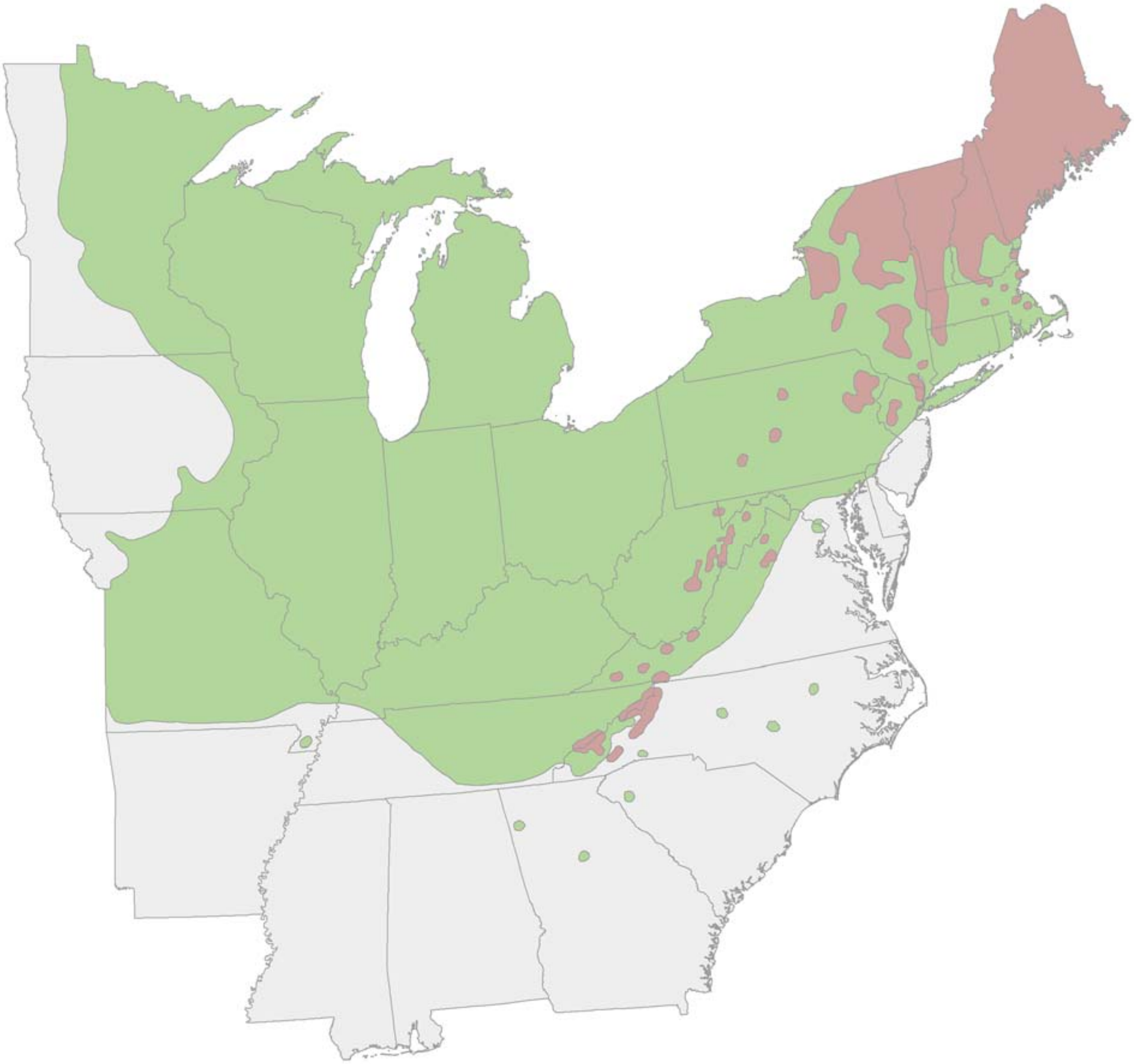


Figure 4.2-5. Distribution of red spruce (rose) and sugar maple (green) in the eastern United States. These two tree species have experienced adverse effects in portions of their ranges that have been attributed to acidification from acidic deposition. Tree distribution data were obtained from Little's Ranges.

Source: Little (1971) http://esp.cr.usgs.gov/data/atlas/little/.

3 to 10 ºC (DeHayes et al., 1999). There is a significant positive association between cold tolerance and foliar Ca in trees that exhibit foliar Ca deficiency. The membrane-associated pool of Ca, although a relatively small fraction of the total foliar Ca pool, strongly influences the

response of cells to changing environmental conditions. The plant plasma membrane plays an important role in mediating cold acclimation and low-temperature injury (U.S. Environmental Protection Agency, 2004). The studies of DeHayes et al. (1999) suggested that direct acidic deposition on red spruce needles preferentially removes membrane-associated Ca. More recently, a link has been established between availability of soil Ca and winter injury (Hawley et al., 2006) based on an experimental addition of Ca at the Hubbard Brook Experimental Forest, New Hampshire. This study demonstrated that Ca depletion from soil was associated with winter injury of red spruce foliage during 2003 when winter injury was unusually high throughout the region (Figure 4.2-6).

In summary, the weight of evidence indicates that changes in soil chemistry have contributed to high mortality rates and decreasing growth trends of red spruce trees in some areas over the past three decades (Sullivan et al., 2002a). In forests where this has occurred, which are mainly located at high elevation, changes in red spruce growth rates are attributable, at least in part, to base cation deficiencies related to decreased availability of Ca and increased availability of Al as a result of acidic deposition effects on soils. Important factors appear to include depletion of base cations in upper soil horizons by acidic deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidic deposition.

Sugar Maple

Sugar maple (*Acer saccharum*) is the deciduous tree species of the northeastern United States that is most commonly associated with adverse acidification-related effects of S and N deposition, though other base cation accumulating hardwoods may also be at risk (Driscoll et al., 2001b). Sugar maple is distributed throughout the northeastern United States and central Appalachian Mountain region as a component of the northern hardwood forest (Figure 4.2-5). Figure 4.2-7 provides a conceptual view of the interactions of acidic deposition and other stressors in sugar maple decline. Several studies, mainly in Pennsylvania, have indicated that sugar maple decline is linked to the occurrence of relatively high levels of acidic deposition and base-poor soils (Horsley et al., 2000; Bailey et al., 2004; Hallett et al., 2006; Moore and Ouimet, 2006).

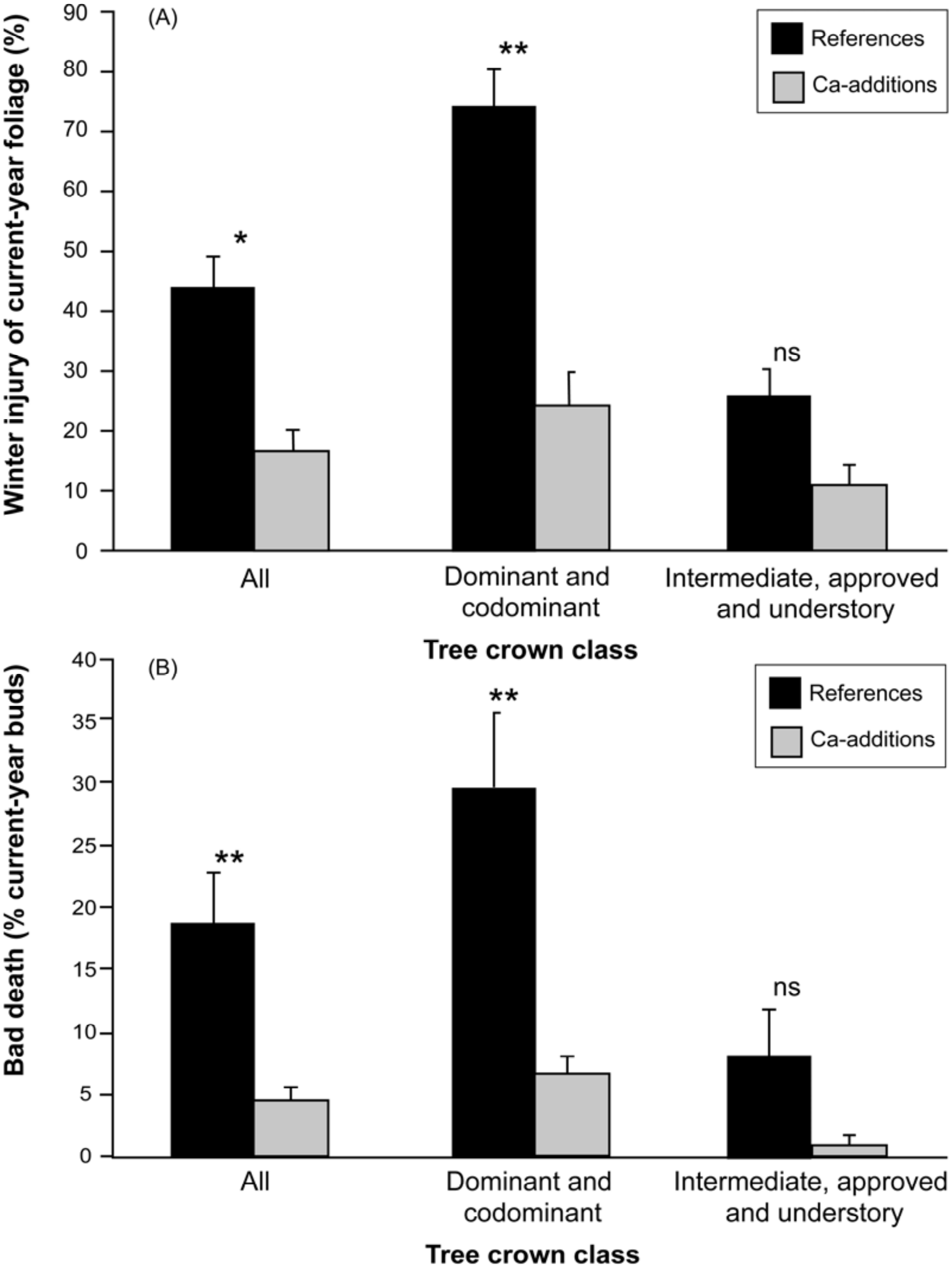


Figure 4.2-6. Mean (± standard error) of current-year red spruce winter injury in reference and calcium-addition watersheds and among crown classes, expressed as foliar injury (A) and bud mortality (B). Watershed means were either not significantly different (ns) or statistically different at $p < 0.05$ (*) or $p < 0.01$ (**) based on nested analyses of variance.

Source: Hawley et al. (2006).

Acidic deposition may be contributing to episodic dieback of sugar maple in the Northeast through depletion of nutrient cations from marginal soils (Figure 4.2-7). Horsley et al. (2000) found that dieback at 19 sites in northwestern and northcentral Pennsylvania and southwestern New York was correlated with combined stress from defoliation and soil deficiencies of Mg and Ca. Dieback occurred predominately on ridgetops and on upper slopes, where soil base cation availability was much lower than on middle and lower slopes (Bailey et al., 2004). A long-term decrease in soil pH since 1960 (0.78 pH unit decrease in the O horizon, and 0.23 pH unit decrease in the A horizon) in Pennsylvania hardwood forests has been documented, along with decreases in soil Ca and Mg concentrations. Declining sugar maples were shown to be deficient in foliar Ca and Mg (Drohan and Sharpe, 1997). More recent research has strengthened understanding of the role of cation nutrition in sugar maple health at a regional scale across a broad range of conditions (Hallett et al., 2006).

Drohan et al. (2002) investigated differences in soil conditions in declining versus non-declining sugar maple plots in northern Pennsylvania from the U.S. Department of Agriculture (USDA) Forest Service's Forest Inventory and Analysis (FIA) program. Soils in plots with declining sugar maple tended to have lower base cation concentrations and pH, and Ca:Al ratio less than 1. Regressions between foliar and soil chemistry showed that foliar nutrition was highly correlated with the chemistry of the upper 50 cm of soil (Drohan et al., 2002).

In general, existing evidence indicates that acidic deposition in combination with other stressors is a likely contributor to the decline of sugar maple trees that occur at higher elevation, on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils having high percentages of rock fragments (Drohan et al., 2002). Such site conditions are representative of the kinds of conditions expected to be most susceptible to adverse impacts of acidic deposition because of probable low initial base cation pools and high base cation leaching losses.

Other Forest Ecosystems

Data on the possible effects of S and N deposition on the acid-base characteristics of forests in the United States, other than the spruce-fir and northern hardwood forest ecosystems, are limited. Ponderosa pine (*Pinus ponderosa*) seedlings exposed to acidic precipitation (pH 5.3,

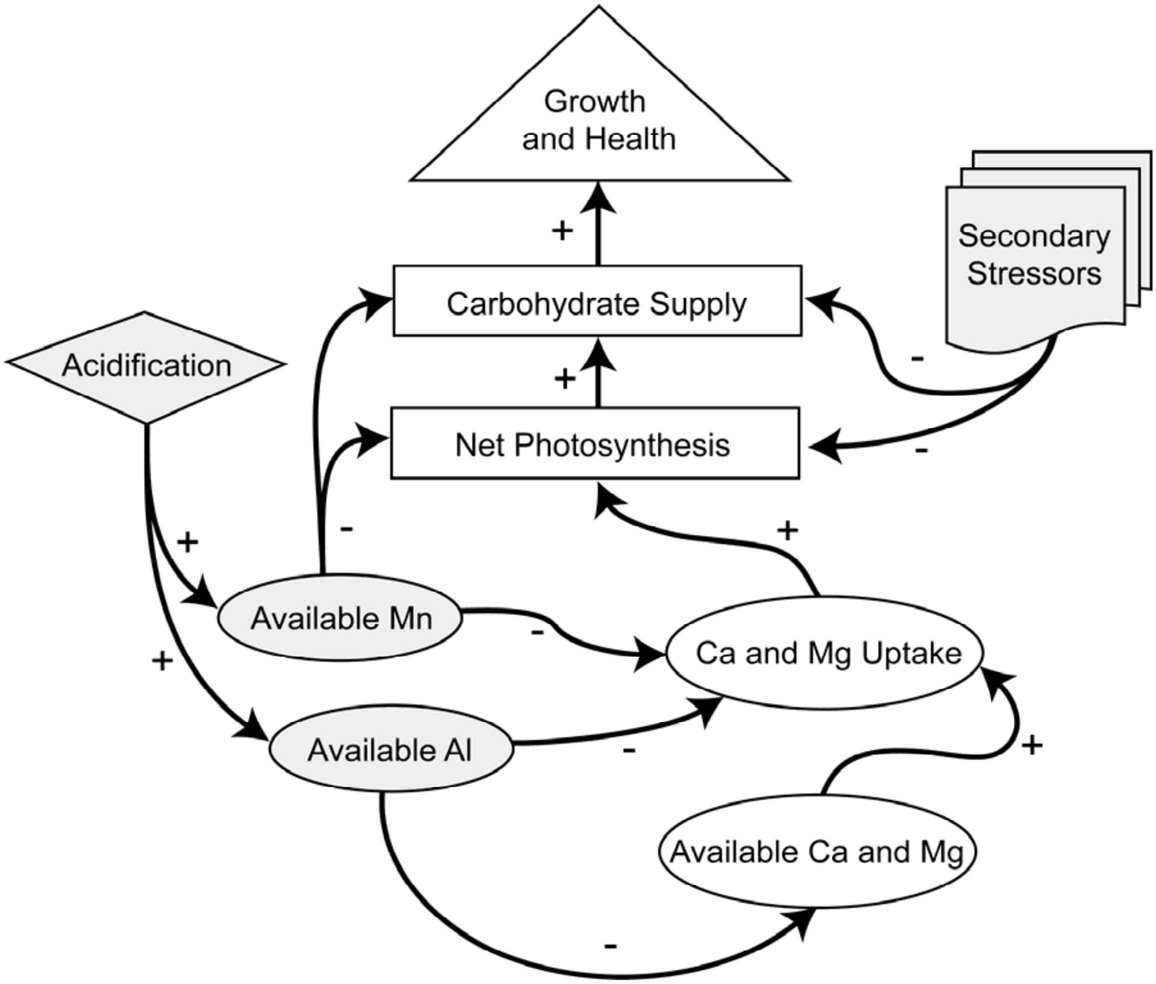


Figure 4.2-7. Conceptual diagram outlining the current understanding of sugar maple decline. Positive and negative signs indicate the nature of the correlative relationship between variables.

Source: Hallett et al. (2006).

4.4, 3.5 of 1:1 NHO_3:H_2SO_4) showed no significant changes in growth (Temple et al., 1992). Fenn et al. (2003a) reported that deposition levels of 20 to 35 kg N ha^{-1} yr^{-1} contributed to increased NO_3^- leaching and soil acidity and decreased base cation saturation in southern California forest ecosystems, but they did not report quantitative measures of growth. Baron et al. (2000) showed that small differences in the N deposition regime between the east (3 to 5 kg N ha^{-1} yr^{-1}) and the west (1 to 2 kg N ha^{-1} yr^{-1}) side of the Rocky Mountains were associated with significant declines in foliar Mg levels and increased foliar N:Mg and N:Ca ratios in old-growth stands of Engelmann spruce (*Picea engelmanii*). It is not known whether such changes in nutrient ratios affect the health or growth of these forests.

4.2.2.2.2 Biodiversity of Forests

Despite the evidence for impacts of acidic deposition on the health and vigor of some terrestrial plant communities, we found a lack of scientific literature directly documenting species loss, reduced biodiversity, or adverse effects on threatened and endangered species. A notable exception is the impact of acidic deposition on lichen abundance and diversity within forest communities (Lichens are discussed in Section 4.2.2.2.3). In eastern North America and central Europe, areas that receive relatively high levels of acidic deposition have experienced noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely (McCune, 1988; Van Haluwyn and Van Herk, 2002). In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas where NO exceeded 40 $\mu g/m^3$ and total N oxides exceeded 70 $\mu g/m^3$. It is also possible that effects of acidification on plant biodiversity may be more widespread than those documented for lichens.

4.2.2.2.3 Health and Biodiversity of Other Plant Communities

Shrubs

Forest trees are not the only vascular plants that are potentially sensitive to acidic deposition. Available data suggest that it is possible, or perhaps likely, that a variety of shrub and herbaceous species are sensitive to base cation depletion and/or Al toxicity. However, conclusive evidence is generally lacking.

Westman et al. (1985) reported a decrease in the number of inflorescences for different shrubs fumigated with SO_2 over 10 weeks, at 0, 0.05, 0.20, and 0.50 ppm. Decreased inflorescences were observed at 0.05-ppm SO_2 for black sage (*Salvia mellifera*), and at 0.20 ppm SO_2 for California sagebrush (*Artemisia californica*), Eastern Mojave buckwheat (*Eriogonum fasciculatum*), and California brittlebush (*Encelia californica*), with progressive declines as SO_2 concentration increased. This suggests impact of exposure to SO_2 on the reproduction of a species rather than solely through impacts on the health of individual plants. We have found no documentation of effects of S deposition, rather than atmospheric exposure, on plant reproduction.

Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in response to acidic deposition. However, such effects are probably more related to the nutrient enrichment effects of N deposition than to the acidification effects of S and N deposition. (See further discussion in Section 4.3.3.1). In summary, whereas some evidence suggests that impacts on shrubs and perhaps herbaceous plants are possible, data in the United States are insufficient to support the use of shrub or herbaceous plant species as indicators of the acidification-related effects of acidic deposition at this time.

Lichens

Typically, lichens and other bryophytes are among the first components of the terrestrial ecosystem to be affected by acidic deposition. Vulnerability of lichens to increased N input is generally greater than that of vascular plants (Fremstad et al., 2005). Even in the Pacific Northwest, which receives uniformly low levels of N deposition, changes from acid-sensitive and N-sensitive to pollution-tolerant and nitrophillic lichen taxa are occurring in some areas (Fenn et al., 2003a). Lichens remaining in areas affected by acidic deposition were found by Davies et al. (2007) to contain almost exclusively the families Candelariaceae, Physciaceae, and Teloschistaceae.

Effects of SO_2 exposure on lichens includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K absorption, and structural changes (Fields, 1988; Farmer et al., 1992). In response to reductions after the 1970s in SO_2 exposure and acidic deposition in London, lichen diversity increased dramatically (Hawksworth, 2002). However, the recovery of lichens in response to reduced S and N inputs is inconsistent. Improvement for bryophytes has been reported to occur in 1 year by Power et al., (2006) and Mitchell et al., (2004), 5 years by Gordon et al., (2001), and 49 years by Strengbom et al., (2001).

Scott (1989a,b) concluded that the S:N exposure ratio was as important as pH in causing toxic effects on lichens, based on experiments on *Cladina rangiferina* and *C. stellaris*. Thus, it is not clear to what extent acidity may be the principal stressor under high levels of air pollution exposure. The toxicity of SO_2 to several lichen species is greater under acidic conditions than under neutral conditions. The impacts of excess N deposition to lichen communities is discussed in Section 4.3.3.1.5.

Grasslands

Due to structural differences and their lower canopy, grasslands are thought to be less sensitive to acidification than woodlands (Blake et al., 1999; Kochy and Wilson, 2001). Among grasslands, those with calcareous soils will be less sensitive than those with acidic soils (Bobbink et al., 1998). Most literature on the effects of atmospheric S and N deposition on grasslands documents effects of fertilization from N deposition, not acidification. Such fertilization effects are discussed in Section 4.3.3.1.2.

Arctic and Alpine Tundra

The possible effects of acidic deposition on arctic and alpine plant communities are also of concern. Especially important in this regard is the role of N deposition in regulating ecosystem N supply and plant species composition (See further discussion of such effects in Section 3.2.2.). Soil acidification and base cation depletion in response to acidic deposition have not been documented in arctic or alpine terrestrial ecosystems in the United States. Such ecosystems are rare and spatially limited in the eastern United States, where acidic deposition levels have been high. These ecosystems are more widely distributed in the western United States and throughout much of Alaska, but acidic deposition levels are generally low in these areas. Key concerns are for listed threatened or endangered species and species diversity. However, for most rare, threatened, or endangered herbaceous plant species, little is known about their relative sensitivities to acidification from atmospheric deposition inputs. Although plant species diversity of arctic and alpine ecosystems is highly valued, it is difficult to document changes in this parameter in response to acidic deposition.

4.2.3 Aquatic Ecosystems

4.2.3.1 Chemical Effects

The changes in major biogeochemical processes and soil conditions caused by acidic deposition have significant ramifications for the water chemistry and biological functioning of associated surface waters. Surface water chemistry indicates the adverse effects of acidification on the biotic integrity of fresh water ecosystems. Because surface water chemistry integrates the sum of soil and water processes that occur upstream within a watershed, it also reflects the results of watershed-scale terrestrial effects, including N saturation, forest decline, and soil acidification (Stoddard et al., 2003). Thus, water chemistry integrates and reflects changes in soil and vegetative properties and biogeochemical processes.

The impacts on aquatic ecosystems can be described by changes in several chemical effects indicators such as: SO_4^+ concentration, NO_3^- concentration, base cation concentration, pH, ANC, and inorganic Al. All of these are of interest, and each can provide useful information regarding both sensitivity to surface water acidification and the level of acidification that has occurred. Importantly, these chemical changes can occur over both long- and short-term timescales. Short-term (hours or days) episodic changes in water chemistry have perhaps the most significant biological impacts. The acidification effects on aquatic biota are most commonly evaluated using either Al or pH as the primary chemical indicator (Table 4.2-3). ANC is also used because it integrates overall acid status and because surface water acidification models do a better job projecting ANC than pH and inorganic Al concentrations. However, ANC does not relate directly to the health of biota. The utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al. The base cation surplus (Lawrence et al., 2007) is an alternate index that integrates acid-base status. It is based on a measurement of ANC (calculated from the charge balance of ionic concentrations in water) and also accounts for the influence of natural organic acidity.

4.2.3.1.1 Surface Water SO_4^+

Measurements of SO_4^+ concentration in surface water provide important information on the extent of cation leaching in soils and how SO_4^+ concentrations relate to ambient levels of atmospheric S deposition. Assessments of acidic deposition effects dating from the 1980s to the present have shown SO_4^+ to be the primary anion in most, but not all, acid-sensitive waters in the United States (Driscoll and Newton, 1985; Driscoll et al., 1988, 2001b; Webb et al., 2004). In an analysis representative of over 10,000 acid-sensitive lakes in the Northeast, inorganic anions represented the majority of negative (anionic) charge in 83% of the lakes, and in this group of lakes, 82% of the total negative charge was due to SO_4^+ (Driscoll et al., 2001b). In contrast, naturally derived organic anions represented an average of 71% of total negative charge in the 17% of lakes in which organic anions predominated (Driscoll et al., 2001b).

Atmospheric deposition of S is widely acknowledged as causing changes in concentrations of SO_4^+ in surface water. No long-term data sets exist to document changes in SO_4^+ in surface waters since the onset of the Industrial Revolution. One of the longest-running monitoring programs exists at the Hubbard Brook Experimental Forest in New Hampshire. Surface water data from this Long-Term Ecological Research site have been used to develop historic estimates of SO_4^+ concentrations using the Photosynthesis and EvapoTranspiration-BioGeoChemical (PnET-BGC) model (Gbondo-Tugbawa et al., 2002). Results from Hubbard Brook suggest that acidic deposition has contributed to a nearly four-fold increase in stream SO_4^+ concentration between 1850 and 1970 (Driscoll et al., 2001b).

Long-term data in other regions suggest similar trends in some cases. For example, a study of seven streams in the Catskill region of New York, Stoddard (1991) identified increasing trends in SO_4^+ concentrations from 1952-54 to 1970 in three streams and no trend in the four other streams.

As emissions and deposition of S have declined over approximately the last 30 years, surface water concentrations of SO_4^+ have decreased in most regions in the eastern United States. For example, Stoddard et al. (2003) found that surface waters monitored in EPA Long-Term Monitoring program showed consistent decreases in SO_4^+ concentrations from 1990 to 2000 in New England lakes (1.77 µeq/L/yr), Adirondack lakes (2.26 µeq/L/yr), Appalachian streams (2.27 µeq/L/yr) and Upper Midwest lakes (3.36 µeq/L/yr). The only exception to the pattern of decreasing SO_4^+ concentration in surface waters during this period was for streams in the Blue Ridge Mountain region of Virginia, which showed a significant increase in SO_4^+ concentrations (0.29 µeq/L/yr) during this period. The increasing trend in Virginia streams is presumably the result of decreased S adsorption and net desorption in the soil in response to decreased S deposition.

In summary, available data indicate a pattern of increasing concentrations of SO_4^+ in surface waters before the year of peak S emissions in 1973, followed by widespread decreasing trends in SO_4^+ concentrations after the peak (with the only exception being the Blue Ridge Mountain region in Virginia). On this basis, continued decreases in S emissions would be expected to result in further decreases in SO_4^+ concentrations in surface waters, although the rate of response is variable and some model results suggest that recovery may be delayed as accumulated S leaches from watersheds, even as emissions and deposition decline.

4.2.3.1.2 Surface Water NO_3^-

Whereas SO_4^+ is generally considered the dominant agent of surface water acidification in affected regions of the United States, NO_3^- plays a large role in acidification of surface waters in some regions, particularly during snowmelt and rainstorm episodes. Prior to the mid-1980s, atmospheric deposition effects research in the United States focused almost exclusively on S. Within the 1980 to 1990 National Acid Precipitation Assessment Program (NAPAP) research program, relatively little attention was paid to N research.

Release of NO_3^- from soil to surface waters may affect nutrient relationships and biological neutralization processes in aquatic ecosystems to a greater extent than SO_4^+ (Kelly et al., 1987; Bukaveckas and Shaw, 1998; Momen et al., 2006). The importance of NO_3^- as an agent of acidification varies by region. Driscoll and Newton, (1985) found that NO_3^- concentrations in 20 lakes in the early 1980s in the Adirondack region of New York averaged 12% of SO_4^+ concentrations, whereas Lovett et al. (2000) found that baseflow NO_3^- concentrations in 1994—97 were an average of 37% of SO_4^+ concentrations in 39 streams in the Catskill region of New York. Murdoch and Stoddard (1993) demonstrated the importance of NO_3^- during high-flow conditions in Catskill streams in which concentrations periodically equaled or exceeded SO_4^+ concentrations. Average concentrations of NO_3^- in most southeastern streams also tend to be considerably less than SO_4^+ concentrations (Webb et al., 2004). However, Cook et al. (1994) documented very high NO_3^- concentrations in stream water at high elevation in the Great Smoky Mountains in North Carolina.

Surface water NO_3^- concentration trends vary by region and over time. Several regions in the northeastern United States showed increased NO_3^- concentrations during the 1980s. For example, in the Catskill Mountains of New York all 16 streams for which data were available showed increasing trends in NO_3^- concentration during that period. A similar increase in NO_3^- concentration was reported for Adirondack lakes in the 1980s (Stoddard et al., 1999). These increasing trends in NO_3^- concentration were initially attributed to N saturation in response to atmospheric deposition (Aber et al., 1998).

More recent information on NO_3^- trends during the 1990s, when atmospheric N deposition was relatively stable, suggest that the relationship between atmospheric N deposition and surface water NO_3^- concentrations is complex. During the 1990s, the only statistically significant change occurred in the two regions with the highest ambient surface water NO_3^- concentrations: lakes in the Adirondack Mountains and streams in the Northern Appalachian Plateau (Figure 4.2-2). Both exhibited small but significant downward trends in NO_3^- concentration during the 1990s. The long-term record of dissolved inorganic N (which is largely NO_3^-) concentrations at the Hubbard Brook Experimental Forest showed a similar pattern: high concentrations in the late 1960s and 1970s, followed by decreases to minimum values in the mid-1990s (Aber et al., 2002). Across New England and the Upper Midwest, where ambient surface water concentrations are much lower than in the Adirondack Mountains and Northern Appalachian Plateau (Figure 4.2-8), NO_3^- concentrations in surface waters were unchanged during the 1990s. The Ridge/Blue Ridge province registered a small, but significant, decrease in NO_3^- concentration during the 1990s, but interpretation of trends for NO_3^- in this region was complicated by an outbreak of gypsy moths, which consumed foliage and caused large increases in the concentration of NO_3^- in soil water and stream water in affected watersheds (Eshleman et al., 1998).

Efforts to explain the inconsistent trends in NO_3^- concentrations under conditions of reasonably stable atmospheric N deposition have focused on both terrestrial and aquatic N cycling. Goodale et al. (2003) reported that lower NO_3^- concentrations measured in the 1990s at streams in New Hampshire could not be accounted for by differences in stream flow or forest succession, but inter-annual climate variation was proposed as a possible cause. In the Adirondacks, Driscoll et al., (2007a) proposed that increased concentrations of atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation. Studies by Mitchell et al. (1996) and Murdoch et al. (1998) provide some evidence of climate effects on trends in NO_3^- concentrations in surface waters in the Northeast. In particular, a region-wide spike in NO_3^- concentrations followed an unusually cold December that may have disrupted soil N cycling processes (Mitchell et al., 1996). Murdoch et al. (1998) also found that mean annual air temperature was strongly related to average annual NO_3^- concentration during most years in a Catskill watershed with elevated NO_3^- concentrations in stream water.

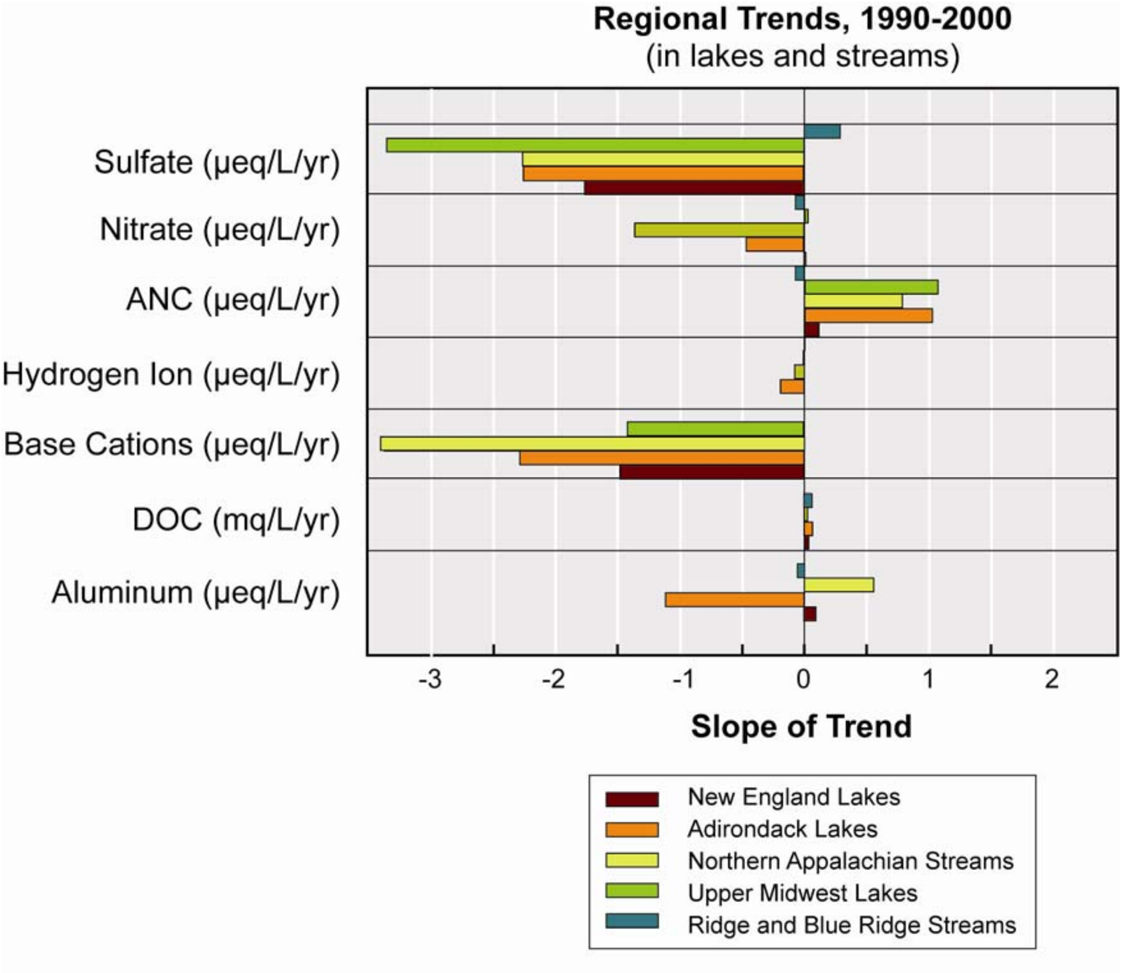


Figure 4.2-8. Summary of regional trends in surface water chemistry from 1990 to 2000 in regions covered by the Stoddard et al. (2003) report.

Source: Stoddard et al. (2003).

Processes within lakes may have also played a role in the measured trends in Adirondack lakes. In a study of 30 of the 48 long-term monitoring lakes investigated by Driscoll et al. (2003c; 2007a) and Momen et al. (2006) found that concentrations of dissolved NO_3^- were inversely correlated with concentrations of chlorophyll *a* in 11 lakes, and that chlorophyll *a* was increasing in concentration in 9 lakes. The increase in pH observed in most of these lakes may have stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

In summary, NO_3^- contributes to the acidity of many lakes and streams in the eastern United States that have been impacted by acidic deposition, especially during spring months and under high-flow conditions. Nevertheless, there is little or no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in surface waters in the eastern United States. This observation is in sharp contrast to observed responses for S deposition and SO_4^+ concentrations. These results likely reflect the complexities of N utilization within terrestrial and aquatic ecosystems. Uptake of atmospherically deposited N by plants and microorganisms in the terrestrial environment precludes drainage water acidification and base cation leaching that would be caused if excess N leached as NO_3^- from the terrestrial to aquatic ecosystems. While great uncertainty exists and the timescales of N saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely (Aber et al., 2003).

4.2.3.1.3 Surface Water Base Cations

The results from several studies in the eastern United States suggest that base cation concentrations in surface waters increased during the initial phases of acidification into the 1970s. This trend reversed and base cations decreased in response to decreasing SO_4^+ and NO_3^- concentrations. For example, the study of Likens et al. (1996) evaluated trends in base cation concentrations in stream water in relation to long-term trends in SO_4^+ plus NO_3^- for the Hubbard Brook Experimental Forest. This record showed an approximately linear increasing relationship between concentrations of base cations and SO_4^+ plus NO_3^- from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994. The slope of the phase with increasing anion concentrations was steeper than the slope for the phase with decreasing anion concentrations. Regional declines in base cation concentrations were measured in the Long-Term Monitoring project from 1990 to 2000 for lakes in New England, the Adirondack Mountains, and the Upper Midwest (Figure 4.2-8). The study of Lawrence et al. (1999) showed decreased concentrations of base cations at a rate that exceeded decreases in (SO_4^+ plus NO_3^-) in Catskill Mountain streams from 1984 to 1997. In streams within western Virginia and in Shenandoah National Park, concentrations of base cations did not exhibit significant trends from 1988 to 2001, perhaps due to the influence of S adsorption to soil on stream water SO_4^+ concentrations.

In some surface waters, interpretation of the effects of, and changes in, the concentration of base cations and ANC is complicated by the influence of naturally occurring organic acidity.

The base cation surplus provides an approach for distinguishing between the effects of organic acidity and acidic deposition (Lawrence et al., 2007). Base cation surplus is defined as the difference between the summed concentrations of base cations (Ca, Mg, Na, K) and strongly acidic inorganic anions (SO_4^+, NO_3^-, chloride), plus an estimate of the strongly acidic organic anions. These strongly acidic organic acid anions are dissociated at low pH, and function essentially as mineral acid anions in terms of their effect on ANC. The calculated base cation surplus is similar to the calculated ANC, but explicitly accounts for strongly acidic organic acids. When the base cation surplus is plotted against inorganic Al concentration, a distinct threshold for Al mobilization occurs at a base cation surplus value that closely approximates 0, regardless of the dissolved OC concentration (Figure 4.2-9) (Lawrence et al., 2007). This threshold provides an unambiguous reference point for evaluating the effects of acidic deposition on mobilization of inorganic Al. To date, this calculated variable has only been used in one large-scale assessment of acidic deposition effects on surface waters (Lawrence et al., 2007).

In summary, decreases in base cation concentrations in surface water in the eastern United States over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^+ concentrations. In most regions, rates of decrease for base cations have been similar to those for SO_4^+ plus NO_3^-, with the exception of streams in Shenandoah National Park, Virginia, which appear to exhibit changes in S adsorption on soils. Decreasing trends of base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

4.2.3.1.4 Surface Water pH

Surface water pH is a commonly used as an indicator of acidification. The pH of water quantifies the hydrogen ion concentration, which is toxic to many forms of aquatic life. In addition, pH correlates with other biologically important components of surface water acid-base chemistry, including ANC, inorganic Al, Ca concentration, and organic acidity. Low pH can have direct toxic effects on aquatic species (Driscoll et al., 2001b). Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Haines and Baker, 1986; Baker et al., 1990a). Common reference values for pH, below which adverse biological effects are anticipated, are 5.0, 5.5, and 6.0. The effects of low pH are specific to the

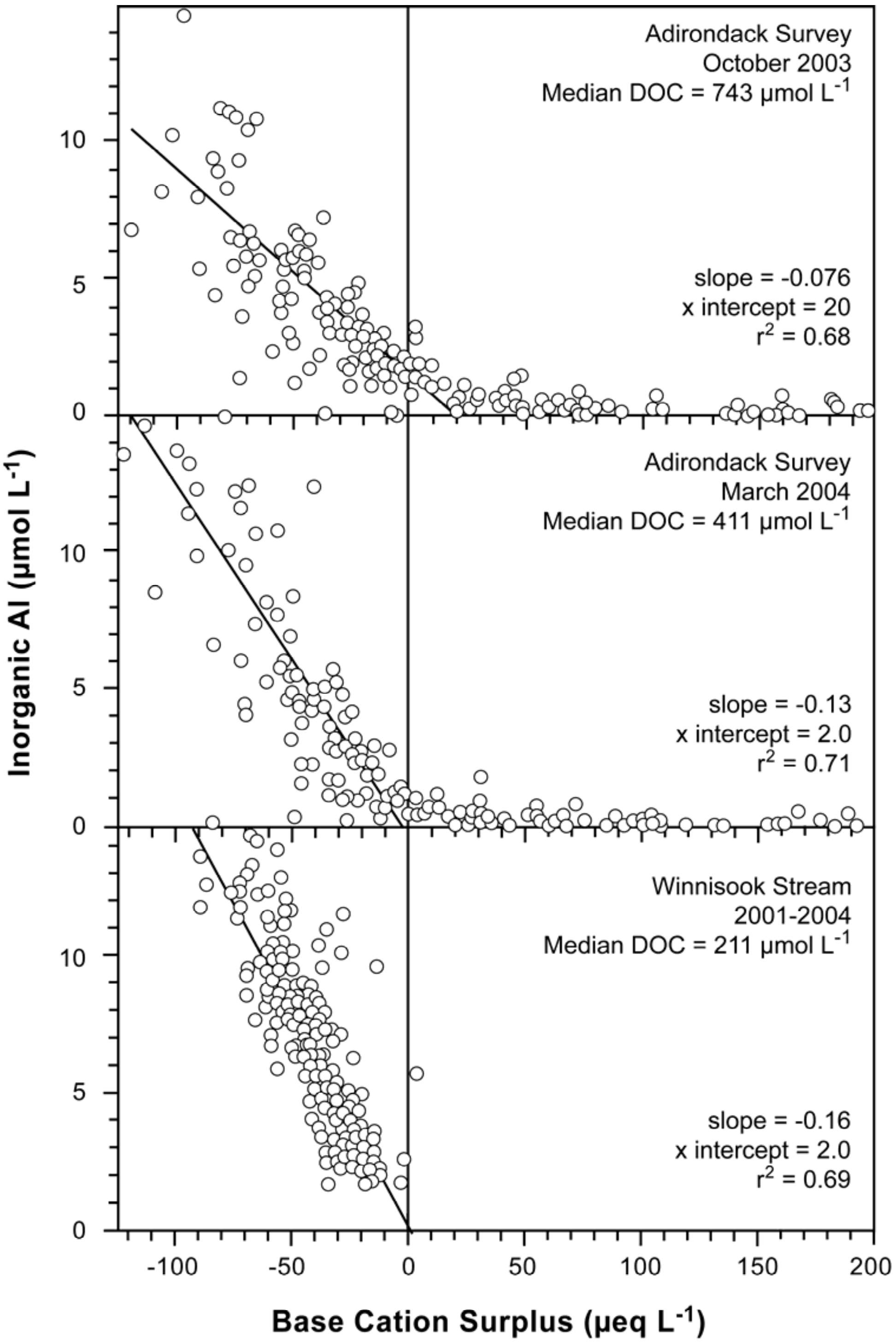


Figure 4.2-9. Concentration of inorganic Al in Adirondack streams as a function of the calculated base cation surplus.

Source: Lawrence et al. (2007).

organism under consideration and depend also upon the concentrations of other chemical constituents in the water, notably inorganic Al and Ca. Species-specific effects are discussed in more detail in Section 4.2.3.2.

Long-term past changes in surface water pH have been inferred for lakes in the Adirondacks through paleolimnological studies (Charles et al., 1989; Sullivan et al., 1990; Cumming et al., 1992, 1994). These studies of algal remains in lake sediments for regionally representative Adirondack lakes suggested that about 25 to 35% of the Adirondack lakes that are larger than 4 ha have acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had ambient pH less than 5.2 in the mid-1980s were inferred to have experienced large declines in pH and ANC since the previous century. About 30 to 45% of the lakes with ambient pH between 5.2 and 6.0 have also acidified. The results suggest that the low-ANC lakes of the southwestern Adirondacks acidified the most since preindustrial time.

Additional information regarding long-term changes in surface water pH has been gained through site-specific dynamic modeling. For example, by applying the PnET-BGC model to the long-term stream chemistry record at the Hubbard Brook Experimental Forest, Gbondo-Tugbawa et al. (2002) estimated that past stream pH (circa 1850) was probably about 6.3, compared with values just above 5.0 in 2000 (Driscoll et al., 2007c).

In recent decades, measurements of pH have been routinely collected in surface waters in the United States where effects of acidic deposition have been monitored, but a long-standing reliance on titrated ANC rather than pH as the primary chemical measurement has limited the amount of pH data published. Overall, between 1980 and 2000 most studies reported slight increases in surface water pH, including lakes in the Adirondack Mountains (rate variable) (Driscoll et al., 2007a) and southern New England (0.002 pH units per year) (Warby et al., 2005), and streams in the Catskill/Poconos region of New York and Pennsylvania (0.008 pH units per year) (Warby et al., 2005).

Through frequent interval monitoring from 1990 to 2000, Stoddard et al. (2003) found a decrease in hydrogen ion (0.19 µeq/L/yr) that was similar to the rate of change observed in the same Adirondack lakes by Driscoll et al. (2007a) from 1992 to 2004 (0.18 µeq/L). Stoddard et al. (2003) also reported an increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq/L/yr) and Upper Midwest lakes (0.01 µeq/L/yr). No trends were found in New England lakes or Appalachian streams in this study (Figure 4.2-8).

In summary, increasing trends in pH (decreasing hydrogen ion concentration) in surface waters in the northeastern United States were common through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have been small. Driscoll et al. (2001a,b; 2007c) attributed the limited pH recovery of lakes in acid-sensitive regions to three factors. (1) The levels of acid-neutralizing base cations in surface waters have decreased markedly because of the depletion of available base cations from the soil, and to a lesser extent, a reduction in atmospheric inputs of base cations. (2) As forests mature, their requirements for N decrease, and they are expected to exhibit increasing losses of NO_3^- as forests develop. (3) Sulfur has accumulated in the soil under previous conditions of high atmospheric S deposition and is now being gradually released to surface water as SO_4^+, even though S deposition has decreased.

4.2.3.1.5 Surface Water ANC

The most widely used measure of surface-water acidification is ANC, determined by Gran titration (titrated ANC). This measurement is the primary chemical indicator used by EPA for assessing past effects of acidic deposition, and the recovery expected from decreasing atmospheric deposition (Bulger et al., 2000; Stoddard et al., 2003). Titrated ANC is useful because it reflects the ANC of the complete chemical system, which is typically reduced by acidic deposition in acid-sensitive landscapes.

In contrast to surface water pH, ANC is more stable and it reflects sensitivity and effects of acidification in a linear fashion across the full range of ANC values. Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated and calculated ANC values are commonly determined in studies aimed at resource characterization or long-term monitoring.

Baker et al. (1990c) used ANC cutoffs of 0, 50, and 200 µeq/L for reporting on national lake and stream population estimates. ANC less than 0 µeq/L is of significance because waters at or below this level have no capacity to neutralize acid inputs. Surface waters with ANC < 50 µeq/L have been termed “extremely acid sensitive” (Schindler, 1988), are prone to episodic acidification in some regions (DeWalle et al., 1987; Eshleman, 1988), and may be susceptible to future chronic acidification at current or increased rates of acidic deposition. Bulger et al. (1999) defined ANC response categories for brook trout in Virginia as less than zero (chronic damage likely), 0 to 20 µeq/L (episodic damage likely), 20 to 50 µeq/L (likelihood of damage not determined), and greater than 50 µeq/L (brook trout not sensitive).

In assessing changes in surface water ANC, it is important to distinguish between *acidic* waters and *acidified* waters. *Acidic* describes a condition that can be measured (i.e., Gran ANC less than or equal to 0). It may be due either to the effects of acidic deposition, or to other causes such as the presence of organic acidity or the weathering of S-containing minerals in the watershed. *Acidified* refers to the consequences of the process of acidifcation (an increase in acidity observed through time). It does not require that the water body be acidic, and does not imply a particular cause for the change in chemistry. The term *anthropogenically acidified* implies that human activity was responsible for the increase in acidity that occurred.

Some of the most detailed studies of ANC have been conducted in the Adirondack Mountains. Model simulations suggested that none of the lakes in the Adirondack target lake population identified by EPA’s Environmental Monitoring and Assessment Program (EMAP) were chronically acidic or had ANC less than 20 µeq/L under preindustrial conditions, but that by 1980 there were hundreds of such lakes (Table 4.2-4). Many lakes were estimated to have had preindustrial ANC below 50 µeq/L, but this estimate more than doubled by 1990. Based on Model of Acidification of Groundwater in Catchments (MAGIC) model outputs extrapolated to the regional population of Adirondack lakes larger than 1 ha that currently have ANC below 200 µeq/L, maximum past acidification occurred by about 1980 or 1990, with median ANC of the lake population of about 61 µeq/L (reduced from a median of 92 µeq/L estimated for the preindustrial period). Changes in ANC produced an increase in not only the percentage of lakes that were chronically acidic, but also in those that were deemed likely to experience episodic acidification and its associated short-term changes in water chemistry (Sullivan et al., in press).

In other regions, responses to reduced levels of acidic deposition required by the Clean Air Act (CAA) and other emissions control legislation were reported by Stoddard et al. (2003). They found tendencies during the 1990s toward increasing surface water Gran ANC in all of the glaciated regions of the eastern United States (i.e., New England, Adirondacks, and Northern Appalachian Plateau) and Upper Midwest, and decreasing Gran ANC in the Ridge/Blue Ridge province. Changes in ANC were relatively modest compared with observed reductions in SO_4^+ concentrations in surface waters. The regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant (Table 4.2-5). Median increases of about +1 µeq/L/yr in the Northern Appalachian Plateau, Adirondacks, and Upper Midwest represent significant movement towards ecological recovery from acidification (Stoddard et al., 2003). Estimated change in the number of acidic surface waters decreased during the 1990s in all regions investigated by Stoddard et al. (2003), except the Ridge and Blue Ridge Provinces in the mid-Appalachian Mountains (Table 4.2-4). For other regions, the change in number of acidic systems ranged from −2% in New England to −68% in the Upper Midwest.

In summary, ANC is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidic deposition. ANC can be measured in the laboratory by Gran titration or calculated on the basis of the difference between the base cation sum and the mineral acid anion sum. Acidic waters are defined as those having ANC below zero. Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern United States. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations. Since about 1990 the ANC of many affected lakes and streams have shown some increase, but such increases have been relatively small.

4.2.3.1.6 Surface Water Aluminum

The concentration of inorganic Al in surface waters is an especially useful indicator of acidic deposition effects because (1) it is widely toxic, and (2) it generally does not leach from the terrestrial soils to surface waters in the absence of acidic deposition (Lawrence et al., 2007), with exceptions such as acid mine drainage and relatively rare geologic deposits. Lawrence et al. (2005) showed that strong organic acid anions can contribute to the mobilization of inorganic Al in combination with SO_4^+ and NO_3^-, but that, in the absence of geologic S, the presence of inorganic Al in surface waters is an ambiguous indication of acidic deposition effects.

Considerable work has been done to define pH sensitivity ranges for a wide variety of aquatic organisms, but when pH values fall below approximately 5.5, inorganic Al generally becomes the greater health risk to biota. Although organically complexed Al (organic Al) can occur in surface waters as a result of natural soil and hydrologic processes, this form of Al is not harmful to aquatic life (Gensemer and Playle, 1999). Inorganic Al, however, has been found to be toxic to plant and animal species throughout the food web (Gensemer and Playle, 1999).

Earlier studies demonstrated reduced growth and survival of various species of fish (Baker and Schofield, 1982; Baker et al., 1996) at inorganic Al concentrations between approximately 2 and 7.5 µmol/L. Most recently, 20% mortality of brook trout young-of-the year was documented in situ during a 30-day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al., 2007). This same study estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

The development of methods to fractionate Al into organic and inorganic forms (Driscoll, 1984; Sullivan et al., 1986) resulted in collection of a considerable amount of data on Al concentrations in surface waters in the 1980s, but most of this sampling was done either once or for a limited period of time (Driscoll and Newton, 1985; Driscoll et al., 1987a; Lawrence et al., 1987; Cronan et al., 1990). Available long-term trend information for inorganic Al is limited. In Adirondack lakes, inorganic Al concentrations decreased slightly (e.g., by 0.02 µM/yr to 0.18 µM/yr; Driscoll et al., 2007a) or remained unchanged between 1982 and 2004 (Stoddard et al., 2003; Driscoll et al., 2007a). There was no trend in inorganic Al for this period in New England lakes, Appalachian streams, or Midwest lakes. Monthly stream chemistry monitoring at the Hubbard Brook Experimental Forest showed decreases in inorganic Al concentrations at four locations along the reference stream for the experimental forest from 1982 to 2000, but no trends at two other locations along this stream (Palmer et al., 2004).

Most recently, Lawrence et al. (in review) found that 49 of 195 streams (25%) in the western Adirondack region had inorganic Al concentrations above 2.0 µM during August base flow. Although there is not a clear benchmark value above which inorganic Al is toxic to aquatic biota, 2 µM is generally recognized as a reasonable threshold for biological effects at a variety of trophic levels (Driscoll et al., 2001b; Baldigo et al., 2007).

In summary, inorganic Al is an important chemical indicator of the effects of acidic deposition on surface water. It has well-documented effects on aquatic biota at specific thresholds. Limited data suggest that acid-sensitive regions of the northeastern United States have elevated inorganic Al concentrations which have been induced by years of acidic deposition and which pose a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern United States during the last two decades in response to decreased levels of acidic deposition.

4.2.3.2 Biological Effects

Aquatic effects of acidification have been well studied in the United States and elsewhere at various trophic levels. These studies indicate that aquatic biota have been affected by acidification at virtually all levels of the food web in acid sensitive aquatic ecosystems. Effects have been most clearly documented for fish, aquatic insects, other invertebrates, and algae.

Biological effects are primarily attributable to a combination of low pH and high inorganic Al concentration. Such conditions occur more frequently during rainfall and snowmelt episodes that cause high flows of water and less commonly during low-flow conditions, except where chronic acidity conditions are severe. Biological effects of episodes center around reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions. High concentrations of Ca, and to a lesser extent other base cations, can lessen the toxicity of low pH and high inorganic Al concentration where they occur.

Biological effects in aquatic ecosystems can be divided into two major categories: (1) effects on health, vigor, and reproductive success, and (2) effects on biodiversity. The first category includes changes in biological indicators such as individual condition factor and recruitment success. The latter can be described by changes in species composition and taxonomic richness.

The following sections define concepts used to measure and evaluate acidification-related effects on aquatic biota. We present measures of changes in (1) health, vigor, and reproductive success, and (2) biodiversity for fish. Finally, the general effects literature is summarized for phytoplankton, zooplankton, benthic invertebrates, amphibians, and fish-eating birds. Specific reference is made to the biological indicators outlined above where such information exists.

4.2.3.2.1 Measures of Health, Vigor, and Reproductive Success

There are few measures of the effects of acidification on the health, vigor, and reproductive success of aquatic species. Condition factor is one measure of sublethal acidification stress that has been used to quantify effects of acidification on an individual fish. Condition factor is an index to describe the relationship between fish weight and length. Expressed as fish weight/length^3, multiplied by a scaling constant, this index reflects potential depletion of stored energy reserves (Everhart and Youngs, 1981; Goede and Barton, 1990; Dennis and Bulger, 1995). Condition factor is interpreted as depletion of energy resources such as stored liver glycogen and body fat in response to increased stress at sublethal levels (Goede and Barton, 1990). Fish with higher condition factor are more robust than fish having low condition factor. Field studies have shown lower condition factor in fish found in more acidic streams (Dennis and Bulger, 1995).

4.2.3.2.2 Measures of Biodiversity

Species composition refers to the mix of species that are represented in a particular ecosystem. Acidification alters species composition in aquatic ecosystems. There are a number of species common to many oligotrophic waters that are sensitive to acidic deposition and that cannot survive, compete, or reproduce in acidic waters. In response to small to moderate changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species, resulting in changes in community composition, but little or no change in total community abundance or biomass. The degree of alteration of surface water biological community composition increases as surface waters become more acidic. There is also a common pattern of lower community diversity with increased acidification.

One important tool that aids in the determination of effects on species composition is the Acid Stress Index (ASI) developed by Baker et al. (1990a). This index uses fish bioassay survival data to predict the probability of fish survival expressed as a percent mortality. Separate ASI models were developed for tolerant, intermediate, and sensitive fish species.

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress on biota. It can be applied at various taxonomic levels. For example, the number of fish species present in a lake or stream can be used as an index of acidification (cf. Bulger et al., 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera) (Sullivan et al., 2003). In the latter cases, the mayfly order was selected for study because it includes a number of genera and species having varying degrees of sensitivity to acidification.

Decreases in ANC and pH and increases in inorganic Al concentration have been shown to contribute to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish (Schindler et al., 1985; Keller and Gunn, 1995). Species richness is positively correlated with pH and ANC (Rago and Wiener, 1986; Baker et al., 1990b) primarily because of the elimination of acid-sensitive species at lower values of pH and ANC (Schindler et al., 1985). Interpretation of species richness can be complicated by the observation that more species tend to occur in larger lakes and streams as compared with smaller ones, irrespective of acidity (Sullivan et al. 2003). Nevertheless, decreases in species richness have been observed for all major trophic groups of aquatic organisms (Baker et al., 1990a), even after adjusting for lake size (Harvey and Lee, 1982; Frenette et al., 1986; Rago and Wiener, 1986; Schofield and Driscoll, 1987; Matuszek and Beggs, 1988).

4.2.3.2.3 Health, Vigor, and Reproductive Success of Fish

Fish populations in acidified streams and lakes of Europe and North America have declined, and some have been eliminated as a result of atmospheric deposition of acids and the resulting changes in water quality (Baker et al., 1990a). A variety of water chemistry variables, including inorganic Al, dissolved OC, and Ca, along with the timing and magnitude of episodic fluctuations in toxic acid and inorganic Al concentrations, are related to the degree to which surface water acidification influences fish survival in natural systems (Baker et al., 1990c; Gagen et al., 1993; Siminon et al., 1993; Van Sickle et al., 1996; Baldigo and Murdoch, 1997).

The effects of acidification on the health, vigor, and reproductive success are manifested through a range of physiological effects on individual life stages and fish species. The primary mechanism for the toxic effects of low pH and elevated inorganic Al on fish involves disruption of normal ion regulation at the gill surface, resulting in increased rates of ion loss and inhibition of ion uptake (McWilliams and Potts, 1978; Leivestad, 1982; Wood and McDonald, 1987; Bergman et al., 1988). Additional effects might include (1) disruption of Ca metabolism (Peterson and Martin-Robichaud, 1986; Gunn and Noakes, 1987; Reader et al., 1988), and (2) decreased hatching success (Runn et al., 1977; Peterson et al., 1980; Haya and Waiwood, 1981; Waiwood and Haya, 1983).

There exists marked variability among species, and among life stages within species, in the specific levels of pH and inorganic Al that produce measurable responses. In general, early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults (Baker and Schofield, 1985; Johnson et al., 1987; Baker et al., 1990a). Also, small fish, especially swim-up fry, are probably less mobile and less able to avoid exposure to adverse chemical conditions than the relatively larger adults (Baker et al., 1996). Here effects are described by life stage. Several studies have shown that the earliest reproductive stages are highly sensitive to low pH. The processes of oogenesis and fertilization in fish are especially sensitive (Muniz, 1991; Havas et al., 1995), most likely due to adverse effects on the female spawner. For instance, Beamish (1976) reported that reduced serum and plasma Ca in female fish in acidified Canadian lakes caused a higher probability of failure in producing viable eggs. A depletion of Ca from bone and increased numbers of females with unshed eggs have also been linked to sensitivity at this life stage (cf. Rosseland, 1986; Muniz, 1991).

After fertilization, the embryo seems to be susceptible to acidic waters throughout the whole period of development. The periods shortly after fertilization and prior to hatching seem to be most critical (Rosseland, 1986). The susceptibility of the embryo can be the result of direct exposure to elevated hydrogen ion concentrations and also to the toxic effects of inorganic Al at intermediate pH-values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to either a prolongation of the hatching or to a reduced hatching success (Rosseland, 1986). Eggs lying in gravel on stream and lake beds are to some extent protected from exposure to rapid changes in pH (Gunn and Keller, 1984b; Lacroix, 1985). Nevertheless, they can experience high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a). Yellowstone cutthroat trout (*O. c. bouveri*) were exposed to 7-day pH depressions by Farag et al. (1993). Of the four life stages studied, eggs were most sensitive to low pH. Eggs exposed for seven days to pH 5.0 test water showed a statistically significant reduction in survival compared with eggs exposed for seven days to pH 6.5 water. Survival of alevin and swim-up larvae were significantly reduced from near 100% at pH 6.5 to near 0% at pH 4.5. Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control (6.5) but not by statistically significant amounts.

Emergent alevins show susceptibility to the adverse effects of inorganic Al and hydrogen ion that increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland (1986) indicated that this increasing sensitivity results from changes that take place in the respiratory system. Shortly after hatching, alevins still respire through their skin but gradually gills become the primary organ of gas and ion exchange. Gills are the locus for interference of hydrogen ion and inorganic Al with iono-regulatory exchange.

Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus clarki*) from the Snake River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory and found that reductions in pH from 6.5 to 6.0 in low-Ca water (70 µeq/L) did not affect survival, but did reduce growth of swim-up larvae. The eggs, alevin, and swim-up larval stages showed significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher at pH 5.0 than at pH 6.5, but only statistically higher for eggs. The authors concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of inorganic Al was pH 5.0 (Woodward, 1991).

In juvenile, young-of-year and adult fish there is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and are unavailable for other functions, such as growth and reproduction (Schreck, 1981, 1982; Wedemeyer et al., 1990). Observed differences in condition factor may occur because maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger, 1999; Sullivan et al., 2003). The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish, 1969; Bulger, 1986).

Prominent physiological disturbances to fish exposed to acid waters are iono- and osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure. Most of these effects can be directly attributed to effects on gill function or structure. The acute toxicity of low pH in acidic waters results in the loss of Ca from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability (McDonald, 1983; Havas, 1986; Exley and Phillips, 1988). Al has been shown to accumulate on the gill surface when fish are exposed to water having high inorganic Al concentration.

The cumulative sublethal effects of physiological impacts can be expressed by changes in condition factor. Condition factor has been developed and applied mainly for blacknose dace. This fish species is widely distributed in Appalachian Mountain streams and is moderately tolerant of low pH and ANC, relative to other fish species in the region. However, the condition factor concept is probably applicable to other species as well. Condition factor may be a useful metric for many species in aquatic ecosystems that are only marginally affected by acidification. Bulger et al. (1999) observed a positive relationship between dace condition factor and pH in streams in Shenandoah National Park. Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. In addition to effects on blacknose dace condition factor, reduced growth rates have been also attributed to acid stress in a number of other fish species, including Atlantic salmon (*Salmo salar*), chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook trout, brown trout (*Salmo trutta*), and arctic char (*Salvelinus alpines*) (Baker et al., 1990a).

In summary, some studies have been conducted on changes in the health, vigor, and reproductive success of fish exposed to water having low pH and high inorganic Al concentration. Blacknose dace have been most thoroughly studied regarding the sublethal effects of acidity on fish condition. Effects tend to vary by life stage; early life stages tend to be particularly sensitive. Adverse effects often involve disruption of gill function, partly due to Al toxicity.

4.2.3.2.4 Fish Biodiversity

Biodiversity loss is a predictable and proven consequence of acidification, and there are abundant examples of this in North America and Europe, mostly focused on fish (cf. Bulger et al., 2000). Population-level fish response to acidification is primarily through recruitment failure, a result of increased mortality of early life stages or indirect effects through the food chain (loss of prey species). Inorganic Al, pH, and Ca have been identified as the variables most likely to have the greatest influence on fish community structure. These changes in water chemistry can alter species composition and species richness, both of which are components of biodiversity.

By 1990, it was well established that changes in pH in the range of 4.0 to 6.5 could cause significant adverse biological effects on fish community composition. As described above, the toxicity of low pH (high hydrogen ion concentration) was, in most cases, the result of impaired body salt regulation. Decreased water pH inhibited the active uptake of Na and chloride and stimulated the passive loss of these ions from the bloodstream (Baker et al., 1990a). Species vary in terms of their sensitivity to such disruptions of physiological condition.

The response of fish to pH, ANC, and inorganic Al is not uniform across species. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH values are lower, there is a greater likelihood that more fish species could be lost without replacement, resulting in decreased richness and diversity. In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than about

5.2 to 5.5. Bioassay experiments using brook trout eggs and fry have demonstrated greater mortality in chronically acidic stream water as compared to water having higher ANC.

The ASI is an index of acidification that uses fish bioassay survival data fitted to a regression model of exposure to water chemistry (pH, Al, and Ca) to predict the probability of fish survival. Approximate ASI reference levels were reported by Baker et al. (1990c) for various fish species, based on logistic regression of fish presence as a function of the sensitive, intermediate, and tolerant ASI values for brown bullhead (*Ameiurus nebulosus*), brook trout, lake trout, and common shiner (*Luxilus cornutus*) (Table 4.2-6).

Fish species richness is an important indicator of acidification response, in part because the public tends to place relatively high value on fisheries resources. As discussed in the previous section, lakes and streams having pH below about 5.0 or ANC below about 0 generally do not support fish. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 µeq/L (Bulger et al., 1999; Cosby et al., 2006; Sullivan et al., 2006a). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is relatively easily determined and is one of the most useful indicators of biological effects of surface water acidification.

Some of the most in-depth studies of the effects of acid stress on fish species richness have been conducted in the streams Shenandoah National Park and the lakes in the Adirondack Mountains. These regions are examined in detail below. However, it is important to note that effects on fish species richness have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York (Stoddard and Murdoch, 1991) and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina (SAMAB, 1996; Bulger et al., 1999, 2000).

The Shenandoah National Park Fish in Sensitive Habitats (FISH) Project evaluated the effects of streamwater acidification on fish communities in streams in Shenandoah National Park, Virginia (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and Bulger, 1995). A statistically robust relationship between stream ANC and fish species richness was documented. Numbers of fish species were compared among 13 Shenandoah

National Park streams spanning a range of pH and ANC conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base status (during the 7-year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 4.2-10). The 3-year FISH study of stream acidification demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al., 1999). Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress associated with acidification. However, an additional causal factor may have been a decrease in the number of available aquatic niches when moving from downstream locations (which are seldom low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region; Sullivan et al., 2003).

South of Shenandoah National Park, the effects of surface water acidification on fish species richness have been studied in some detail in the St. Marys River in Virginia. Fish species richness was closely associated with surface water acid-base chemistry. The number of fish species in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*] are tolerant of low pH and are typically the only fish species present in streams having similar levels of acidity in nearby Shenandoah National Park (Bulger et al., 1999).

Dynamic water chemistry model projections have been combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the Shenandoah National Park data was used by Sullivan et al. (2003), along with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present and future chemical conditions simulated for each stream. Results suggest that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic bedrock; 1.6 species lost), with fewer lost species on granitic bedrock and basaltic bedrock (average of 0.4 species lost).

In the Adirondack Mountains, lakewater acidification and the associated elevated concentrations of inorganic Al have adversely affected fish populations and communities in sensitive areas (Baker and Schofield, 1982; Johnson et al., 1987; Schofield and Driscoll, 1987; Baker et al., 1990b; Siminon et al., 1993). Of the 53 fish species recorded in Adirondack lakes

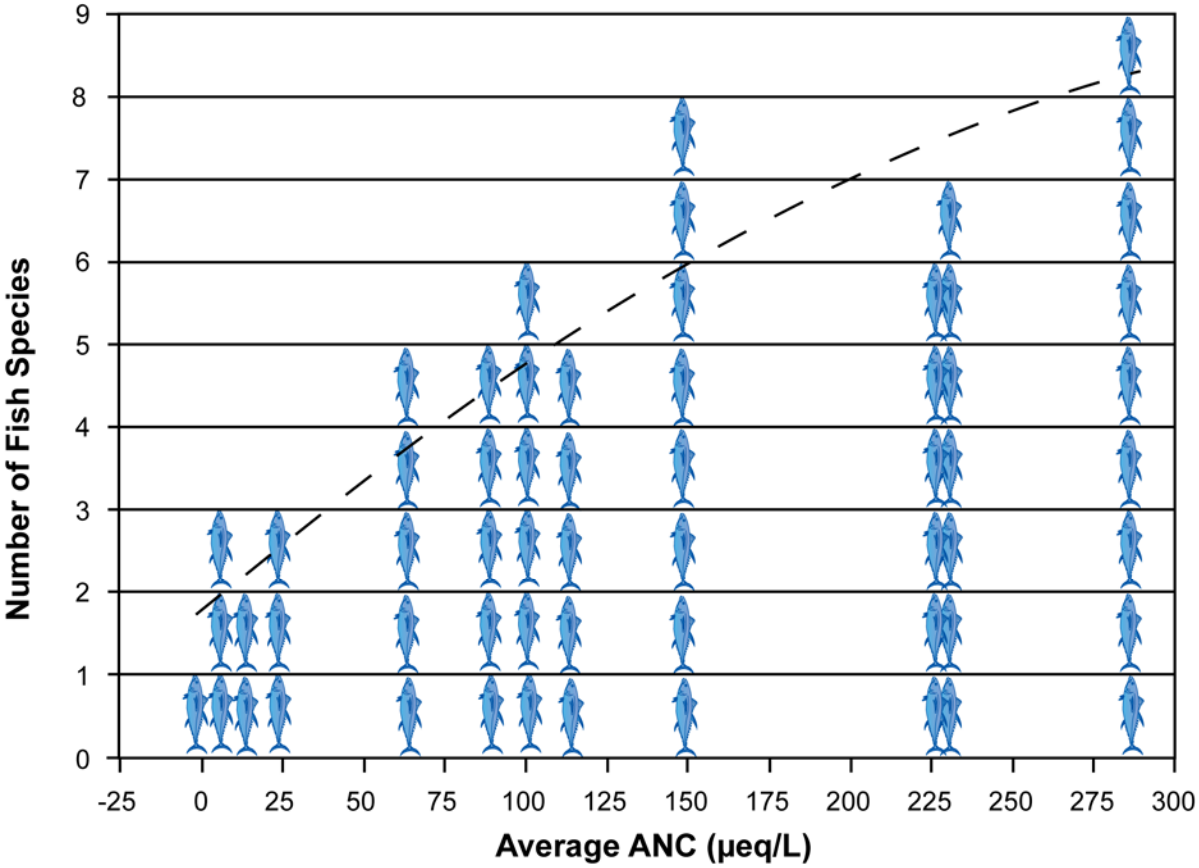


Figure 4.2-10. Number of fish species as a function of mean stream ANC among 13 streams in Shenandoah National Park, Virginia. Values of ANC are means based on quarterly measurements, 1987-1994. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently < 75 µeq/L had three or fewer species.

Source: Redrawn from Bulger et al. (1999).

by the Adirondack Lakes Survey Corporation, about half (26 species) were absent from lakes with pH below 6.0. Among the absent species were several important recreational species (Baker et al., 1990b), plus ecologically important minnows that serve as forage for sport fish. Fully 346 of 1,469 lakes surveyed supported no fish at all at the time of the survey. These lakes were significantly lower in pH, dissolved Ca, and ANC, and had higher concentrations of inorganic Al than lakes hosting one or more species of fish (Gallagher and Baker, 1990). Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH higher than 6.5 (Baker et al., 1990b; Driscoll et al., 2001a).

High-elevation lakes are more likely to be fishless than larger lakes at low elevation (Gallagher and Baker, 1990). This observation has been attributed to the fact that high elevation lakes tend to have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to periodic winter kills. Small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless high-elevation lakes; acidity is likely to play an important role in the absences of fish from such lakes (Driscoll et al., 2001b).

Sullivan et al. (2006a) developed a relationship between fish species richness and ANC class for Adirondack lakes. Under chronically acidic conditions (summer index or annual average ANC < 0 µeq/L), Adirondack lakes are generally without fish. There was a marked increase in mean species richness with increases in ANC up to values of approximately 50 to 100 µeq/L (Figure 4.2-11). The asymptote for the fish species equation was 5.7 species. This analysis suggests that there could be loss of fish species with decreases in ANC below approximately 50 to 100 µeq/L.

It is important to note that the absence of fish from a given lake or stream in an area that experiences surface water acidification does not necessarily imply that acidification is responsible for the absence of fish. For example, results of fisheries research in the Adirondacks has indicated that many Adirondack lakes always had marginal spawning habitat for brook trout (Schofield, 1993). However, multivariate regression of the presence or absence of brook trout in Adirondack waters produced a ranking of factors that appeared to influence the presence of brook trout when biological factors were excluded from the analysis (stocking, presence of associated species, presence of competitors). Among contributing factors, including silica (Si), ANC, dissolved OC, substrate type, and distance to the nearest road, pH ranked first as a predictor of brook trout presence (Christensen et al., 1990). The results of this analysis supported that 1990 levels of pH and related variables restricted the distribution of fish in some Adirondack lakes.

In summary, acidic conditions characterized by low pH, low ANC, and high inorganic Al exert considerable influence on the fish species composition of sensitive surface waters, particularly in the eastern United States. Low pH and ANC, and high inorganic Al

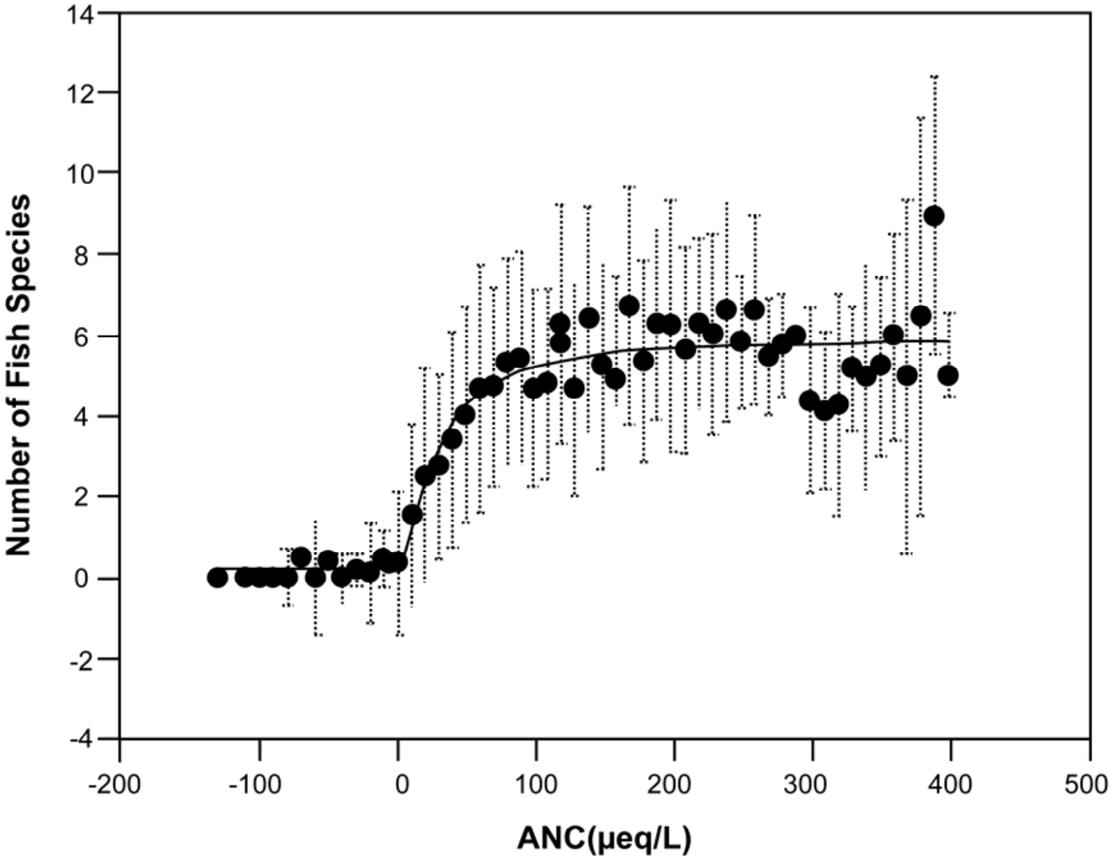


Figure 4.2-11. Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 μeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

Source: Sullivan et al. (2006a).

concentrations, contribute to loss of the most acid-sensitive fish species. Species richness is a common indicator used to reflect the effects of water acidification on aquatic biota. This index is most often applied to fish. Few or no fish species are found in lakes and streams that have low ANC (near zero) and low pH (near 5.0). The number of fish species generally increases at higher ANC and pH values. This relationship is complicated to some extent by the tendency of smaller lakes and streams (which are more likely to have low ANC and pH) to host fewer fish species, regardless of acid-base chemistry. Nevertheless, available data suggest that acid stress is a major factor governing the observed relationship between fish species richness and surface water acidity.

4.2.4 Characterization of Most Sensitive and Most Affected Ecosystems and Regions

4.2.4.1 Characteristics of Sensitive Ecosystems

The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is geology. Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been used in numerous acidification studies (e.g., Bricker and Rice, 1989; Stauffer, 1990; Stauffer and Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007). Other factors contribute to the sensitivity of soils and surface waters to acidic deposition, including topography, soil chemistry, land use, and hydrologic flowpath.

Several studies have confirmed the importance of geology in regulating terrestrial and aquatic ecosystem sensitivity to acidification, and highlighted other key factors responsible for terrestrial and aquatic sensitivity to acidic deposition throughout the southeastern United States. In terrestrial ecosystems, sensitive systems often occur in high-elevation spruce-fir forests dominated by relatively unreactive bedrock in which base cation production via weathering is limited (Elwood et al., 1991). Soils in such areas tend to have thick organic horizons, high organic matter content in the mineral horizons, and low pH (Joslin et al., 1992). Because of the largely unreactive bedrock, base-poor litter and organic acid anions produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these high-elevation forests tends to be below about 10% and the soil cation exchange complex is generally dominated by Al (Johnson and Fernandez, 1992; Eagar et al., 1996).

Galloway (1996) further attributed forest soil sensitivity to acidification in the southeastern United States to atmospheric deposition level, soil age, weathering rate, and S adsorption capacity. Moncoulon et al. (2004) suggested that forest ecosystem sensitivity to acidification varies mainly with weathering rate. In a review of 241 ecosystem types in France (classified by pedologic and geologic characteristics), the ecosystems most susceptible to acidification were those with low weathering rates and thus limited buffering capacity (Moncoulon et al., 2004).

In hardwood forests, species nutrient needs, soil conditions, and additional stressors work together to determine sensitivity to acidic deposition. Stand age and successional stage also can affect the susceptibility of hardwood forests to acidification effects. In northeastern hardwood forests, older stands exhibit greater potential for Ca depletion in response to acidic deposition than younger stands. Thus, with the successional change from pin cherry (*Prunus pensylvanica*), striped maple (*Acer pensylvanicum*), white ash (*Fraxinus americana*), yellow birch and white birch (*Betula papyrifera*) in younger stands to beech and red maple in older stands, there is an increase in sensitivity to acidification (Hamburg et al., 2003).

Land use influences watershed sensitivity to acidification mainly through land disturbance and consequent exposure of S-bearing minerals to oxidation, loss of base cations through erosion and timber harvesting, and change in N status of the forest through timber management. Each of these types of activity can influence the relative availability of mobile mineral acid anions (SO_4^+, NO_3^-) in soil solution and base cations (Ca, Mg, K, Na) on the soil ion exchange sites and in drainage water.

The movement of water through the soils into a lake or stream, and the interchange between drainage water and the soils and sediments, strongly regulate the type and degree of watershed response to acidic inputs (Sullivan, 2000). Surface waters in the same setting can have different sensitivities to acidification depending on the relative contributions of near-surface drainage water and deeper groundwater (Eilers et al., 1983; Chen et al., 1984; Driscoll et al., 1991).

In summary, lakes and streams in the United States that are sensitive to episodic and chronic acidification in response to SO_X, and to a lesser extent NO_X, deposition tend to occur at relatively high elevation in areas that have base-poor bedrock, high relief, and shallow soils. For example, in the Southern Appalachian region, Sullivan et al. (2002a, 2007) determined that underlying bedrock geology dominated by sandstone or related rock types and elevations greater than 1000 m (3250 ft) could be used to identify landscapes in the region most likely to contain acidic streams.

4.2.4.2 Extent and Distribution of Sensitive Ecosystems

4.2.4.2.1 Surface Waters

Several regions of the United States contain appreciable numbers of lakes and streams with low ANC (less than about 50 µeq/L), including portions of the Northeast (especially New England, the Adirondacks, and the Catskill Mountains), Southeast (the Appalachian Mountains and northern Florida), Upper Midwest, and western United States (Charles, 1991). The Adirondack and Appalachian Mountains, and to a lesser extent the Upper Midwest, include many acidified surface waters that have been impacted by acidic deposition. Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidic deposition in these areas is less clear. The western United States contains many of the surface waters most susceptible to potential acidification effects, but with the exception of the Los Angeles Basin and surrounding areas, the levels of acidic deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has likely been very limited.

Several national assessments have been conducted to estimate the distribution and extent of surface water acidity in the United States. During summer baseflow of 2004, the EPA conducted a National Wadeable Stream Assessment (WSA) survey of 1,392 randomly selected sites across the conterminous 48 United States to assess the ecological condition of wadeable streams (U.S. Environmental Protection Agency, 2006c). Because this sampling was conducted during baseflow in the summer, which exhibits the least acidic conditions of the year, only the most chronically acidified streams were identified as acidic. Therefore, the extent of potential seasonal acidification was underestimated by this approach (Lawrence et al., in review). Overall, less than 1% of the 1,020,000 km of stream in the target population (based on the 1:100,000-scale U.S. Geological Survey (USGS) map blue line network) was acidic due to acidic deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams attributable to acidic deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0-25 µeq/L) streams likely exposed to episodic acidification were found in the Northern Appalachians (2.7% of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of 204,000 km).

Even though the WSA had over 1,300 sample sites, it was still a very coarse sample of the nation's streams with respect to acidic deposition effects, which are only observed in spatially restrictive subpopulations. More precise survey estimates of the effects of surface water acidification were made in the National Surface Water Survey (NSWS) in the mid 1980s. By statistically selecting representative lakes and streams in each surveyed region, the NSWS estimated chemical conditions of 28,300 lakes and 56,000 stream reaches (Baker et al., 1990c). The NSWS concluded that 4.2% of lakes larger than 4 ha and 2.7% of stream segments in the acid-sensitive regions of the eastern United States were acidic. The NSWS documented the status and extent of surface water acid-base chemistry during probability surveys of lakes and streams conducted from 1984 through 1988 in the major acid sensitive regions of the United States (Linthurst et al., 1986a; Landers et al., 1987; Kaufmann et al., 1988). The data collected by the NSWS allowed EPA and the states to focus monitoring efforts on those areas that contain the majority of anthropogenically acidified waters in the United States, and that are most likely to respond to changes in deposition as a result of the 1990 Amendments to the CAA (CAAA) and other air pollution control legislation.

The stream component of the NSWS, the National Stream Survey (NSS), was focused in the northern and southern Appalachians and Coastal Plain of the eastern United States (Kaufmann et al., 1991). The NSS included 500 stream reaches selected from 1:250,000 scale USGS topographic maps using a systematic, randomized sample. Study reaches were sampled at both the upstream and downstream end of each selected reach. Population estimates were made for chemistry at both reach ends and for stream length by interpolating chemical results between reach ends.

Overall, out of the estimated 57,000 stream reaches in the NSS, after excluding streams acidic due to acid mine drainage, 6.2% of the upstream and 2.3% of the downstream reach ends were acidic during spring baseflow (Kaufmann et al., 1991). After interpolation, this corresponded to 2.7% of the 201,000 km of stream in the study region. In acidic and low-ANC NSS reaches, ANC usually increased with downstream distance. Acidic (ANC $\leq$0) streams were located in the highlands of the Mid-Atlantic Region (southern New York to southern Virginia, 2320 km), in coastal lowlands of the Mid-Atlantic (2530 km), and in Florida (461 km). Acidic streams were rare (less than 1%) in the highlands of the Southeast and Piedmont. Inorganic monomeric Al concentrations were highest in acidic streams of the Mid-Atlantic Highlands, where over 70% of the acidic streams had inorganic Al greater than 3.7 µM (100 µg/L), a concentration above which deleterious biological effects have frequently been reported.

Anion composition of the NSS stream samples was examined in order to evaluate the most probable sources of stream acidity in acidic and low-ANC sites (Baker et al., 1991; Herlihy et al., 1991). Acidic streams that had minimal organic influence (organic anions constituted less than 10% of total anions), and SO_4^+ and NO_3^- concentrations indicative of evaporative concentration of atmospheric deposition, were classified as acidic due to acidic deposition. These acidic streams were located in small (<30 km^2) forested watersheds in the Mid-Atlantic Highlands (an estimated 1980 km of stream length) and in the Mid-Atlantic Coastal Plain (1250 km). Acidic streams affected primarily by acidic deposition but also influenced by naturally occurring organic anions accounted for another 1210 km of acidic stream length and were mainly located in the New Jersey Pine Barrens, plateau tops in the Mid-Atlantic and Southeast Highlands, and the Florida Panhandle. The total length of streams that were identified as acidic due to acid mine drainage in the NSS (4590 km) was about the same as the total length of acidic streams likely affected by acidic deposition (4455 km). Acidic streams whose acid anion composition was dominated by organics were mainly located in Florida and the Mid-Atlantic Coastal Plain. In Florida, most of the acidic streams were organic-dominated, whereas about half of the acidic streams in the Mid-Atlantic Coastal Plain were organic-dominated. Organic-dominated acidic streams were not observed in the Mid-Atlantic or Southeast Highlands.

Stoddard et al. (2003) presented a map of acid-sensitive regions of the eastern United States where lakes and streams occur that are likely to be affected by acidic deposition (Figure 4.2-12). The map shows considerable overlap with the areas of high interest identified by Baker et al. (1990c). Surface waters in most other regions of the United States are not sensitive to the impacts of acidification due largely to the nature of the local geology (Stoddard et al., 2003). An exception is the region surrounding the Los Angeles Basin, which receives high N deposition (>20 kg N ha^{-1} yr^{-1} in some areas) and includes streams with very high NO_3^- concentrations (>50 µeq/L).

In addition to the large water chemistry databases developed by the EPA that help to identify the spatial distribution of acid-sensitive and acid-impacted surface waters in the United States, there are also some important supplemental regional databases in New England, the

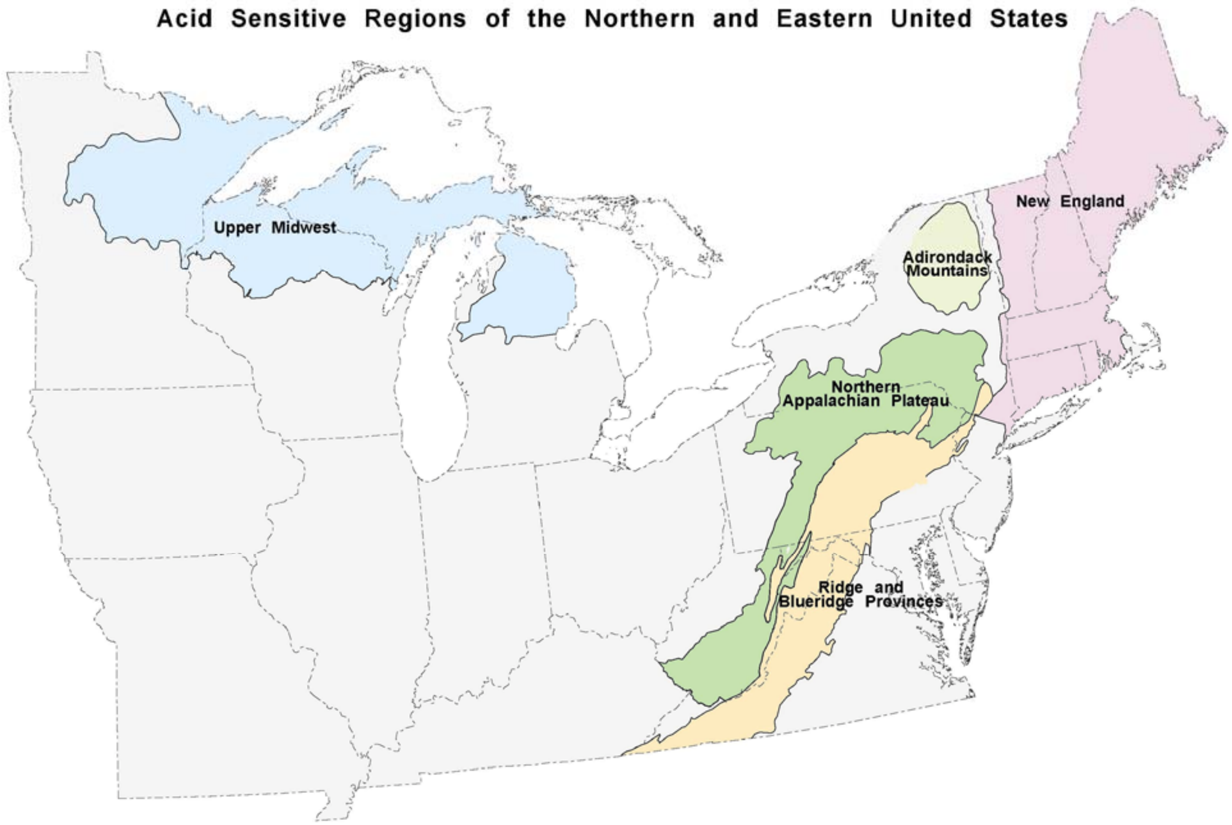


Figure 4.2-12. Regions of the eastern United States that contain appreciable numbers of lakes and streams that are sensitive to acidification from acidic deposition.

Source: Stoddard et al. (2003).

Adirondacks, the mid-Appalachian region, the Florida Panhandle, the Upper Midwest, and the Western United States. Results from these studies are summarized below.

New England

For the New England region, results from EPA's TIME program indicate that 5.6% of the regional lake population (386 lakes) in New England exhibited ANC < 0 µeq/L during the period 1991 to 1994. This result is similar to the Environmental Monitoring and Assessment Program (EMAP) findings, which indicate that 5% of lakes in New England had ANC values less than 0 µeq/L. The EMAP survey was a probability based survey representative of lakes with surface area greater than 1 ha (1,812 lakes). The survey was conducted during low-flow summer conditions, and the results therefore likely reflect the highest ANC values for the year. The EMAP analysis also estimated that an additional 10% of the population had low ANC values, between 0 and 50 µeq/L, and were probably sensitive to episodic acidification (Driscoll et al., 2001b).

Adirondacks

A study by Driscoll et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the extent of acidic lakes in the Adirondacks for that period. Results from the survey indicate that 10% of the population of Adirondack lakes were chronically acidic (ANC values of less than 0) and 31% were sensitive to episodic acidification (ANC values between 0 and 50) during the study period (Driscoll et al., 2001b).

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

Mid-Appalachian Region

A compilation of survey data from the mid-Appalachians yields a consistent picture of the acid-base status of streams. In the subpopulation of upland forested streams, which comprises about half of the total stream population in the mid-Appalachian area, data from various local surveys showed that 5% to 20% of the streams were acidic, and about 25 to 50% had ANC < 50 µeq/L (Herlihy et al., 1993). NSS estimates for the whole region showed that there were 2330 km of acidic streams and 7500 km of streams with ANC < 50 µeq/L. In these forested reaches, 12% of the upstream reach ends were acidic and 17% had pH ≤5.5. SO_4^+ from atmospheric deposition was the dominant source of acid anions in acidic mid-Appalachian streams.

Cosby et al., (2006) provided a detailed characterization of streamwater acid-base chemistry in Shenandoah National Park, Virginia, which has been the most thoroughly studied area within the mid-Appalachian Mountain region with respect to acidification from acidic deposition. Based on MAGIC model simulations and extrapolation using landscape characteristics, Cosby et al. (2006) developed maps showing the distribution of streamwater conditions in the park for the preindustrial past, current conditions, and anticipated future conditions.

Florida Panhandle

According to the EPA's Eastern Lakes Survey conducted in 1984, 75% of the Florida Panhandle lakes were acidic at that time, as were 26% of the lakes in the northern peninsula. Most of the acidic lakes were clear water (dissolved OC < 400 µM) seepage lakes in which the dominant acid anions were chloride and SO_4^+. Most of the acidic and low-ANC lakes were located in the Panhandle and northcentral lake districts. Acidic streams were located in the Panhandle and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-corrected sum of base cations (mean 21 µeq/L) and sea salt-corrected SO_4^+ concentrations (mean 16 µeq/L). One-fourth of these acidic Panhandle streams were organic-dominated but the remaining sites all had dissolved OC < 2 mg/L. Inorganic monomeric Al concentrations in these acidic streams were very low (mean 11 µg/L). In these low dissolved OC, low ANC Panhandle streams, it was suggested that the degree of SO_4^+ and NO_3^- retention in soil was an important control on streamwater ANC (Baker et al., 1990c).

Upper Midwest

Based on the Eastern Lakes Survey, the Upper Midwest has a large population of lakes having ANC ≤200 µeq/L, (Linthurst et al., 1986a,b); only 6% of the lakes had ANC ≤50 µeq/L. Groundwater recharge lakes (those having Si concentration less than 1 mg/L, indicating little groundwater input) constituted 71% of the seepage lakes in the Upper Midwest, and were more frequently low in pH and ANC. Five percent were acidic and 9% had pH ≤5.5. Nearly 90% of Upper Midwestern lakes that had ANC ≤50 µeq/L were in the groundwater recharge category (Baker et al., 1991). Such lakes tend to be susceptible to acidification from acidic deposition.

Acidic lakes in the Upper Midwest are primarily small, shallow, seepage lakes that have low concentrations of base cations and Al and moderate SO_4^+ concentrations. Organic anions, estimated by both the Oliver et al. (1983) method and the anion deficit, tend to be less than half the measured SO_4^+ concentrations in the acidic lakes (Eilers et al., 1988), but much higher in many of the drainage lakes that are less sensitive to acidification from acidic deposition.

West

Landers et al. (1987) identified subregions in the West with acid-sensitive lakes, based on results of EPA's Western Lakes Survey. The surface water chemistry data for the West indicate that the Sierra Nevada and Cascade Mountains constitute the mountain ranges with the greatest number of sensitive lake resources. Surface waters in this region are among the most poorly buffered surface waters in the United States (Landers et al., 1987; Melack and Stoddard, 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute, mildly acidic snowpack.

Many Cascade and Rocky Mountain lakes are highly sensitive to potential acidic deposition effects (Nelson, 1991; Turk and Spahr, 1991). It does not appear that chronic acidification has occurred to any significant degree, although episodic acidification has been reported for lakes in the Colorado Front Range (Williams and Tonnessen, 2000).

Along the eastern edge of the Continental Divide in Colorado and southeastern Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in the mountainous areas that are exposed to relatively high (by western standards) deposition of N. A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically acidic (ANC < 0), although several had ANC < 10 µeq/L, and more than 10% of the lakes had ANC < 50 µeq/L.

Forest Ecosystems

No systematic national survey of terrestrial ecosystems in the United States has been conducted to determine the extent and distribution of terrestrial ecosystem sensitivity to acidic deposition. The scarcity of information on sensitive terrestrial ecosystems is due in part to sparse soils data. In general, forest ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachians are considered to be the regions most sensitive to terrestrial acidification effects from acidic deposition.

One national and a few regional efforts have been undertaken to characterize forest sensitivity to acidic deposition using a critical loads approach. In this context, acid-sensitive soils are those which contain low levels of exchangeable base cations and low base saturation. On a broad national scale, McNulty et al. (2007) used a simple mass balance equation and available national databases to estimate forest soil critical acidic loads (for wet and dry deposition of S and N) and exceedences for forest soils. Exceedences are pollutant loads that are greater than the estimated critical load. They found that approximately 15% of forest soils in the United States exceed the estimated critical load of wet and dry deposition of S and N by more than 250 eq ha^{-1} yr^{-1} (McNulty et al., 2007). The areas where exceedences reach this level could be considered to represent those areas that are likely most sensitive to continued high levels of acidic deposition. Thus, there is not a national survey of soil sensitivity to acidification, but there are approaches available with which to identify areas likely to include sensitive soils.

It should be noted that the McNulty et al. (2007) paper represents the beginning of an iterative process to identify more precise critical loads for terrestrial acidity. The authors note that the actual area in exceedence of the forest soil critical acid load may be higher than the mapped estimates for several reasons (McNulty et al., 2007). First, their estimated total deposition did not include cloud deposition. Second, base cation deposition to near-coastal areas was not corrected for marine aerosol contributions. Third, the 1-km squared grid size of the mapping resulted in averaging of soil and deposition data, which removed extreme values from the analysis (McNulty et al., 2007). The authors take care to describe their results as “preliminary” and note that a more systematic analysis of model-predicted and measured forest soil critical acid load exceedance is needed before this approach can be used as a tool for identifying areas of potential forest health concern (McNulty et al., 2007). For these reasons, and because of the significant uncertainty associated with many of the large national databases used in the analysis, the appropriate use of this information is not for the actual determination of critical loads at specific locations or for predictions of forest health effects, but rather for increased understanding of relative differences in forest soil sensitivity at a national scale. In general, the Northeast, the Southern Appalachians, parts of Florida and the Upper Midwest have the highest proportion of soils that exceed the estimated critical acid load by at least 250 eq ha^{-1} yr^{-1} and could therefore be termed vulnerable. Where the exceedances are highest, forest soils are likely most sensitive to continued impacts from acidic deposition.

Another approach to identification of sensitive forest lands is to map the distribution of tree species thought be most sensitive to adverse impacts. The effects of acidic deposition are particularly well documented for red spruce trees that occur in the northeastern United States and southern Appalachian Mountains (Figure 4.2-5 shows the distribution). In the Northeast, red spruce grows at elevations from near sea level to about 4500 feet. In the Appalachian Mountains, spruce-fir forests are generally found at relatively high elevation, for example above about 1400 m in the southern Appalachian Mountains (SAMAB, 1996). Northern hardwood forests have also been identified as forest resources experiencing air pollution impacts. Impacts are best documented for sugar maple trees which are broadly distributed across the northern hardwood forests in the northeastern United States (Figure 4.2-5 shows the distribution). The areas where sugar maple appears to be at greatest risk are along ridges and where it occurs on nutrient-poor soils.

4.2.4.3 Levels of Deposition at Which Effects are Manifested

The effects of S and N deposition are manifested at a range of deposition levels, depending on the inherent sensitivity of the natural resources, as described in the previous sections, and the historical deposition loading. The intersection between current loading, historic loading, and sensitivity defines the ecologic vulnerability to the adverse effects of acidification. Few studies in the United States have defined deposition levels that are associated with effects over large areas.

Some degree of surface water acidification, and perhaps also of soil acidification, can occur at very low levels of S deposition (only a few kg ha^{-1} yr^{-1}). These highly sensitive soils are characterized by very low levels of exchangeable base cations and base saturation. They provide limited neutralization of acidic drainage water.

Effects levels for N deposition can be established based on changes to stream and soil chemistry that signal alteration of nutrient cycling, causing NO_3^- leaching. Analyses have been conducted in the northeastern United States and Europe to examine the relationships between N deposition and NO_3^- leaching to surface waters. The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N ha^{-1} yr^{-1}. Aber et al. (2003) concluded that loss of NO_3^- to surface waters during the growing season in forested watersheds often occurs above a threshold of total (wet plus dry) atmospheric N deposition of about 8 to 10 kg N ha^{-1} yr^{-1}.

The effects of N addition on forests have been shown to be wide-ranging. Additions of 25 kg N ha^{-1} yr^{-1} to spruce plots in Vermont (ambient bulk deposition 5.4 kg N ha^{-1} yr^{-1}), in which net nitrification did not occur prior to treatment, triggered net nitrification in the second year of treatment (McNulty et al., 1996). Similar results were seen in Colorado, where additions of 25 kg N ha^{-1} yr^{-1} to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition 4 to 5 kg N ha^{-1} yr^{-1}) doubled N mineralization rates and stimulated nitrification. In marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest, Massachusetts, which received additions of 150 kg N ha^{-1} yr^{-1} (Magill et al., 2004). Concentrations of NO_3^- plus NH_4^+ in hardwood plots receiving 50 kg N ha^{-1} yr^{-1} were not yet detectable in the 15th year of treatment.

Many of the changes in plant species composition, species diversity, and nitrification and mineralization rates in response to atmospheric N deposition are associated with nutrient N fertilization, rather than acidification. They are discussed in more detail in Section 4.3.

4.2.4.3.1 Critical Loads and Timeframes of Response

Critical loads one way one way to express the amount of deposition of an atmospheric pollutant (a “load”) or the concentration of an airborne pollutant that can be tolerated by natural or synthetic systems without significant harm or change occurring in those systems. The generally accepted definition of a critical load of atmospheric pollutant deposition emerged from a pair of international workshops held in the late 1980s (Nilsson, 1986; Nilsson and Grennfelt, 1988). The workshop participants defined a critical load as:

> “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.”

Further background information on the concept of critical loads, how a critical load is developed, spatial scale issues, and current United States and Canadian efforts is provided in Section 4.1.2.

It is important to note that critical loads developed to date in the United States have largely been at sub-regional scales or for individual sites and usually used a catchment-based approach. The definitions of adversity and harm in critical load applications are specific to the resource under consideration. Therefore, there is no single “definitive” critical load for a natural resource. Rather, there is a range of values, each of which is applicable to a particular sensitive resource element. The chemical indicators and linkages to biological receptors articulated through the critical loads process can provide a framework for documenting ecosystem responses to changing emissions and deposition. For example, surface water monitoring data collected from 1990 to the present provide information on the extent to which lakes and streams are responding to reductions in SO_2 emissions. This information is then used in models to estimate how ecosystems may respond in the future. The response of surface waters since the 1990s and projected future responses in terrestrial and aquatic ecosystems in sensitive regions are summarized below using many of the indicators identified through the various critical loads initiatives.

4.2.4.3.2 Chemical Response

As discussed in Section 4.2.1.6, surface water chemistry has responded to changes in emissions and deposition of S and N over the past two to three decades. Monitoring data collected within EPA's Long-Term Monitoring (LTM) and TIME projects, as well as other monitoring programs, have been key to understanding chemical responses. See discussion of major monitoring programs in Annex 3. Surface water chemistry monitoring data generated through TIME and LTM (Stoddard et al., 2003) suggest that the following important changes in lake and stream chemistry have occurred over the past one to two decades in the eastern United States:

- SO_4^+ concentration has decreased as a percentage of total ion concentration in surface waters.
- ANC has increased modestly in three of the five regions studied.
- Dissolved OC and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidic deposition has decreased.
- Inorganic Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

The significant decreases in SO_4^+ concentration which have been observed in many areas have not necessarily brought large changes in the acidity of lakes and streams. For example, the decline in Adirondack lakewater SO_4^+ during the 1980s was charge-balanced by a nearly equivalent decrease in concentrations of base cations in many of the low-ANC lakes, and this limited the increase in ANC and pH that occurred in response to lower SO_4^+ concentrations. Overall, improvements in lakewater acid-base chemistry since 1990 have been measurable but modest. Similar patterns have been observed in most other regions. There are currently no data in the United States that indicate increases in soil pH associated with recent declines in acidic deposition levels.

Dynamic models have been used in certain regions to help determine whether the changes in surface water chemistry that have occurred over the past one to two decades will continue and whether they will reach levels needed to support biological recovery. The most commonly used models are described in Annex 3, and details of these analyses are discussed below. In general, model forecasts indicated that under base case conditions (those expected under existing or anticipated emissions controls) surface water ANC in the southern Appalachians and parts of the Adirondacks would be likely to decline in the future. Results from northern New England suggest mixed responses with less sensitive areas showing continued improvement. Recently mandated emissions controls under the Clean Air Interstate Rule (CAIR) may modify this expectation. In terms of soil chemistry, projected future improvements in both the Adirondacks and southern Appalachian Mountains appear to be extremely slow and in most cases do not reach a base saturation of 20% or more within the next 100 years.

In the eight-state Southern Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC class. The model runs were based on three emissions control strategies (A2, B1, and B3). A2 is the base case that represents best estimates for air emission controls under regulations for which implementation strategies were relatively certain at the time of the study (about the year 2000), including the acid rain controls under Title IV of the 1990 Amendments to the CAA, the 1-h ozone (O_3) standard, NO_X reductions required under EPA’s call for revised State Implementation Plans (SIPs), and several highway vehicle and fuel reductions. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight states in the southern Appalachian Mountains region, but covering all emissions sectors.

The results for the portion of the region south of Virginia and West Virginia suggest that the percentages of streams having ANC below zero and below 20 µeq/L will actually increase through the year 2040 under all except the most restrictive emissions control strategies (Sullivan et al., 2005). Most simulated changes in stream water ANC from 1995 to 2040 were rather modest, given the very large estimates of future decrease in S deposition. Few modeled streams showed projected change in ANC of more than about 20 µeq/L (Sullivan et al., 2005). Some of the largest changes were simulated for some of the streams that were most acidic in 1995. For such streams, however, even relatively large increases in ANC would still result in stream water having negative ANC, and therefore little biological improvements would be expected from the simulated improvement in chemistry (Sullivan et al., 2005).

Similarly, Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in total S deposition of 40% and 70% from 1991 levels S. Bulger et al. (2000) estimated that 1991 ambient stream chemistry was marginal or unsuitable for brook trout in half of the streams in western Virginia that were considered in the study. The model projections suggest that neither the 40% nor the 70% reductions in S deposition would be expected to increase the number of streams that were suitable for brook trout above the ambient 50% (Bulger et al., 2000). In fact, the results suggest that a 70% reduction in deposition would be needed in the long term just to maintain the number of streams that were considered suitable for brook trout (Bulger et al., 2000). Because of the length of time required to restore buffering capacity in watershed soils (typically more than 100 years), most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

Sullivan et al. (2002b) used the NuCM model to evaluate potential changes in soil chemistry in response to acidic deposition in the southern Appalachian Mountains. The results suggest that spruce-fir forests in the region are likely to experience decreased Ca:Al ratios in soil solution under virtually all strategies of reduced future acidic deposition considered. This result was partly because S adsorption in soils is likely to decline, even with dramatically reduced S deposition. In addition, many spruce-fir forests in the region are N-saturated, and continued N deposition at moderate or high levels would be expected to contribute to elevated NO_3^- concentrations in soil water, which could further enhance base cation leaching and mobilization of Al from soils to soil solution.

In the Adirondacks, model results produced by several studies suggest that the trend of increasing lakewater ANC for the most acid-sensitive lakes might not continue in coming decades. These results are discussed below in the Adirondack case study.

In a regional application of PnET-BGC, Chen and Driscoll (2005) analyzed 60 DDRP (Direct Delayed Response Project) lake watersheds within northern New England under three future emissions reduction scenarios. Most of the lakes had surface water ANC values greater than 50 µeq/L in 1984 and were therefore not considered chronically acidic. The authors reported that ANC was projected to increase under all three scenarios, with greater rates of recovery occurring with deeper emissions reductions. Soil improvements were slow and modest under all scenarios. Simulations suggested that 80% of the northern New England sites and 60% of the Maine sites will have soil base saturation below 20% in 2050 (Chen and Driscoll, 2005). They concluded that the decreases in SO_4^+ and NO_3^- concentrations in surface water were coupled with nearly stoichiometric decreases in base cation concentrations. Simulated improvements in ANC in response to reduced acidic deposition were minor. Therefore, while further declines in atmospheric deposition in S and N will bring some improvements, most ecosystems in the study were not expected to recover to background conditions by 2050.

In summary, declines in SO_2 and NO_X emissions have brought about measurable improvements in streamwater chemistry in sensitive regions of the United States since 1990. However, model forecasts suggest that a reversal in chemical recovery could occur under base case emissions and deposition levels in many sensitive ecosystems and that further reductions beyond those required by the 1990 Amendments to the Clean Air Act may be needed to prevent continued adverse effects and to support biological recovery of terrestrial and aquatic ecosystems.

4.2.4.3.3 Biological Response

Biological recovery can occur only if chemical recovery is sufficient to allow survival and reproduction of acid-sensitive plants and animals. The time required for biological recovery is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored because of the long life of many plant species and the complex interactions of soil, roots, microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate populations may recover relatively rapidly (within approximately 3 years), whereas lake populations of zooplankton recover more slowly (Gunn and Mills, 1998).

There is currently no theoretical basis on which to predict the pathway and timing of biological recovery. Biological recovery of previously acidified surface waters can lag behind chemical recovery because of such factors as (1) limits on dispersal and recolonization, (2) barriers imposed by water drainage patterns (Jackson and Harvey, 1995), (3) the influence of predation (McNicol et al., 1995), and (4) other environmental stressors (Gunn et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996a,b). Full biological recovery may take decades from the onset of chemical recovery. The results of biological recovery research from the Sudbury region of Canada and several experimental lakes is summarized below.

The Sudbury region of Ontario, Canada has been important for studying both the chemical and biological effects of S deposition. Mining and smelting of copper-nickel ore began in the 1880s. By the 1950s and 1960s, SO_2 emissions from the mining and smelting operations peaked at over 5,000 tons/day and extensive acidification of nearby surface waters was documented (Beamish and Harvey, 1972). Emissions of SO_2 then decreased during the 1970s to less than one-third of the peak values. S emission reductions resulted in improved water quality in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries recovery was also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and Keller (1992) found changes in the occurrence and abundance of benthic invertebrates that were consistent with a direct effect of reduced lakewater acidity. A more recent assessment of recovery of ecosystems in Canada provided further evidence of biological recovery, but also showed that the spatial extent of recovery was limited to lakes that had been severely acidified by the Sudbury smelter (Jeffries et al., 2003). Research at Sudbury clearly documented that chemical recovery of lakes was possible upon reduced emissions and deposition of S, and also that biological recovery, involving multiple trophic levels, could follow. Major findings of the research at Sudbury and elsewhere are summarized below.

Phytoplankton

Studies of phytoplankton recovery from experimental acidification indicate that there is an increase in phytoplankton species richness and diversity as pH increases. In Lake 223 in the Experimental Lakes area of Ontario, there was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian, 1996). In Lake 302S, profound change began at pH 5.5; phytoplankton assemblages at pH below 5.5 resembled acidified lakes.

Zooplankton

Zooplankton recovery in response to experimental de-acidification has been reported for lakes in Ontario, Canada and Minnesota. Zooplankton recovery in experimentally acidified Lake 223 as pH returned back to 6.1 was reported by Malley and Chang (1995). Species diversity that had been reduced during the acidification phase had partially returned to pre-acidification levels. Rotifers had recovered less than crustaceans.

One decade after cessation of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton community was complete (Frost et al., 2006). Recovery did not follow the same trajectory as the initial acidification, however, indicating a substantial hysteresis in zooplankton community recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to recover to levels that occurred in the neutral reference basin.

Benthic Invertebrates

There has been some research conducted on the recovery of benthic invertebrate communities in surface waters exhibiting chemical recovery from acidification. In Scotland, Soulsby et al. (1995) reported an increase in acid-sensitive mayflies in some streams that showed recent ANC increases. However, no increases in invertebrates were observed in the most acidic streams despite observed increases in ANC. They suggested that further acidic deposition reductions and sufficient time for reversal of soil acidification may be required before aquatic biotic recovery can occur. The extent to which benthic invertebrates in streams in the United States may have recovered in response to any recent increases that may have occurred in stream ANC and pH is not known.

Fish

Fish populations have recovered in acidified lakes when the pH and ANC have been raised through liming or reduction of acidic deposition (Hultberg and Andersson, 1982; Beggs and Gunn, 1986; Dillon et al., 1986; Keller and Pitblado, 1986; Raddum et al., 1986; Gunn et al., 1988; Kelso and Jeffries, 1988). The timing of fish recovery is uncertain and probably depends heavily on dispersal opportunities. Stocking could accelerate fish population recovery (Driscoll et al., 2001b). Limitations on dispersal and recolonization can hamper biological recovery from acidification.

Continued periodic episodic acidification might hamper biological recovery of a lake or stream that is experiencing improvement in chronic chemistry. If fish move into refuge areas during episodes of low pH and then return, behavioral avoidance would reduce the overall effect of episodic acidification on fish populations. If fish move out of the stream system in response to acidic episodes, as suggested by Baker et al. (1996), and do not return or return in smaller numbers, then the population level effects of episodic acidification would be greater than predicted based on mortality tests alone.

Baker et al. (1990a) used field-based models to test the potential for biological recovery. For each species considered, the current presence or absence of the species was analyzed as a function of the water quality variables associated with acidification (e.g., pH, Al, Ca, ANC, and dissolved OC) using maximum likelihood logistic regression (Reckhow et al., 1987). The results from the various models were compared to their prediction of the change in the number of Adirondack lakes with unsuitable acid-base chemistry, given a 50% decrease or a 30% increase in S deposition relative to the existing conditions at the time of the Eastern Lakes Survey (1984). Most of the models provided similar results and suggest that a 30% increase in S deposition would increase the unsuitable fish habitat in Adirondack DDRP lakes by 15% to 28% for brook trout, lake trout, and common shiner. A 50% decrease in S deposition was projected to increase suitable habitat by 8% to 18%.

Waterfowl

Few studies have been conducted on the recovery of higher trophic level organisms such as waterfowl. However, breeding distribution for the common goldeneye (Bucephala clangula), an insectivorous duck, may be impacted by changes in acidic deposition (Longcore and Gill, 1993). Similarly, reduced prey diversity and quantity have been observed to create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

Logistic regression modeling with measured pH and species occurrence data for acid-sensitive lakes in the Algoma region of Ontario showed that the occurrences of fish, common loons, and common mergansers were positively related to lake water pH (McNicol, 2002).

Predictions of common loon and merganser recovery for this area were made using the Waterfowl Acidification Response Modeling System (WARMS) under varying S emissions control scenarios targeted for 2010 (McNicol, 2002). The number of lakes projected to be suitable for supporting breeding pairs and broods increased with Lake PH and stricter emissions controls (McNicol, 2002). Marginal improvements in fish-eating bird habitat were predicted to occur by 2010, with more significant improvements expected under hypothetical S emissions reductions of 50% and 75% for lakes with pH below 6.5 (McNicol, 2002). Fundamental to the predicted improvement of these fish-eating bird populations is the expected increase in food availability with lake pH recovery.

4.2.4.4 Acidification Case Study #1: Adirondack Region of New York

4.2.4.4.1 General Description of Region

The Adirondack Mountains region is situated in northeastern New York State. It is characterized by dense forest cover and abundant surface waters, with 46 peaks that extend up to 1600 m in elevation. The Adirondack Park has long been a nationally important recreation area for fishing, hiking, boating, and other outdoor activities.

The Adirondack region, and the southwestern Adirondacks in particular, is sensitive to acidic deposition because it receives high precipitation, has shallow base-poor soils, and is underlain by igneous bedrock with low weathering rates and buffering capacity (Driscoll et al., 1991; Sullivan et al., 2006b). The Adirondack region is among the most severely acid-impacted regions in North America (Landers et al., 1988; Driscoll et al., 2003b). It has long been used as an indicator of the response of forest and aquatic ecosystems to United States policy on atmospheric emissions of SO_2 and N oxides (U.S. Environmental Protection Agency, 1995b; NAPAP, 1998; GAO, 2000).

4.2.4.4.2 Levels of Acidic Deposition

Current rates of wet deposition of S and N in the western Adirondacks remain among the highest in the nation. Spatial patterns in wet deposition of S and N from 1988 to 1999 were developed by Ito et al. (2002), using data from 24 precipitation and 4 wet deposition monitoring stations. Results from this effort suggest that wet S deposition ranged from 2.3 to 12.9 kg S ha^{-1} yr^{-1} and wet nitrate-N deposition rates ranged from 1.7 to 5.1 kg N ha^{-1} yr^{-1} (Ito et al., 2002)

(Figure 4.2-13). In general, deposition rates are highest in the southwestern Adirondacks and decrease to the northeast. Rates of dry deposition are less well known, but probably constitute 25% to 50% or more of total wet deposition.

Deposition trends have changed with the implementation of federal and state emissions control regulations. For example, by 1990 average wet S deposition in the Adirondack region had declined by approximately 30% from its peak in the 1970s (Sullivan et al., 1990). Deposition of S has continued to decline (Figures 4.2-14 and 4.2-15) in response to implementation of the Clean Air Act Amendments of 1990. Until recently, wet N deposition had been fairly consistent over the previous two decades. N deposition now appears to be decreasing (http://nadp.sws.uiuc.edu/).

4.2.4.4.3 Soil Retention and Leaching of Sulfur and Nitrogen

As discussed in Section 4.2.4.4, acidic deposition has resulted in the accumulation of S and N in Adirondack soils. Although input-output budgets for S developed in the 1980s suggested that the amount of S exported was approximately equal to the S inputs from atmospheric deposition, more recent studies show that watershed loss of SO_4^+ now exceeds atmospheric S deposition inputs (Driscoll et al., 1998). This pattern suggests that decades of atmospheric S deposition have resulted in the accumulation of S in forest soils. With recent declines in atmospheric S deposition and a possible warming-induced enhancement of S mineralization from soil organic matter, previously retained S is gradually being released to surface waters (Driscoll et al., 1998). This release of SO_4^+ from soils could contribute to a delay in the recovery of surface waters in response to SO_2 emissions controls.

N dynamics are quite different from those of S. Since N is a growth-limiting nutrient for many forest plants, retention in forest ecosystems under low levels of air pollution is generally high and NO_3^- loss to streams is relatively low. However, recent research suggests that N has accumulated in soils over time in the Adirondacks and that some forests have exhibited declining retention of N inputs. The result has been increased leaching of NO_3^- to surface waters. The extent and degree of leaching appear to be linked to climatic variation, land-use history, and vegetation type (see Section 4.2.1.3).

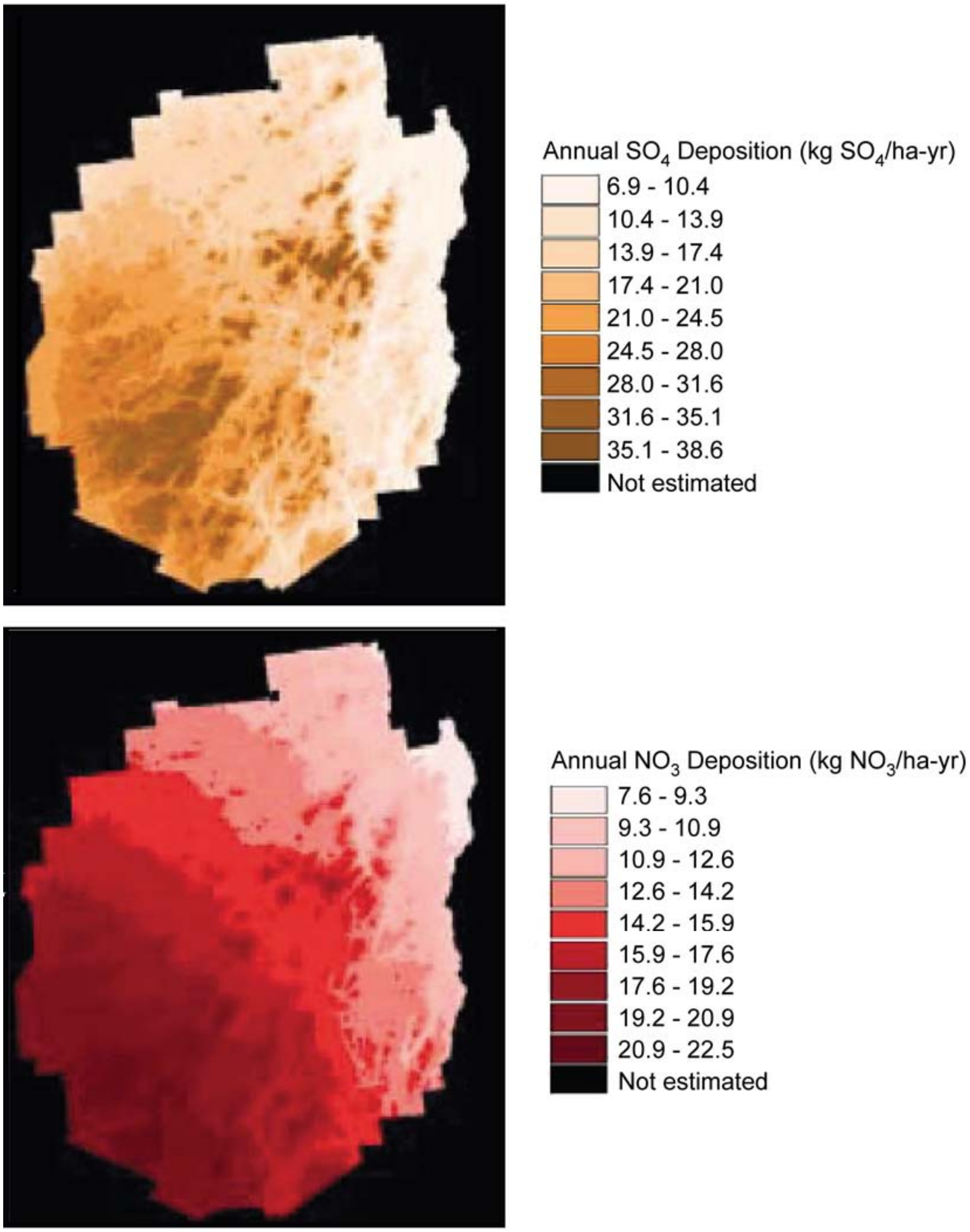


Figure 4.2-13. Spatial patterns in predicted wet sulfate and nitrate deposition in the Adirondack Park during the period 1988 to 1999.

Source: Ito et al. (2002).

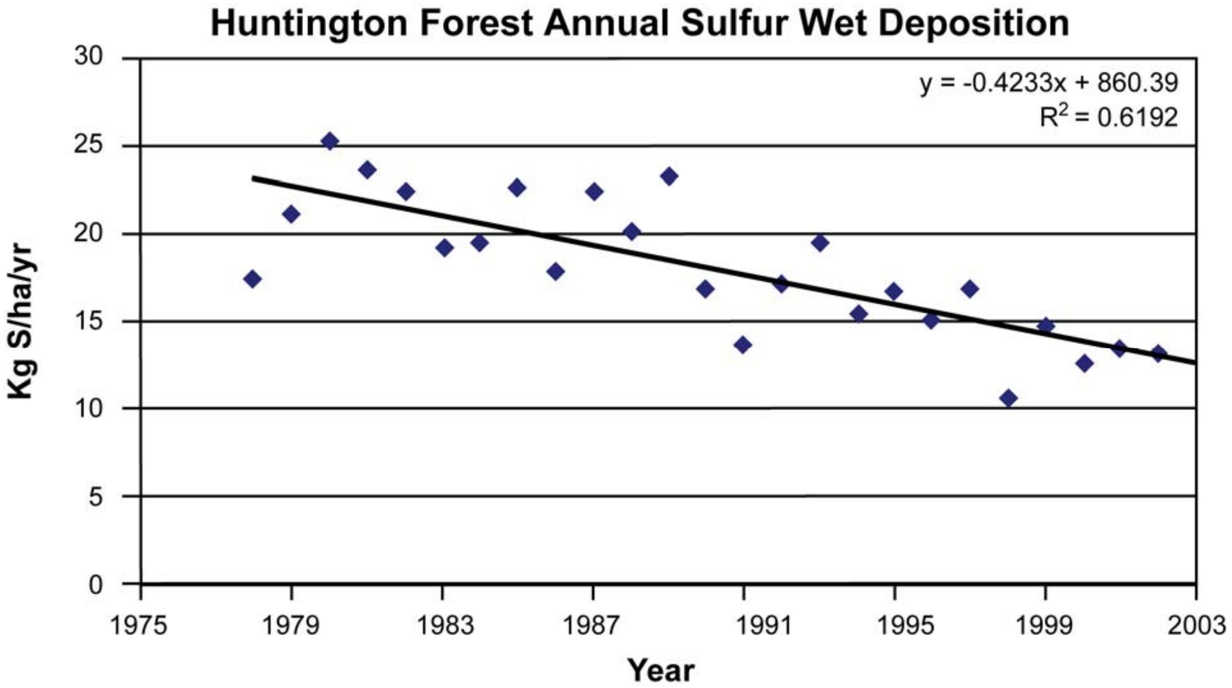


Figure 4.2-14. Measured wet deposition of sulfur and inorganic nitrogen at the Huntington Forest NADP/NTN monitoring station.

Source: Sullivan et al. (2006a).

The leaching of both SO_4^+ and NO_3^- into drainage water has contributed to the displacement of cations from soil, acidification of surface waters (Driscoll et al., 2001a), and the associated chemical and biological effects discussed below.

4.2.4.4.4 Soil Acidification and Base Cation Depletion

The hydrogen deposited atmospherically can have a direct effect on soil pH. Net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter and uptake of nutrient cations. In the only repeated soil sampling in the United States in which the original sampling predated acidic deposition, Johnson et al. (1994b) found significantly higher soil pH values in 1930 than in 1984 in the Oa horizon of Adirondack soils that had an initial pH of 4.0-5.5, but no decrease in pH in soils with an initial pH of <4.0. Johnson et al. (1994b) also documented a decrease in exchangeable Ca

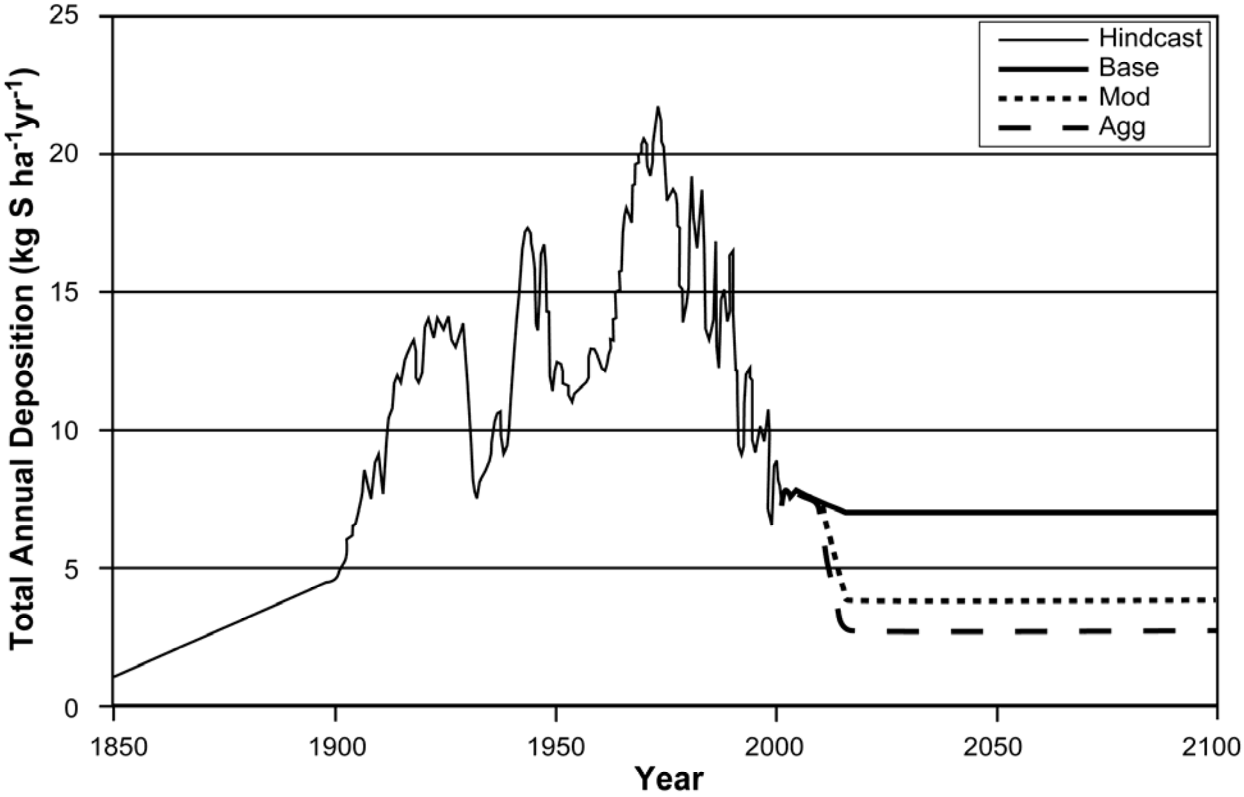


Figure 4.2-15. Estimated time series of S deposition at one example watershed in the southwestern Adirondack Mountains used by Sullivan et al. (2006b) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidic deposition. Future deposition estimates were based on three emissions control scenarios (Base Case [solid line], Moderate Additional Controls [dotted line], Aggressive Additional Controls [dashed line]).

Source: Sullivan et al. (2006b).

concentrations in both the O (combined Oa and Oe horizons) and B horizons from 1930 to 1984. The decrease in soil pH and Ca concentrations was attributed to a combination of acidic deposition and changing vegetation dynamics.

In a regional assessment of changes in soil-exchange chemistry, Sullivan et al. (2006a) found that base saturation and exchangeable Ca concentrations in the Adirondack region appeared to have decreased in the B horizon between the mid 1980s and 2003 in watersheds of lakes with acid-neutralizing capacity less than 200 μeq/L. Although this study did not involve repeated sampling of the same sites, the comparison could be made on a regional basis because the sampling locations were selected randomly in both the mid 1980s and in 2003, and a large and similar number of sites were included in both samplings.

4.2.4.4.5 Effects of Acidic Deposition on Adirondack Surface Water Chemistry

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

In addition to low pH and ANC, many acidic surface waters in the Adirondacks are characterized by high concentrations of inorganic Al. For example, a study of 12 subbasins in the watershed of the North Branch of the Moose River by Driscoll et al. (1987b) determined that the concentration of inorganic Al in lakewater was higher in lakes having pH below 6.0. Recently, Lawrence et al. (2007) determined that 66% of 188 streams sampled in the western Adirondack region during snowmelt in 2004 had measurable concentrations of inorganic Al, an indicator of acidification by acidic deposition.

Historical changes in lakewater chemistry from the mid-1800s to recent times have been estimated for the Adirondacks using paleolimnological techniques. Fossil remains of diatoms and chrysophytes in sediment cores have been used to reconstruct chemical histories.

The PIRLA I and II projects (Paleoecological Investigation of Recent Lake Acidification) used the remains of diatoms preserved in lake sediments to estimate historical changes in lakewater chemistry across the Adirondack region. The PIRLA-II project focused on lakes that are 4 ha or larger that represented a subpopulation of 675 Adirondack lakes. The results from these analyses suggest that nearly all lakes with estimated preindustrial pH less than 6.0 had acidified between 0.3 and 1.0 pH units during the 20th century. Based on an analysis of data from Cumming et al. (1992) and Baker et al. (1990b), low-pH lakes were uncommon or rare in the preindustrial Adirondacks; the number of lakes with pH less than 5.5 had at least doubled by the mid 1980s and the number with pH less than 5.0 had increased by 5 to 10 times.

The PIRLA results are generally consistent with projections from model hindcasts. Sullivan et al. (2006a) modeled past changes in the acid-base chemistry of 70 Adirondack lake watersheds, including 44 that were statistically selected to be representative of the approximately 1,320 Adirondack lake watersheds that have lakes larger than 1 ha and deeper than 1 m and that have ANC ≤200 µeq/L. Model hindcasts were constructed using both the MAGIC and PnET-BGC models. Based on MAGIC model outputs, maximum past acidification occurred by about 1980 or 1990, with a median ANC for the study population of about 61 µeq/L (reduced from a median of 92 µeq/L estimated for the preindustrial period). By 1990, 10% of the population target lakes had decreased in ANC to below −16 µeq/L and 25% had ANC < 28 µeq/L. The model simulations suggest that none of the target lakes were chronically acidic (had ANC < 0 µeq/L) under preindustrial conditions, but that by 1980 there were about 204 chronically acidic Adirondack lakes.

PnET-BGC model simulations generated output that was generally similar to results provided by MAGIC model simulations. Results from PnET-BGC suggest that none of the lakes in the Adirondack population had preindustrial ANC below 20 µeq/L. By 1990, there were 289 lakes having ANC < 20 µeq/L and 217 chronically acidic (ANC ≤0 µeq/L) lakes according to PnET-BGC simulations. There were 202 lakes in the population simulated to have had preindustrial ANC below 50 µeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations.

Zhai et al. (2007) reported PnET-BGC hindcasts for the 44 EMAP lakes. They report that simulated median values of pH, ANC, and soil percent base saturation were 6.63, 67.7 µeq/L, and 12.3%, respectively, in 1850 compared to current measured values of 5.95, 27.8 µeq/L, and 7.9%. They also calculated F factors for the PnET-BGC model projections of historical acidification. The F-factor (Henriksen, 1984; Husar et al., 1991) reflects the proportion of the increase in lakewater SO_4^+ plus NO_3^- concentration that is charge balanced by an equivalent increase in base cation concentrations. The remaining proportion (1-F) is attributed to increase in the potentially toxic cations, hydrogen and inorganic Al. Based on PnET-BGC hindcast simulations, F-factors for the EMAP lakes ranged from 0.3 to slightly over 1.0, with a mean value of 0.7 (Figure 4.2-16). The F-factor increased with ambient lakewater ANC. These results are in close agreement with paleolimnological analyses reported by Sullivan et al. (1990), which showed historic F-factors ranging from about 0.5 to above 1.0.

4.2.4.4.6 Biological Effects

The Adirondack region has a rich aquatic biota dataset from which to examine relationships among lake water chemistry and species abundance, composition, and richness. In

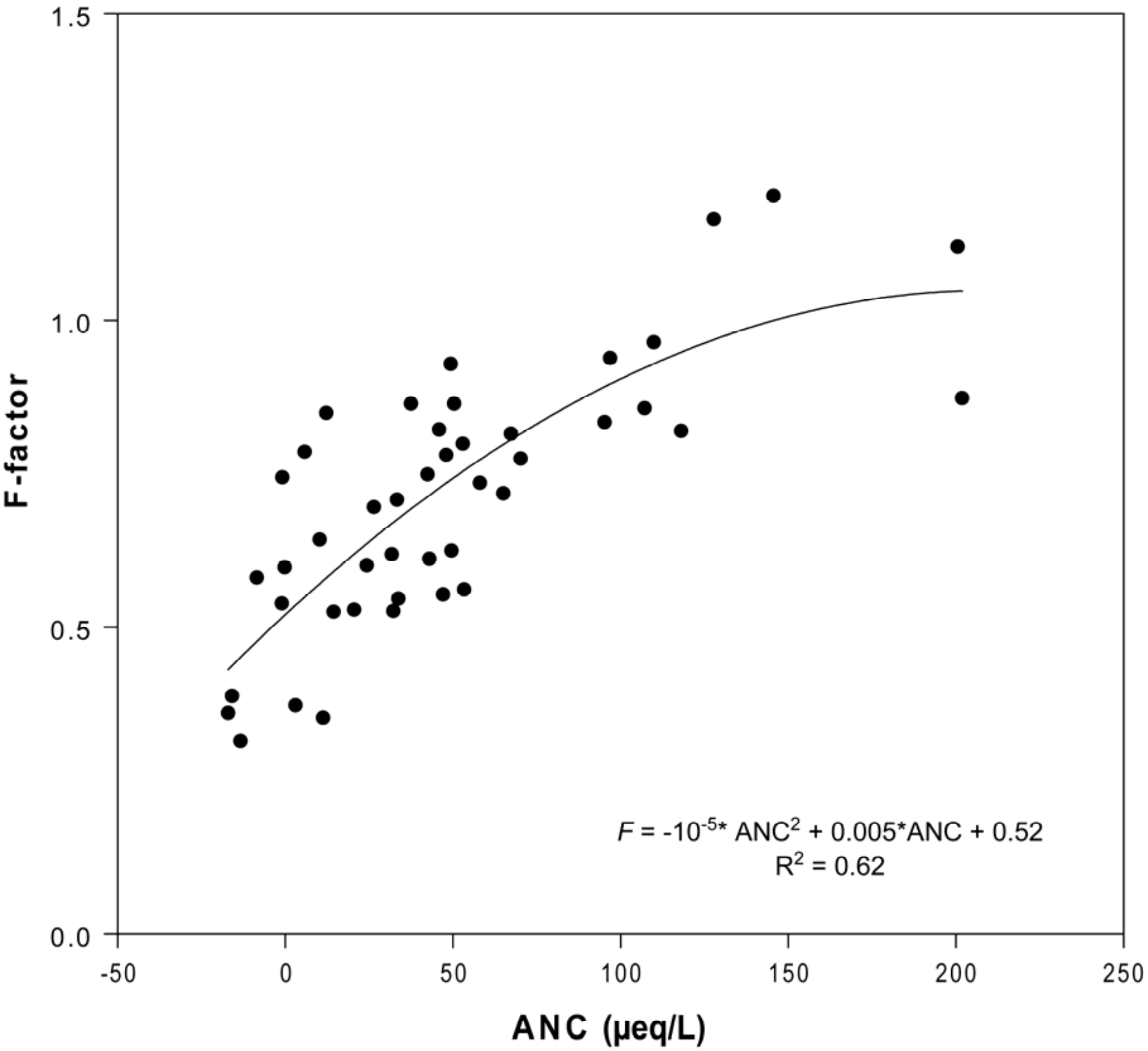


Figure 4.2-16. F-factors (ΔSBC/Δ[SO_4 + NO_3], where SBC is the sum of the base cation concentrations, with all units in µeq/L) calculated from model results for the period 1850 to 1980 as a function of simulated ANC in 1980 for 44 statistically selected EMAP lakes in the Adirondack region of New York.

Source: Zhai (2007).

general, there tends to be a negative relationship in Adirondack lakes between pH, ANC, and inorganic Al chemical variables and the diversity and abundance of fish (Baker and Laflen, 1983; Baker et al., 1990c; Havens et al., 1993), phytoplankton, and zooplankton (Confer et al., 1983; Siegfried et al., 1989).

Through the Adirondack Lakes Survey, 1,469 lakes were sampled between 1984 and 1987, representing 80% of the estimated population of Adirondack lakes larger than 1 ha in area (Whittier et al., 2002). The goal of the survey was to characterize the biological, physical, and chemical characteristics of the lakes and evaluate the relationships between fish communities and water chemistry. The major results were reported by Baker et al. (1990b). The key findings are summarized in the bullet list below and accompanying figures.

- Seventy-six percent of the lakes had fish; 24% (346 lakes) were fishless.
- The most common fish caught were native acid-tolerant species: brown bullhead, brook trout, and white sucker.
- As pH decreases, fish diversity also decreases. The average number of fish species declines from six fish species in lakes with pH higher than 6.5 to two or fewer fish species in lakes with pH of 5.0 or less.
- As pH decreases, the number of fishless lakes increases. Few lakes with pH of 5.5 or higher are fishless. Below pH 5.0, approximately 75% of the lakes are fishless.
- After accounting for other conditions that could explain the absence of fish, such as organic acidity or unsuitable habitat, 32% of the fishless lakes or 8% of all the lakes sampled were considered fishless due to the inputs of mineral acids by acidic deposition.

Researchers in the Adirondacks were among the first in the United States to demonstrate that fish mortality increases during acid episodes, which are common to lakes and streams in the Adirondacks during spring runoff. Driscoll et al. (1987a) documented surface water chemistry changes associated with periods of high flow. They found that pH and ANC dropped substantially during hydrological episodes and inorganic Al concentrations commonly exceeded thresholds harmful to fish. These relationships were further documented by the Episodic Response Project as shown in the example for Bald Mountain Brook in the Adirondacks (Wigington et al., 1996). Subsequent work by Van Sickle et al. (1996) and others linked these chemical changes to fish mortality in small streams. They determined that blacknose dace were highly sensitive to low pH and could not tolerate inorganic Al concentrations above about 3.7 µM for extended periods of time. After 6 days of exposure to high inorganic Al, dace mortality increased rapidly to nearly 100% (Van Sickle et al., 1996). Brook trout were less sensitive, but still showed high mortality during many acid episodes.

Several efforts have been made to link changes in fish populations with historical changes in water chemistry associated with acidic deposition. Among the most widely cited is the work of Baker et al. (1990b; 1996). They analyzed 988 Adirondack Lake Survey lakes for which data existed for the period before 1970 and for the 1980s. Of the 2,824 fish populations confirmed by pre-1970 surveys, 30% had apparently been lost by the 1980s (Baker et al., 1990b). An estimated 23% of the fish population losses were related to acidic deposition. This relationship was strengthened by evidence from the PIRLA projects. In the 32 lakes that had both historic fish data and paleolimnological chemical reconstructions, the lakes that had acidified the most or that were originally the most acidic were the same ones that were judged to have lost fish populations (Baker et al., 1996).

4.2.4.4.7 Recent Trends in Surface Water Chemistry and Projections of Future Change

Several studies have been conducted to analyze trends in lake chemistry in the Adirondacks. Driscoll et al. (2003c) evaluated changes from 1982 to 2000 in 16 LTM lakes and from 1992 to 2000 in an additional 48 LTM lakes that had been more recently added to the monitoring program. They found that nearly all study lakes showed marked decreases in SO_4^+ concentration over the period of record and several lakes showed declines in NO_3^- concentration. Data for one example monitoring lake are given in Figure 4.2-17. They found that 7 of the 16 original monitoring lakes showed a statistically significant increase in ANC (Figure 4.2-18), with a mean rate of increase of 0.78 µeq/L/yr (Driscoll et al., 2003c). Twenty-nine of the group of 48 lakes showed increasing ANC trends from 1992 to 2000 with a mean rate of increase of 1.60 µeq/L/yr (Driscoll et al., 2003b). The authors attributed this recent increase in ANC to declines in both SO_4^+ and NO_3^- concentrations (Driscoll et al., 2003b).

Despite these recent improvements in lake water chemistry in the Adirondack Long-Term Monitoring lakes, 34 of the 48 lakes still had mean ANC values less than 50 µeq/L in 2000, including 10 lakes with ANC less than 0 µeq/L. Thus, current chemistry data suggest that most of these lakes exhibit chemical conditions that continue to pose a risk to aquatic biota.

Model projections of future acid-base chemistry of lakes in the Adirondack Mountains under three scenarios of future atmospheric emissions controls were presented by Sullivan et al.

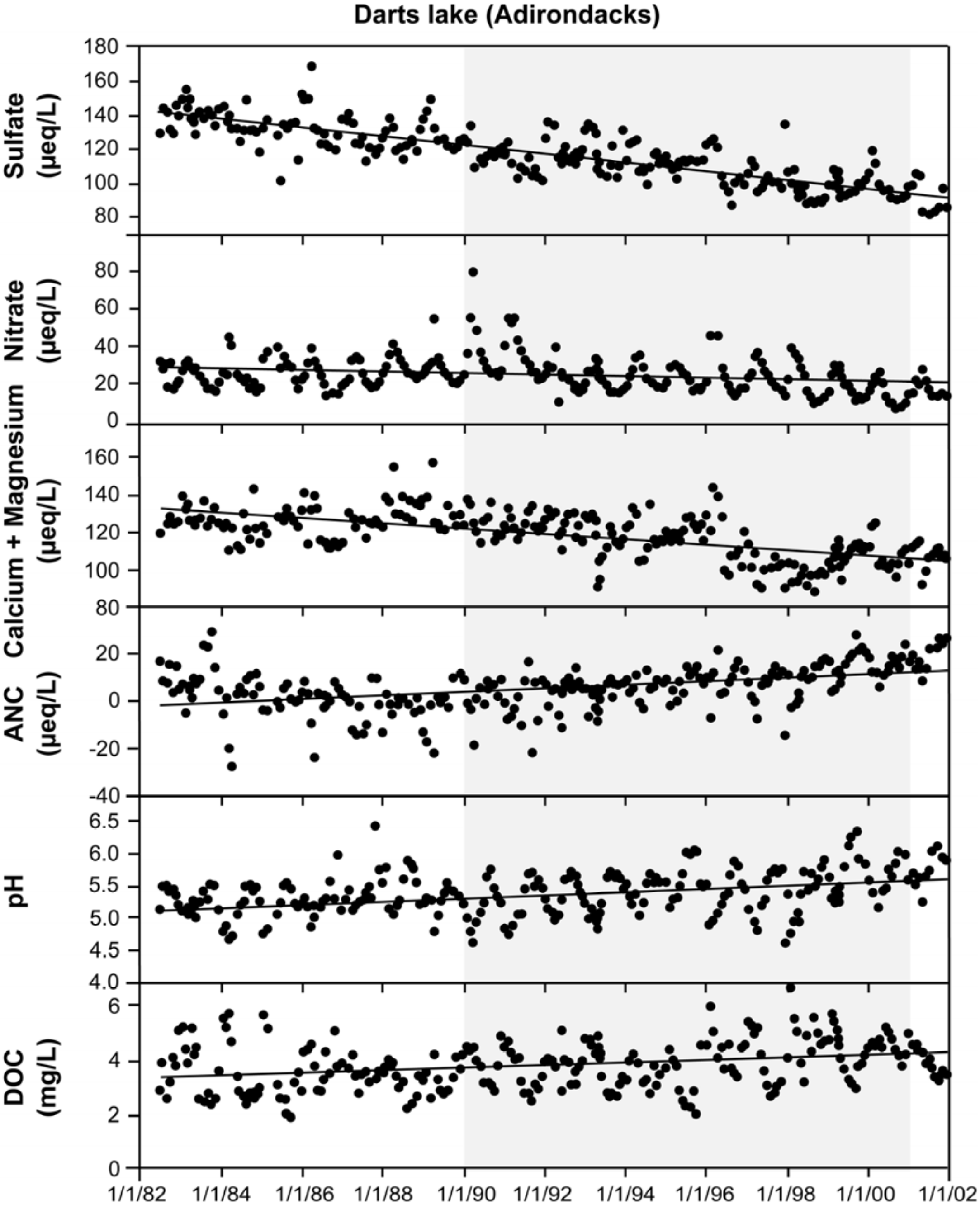


Figure 4.2-17. Time series data for sulfate, nitrate, base cations [Ca plus Mg], Gran ANC, pH, and dissolved organic carbon in one example Long-Term Monitoring Lake in the Adirondack Park. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Source: Stoddard et al. (2003).

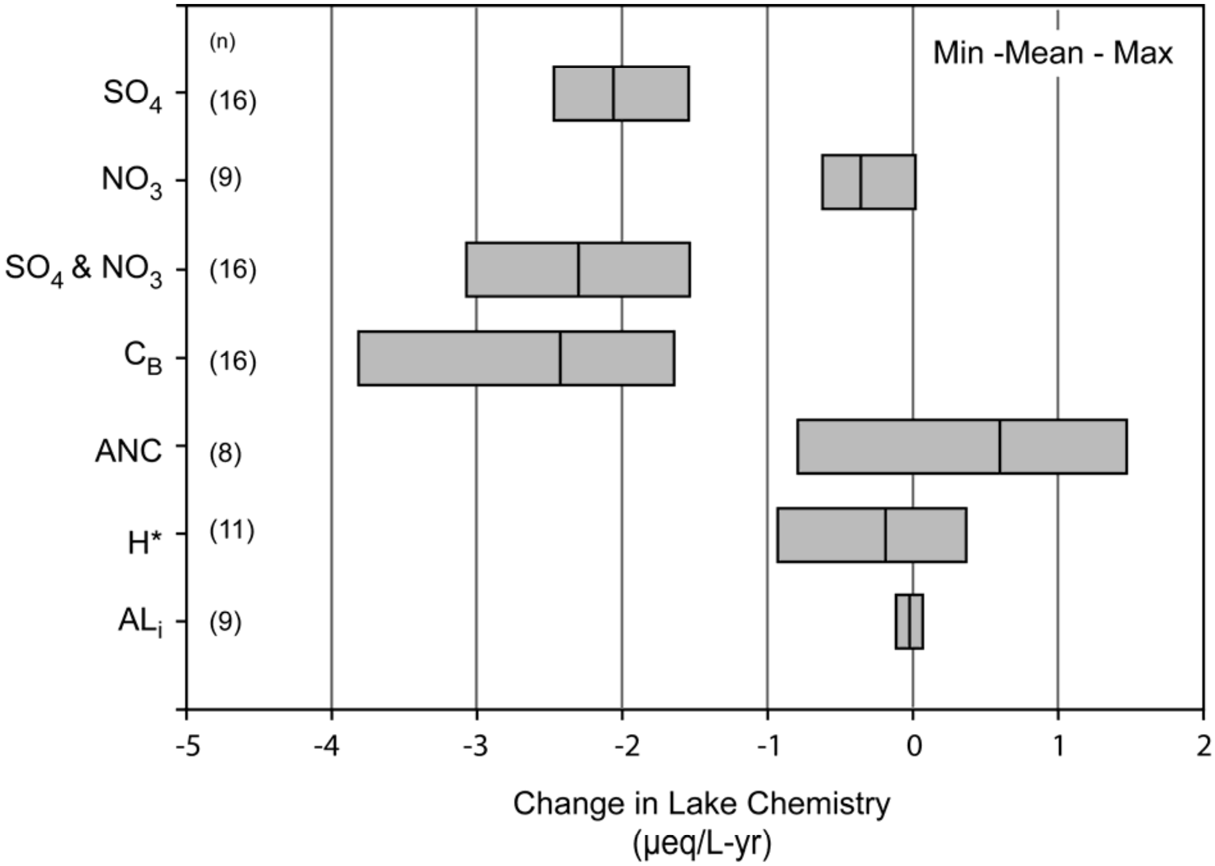


Figure 4.2-18. Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in µeq/L/yr, except for concentrations of inorganic monomeric aluminum (Ali), which is expressed in µM/yr.

Source: Driscoll et al. (2001b).

(2006b) to evaluate the extent to which lakes might be expected to continue to increase in ANC in the future. Estimated levels of S deposition at one representative watershed are shown in Figure 4.2-15 for the hindcast period and in the future under the three emissions control scenarios. Model simulations for 44 statistically selected Adirondack lakes using the MAGIC and PnET-BGC models were extrapolated to the regional lake population. Cumulative distribution frequencies of ANC response projected by MAGIC are shown in Figure 4.2-19 for the past (1850), peak acidification period (approximately 1990), and future (2100). Results for the future are given for each of the scenarios.

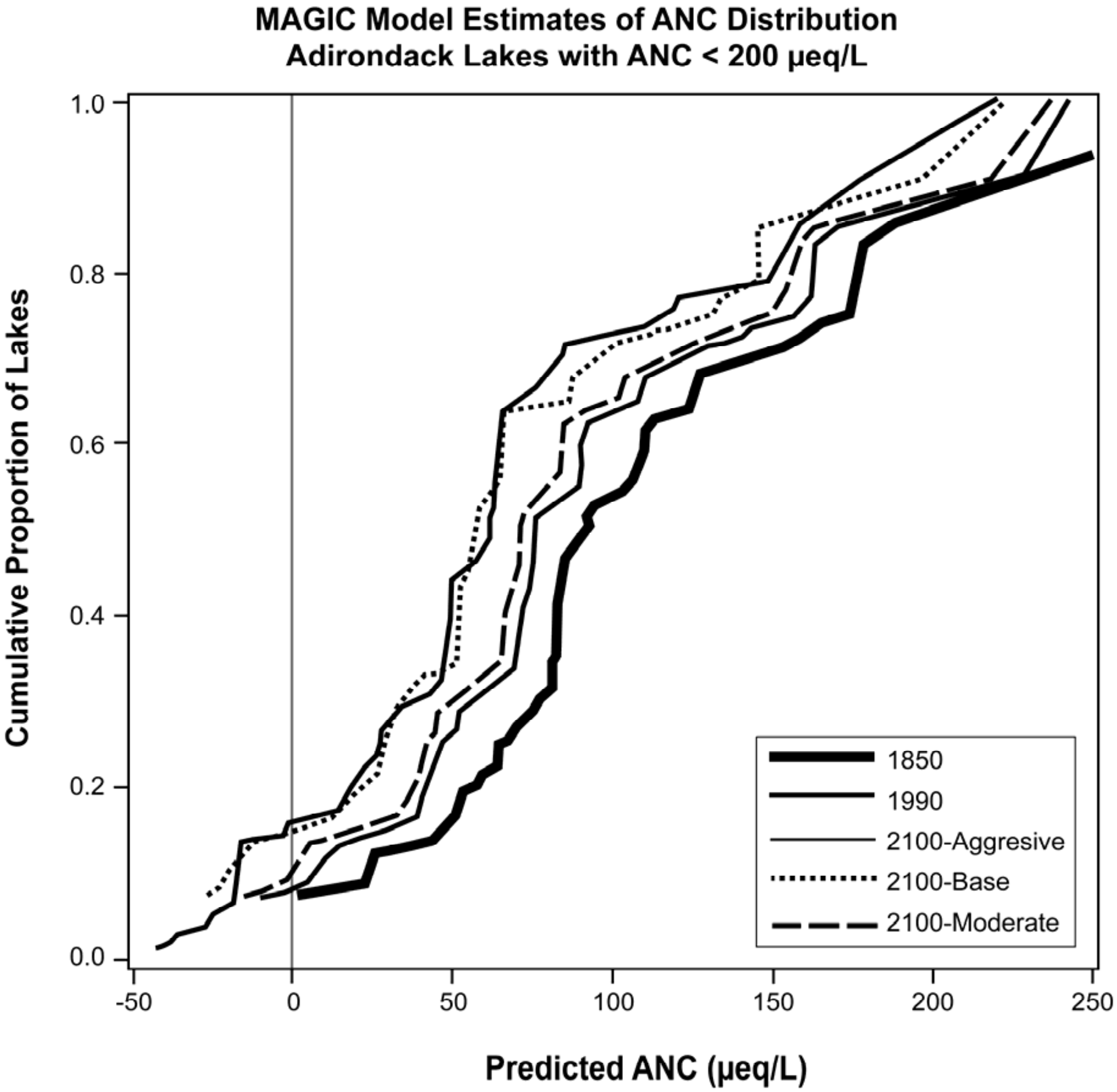


Figure 4.2-19. Simulated cumulative frequency distributions of lakewater ANC at three points in time for the population of Adirondack lakes, based on MAGIC model simulations reported by Sullivan et al., 2006. Conditions for the year 2100 are presented for three emissions control scenarios: Base Case, Moderate Additional Controls, and Aggressive Additional Controls. (See Figure 4.2-10.)

Source: Sullivan et al. (2006b).

Forecasting results suggested that the ongoing trend of increasing lakewater ANC for the most acid-sensitive lakes would not continue under future emissions and deposition levels anticipated as of 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC below 20 and below 50 µeq/L were projected to increase between 2000 and 2100 under that scenario, and the number of chronically acidic Adirondack lakes (i.e., ANC less than 0) was projected to stabilize at the level reached in 2000. This projected partial reversal of chemical recovery of acid-sensitive lakes was due to a continuing decline in the simulated pool of exchangeable base cations in watershed soils. Simulations suggested that re-acidification might be prevented with further reductions in emissions and deposition.

Chen and Driscoll (2004) applied the PnET-BGC model to 44 EMAP lake watersheds in the Adirondacks. The model was applied to three future emissions scenarios: base case, moderate emissions reductions, and aggressive emissions reductions. A case study for Indian Lake in the Adirondacks illustrated that larger reductions in deposition caused greater decreases in SO_4^+ and base cation concentrations in lake water and greater recovery in pH and ANC. Within the full population of lake-watersheds, some showed decreasing ANC and pH values from 1990 to 2050 even under the moderate and aggressive reduction scenarios. By 2050 to 2100, however, nearly all lakes were simulated to experience increasing ANC and pH. The modeled soil base saturation increased very slowly over the modeled time period compared to changes in surface water chemistry. For 95% of the lake-watersheds studied, simulated soil base saturation remained below 20% in 2100 under all emissions scenarios.

4.2.4.4.8 Multipollutant Interaction: Biological Mercury Hotspots in the Adirondacks

The Adirondacks has been identified as a region at risk from the combined effects of acidic deposition and Hg deposition (Driscoll et al., 2007b). The relationship between atmospheric deposition of S and enhanced Hg methylation is discussed in Section 4.4. In general, the solubility of Hg increases with increasing sulfide concentrations in anoxic waters through complexation reactions, potentially increasing the pool of Hg available for methylation (Benoit et al., 2003; Driscoll et al., 2007b). Evers et al. (2007) identified a biological Hg hotspot in the western Adirondacks based on Hg concentrations in yellow perch and common loons. Mean yellow perch Hg concentrations in the Adirondack hotspot were 1.5 to 2.5 times higher than the EPA and U.S. Food and Drug Administration's reference dose used for fish consumption advisories (Evers et al., 2007). The authors hypothesized that the occurrence of the biological hotspot was due in part to the combination of high Hg deposition and sensitive water chemistry, such as low ANC and pH, which is associated with both natural acidity and the long-term effects of acidic deposition (Evers et al., 2007).

4.2.4.5 Acidification Case Study #2: Shenandoah National Park, Virginia

Shenandoah National Park is located along the crest of the Blue Ridge Mountains in Virginia. Air pollution within Shenandoah National Park, including S and N deposition and O_3 concentration, is higher than in most other national parks in the United States. Measured wet S deposition in the park has ranged from 8 to 10 kg S ha^{-1} yr^{-1} in the early 1980s to near 6 kg S ha^{-1} yr^{-1} since 2000 (Figure 4.2-20). Dry S deposition may be nearly as high as wet deposition (Sullivan et al., 2003). Most acidification effects in the park have been linked with S deposition.

The sensitivity of streams in the park to acidification from acidic deposition is determined mainly by the types of rocks found beneath the stream and the characteristics of the watershed soils that surround it. If the underlying geology is Si-based, the soil and water in the watershed generally have poor ability to neutralize acids deposited from the atmosphere. About one-third of the streams in the park are located on this type of geology. Model estimates using the MAGIC model suggest that such streams have typically lost most of their natural ANC, largely in response to a century of industrial emissions and acidic deposition. As a consequence, stream pH values in many streams are low, especially during winter and spring. Prior to human-caused air pollution, most streams in Shenandoah National Park probably had pH above about 6. Many park streams currently have pH as low as about 5 (Sullivan et al., 2003; Cosby et al., 2006).

The effects of acidic deposition on Shenandoah National Park streams have been studied for over 25 years by the Shenandoah Watershed Study, the longest-running watershed study program in any of the national parks (Sullivan et al., 2003; Cosby et al., 2006; see http://swas.evsc.virginia.edu). This program has determined that the high rate of atmospheric deposition of S, combined with naturally low contributions from some rock types of Ca and other base cations (that serve to neutralize acidity), are the most important causes of low streamwater ANC in many park streams. Some park streams can also become temporarily acidic for short periods (hours to days) during rainstorms or snowmelt.

The acidification of streams in the park is linked to effects that are occurring in the watershed soils. Over time, the ability of soils to adsorb S, thereby effectively negating S’s potential to acidify water, is decreasing. In addition, the amount of stored Ca and Mg in the soil is gradually declining in response to acidic deposition. Therefore, streams are expected to

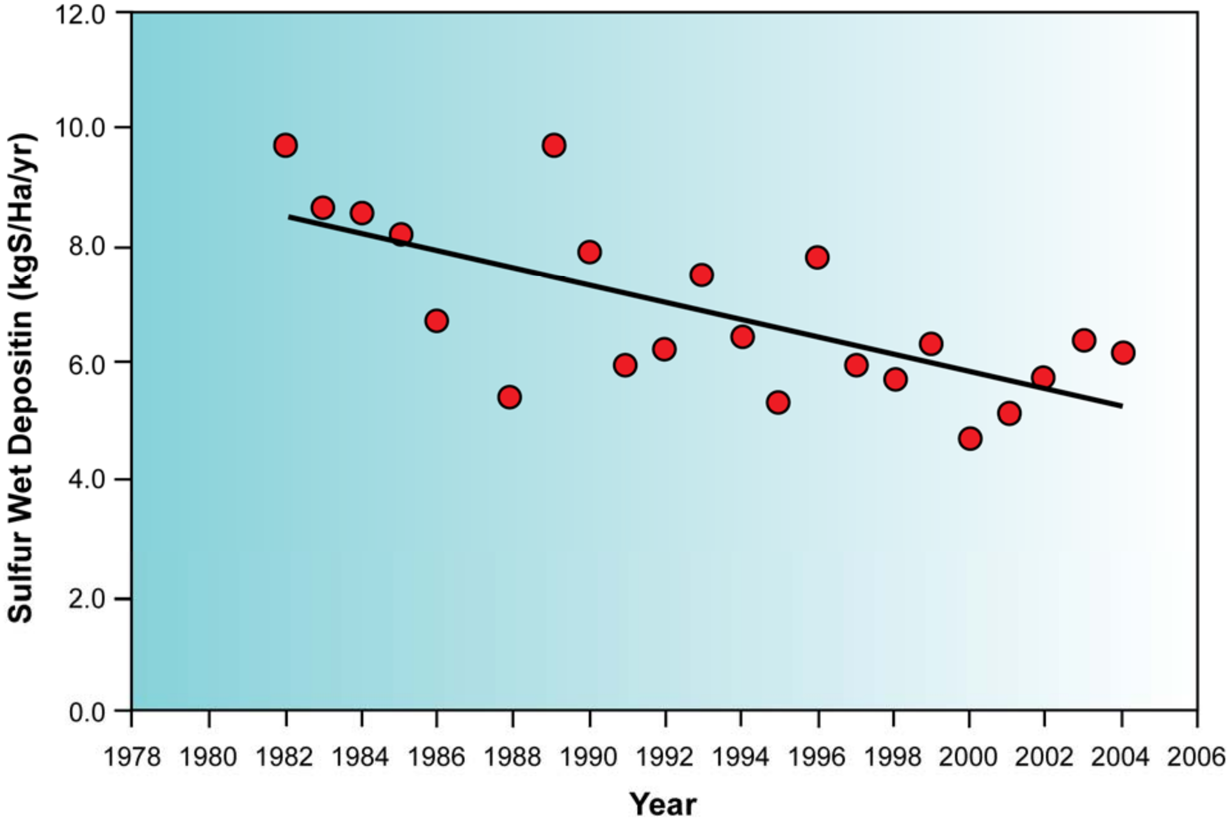


Figure 4.2-20. Wet sulfur deposition for the period of record at the Big Meadows NADP/NTN monitoring station in Shenandoah National Park.

Source: Sullivan et al. (2003).

acidify more in the future than they have so far, relative to the amount of acidic deposition received. This prognosis is consistent with recent analysis of national lake and stream response to reductions in air pollution emissions (Stoddard et al., 2003). Unlike a number of other regions of the country, streams in the region that includes Shenandoah National Park are generally not recovering from acidification.

A great deal of research has been conducted in the park on the effects of S and N deposition on soil and water acidification. This park was a major site of early research on acidification processes (cf. Galloway et al., 1983). This early work provided much of the foundation for development of the MAGIC model (Cosby et al., 1985), which has been the most widely used dynamic watershed acid-base chemistry model worldwide for the past two decades.

Although research on many aspects of acidification effects science has been conducted in the park, it has been particularly noteworthy for studies on episodic acidification; biological effects of stream acidification; and dynamic modeling of acidification, recovery, and critical loads. Research within Shenandoah National Park on each of these topics is discussed below.

4.2.4.5.1 Episodic Acidification

A number of studies of episodic acidification have been conducted in streams within Shenandoah National Park. Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a 3-year period. During the study, 33 discrete storm events were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (~0) Paine Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^+, and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 µeq/L (median 7 µeq/L) during the episodes studied.

At the intermediate-ANC (~60 to 120 µeq/L) Staunton River site on granitic bedrock, increases in SO_4^+ and organic acid anions, and to a lesser extent NO_3^-, were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 µeq/L during the episodes (median decrease in ANC was 21 µeq/L).

At the high-ANC (~150 to 200 µeq/L) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other two sites where base cation concentrations increased). SO_4^+ and NO_3^- usually increased. The change in ANC during the episodes studied ranged from 9 to 163 µeq/L (median 57 µeq/L) (Eshleman and Hyer, 2000). Changes in base cation concentrations during episodes contributed to the ANC of Paine Run, had little effect in Staunton River, and consumed ANC in Piney River.

The most acidic conditions in Shenandoah National Park streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. There are several different mechanisms of episodic acidification in operation in these streams, depending at least in part on the bedrock geology of the stream watershed. The relative importance of the major processes that contribute to episodic acidification varies among the streams, in part as a function of bedrock geology and baseflow streamwater ANC. S-driven acidification was an important contributor to episodic loss of ANC at all three study sites, probably because S adsorption by soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to diminished contact between drainage water and potentially adsorbing soil surfaces. Dilution of base cation concentrations during episodes was most important at the high-ANC site.

Thus, episodic acidification of streams in Shenandoah National Park can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-episode ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse effects on fish populations. However, not all of the causes of episodic acidification are related to acidic deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of HNO_3, indicated by increased NO_3^- concentrations, has evidently been (at least for streams in the park) related to forest defoliation by the gypsy moth (Webb et al., 1995; Eshleman et al., 1998). Significant contributions of H_2SO_4, indicated by increased SO_4^+ concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer, 2000).

A recent study by Deviney et al. (2006) used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the catchments using catchment geology and topography. On the basis of the models, they concluded that large number of streams in the park have 6- to 168-h periods of low ANC values, which may stress resident fish populations (Deviney et al., 2006). Specifically, on the basis of a 4-year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions for 72 continuous hours that are indeterminate with respect to brook trout suitability (ANC 20 to 50), episodically acidic (ANC 0 to 20), or chronically acidic (ANC less than 0). Many catchments were predicted to have successive years of low-ANC values potentially sufficient to extirpate some species (Deviney et al., 2006). The authors of the study reported that smaller catchments are more vulnerable to episodic acidification than larger catchments underlain by the same bedrock. Catchments with similar topography and size are more vulnerable if underlain by less basaltic and carbonate bedrock.

4.2.4.5.2 Biological Effects of Acidification

A robust relationship between acid-base status of streams and fish species richness was documented in Shenandoah National Park in the 3-year Fish in Sensitive Habitats (FISH) study (Bulger et al., 1999). Numbers of fish species were compared among 13 streams spanning a range of pH and ANC conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base status (during the 7-year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 4.2-10). This study demonstrated biological differences in low- versus high-ANC streams, including species richness, population density, condition factor, age, size, and field bioassay survival. Of particular note was that both episodic and chronic mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger, 1995), and that blacknose dace (*Rhinichthys atratulus*) in low-ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis et al., 1995; Dennis and Bulger, 1995).

Bulger et al. (1999) observed a positive relationship between condition factor and pH in streams in Shenandoah National Park (Figure 4.2-21). Dennis and Bulger (1995) also found a reduction in condition factor for blacknose dace in waters near pH 6.0. The four populations depicted on Figure 4.2-21 with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects for blacknose dace are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. Comparisons with the work of Schofield and Driscoll (1987) and Baker et al. (1990b) suggest that pH values in the low-pH streams are also near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan et al., 2003).

MacAvoy and Bulger (1995) used multiple bioassays over 3 years in one of the low-ANC streams as part of the FISH project to determine the effect of stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry. Simultaneous bioassays took place

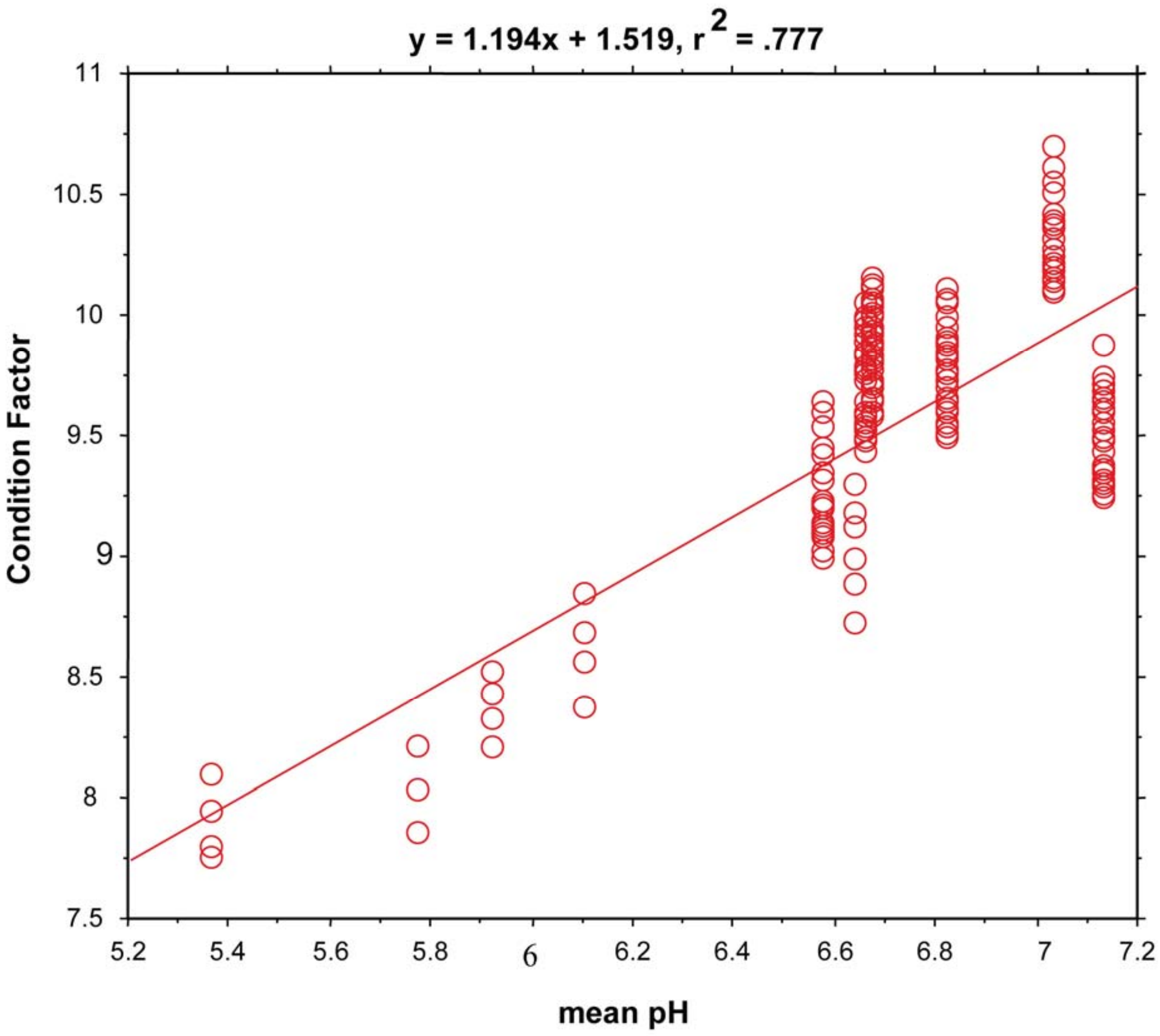


Figure 4.2-21. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The regression analysis showed a highly significant relationship ($p < 0.0001$) 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).

in mid- and higher-ANC reference streams. Acidic episodes, with associated low pH and elevated inorganic Al concentrations and high streamwater discharge, induced rapid fish mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger et al., 1999).

4.2.4.5.3 Modeling of Acidification, Recovery, and Critical Loads

Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels using data from streams in and near Shenandoah National Park. Projections were based on four brook trout stream categories: Suitable, ANC > 50 µeq/L; Indeterminate, ANC 20 to 50 µeq/L; Marginal, ANC 0 to 20 µeq/L; and Unsuitable, ANC < 0 µeq/L. Three scenarios of future acidic deposition were modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values, approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout because they were either episodically (24%) or chronically (6%) acidic. In addition, another 20% of the streams were classified as indeterminate, and brook trout in these streams may or may not have been affected. Based on the model simulations, 82% of these streams would not have been acidic prior to the onset of acidic deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidic deposition would be expected to increase the number of streams that were suitable for brook trout above the ambient 50%. In fact, the results suggested that a 70% reduction in deposition would be needed in the long term just to maintain the number of streams that were considered suitable for brook trout. Because of the length of time required to restore buffering capacity in watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

MAGIC model simulations for streams in Shenandoah National Park by Sullivan et al. (2003) also suggested that acidic deposition would have to be decreased substantially in order to improve and maintain acid-sensitive streams at levels of ANC that would be expected to protect against ecological harm. In addition, it took a long time for these streams to acidify in the past; because of complexities related to soil conditions, it will take even longer for them to recover in the future. In order to protect against chronic acidity in the year 2100, with associated probable lethal effects on brook trout, S deposition to the most sensitive Si-based watersheds in the park will have to be kept below about 9 kg per hectare per year for the next 100 years (Sullivan et al., 2007a). Prior to the industrial revolution, most streamwater in the park had ANC higher than about 50 μeq/L. In order to promote ANC recovery to 50 μeq/L in the future, to protect against general ecological harm, S deposition to Si-based watersheds in the park will have to be kept below about 6 kg per hectare per year. Some watersheds will likely not recover streamwater ANC to values above 50 μeq/L over the next century even if S deposition is reduced to zero (Sullivan et al., 2007a).

Simulation and mapping of watershed responses to historical changes in acidic deposition (from preindustrial to current) by Cosby et al. (2006) suggest that large areas of Shenandoah National Park have suffered deterioration of both soil and stream conditions. The changes in soil condition have been relatively modest up to the present time, with small areas in the southern district of the park moving from classification of "moderate concern" (watershed average mineral soil percent base saturation 10% to 20%; the historical baseline) to "elevated concern" (average mineral soil percent base saturation 5% to 10%) as a result of leaching of base cations from the soils in response to S deposition. Simulation results indicated that deterioration in stream conditions has been more severe than for soil conditions, with large areas in the southern district and some smaller areas in the central and northern districts moving from "moderate concern" (average stream ANC 50 to 100 μeq/L) to "elevated concern" (average stream ANC 0 to 50 μeq/L). Neither soil nor stream conditions have shown any improvement from 1980 to the present in response to the decline in acidic deposition that has occurred over the last 25 years.

Simulation and mapping of watershed responses to predicted future changes in acidic deposition by (Cosby et al., 2006) were developed following EPA methods for preparation of emissions inventory inputs into air quality modeling for policy analysis and rule making purposes. These alternate emissions scenarios were based on existing emission control regulations and several proposed alternatives. The model output suggested that the responses of soil conditions to changes in S deposition are expected to be relatively slow. In the short term (by the year 2020), neither improvement nor further deterioration is likely to be observed in soil condition regardless of the future deposition scenario considered. However, model results suggested that constant deposition at 1990 levels would produce worsening soil conditions in the park by the year 2100 with the development of areas of "acute concern" (average percent soil base saturation below 5%) in the southern district. Although the scenarios of possible reduced future deposition did not produce worsening soil conditions, neither did they indicate any improvement in soil condition, even in the long term.

Simulated responses of stream conditions were more rapid than those of soils. In the short term (by the year 2020), constant deposition at 1990 levels would likely produce further deterioration in stream condition. The scenarios of future deposition reductions failed to reverse the deterioration of stream condition that has occurred during the last century. In the long term (by year 2100), the effects of the deposition reduction scenarios begin to diverge. The moderate S deposition reduction scenario (69% reduction from 1990 values) did not produce improvement in stream chemistry relative to current conditions. The larger deposition reduction scenario (75%), by contrast, produced modest improvements in stream chemistry by 2100. However, even the relatively large S deposition reductions of this scenario did not result in a simulated return of stream conditions to the preindustrial state.

To develop projections of probable past and future responses of aquatic biota to changing S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al. (2003) with several empirical models that linked biological response to past and future model projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the biological effects estimates were based on observed empirical relationships rooted in correlation and expressed as linear relationships. Correlation does not necessarily imply causality, but an observed pattern of covariation between variables does provide a quantitative context for extrapolation. In this case, the projections did not require extrapolation beyond the observed ranges of observations, and therefore the projections were statistically robust. To the extent that the observed empirical relationships used in the coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were also biologically robust.

Dynamic water chemistry model projections were combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the data in Figure 4.2-10 was used by Sullivan et al. (2003) with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present, and future chemical conditions simulated for each stream. The coupled geochemical and biological model predictions were evaluated by comparing the predicted species richness in each of the 13 streams with the observed number of species that occur in each stream. The agreement between predicted and observed species numbers was good, with a root mean squared error in predicted number of species across the 13 streams of 1.2 species. The average error was 0.3 species, indicating that the coupled models were unbiased in their predictions. Model reconstructions of past species richness in the streams suggested that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic). The average number of species lost from streams on the three bedrock types examined were estimated as 1.6 species on siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4 species on basaltic bedrock. In the case of the siliciclastic streams, the projected past changes were much larger than the average error and root mean squared error of the coupled models, suggesting that the projections were reasonably robust.

4.3 NITROGEN NUTRIENT ADDITION

For convenience, N can be divided into two groups, nonreactive (N_2 gas) and reactive (N_r) N. N gas composes 80% of the total mass of the Earth's atmosphere, but most atmospheric N is not biologically available until transformed into to biologically active reduced forms of N. Reactive N includes all biologically active N compounds in the Earth's atmosphere and biosphere (Galloway et al., 2003). The N_r class includes inorganic reduced forms of N (e.g., NH_3 and NH_4^+), inorganic oxidized forms (e.g., NO_X, HNO_3, N_2O, NO_3^-), and organic N compounds (e.g., urea, amine, proteins, nucleic acids) (Galloway et al., 2003). Assessment of ecosystem effects of N deposition requires consideration of multiple forms of N, including but not limited to oxidized forms. N species that are contained in atmospheric deposition, and that influence nutrient dynamics, include both multiple oxidized and reduced forms of inorganic N and also C-bonded N.

Once in a reactive form, N is transported easily between air, water and soils in what is known as the N cascade (See Section 4.3.1). A single N-containing molecule can have a series of impacts on the environment because it can move so easily from the atmosphere, into soils and onto other surfaces, into waterways, and back again. Atmospheric deposition, generates a series of effects contributing to both acidification (see Section 4.2) and N pollution, the latter, by causing inadvertent fertilization of trees and grasslands, creating unnatural growth rates, nutrient imbalances, and ultimately decreasing ecosystem health and biodiversity. Leaching out of the soil, reactive N can pollute groundwater and surface water, rendering it unfit for human consumption. Reactive N also promotes eutrophication in coastal ecosystems, ultimately reducing biodiversity due to a lack of oxygen needed for the survival of many species of aquatic plants and animals. The cascade is interrupted only when reactive N is stored in inaccessible places or converted back to N_2 gas through denitrification. Even where denitrification occurs, not all the reactive N is always converted to unreactive N_2. Instead a portion is often converted by denitrifying bacteria to the intermediate product, nitrous oxide, which contributes to both the greenhouse effect and to stratospheric O_3 depletion. The following sections begin with a discussion of the N cascade, which is the foundation from which to discuss the effects of N_r on terrestrial, transitional, and aquatic ecosystems within the United States.

4.3.1 Reactive Nitrogen and the Nitrogen Cascade

N is required by all organisms because it is a major constituent of both the nucleic acids that determine the genetic character of all living things and the enzyme proteins that drive the metabolism of every living cell (U.S. Environmental Protection Agency, 1993b; Galloway, 1998; Galloway and Cowling, 2002). N is one of the most important, and often limiting, nutrients in virtually all ecosystems on earth (Vitousek and Howarth, 1991). It is mainly because of its importance as a limiting nutrient that N deposition from air pollution causes ecological problems. N is typically the most important limiting nutrient for terrestrial plant growth. It is of critical importance in plant metabolism and it often governs the utilization of phosphorus (P), K, and other nutrients. In aquatic ecosystems, either N or P is typically the most important limiting nutrient. N commonly limits algal production in estuaries, near-coastal marine waters, and remote oligotrophic lakes.

An increase in global reactive N has occurred over the past century, largely due to three main causes: (1) widespread cultivation of legumes, rice, and other crops that promote conversion of N_2 gas to organic N through biological N fixation; (2) combustion of fossil fuels, which converts both atmospheric N_2 and fossil N to reactive NO_X; and (3) synthetic N fertilizer production via the Haber-Bosch process, which converts nonreactive N_2 to N_r to sustain food production and some industrial activities (Galloway and Cowling, 2002; Galloway et al., 2003). Food production accounts for much of the conversion from N_2 to N_r, and accounts for geographic redistribution of N as food is shipped to meet population demands.

Reactive N is accumulating in the environment on local, regional, and global scales (Galloway, 1998; Galloway and Cowling, 2002; Galloway et al., 2003). This accumulation occurs in the atmosphere, soil, and water (Galloway and Cowling, 2002), with a multitude of effects on humans and ecosystems (Galloway, 1998; Rabalais, 2002; Van Egmond et al., 2002; Townsend et al., 2003). A single atom of new N_r can alter a wide array of biogeochemical processes and exchanges among environmental reservoirs. The sequence of transfers, transformations, and environmental effects is referred to as the "N cascade" (Figure 4.3-1) (Galloway and Cowling, 2002; Galloway et al., 2003).

The results of the N cascade and the various transformations in the N cycle can be both beneficial and detrimental to humans and to ecosystems (Galloway and Cowling, 2002; Galloway et al., 2003). Among the most adverse effects of chronic N deposition are changes in terrestrial plant biodiversity, aquatic eutrophication, disruptions in nutrient cycling, increased soil emissions of nitrous oxide (a potent GHG), accumulation of N compounds in the soil with enhanced availability of NO_3^- or NH_4^+, soil-mediated effects of acidification, and increased susceptibility of plants to stress factors (Aber et al., 1989, 1998; Bobbink et al., 1998; Fenn et al., 1998; Driscoll et al., 2003a). Important ecological effects known or suspected to occur in the western United States are summarized in Table 4.3-1.

4.3.2 Biogeochemical Processes and Chemical Effects Indicators

The following sections address the net impacts of excess reactive N on terrestrial and aquatic ecosystems via nutrient enrichment pathways. They are organized topographically, starting with impacts on upland terrestrial ecosystems, followed by effects on associated transitional and freshwater systems, and concluding with downstream changes to estuaries and coastal marine waters.

4.3.2.1 Terrestrial Ecosystems

N saturation is a process by which elevated N inputs give rise to a series of changes in terrestrial and aquatic ecosystems. The term N-saturation refers to the condition whereby the input of N to the ecosystem exceeds the requirements of terrestrial biota, and consequently an elevated fraction of the incoming N leaches out of soils to surface waters. The original description of N saturation by Aber et al. (1989) described four stages. It was revised by Stoddard (1994) and Aber et al. (1998) (Figure 4.3-2). In Stage 0, N inputs are low and

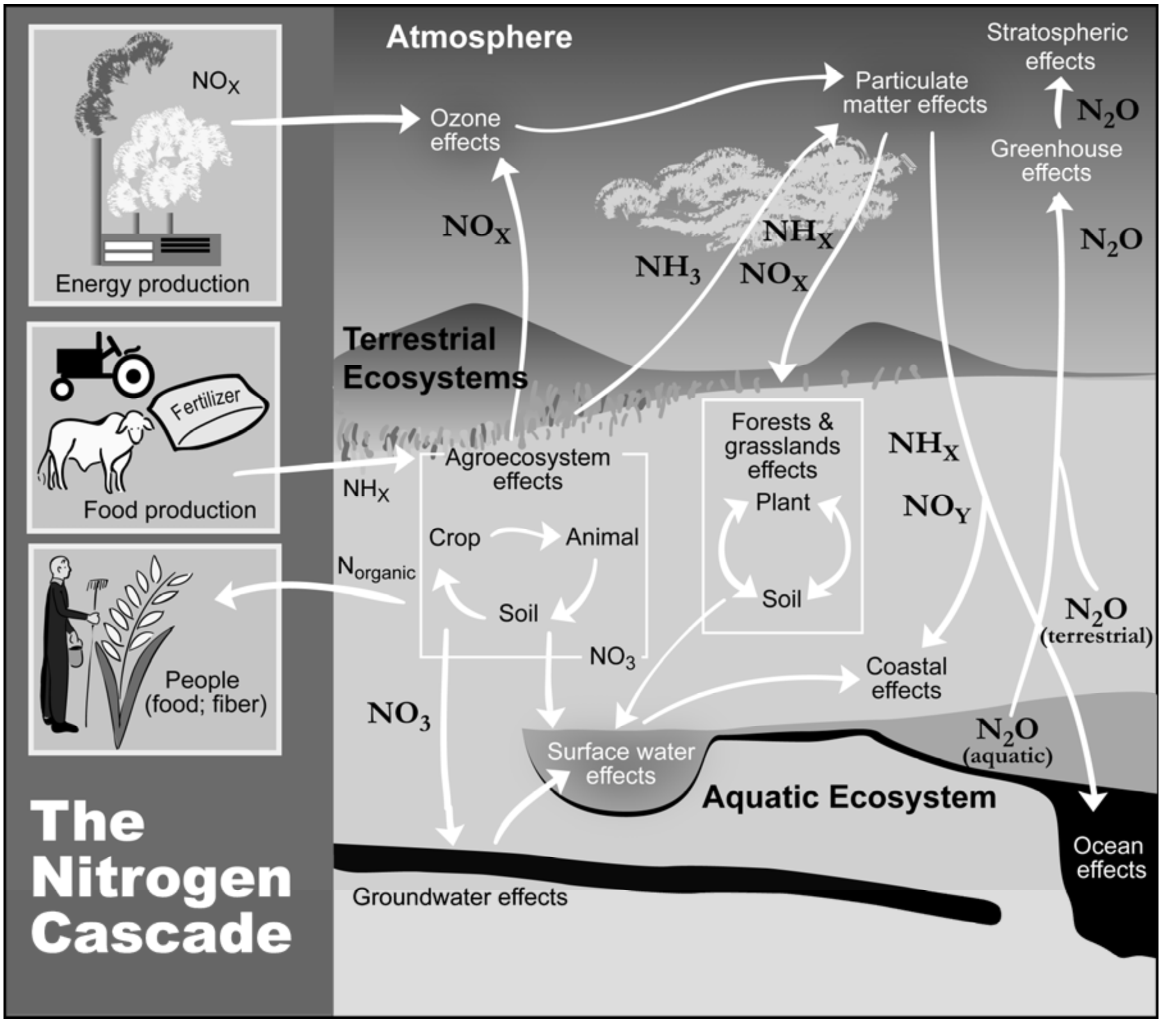


Figure 4.3-1. Illustration of the nitrogen cascade showing the movement of the human-produced reactive nitrogen (N_r) as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and aquatic ecosystems.

Source: Galloway et al. (2003).

there are strong N limitations on growth. Stage 1 is characterized by high N retention and a fertilization effect of added N on tree growth. Stage 2 includes the induction of nitrification and some NO_3^- leaching, though growth may still be high. In Stage 3 tree growth declines and nitrification and NO_3^- loss continue to increase, but N mineralization rates begin to decline. While not all terrestrial ecosystems move through the stages of N saturation at the same rate or in response to the same N loading, several experimental N addition studies and a survey

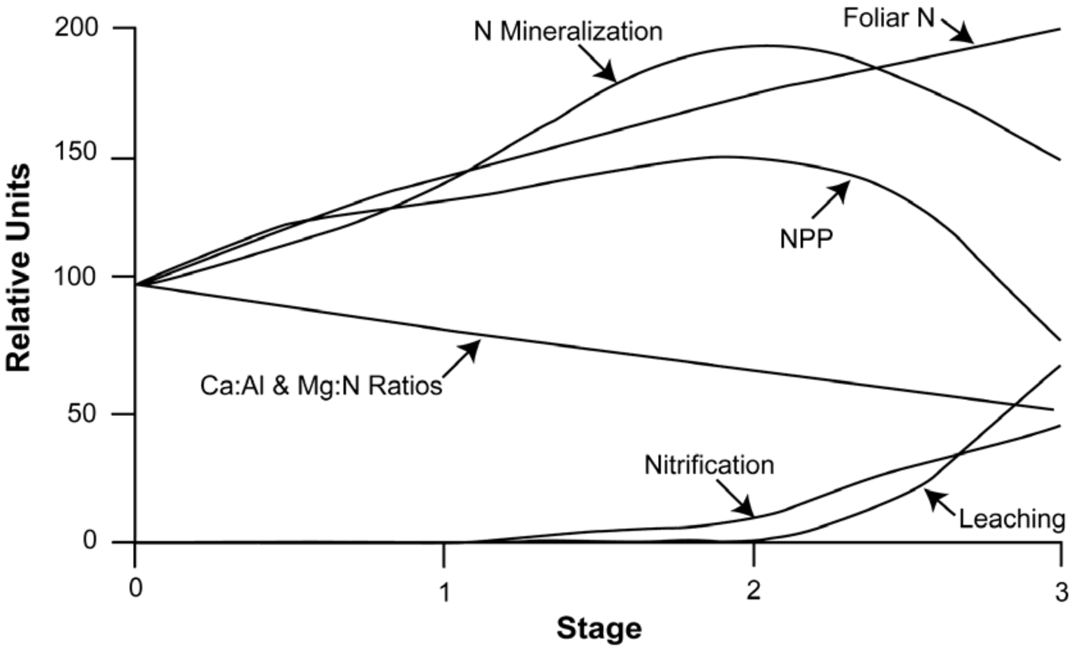


Figure 4.3-2. Schematic illustration of the response of temperate forest ecosystems to long-term, chronic N additions. Changes from initial hypotheses of Aber et al. (1989) include the reduction in N mineralization in stage 3 and the addition of foliar Ca:Al and Mg:N ratios.

Source: Aber et al. (1998).

of 161 spruce-fir stands along a N deposition gradient support the basic N saturation concept from the onset of increase in net nitrification and NO_3^- leaching loss to the eventual decline in tree growth and increase in tree mortality (Aber et al., 1998).

Decades of atmospheric deposition of N have increased the availability of NO_3^- and NH_4^+ in some terrestrial ecosystems to levels where excess N availability results in net nitrification and associated NO_3^- leaching in drainage water. Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (Webb et al., 1995) and deplete soils of nutrient base cations, especially Ca and Mg (Likens et al., 1998). The effects of NO_3^- leaching associated with acidification are discussed in Section 4.2.1.3. NO_3^- leaching from soils may also eutrophy estuaries and marine waters (Fisher and Oppenheimer, 1991), this topic is discussed in Section 4.3.3.4. The following section discusses the variability of N retention among terrestrial ecosystems.

Experimental additions of N to plots and watersheds demonstrate that rates of leaching and nitrification associated with N saturation vary among terrestrial ecosystems. Additions of N to hardwood watersheds in Maine (25 kg N ha^{-1} yr^{-1}) and West Virginia (35.5 kg N ha^{-1} yr^{-1}), which were releasing NO_3^- to surface waters prior to the additions, resulted in substantial increases in NO_3^- concentrations in soil water and stream water within the first treatment year (Kahl et al., 1993; Peterjohn et al., 1996). Additions of 25 kg N ha^{-1} yr^{-1} to spruce plots in Vermont (ambient bulk deposition 5.4 kg N ha^{-1} yr^{-1}), in which net nitrification did not occur prior to treatment, triggered net nitrification in the second year of treatment, whereas nitrification was not triggered until the third year in plots receiving 19.8 kg N ha^{-1} yr^{-1} (McNulty et al., 1996). Similar results were seen in two studies from Colorado. Additions of 25 kg N ha^{-1} yr^{-1} to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition ~4-5 kg N ha^{-1} yr^{-1}) doubled N mineralization rates and stimulated nitrification, while the addition of the same amount to plots receiving ambient bulk deposition of ~2.0 kg N ha^{-1} yr^{-1} in Fraser Experimental Forest elicited no microbial response but significantly increased foliar and organic soil horizon N (Rueth et al., 2003). A comparison study of old-growth spruce plots across a depositional gradient in Colorado found mineralization rates to be higher where N deposition ranged from 3 to 5 kg N ha^{-1} yr^{-1} than where N deposition ranged from 1 to 2 kg N ha^{-1} yr^{-1}, with measurable nitrification rates at sites with the highest deposition amounts (Rueth and Baron, 2002). In marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest, which received additions of 150 kg N ha^{-1} yr^{-1} (Magill et al., 2004). Concentrations of (NO_3^- plus NH_4^+) in hardwood plots receiving 50 kg N ha^{-1} yr^{-1} were not yet detectable in the 15th year of treatment. The same treatments were applied to red pine (*Pinus resinosa*) plots, which exhibited elevated concentrations of (NO_3^- plus NH_4^+) in soil water after 1 year of 150 kg N ha^{-1} yr^{-1} doses, and after 5 years of 50 kg N ha^{-1} yr^{-1} doses.

Severe symptoms of N saturation have been observed (1) in the northern hardwood watersheds at Fernow Experimental Forest near Parsons, West Virginia (Peterjohn, 1996), (2) in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains (Cook, 1994), (3) throughout the northeastern United States (Aber, 1989, 1998). Mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998).

There are examples of N saturation in lower-elevation eastern forests, especially in West Virginia. For example, progressive increases in streamwater NO_3^- and Ca concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s (Edwards and Helvey, 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000). This watershed has received higher N deposition (average throughfall input of 22 kg ha^{-1} yr^{-1} of N in the 1980s) than is typical for low-elevation areas of the eastern United States, however (Eagar et al., 1996), and this may help to explain the observed N saturation.

Rueth and Baron (2002) compared Engleman spruce (*Picea englemanii*) forest stands east and west of the Continental Divide in Colorado. N deposition, arising mainly from agricultural and urban areas of the South Platte River Basin, was moderate (3 to 5 kg N ha^{-1} yr^{-1}) on the east slope, but only 1 to 2 kg N ha^{-1} yr^{-1} on the west slope. East slope sites showed lower soil organic horizon C:N ratio, lower foliar C:N ratio, higher potential net mineralization, and higher percent N, N:Mg ratio, and N:P ratio in foliage. These results suggested that even moderate levels of N deposition input can cause measurable changes in spruce forest biogeochemistry.

In general, it is believed that deciduous forest stands in the eastern United States have not progressed toward N-saturation as rapidly or as far as coniferous stands. Deciduous forests may have a greater capacity for N retention than coniferous forests. In addition, deciduous forests tend to be located at lower elevation and receive lower atmospheric inputs of N. Many deciduous forests have higher rates of N uptake and greater N requirement than coniferous forests (Aber, 1998).

The varying degree of N assimilation, leaching and microbial transformation illustrated by the following examples often reflect differences in N status of the treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more (Goodale and Aber, 2001). Sites which have undergone disturbances that cause loss of soil N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and experimental inputs of N. N retention capability often decreases with stand age, which suggests that older forests are more susceptible than younger forests to becoming N-saturated (Hedin et al., 1995). Aber et al. (1998) surmised that land use history may be more important than cumulative atmospheric deposition of N in determining the N status of a forest ecosystem.

The extent to which N saturation occurs across the landscape also depends, in part, on past land use and on rates of denitrification. Land use can modify the amount of N stored in the soil and influence the extent of N uptake by growing vegetation. Denitrification refers to the conversion of oxidized forms of reactive N (e.g., NO_3^- and nitrite) to gaseous N that is released to the atmosphere. Through this process, denitrification removes atmospherically deposited N from terrestrial, transitional, and aquatic ecosystems, thereby limiting the extent of environmental effects associated with acidification and nutrient enrichment. Denitrification occurs under anaerobic conditions, where and when there is also sufficient NO_3^- and OC to fuel the facultative anaerobic bacteria that are responsible for denitrification. Hence, most terrestrial denitrification is controlled by "hotspots" and "hot moments," which represent sporadically wet places or times or anaerobic soil microsites (McClain et al., 2003; Seitzinger et al., 2006). In upland terrestrial ecosystems, the extent of NO_3^- removal via denitrification is usually small, with some of the highest rates reported from experimental studies in which 3% to 8% of the N added to fertilized pine stands at the Harvard Forest was removed via NO emissions (Venterea et al., 2003, 2004).

4.3.2.2 Transitional Ecosystems

N dynamics in wetland ecosystems are variable in time and with type of wetland and environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren, 1994; Mitchell et al., 1996).

Wetlands represent a convergence of conditions of NO_3^-, oxygen, and C availability that are favorable for denitrification. As such, wetlands and other transitional ecosystems can remove NO_3^- via denitrification. This is especially true if N supply is limiting the rates of denitrification in wetland soils (Hayden and Ross, 2005). Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983;

Broderick et al., 1988; Cooper, 1990). This process increases the contribution of nitrous dioxide (a GHG) and NO (a precursor to O_3) to the atmosphere, but limits NO_3^- levels in soils and leaching into drainage waters and the associated environmental effects. However, increased N inputs to wetland systems would only be expected to stimulate denitrification if there is an adequate C supply (Groffman, 1994). Although denitrification has been observed to increase with N addition, N mineralization has also been shown to increase, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

Denitrification is also a major factor governing the loss of N from estuarine and marine ecosystems. Previously, it was believed that denitrification was responsible for virtually all of the transfer of N_r in the ocean to the atmosphere as N_2 gas. It now appears that anaerobic NH_4^+ oxidation (anammox) may account for up to 50% of the N_2 production in the oceans (Devol, 2003; Ward, 2003; Dalsgaard et al., 2005; Kuypers et al., 2005).

Increased N loading to transitional ecosystems can affect both methane (CH_4)-producing and CH_4-oxidizing microbial activity. The difference between the CH_4 production and oxidation determines the magnitude of CH_4 emission from soils. NO_3^- can decrease CH_4 production by acting as a redox buffer during organic decomposition in anaerobic sediments. NH_4^+ compounds are generally considered to reduce CH_4 oxidation (Steudler et al., 1989; King and Schnell, 1994; Gulledge et al., 1997), but have also been observed to increase methanotropic bacterial activity (Bodelier et al., 2000).

CH_4 emissions from saturated soils have been observed to increase with N addition (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). The prevailing hypothesis for explaining this effect is that increased vegetative cover increases C availability through root exudates, which in turn stimulates methanogenic bacteria and CH_4 emissions (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). Saarnio et al. (2003) observed moderate increases in CH_4 emissions from boreal wetland soils with N fertilization rates of 30 kg N ha^{-1} yr^{-1} as NH_4NO_3. Comparable N application rates and effects on CH_4 emissions were also observed by Granberg et al. (2001) in a similar ecosystem type. Zhang et al. (2007) observed elevated CH_4 emissions from freshwater wetland soils with experimental N additions of 240 kg N ha^{-1} yr^{-1}. They postulated that additional N increased abundance of *Deyeucia angustifolia* which increased CH_4 emissions by supplying methanogenic bacteria with additional substrate in the form of root exudates. Other studies have shown that N addition had little or no effect on CH_4 emissions across a variety of ecosystem types (Saarnio et al., 2000; Silvola et al., 2003; Ambus and Robertson, 2006).

It is important to note that the N enrichment rates employed in all of the above reported studies related to N effects on soil CH_4 emissions were much greater (30 to 240 kg N ha^{-1} yr^{-1}) than atmospheric N inputs in most areas of the United States that are heavily impacted by elevated atmospheric N deposition. Nevertheless, an increase in CH_4 emissions from wetland soils in response to N loading is important, especially because CH_4 is an effective GHG contributing to global warming (Saarnio et al., 2000). Changes in the C cycle in wetlands, especially within the geographically extensive boreal zone, could have an important influence on climate. The reason(s) for the observed difference in response are not known.

The nutrient enrichment effects of N deposition are likely to be more pronounced in ombrotropic bogs and nutrient-poor fens than in other kinds of wetlands. This is because these kinds of wetlands have evolved under conditions of very low nutrient, including N, supply. Even relatively low additions of N in atmospheric deposition can stimulate the growth of some plant species at the expense of others. Ombrotrophic bogs are hydrologically isolated from the surrounding landscape and therefore receive most of their N supply from atmospheric deposition. Nutrient-poor fens receive ground water inputs but they are low in N; as a consequence, atmospheric deposition constitutes a major component of the total N input. N deposition to nutrient-poor wetland environments may lead to a decrease in species diversity and increased risk of extinction for some of the more sensitive and rare species (Moore et al., 1989). These are the most vulnerable transitional ecosystems to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Kooijman and Bakker, 1994; Berendse et al., 2001; Tomassen et al., 2004).

4.3.2.3 Aquatic Ecosystems

Anthropogenic sources of N to freshwater and coastal ecosystems are varied and include atmospheric deposition, wastewater discharge, agricultural runoff, and urban runoff. A large fraction of atmospheric N deposition is retained in most forests. Nevertheless, the fraction that does leach to streams can make a substantial contribution to total N inputs to downstream large rivers and estuaries, especially in the eastern United States. Direct atmospheric N deposition to the estuary surface constitutes an additional important N source, especially to estuaries which have a large surface area relative to their watershed area. N deposition effects on the nutrient dynamics of aquatic ecosystems are described by the process of eutrophication, 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. The following sections discuss the biogeochemical processes associated with N loading in freshwater and estuarine ecosystems.

4.3.2.3.1 Freshwater Aquatic Ecosystems

A freshwater lake or stream must be N-limited in order to be sensitive to N-mediated eutrophication. Although conventional wisdom holds that most lakes and streams in the United States are limited by P, recent evidence illustrates examples of lakes and streams that are limited by N and show symptoms of eutrophication in response to N addition. For example, surveys of lake N concentrations and trophic status along gradients of N deposition show increased inorganic N concentration and productivity to be correlated with atmospheric N deposition (Bergström and Jansson, 2006). Additional information supporting the connection between N loading and eutrophication in freshwater systems is provided in Section 4.3.3.3 below.

The predominant chemical consequences of excess atmospheric and non-atmospheric N loading to the watershed of fresh surface waters are (1) elevated NO_3^- concentration in surface water and (2) NO_3^- leaching downstream. As described in Section 4.2.1.6, surface water NO_3^- concentrations are elevated in some of the lakes and streams that have been impacted by acidic deposition in the Northeast. A survey of 220 lakes and streams in the northeastern region documented NO_3^- concentrations ranging from less than 2 up to 42 µeq/L, with the highest median values occurring in the Adirondacks (Figure 4.3-3).

The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N ha^{-1} yr^{-1}, which probably corresponds with a total

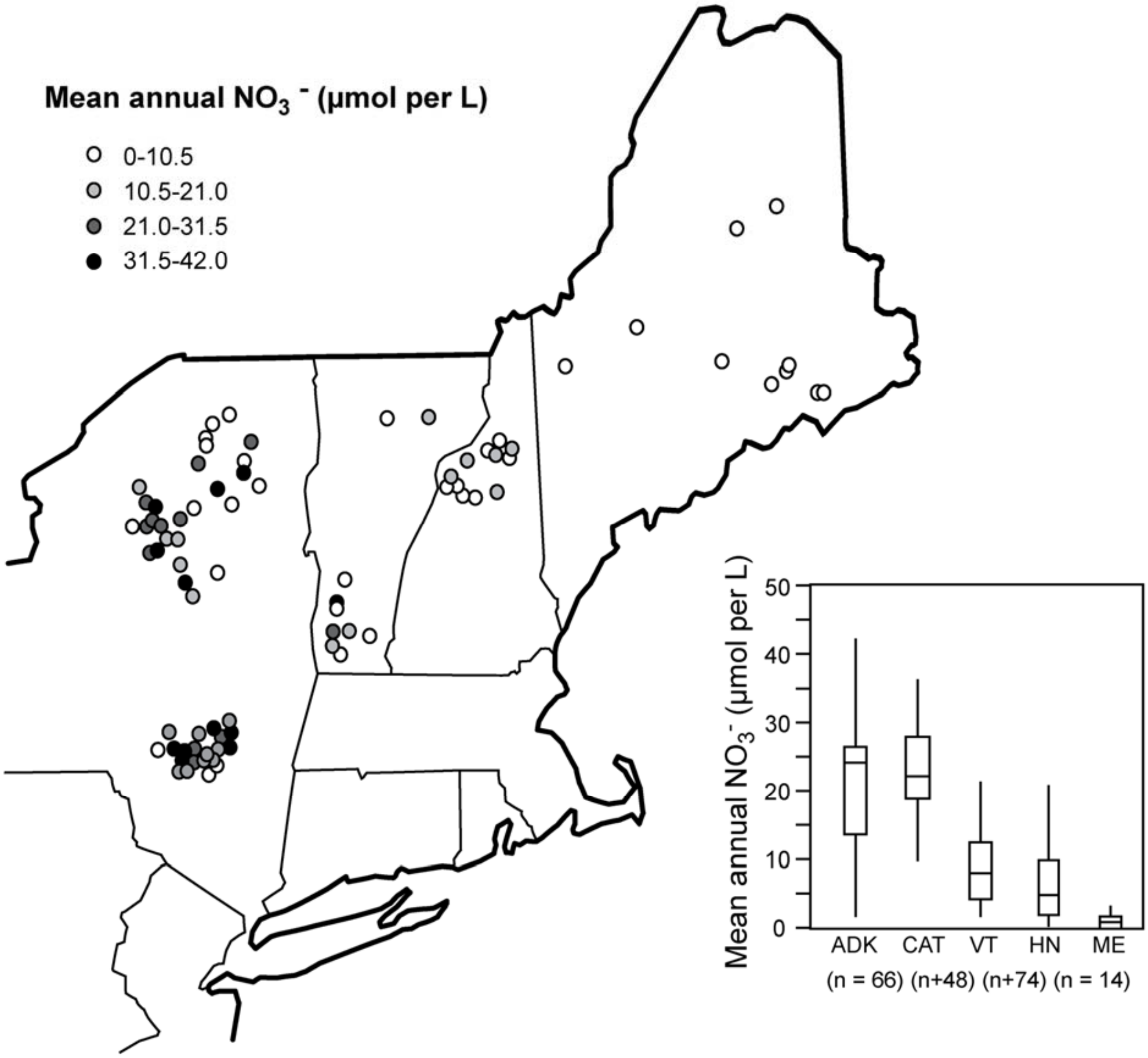


Figure 4.3-3. Mean annual nitrate (NO_3^-) concentrations in 230 lakes and streams across the northeastern United States. Inset indicates the median, quartile, and 90% range of mean annual NO_3^- in the Adirondacks (ADK), the Catskills (CAT), Vermont (VT), New Hampshire (NH), and Maine (ME).

Source: Aber et al. (2003).

N deposition input of about 8 to 10 kg ha^{-1} yr^{-1}. Stoddard (1994) presented a geographical analysis of patterns of watershed loss of N throughout the northeastern United States.

In the western United States, NO_3^- concentrations of freshwater ecosystems have been shown to increase with proximity to urban areas. Results from the Western Lake Survey (WLS) conducted by the EPA (Eilers et al., 1987), document enhanced N concentrations in high elevation lakes adjacent to and downwind of urban centers (Fenn et al., 2003a), such as those found in the Sierra Nevada and Colorado Front Range (Figure 4.3-4). For example, NO_3^- concentrations in streamwater during the growing season in the Sierra Nevada were reported to range from 4 to 19 µeq/L (Fenn et al., 2003b).

An interesting example from the Colorado Front Range indicates that lakes on the eastern and western slopes can experience significantly different levels of NO_3^-. A survey of 44 lakes east and west of the Continental Divide indicated that lakes on the western side of the Continental Divide averaged 6.6 µeq/L of NO_3^-, whereas lakes on the eastern side of the divide averaged 10.5 µeq/L of NO_3^- concentration. NO_3^- concentrations above 15 µeq/L have commonly been measured in lakes on the eastern slope of the Front Range, suggesting some degree of N saturation (Baron, 1992), and extreme values as high as 40 µeq/L have also been reported (Campbell et al., 2000). Williams et al. (1996b) contended that N-saturation is occurring throughout high-elevation catchments of the Colorado Front Range. Many lakes in the Colorado Front Range have chronic NO_3^- concentrations greater than 10 µeq/L and concentrations during snowmelt are frequently much higher, due at least in part to leaching from tundra, exposed bedrock, and talus areas.

In the Uinta Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of the lakes included within the Western Lakes Survey had NO_3^- concentrations greater than 10 µeq/L. This suggests that N deposition in these areas may have exceeded the capability of these lakes to assimilate N. It is unknown if these concentrations of NO_3^- represent effects from anthropogenic sources or if this constituted a natural condition associated with inhibited NO_3^- assimilation in cold alpine environments.

In summary, elevated surface water NO_3^- concentrations in both the eastern and western United States suggest that some areas may have experienced measurable water chemistry changes in response to N inputs. However, as described in Section 4.3.3.3, the chemical changes generally are not large enough to cause direct biological harm to fish or other vertebrates but may contribute to increased productivity and species shifts in algal communities.

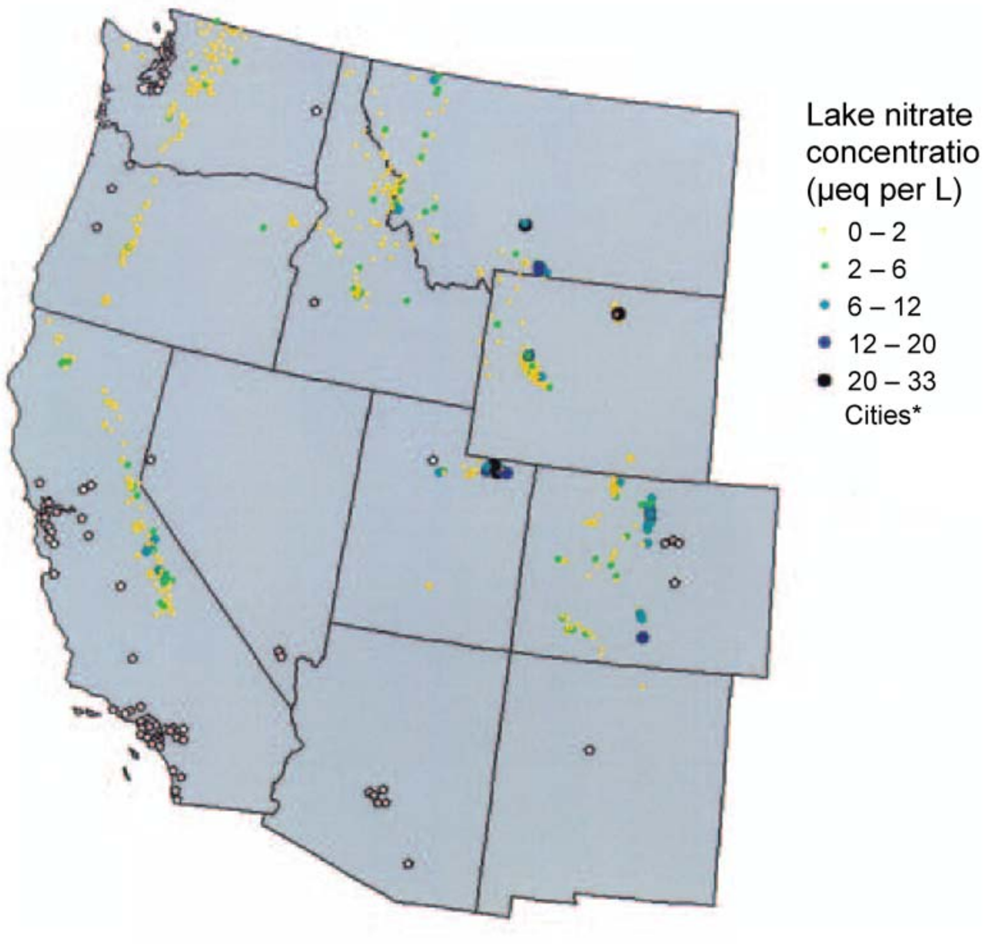


Figure 4.3-4. Nitrate concentrations in high-elevation lakes in western North America. Stars represent cities with a population greater than 100,000.

Source: Fenn et al. (2003a).

4.3.2.3.2 Estuarine and Coastal Marine Ecosystems

Estuarine and coastal marine ecosystems experience a range of ecological problems associated with nutrient enrichment. Because the productivity of estuarine and nearshore marine ecosystems is generally limited by the availability of N_r, excessive contribution of N_r from sources of water and air pollution can contribute to eutrophication. Some of the most important environmental effects include increased algal blooms, depletion of dissolved oxygen in bottom waters, and reduction in fisheries and sea grass habitats (Valiela and Costa, 1988; Valiela et al., 1990; Boynton et al., 1995; Paerl, 1995, 1997; Howarth et al., 1996). The general process of estuarine eutrophication is depicted in Figure 4.3-5.

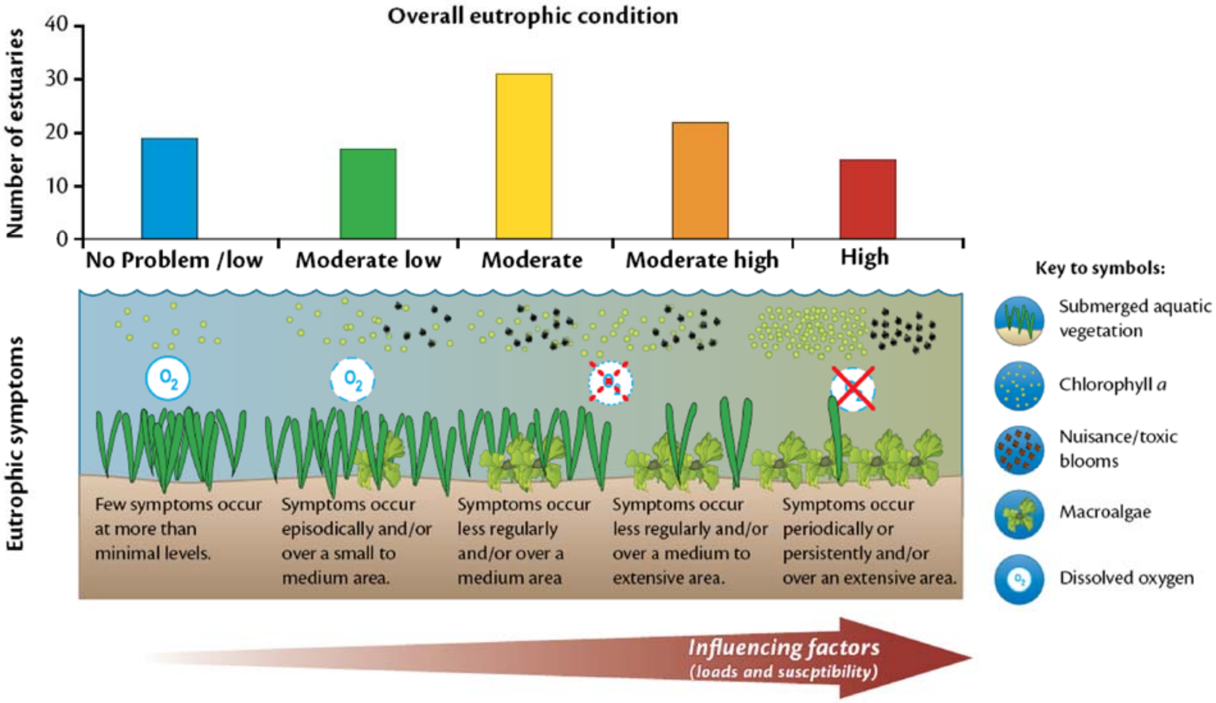


Figure 4.3-5. A conceptualization of the relationship between overall eutrophic conditions, associated eutrophic symptoms, and influencing factors (N loads and susceptibility). Overall eutrophic condition was assessed for estuaries throughout the United States. (See also Figure 4.3-10.)

Source: Bricker et al. (2007).

There is broad scientific consensus that N-driven eutrophication of shallow estuaries in the United States has increased over the past several decades and that environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl et al., 2001). For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer et al., 1984), Pamlico estuary in North Carolina (Paerl et al., 1998), and along the continental shelf adjacent to the Mississippi and Atchafalaya River discharges to the Gulf of Mexico (Eadie et al., 1994). A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions (Bricker et al., 2007). Estuaries with high overall eutrophic conditions were generally those that received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al., 2007).

Anthropogenic sources of N to estuarine and coastal ecosystems are varied and include atmospheric deposition, wastewater discharge, agricultural runoff, and urban runoff. Estimates of the relative contribution of each major source have been developed by using the Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N) model (Castro and Driscoll, 2002). Driscoll et al. (2003a,b) estimated the contributions of various N sources to the nutrient budgets of estuaries draining eight large watersheds in the northeastern United States. They reported that atmospheric deposition, either through direct deposition to the estuary or through watershed runoff of atmospheric deposition, was generally the second highest source of N and ranged from 14 to 35% of the total (Figure 4.3-6). These results are consistent with the findings of Boyer et al. (2002) for 16 catchments from Maine to Virginia. However, Boyer et al. attributed the highest N input to atmospheric deposition in part because their budgets were based on the drainage area upstream of major U.S. Geological Survey (USGS) gages and therefore do not generally account for wastewater inputs to larger rivers and estuaries.

Atmospheric N deposition has been estimated to account for only a few percent to more than 40% of total external N loading to estuaries in North America and Europe. Valigura et al. (2000) estimated that direct atmospheric deposition to the estuary surface generally constitutes at least 20% of the total N load for estuaries that occupy more than 20% of their watershed. U.S. Environmental Protection Agency (1999b) estimated that between 10% and 40% of the total N input to estuaries in the United States is typically derived from atmospheric deposition. NRC (2000) judged that U.S. Environmental Protection Agency (1999a) underestimated the importance of atmospheric deposition as a contributor to the total N load.

One the challenges in determining the contribution of atmospheric N deposition to estuaries is estimating the inputs from upstream river basins. Smith et al. (1997) applied the SPAtially Referenced Regressions on Watershed Attributes (SPARROW) model to streamwater chemistry data from the National Stream Quality Accounting Network in order to evaluate NO_3^- leaching in large river basins. Leaching losses of N in large river systems provide important sources of N to estuaries and coastal marine waters. Smith et al. (1997) concluded that much of the United States probably exports less than 5 kg N ha^{-1} yr^{-1}, but that N export in watersheds of

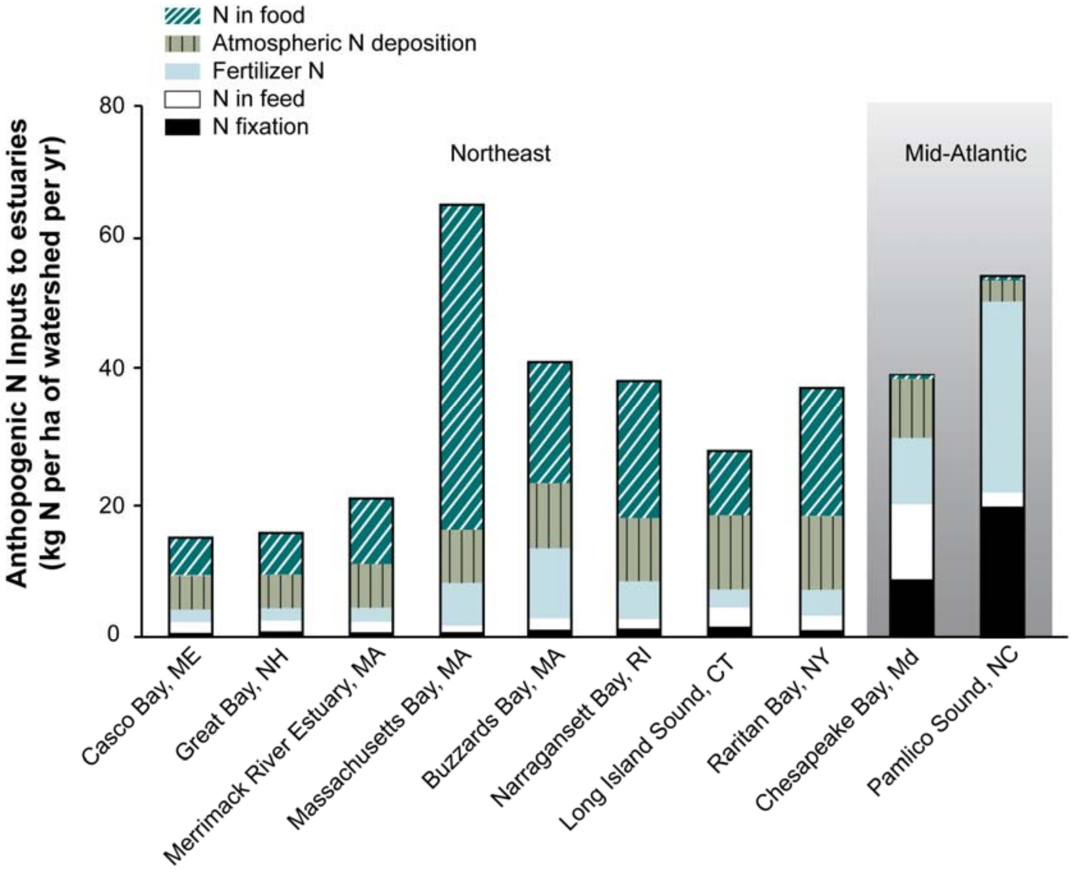


Figure 4.3-6. Estimated anthropogenic nitrogen inputs to the estuaries of the northeastern United States, in kg ha^{-1} yr^{-1}.

Source: Driscoll et al. (2001b).

the northeastern United States is probably higher. For the watersheds that export more than 10 kg N ha^{-1} yr^{-1}, Smith et al. (1997) concluded that fertilizer was the largest source of N (48%), followed by atmospheric deposition (18%) and livestock wastes (15%). In this analysis, fertilizer used for human food production was considered to be the ultimate source of N contributed to waterways through waste water treatment plants. If the analysis of N sources to estuarine water is restricted to only nonpoint sources of N, atmospheric deposition is often considered to be the largest individual source (Howarth et al., 1996; Jaworski et al., 1997; Smith et al., 1997; NRC, 2000; Howarth, 2007).

Overall, these estimates of the relative importance of atmospheric deposition, compared to non-atmospheric sources of N, typically involve many assumptions regarding dry deposition, riverine fluxes, and the relationship between human populations and wastewater inputs. Thus, such estimates entail considerable uncertainty. It is clear, however, that the relative contribution of atmospheric deposition to total N loading varies with the atmospheric N deposition level, land use, watershed and estuary areas, and hydrological and morphological estuarine characteristics. It is also clear that atmospheric deposition is generally an important contributor to the overall N load that stimulates eutrophication of estuaries in the eastern United States (Paerl et al., 2001; Boyer et al., 2002; Driscoll et al., 2003a).

4.3.3 Biological Effects

The major biological effects of N enrichment on biota in terrestrial ecosystems in the United States are attributable to changes in productivity and competitive interactions. Addition of an important plant nutrient (N) from atmospheric deposition is expected to benefit those species that are best able to take advantage of the increased availability of that nutrient. Other species can experience harm, or be eliminated, because they are out-competed by species that are more successful under enhanced N availability. Effects have been most clearly documented for lichens. In the San Bernardino Mountains, California, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared, with a disproportionate number of locally extinct species being epiphytic cyanolichens (Nash and Sigal, 1999; Fenn et al., 2003a).

4.3.3.1 Terrestrial Ecosystems

Terrestrial ecosystem health and vigor can be evaluated using changes in rates of NO_3^- leaching, and the growth and productivity of ecosystem-specific indicator species. Changes in biodiversity are reflected in shifts in species composition and richness as well as impacts on rare or threatened species. Atmospheric inputs of N can alleviate deficiencies and increase growth of some plants at the expense of others. Thus, N deposition can alter competitive relationships among plant species and therefore alter species composition and diversity (Ellenberg, 1987; Kenk and Fischer, 1988; U.S. Environmental Protection Agency, 1993b). Wholesale shifts in species composition are more probable in short-lived ecosystems such as annual grasslands or in the forest understory or mycorrhizal associations than for forest trees. These kinds of species shifts and ecosystem changes can occur even if the ecosystem does not exhibit signs of

N saturation. Recent research on changes in species richness and composition in terrestrial ecosystems is summarized below.

4.3.3.1.1 Forests

Over 50% of plant N is used for photosynthetic enzymes. Because N is so crucial to photosynthesis, rates of photosynthesis and net primary productivity is typically correlate with metrics of N availability such as leaf N content and net N mineralization rate (Field and Mooney, 1986; Reich et al., 1997a,b; Smith et al., 2002). Because N availability often limits rates of net primary productivity, many modeling analyses expect atmospherically deposited N to increase growth of vegetation (e.g., Townsend et al., 1996; Holland et al., 1997; Ollinger et al., 2002).

In order to understand the effects of added N to forest ecosystems, it is helpful to examine the results of modeling projects and experimental N additions. Experimental N additions to forest ecosystems have elicited positive growth responses in some, but certainly not all, organisms (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006). Forest growth enhancement, to the extent that it occurs, can potentially exacerbate other nutrient deficiencies, such as Ca, Mg, or K, thereby causing problems with forest health. Multiple long-term experiments have demonstrated transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).

Experimental N addition studies on forest ecosystems show a range of responses in terms of mortality and productivity. In general, the results from several studies suggest that moderate to high additions of N lead to either no significant change in growth rates or increased growth in early years followed by declines in most species. Decreased growth and increased mortality have more commonly been observed in high-elevation coniferous stands than in lower elevation hardwood forests, and these differences have been partially attributed to higher inputs of N at higher elevation and to coniferous, as opposed to deciduous, trees (Aber et al., 1998).

It is expected that low to moderate levels of N deposition should result in increased forest growth (Aber et al., 1998). However, there is little direct evidence for regional increases in overall forest productivity in the United States in response to atmospheric deposition of N. Evaluation of tree growth rates in five states (Minnesota, Michigan, Virginia, North Carolina, and Florida) found little evidence for growth enhancement due to any factor examined, including N deposition, carbon dioxide (CO_2) fertilization, or climate change (Caspersen et al., 2000).

Analyses of satellite observations of canopy greenness over the last 20 years across North America suggest enhancement of net primary production in some regions, corresponding to observed changes in climate and forest management, but few such changes in the northeastern United States, where rates of N deposition are relatively high (Hicke et al., 2002). In a broader study, Magnani et al. (2007) recently reported a strong correlation between estimated average long-term net ecosystem productivity and estimated 1990 wet N deposition (Holland et al. 2005) for forest stands mostly in western Europe and the conterminous United States. This study provides some evidence that productivity of forests in high latitudes in the Northern Hemisphere may be stimulated by a moderate level of wet N deposition (estimated up to 9.8 kg N ha^{-1} yr^{-1}). However, this study did not evaluate forest stands that receive higher levels of N deposition that may be showing negative symptoms of N saturation.

In Europe, forest biomass is accumulating, largely in response to increases in forest area and improved management, but other possible mechanisms of growth enhancement cannot be ruled out (Kauppi et al., 1992; Spiecker et al., 1996). One of the most comprehensive analyses of regional forest growth trends was an analysis of tree increment cores from more than 31,000 plots in Norway. In this study, growth increased during the 1960s and 1970s and then declined in the 1990s, especially in southern regions exposed to the highest rates of N deposition (Figure 4.3-7) (Nellemann and Thomsen, 2001).

Conifer forests that receive high inputs of reactive N appear to exhibit decreases in productivity and increases in mortality (Fenn et al., 1998). Multiple long-term experiments have demonstrated transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).

One of the longest of these fertilization studies examined a Scots pine forest in northern Sweden, and found that chronic fertilization at 30 kg N ha^{-1} yr^{-1} continued to stimulate stemwood production even after 30 years, whereas a higher application (90 kg N ha^{-1} yr^{-1}) decreased stem volume growth, and an intermediate application (60 kg N ha^{-1} yr^{-1}) had little positive or negative effect relative to the control plots (Högberg et al., 2006). Note that the lower rates of application in this study are low by fertilization standards, but are still higher than the level of atmospheric N deposition in almost all areas of the United States.

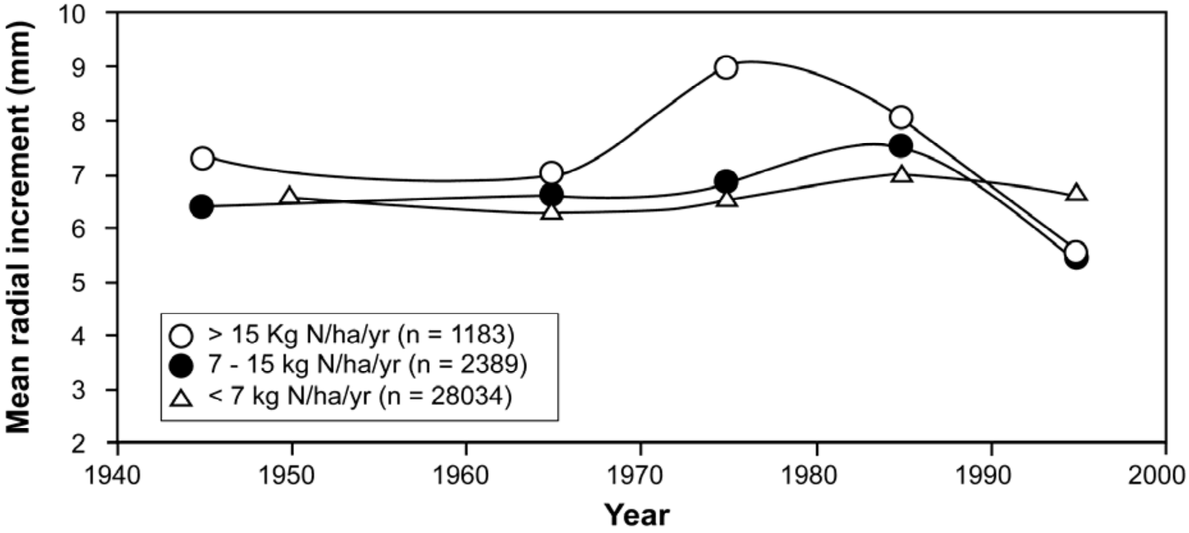


Figure 4.3-7. Mean 5-y radial increment from 31,606 core samples from *Picea abies* during the period 1945 to 1996 for three atmospheric N deposition zones (high, medium, and low wet N-deposition in 1990), respectively. Note that the decline in radial increment after 1975 corresponds with the peak in exceedances for critical loads for the same areas. The increase and subsequent decline from 1965 to 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).

At the Bear Brook, Maine, acidification study, basal area increment of sugar maple was enhanced 13 to 104% by addition of 25 kg N ha^{-1} yr^{-1} as ammonium sulfate ($(NH_4)_2SO_4$), whereas red spruce was not significantly affected (Elvir et al., 2003). In a comparable experiment at the Fernow Experimental Forest, WV, application of 35 kg N ha^{-1} yr^{-1} as $(NH_4)_2SO_4$ enhanced growth of black cherry and yellow poplar during the first 7 years, but led to reduced growth of these species relative to control trees in years 9 through 12, with no change in red maple or sweet birch (DeWalle et al., 2006). Chronic fertilization combined with drought led to significant mortality in a 70-year old red pine stand at Harvard Forest, Massachusetts (Magill et al., 2004). As red pine has died, striped maple, black cherry, and black birch have increased their contributions to annual litterfall production. At the same site, N fertilization of a 50-year-old red-oak/red maple stand largely stimulated productivity, although the drought in 1995 induced significant mortality in fertilized small red maple trees (Magill, 2004).

In western forests, areas of chaparral and mixed conifer forests that receive very high levels of dry N deposition in southern California have experienced significant environmental change over the past several decades (Fenn et al., 1996, 2003a). In a review of acidic deposition effects on mixed conifers in California, Takemoto et al. (2001) reported that some southern California forests experience N deposition up to 45 kg N ha^{-1} yr^{-1}, and that increased N deposition caused increased growth of Jeffrey and ponderosa pine stands. Additionally, N fertilization has been shown to cause increased litter accumulation and C storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires (Fenn et al., 2003a).

Results from a study of 46 forest plots on six sites in North Carolina and Virginia dominated by American beech, sugar maple, and yellow birch suggested that N deposition is associated with changes in basal area, foliar chemistry, and nitrification and mineralization rates (Boggs et al., 2005). Growth rates for the three tree species were similar at the lowest rates of N deposition, and then diverged as N deposition increased, with growth of yellow birch and American beech decreasing at the high N deposition loads (Boggs et al., 2005). These differential growth rates have the potential to affect forest structure and biodiversity.

Disturbance can affect N cycling and the response of forest ecosystems to N deposition. Disturbance can be human-caused (e.g., timber harvesting, road-building, agricultural development) or natural (e.g., wind storm, wildfire, drought). The extent to which disturbance influences leaching of NO_3^- and base cations from soils to drainage waters depends on rates of primary productivity, nutrient uptake by plants and microorganisms within the terrestrial ecosystem, and hydrological pathways for transferring nutrients to drainage water. Historical land use also influences N leaching from currently forested watersheds that receive moderate to high levels of atmospheric N deposition. The severity of effect and length of the recovery period probably vary according to the nature of the past disturbance. Past logging and agricultural cultivation appear to have considerable and long-lasting effects on nutrient cycling.

There is very little information on the effect of N deposition on the biodiversity of overstory trees in the United States. However, some effects have been documented on other plant communities and on understory species, lichens, mycorrhizae, and microbial diversity within forests. See the sections below for explanations of these effects.

4.3.3.1.2 Grasslands

Grasslands are well known to respond to increased N availability through changes in growth rates of both native and exotic species. Under high N supply, exotic grasses often out-compete other species, and cause changes in plant community composition. Lowe et al. (2002) tested the response of two native (blue grama and western wheatgrass) and four exotic (cheatgrass, leafy spurge, Canada thistle, and Russian knapweed) grassland species to increased N availability (0, 10, 40, 70, or 100 kg N ha^{-1} yr^{-1}) in a 75-day greenhouse experiment. They found that all of the grass species exhibited increased growth with increased N availability. Native species did not consistently grow better at low N levels than the exotic species. Two of the exotic grasses exhibited the greatest increase in growth, while another of the exotics exhibited the smallest increase in growth.

From studies of N additions in tallgrass prairie (0.1, 1, 3 mmol N addition for 80 days), Lane and BassiriRad (2002) suggested that increasing N deposition levels could cause species-specific growth and plant tissue quality changes, which in turn could lead to changes in ecosystem dynamics and community structure. In interior coastal grasslands at Jasper Ridge Biological Preserve in California, additions of 70 kg N ha^{-1} yr^{-1} over three years led to decreased forb production concomitant with increased grass productivity (Zavaleta et al., 2003).

In a European study involving 15 herb and 13 grass species, Falkengren-Grerup (1998) found that, in general, grasses grew better than herbs in response to experimental addition of N. At the highest experimental N deposition rates, growth was limited for most species by the supply of nutrients other than N.

Several grassland studies have demonstrated that increased N availability can lead to an overall decrease in plant species richness and an increase in exotic nitrophilous grasses that displace native grass and forb species. Change in species composition in response to N deposition have been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Stevens et al., 2004; Bobbink et al., 1992, 1998; Bobbink, 1998).

Wedin and Tilman (1996) conducted studies of N enrichment over a 12-year period on Minnesota grasslands and found that plots initially dominated by native warm-season grasses shifted to low-diversity mixes of species dominated by cool-season grasses at all but the lowest rates of N addition. Grasslands with high N retention and C storage rates were the most vulnerable to loss of species and major shifts in N cycling in response to experimental N enrichment.

From a study of interior coastal grasslands in California, Zavaleta et al. (2003) found increased N deposition led to a decline in total species richness. After three years of N additions (70 kg N ha^{-1} yr^{-1}), species diversity decreased by 5% and all three N-fixing forbs disappeared.

In the San Francisco Bay area of California, which receives N deposition levels of 10 to 15 kg N ha^{-1} yr^{-1}, exotic nitrophilous grasses have been reported to have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system (Fenn et al., 2003a).

Not all studies have shown an effect of N addition on species richness or diversity. In old agricultural fields in Michigan, increased N deposition changed neither the successional timing nor the gain or loss of species numbers (Huberty et al., 1998). A lack of response in species richness may have been due to application of mid-growing season fertilization in the experimental design. Huberty and colleagues (1998) suggested that N additions may change the dominance structure of these successional old-field communities. Other studies in Michigan also indicated that successional grasslands were not N-saturated (Ambus and Robertson, 2006) and showed no response to N application of 1 g $N/m^2/yr$, equivalent to about 2.5 times ambient deposition rates.

4.3.3.1.3 Arid and Semi-Arid Land Ecosystems

Some arid, semi-arid, and desert ecosystems in the southwestern United States are considered sensitive to N enrichment effects and receive high levels of atmospheric N deposition. However, water is generally more limiting than N in these systems. Nevertheless, enhanced N could play a role in the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate.

In semi-arid ecosystems, results from several N fertilization experiments showed (1) increased biomass of nonnative plant species over native species, (2) decreased soil moisture under some conditions, and (3) increased fire risk where dense mats of grasses replaced shrub cover (Eliason and Allen, 1997; Yoshida and Allen, 2001). For example, in the coastal sage shrub community of southern California, dry N deposition is above 30 kg N ha^{-1} yr^{-1} in some places. Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Eliason and Allen, 1997; Yoshida and Allen, 2001; Cione et al., 2002). The coastal sage shrub community in California has been declining in land area and in shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Allen et al., 1998; Padgett and Allen, 1999; Padgett et al., 1999). N deposition is considered a possible cause or contributor to this ecosystem alteration. More than 30 kg N ha^{-1} yr^{-1} of atmospheric N is deposited to this ecosystem in portions of the Los Angeles Air Basin (Bytnerowicz and Fenn, 1996). Decreases in the diversity of native plants paralleled increases in exotic grass biomass. Biodiversity impacts have also been documented for microbial communities in coastal sage scrub ecosystems. It has been hypothesized that the decline in coastal sage shrub species could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and Allen, 2000). Refer to Section 4.3.3.1.6 for more on mycorrhizae.

Similar responses to N fertilization have been reported in other arid land ecosystems. Fertilization experiments in the Mojave Desert showed that increased levels of N deposition could favor the establishment of nonnative species where the nonnatives are already prevalent (Brooks, 2003). At application rates of 32 kg N ha^{-1} yr^{-1} over two years, biomass of nonnative plants increased 54%, while native species biomass declined by about 39%. A fertilization experiment in the Chihuahuan Desert, with inputs of 100 kg N ha^{-1} yr^{-1} over about a decade, resulted in a 30% increase in cover of warm season grasses and a 52% reduction in cover of legumes (Baez et al., 2007). The effect on legumes may be attributable to the fact that legumes, which are N fixers, often compete better under low N supply.

Another fertilization experiment in an arid grassland on the Colorado Plateau demonstrated a large difference in the response of native and nonnative plants. The increased N application hastened the onset of water stress and a nonnative species, Russian thistle (*Salsola iberica*), showed a rapid growth response to the highest fertilization rate in the first summer, when rainfall was above average. In Joshua Tree National Park, California, which receives moderate levels of air pollution from the Los Angeles Basin, N fertilizer was applied at levels of 5 and 30 kg N ha^{-1} yr^{-1} at four sites over a two-year period. Nonnative grass biomass increased significantly at three of four treatment sites that received 30 kg N ha^{-1} yr^{-1}, but not at the sites that received 5 kg N ha^{-1} yr^{-1} (Allen et al., 2007).

Vegetative changes stimulated by nutrient enrichment from N deposition may affect the frequency and severity of subsequent disturbance. Several lines of evidence suggest that N deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of ecosystem types. Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations (Fenn et al., 2003a).

In summary, N fertilization experiments in arid and semi-arid plant communities have shown that changes in plant biomass associated with increased N deposition tend to alter species composition, with negative impacts on biodiversity. Such plant community changes resulting from experimental fertilization have been reported in the Chihuahuan Desert, Colorado Plateau, Mojave Desert, and Joshua Tree National Park in California.

4.3.3.1.4 Herbaceous Plants and Shrubs

The negative effects of increasing N deposition on herbaceous plants was reviewed by Gilliam (2006). Reported effects include (a) species shifts towards nitrophilous and more acid-tolerant plant species along a deposition gradient from 6 to 20 kg N ha^{-1} yr^{-1} in Swedish oak forests; (b) a decline in abundance and cover of ericaceous shrubs along a deposition gradient from <3 to >12 kg N ha^{-1} yr^{-1} in the boreal forest in Sweden; and (c) a decline in herbaceous cover under hardwoods following 3 years of N additions applied as $(NH_4)_2SO_4$ at rates ranging from 14 to 28 kg N ha^{-1} yr^{-1}. The decline in herbaceous cover in the latter study was attributed to increased shading by ferns, and the effect was more pronounced at sites that experienced lower ambient atmospheric N inputs.

Mixed results have been reported in other studies. Research at Fernow Experimental Forest, West Virginia, indicated that application of 35 kg N ha^{-1} yr^{-1} applied as $(NH_4)_2SO_4$ for 6 years had no significant impact on the herbaceous layer in an Appalachian hardwood forest (Gilliam et al., 2006). Fernow has been the recipient of high levels of N deposition for decades, raising the possibility that the herbaceous layer responded long ago to changes in N availability.

Brunet et al. (1998) and Falkengren-Grerup (1998) reported the effects of excessive N deposition on mixed-oak forest vegetation along a depositional gradient. Results of this study suggest that N deposition had affected nonwoody vegetation directly by increased N availability and, indirectly, by accelerating soil acidity. Time series studies indicated that 20 of the 30 nonwoody plant species that were associated most closely with high N deposition had increased in abundance in those areas in Europe that received high N deposition.

4.3.3.1.5 Lichens

Lichens are frequently used as indicators of air pollution and atmospheric deposition levels. In addition to being good subjects for biomonitoring, they constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997).

Epiphytic macro lichens (those that grow attached to trees or other plants) exhibit different sensitivities to atmospheric pollutants, with some species being adversely impacted at air pollution levels that may not be considered high relative to other sensitive receptors. Particularly sensitive genera include *Alectoria*, *Bryoria*, *Ramalina*, *Lobaria*, *Pseudocyphellaria*, *Nephroma*, and *Usnea* (McCune and Geiser, 1997; Blett et al., 2003).

Lichens that include a cyanobacterium as the photobiont are adversely affected by N deposition as well as acidity. In contrast, those that include a green algal photobiont tend to be only sensitive to acidity. The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N ha^{-1} yr^{-1} (Bobbink et al., 1998). In fact, epiphytic cyanobacteria-containing lichens may be among the most sensitive species in humid forested ecosystems to atmospheric N deposition (Hallingbäck, 1991; Bobbink et al., 1998).

Community composition of epiphytic lichens in the United States can be altered by relatively small increases in N deposition (Fenn et al., 2003a). Most epiphytic lichens meet their nutritional requirements from atmospheric deposition and can store N in excess of their nutritional needs (van Herk, 1999). In the San Bernardino Mountains, California, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared, with a disproportionate number of locally extinct species being epiphytic cyanolichens (Nash and Sigal, 1999; Fenn et al., 2003a).

The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn et al., 2003a). However, in urban areas, intensive agricultural zones, and downwind of major urban and industrial centers in the Pacific Northwest, there are few air pollution-sensitive lichen species, such as epiphytic cyanolichens, and high N concentrations have been measured in lichen tissue (Fenn et al., 2003a). With N enrichment, especially around urban and agricultural areas, there is a shift towards weedy, nitrophilous lichen species (Fenn et al., 2003a). Replacement of sensitive lichens by nitrophilous species has undesirable ecological consequences. In late-successional, naturally N-limited forests of the Coast Range and western Cascade Mountains, for example, epiphytic cyanolichens make important contributions to mineral cycling and soil fertility (Pike, 1978; Sollins et al., 1980; Antoine, 2001), and together with other large, pollution-sensitive macrolichens, are an integral part of the food web for mammals, insects, and birds (McCune and Geiser, 1997). Sensitive lichen species appear to be negatively affected by N inputs as low as 3 to 8 kg N ha^{-1} yr^{-1} (Fenn et al., 2003a).

4.3.3.1.6 Mycorrhizal and Microbial Diversity

Mycorrhizal and microbial biodiversity can also be affected by N enrichment. Interactions between atmospherically deposited N and terrestrial vegetation frequently occur in the rhizosphere. The rhizosphere includes the soil that surrounds and is influenced by plant roots (Wall and Moore, 1999). Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. Mycorrhizal fungal diversity has been shown to be associated with above-ground plant biodiversity and ecosystem productivity (Wall and Moore, 1999) and to be adversely affected by increased N availability (Egerton-Warburton and Allen, 2000). The loss of mycorrhizal function has been hypothesized as a key process contributing to reduced N uptake by vegetation and increased NO_3^- mobility from soil into drainage water under conditions of high N supply (U.S. Environmental Protection Agency, 2004).

It has been hypothesized that the decline in coastal sage shrub species in California could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and Allen, 2000). They discerned a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along a deposition gradient (2 to 57 µg N/g as soil NO_3^-). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by Mediterranean annual grasslands. Larger-spored fungal species (*Scutellospora* and *Gigaspora*) have decreased in number due to a failure to sporulate, with a concomitant proliferation of small-spored species. This suggests selective pressure favoring the smaller spored species of fungi (Egerton-Warburton and Allen, 2000), and that N enrichment of the soil might alter the arbuscular mycorrhizal species composition and diversity.

Progressive decline in ectomycorrhizal fungal species richness in Alaskan coniferous forest (white spruce [*Picea glauca*] dominant) occurred along a local N deposition gradient, from 1 to 20 kg N ha^{-1} yr^{-1}, downwind from an industrial complex (Lilleskov et al., 2002). Ectomycorrhizal fungal communities are important in tree nutrition, and ectomycorrhizal fungal trees tend to be dominant in N-limited forest ecosystems. A shift in ectomycorrhizal fungal community structure could result in a shift in dominant tree species and in nutrition.

N fertilization at rates of 54 and 170 kg N ha^{-1} yr^{-1} (as NH_4NO_3) led to a decline in ectomycorrhizal fungal diversity and species composition in an oak savanna at Cedar Creek Natural History Area in Minnesota (Avis et al., 2003). In the control plots, five species collectively accounted for more than 40% cover versus four plant species in the lower N addition plots. In the higher N addition plots, a single plant species accounted for more than 40% cover.

Compton et al. (2004) investigated the effects of 11 years of experimental N addition on forest soil microbial ecology. Experimental N addition decreased the C content of microbial biomass in the O horizon of both experimental forest stands, based on chloroform fumigation-extraction. In addition, the use of N-containing substrates by microbes appeared to be reduced by N addition in the pine stand, but not in the hardwood stand.

4.3.3.2 Transitional Ecosystems

Ombrotrophic bogs, peatlands, and coastal marshes are the transitional ecosystems that appear to be most sensitive to the effects of excess N deposition. Many bogs receive the majority of their nutrients, including N, from atmospheric deposition. If atmospheric N loading increases substantially to a bog ecosystem, it is expected that productivity will increase and may be accompanied by changes in species composition to favor those species that are adapted to higher nutrient levels. U.S. Environmental Protection Agency (1993b) reviewed field experiments involving N fertilization of wetlands. Results of those experiments confirmed the belief that wetland vegetation is commonly limited by N availability.

Most of the documented impacts of elevated N on wetlands relate to changes in species diversity. Especially important is the effect of elevated nutrient concentrations on the distribution and biomass of nonnative and invasive species.

The sensitivity of wetlands to N enrichment is particularly important given that they contain a disproportionately high number of rare plant species (Figure 5-10; Moore et al., 1989). EPA reported that, of the 130 plant species from the conterminous United States that were listed as threatened or endangered in 1987, 14% occurred principally in wetlands (U.S. Environmental Protection Agency, 1993b). Bedford and Godwin (2003) indicated that a disproportionately high number of rare plant species occur in fens relative to their percent land cover (Table 5-2; Bedford and Godwin, 2003).

Marler et al. (2001) evaluated the potential impacts of experimentally elevated stream water nutrient concentrations on three riparian wetland tree species: Fremont cottonwood (*Populus fremontii*), Goodding willow (*Salix gooddingii*), and exotic saltcedar (*Tamarix ramosissima*) in the riparian zone of the Salt River near Phoenix, Arizona. The results from this 43-day experiment showed that growth of all three riparian plant species responded positively to increased nutrient supply (treatment 3 and 4) (Marler et al., 2001). The exotic and invasive saltcedar showed the greatest increases in biomass at high nutrient supply. Other studies have also found that exotic plant species often respond more rapidly than native vegetation to increased nutrient supply (Milberg et al., 1999; Paschke et al., 2000). This experiment was conducted to simulate impacts of wastewater effluent on riparian zones, and N additions were therefore very large. Elevated nutrient supply to riparian systems via atmospheric N deposition in the United States is more typically in the range of treatments in this experiment that showed minimal response to N addition.

The form of added N may partially regulate wetland response to N deposition. Experimental applications of NO_3^- may have been less effective at stimulating wetland plant productivity than applications of NH_4^+ (U.S. Environmental Protection Agency, 1993b). This may reflect higher rates of denitrification in response to the added NO_3^-, suggesting the importance of competition between plants and microbes for bioavailable N. Plants appear to compete more successfully for NH_4^+ and microbes to compete more successfully for NO_3^-. An important caveat expressed by EPA (1993), however, was that the results of relatively short-term

N fertilization experiments are not necessarily good predictors of long-term wetland community responses to increased N inputs.

In wet heathlands in Europe, changes in plant species composition have been attributed to elevated atmospheric N deposition (Roem and Berendse, 2000). Diverse plant communities consisting of *Erica tetralix*, *Calluna vulgaris*, *Gentiana pneumonanthe*, *Drosera intermedia*, and *Lycopodium inundatum* have been replaced by monospecific stands of the grass *Molina caerulea* or *Deschampsia flexuosa* in Dutch wet heathlands (Aerts and Berendse, 1988; Houdijk et al., 1993).

In other studies, wetland species such as *Calluna vulgaris* can successfully compete with grasses even at relatively high rates of N deposition, as long as the vegetative canopies are closed (Aerts et al., 1990). However, N deposition causes nutrient imbalances, and increased plant shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost stress, and attack by insect pests (Heil and Diemont, 1983). These can result in gaps in the canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in using the additional N and therefore gain a competitive advantage (Krupa, 2003).

Biodiversity

Increased N availability in nutrient-poor wetland environments may lead to a decrease in species diversity and increased risk of extinction for some of the more sensitive and rare species (Moore et al., 1989). Peatlands and bogs are among the most vulnerable transitional ecosystems to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker, 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the United States and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York.

For two ombrotrophic bogs in the northeastern United States (Vermont and Massachusetts) model estimates of extinction risk for the northern pitcher plant (*Sarracenia purpurea*) were calculated under varying N deposition scenarios (Gotelli and Ellison, 2002). Modeled extinction risk within the next 100 years was relatively low under precipitation

N concentrations equivalent to those at the time of the study (0.391 to 0.477 mg N/l/yr). However, model estimates showed increased extinction risk under elevated N deposition scenarios (Gotelli and Ellison, 2002).

4.3.3.3 Freshwater Ecosystems

There are a variety of potential eutrophication effects of excess N deposition to the watersheds of lakes, streams, rivers, and estuaries. Primary productivity in many coastal waters and some freshwaters can be increased with the addition of even very low amounts of N. Effects on freshwater ecosystems are discussed here; effects on estuarine and marine ecosystems are discussed in Section 4.3.3.4.

Eutrophication typically increases algal biomass, alters algal species assemblages, and may affect aquatic biota at all trophic levels. Biological changes in freshwater ecosystems attributed to nutrient enrichment from atmospheric N deposition are likely to be most pronounced in high-elevation aquatic ecosystems in the western United States. Important effects can include changes in biomass, species composition, and diversity of algae, especially diatoms.

In freshwater ecosystems, excess contribution of N to N-limited systems can stimulate ecosystem productivity and contribute to eutrophication. Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition showed strong correlations between N limitation and productivity where N deposition was low. P (or N plus P) limitations occurred where N deposition was higher (Fenn et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006). Paleolimnological studies provide additional evidence suggesting N-limitation or N and P co-limitation of some high-elevation oligotrophic lakes in the western United States (Saros et al., 2005; Wolfe et al., 2006). A recent meta-analysis of 990 freshwater field experiments to determine patterns of autotrophic nutrient limitation found that N limitation of stream benthos, lake benthos, and phytoplankton was as common as P limitation from sites in all biomes worldwide (Elser et al., 2007).

4.3.3.3.1 Chlorophyll **a**

The most widely used index of biological change in response to nutrient addition is measurement of chlorophyll *a* concentration in water. Surveys and fertilization experiments show increased inorganic N concentration and aquatic ecosystem productivity (as indicated by chlorophyll *a* concentration) to be strongly related. For example, a series of in situ meso- and microcosm N amendment experiments more than 30 years ago showed increases in lake algal productivity. Lake 226S in Ontario's Experimental Lake District (ELD) showed doubling of average epilimnetic chlorophyll *a* over five years of fertilization. However, because the response to P fertilization was much greater, the effects of N received less attention (Schindler, 1980). Other ELD lakes that had relatively low N to P concentration ratios experienced 3 to 10 times greater increases in chlorophyll *a* than Lake 226S (Schindler, 1980). Similar experiments at Castle Lake, California, the Snowy Range of southern Wyoming, and Alaskan arctic foothill lakes yielded measurable increases in chlorophyll *a* and primary productivity with N amendments (Axler and Reuter, 1996; Levine and Whalen, 2001; Nydick et al., 2003, 2004a; Lafrancois et al., 2004). Long-term data from 28 years of study in Lake Tahoe, California showed that primary productivity doubled during that period, while water clarity associated with chlorophyll *a* concentration declined, mostly as a result of atmospheric N deposition (Goldman, 1988; Jassby et al., 1994).

4.3.3.3.2 Phytoplankton Biomass

Studies have shown an increase in lake phytoplankton biomass with increasing N deposition in several regions, including the Snowy Range in Wyoming (Lafrancois et al., 2003), the Sierra Nevada Mountains in California (Sickman et al., 2003), throughout Sweden (Bergström et al., 2005), and across Europe (Bergström and Jansson, 2006).

Chemical data from 3,907 lakes and phytoplankton biomass from 225 lakes from Swedish monitoring programs were used to identify clear north-south gradients of increasing lake algal productivity related to the pattern of increasing N deposition input (Bergström et al., 2005). The lowest productivity was found at sites where wet inorganic N deposition was about 1.3 kg N ha^{-1} yr^{-1}; higher productivity occurred at N deposition levels above 2.2 kg N ha^{-1} yr^{-1} (Bergström et al., 2005). Although these lakes are all in Sweden, the sheer number of them used to derive a strong correlation between productivity and atmospheric deposition makes the results of interest to North American audiences.

Experiments conducted with mesocosms in lakes where NO_3^- was below the detection level found a strong response in phytoplankton biomass with additions of N (bringing concentrations to ~1.0 mg N/L) and even stronger responses to additions of N plus P, but not P alone (Lafrancois et al., 2004). The reverse was also found in Colorado Front Range lakes with ambient NO_3^- concentrations of ~1.0 mg/L: productivity increased with additions of N plus P or P only, but not NO_3^- alone (Lafrancois et al., 2004).

A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America, including many of the studies described above, found algal growth enhancement from N amendments to be common in slightly less than half the studies (Elser et al., 1990). There was a mean increase in phytoplankton biomass of 79% in response to N enrichment (average of 46.3 µeq/L N) (Elser et al., 1990).

4.3.3.3.3 Periphyton Biomass

N effects have been observed in periphyton which grow on rocks or sediment in lakes and streams where there is sufficient light for photosynthesis. Several studies found stimulated growth with N amendments from ecosystems throughout the United States, including streams in Alaska, Arizona, Iowa, Texas, Minnesota, Missouri, and lakes in California, Colorado, and Massachusetts. Growth stimulation occurred with N additions ranging from 8 to 50 µM/L, or with exposure to 0.5 M N concentrations on agar substrate (e.g., Bushong and Bachmann, 1989; Allen and Hershey, 1996; Wold and Hershey, 1999; Smith and Lee, 2006). Additional lake bioassay experiments that enriched the water column down into the sediments found enhancement of periphyton growth on bioassay container walls in experiments in California, Wyoming, and Massachusetts (Axler and Reuter, 1996; Nydick et al., 2004b; Smith and Lee, 2006).

The implications of these studies are that the productivity of many freshwater ecosystems is currently limited by the availability of N, European and North American lakes may have been N-limited before human-caused disturbance, and remote lakes may have remained N-limited until slight increases in atmospheric N deposition brought about an increase in phytoplankton and periphyton biomass and induced P limitation. Increases in algal biomass are associated with changes in algal assemblages that favor certain species over others. These effects are described below in the discussion of biodiversity.

4.3.3.3.4 NO_3^- Toxicity

In addition to the biological effects described above, NO_3^- in freshwater at extremely high concentrations can have direct adverse effects on many life stages of fish, as well as on invertebrates and amphibians. These effects occur at levels that are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition, and therefore NO_3^- concentration has not been defined as a primary biological indicator. Nevertheless, these effects are described in Annex 5.

4.3.3.3.5 Biodiversity

Some freshwater algae are particularly sensitive to the effects of added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Interlandi and Kilham, 1998; Baron et al., 2000; Wolfe et al., 2001, 2003; Saros et al., 2003, 2005). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains (Figure 4.3-8). These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

Further evidence for the relationship between N enrichment and algal changes has been provided by N addition studies. For example, the growth of *A. formosa* has been stimulated with N amendments during in situ mesocosm incubations (6.4 to 1616 µM N, McKnight et al., 1990; 76 µM N/L, Lafrancois et al., 2004; 18 µM N, Saros et al., 2005). In situ incubations in large lakes of Yellowstone National Park, Wyoming also stimulated *F. crotonensis* (Interlandi and Kilham, 1998), although this publication did not reveal how much N was added to the incubations. The N requirements for *A. formosa* and *F. crotonensis* were determined to be 0.041 µM and 0.006 µM, respectively, and higher concentrations stimulated growth (Michel et al., 2006). *A. formosa* and *F. crotonensis* have extremely low P requirements, enabling them to outcompete other algae under relatively low P conditions.

Differences in resource requirements allow some species to gain competitive advantage over others upon nutrient addition, causing changes in species composition (Wolfe et al., 2001, 2003; Lafrancois et al., 2004; Saros et al., 2005). This is in keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species diversity was maintained when N levels were low (<3 µM) in lakes in the Yellowstone National Park region.

The implication of this research is that species diversity declines with increasing availability of N. In studies of lake sediment diatom remains, typical oligotrophic species such

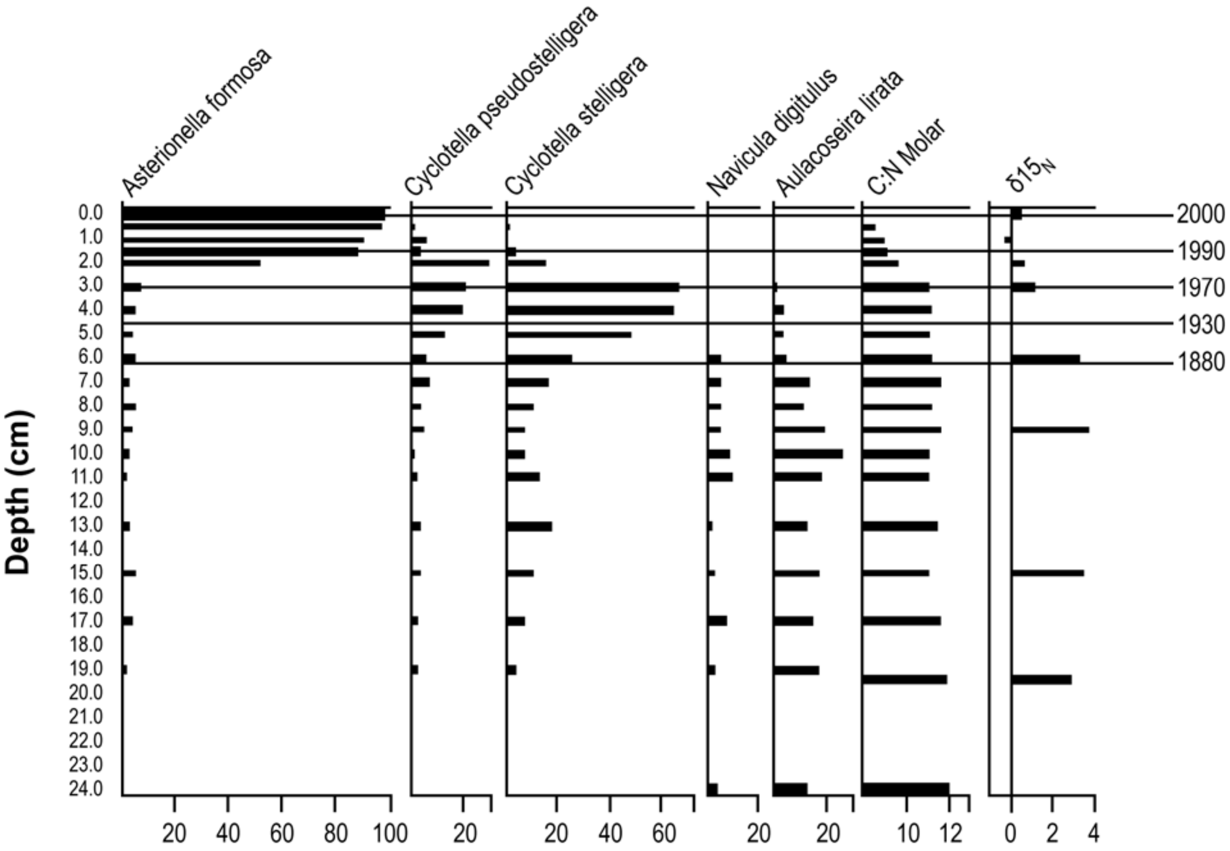


Figure 4.3-8. Diatom assemblage sediment patterns in Emerald Lake, WY.

Source: Saros et al. (2003).

as *Aulacoseria perglabra*, *Cyclotella steligera*, and *Achnanthes* spp. declined coincident with the rise in dominance of *A. formosa* and *F. crotonensis* (Wolfe et al., 2001, 2003).

Community shifts in phytoplankton other than diatoms have also been observed under conditions of elevated N availability. Mesocosm experiments in oligotrophic Snowy Range, Wyoming lakes illustrated a shift away from a general dominance by chrysophyte species to dominance primarily by large chlorophytes and the dinoflagellate Gymnodinium (Lafrancois et al., 2004). A similar positive correlation between the proportion of the phytoplankton comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of 15 Snowy Range lakes (Lafrancois et al., 2003). Chlorophytes, like the two diatom species identified above, generally have a preference for high concentrations of N and are able to rapidly dominate the flora when N concentrations increase (Findlay et al., 1999). This occurs in both circumneutral and acidified waters (Wilcox and Decosta, 1982; Findlay et al., 1999).

Available data suggest that the increases in total N deposition do not have to be large in order to elicit an ecological effect; a model hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N ha^{-1} yr^{-1} (Baron, 2006). Similar changes inferred from lake sediment cores in the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N ha^{-1} yr^{-1} deposition (Saros et al., 2003). Preindustrial inorganic N deposition in the western United States was estimated by Holland et al. (1999) to range from about 0.4 to 0.7 kg ha^{-1} yr^{-1}.

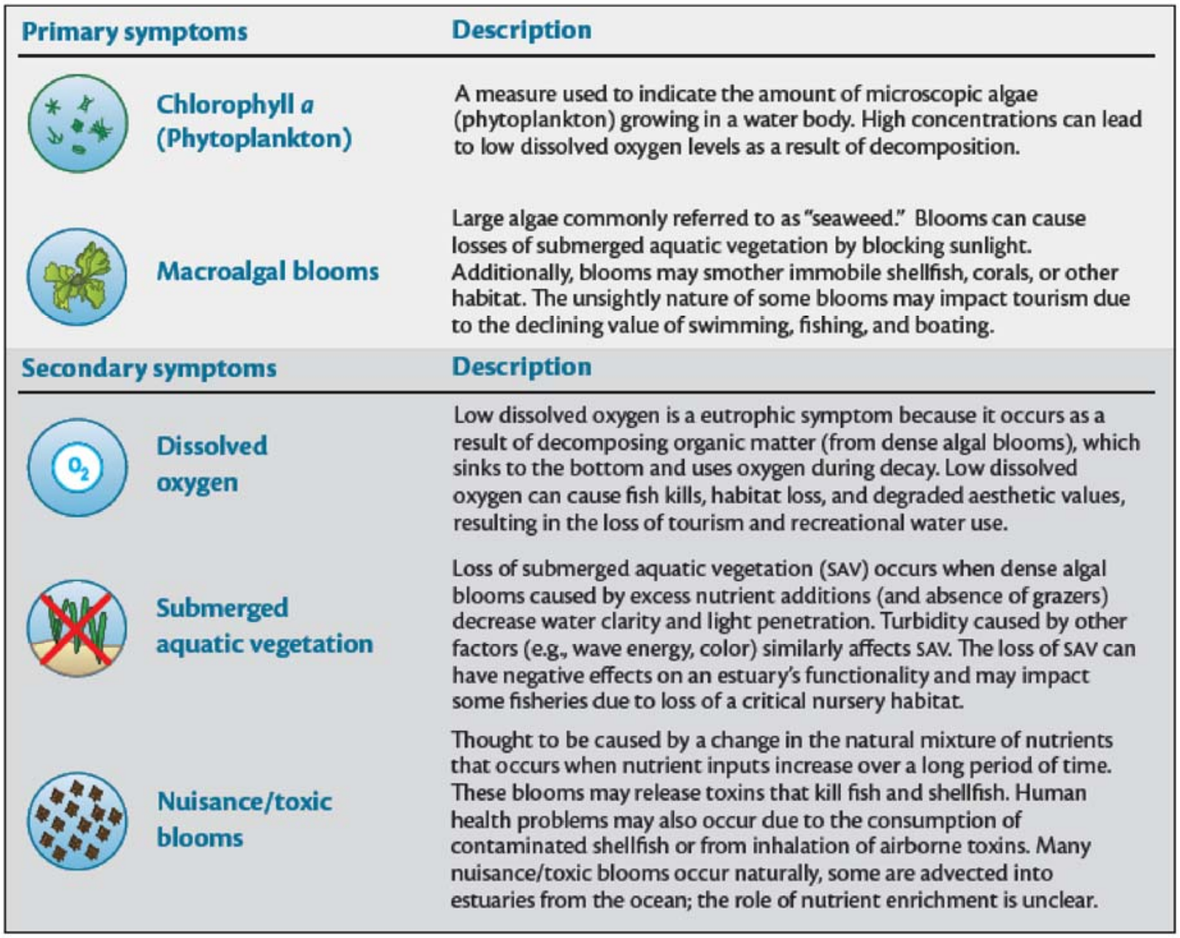
In summary, survey data and fertilization experiments demonstrate that increase in algal productivity, as well as species changes and reductions in biodiversity, have occurred at sensitive high elevation lakes in the western United States in response to increased availability of N.

4.3.3.4 Estuarine and Marine Ecosystems

N is an essential nutrient for estuarine and marine ecosystem fertility, and is often the algal growth limiting nutrient. Excessive N contributions can cause habitat degradation, algal blooms, toxicity, hypoxia (reduced dissolved oxygen), anoxia (absence of dissolved oxygen), fish kills, and decrease in biodiversity (Paerl, 2002). In order to evaluate these impacts, five biological indicators were used in the recent national assessment of estuary trophic condition: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and submerged aquatic vegetation (SAV) (Bricker et al., 2007) (Figure 4.3-9). Each of these indicators is discussed below regarding its relationship with the health and vigor of aquatic species and ecosystem biodiversity.

4.3.3.4.1 Chlorophyll a

Chlorophyll *a* concentration in estuarine or marine water is an indicator of total phytoplankton biomass. It can signal an early stage of water quality degradation related to nutrient loading. High concentration of chlorophyll *a* suggests that algal biomass is sufficiently high that it might contribute to low dissolved oxygen concentration due to increased decomposition of dead algae. In the national estuary condition assessment, high chlorophyll *a*



Primary symptoms	Description
Chlorophyll *a* (Phytoplankton)	A measure used to indicate the amount of microscopic algae (phytoplankton) growing in a water body. High concentrations can lead to low dissolved oxygen levels as a result of decomposition.
Macroalgal blooms	Large algae commonly referred to as "seaweed." Blooms can cause losses of submerged aquatic vegetation by blocking sunlight. Additionally, blooms may smother immobile shellfish, corals, or other habitat. The unsightly nature of some blooms may impact tourism due to the declining value of swimming, fishing, and boating.
Secondary symptoms	**Description**
Dissolved oxygen	Low dissolved oxygen is a eutrophic symptom because it occurs as a result of decomposing organic matter (from dense algal blooms), which sinks to the bottom and uses oxygen during decay. Low dissolved oxygen can cause fish kills, habitat loss, and degraded aesthetic values, resulting in the loss of tourism and recreational water use.
Submerged aquatic vegetation	Loss of submerged aquatic vegetation (SAV) occurs when dense algal blooms caused by excess nutrient additions (and absence of grazers) decrease water clarity and light penetration. Turbidity caused by other factors (e.g., wave energy, color) similarly affects SAV. The loss of SAV can have negative effects on an estuary's functionality and may impact some fisheries due to loss of a critical nursery habitat.
Nuisance/toxic blooms	Thought to be caused by a change in the natural mixture of nutrients that occurs when nutrient inputs increase over a long period of time. These blooms may release toxins that kill fish and shellfish. Human health problems may also occur due to the consumption of contaminated shellfish or from inhalation of airborne toxins. Many nuisance/toxic blooms occur naturally, some are advected into estuaries from the ocean; the role of nutrient enrichment is unclear.

Figure 4.3-9. Description of the eutrophic symptoms included in the national estuary condition assessment.

Source: Bricker et al. (2007).

concentration was the most widespread documented symptom of eutrophication (Bricker et al., 2007) (Figure 4.3-10). Half of the estuaries for which there were available data exhibited high chlorophyll *a* concentration (Bricker et al., 2007). San Francisco Bay, California is an example of an estuary that has experienced considerable increases in chlorophyll *a* concentrations in recent years. Phytoplankton biomass in much of the bay has increased by more than 5% per year from 1993 to 2004. During this time, modeled primary production has doubled and nutrient loading is identified as one of eight possible causes (Cloern et al., 2006).

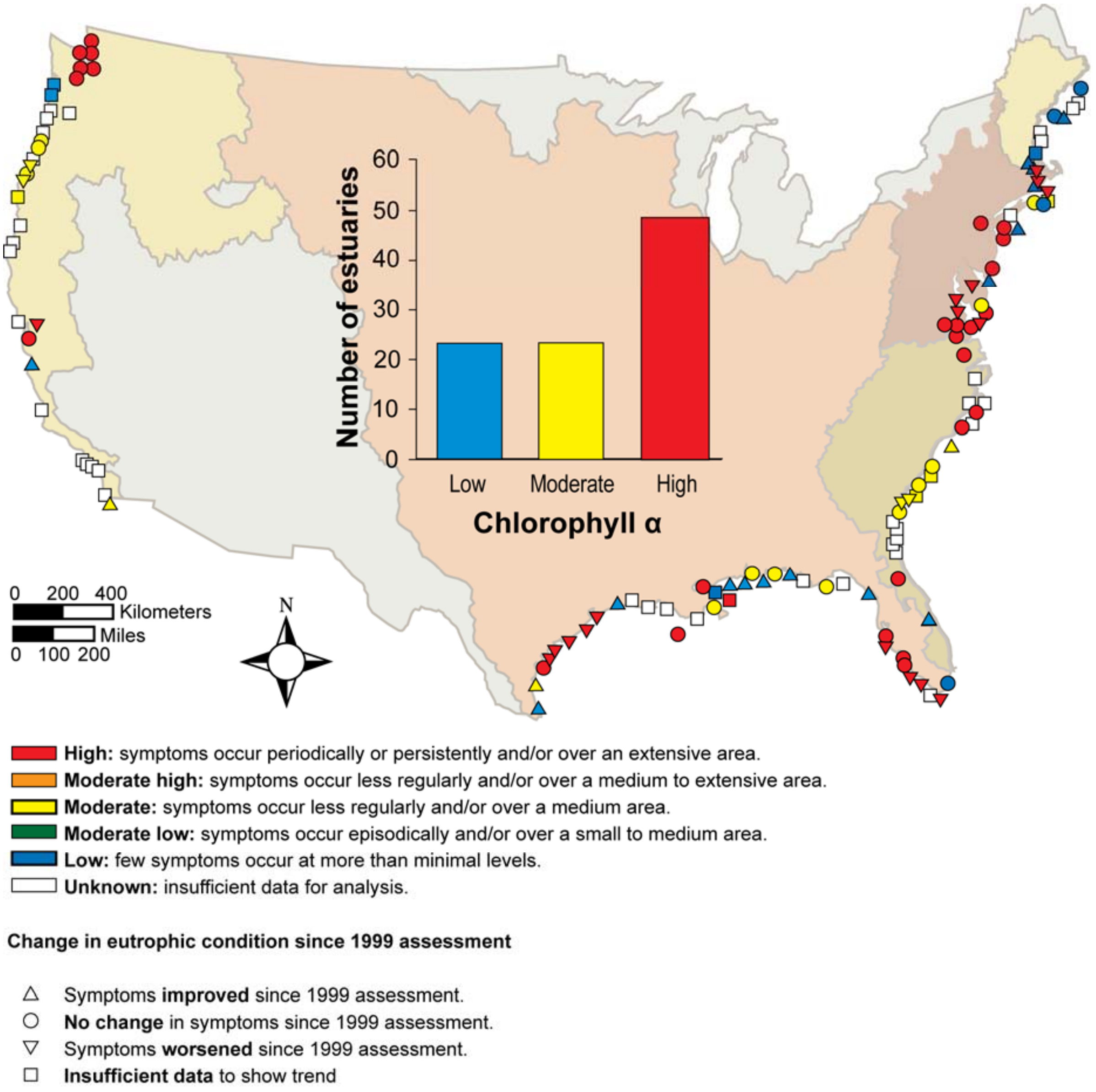


Figure 4.3-10. A high chlorophyll *a* rating was observed in a large number of the nation's estuaries. White squares indicate that data were not available for a particular estuary.

Source: Bricker et al. (2007).

4.3.3.4.2 Macroalgal Abundance

Macroalgae are generally referred to collectively as seaweed. Macroalgal blooms can contribute to loss of important SAV by blocking the penetration of sunlight into the water column. Although macroalgal data for estuaries in the United States were generally sparse, the national estuary condition assessment reported that conditions were moderate or high for 33 of the estuaries evaluated (Bricker et al., 2007).

4.3.3.4.3 Dissolved O_2

The decomposition of organic matter associated with increased algal abundance consumes dissolved oxygen and can reduce dissolved oxygen concentrations in eutrophic waters to levels that cannot support aquatic life. Decreased dissolved oxygen can lead to development of hypoxic or anoxic zones that are inhospitable to fish and other life forms. Perhaps the most important environmental effect of N input to coastal waters is the development of hypoxia. The largest zone of hypoxic coastal water in the United States has been documented in the northern Gulf of Mexico on the Louisiana-Texas continental shelf. During midsummer, this hypoxic zone has regularly been larger than 16,000 km^2 (Rabalais, 1998). The timing, duration, and spatial extent of hypoxia in this case are related mostly to the nutrient flux from the Mississippi River (Justic et al., 1993, 1997; Rabalais et al., 1996; Lohrenz et al., 1997; Paerl et al., 2001).

Although impacts on dissolved oxygen can be quite severe in the areas where they are manifested, the national assessment reports that the severity of dissolved oxygen impacts related to eutrophication are relatively limited in many of the systems assessed (Bricker et al., 2007). In the shallow estuary of Long Island Sound, the existence of extended periods of low dissolved oxygen is a notable problem, and atmospheric deposition is considered to comprise a significant fraction of the total N loading. Dissolved oxygen levels below 3 mg/L are common, and levels below 2 mg/L also occur. During some years, portions of the Long Island Sound bottom waters become anoxic (<1 mg/L; Figure 4.3-11) (Bricker et al., 2007).

4.3.3.4.4 Nuisance/Toxic Algal Blooms

Nuisance or toxic algal blooms reflect the proliferation of a toxic or nuisance algal species that negatively affects natural resources or humans. Such blooms can release toxins that kill fish and shellfish and pose a risk to human health. Unlike the other indicators of estuarine eutrophication, the role of nutrients in stimulating toxic algal blooms is less clear. Of the 81 estuary systems for which data were available, 26 exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker et al., 2007).

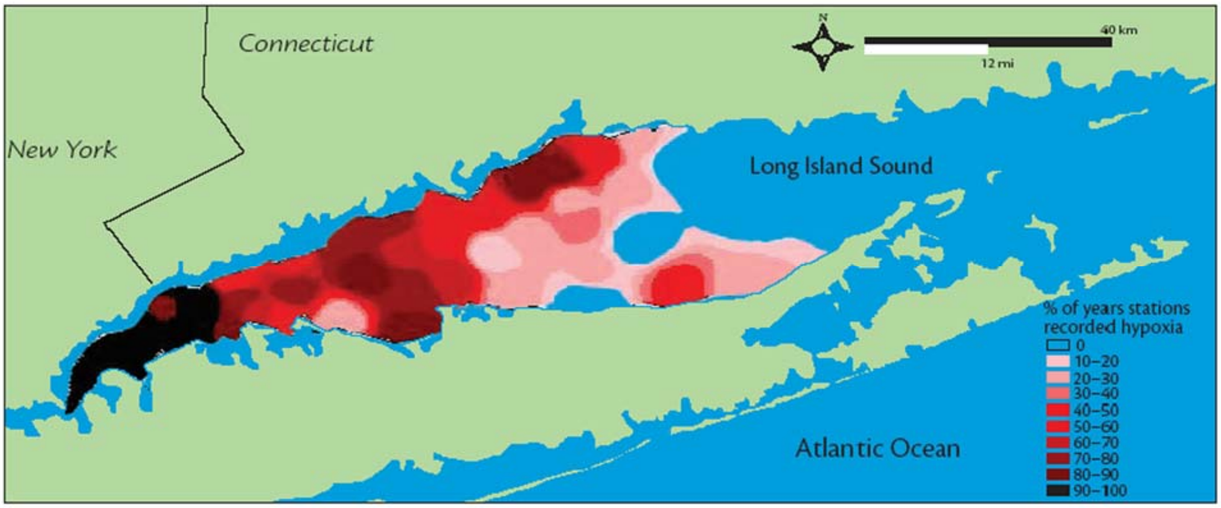


Figure 4.3-11. Frequency of hypoxia in Long Island Sound, 1994 to 2002.

Source: Bricker et al. (2007).

4.3.3.4.5 Biodiversity

Phytoplankton

In addition to causing increased phytoplankton biomass, as indicated by chlorophyll *a* measurements, excess N can contribute to changes in phytoplankton species composition. N enrichment of marine and estuarine waters can alter the ratios among nutrients and affect overall nutrient limitation. For example, excessive N loading to Chesapeake Bay and its tributaries during spring high runoff periods contributes to periods of P limitation and co-limitation (Boynton et al., 1995). The ecosystem then returns to N limitation during low flow summer months (Paerl, 2002). High loadings of N and P can also increase the potential for Si limitation, with associated changes in diatoms. Such changes to the phytoplankton community can also affect higher trophic levels. For example, Officer and Ryther (1980) and Turner et al. (1998) suggested that a shift in the Si-to-N atomic ratio to less than 1 would alter the marine food web. Specifically, the diatom-to-zooplankton-to-higher tropic level ratios would decrease, whereas flagellated algae (including those that often contribute to hypoxia) would increase (Paerl et al., 2001).

Phytoplankton production and community composition in estuarine and marine environments also respond to differences in the form of atmospheric N input. Atmospheric deposition of reduced N has increased relative to oxidized N in the eastern United States, and this trend is expected to continue in the future under existing emissions controls. Such patterns can influence marine eutrophication responses. Large diatoms tend to dominate coastal waters when NO_3^- is supplied (Stolte et al., 1994; Paerl et al., 2001), whereas smaller diatom species have a greater preference for NH_4^+ uptake. Thus, ongoing trends of decreasing NO_3^- deposition and increasing NH_4^+ deposition might lead to changes in species distributions and size distributions of estuarine phytoplankton, with cascading effects on trophic structure and biogeochemical cycling (Paerl et al., 2001).

Changes in phytoplankton species abundances and diversity have been further documented through in situ bioassay experiments such as the results reported by Paerl et al. (2003) for the Neuse River Estuary in North Carolina. Effects were species-specific and varied dramatically depending on whether, and in what form, N was added. The findings illustrate the potential impacts of N additions on phytoplankton community structure (Figure 4.3-12).

Changing phytoplankton community composition has numerous potential ecological ramifications, including modifications to the ecosystem food web and nutrient dynamics. For example, if the nutrient mix favors species that are not readily grazed (e.g., cyanobacteria and dinoflagellates), trophic transfer will be poor and relatively large amounts of unconsumed algal biomass will settle to the bottom, which could stimulate decomposition, oxygen consumption, and the potential for hypoxia (Paerl et al., 2003).

Submerged Aquatic Vegetation

Submerged aquatic vegetation (SAV) provides important nursery grounds to many estuarine fish. There are few data documenting the long-term response of SAV in coastal ecosystems to N loading. The national assessment (Bricker et al., 2007) suggested that only a small fraction of the estuary systems evaluated reported high severity of SAV loss. Most of those that did report moderate or high loss were located in the Mid-Atlantic region. However, where SAV loss is a problem, the results can be severe, and there is evidence suggesting a correlation with increases in N loading. For example, at Waquoit Bay, Massachusetts, Driscoll

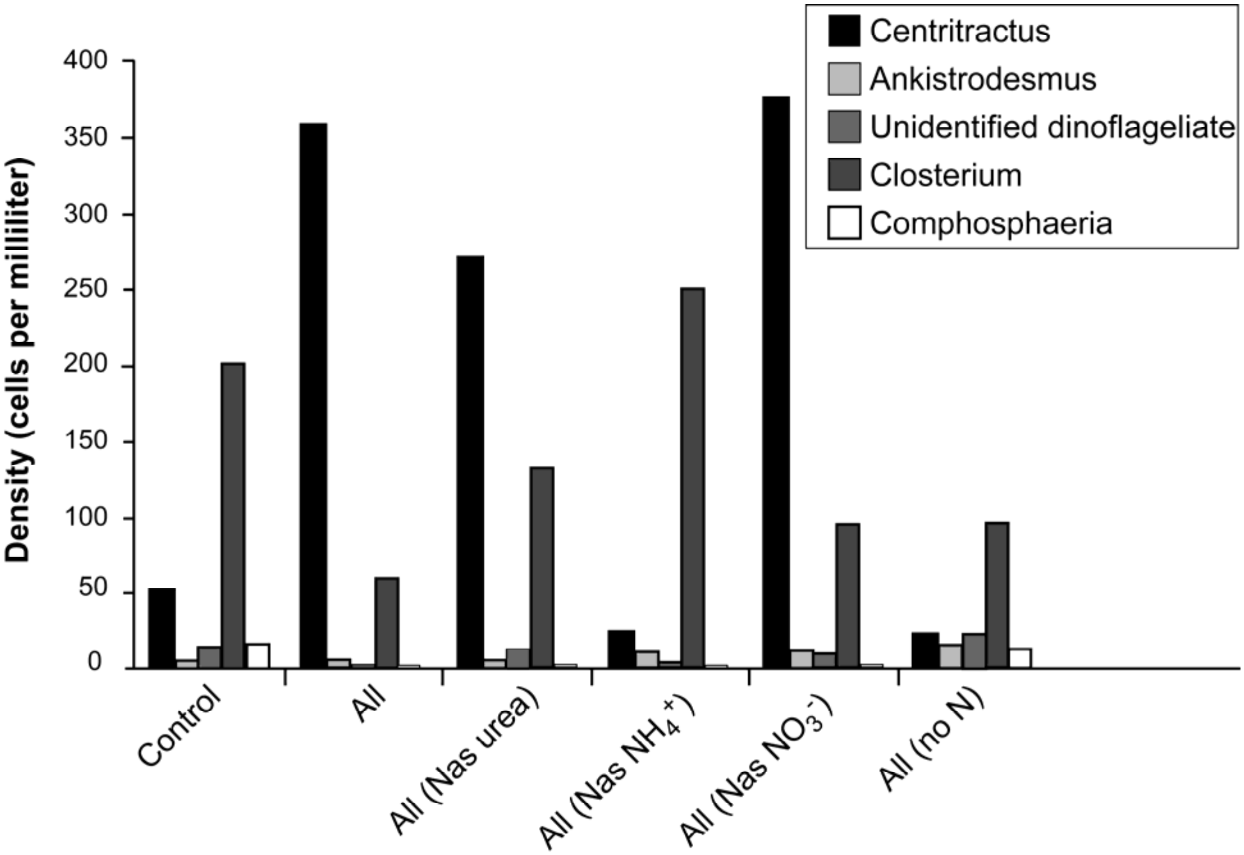


Figure 4.3-12. Microscopic counts of phytoplankton species composition in the Neuse River Estuary, NC following 36-h in situ bioassays to manipulate available forms of nitrogen (N). Treatments included a control (unamended estuarine water sample), all nutrients (N, P, vitamins, trace metals, and Si), all with urea as the N form, all with ammonium (NH_4^+) as the N form, all with nitrate (NO_3^-) as the N form, and all with no N. Bars represent the mean density of cells present (three replicate counts for each treatment).

Source: Paerl et al. (2003).

et al. (2003b) reported a strong negative relationship between modeled N loading and measured eelgrass area based on measurements of eelgrass coverage from 1951 to 1992.

4.3.3.5 Effects on Rare and Endemic Species

Changes in species composition, taxonomic richness, and species diversity are important in their own right. Of particular importance, however, is the extent to which such changes in species occurrence might impact rare species, especially those that are federally listed as threatened or endangered. The coastal sage shrub community in California is of particular interest because about 200 sensitive plant species and several federally listed threatened or endangered animal species are found in the area (Allen et al., 1998). It is not clear to what extent changes that occur in biodiversity within this community in response to N deposition may have affected any of the rare species known to occupy these habitats.

Changes in grass species composition at ambient N deposition levels of 10 to 15 kg N ha^{-1} yr^{-1} has been associated with the decline of the bay checkerspot butterfly (*Euphydryas editha bayensis*), which is a federally threatened species that is native to California. Since the 1980s, the population of checkerspots has been in serious decline. According to the U.S. Fish and Wildlife Service, the bay checkerspot butterfly historically occurred east, west, and south of San Francisco Bay before the invasion of nonnative grasses. Today, their habitat is limited to approximately 19,000 acres on serpentine soils.

The proposed plan for designating critical habitat for the bay checkerspot butterfly developed by the U.S. Fish and Wildlife Service cites the impacts of N deposition as a key factor in the loss of bay checkerspot butterfly habitat (Federal Register, 2007). Specifically, they note that the serpentine and serpentine-like grasslands had previously supported uncommon plants including the bay checkerspot butterfly's larval host plants *Plantago erecta*, *Castilleja densiflora*, and *Castilleja exserta*. These remnant native grasslands are being invaded by nonnative grass species, and this has been partially attributed to N deposition that is primarily caused by air pollution (Weiss, 1999; Federal Register, 2007).

4.3.4 Characterization of Most Sensitive and Most Affected Ecosystems and Regions

4.3.4.1 Extent and Distribution of Sensitive Ecosystems

The following discussion of sensitive ecosystems is organized into three ecosystem categories: terrestrial, transitional, and aquatic. Table 4.3-2 gives an overview of the sensitive ecosystems. Changes in terrestrial and aquatic plant or algal community composition that occur in response to increased N deposition will be most obvious in ecosystems that are naturally deficient in N. This is because species that are adapted to low N supply will often be more readily outcompeted by species that have higher N demand when the availability of N is increased (Aerts, 1990; Tilman and Wedin, 1991; Krupa, 2003). As a consequence, some native species can be eliminated by N-enhanced eutrophication (Ellenberg, 1985; Falkengren-Grerup, 1986, 1989; Roelofs, 1986; Stevens et al., 2004).

Terrestrial

Little is known about the full extent and distribution of the terrestrial ecosystems in the United States that are most sensitive to adverse impacts caused by nutrient enrichment from atmospheric N deposition. Effects are most likely to occur where areas of relatively high atmospheric N deposition intersect with N-limited plant communities. The factors that govern the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation, rates and form of N deposition, elevation, species composition, length of growing season, and soil N retention capacity.

Alpine tundra is believed to be among the terrestrial systems most sensitive to N enrichment. Factors that govern the sensitivity of alpine tundra to N deposition include low rates of primary production, short growing season, low temperature, and wide variation in moisture availability in the alpine environment (Bowman and Fisk, 2001). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this also contributes to their N-sensitivity (Bowman et al. 2006).

Regions and ecosystems in the **western** United States where N enrichment effects have been documented in terrestrial ecosystems are shown on Figure 4.3-13 (Fenn et al., 2003a). The alpine ecosystems of the Colorado Front Range (see case study), chaparral watersheds of the Sierra Nevada, lichen communities in the San Bernadino Mountains and the Pacific Northwest, and the southern California coastal sage scrub community are among the most sensitive terrestrial ecosystems (see Section 4.3.3.1 for description of effects).

In the **eastern** United States, the degree of N saturation of the terrestrial ecosystem is often assessed in terms of the degree of NO_3^- leaching from watershed soils into ground water or surface water. Stoddard (1994) estimated the number of surface waters at different stages of saturation across several regions in the eastern United States. Of the 85 northeastern watersheds examined, 40% were in N-saturation Stage 0, 52% in Stage 1, and 8% in Stage 2. Of the

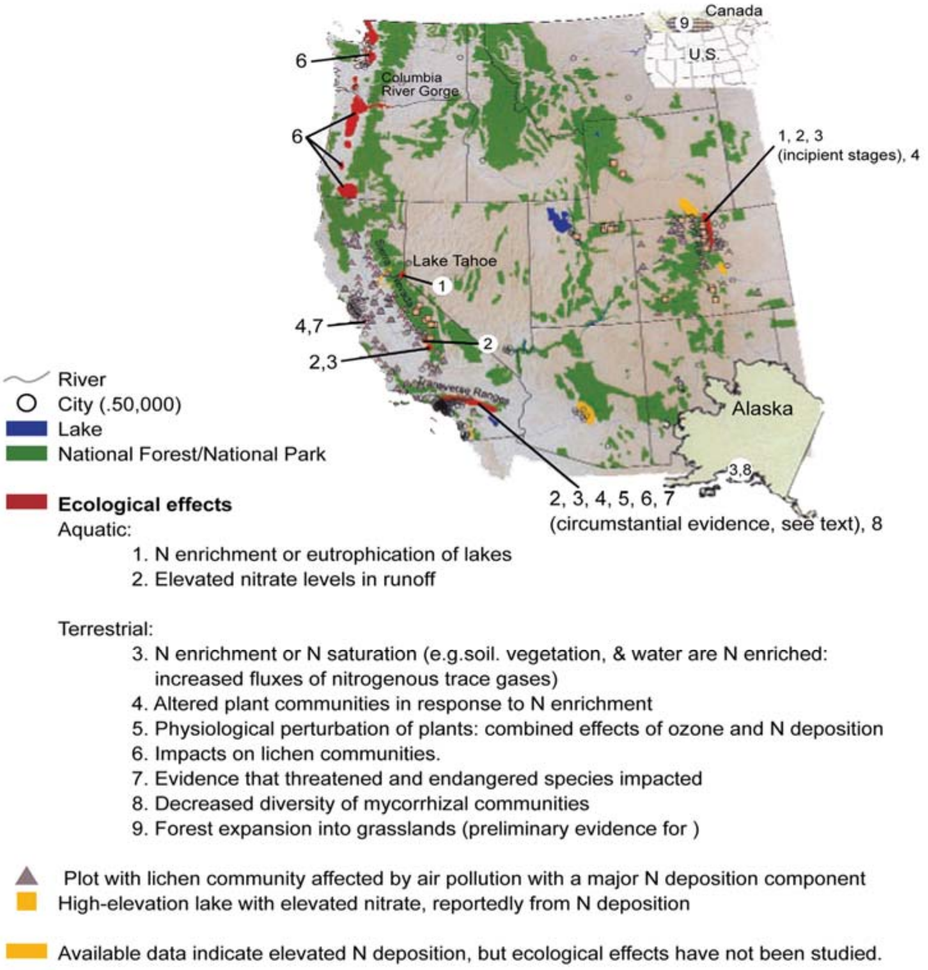


Figure 4.3-13. Map of the western United States showing the primary geographic areas where N deposition effects have been reported. Eutrophication effects are more widespread and of greater importance than acidification effects in western North America. Areas where effects of air pollution on lichen communities have been reported in California are represented by pink triangles. The plots in northcentral Colorado where lichen community changes were observed are exposed to emissions of both N and sulfur (S) from two large power plants in Craig and Haydens, Colorado (Peterson and Neitlich, 2001). The areas shown in red in Oregon and Washington (lichen communities affected by N deposition) are kriged data (Geiser and Neitlich, 2007). Only lakes at an elevation greater than 1000 m and with a nitrate concentration of more than 5 μeq/L (measured in fall surveys or on an annual volume-weighted basis) are shown in this figure. Other high-elevation lakes in the West also had elevated nitrate concentrations, but were excluded because N sources other than N deposition may have contributed to the elevated concentrations of nitrate.

Source: Fenn et al. (2003a).

northeastern sites for which adequate data were available for assessment, those in Stage 1 or 2 were most prevalent in the Adirondack and Catskill Mountains. Effects on individual plant species have not been well studied in the United States. More is known about the sensitivity of particular plant communities. Based largely on results obtained in more extensive studies conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems.

Transitional

Wetlands considered sensitive to N deposition typically host plant species that evolved under N-limited conditions. It is believed that the balance of competition among plant species in some sensitive wetland ecosystems can be altered by N addition, with resulting displacement of some species by others that can utilize the excess N more efficiently (U.S. Environmental Protection Agency, 1993a). Data are not available with which to evaluate the extent to which wetlands in the United States have been affected by nutrient enrichment from N deposition. Wetlands are widely distributed, including some areas that receive moderate to high levels of N deposition.

Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the effects of N deposition. In the conterminous United States, peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S. Environmental Protection Agency, 1993a). In Alaska, these ecosystems are common in poorly drained locations throughout the state. Other types of wetlands occur across broad areas of the United States. It is not clear whether current levels of N deposition cause eutrophication to these ecosystems.

Coastal marsh ecosystems, unlike bog ecosystems, often receive large N inputs in tidal water, groundwater, and surface runoff. At many locations, especially along the Atlantic and Gulf coasts, atmospheric N inputs probably contribute to eutrophication problems in coastal marshes. Atmospheric inputs to these systems are important because any N addition has the potential to contribute to eutrophication of coastal marshes and nearby marine and estuarine ecosystems (Paerl, 2002; Galloway et al., 2003).

Nutrient concentrations in wetland waters associated with the Great Lakes suggest that coastal Great Lakes wetlands are N-limited. Hill et al. (2006) found that more wetlands were N- than P-limited at each of the five Laurentian Great Lakes. This result is consistent with the apparent N-limitation of most North American marsh lands (Bedford et al., 1999). Nutrient loading to lakeshore wetlands is a concern throughout the lower lakes (Lakes Erie, Ontario, and the southern part of Lake Michigan) and in some localized areas of the upper lakes (Hill et al., 2006). Both agricultural and atmospheric sources of nutrients contribute to this stress.

Aquatic

Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of greatest concern in lakes and streams that have very low productivity and nutrient levels and that are located in remote areas. In more productive freshwaters, nutrient enrichment from N deposition usually does not stimulate productivity or community changes because P is more commonly the limiting nutrient. Also, in many places with even minor levels of human disturbance, nutrient enrichment with both N and P from non-atmospheric sources is common. Thus, eutrophication effects from N deposition are most likely to be manifested in undisturbed, low-nutrient surface waters such as those found in the higher elevation areas of the western United States. The most severe eutrophication from N deposition effects are expected downwind of major urban and agricultural centers.

High concentrations of lake or streamwater NO_3^-, indicative of ecosystem saturation, have been found at a variety of locations throughout the United States, including the San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the Front Range of Colorado (Baron et al., 1994; Williams et al., 1996a), the Allegheny Mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al., 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994). All of these regions, except Colorado, received more than about 10 kg N ha^{-1} yr^{-1} atmospheric deposition of N throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives up to about 5 kg N ha^{-1} yr^{-1} of total (wet plus dry) deposition (Sullivan et al., 2005), less than half of the total N deposition received at many of these other locations.

High concentrations of NO_3^- in surface waters in the western United States are not widespread. NO_3^- concentrations during the fall sampling season were low in most western lakes sampled in the Western Lakes Survey. Only 24 sampled lakes were found to have NO_3^-

concentrations greater than 10 μeq/L. Of those, 19 lakes were situated at high elevation, most above 3,000 m (Eilers et al., 1987).

There is some evidence suggesting that reductions in atmospheric N deposition could decrease the extent of eutrophication in at least some of the Great Lakes. It has generally been believed that the Laurentian Great Lakes are P-limited (Schelske, 1991; Downing and McCauley, 1992; Rose and Axler, 1998). Water quality in the open waters of these lakes has been improving in recent years in response to controls on point sources of P (Nicholls et al., 2001). Work by Levine et al. (1997), however, suggested a more complicated pattern of response to nutrient addition for Lake Champlain. They added nutrients to in situ enclosures and measured indicators of P status, including alkaline phosphatase activity and orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during summer, N addition also resulted in algal growth stimulation. P sufficiency appeared to be as common as P deficiency. During spring, phytoplankton growth was not limited by P, N, or Si, but perhaps by light or temperature (Levine et al., 1997).

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia et al., 1986; Howarth and Marino, 2006). This is at least partly because the rate of denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997).

The national estuary condition assessment conducted by Bricker et al. (2007) found that the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. Other regions had mixtures of low, moderate, and high degree of eutrophication (Figure 4.3-14). The estuaries with the greatest extent of eutrophication corresponded with conditions related to both the degree of N loading and the inherent sensitivity of the estuary, as influenced by morphology and water flushing dynamics. The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker et al., 2007).

Bricker et al. (2007) evaluated the future outlook of the nations estuaries based on population growth and future management plans. They predicted that trophic conditions would worsen in 48 estuaries, stay the same in 11, and improve in only 14 by the year 2020. Between 1999 and 2007, an equal number of estuary systems have improved their trophic status as have

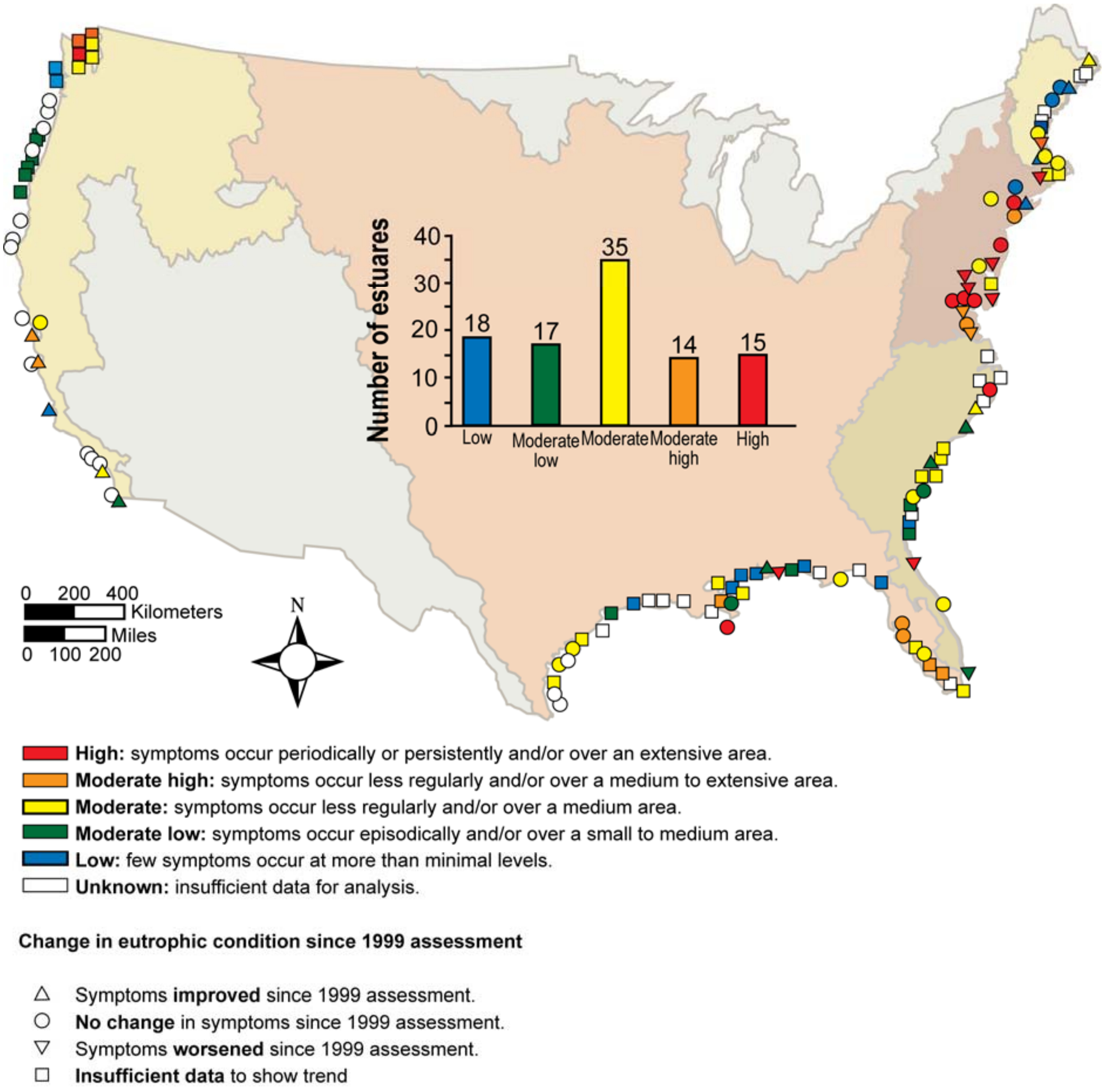


Figure 4.3-14. Overall eutrophication condition on a national scale.

Source: Bricker et al. (2007).

worsened. The assessed estuarine surface area with high to moderate/high eutrophic conditions have stayed roughly the same, from 72% in 1999 (Bricker et al., 1999) to 78% in the recent assessment (Bricker et al., 2007).

Efforts in the scientific literature to link changes in estuary nutrient status to atmospheric N deposition have been limited, though it should be noted that many states are addressing atmospheric inputs as part of their development of Total Maximum Daily Load plans to address estuarine water quality impairments, including those associated with low dissolved oxygen. In an effort to evaluate the contribution of atmospheric N deposition to the future reduction in N loading to estuaries, Castro and Driscoll (2002) reported model calculations that suggested that considerable reductions (more than 25%) in atmospheric N deposition will be needed to significantly reduce the contribution made by atmospheric N deposition to the total N loads to their study estuaries in the northeastern United States. A simulated reduction in atmospheric deposition of 25% of ambient deposition rates reduced the contribution made by atmospheric deposition to the total estuarine N loads by only 1% to 6% (Castro and Driscoll, 2002). In a later study, Driscoll et al. (2003b) estimated that reduction of both mobile N emissions sources and electric utilities would produce an estimated reduction in estuarine N loading in Casco Bay, Maine of 13% (Driscoll et al., 2003). Casco Bay receives the lowest atmospheric and non-atmospheric N loading per unit area of watershed (4 kg N ha^{-1} yr^{-1}) of the eight estuaries in the northeastern United States evaluated by Driscoll et al. (2003) (Figure 4.3-6).

4.3.4.2 Levels of Atmospheric Nitrogen Deposition at Which Effects are Manifested

N levels at which effects are manifested in terrestrial and associated freshwater ecosystems have been documented through gradient and fertilization studies. The results from several major studies are summarized in Table 4.3-1. In terrestrial ecosystems, the reported effect levels range from 4 to 5 kg N ha^{-1} yr^{-1} for changes in the abundance of individual sensitive alpine plant species, to 20 kg N ha^{-1} yr^{-1} for community level changes in alpine plant communities. Differences in the levels at which increased nitrification and NO_3^- leaching have been observed in eastern and western watersheds. For example, Rueth (2002) observed increased rates of nitrification in old-growth forests in Colorado at approximately 5 kg N ha^{-1} yr^{-1}, whereas Aber et al. (2003) associated the onset of NO_3^- leaching in eastern forests with deposition levels of 7 to 10 kg N ha^{-1} yr^{-1}. Changes in aquatic ecosystems in the western United States in response to N deposition are highlighted in Table 4.3-3.

4.3.4.3 Critical Loads and Timeframes of Response

Empirical models of critical loads for nutrient-N have been in use in Europe for some time (e.g., UNECE, 2004). Within the United Nations Economic Commission for Europe (UNECE) Long Range Transboundary Air Pollution (LRTAP) convention, empirical procedures have been developed to set critical loads for atmospheric N deposition to protect against effects caused by nutrient enrichment. Empirical critical loads of N deposition for natural and semi-natural terrestrial and wetland ecosystems were first presented in a background document for the 1992 LRTAP workshop on critical loads held at Lökeberg, Sweden (Bobbink et al., 1992).

Since the identification of N deposition as one of the main drivers behind the general loss of biodiversity in Europe, a number of European expert workshops have taken place in order to reach agreement among specialists regarding the impacts of N deposition on various ecosystems and related critical loads (Nilsson and Grennfelt, 1988; Bobbink et al., 1992; Hornung et al., 1995; Bobbink et al., 1996; Achermann and Bobbink, 2003). Efforts have begun to develop similar empirical relationships in the United States, particularly for western ecosystems (Baron et al., 1994, 2000; Williams and Tonnessen, 2000; Fenn et al., 2003a; Burns, 2004; Nydick et al., 2004b). See Section 4.1.2 for additional general information on critical loads.

4.3.4.4 Nutrient Enrichment Case Study #1: Alpine and Subalpine Communities of the Eastern Slope of the Rocky Mountains in Colorado

Research on N enrichment effects on alpine and subalpine ecosystems in the western United States has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge Long-Term Ecosystem Research site, both located east of the Continental Divide in Colorado. Research has been conducted in this region on both the terrestrial and aquatic effects of nutrient enrichment.

Terrestrial Effects

Changes in biomass production and NO_3^- leaching are indicative of effects on the health and vigor of plants in alpine and subalpine ecosystems. Biomass production responses of alpine communities to increased N deposition are dependent on moisture regimes (Fisk et al., 1998) and are driven by shifts in species composition. In a fertilization experiment, the addition of 25 kg N ha^{-1} yr^{-1} during summer caused a community shift towards greater dominance of hairgrass (*Deschampsia sp.*) in wet alpine meadows, but the increase in plant biomass (+67%) and plant

N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows than in forb-dominated wet meadows (+53% plant biomass, +64% standing N crop, respectively) (Bowman et al., 1995; Burns, 2004).

Alteration of plant productivity and species richness have been observed in fertilization experiments. Seastedt and Vaccaro (2001) showed that four years of N addition to alpine vegetation at rates ranging between 100 and 200 kg N/ha (depending on the year) caused marginal increases in plant foliage productivity but reduced species richness. In a follow-up study at Niwot Ridge, additions of 20, 40, and 60 kg N ha^{-1} yr^{-1} (on top of ambient N deposition near 5 kg N ha^{-1} yr^{-1}) over an 8-year period to a dry alpine meadow led to an increase in plant biomass, and an increase in tissue N concentration at all treatment levels within three years of application. Much of the response was due to increased cover and total biomass of sedges (*Carex spp.*). There was a significant decrease in Kobresia biomass with increasing N input.

High elevation alpine zones exhibit a relatively low capacity to sequester atmospheric deposition of N because of steep slopes, shallow soils, sparse vegetation, short growing season and other factors (Baron et al., 1994; Williams et al., 1996a). Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at deposition levels less than 10 kg N ha^{-1} yr^{-1} (Baron et al., 1994; Williams and Tonnessen, 2000). The changes in plant species that occur in response to N deposition in the alpine zone can result in further increased leaching of NO_3^- from the soils, because the plant species favored by higher N supply are often associated with greater rates of N mineralization and nitrification than the preexisting species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al., 2006).

Effects of N_r deposition to alpine terrestrial ecosystems in this region include community-level changes in plants, lichens, and mycorrhizae. Alpine plant communities are sensitive to changes in species composition in response to added N (Bowman et al., 1995; Seastedt and Vaccaro, 2001). Plant species composition likely responds at lower N input levels than those that cause measurable changes in soil inorganic N content. For example, Bowman et al. (2006) conducted a N-addition experiment in the Colorado Front Range with 20, 40, or 60 kg N ha^{-1} yr^{-1}. Experimental sites were monitored for 8 years along with a control site that received about 5 kg N ha^{-1} yr^{-1} total ambient deposition. Changes in plant species composition associated with the treatments occurred within 3 years of the initiation of the experiment, and were significant at all levels of N addition (Figure 4.3-15). Using changes of individual species abundance and ordination scores to evaluate critical load, the critical load for total N deposition was estimated for change in individual species to be 4 kg N ha^{-1} yr^{-1} and for overall community change to be 10 kg N ha^{-1} yr^{-1} (Bowman et al., 2006). In contrast, increases in NO_3^- leaching, soil solution inorganic NO_3^-, and net nitrification were detectable at levels above 20 kg N ha^{-1} yr^{-1} (Bowman et al., 2006). These results indicate that changes in plant species composition may be detectable at lower N deposition rates than the level at which the traditional soil indicators signal ecosystem responses to N deposition. This response suggests that changes in species composition are probably ongoing in alpine dry meadows of the Front Range of the Colorado Rocky Mountains at current atmospheric N deposition levels. This research also demonstrated that long-term experimental fertilization plots illustrate a clear response of alpine flora to N addition, including shifts toward graminoid plants that shade smaller flowering species, and accompanying changes in soil N cycling (Bowman et al., 2006).

Changes in alpine plant species composition have also been documented on Niwot Ridge, where increased cover of plant species that are most responsive to N fertilization has occurred in some of the long-term monitoring plots (Korb and Ranker, 2001; Fenn et al., 2003a). These changes have probably developed in response to changes in N deposition. However, the influences of climatic change, particularly changes in precipitation (Williams et al., 1996a), and pocket gopher disturbance (Sherrod and Seastedt, 2001) could not be ruled out (Fenn et al., 2003a). The altered N cycling provided the potential for replacement of some native plant species by more competitive, faster growing native species (Bowman and Steltzer, 1998; Baron et al., 2000; Bowman, 2000).

Aquatic Effects

Rocky Mountain National Park has been the site of research addressing the effects of N deposition on algal species abundance in freshwater lakes. Wolfe et al. (2001) analyzed sediments from Sky Pond and Lake Louise, two small alpine lakes located at more than 3300 m elevation on the east slope of the Colorado Front Range in Rocky Mountain National Park. Prior to 1900, the diatom flora was typical of oligotrophic Rocky Mountain lakes, dominated by such species as *Aulacoseira distans*, *A. perglabra*, *Fragilaria pinnata*, *F. construens,* and various *Achnanthes* spp. The mesotrophic planktonic species *Astrionella formosa* and *Fragilaria*

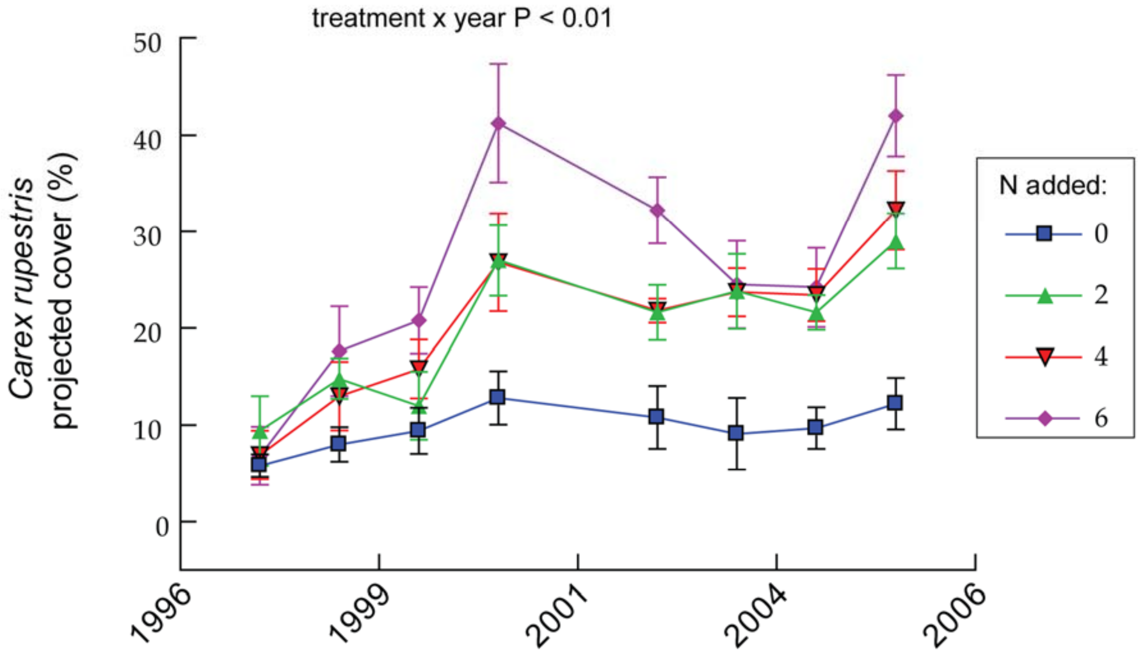


Figure 4.3-15. Changes in plant species composition associated with nitrogen addition treatments in an alpine dry meadow of the Colorado Front Range. Within 3 years of the initiation of the experiment, statistically significant changes in the cover of *Carex rupestris* occurred at all treatment levels.

Source: Bowman et al. (2006).

crotonensis were present in trace frequencies, but became common elements of the diatom flora during the 20th century. Between 1950 and 1970, *A. formosa* became the dominant taxa in both lakes. It is known from studies in other locations as an opportunistic alga that responds rapidly to disturbance and nutrient enrichment (Renberg et al., 1993; Anderson et al., 1995; Reavie and Smol, 2001). This shift in diatom species is apparently the result of environmental stimulation, rather than recent colonization, as evidenced by the presence of these mesotrophic taxa in the older sediment record.

Additional corroborative evidence for the linkage between atmospheric N deposition and the observed diatom shifts in these alpine lakes is provided by the results of laboratory (Interlandi and Kilham, 1998) and in-lake (McKnight et al., 1990) N addition experiments. In both sets of experiments, growth of *A. formosa* and *F. crotonensis* was accelerated by experimental N addition. The post-1950 period of rapid shifts in diatom species composition in Sky Pond and Lake Louise corresponded with intensification of agricultural practices, animal husbandry, and population growth in adjacent regions to the east of Rocky Mountain National Park (Wolfe et al., 2001). Nevertheless, N deposition at that time was estimated to be low, probably less than 2 kg N ha^{-1} yr^{-1} (Baron, 2006).

4.3.4.5 Nutrient Enrichment Case Study #2: Chesapeake Bay

Chesapeake Bay is the largest estuary in the United States and one of the most sensitive to N inputs (Bricker et al., 1999; Howarth, 2007). Eutrophication effects have been pronounced in Chesapeake Bay (Howarth, 2007) and it is perhaps the best known example in the United States of human activities leading to accelerated estuarine eutrophication and its associated negative effects. In the recent national assessment of eutrophic conditions in estuaries, the Chesapeake Bay stands out as a system with both physical features and N loading levels that make it particularly vulnerable to eutrophication (Bricker et al., 2007).

The role of atmospheric N deposition in estuary eutrophication in the United States was ignored until Fisher and Oppenheimer (1991) suggested that it could constitute up to 40% of the total N inputs to the Chesapeake Bay. Although their analysis was preliminary, and has been updated by more conservative estimates (e.g., Boyer et al., 2002; Boyer and Howarth, 2002), it served to focus attention on the role of atmospheric deposition as an important contributor to the overall budget of estuaries in the eastern United States. N inputs to the Chesapeake Bay have increased substantially over the last 50 to 100 years. The increase is attributed to rapid acceleration of the use of chemical fertilizers in agriculture, the increasing human population density and associated wastewater discharge, and rising atmospheric N emissions within the airshed and consequent deposition within the Chesapeake Bay watershed. Atmospheric deposition of N is currently estimated to contribute about one-fourth of the total N loading to Chesapeake Bay (Boyer et al. 2002; Howarth, 2007).

Human activities have increased the susceptibility of the Chesapeake Bay to the effects of atmospheric N deposition. For example, the filling in of wetlands and deforestation for agricultural and urban development, have reduced the ability of natural ecosystem processes to remove or trap nutrients, thereby further accelerating nutrient delivery to the bay. In addition, diseases and over-harvesting led to a dramatic decline of the once highly abundant eastern oyster, seriously reducing the natural filtering of algae and other organic matter from the water column.

As a result of these changing conditions, eutrophic symptoms intensified in the Chesapeake Bay from the mid-1950s to the mid-1980s. The most apparent symptoms were (1) high production of algae, (2) increasingly turbid water, (3) major declines in SAV abundance and species, and (4) increasingly worsening anoxia and hypoxia (Boesch et al., 2001). The recent national estuary condition assessment (Bricker et al., 2007) reported that chlorophyll *a*, dissolved oxygen, nuisance/toxic algal blooms, and SAV rated "high" in Chesapeake Bay in terms of severity of effects associated with eutrophication. In addition, macroalgae and toxic algal bloom conditions have worsened since the previous national assessment in 1999 (Bricker et al., 1999, 2007).

Concentrations of chlorophyll *a* in the surface mixed layer have increased tenfold in the seaward regions of the bay and one-and-one-half- to twofold elsewhere, paralleling estimates of increased loading of N and P to the bay since 1945 (Harding and Perry, 1997).

SAV began to decline as a result of nutrient enrichment during the mid-1960s, disappearing entirely from the Patuxent and lower Potomac Rivers. By 1980, many areas of the bay that once contained abundant SAV beds had none or only very small remnants left (Orth and Moore, 1984). Research indicated that the major driving factor in the decline of SAV was nutrient enrichment, which was causing excessive growth of algae in the water column and on SAV leaf blades (epiphytic algae). This algal growth decreased light availability to the submerged plants to the point that they could not survive (Kemp et al., 1983; Twilley et al., 1985).

There is an annual cycle of *oxygen depletion* in the Chesapeake Bay that begins as the water starts to warm in spring, and oxygen depletion accelerates during and following the spring freshet. The spring accumulation of algal biomass is more than sufficient to create conditions for oxygen depletion and summer anoxia (Malone, 1991, 1992). Hypoxia (very low dissolved oxygen concentration) and anoxia (absence of dissolved oxygen) generally occur from May through September, with the most severe conditions observed in mid-summer. Seasonal hypoxia has been a feature of the Chesapeake Bay since deforestation during the colonial period (Cooper and Brush, 1991; Malone, 1991), but evidence suggests an increase in the extent of the problem in recent decades (Officer et al., 1984; Malone, 1991). Estuarine eutrophication is sometimes accompanied by increases in the populations of species of algae, often cyanobacteria that produce toxins. Such chemicals can affect people, fish, shellfish, and other organisms. Blooms of algae that produce toxins in Chesapeake Bay have become more extensive over approximately the past decade (Bricker et al., 2007).

In 1983, EPA, District of Columbia, and states of Virginia, Maryland, and Pennsylvania signed the first Chesapeake Bay Agreement, which established the Chesapeake Bay Program—a voluntary government partnership that directs and manages bay cleanup efforts. Scientific findings from the program led to the signing of the second Chesapeake Bay Agreement in 1987, in which it was agreed to reduce by 40% the N and P entering the Chesapeake Bay by the year 2000. Point source reductions have been most successful, especially for P. Between 1985 and 1996, P point sources were reduced by 58% and N by 15%. Nonpoint source reductions have been slower, largely because nonpoint sources of nutrients are more difficult to control. Nonpoint sources of N and P have been reduced by only 7% and 9%, respectively (Boesch et al., 2001). Effective reduction of nonpoint source nutrients will require such changes as adoption of better agricultural practices, reduction of atmospheric N deposition, enhancement of wetlands and other nutrient sinks, and control of urban sprawl.

4.4 OTHER WELFARE EFFECTS

4.4.1 Nonacidification Effects of Sulfur

As discussed in Section 4.2, a number of environmental effects are associated with S deposition, in particular, soil and water acidification. However, S deposition also contributes to nutrient enrichment, toxicity, and secondary effects on the cycling and bioavailability of Hg, a highly neurotoxic contaminant. High concentrations of SO_2 can harm vegetation by causing foliar injury, decreasing plant growth, and eliminating sensitive plant species, although atmospheric concentrations of SO_2 are seldom high enough to cause these effects on vegetation at ambient air pollution levels in the United States. The biogeochemical cycling of S is closely linked with the cycling of other important elements, including C, N, P, Al, and Hg. Therefore, S deposition can influence the cycling of these elements in ways that influence nutrient availability or contaminant toxicity. In particular, current research suggests that S deposition influences the cycling of Hg in transitional and aquatic ecosystems by stimulating SO_4^+-reducing bacteria, which are also associated with Hg methylation, a key process that increases the bioavailability of Hg.

4.4.1.1 Biological Role of Sulfur

S is an essential plant nutrient. Low dosages of S serve as a fertilizer, particularly for plants growing in S-deficient soil (Hogan et al., 1998). A certain level of foliar SO_4^+ is likely necessary for adequate S nutrition (Johnson and Mitchell, 1998), and S deficiency has been shown to occur at foliar SO_4^+ levels below 80 µg/g (Turner and Lambert, 1980). Nevertheless, the annual increment of S in vegetation is usually small compared to atmospheric deposition and leaching fluxes. Plants require similar levels of S and P, but S is generally available in much higher concentrations in soil. Storage of S in vegetation is of minor significance in the retention or loss of S in most forests (Mitchell et al., 1992; Johnson and Mitchell, 1998).

Current levels of S deposition throughout much of the United States exceed the capacity of most plant communities to immobilize the deposited S (Johnson, 1984; Lindberg, 1992). There are few field demonstrations of foliar SO_4^+ uptake (Krupa and Legge, 1986, 1998; U.S. Environmental Protection Agency, 2004). Rather, SO_4^+ in throughfall is often enriched above levels in precipitation. The relative importance to this enrichment of foliar leachate versus prior dry-deposited SO_4^+ particles is difficult to quantify (Cape et al., 1992).

S is a major component of plant proteins and, as such, is an essential plant nutrient. The most important source of S to vegetation is SO_4^+, which is taken up from the soil by plant roots (Marschner, 1995). The major factor controlling the movement of S from the soil into vegetation is the rate of release through microbial decomposition of S from organic to inorganic forms (May et al., 1972; U.S. Environmental Protection Agency, 1982c, 1993a; Marschner, 1995). S also plays a critical role in agriculture, and is an essential component of fertilizers used to increase food production (Ceccotti and Messick, 1997).

Atmospheric deposition is an important component of the S cycle. This is true not only in polluted areas where atmospheric deposition is very high, but also in areas of low S deposition. Biochemical relationships between S and N are involved in plant protein synthesis and metabolism. S deficiency reduces NO_3^- reductase and glutamine synthetase activity. N uptake in forests, therefore, could be loosely regulated by S availability, but SO_4^+ additions in excess of needs do not necessarily lead to injury (Turner and Lambert, 1980; Hogan et al., 1998).

S deficiency in forest soil is rare, but has been reported in remote areas that receive very low levels of atmospheric S deposition and that have inherently low S levels in soil (Turner et al., 1977, 1991). In such cases, atmospheric S deposition might be taken up by vegetation, with little SO_4^+ leaching. Within areas of the United States influenced by acidic deposition, this is not expected to be a common phenomenon. To some extent, plant uptake of S is determined by the availability of N. This is because most S in plant tissue is in protein form, with a specific S:N ratio (Turner et al., 1977, 1991; Johnson et al., 1982b).

S deposition can have direct effects on plants via nutrient enrichment pathways. S is an essential nutrient for protein synthesis in plants. Adequate S supply for sustaining plant health is 0.01 to 0.05% in soils (Nriagu, 1978). SO_4^+ is the dominant form of bioavailable S in soils. Plants can also utilize volatile S compounds such as SO_2 in the atmosphere to fulfill nutrient requirements (Rennenberg, 1984). This S is directly available for diffusive uptake through the leaf surface to support plant growth (Jager and Klein, 1980), and can also become bioavailable in the soil for plant root uptake (Moss, 1978).

With the discovery of S deficiencies in some unpolluted regions (Kelly and Lambert, 1972; Humphreys et al., 1975; Turner et al., 1977; Schnug, 1997) and excesses associated with acidic deposition in other regions (Shriner and Henderson, 1978; Meiwes and Khanna, 1981; Johnson et al., 1982a), interest in S nutrition and cycling in forests has heightened (U.S. Environmental Protection Agency, 2004). General reviews of S cycling in forests were written by Turner and Lambert (1980), Johnson (1984), Mitchell et al. (1992), and Hogan et al. (1998). The influence of atmospheric deposition on the S cycle was summarized by Johnson and Mitchell (1998).

4.4.1.2 Role of Sulfur in Methylation of Mercury

A key step in the entrance of Hg into the food chain is methylation, which converts inorganic Hg to organic compounds of Hg which are highly bioavailable and can accumulate in fish tissue. Methylation rates are influenced by oxygen content, temperature, pH, and the concentration of organic acids in solution (Nagase et al., 1982; Xun et al., 1987; Winfrey and Rudd, 1990; U.S. Environmental Protection Agency, 1996). The EPA's Science Advisory Board concluded that there is a large degree of scientific uncertainty and variability among water bodies concerning the processes that methylate Hg (U.S. Environmental Protection Agency, 1996). Experimental observations show that when SO_4^+ is added to wetlands or lakes, SO_4^+ reduction is enhanced, leading to increased methylation and CH_3Hg^+ export, at least up to a point (Branfireun et al., 1999; Benoit et al., 2003; Watras et al., 2006).

Methylating bacteria convert inorganic Hg (often Hg^{2+}) into CH_3Hg^+, which is the form that bioaccumulates in fish and other biota. SO_4^+ provides the necessary terminal electron acceptor for methylating bacteria (Gilmour et al., 1992). Many studies have also illustrated an association between low lake water pH and high Hg concentrations in fish (Grieb et al., 1990; Suns and Hitchin, 1990; Driscoll et al., 1994; Kamman et al., 2004). Hrabik and Watras (2002) found that decreases in fish Hg concentration in an experimentally de-acidified lake basin exceeded those in the reference lake basin by a factor of two over a 6-year period of experimental de-acidification. On the other hand, in a study of over 600 randomly selected streams and rivers throughout the western United States, Peterson et al. (2007) found little relationship between fish tissue Hg concentrations and surface water pH, SO_4^+, or dissolved OC. They attributed the lack of a chemical relationship to the fact that low pH (<7) and high dissolved OC systems were rare in the West. The major factors controlling fish tissue Hg concentrations in western streams and rivers were fish size and feeding group, not water chemistry. In comparing CH_3Hg^+ levels in fish, it is necessary to control for differences in fish size and trophic position because highest CH_3Hg^+ concentrations are found in large piscivorous fish.

4.4.1.2.1 Conditions Conducive to Mercury Methylation

Hg in fish muscle tissue occurs mainly as CH_3Hg^+ (MeHg), (Bloom, 1992; Harris et al., 2003). Hg methylation is largely attributed to SO_4^+-reducing bacteria, which are commonly found in anoxic wetland and lake bottom sediments (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Gilmour et al., 1992). Under increased S load, there are increases in the numbers and activity of SO_4^+-reducing bacteria. The mechanisms for Hg methylation, as mediated by SO_4^+-reducing bacteria, have been discussed by Choi et al. (1994), Ekstrom et al. (2003), and Ekstrom and Morel (2004). Abiotic mechanisms responsible for Hg methylation also exist (Weber, 1993; Hintelmann and Evans, 1997; Siciliano et al., 2005), but have not been shown to be important.

Wetland environments have been shown to be significant areas of CH_3Hg^+ production and sources of export to downstream receiving waters (St. Louis et al., 1994). Experimental wetland studies have found that SO_4^+ addition can increase SO_4^+-reducing bacteria activity and cause increased CH_3Hg^+ production (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006). For example, SO_4^+ additions of both 2.8 kg/ha and 28 kg/ha to a nutrient-poor fen peatland in Ontario, Canada showed enhanced pore water CH_3Hg^+ production (Branfireun et al., 1999). Gilmour et al. (1992) found increased CH_3Hg^+ production within anoxic sediments of a reservoir located in central Massachusetts in response to SO_4^+ addition in both experimental laboratory slurries and intact sediment cores. Gilmour et al. (1992) also showed that CH_3Hg^+ production was substantially reduced with addition of a known SO_4^+-reducing bacteria inhibitor (Na_2MoO_4). These results are in agreement with observations of Hg methylation mediated by SO_4^+-reducing bacteria in salt marsh sediments (Compeau and Bartha, 1985). SO_4^+ addition has also been observed to enhance Hg methylation in freshwater wetland sediments (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006).

Wetland CH_3Hg^+ production has been measured at rates 26 to 79 times higher than in upland areas of a Canadian boreal forest (wetland: 1.84 to 5.55 mg ha^{-1} yr^{-1}; upland: 0.07 mg ha^{-1} yr^{-1}) (St. Louis et al., 1994). Watersheds containing 14.0% to 16.3% wetland yielded 5 to 14 times more CH_3Hg^+ than upland catchments that lacked wetlands (St. Louis et al., 1994). In the same region, St. Louis et al. (1996) found that all watersheds were net sinks for total Hg, but that watersheds containing wetlands regularly exported CH_3Hg^+ (St. Louis et al., 1996). However, CH_3Hg^+ export from these watersheds was not directly proportional to percent wetland coverage, indicating that other variables are also involved in the major processes that regulate CH_3Hg^+ production and export. In particular, the level of atmospheric Hg deposition and the acid-base chemistry of drainage water may be important.

Branfireun et al. (1996) measured highest peat and pore water CH_3Hg^+ concentrations in wetland areas that exhibited characteristics of a poor fen environment (i.e., interaction with nutrient-poor ground water). St. Louis et al. (1996) observed that high water yield resulted in high CH_3Hg^+ export. Thus, the proportion of upland to wetland land area within a watershed was not the only control on CH_3Hg^+ export, but wetland type and annual water yield also played important roles (St. Louis et al., 1996).

Hg methylation occurs in anoxic sediments that contain a sufficient C source to support SO_4^+-reducing bacterial activity along with an adequate supply of SO_4^+ for SO_4^+-reducing bacteria-mediated SO_4^+ reduction. These conditions are found in lake and pond bottom sediments (Gilmour et al., 1992), freshwater wetland sediments (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006), and salt mash sediments (Compeau and Bartha, 1985). Hg must also be present and bioavailable to SO_4^+-reducing bacteria for methylation to occur (Benoit et al., 1999). Microbial SO_4^+ reduction can further enhance the reducing conditions in sediments and bottom waters via the production of sulfide. These wetland systems that are likely to exhibit high levels of Hg methylation can be found throughout the United States.

Several studies have shown a strong negative correlation between surface water pH and Hg concentration in fish tissue, but the mechanisms responsible for this linkage are not clear. Hg concentrations in fish have also been shown to be less strongly correlated with a variety of other variables, including dissolved inorganic carbon (IC), Ca, Mg, dissolved OC, Na, lake area, and watershed area (U.S. Environmental Protection Agency, 1996).

Driscoll et al. (2007b) developed indicators of Hg sensitivity using two stratified, random-probability surveys of northeastern lakes combined with the survey data sets of Chen et al. (2005). This analysis showed that lakes with Hg levels above the EPA criterion of 0.3 µg/g in yellow perch had significantly higher dissolved OC, and lower pH, ANC, and total P than lakes with fish Hg concentrations below 0.3 µg/g (Driscoll et al., 2007b). Based on the probability surveys, they calculated that about 20% of lakes in the region had total P concentrations above 30 µg/L and yellow perch Hg concentrations below 0.3 µg/g. In the remaining 80% of lakes, 75% had yellow perch Hg concentrations exceeding 0.3 µg/g when surface water dissolved OC levels exceeded 4.0 mg C/L, a pH of less than 6.0, or an ANC of less than 100 µeq/L.

Most Hg in the water column of freshwaters is bound to organic matter, either to dissolved OC or to suspended particulate matter. Therefore, total Hg and CH_3Hg^+ concentrations are often positively correlated with dissolved OC in lake waters (Mierle and Ingram, 1991; Driscoll et al., 1994; U.S. Environmental Protection Agency, 1996). Dissolved OC, in turn, has an important influence on pH. Thus, several interrelated factors also seem to be related to Hg contamination. For example, Driscoll et al. (1995) found one or more yellow perch exceeding the 0.5 µg/g action level in 14 of 16 Adirondack study lakes despite wide ranges in pH (to above 7) and ANC (to above 200 µeq/L) (Mierle, 1990).

Several researchers have suggested that the export of Hg from terrestrial watersheds to lakes may be controlled in large part by the nature of watershed soils and the movement of naturally occurring organic acids (Mierle, 1990; Meili, 1991; Mierle and Ingram, 1991;

Engstrom et al., 1994). This suggestion is based partly on the fact that dissolved organic matter strongly binds with Hg and partly on the observed positive correlation between Hg accumulation in lake sediments and the ratio of the watershed area to the lake area in relatively undisturbed watersheds ($r^2 = 0.91$; $r^2 = 0.91$) (Engstrom et al., 1994). Engstrom et al. (1994) concluded that Hg export from the terrestrial watershed to lake water may be explained by factors regulating the export of fulvic and humic matter and by watershed area. They based this conclusion on the close correlation between Hg concentration and humic matter in surface waters, the observation that peak concentrations of both Hg and dissolved organic matter tend to occur during periods of high runoff, and the experimental determination that Hg transport occurs primarily in upper soil horizons.

Driscoll et al. (1994) concluded that the most obvious factor regulating the concentration and availability of both total Hg and CH_3Hg^+ in Adirondack lakes is dissolved OC. Driscoll et al. (1994) found increased fish Hg concentrations with increasing dissolved OC up to dissolved OC concentrations of about 8 mg/L, followed by lower concentrations in the highly distrophic Rock Pond (dissolved OC = 26 mg/L). They hypothesized that dissolved OC may bind with CH_3Hg^+ at very high dissolved OC concentration, limiting the bioavailability of the Hg.

In addition, calculations made by Driscoll et al. (1995) with the Hg Cycling Model suggested that increases in dissolved OC result in increasing concentrations of Hg in biota but decreases in the bioconcentration factor of Hg in fish tissue. Because the transport of Hg to Adirondack lakes appeared to be linked to dissolved OC production from wetlands within the watersheds of the study lakes, Driscoll et al. (1995) concluded that dissolved OC is important in regulating Hg concentrations in the lakes, and ultimately the supply to fish.

In a recent study of biological Hg hotspots in the northeastern United States and southeastern Canada, Evers et al. (2007) analyzed more than 7,300 observations of Hg levels in seven species in three major taxonomic groups to quantify the spatial heterogeneity in tissue Hg concentrations. Using published effect thresholds for Hg tissue concentrations, they identified five known and nine possible biological Hg hotspots. They reported that two of the biological hotspots, located in the Adirondack Mountains of New York and south-central Nova Scotia, occur in areas with relatively low to moderate atmospheric Hg deposition and high landscape sensitivity, as determined by the abundant forest and wetland cover as well as the acidic surface water conditions (Evers et al., 2007).

4.4.1.2.2 Effects of Mercury Methylation

A variety of biological effects can result from S deposition, in addition to the acidification effects discussed in Section 4.2. In particular, the enhanced methylation (and consequent enhanced bioavailability) of Hg that occurs in response to S addition can have adverse effects on fish and on species that consume large quantities of fish. CH_3Hg^+ is a potent neurotoxin to piscivorous mammals and birds (Scheuhammer et al., 2007). Thus, enhanced bioavailability of Hg poses a public health risk to people who consume fish. Hg bioaccumulates at higher trophic levels, and therefore fish-eating wildlife can be affected. Piscivorous birds generally have higher tissue Hg concentrations than non-piscivorous birds (Boening, 2000).

A range of effects has been demonstrated, including behavioral, reproductive, neurochemical, and hormonal effects (Scheuhammer et al., 2007). Exposure of fish and wildlife to Hg occurs primarily through the diet. Top predatory, especially piscivorous, animals feeding on aquatic food chains are at greatest risk for Hg accumulation and toxicity (Scheuhammer et al., 2007). Wildlife living in inland lake habitats tends to accumulate higher tissue concentrations of Hg than those living in coastal habitats (Frederick et al., 2002; Evers et al., 2005).

S deposition is most likely to result in enhanced Hg methylation in regions that receive relatively high levels of atmospheric Hg and S deposition and that exhibit characteristics conducive to methylation. These include low ANC and low pH surface waters, with large upstream or adjoining wetlands (Scheuhammer and Blancher, 1994; Wiener et al., 2003; Chen et al., 2005; Scheuhammer et al., 2007). Such sensitive ecosystems are prevalent in portions of the northeastern United States and southeastern Canada. Studies of Hg concentration in feathers, blood, and eggs of the common loon (Gavia immer) indicate decreasing concentrations from west to east in this region (Evers et al., 1998, 2003). This pattern is in general agreement with patterns of deposition of both Hg and S.

Available data suggest that numerous wild populations of fish, birds, and mammals experience CH_3Hg^+ exposures that are high enough to cause substantial reproductive, behavioral or health impairment. Reproduction is the component of response that appears to be most affected (Scheuhammer et al., 2007).

CH_3Hg^+ exposure can affect growth, reproductive ability, morphological characteristics, and feeding efficiency in fish. Friedman et al. (1996) investigated the effects of low-level (0.137 μg Hg/g) and high-level (0.987 μg Hg/g) dietary Hg concentrations (as CH_3Hg^+) on hatchery juvenile walleye (*Stizostedion vitreum*). These experimental Hg exposures were chosen to reflect dietary Hg concentrations commonly encountered in North American lakes and streams. Results showed impaired fish growth and impaired gonad development in males.

Fjeld et al. (1998) exposed grayling (*Thymallus thymallus*) embryos to varying concentrations of CH_3Hg^+ (0.16, 0.8, 4.0, and 20 μg Hg/L) during their first 10 days of development. This exposure resulted in body tissue CH_3Hg^+ concentrations of 0.09, 0.27, 0.63, and 3.80 μg Hg/g respectively. Morphological deformities were observed in fish exposed to the highest level of CH_3Hg^+. Samson and Shenker (2000) also observed morphological disturbance in zebrafish (*Danio rerio*) at embryonic CH_3Hg^+ exposure levels of 20 and 30 μg CH_3HgCl/L. Other fish such as mummichog (*Fundulus heteroclitus*) and rainbow trout (*Oncorhynchus mykiss*) have also been observed to have teratogenic effects such as cyclopia, tail flexures, cardiac malformations, jaw deformities, twinning, and axial coiling from embryonic CH_3Hg^+ exposure (Samson and Shenker, 2000).

Fish survival and subsequent population status can be jeopardized as a result of exposure to CH_3Hg^+. Fathead minnows (*Pimephales promelas*) showed impaired feeding efficiency after exposure to both 6.79 and 13.57 μg $HgCl_2$/L (Grippo and Heath, 2003). Reduced feeding efficiency and competitive ability was also observed in grayling exposed to 0.8 to 20 μg Hg/L as embryos (Fjeld et al., 1998).

4.4.1.3 Summary

The most important nonacidification effect of S deposition in areas of the United States that receive high levels of S deposition concern the influence of S supply on Hg methylation. The extent of methylation governs the bioavailability of Hg to biota. High concentrations of CH_3Hg^+ in fish can constitute an important health concern for people who consume large quantities of fish and can affect the health and reproduction of piscivorous wildlife, including the common loon, bald eagle (*Haliaeetus leucocephalus*), and river otter (*Lutra canadensis*). Hg methylation occurs mostly in wetland soils and bottom sediments of lakes and ponds. S deposition to these ecosystems can enhance S reduction and Hg methylation processes. Although S can also be directly toxic to terrestrial vegetation, levels of S in ambient air pollution and levels of S deposition commonly found in the United States are generally not high enough to cause substantial direct adverse effects on plants.

4.4.1.4 Sulfur Nutrient Enrichment Case Study: Interactive Effects of Sulfur and Mercury in Little Rock Lake, Wisconsin

Little Rock Lake is an 18-ha precipitation-dominated seepage lake located in a forested and undisturbed catchment of northcentral Wisconsin. The extensive experimental work conducted at Little Rock Lake was described by Hrabik and Watras (2002). The research at Little Rock Lake provides considerable insight into the interactions of S and Hg in the lake, and also bioaccumulation of Hg in fish in freshwater ecosystems.

In 1984, the lake was divided into two basins by placing an impermeable curtain across a narrow lake section. One of the basins was experimentally acidified from pH 6.1 to 4.7 by mixing H_2SO_4 into the surface water over a period of 6 years (Watras and Frost, 1989). The other basin was left undisturbed to serve as a reference. Beginning in 1990, the treated basin was left to de-acidify naturally.

Hg accumulation in yellow perch showed significant declines in fish in both the experimental and reference basins between 1994 and 2000, commensurate with declines in atmospheric deposition of Hg. Fish Hg concentrations in the experimental basin were 57% higher in 1994 than in 2000, whereas concentrations were 36% higher in the reference basin (Hrabik and Watras, 2002). The authors determined that half of the decrease in fish Hg concentration was attributable to lakewater de-acidification and the other half was associated with regional declines in atmospheric Hg deposition. In the reference basin, which had higher pH and exhibited a lower rate of de-acidification, 15% of the decrease in fish Hg concentration was due to de-acidification (Hrabik and Watras, 2002).

These findings were consistent with the hypothesis that SO_4^+ and newly added Hg synergistically contribute to enhanced bioaccumulation of Hg in fish. In subsequent analyses, Watras et al. (2006) found that maximum CH_3Hg^+ concentrations in hypolimnetic waters were directly correlated with the SO_4^+ deficit and they observed a correlation between CH_3Hg^+ and lakewater SO_4^+ concentrations. The tracking of external loads of Hg and S, and internal loads of Hg and CH_3Hg^+ suggested a tight biogeochemical connection among atmospheric deposition, SO_4^+ reduction, and Hg methylation. However, these relationships did not fully explain the observed large inter-annual variability in CH_3Hg^+ accumulation. The variability appeared to be influenced by OC, terrestrial runoff and temperature.

The results from the Little Rock Lake acidification experiment suggest that S deposition plays an important role in the accumulation and methylation of Hg in freshwater ecosystems, and that acid deposition and Hg deposition have a disproportionately larger effect together than either would have separately (Watras et al., 2006).

4.4.2 Direct Phytotoxic Effects of Gaseous Nitrogen and Sulfur on Vegetation

This section is intended to be a brief overview of the exposure and phytotoxic effects of gaseous N and S compounds on vegetation. This recognizes that the major focus of this review is the acidic and N deposition on to vegetation and ecosystems. However, direct effects of gaseous N and S could augment the effects of deposition on vegetation and there may be effects of gaseous N and S that may occur in some areas.

The effects of major gaseous pollutants such as SO_2, nitrogen dioxide (NO_2), and O_3 on vegetation have been studied since the 1950s and 1960s. Methodologies have been developed to study these effects in the lab, greenhouse, and in the field. The methodologies to study gaseous pollutants effects on vegetation have been recently reviewed in the O_3 AQCD (U.S. Environmental Protection Agency, 2006a). Readers are referred to the Section AX9.1 of the O_3 AQCD (U.S. Environmental Protection Agency, 2006a) and Section 9.2 in the 1993 NO_2 AQCD (U.S. Environmental Protection Agency, 1993a) for a thorough description of all the methodologies used to expose vegetation to gaseous pollutants.

Uptake of gaseous pollutants in a vascular plant canopy is a complex process involving adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants penetrate into leaves primarily in gaseous form through the stomata, although there is evidence for limited pathways via the cuticle. Pollutants must travel from the bulk air to the leaf boundary layer in order to get to the stomata. Although the movement of pollutants through a boundary layer into the stomata region is known to be important, and even rate limiting in many cases of low wind velocity, its description has been defined from aeronautical concepts and usually relates to smooth surfaces that are not typical of leaf-surface morphology; however, it is nearly the only treatment available (Gates, 1968). Once through the boundary layer, the gas must enter the leaf through the stomata. The entry of gases into a leaf is dependent upon the physical and chemical processes of gas phase and surfaces as well as the stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as humidity, temperature, and light intensity. When the stomata are closed, as occurs under dark or drought conditions, then resistance to gas uptake is very high and the plant has a very low degree of susceptibility to injury (Figure 4.4-1). The stomatal control of uptake of gaseous pollutants is described in more detail in AX9.2 of the O_3 AQCD (U.S. Environmental Protection Agency, 2006a) and Section 9.3.1.5 of the oxides of nitrogen AQCD (U.S. Environmental Protection Agency, 1993a). It should be noted that unlike higher plants, mosses and lichens do not have a protective cuticle barrier to gaseous pollutants, a major reason for their sensitivity to gaseous S and N.

4.4.2.1 Direct Phytotoxic Effects of SO_2 on Vegetation

It has been known since the early 1900s that exposure of plants to SO_2 can cause damage and death (Wislicenus, 1914). The large sources of SO_2 were ore smelters. Sulfides in the ore were oxidized during smelting and resulted in large releases of SO_2. Emissions from large ore smelters in the United States and Canada resulted in large areas denuded of vegetation surrounding these facilities (Swain 1949; Thomas 1951). Much of the damage to the vegetation was due to acute effects of high concentrations of SO_2. However, as early as 1923 researchers recognized that SO_2 might reduce plant growth without acute symptoms of foliar injury (Stoklasa 1923). In the 1950s through the early 1980s, there was much research on the effects of lower levels of SO_2 as well as the interaction with other pollutants such as O_3 and NO_2. Since then, there has been much less research on the effects of SO_2 on vegetation, especially in the United States, due to the decreasing ambient concentrations of SO_2. This section will briefly recap what is known about the effect of SO_2 on vegetation and summarize some of the limited recent literature.

Currently, SO_2 is the only Criteria Pollutant with a secondary NAAQS distinct from the primary standard. This standard is to protect acute foliar injury resulting from SO_2 exposure. The standard is a 3-h average of 0.50 ppm and was promulgated in 1970 to protect against acute foliar injury in vegetation. The last review of the SO_2 secondary standard was completed in 1982 and concluded that controlled experiments and field observations supported retaining this secondary standard (U.S. Environmental Protection Agency, 1982a,b). Acute foliar injury

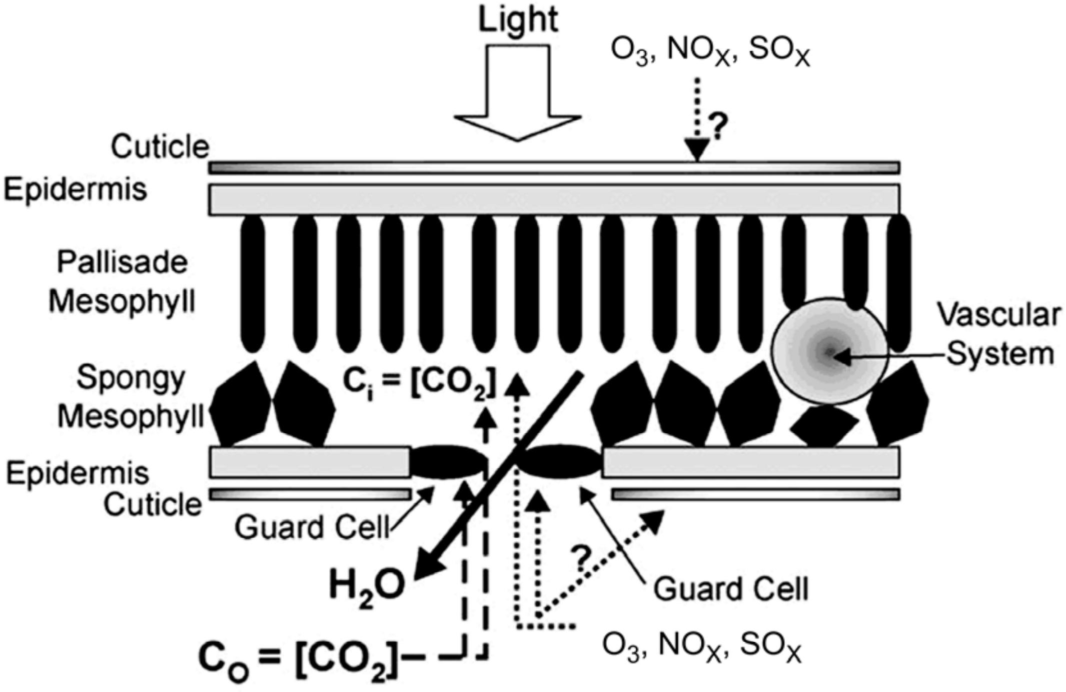


Figure 4.4-1. The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial leaf surface. CO_2, SO_X, NO_X, and O_3 gases generally enter through the stomata on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).

usually happens with hours of exposure, involves a rapid absorption of a toxic dose and involves collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and is usually a result of variable SO_2 exposures over the growing season. After entering the leaf, SO_2 is converted to sulfite and bisulfite, which may be oxidized to SO_4^+. SO_4^+ is about 30 times less toxic than sulfite and bisulfite. The conversion of sulfite and bisulfite to SO_4^+ results in net H^+ production in the cells. Kropff (1991) proposed that the appearance of SO_2-induced leaf injury was likely due to a disturbance of intracellular pH regulation. Kropff (1991) pointed out several studies that the pH of homogenates only shifted towards greater acidity when plants were lethally damaged from long-term SO_2 exposures (Grill 1971; Jager and Klein, 1977; Thomas et al., 1944). The appearance of foliar injury can vary significantly between species and growth conditions affecting stomatal conductance. Currently there is not regular monitoring for SO_2 foliar injury effects in the United States.

Besides foliar injury, long-term lower SO_2 concentrations can result in reduced photosynthesis, growth, and yield of plants. These effects are cumulative over the season and are often not associated with visible foliar injury. As with foliar injury, the effects of foliar injury vary among species and growing environment. The 1982 SO_2 AQCD summarized the concentration-response information available at the time (U.S. Environmental Protection Agency, 1982a). Effects on growth and yield of vegetation were associated with increased SO_2 exposure concentration and time of exposure. However, that document concluded that more definitive concentration-response studies needed before useable exposure metrics could be identified. Because of falling ambient SO_2 concentrations and focus on O_3 vegetation effects research, few studies have emerged to better inform a metric and levels of concern for effects of SO_2 growth and productivity of vegetation. Most research has been performed in areas of Europe where ambient SO_2 concentrations are generally higher than in the United States.

4.4.2.2 Direct Phytotoxic Effects of Gaseous NO_2 on Vegetation

4.4.2.2.1 NO and NO_2

It has been well known that in sufficient concentrations nitric oxide (NO) and NO_2 have the potential to have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (U.S. Environmental Protection Agency, 1993a). The 1993 NO_X AQCD concluded that concentrations of NO_2 or NO in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (U.S. Environmental Protection Agency, 1993a). Since the 1993 AQCD, very little new research has been done on these phytotoxic effects to alter this conclusion. However, it is known that these gases could be altering the N cycle in some ecosystems, especially in the western United States, and contributing N saturation (Fenn et al., 2003a; Bytnerowicz and Fenn, 1996). See Section 4.3 for a discussion of the nutrient effects of N.

In general, NO and NO_2 enters leaves through stomata (Saxe, 1986). However, it has also been shown that the leaf cuticle may be an important receptor for NO_2 and there is evidence of transport of NO and NO_2 across isolated cuticles (Lendzian and Kerstians, 1988). After entering the leaves, NO_2 dissolves in the extracellular water of the sub-stomatal cavity to form

HNO_2 and HNO_3, which then dissociate to form nitrite, NO_3^-, and protons (Bytnerowicz et al., 1998). Both cell and tonoplast membranes contain ATP-dependent H^+ pumps and the tonoplast pumps are strongly inhibited by NO_3^- (Bytnerowicz et al., 1998). If extra protons are deposited in vacuoles of the plant cells during normal cellular regulation, then additional acidity will occur in combination with additional NO_3^-. This combination can cause disruptions in cellular control (Taylor and MacLean, 1970). NO_3^- and nitrite are metabolized to amino acids and proteins through a series of enzymatic reactions mainly involving NO_3^- and nitrite reductases (Amundson and MacLean 1982). The effectiveness of plants to reduce NO_3^- and nitrite to amino acids and proteins determines the potential of the plant to detoxify NO and NO_2 (Wellburn, 1990). Reduction of NO_3^- takes place outside of the chloroplast while the reduction of nitrite is coupled with the light reactions of photosynthesis. Therefore, when leaves are exposed to NO and NO_2 in the dark, highly phytotoxic levels of nitrite accumulate and may lead to greater toxicity to NO and NO_2 at night (Amundson and MacLean, 1982). Exposure to NO produces both NO_3^- and nitrite in the leaves, but the rate of NO_3^- accumulation is much slower than nitrite. Thus, plants exposed to high NO could be at risk to elevated concentrations of nitrite (Wellburn, 1990). More detailed information on the cellular effects of NO and NO_2 can be found in the 1993 NO_X AQCD.

Necrotic lesions and excessive defoliation may occur as a result of accidental releases of NO or NO_2 from point sources during relatively short periods of exposure (MacLean et al., 1968). With the normal ranges of concentrations occurring in large U.S. cities, detrimental effects on long-term photosynthesis and growth of plants may have the potential to occur, but this effect has not been quantified or studied. Significant foliar injury due to exposure to NO or NO_2 is not expected to occur.

4.4.2.2.2 Peroxyacetyl Nitrate (PAN)

Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant, often co-occurring with O_3 during high photochemical episodes, which has been shown to cause injury to vegetation (See reviews by Cape, 2003, 1997; Kleindienst, 1994; Smidt, 1994; Temple and Taylor, 1983). Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species include spinach, Swiss chard, lettuces, and tomatoes. Petunias have also been characterized as sensitive to PAN exposures and have been used as bioindicators of in areas of Japan (Nouchi et al., 1984). Controlled experiments have also shown significant negative effects on the net photosynthesis and growth of petunia (*Petunia hybrida* L.) and kidney bean (*Phaseolus vulgaris* L.) after exposure of 30 ppbV of PAN for four hours on each of three alternate days (Izuta et al., 1993). As mentioned previously, it is known that oxides of N, including PAN, could be altering the N cycle in some ecosystems, especially in the western United States, and contributing N saturation (Fenn et al., 2003a; Bytnerowicz and Fenn, 1996). See Section 4.3 for a discussion of the nutrient effects of N. Although PAN continues to persist as an important component of photochemical pollutant episodes, there is little evidence in recent years suggesting that PAN poses a significant risk to vegetation in the United States.

4.4.3 N_2O as a GHG and Interactions between Nitrogen Deposition and Biogenic N_2O Emissions.

4.4.3.1 GHG

As discussed in Chapter 2, N_2O is a GHG with a global warming potential (GWP) on the conventional 100-year time horizon of ~296 (i.e., N_2O is nearly 300 times more effective for trapping heat in the atmosphere than CO_2 over a 100-year period (IPCC, 2007). The largest fraction of U.S. GHG emissions are from CO_2, followed by CH_4 and N_2O (83.3%, 7.4%, and 6.5% of total GHG emissions from the United States on a Tg CO_2 equivalents basis, respectively) in 2005 (U.S. Environmental Protection Agency Inventory, 2007a). GHGs force global climate change by trapping infrared radiation. A rigorous assessment of this process is provided by the Intergovernmental Panel on Climate Change (IPCC, 2007). It is important to note the process of climate change is projected to alter meterological patterns that include temperature extremes and patterns of precipitation, including the projected likelihood of extreme precipitation events. Changes in meteorological patterns are one factor associated with climate change that will alter ecosystems. In Annex 7, Table 7-1 provides a short-list of GHGs and the environmental factors indicated to change because of climate change. A comprehensive discussion of the adverse effects of climate change on ecosystems and other welfare effects in North America are assessed in chapter fourteen of the IPCC working group II assessment (Field et al., 2007).

In addition to directly and indirectly altering climate change, human activities may also affect the biogenic production of N_2O (e.g., anthropogenic N additions to ecosystem increasing the production of N_2O). The indications of a potential feedback between climate change, N deposition, and N_2O emissions are discussed below.

4.4.3.2 Interactions between Nitrogen Deposition and N_2O Production

Human activities can significantly enhance the natural processes that lead to N_2O formation. For example, the N nutrient loading in water bodies due to fertilization and run-off to streams can enhance N_2O emissions from these natural sources.

Terrestrial Ecosystems

Numerous studies that show that N_2O emissions from soils increase upon artificial N additions (Brumme and Beese, 1992; Matson et al., 1992; Klemedtsson et al., 1997; Papen et al., 2001). Regions with elevated atmospheric N-deposition due to anthropogenic activity also show 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 growth deciduous (40-60 year old) coniferous and successional grasslands that they stimulated by introducing an additional 1-3 g N m^{-2} yr^{-1} (0.84 g N m^{-2} yr^{-1} ambient). They compared the field results to a second experiment conducted in a laboratory setting that simulated the field conditions. The results indicate no change in N_2O emissions for conifer forest and grasslands. The deciduous forest studied showed increased N mineralization, suggesting the system was approaching N saturation. The additional lab study showed a significant and positive relationship between N deposition and N_2O efflux with N additions up to 10 g m^{-2} in both coniferous and deciduous forests (Ambus and Robertson, 2006). Investigation of N_2O emissions from a 145 yr old Beech tree stand in Stollig Germany that compared ambient N deposition (35 kg N ha^{-1} yr^{-1}) to elevated N deposition (145 kg N ha^{-1} yr^{-1}) indicated elevated N deposition stimulated annual N_2O emissions (5.6 to 7.8 kg N ha^{-1} yr^{-1}, respectively [Brumme and Beese, 1992]). Investigation of sites with similar species composition and climate across Europe, yet with differing rates of wet N deposition (measured as NH_4^+) showed a significant and positive correlations between increasing N deposition and increasing N_2O flux ($f(x) = 4.7 + 1.4x$, $r^2 = 0.38$, $P < 0.001$) (Butterbach-Bahl et al., 1998).

Other studies show N deposition to switch ecosystems from a sink to a source of biogenic N_2O. For example, a study of a mixed spruce, fir and pine stand (85-125 yrs old) showed the ecosystem was a sink on 7 of 9 sampling dates under ambient N deposition (10 kg N ha^{-1} yr^{-1}). However, the ecosystem was functioning as a source 6 of 9 sampling dates under elevated N deposition (150 kg ha^{-1} yr^{-1}). This switch in ecosystem function from sink to source was attributed to a stimulation of nitrification rather than denitrification (Papen et al., 2001).

Soil Moisture and Rainfall

Soil moisture plays an important role affecting N_2O production. A study of mixed spruce, pine and birch forest (100 yrs old) under well- and poorly drained soil moisture conditions indicated poorly drained soils produced 1/3 more N_2O (118 g N_2O^-N ha^{-1} yr^{-1}). When N deposition was increased in the poorly drained soil from ambient (12 kg N ha^{-1} yr^{-1}) to elevated (42 kg N ha^{-1} yr^{-1}), N_2O emissions increased by a factor of more than 2 (254 kg N ha^{-1} yr^{-1}) (Klemedtsson et al., 1997).

Rainfall events are an important feature controlling N_2O produced via denitrification. Rainfall inhibits oxygen diffusion into the soil creating anoxic conditions, which increases rates of denitrification. A study of a spruce forest under ambient and elevated N deposition (20 and 30 kg N ha^{-1} yr^{-1}, respectively) revealed through most of the study period N_2O emission was equivalent (Mohn et al., 2000). However, after rainfall events the maximum rate of N_2O emission was much higher for the +N plots, especially when rainfall caused low soil redox potential (an indicator of anoxic conditions).

Modeling under Climate Variations

The PnET-N-DNDC model is designed to simulate and predict soil C and N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N_2O and NO from forest soils. The model couples the PnET model (Photosynthesis-Evapotranspiartion-Model), the Denitrification-Decomposition (DNDC) model, and an N module that are further described in Li et al. (1992, 1996, 2000), Li (2000), and Stange et al. (2000). The capacity of this model to simulate N trace gas emissions from forest soils was tested by comparing model results with results form field measurements at 19 different field sites across Europe and 1 site in the United States (Kesik et al., 2005). Denitrification is described in the model as a series of sequential reductions driven by microorganism using N oxides as electron acceptors under anaerobic conditions. As intermediates of the processes, NO and N_2O are tightly controlled by the kinetics of each step in the sequential reactions. Possible feedbacks of temperature change on forest soil NO and N_2O emissions in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006). Interactions between temperature, precipiationa, and forest soil NO and N_2O emissions in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006), abiotic parameters are summarized in Table 4.4-1. The model results indicate areas with light texture soils (below 15%) that decreasing precipitation and increasing temperature resulted in decreased soil moisture values; in turn, soil aeration increased while N_2O production by denitrification decreases. Under these same environmental conditions, NO production by nitrification increases. Most laboratory studies show increasing Temp increases N_2O production, however if water filled pore space (WFPS) increases to 70-80% then N_2 rather than N_2O is the main product of denitrification and N_2O emissions go down.

4.4.4 Atmospheric Sources of NO_3^- in Drinking Water

High-quality potable water is an ecosystem services that may be impaired by atmospheric N pollution. Elevated NO_3^- levels in drinking water have been link to human health risks (Towsend et al., 2003). Elevated NO_3^- in stream and groundwater raise concerns about drinking water quality (Fenn et al., 1998). In regions of the United States such as southern California, NO_3^- concentrations in stream and groundwater from montane watersheds are the highest reported in North America, with concentrations reaching as much as 370 µeq/L (Fenn et al., 2003a). Furthermore, ground water is elevated in these areas (Towsend et al., 2003) and these watersheds serve as sources of drinking water for nearby urban areas. Similar situations may exist in other areas of the United States; however, there is little information available about the extent to which atmospheric N deposition contributes to NO_3^- levels in groundwaters used for drinking.

TABLE 4.2-1. EXAMPLES OF CHEMICAL INDICATORS OF EFFECTS FROM ACIDIC DEPOSITION ON TERRESTRIAL ECOSYSTEMS

Examples of Chemical Indicators	Example Possible Impact Threshold	References
Soil base saturation	10-20%	Lawrence et al. (2005) Driscoll et al. (2001) Cronan et al. (1990)
Soil solution Ca:Al ratio	1.0	Cronan and Grigal (1995)
Soil C:N ratio	20-25	Aber et al. (2003)

TABLE 4.2-2. EXAMPLE BIOLOGICAL EFFECTS INDICATORS IN TERRESTRIAL ECOSYSTEMS

Indicator Species	Example of Health Indices	References
Red spruce	Percent dieback of canopy trees	Shortle et al. (1997) DeHayes et al. (1999)
Sugar maple	Basal area dead sugar maple (as %) Crown vigor index Fine twig dieback	Bailey et al. (1999) Drohan and DeWalle (2002)

TABLE 4.2-3. EXAMPLES OF CHEMICAL INDICATORS OF EFFECTS FROM ACIDIC DEPOSITION ON AQUATIC ECOSYSTEMS

Chemical Indicator	Examples of Potential Thresholds	References
Surface water pH	5.0-6.0	Baker et al. (1990)
Surface water ANC	0-50 µeq/L	Bulger et al. (1999)
Inorganic Al	2-4 µmol/L	Wigington Jr. et al. (1996) Driscoll et al. (2001) Baldigo et al. (2007)

TABLE 4.2-4. 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

Results of Regional Survey					**Results of Monitoring during 1990s**			
Region	**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%
N. Appalachians	42,426 km	5,014 km	11.8%	1993-94	+0.7	3,600 km	8.5%	−28%
Ridge/Blue Ridge	32,687 km	1,634 km	5.0%	1987	−0.0	1,634 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 4.2-5. REGIONAL TREND RESULTS FOR LONG-TERM MONITORING LAKES AND STREAMS FOR THE PERIOD 1990 THROUGH 2000 (values are median slopes for the group of sites in each region)

Region	SO_4^{2-} (µeq/L/yr)	NO_3^- (µeq/L/yr)	Base Cations [Ca + Mg] (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

Source: Stoddard et al. (2003).

TABLE 4.2-6. 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 FISH SPECIES

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. (1990b).

TABLE 4.2-7. OBSERVED RELATIONSHIPS BETWEEN ZOOPLANKTON SPECIES RICHNESS AND LAKEWATER ANC IN THE ADIRONDACK MOUNTAINS

Taxonomic Group	Equation	r^2	p
Total zooplankton	Richness = 15.65 + 0.089 ANC	0.46	0.001
Crustaceans	Richness = 6.35 + 0.028 ANC	0.47	0.001
Rotifers	Richness = 9.04 + 0.053 ANC	0.30	0.001

Source: Sullivan et al. (2006b).

TABLE 4.2-8. STUDIES THAT EITHER DID (YES) OR DID NOT (NO) YIELD EVIDENCE THAT ACIDIC DEPOSITION AFFECTED CERTAIN SPECIES OF BIRDS

	Diet/ Foraging		Breeding Distribution		Reproductive Measures		
Species	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**	**Reference[a]**
Common loon	x		x	x	x	x	1-3, 22-24
Arctic loon						x	4
Common merganser			x		x		5, 22
Belted kingfisher			x				6
Osprey	x		x		x		7, 8
Black duck	x		x		x[b]		9-12
Common goldeneye			x[b]				5, 10
Ring-necked duck	x				x		13, 14
Eurasian dipper	x		x		x		15-17
Eastern kingbird				x	x		18
Tree swallow	x			x	x		19-21

[a] 1 = Alvo et al. (1988)
2 = Parker (1988)
3 = Wayland and McNicol (1990)
4 = Eriksson (1987)
5 = McNicol et al. (1987b)
6 = Goriup (1989)
7 = Eriksson (1983)
8 = Eriksson (1986)
9 = Hunter et al. (1986)
10 = DesGranges and Darveau (1985)
11 = Rattner et al. (1987)
12 = Harasmis and Chu (1987)
13,14 = McAuley and Longcore (1988a,b)
15,16 = Ormerod et al. (1985, 1986)
17 = Ormerod and Tyler (1987)
18 = Glooschenko et al. (1986)
19,20 = Blancher and McNicol (1988, 1991)
21 = St. Louis et al. (1990)
22 = Blancher and McNicol (1991)
23 = DesGranges and Houde (1989)
24 = Blair (1990)

[b] The effect was beneficial.

Source: Longcore and Gill (1993).

TABLE 4.2-9. 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	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.
	Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).
6.0 to 5.5	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.
	Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.
	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.
	Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.
5.5 to 5.0	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.
	Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.
	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.
	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.
	Inhibition of nitrification.

TABLE 4.2-9 (cont'd). GENERAL SUMMARY OF BIOLOGICAL CHANGES ANTICIPATED EITH SURFACE WATER ACIDIFICATION, EXPRESSED AS A DECREASE IN SURFACE WATER pH

pH Decrease	General Biological Effects
5.0 to 4.5	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). Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling. 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. Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans. Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.

Source: Baker et al. (1990a).

TABLE 4.3-1. ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION IN TERRESTRIAL ECOSYSTEMS 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
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	N 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, 2003c), Allen et al. (1998), Fenn and Poth (1999), Padgett and Allen (1999), Baron et al. (2000), Rueth and Baron (2002)
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), Fenn and Poth (2001)
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), Siguenza (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)
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.	Allen et al. (1998), Weiss (1999), Allen et al. (2007)
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.	McCune et al. (1998), Nash and Sigal (1999), Peterson and Neitlich (2001), Geiser and Neitlich (2007)
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), Service (2002), 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. (2007)
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), Fenn and Poth (2001)

TABLE 4.3-1 (cont'd). ECOLOGICAL EFFECTS OF NITROGEN DEPOSITION IN TERRESTRIAL ECOSYSTEMS 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
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)
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.	Kochy 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. (2003b), IMPROVE data, *http://vista.circa.colostate.edu/improve* (2003)
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; NO_3^-, nitrate; NO_X, nitrogen oxides; O_3, 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 4.3-2. OVERVIEW OF MOST SENSITIVE AND MOST AFFECTED ECOSYSTEMS TO N DEPOSITION

Ecosystem	Type	Factors that Govern Vulnerability
Terrestrial	Forest	• Receives relatively high levels of N deposition • Naturally adapted to very low nutrient supply • Experienced depletion of soil base cations associated with high levels of acidic deposition
	Grassland	• Sensitive to N enrichment
	Alpine	• Low rates of primary production • Short growing season • Low temperature • Wide variation in moisture availability
Transitional	Peat-forming bog	• Typically contain plants species that have evolved under N-limited conditions
	Coastal marsh	• Often receive large N inputs in tidal water, groundwater, and surface runoff; thus, atmospheric inputs are important because any N addition has the potential to contribute to eutrophication
	Wetland	• Typically contain plants species that have evolved under N-limited conditions; thus, N additions may lead to displacement of some species by others that can utilize the excess N more efficiently
Aquatic	Fresh waters	• Low productivity • Low nutrient levels • Located in remote areas and/or high elevations • Downwind of major urban and agricultural centers
	Estuarine and coastal waters	• Tend to be N-limited and are therefore inherently sensitive to increased N loading • The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates

TABLE 4.3-3. CHANGES IN AQUATIC ECOSYSTEMS ASSOCIATED WITH ELEVATED NITROGEN LOADINGS IN THE WESTERN UNITED STATES

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
Effects in Aquatic Systems				
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 littler information from low-elevation systems in the Sierra Nevada and elsewhere.	Williams et al. (1996b), Fenn and Poth (1999), Fenn et al. (2003a)
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. (2003)
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)

Source: Fenn et al. (2003a).

TABLE 4.4-1. PARAMETERS INCLUDED IN THE PnET-N-DNDC MODEL AS MODELED FOR EUROPEAN FOREST BY KESIK (2006)

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

5. FINDINGS AND CONCLUSIONS

5.1 INTRODUCTION

The previous chapters have presented the most policy-relevant science integrated across disciplines pertaining to sulfur and nitrogen oxides (SO_X and NO_X, respectively) and their ecological effects. The goal of this chapter is to summarize key findings and draw conclusions from this information in part to help inform decisions related to ecological exposure and risk assessment. This chapter has these sections: (1) this introduction, (2) atmospheric sciences, (3) emissions and exposures, (4) ecosystem acidification, (5) ecosystem nitrogen nutrification, and (6) other welfare effects.

In this review of information pertinent to an environmental welfare standard, multiple species of nitrogen and sulfur oxides were considered because of their complex multi-phase and multi-component roles in ecological systems. For example, details of the atmospheric chemistry of NO_X and SO_X would be incomplete with consideration only of gas-phase compounds; hence, descriptions of present-day ambient concentrations and deposition amounts related to the particulate forms of nitrogen (N) and sulfur (S) are given in Chapter 2 and supplemented in Annex 2. In this regard, the roles of other atmospheric pollutants, including mercury (Hg), ozone (O_3), ammonia (NH_3) and ammonium ion (NH_4^+), that interact with NO_X and SO_X to produce demonstrable welfare effects are also considered.

5.2 ATMOSPHERIC CHEMISTRY

5.2.1 Significant Chemical Species

- NO_X is the category label for oxides of nitrogen that includes a range of chemical species, chief among which are nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and peroxyacetyl nitrate (PAN) in the gas phase, and particulate nitrate (pNO_3) in the particle phase. Some of these species are directly emitted; others are formed as secondary products from the emitted species.
- SO_X is the category label for oxides of sulfur including sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and disulfur monoxide (S_2O), though only SO_2 is

present in concentrations relevant for atmospheric chemistry and ecological exposures.

  - Aqueous oxidation dominates production of sulfate ion (SO_4^{2-}) from SO_2; gas-phase oxidation is responsible for only ~20% of the SO_4^{2-} total. By contrast, there is little aqueous-phase oxidation of NO_2 to nitrate (NO_3^-) owing to its low solubility.
  - NH_3 and NH_4^+ (category label is NH_X) play significant roles in controlling SO_2 oxidation by neutralizing acidity on particles and in cloud, fog, and rain water, and in determining the range and extent of N deposition both in themselves as reduced N and through combining to form ammonium nitrate (NH_4NO_3).
  - Oxidation of NH_3 is a minor source of total NO_X.
  - Excess NH_3 is an actor alone and with NO_X in the N cascade leading to nitrification in aquatic and terrestrial ecosystems.
- Nitrous oxide (N_2O) is a constituent oxide of nitrogen having effectively no chemical or ecological effects in the troposphere, thus giving it an atmospheric lifetime of ~114 yr. N_2O is also a greenhouse gas (GHG) with a greenhouse warming potential (GWP) on the standard 100-year basis of ~296 times that of carbon dioxide (CO_2).
- Sea salt and other natural and anthropogenic particles provide surfaces for conversion of gas-phase N species to the particle phase, which can substantially alter the areal extent and magnitude of N deposition to the environment.

5.2.2 Field Sampling and Analysis

- Techniques for routine regulatory monitoring of gas-phase NO_X and SO_2 are adequate but have important limitations.
  - Routine NO_2 measurements by chemiluminescence (the Federal Register Method [FRM]) are contaminated by unknown and varying concentrations of higher-order oxidized N species (category label is NO_Z).
  - SO_2 measurements by the FRM in the standard regulatory network are now mostly at or below the instrument's operating limit of detection, producing irresolvable uncertainty in these data.

  - Routine field sampling techniques for NH_3 are at present limited to integrated values–from several days to one week–because higher frequency semi-continuous methods are not yet sufficiently robust to deploy in regulatory networks.
  - Routine regulatory sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are also subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the measurement.
- Despite the aforementioned limitations, for the purposes of identifying and quantifying the atmospheric concentrations and deposition totals causing ecological effects, these measurement techniques and sampling frequencies are fully adequate. Nevertheless, the coverage of the networks is very thin over large expanses of the interior United States.

5.3 EMISSIONS AND EXPOSURES

5.3.1 Emissions and Atmospheric Concentrations of NO_X and SO_X

- Policy-relevant background concentrations of NO_2 (i.e., concentrations calculated to exist without anthropogenic emissions from North America) are <300 parts per trillion (ppt) over most of the conterminous United States (CONUS) and <100 ppt in the eastern United States on an annual average basis.
- 24-h ambient NO_2 concentration in the consolidated metropolitan statistical areas (CMSAs) where most monitors are located were, on average, <20 parts per billion (ppb) with a 99%ile value <50 ppb for the years 2003–2005. Annual average NO_2 concentrations ([NO_2]) over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.
- Annual average policy-relevant background [SO_2] are <10 ppt over most of the CONUS, or <1% of observed [SO_2] everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.
- Energy production at electrical generating units (EGUs) accounts for nearly all SO_X emissions in the United States; very little SO_X is emitted by transportation-related and other sources. Ambient annual [SO_X] has decreased ~50% over the years 1990–2005.

- Combustion at stationary sources, such as electrical utilities and industrial sites, contribute roughly one-half of the total anthropogenic NO_X emissions; mobile source emissions make up most of the rest. Ambient annual [NO_X] has decreased <35% over the years 1990–2005.
- Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils. NO and N_2O can be emitted from soils as intermediate products from denitrification, either naturally; or as stimulated by addition of N-containing fertilizers to crops and other soil management practices.
- N_2O is a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2-equivalent basis in 2005, and its U.S. emissions decreased ~3% in the years 1990–2005, though there remains considerable interannual variation in this number.
- NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices.

5.3.2 Deposition of Nitrogen and Sulfur

- Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere.
- NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the United States and comprises ~50 to 75% of the total.
- Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes that are high in N, of which 30% to 70% may be emitted as NH_3. This increase in NH_3 emissions, and consequent increase in NH_4^+ deposition, correlates well with the local and regional increases in agricultural intensity.
- For 2004–2006, regulatory monitoring networks report the mean N deposition was greatest in the Ohio River valley, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg ha^{-1} yr^{-1}, respectively.
  - N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central United States, Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg ha^{-1} yr^{-1}, respectively.

  - Deposition primarily occurred as wet NO_3 and NH_4 followed by dry HNO_3, dry NH_4, and dry NO_3. Although deposition in most areas of the United States occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.
- For 2004–2006, mean S deposition in the United States was greatest east of the Mississippi River with the highest deposition amount (21.3 kg ha^{-1} yr^{-1}), in the Ohio River valley where most recording stations reported three-year averages >10 kg ha^{-1} yr^{-1}.
  - Numerous other stations in the East reported S deposition >5 kg ha^{-1} yr^{-1}.
  - Data are sparse for the central United States between the 100th meridian and the Mississippi River; but, where available, deposition values there are lower than most of the eastern United States, ranging from 4.1 to 5.3 kg ha^{-1} yr^{-1}.
  - Total S deposition in the United States west of the 100th meridian is relatively low, with all recording stations reporting less than 2 kg ha^{-1} yr^{-1} and many reporting less than 1.0 kg ha^{-1} yr^{-1}.
  - S was primarily deposited as wet SO_4 followed by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry SO_4.
- N from atmospheric deposition is estimated to comprise 10% to 40% of the total input of N to many coastal estuaries, and could be higher for some. Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape are then computed using measurements of wet and dry N deposition where these are available and interpolated with or without a set of air quality model predictions.
  - Direct atmospheric inputs (directly to the water surface) of reactive N to coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of external N loadings to these systems: 11, 5.6, and 5.6 kg N ha^{-1} for the northeast Atlantic coast of the United States, the southeast Atlantic coast of the United States, and the U.S. eastern Gulf of Mexico, respectively.
  - Atmospheric N loads to great waters and estuaries in the United States are estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the Catherines-Sapelo estuary (Castro et al. 2003) on the highest.

- At Chesapeake Bay, where N and S deposition and ecological effects have been extensively studied, total atmospheric deposition of atmospheric NO_3 is estimated to contribute from 20% to 30% of total N and 14% of the NH_4 loadings to the Bay.

5.4 ECOLOGICAL EFFECTS OF ACIDIFICATION

Oxides of nitrogen and sulfur act in tandem to cause acidification of ecosystems. The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is geology. Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been used in numerous acidification studies (e.g., Bricker and Rice, 1989; Stauffer, 1990; Stauffer and Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007a). Other factors contribute to the sensitivity of soils and surface waters to acidic deposition, including topography, soil chemistry, land use, and hydrologic flowpath. Vulnerability of ecosystems and regions to acidification lies at the intersection between the inherent sensitivity and the atmospheric loading of NO_X and SO_X.

5.4.1 Terrestrial

In the 1982 Air Quality Criteria Document (AQCD) for SO_X, the foliar and root uptake pathways for sulfur oxides were understood, as well as the role of S as a plant nutrient. Though small amounts of SO_2 may be beneficial, it was understood that large amounts and high frequency of SO_2 exposure and S deposition can be detrimental in the long run. At that time, there were no documented observations or measurements of changes in natural terrestrial ecosystems that were directly attributed to acidic precipitation. However, the AQCD authors made it clear that this did not necessarily indicate that no change was occurring.

The 1993 NO_X AQCD indicated that there were very few documented cases in which excessive atmospheric N deposition was linked to soil acidification. The process of soil acidification was already well understood, whereby increased concentrations of NO_3^- or other mineral acid anions (e.g., SO_4^{2-} or Cl^-) in soil solution can lead to leaching of base cations from soil in order to maintain charge balance in solution. Since the preparation of these assessments, direct links between NO_X and SO_X deposition and many adverse affects associated with ecosystem loading have been reported.

5.4.1.2 Ecological Effects

5.4.1.2.1 Biogeochemistry and Chemical Effects

Soil acidification occurs in response to inputs of sulfuric acid (H_2SO_4) and nitric acid HNO_3; the effect can be neutralized by weathering or base cation exchange. Soil acidification is a natural process, but is often exacerbated by acidic deposition. Acidic deposition has been shown to be an important factor causing decreases in concentrations of exchangeable base cations in soils. The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidic deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

The nitrification process is mediated by autotrophic bacteria that derive energy by reducing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters.

There are three useful indicators of chemical changes and acidification effects on terrestrial ecosystems: soil base saturation, aluminum (Al) concentration in soil water, and soil carbon-to-nitrogen (C:N) ratio. In the United States, terrestrial effects of acidification are best described for forested ecosystems, with supplemental information on other plant communities, including shrubs and lichens. Grasslands are thought to be less sensitive to acidification than woodlands.

- Soil base saturation expresses the concentration of exchangeable bases as a percent of the total soil cation exchange capacity. Once base saturation decreases to a critical level (approximately 15-20% see Table 5.4-1), inputs of H_2SO_4 and HNO_3 are increasingly buffered by release of inorganic Al through cation exchange.
- Aluminum is toxic to tree roots. Plants affected by high Al concentrations in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially calcium (Ca) (Parker et al., 1989; see Table 5.4-1).

- The C:N ratio of soil indicates alterations to the nitrogen biogeochemical cycle. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils (see Table 5.4-1).

5.4.1.2.2 Biological Effects

Acidic deposition can affect terrestrial ecosystems by causing direct impacts on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum toxicity and decreased ability of plant roots to take up base cations. There are several indicators or indices of stress on terrestrial vegetation (see Table 4.2-2), including percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback.

Species Level

- Changes in soil chemistry (depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water) have contributed to high mortality rates and decreasing growth trends of red spruce trees (*Picea rubens*) in some areas of the East over the past three decades.
- Acidic deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple (*Acer saccharum*) trees that occur at higher elevation, in some portions of the eastern United States, on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils.
- Lichens and bryophytes are among the first components of the terrestrial ecosystem to be affected by acidic deposition. Effects of SO_2 on lichens include reduced photosynthesis and respiration, damage to the algal component of lichen, leakage of electrolytes, inhibition of N fixation, reduced potassium (K) absorption and structural changes.
- There are insufficient data to draw conclusions for other species

Community Level

- Species loss, and reduced biodiversity of forests, shrubs, and meadow plant communities may occur, but have not been clearly demonstrated in the United States.

5.4.1.2.3 Regional Trends

There has been no systematic national survey of terrestrial ecosystems to determine the extent and distribution of terrestrial ecosystem sensitivity to the effects of acidic deposition. However, one preliminary national evaluation estimated that approximately 15% of forest ecosystems in the United States exceed the estimated critical load of wet and dry deposition of S and N by more than 250 eq ha^{-1} yr^{-1}.

- Forest ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachians are considered to be the regions most sensitive to terrestrial acidification effects from acidic deposition. It is not known if terrestrial acidification effects in these areas are continuing to develop, or if some recovery is occurring in response to recent reductions in acidic deposition.

5.4.2 Aquatic

5.4.2.1 1982 SO_X and 1993 NO_X AQCD

The 1982 AQCD for SO_X (U.S. Environmental Protection Agency, 1982c) discussed the growing environmental concern about acidic deposition and its role in the acidification of aquatic ecosystems in the United States. As in the more recent 1993 AQCD for NO_X (U.S. Environmental Protection Agency, 1993a), chronic and episodic acidification were discussed and the most vulnerable regions were identified, including the Adirondack Mountains of New York. The following conclusions were drawn from the 1982 AQCD regarding significant changes that have occurred in aquatic ecosystems with increasing acidity, particularly as the pH drops below about 5.5. Changes in community structure occur at all levels in the food web. Bacterial decomposition is reduced, and fungi that feed on organic debris may become dominant in aquatic communities. Consequently, organic matter accumulates rapidly, tying up nutrients and limiting nutrient mineralization and cycling. Phytoplankton productivity may be reduced because of changes in nutrient cycling and increased acidity. Biomass and total productivity of benthic macroscopic plants and algae may increase, in part because of increased lake transparency. Species diversity and total numbers of species of aquatic plants and animals (especially invertebrates and fish) are reduced. Acid-tolerant species predominate.

The 1993 AQCD for oxides of nitrogen expanded our knowledge of the role of N deposition in the acidification of aquatic ecosystems. This was especially the case with respect to episodic acidification, which is far more common than chronic acidification and has been well documented for streams and lakes in the eastern United States. The most prominent examples exist in the Adirondack and Catskill Mountains of the Northeast as well as in the Great Smoky Mountains of the Southeast. Instances of episodic acidification were also reported in the western United States but to a much lesser extent than in the East.

5.4.2.2 Ecological Effects

The status of surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less buffering of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits lower pH and acid neutralizing capacity (ANC) during episodes than during baseflow conditions. One of the most significant impacts of acidic deposition on surface water chemistry is the short-term change in chemistry that is termed “episodic acidification.” Some streams may exhibit chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the eastern United States caused partly by acidic deposition and partly by natural processes.

5.4.2.2.1 Biogeochemical Effects

Surface water chemistry integrates the sum of upstream soil and water processes; and reflects the results of watershed-scale terrestrial effects of S and N deposition, including N saturation, forest decline, and soil acidification (Stoddard et al., 2003). In many cases, surface water chemistry indicates the adverse effects of acidification on the biotic species and communities found in fresh water ecosystems. Changes in surface water chemistry include concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and Ca, surface water pH, sum of base cations, ANC, and the base cation surplus.

Acidification effects on aquatic life are most commonly evaluated using either Al or pH as the primary chemical indicator. ANC is also used because it integrates overall acid status (although ANC does not relate directly to the health of biota). The utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

Sulfate, Nitrate, and Base Cations

Changes in water chemistry in response to acidic deposition typically include changes in sulfate, nitrate, and base cation concentrations. Each plays an important role in the acid-base chemistry of water, but none are directly toxic at levels commonly encountered in natural waters (see Table 5.4-2).

- Sulfate is the primary inorganic anion found in most acid sensitive waters. Continued decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in surface waters. However the rate of decrease in surface water sulfate concentrations may be delayed as accumulated S leaches from watershed soils in some regions of the country, especially the Blue Ridge.
- The importance of NO_3^- as an agent of acidification varies by region, but it is particularly important during periods of high hydrologic flow from soils to streams such as those that occur in snowmelt and rain runoff events. The relationship between atmospheric N deposition and surface water NO_3^- concentration is complex and involves the cycling of nitrogen and other elements in both terrestrial and aquatic ecosystem compartments. NO_3^- contributes to the acidity of many lakes and streams in the eastern United States, but there is no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in these surface waters (in contrast to observed responses for S deposition and SO_4^{2-} concentrations). This suggests that the time scales of N saturation may be longer than previously considered (e.g., centuries rather than decades). Nevertheless, long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely (Aber et al., 2003).
- Decreases in base cation concentrations in eastern U.S. surface waters over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-}

concentrations. Rates of decrease for base cations have been similar to those for SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is notable exception). Decreasing trends in base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

pH, Acid Neutralizing Capacity, and Aluminum

Changes in pH, ANC, and inorganic aluminum concentration accompany acidification of surface water. Low pH and high inorganic aluminum concentration can be directly toxic to aquatic biota (see Table 5.4-2).

- The pH of freshwater streams and lakes is a common metric used to link acidification to adverse effects on aquatic biota. Decreases in pH of one unit or more typically result in species loss of benthic invertebrates, plankton species, and fish. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a greater likelihood that more aquatic species could be lost without replacement, resulting in decreased richness and diversity. (See the following discussion on biota).
- ANC is a variable that reflects the difference between base cations and anions of strong acids in solution and is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidic deposition. Acidic waters are defined as those having ANC at or below zero. Waters with ANC of <50 μeq/L are considered “extremely acid sensitive” (Schindler, 1988) and are prone to episodic acidification in some regions (DeWalle et al., 1987; Eshleman, 1988. Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the eastern United States. Since about 1990 the ANC of many affected lakes and streams has shown some increase, but such increases have been relatively small. The number of acidic surface waters has decreased some areas of the Northeast, but not in the mid-Appalachian Mountains.
- Dissolved inorganic Al is an important chemical indicator of the effects of acidic deposition on surface water because it is toxic to aquatic life and generally does not

leach from soils in the absence of acidification. When pH values fall below approximately 5.5, inorganic Al generally becomes the greater health risk to biota. Limited data suggest that acid-sensitive regions of the northeastern United States have elevated inorganic Al concentrations induced by years of acidic deposition posing a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern United States during the last two decades in response to decreased levels of acidic deposition.

5.4.2.2.2 Biological Effects

Acidification affects aquatic biota at virtually all levels of the food web in acid sensitive aquatic ecosystems. Many species of phytoplankton, zooplankton, macroinvertebrates, and fish are sensitive to acidification. Few studies have been conducted on the effects of acidic deposition on higher trophic levels other than piscivorous birds. Acidification can result in the loss of acid-sensitive species, and more species are lost with higher degrees of acidification. Biological effects are linked to changes in water chemistry that include ANC, pH, and Al. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur over both long- and short-term time scales, with further effects on biologic systems. Short-term (hours or days) episodic changes in water chemistry can have the most serious biological effects, including reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions.

Species

- Logistic regression modeling showed that the occurrence of two piscivorous birds, common loons and common mergansers, are positively related to the pH of acid-sensitive lakes in the Algoma region of Ontario. Model estimates suggested that the number of lakes projected to be suitable for supporting breeding pairs and broods of these bird species increased with increasing lake pH.
- High levels of acidification (to pH values below 5) virtually eliminate all mayflies, crustaceans, and mollusks from French streams.

- In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.2 to 5.5.
- Twenty percent mortality of brook trout young-of-the year was documented during a 30-day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al., 2007). It was estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

Community

Community-level effects have been observed in the Adirondacks and Shenandoah National Park where taxonomic richness is lower in lakes and streams having low ANC and pH.

- Decreases in pH and increases in inorganic Al concentrations have diminished the species richness of plankton, invertebrates, and fish in acid-impacted surface waters.
- Invertebrate taxa that are most sensitive to acidification include mayflies, amphipods, snails, and clams.
- In the Adirondacks, a significant positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes. A number of synoptic surveys indicated suggested loss of species diversity and absence of several sensitive fish species in the pH range of 5.0 to 5.5.
- In Shenandoah National Park, the number of species of fish present in streams decreases with decreasing stream ANC. On average, richness is lower by one fish species for every 21 µeq/L decrease in ANC.
- Short-term episodes of acidity are particularly harmful to aquatic biota. Early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults. Episodes are most likely to affect biota if the water had pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. Episodic acidification can have long-term adverse effects on fish populations.

5.4.2.2.3 Regional Trends

The effects of acidifying deposition have been assessed by several national surveys since the 1980s, including: the National Surface Water Survey (NSWS) and the National Stream Survey (NSS) in the mid 1980s; the Wadeable Streams Assessment (WSA) in 2004; U.S.

Environmental Protection Agency (EPA)'s Long-Term Monitoring (LTM) program since 1983; and Temporally Integrated Monitoring of Ecosystems (TIME) probability surveys since 1991. These surveys indicate that acidic deposition has acidified surface waters in the (1) southwestern Adirondacks, (2) New England uplands, (3) low-silica eastern Upper Midwest, (4) forested Mid-Atlantic Highlands, and (5) Mid-Atlantic Coastal Plain.

The Northeast and mountainous West of the United States contain many of the surface waters most sensitive to potential acidification effects. Levels of acidic deposition in the West are low in most areas, acidic surface waters are rare, and the extent of *chronic* surface water acidification that has occurred to date has likely been very limited. Episodic acidification does occur. In both the West and the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. On average, spring ANC values of acid-sensitive surface waters in New England, the Adirondacks, and the northern Appalachian Plateau were about 30 µeq/L lower than summer values during the period 1990 to 2000. This implies that lakes and streams in these regions would need to recover to chronic ANC values above about 30 µeq/L or more before they could be expected not to experience acidic episodes (Stoddard et al., 2003).

It is important to address whether or not surface waters recovered chemically in response to reduced acidic deposition over the past few decades. The following section summarizes recent regional trends in acidification recovery.

- About one-quarter to one-third of the lakes and streams that were chronically acidic in the 1980s were no longer chronically acidic in the year 2000. These improvements in water chemistry are largely attributed to decreases in S deposition. Throughout the northeastern United States, the concentration of SO_4^{2-} in surface waters has decreased substantially in response to decreased emissions and atmospheric deposition of S. Decreased concentrations of SO_4^{2-} in lakes and streams of a third, or more, have been commonly observed.
- EPA's LTM and TIME projects suggest that the following important changes in lake and stream chemistry occurred during the 1990s in response to S and N emissions reductions: (1) SO_4^{2-} concentration decreased as a percentage of total ion concentration in surface waters, (2) ANC increased modestly in three of the five regions included in surface water LTM efforts, (3) Dissolved organic carbon (DOC)

and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidic deposition decreased, and (4) Inorganic, and potentially toxic, Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

- In 2004, the EPA conducted a national WSA survey and found that, overall, less than 1% of the 1,020,000 km of stream in the target population was acidic due to acidic deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams attributable to acidic deposition were found in the (1) Northern Appalachians (2.8% of 96,100 km of stream), and (2) the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0 to 25 µeq/L) streams likely exposed to episodic acidification were found in (1) the Northern Appalachians (2.7% of 96,100 km of stream), (2) the Coastal Plain (6.3% of 119,000 km), and (3) the Mountainous West (0.6% of 204,000 km).

5.4.3 Case Studies

5.4.3.1 Adirondacks

The Adirondack region is presented as a case study in this ISA to demonstrate a geographical region that continues to experience the adverse affects of acidification due to atmospheric deposition of NO_X and SO_X. This region is particularly sensitive to acidic deposition because it receives high precipitation, has shallow base-poor soils, and is underlain by igneous bedrock with low weathering rates and buffering capacity.

Hindcast modeling conducted for the Adirondack ecoregion using Paleocological Investigation of Recent Lake Acidification (PIRLA) diatom reconstructions, Model of Acidification of Groundwater in Catchments (MAGIC) model, and Photosynthesis and EvapoTranspiration-BioGeoChemical (PnET-BGC) model simulations are useful to understand changes to surface water chemistry over decadal time scales. . Maximum past acidification occurred by about 1980 or 1990, with median ANC of the lake population of about 61 µeq/L (reduced from a median of 92 µeq/L estimated for the preindustrial period). Many lakes were estimated to have had pre-industrial ANC below 50 µeq/L, but this estimate more than doubled by 1990. During the 1990s, ANC increased in Adirondack lakes at a rate of about

+1 µeq L^{-1} yr^{-1}. Surface water pH also increased, and inorganic Al concentrations declined slightly in many of the most acid-impacted. Overall improvements in lake water acid-base chemistry have been modest. Dynamic model simulations estimate a limited chemical recovery (3 to 5 µeq/L on average) and the ongoing trend of increasing lake water ANC for the most acid-sensitive Adirondack lakes would not continue under future emissions and deposition levels anticipated as of 2003 (modeled as a Base Case Scenario).

Many acidic surface waters in this region are currently characterized by high levels of inorganic Al (66% of 188 streams in 2004). Forecasting projections show that lower deposition levels would lead to either stabilization of the number of chronically acidic lakes or increasing levels of ANC and pH. In addition, a number of biological effects findings have been identified between 1984 and 1987:

- 76% of lakes had fish; 24% (346 lakes) were fishless.
- The most common fish caught were native acid-tolerant species: brown bullhead, brook trout, and white sucker.
- As pH decreases, fish richness also decreases and the number of fishless lakes increases.
- After accounting for other conditions that could explain the absence of fish, 32% of the fishless lakes, or 8% of all the lakes sampled were considered fishless due to the inputs of acids by acidic deposition.
- Mean yellow perch mercury (Hg) conditions in the Adirondack hotspot were 1.5 to 2.5 times higher than the EPA and U.S. Food and Drug Administration (FDA) reference dose used for fish consumption advisories, particularly due to the *combined effects of acidic deposition and Hg deposition.*

5.4.3.2 Shenandoah National Park, Virginia

Shenandoah National Park (SNP) in Virginia received relatively high deposition of S and N (and high O_3 concentrations). Measured wet S deposition ranged from 8 to 10 kg S ha^{-1} yr^{-1} (in the early 1980s) to near 6 kg S ha^{-1} yr^{-1} since 2000. Dry S deposition may be nearly as high as wet deposition (Sullivan et al., 2003). Most acidification effects in the park have been linked to S deposition. One third of SNP streams drain watersheds with silica (Si)-based underlying geology and consequently have low ANC. These streams have probably lost much of their natural ANC from the past century of acidifying deposition that came primarily from industrial sources. Stream pH is now as low as 5 in many streams, versus an estimated 6 for most streams prior to elevated deposition from human sources of air pollution.

High rates of atmospheric deposition of S, combined with naturally low contributions from some rock types of Ca and other base cations (that serve to neutralize acidity), are the most important causes of low stream water ANC in many park streams. In general, SNP streams do not show recent recovery from acidification despite reductions in deposition. In fact, many streams are expected to acidify more in the future unless deposition is further reduced. This is because: (1) S adsorption on soil has decreased due to the cumulative effects of long-term S deposition and (2) stored Ca and magnesium (Mg) is being depleted (due to acid deposition).

5.5 ECOLOGICAL EFFECTS OF NITROGEN NUTRIENT ENRICHMENT

Terrestrial ecosystems typically respond to total reactive N loading and, with few exceptions, have limited differential responses to the specific chemical species of deposited N. Nitrogen compounds that are contained in atmospheric deposition, and that influence nutrient dynamics, include both multiple oxidized and reduced forms of inorganic N. Excess N in ecosystems causes inadvertent fertilization of trees and grasslands, creating unnatural growth rates in some species and change in the competitive interactions among species, nutrient imbalances, and ultimately decreasing ecosystem health and biodiversity. Reactive nitrogen (N_r) can leach from the soil and pollute groundwater and surface water. Reactive nitrogen also promotes eutrophication in coastal ecosystems, ultimately reducing biodiversity due in part to depletion of oxygen needed for the survival of many species of aquatic plants and animals. The cascade of N effects in the environment is interrupted only when N_r is stored in inaccessible places or converted back to N_2 gas through denitrification. It is important to note that not all N_r is converted to unreactive N_2 in the process of denitrification; a portion is often converted to the intermediate products, NO and N_2O.

5.5.1 Terrestrial

The 1993 AQCD concluded that N deposition could have large impacts on terrestrial systems and the impact of N deposition should consider total N in the system rather than just the oxidized forms. Nitrogen deposited to an N-deficient ecosystem is generally expected to increase growth. If N is deposited on an ecosystem with adequate N or saturated with N, NO_3^- leaching is expected to occur. Much of the information presented in the 1993 AQCD was based on results from studies of forest systems. N saturation was known to be more common in older forests. Disturbances such as fire and harvesting would push ecosystems to a state of lower N saturation. Forest fertilization was known to produce growth increases in N-deficient forests in the short-term. However little was known about long-term effects of N fertilization and the differential growth effects on various tree and herbaceous plant species. It was known that plants do not necessarily benefit from added N. When N is to the point that it no longer limiting, deficiencies of other nutrients can occur (Aber et al., 1989). A few studies documented the deleterious affects of excessive N on tree growth and grassland biodiversity. Alpine ecosystems, were identified as particularly sensitive to N deposition. The studies published since the 1993 AQCD generally support the conclusions of the 1993 AQCD, provide more information on the long-term effects of N deposition, and expand the knowledge of effects to include more ecosystems and species.

5.5.1.2 Ecological Effects

Factors that govern the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation, rates and form of N deposition, elevation, species composition, length of growing season, and soil N retention capacity. Very little is known about the extent and distribution of the terrestrial ecosystems in the United States that are most sensitive to adverse impacts due to nutrient enrichment from atmospheric N deposition. Based largely on results obtained in more extensive studies in Europe, it is expected that the more sensitive ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and nutrient-poor grassland ecosystems. Effects are most likely where areas of relatively high atmospheric N deposition intersect with N-limited plant communities. Table 4.3-1 summarizes the ecological effects of N deposition on terrestrial ecosystems in the western United States where N effects are likely to be important and have been studied in recent years.

5.5.1.2.1 Biochemical Effects

Decades of atmospheric deposition of N have increased the availability of NO_3^- and NH_4^+ in some terrestrial ecosystems. It is important to note that N saturation does not need to occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation does occur to levels at which excess N availability results in net nitrification and associated NO_3^- leaching in drainage water. Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (See section 5.4.2) and deplete soils of nutrient base cations, especially Ca and Mg (Likens et al., 1998).

5.5.1.2.2 Biological Effects: Plant, Lichen, and Mycorrhizae Communities

Atmospheric inputs of N cause increased growth rates of some vascular and non-vascular plants species. Thus, N deposition can alter competitive relationships among species, which may alter species composition and diversity of plant communities. These kinds of species shifts and ecosystem changes can occur even if the ecosystem does not exhibit signs of N saturation. In general, the most sensitive forest ecosystems in the United States are expected to be those that are naturally adapted to very low nutrient supply.

Forest Plant Communities

This section includes both woody and herbaceous vascular plants that occur in forest ecosystems. In general forest ecosystems in the United States that are most impacted by nutrient enrichment from nitrogen deposition are expected to be those that now receive high levels of N deposition and that are naturally adapted to very low nutrient supply. Such forests are known to exist in the greater Los Angeles area. Nitrogen saturation has also been found to occur in the red spruce and northern hardwood forests of the northeastern United States, at high-elevation in the southeastern United States, and in the unglaciated regions of the mid-Atlantic that have been impacted by acidic deposition.

- In most upland forested areas in the United States, most N received in atmospheric deposition is retained in soil (Nadelhoffer et al., 1999). Several different data compilations indicate that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems that receive less than about 10 kg N ha^{-1} yr^{-1} (Dise and Wright, 1995; Sullivan, 2000; MacDonald et al., 2002; Aber et al., 2003; Kristensen et al., 2004).
- Two of the primary indicators of N enrichment in forested watersheds are the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season (Stoddard, 1994). The concentration of NO_3^- in

surface water provides an indication of the extent to which atmospherically deposited (or otherwise added) N leaches from the terrestrial ecosystem. In northeastern and some southeastern forests that receive atmospheric N deposition higher than about 10 kg ha^{-1} yr^{-1}, elevated concentrations of NO_3^- in surface waters are common (Aber et al., 2003), which suggests that their watersheds are also receiving excess N input above vegetative demand.

- Experimental N additions to forest ecosystems have elicited positive growth responses in some, but not all, species (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006).
- Forest growth enhancement can potentially exacerbate other nutrient deficiencies, such as Ca, Mg, or K, thereby causing problems with forest health.
- Enhanced growth generally occurs mainly above ground level. This can cause changes in the shoot-to-root ratio, which can be detrimental to the plant because of decreased resistance to environmental stressors, such as drought.
- In conifer forests, multiple long-term experiments have demonstrated transient growth increases (generally at deposition lower than 10 kg N ha^{-1} yr^{-1}) followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).
- In the western United States, atmospheric N deposition has been shown to cause increased litter accumulation and carbon storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires (Fenn et al., 2003a).
- N deposition could be increasing growth of forest trees slightly in some regions, especially in portions of the eastern United States where O_3 levels and drought occurrence are low.
- Negative effects on understory herbaceous communities of increasing N deposition include species shifts towards nitrophilous and more acid-tolerant plant species along a deposition gradient from 6 to 20 kg N ha^{-1} yr^{-1} in Swedish oak forests, decline in abundance and cover of ericaceous shrubs along a deposition gradient from less than 3 to more than 12 kg N ha^{-1} yr^{-1} in the boreal forest in Sweden, and decline in

herbaceous cover under hardwoods following 3 years of N additions applied as $(NH_4)_2SO_4$ at rates ranging from 14 to 28 kg N ha^{-1} yr^{-1} (Gilliam, 2006).

Grasslands

Grasslands communities that are adapted to low nutrient supply can exhibit substantial sensitivity to nutrient enrichment effects of N deposition. Several grassland studies have demonstrated that increased N availability led to an overall decrease in plant species richness and an increase in exotic nitrophilous grasses that displace native species.

- In the San Francisco Bay area of California, which receives N deposition levels of 10 to 15 kg N ha^{-1} yr^{-1}, exotic nitrophilous grasses have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system (Fenn et al., 2003a).
- Change in species composition and richness in response to N deposition have been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Stevens et al., 2004; Bobbink et al., 1992, 1998; Bobbink, 1998). Stevens et al. (2004) report a linear relationship between species diversity and N deposition.
- In general, data with which to quantify grassland sensitivity in the United States are largely not available. Nevertheless, it is expected that increased N supply can alter species composition, increase productivity, and contribute to increased herbivory (Tilman and Wedin, 1991; Wedin and Tilman, 1996; Stevens et al., 2004; Throop and Lerdau, 2004).

Arid and Semi-Arid Lands

Arid and semi-arid plant community changes resulting from experimental nitrogen fertilization have been reported in the Chihuahuan Desert, Colorado Plateau, Mojave Desert, Joshua Tree National Park in California, and the coastal sage shrub community of southern California.

- In semi-arid ecosystems, results from several N fertilization experiments showed (1) increased biomass of non-native plant species over native species, (2) decreased soil moisture under some conditions, and (3) increased fire risk where dense grasses replaced shrub cover. More than 30 kg N/ha/year of atmospheric nitrogen is deposited to this ecosystem in portions of the Los Angeles Air Basin (Bytnerowicz and Fenn, 1996).

- In the coastal sage shrub community of southern California, dry N deposition is very high. Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Eliason and Allen, 1997; Yoshida and Allen, 2001; Cione et al., 2002). The coastal sage shrub community in California has been declining in land area and in shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Allen et al., 1998; Padgett and Allen, 1999; Padgett et al., 1999). N deposition is considered a possible cause or contributor to this ecosystem alteration.
- Several lines of evidence suggest that N deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of ecosystem types. Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations. The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of shrub vegetation types to grassland in southern California.

Alpine Plant Communities

Alpine plant communities are considered among most sensitive terrestrial communities to nutrient-enrichment from atmospheric N deposition.

- Factors that govern the sensitivity of alpine tundra to N deposition include low rates of primary production, short growing season, low temperature, and wide variation in moisture availability in the alpine environment (Bowman and Fisk, 2001). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this also contributes to their N-sensitivity.
- The western United States contains extensive land areas that receive low levels of atmospheric N deposition, interspersed with hot spots of relatively higher N

deposition downwind of large metropolitan centers and agricultural areas. Some of these areas of higher nitrogen deposition occur at high elevation.

- Effects of N deposition on alpine ecosystems in the western United States are thought to include community-level changes in plants, lichens, and mycorrhizae. Subtle effects have been shown to occur at what would be considered relatively low levels of N deposition (about 3 to 5 kg N ha^{-1} yr^{-1}).
- N deposition to the alpine tundra of Niwot Ridge in the Colorado Front Range altered N cycling and provided the potential for replacement of some native plant species by more competitive, faster growing species.

Lichens

- Sensitive lichen species appear to be negatively affected by N inputs as low as 3 to 8 kg ha^{-1} yr^{-1} (Fenn et al., 2003a).
- In the San Bernardino Mountains, California, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared (Nash and Sigal, 1999; Fenn et al., 2003a).
- The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn et al., 2003a). In this area, lichen communities are beginning to show evidence of changes in response to increased N pollution, including decreased distribution of sensitive lichen taxa, and their replacement with nitrophilous species (Geiser and Neitlich, 2007).

Mycorrhizae

- Biodiversity impacts on microbial communities have been documented in coastal sage scrub ecosystems. It has been hypothesized that the decline in coastal sage shrub species could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and Allen, 2000).
- Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. Changes in soil N can influence mycorrhizal-plant relationships in the rhizosphere. Mycorrhizal fungal diversity has been shown to be associated with above-ground plant biodiversity and ecosystem

productivity (Wall and Moore, 1999) and to be adversely affected by increased N availability (Egerton-Warburton and Allen, 2000).

5.5.2 Transitional

Anaerobic conditions of water-logged soils in wetlands result in slow decomposition of organic matter and rapid denitrification. N cycles of two types of wetland, ombrotrophic bogs and coastal salt marshes, were discussed in 1993 AQCD for oxides of nitrogen. Ombrotrophic bogs are generally considered the most sensitive to atmospheric N deposition because they are nutrient poor, with a closed N cycle in which the predominant source of N is rainfall. The 1993 AQCD found that the three main ecological effects of N deposition on wetland ecosystem are: (1) increasing primary production; (2) modifying microbial processes; and (3) reducing biodiversity and altering ecosystem structure. The studies since 1993 support and extend the conclusions in the 1993 AQCD, especially with regard to the impacts of N deposition on species diversity.

5.5.2.2 Ecological Effects

5.5.2.2.1 Biochemical Effects

N dynamics in wetland ecosystems are variable in time and with type of wetland and environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren, 1994; Mitchell et al., 1996).

Wetlands and other transitional ecosystems can remove NO_3^- via denitrification. Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process increases the contribution of NO_2 and NO to the atmosphere, each of which can have adverse consequences. However, denitrification reduces NO_3^- levels in soils and leaching into drainage waters and associated environmental effects. Although denitrification has been observed to increase with N addition, N mineralization has also been shown to increase, and this can cause a net increase in wetland N export to adjacent surface water (Groffman, 1994). Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

5.5.2.2.2 Biological Effects

Ecosystem Function

- Primary production of transitional ecosystem is commonly limited by N availability. Typically, phosphorous is secondarily limiting after N. N fertilization experiments in salt marsh ecosystems show biomass stimulation from 6 to 413% with application rates ranging from 7 to 3120 kg N ha^{-1} yr^{-1}, and the change of plant production is not a linear function of the rate of N application (U.S. Environmental Protection Agency, 1993a).
- The form of N applied is shown to regulate plants and microbial responses in transitional ecosystem. NH_4^+ produces a greater stimulation of plant productivity than NO_3^- does because plants have a preference for NH_4^+ over NO_3^- as an N source. Increasing soil NH_4^+ concentration inhibits the activity of N-fixing bacteria, whereas increased NO_3^- concentration favors N_2O production and inhibits N_2 production via denitrification process.
- Elevated atmospheric N deposition stimulates leaf growth more than root growth and can cause changes in plant carbon allocation, such as increase plant shoot-to-root ratio. Increasing N availability can also increase N concentration in leaf tissues, which has been shown to increase microbial litter decomposition activity.
- Increases in biomass linked to N deposition, have also increased evapotranspiration (Howes, 1986). This changed the soil water balance of water and may influence the direction of plant community succession. Model results suggest 7 kg N ha^{-1} yr^{-1} is the threshold in which an oligotrophic bog would be influenced to become a mesotrophic bog dominated by trees (conclusion from 1993 NO_X AQCD).

Species and Community-Level

- Wetlands considered sensitive to nitrogen deposition typically contain plant species that have evolved under nitrogen-limited conditions.

- Wetlands contain a disproportionately high number of rare plant species. Excess N deposition can cause shifts in wetland communities composition by altering competitive relationships among species, which potentially leads to effects such as decreasing biodiversity, increasing non-native species establishment and increasing the risk of extinction for sensitive and rare species.
- Changes in plant species composition caused by elevated atmospheric N deposition haven been demonstrated in Europe. Diverse plant communities have been converted into monospecific stands dominated by *Molina caerulea* or *Deschampsia flexuosa* in Dutch wet heathlands. However, it is not clear to what extent such effects occur under ambient N deposition levels in the United States.
- Some wetland species, such as *Sphagnum squarrosum*, *Sphagnum fallax*, and *Drosera rotundifolia*, are adapted to low-N environments. High levels of atmospheric N deposition will increase the risk of decline and extinction of those sensitive species.
- *Sarracenia purpurea* can be used as a biological indicator of local N deposition in some locations (Ellison and Gotelli, 2002). *S. purpurea* is a perennial pitcher plant native to Canada and the eastern United States that grows in nutrient-poor peatlands and is sensitive to changes in N availability. Within a single growing season, increasing N availability switches the plant from producing carnivorous pitchers to producing more photosynthetically efficient phyllodia.

5.5.2.2.3 Regional Trends

- Bogs are among the most sensitive transitional ecosystems to the effects of N deposition. In the CONUS, peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S. Environmental Protection Agency, 1993a).
- N input and output rates of fens are intermediate between bogs and coastal marshes. N deposition could drastically change species composition, increase primary productivity and increase methane emission in fens (Pauli et al., 2002; Aerts and de Caluwe, 1999).

- Atmospheric N inputs probably contribute to eutrophication problems in coastal marshes at many locations, especially along the Atlantic and Gulf coasts.
- Table (5.5-1) compares N fluxes (g N m^{-2} yr^{-1}) from wetlands classified according to the importance of atmospheric deposition to the total N budgets.

5.5.3 Freshwater Aquatic

General conclusions of the 1993 AQCD for oxides of nitrogen indicated that productivity of fresh water is usually limited by the availability of phosphorus. However, it was noted high inputs of phosphorus from anthropogenic sources could lead to N limitation occurring. The ratio of dissolved organic N to total phosphorous was used as an indicator for nutrient limitation, with values less than 2 indicating N limitation. The proportions of N limited lakes show wide regional variation: Pacific Northwest (27.7%), Upper Midwest (19%), Northeast (5%), Southeast (2.5%). All sub regions of the West contain substantial numbers of N limited lakes.

5.5.3.2 Ecological Effects

A freshwater lake or stream must be N-limited in order to be sensitive to N-mediated eutrophication. Although conventional wisdom holds that most lakes and streams in the United States are limited by phosphorus, recent evidence illustrates examples of lakes and streams that are limited by N and show symptoms of eutrophication.

5.5.3.2.1 Biogeochemcal Effects

In agreement with the 1993 AQCD, productivity of freshwater ecosystems is generally limited by the availability of phosphorus. However, new information indicates many surface waters in remote locations are limited by nitrogen. Such waters receive low atmospheric inputs of nitrogen, and this may explain their nitrogen-limited condition.

5.5.3.2.2 Biological Effects

The following biological indicators can be used to assess the eutrophic condition of aquatic ecosystems:

- Chlorophyll *a*: Increased N deposition leads to increased productivity and increased chlorophyll *a*, resulting in decreased water clarity as well as decreased dissolved oxygen.

- <u>Phytoplankton Biomass</u>: Increased N deposition leads to increased phytoplankton biomass.
- <u>Periphyton Biomass</u>: N deposition generally stimulated periphyton biomass productivity in N-limited lakes.
- <u>Nitrate Toxicity</u>: Extremely high NO_3^- concentrations can have direct adverse effects on fish, invertebrates and amphibians, but the concentrations required to elicit such effects are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition. For example, mortality of rainbow trout eggs and fry occurred after 30-day incubations in concentrations greater than 79 µg N/L; adverse effects on amphibians and insects occur at even higher concentrations.

Increased N deposition can cause a shift in community composition and reduce algal biodiversity.

- Elevated N deposition results in changes in algal species composition, especially at sensitive high elevation lakes in the western United States.
- Opportunistic algae, such as *Asterionella formosa* and *Fragilaria crotonensis*, respond rapidly to nutrient enrichment and gain competitive advantage over others species.

5.5.3.2.3 Regional Trends

Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of greatest concern in lakes and streams that have very low productivity and nutrient levels and that are located in remote areas.

- In the western United States, high-elevation lakes are considered the most sensitive aquatic ecosystems to N deposition. Some examples include the Snowy Range in Wyoming, the Sierra Nevada Mountains, and Lake Tahoe in California, and the Colorado Front Range.
- The most severe eutrophication from N deposition effects are expected downwind of major urban and agricultural centers.
- N deposition appears to have stimulated productivity and altered algal species assemblages in some high-elevation lakes in the western United States at low deposition rates of 1.5 to 2.2 kg N ha^{-1} yr^{-1}. It appears that many high-elevation

oligotrophic western lakes may be N limited, whereas lower elevation lakes are more typically phosphorus limited.

- The change in lake algae that occurred in Rocky Mountain National Park between 1950 and 1964, based on the paleolimnological record, was associated with a level of wet N deposition that was estimated to have been only about 1.5 kg N/ha.

5.5.4 Estuarine Aquatic

The 1993 AQCD for Oxides of Nitrogen concluded that the primary N nutrient addition effect on aquatic ecosystems is eutrophication of estuarine and near-coastal marine waters, which results in an increase of algal biomass and changes in community composition. Studies published since 1996 generally support the conclusions of 1993 AQCD. The data for estimating the contribution of N deposition to the nutrient budget of aquatic ecosystems were very sparse and mainly limited to the Chesapeake Bay before 1993. The contribution of nitrogen deposition to estuarine eutrophication is now better understood in the Chesapeake Bay and other estuaries.

5.5.4.2 Ecological Effects

A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions and generally received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al., 2007). Estuarine and coastal marine ecosystems experience a range of ecological problems associated with nutrient enrichment. Because the productivity of estuarine and near shore marine ecosystems is generally limited by the availability of N_r, excessive contribution of N_r from sources of water and air pollution can contribute to eutrophication.

5.5.4.2.1 Biogeochemical Effects

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D’Elia et al., 1986; Howarth and Marino, 2006). This is at least partly because denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997). However, other limiting factors occur in some locations and during some seasons. Levels of N limitations are affected by seasonal patterns. N-deficient conditions are likely to be found during the peak of annual productivity in the summer.

Excess N inputs will affect the Si:N ratio in water. If the Si:N ratio drops below about 1, the marine food web structure would be expected to change, with decreasing diatom-to-zooplankton-to-higher tropic level ratios and increasing abundance of flagellated algae.

5.5.4.2.2 Biological Effects

Increased N deposition can cause shifts in community composition reduce algale biodiversity, and mortality of submerged aquatic vegetation (SAV). The form of deposited N can significantly affect phytoplankton community composition in estuarine and marine environments. Small diatoms are more efficient in using NO_3^- than NH_4^+. Increasing NH_4^+ deposition relative to NO_3^- in the eastern United States favors small diatoms at the expense of large diatoms. This alters the foundation of the food web. SAV is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor contributing to declines in SAV coverage. The Mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of SAV due to eutrophication.

The following biological measurements can be used to assess the eutrophic condition of estuarine and coastal waters:

- Chlorophyll *a*: excess N input will stimulate primary productivity. High levels of chlorophyll *a* indicates a high phytoplankton biomass.
- Macroalgal Abundance: Macroalgal blooms were moderate or high for half of the nation’s assessed estuaries (Bricker et al., 2007). Macroalgal blooms can cause the loss of important SAV by blocking sunlight.
- Dissolved Oxygen: Dissolved oxygen concentration decreases with increasing algal abundance under elevated N, because microbes consume oxygen as they decompose dead algae. Increased atmospheric N deposition if sufficiently high, could stimulate the development of hypoxic or anoxic zones. The northern Gulf of Mexico is the largest documented zone of hypoxic coastal water in United States.
- Nuisance/Toxic Algal Blooms: Excess N input can cause nuisance or toxic algal blooms, which release toxins in the water that can poison aquatic animals and threaten human health. About one third of the nation’s assessed estuary systems

exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker et al., 2007).

5.5.4.2.3 Regional Trends

The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker et al., 2007). The national estuary condition assessment conducted by Bricker et al. (2007) found the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. Other regions had mixtures of low, moderate, and high degree of eutrophication. The regional assessment results from the report of Bricker et al. (2007) are summarized in Table 5.5-2.

5.5.5 Case Studies

5.5.5.1 Chesapeake Bay

The Chesapeake Bay is the largest estuary in United States. Its watershed covers 64,299 square miles ² and the surface area of the bay and its major tributaries is 4,479 square miles (Pyzik et al., 2004). The Chesapeake Bay is perhaps the best-documented case study in the United States of the effects of human activities on estuarine eutrophication. Recent studies (Boyer et al., 2002; Howarth, 2007) indicated that atmospheric deposition makes a substantial contribution (about 25%) to the overall N budget of Chesapeake Bay. Human disturbances, such as landscape changes, have exacerbated the negative impacts of N deposition by reducing N removal and retention in the upper watershed region. Anthropogenic N inputs have substantially altered the trophic condition of Chesapeake Bay over the last 50 to 100 years. Symptoms of eutrophication in the bay include high algal production, low biodiversity, and large hypoxia and anoxia zones. SAV was once abundant in Chesapeake Bay, covering about 200,000 acres along the shallows and shorelines. Increased nutrient inputs caused SAV declines since the mid-1960s and the SAV community had fallen to about 38,000 acres by 1984. Eutrophication has been implicated in declines and disappearance of striped bass (*Morone saxatilis*) and blue crab (*Callinectes sapidus*) in Chesapeake Bay.

5.5.5.2 Alpine and Subalpine Communities of the Eastern Slope of the Rocky Mountains in Colorado

Research on N enrichment effects on alpine and subalpine ecosystems in the western United States has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge Long Term Ecosystem Research site, both located east of the Continental Divide in Colorado. Research has been conducted in this region on both the terrestrial and aquatic effects of nutrient enrichment. Some key findings are summarized below:

- Changes in plant species composition may be detectable at lower N deposition rates than the level at which the traditional soil indicators signal ecosystem responses to N deposition, and changes in species composition are probably ongoing in alpine dry meadows of the Front Range of the Colorado Rocky Mountains at current ambient atmospheric N deposition levels.
- Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at input levels less than 10 kg N ha^{-1} yr^{-1} (Baron et al., 1994; Williams and Tonnessen, 1999).
- Rocky Mountain National Park has been the site of research addressing the effects of N deposition on algal species abundance in freshwater lakes. Two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane lakes, and this has been attributed to atmospheric N deposition.

5.6 OTHER WELFARE EFFECTS

5.6.1 Deposition of Sulfur Oxides Affect Mercury Methylation

S deposition contributes to secondary effects on the cycling and bioavailability of Hg, a highly neurotoxic contaminant. Research suggests that S deposition influences the cycling of Hg in wetland and aquatic ecosystems by stimulating SO_4^{2-}-reducing bacteria associated with Hg methylation, a key process that increases the bioavailability of Hg. The rates of methylation are influenced by oxygen content, temperature, pH, and the concentration of organic acids in solution. Mercury methylation occurs in anoxic sediments that contain a sufficient carbon source to support SO_4^{2-}-reducing bacterial activity along with an adequate supply of SO_4^{2-}. Wetland environments are significant areas of methylmercury (CH_3Hg) production and sources of export to downstream receiving waters (St. Louis et al., 1994). The wetland ecosystems that are likely to exhibit high levels of Hg methylation can be found in the northeastern United States and southeastern Canada.

Chemical Indicators

- Studies have shown a strong negative correlation between surface water pH and Hg concentration in fish tissue, but the mechanisms responsible for this linkage are not clear. Hg concentrations in fish have also been shown to be less strongly correlated with a variety of other variables, including (DIC), Ca, Mg, (DOC), sodium, lake area, and watershed area.
- Total Hg and CH_3Hg concentrations are often positively correlated with DOC in lake waters. Dissolved organic carbon, in turn, has an important influence on pH. DOC may bind with CH_3Hg at very high DOC concentration, limiting the bioavailability of the Hg.
- One study showed that lakes with Hg levels above the EPA criterion of 0.3 µg/g in yellow perch had significantly higher DOC, and lower pH, ANC, and total phosphorus than lakes with fish Hg concentrations below 0.3 µg/g (Driscoll et al., 2007b).

Case Study

- Little Rock Lake is an 18 ha precipitation-dominated seepage lake located in a forested and undisturbed catchment of north-central Wisconsin. Results from the Little Rock Lake acidification experiments suggest that S deposition plays an important role in the accumulation and methylation of Hg in freshwater ecosystems.

5.6.2 Direct Phytotoxic Effects of Gaseous Sulfur and Nitrogen on Vegetation

5.6.2.1 SO_2

The current secondary standard for SO_2 is a 3-h average of 0.50 ppm, which is designed to protect vegetation against acute foliar injury. There has been limited research on acute foliar injury since the last SO_2 AQCD and there is no clear evidence of acute foliar injury below the level of the current standard.

Effects on growth and yield of vegetation are associated with increased SO_2 exposure concentration and time of exposure. The 1982 SO_2 AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Because of falling ambient SO_2 concentrations and focus on O_3 vegetation effects research, few studies have emerged to better inform a metric and levels of concern for effects of SO_2 on growth and productivity of vegetation.

5.6.2.2 NO and NO_2

It has been well known that in sufficient concentrations NO and NO_2 have the potential to have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (U.S. Environmental Protection Agency, 1993a). The 1993 NO_X AQCD concluded that concentrations of NO_2 and NO in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (U.S. Environmental Protection Agency, 1993a). Since the 1993 AQCD, very little new research has been done on these phytotoxic effects to alter this conclusion.

5.6.2.3 Peroxyacetyl Nitrate (PAN)

Although peroxyacetyl nitrate (PAN) remains an important component of photochemical pollutant episodes and negative effects on plants have been observed, there is little evidence in recent years suggesting that PAN poses a significant risk to vegetation in the United States.

5.6.3 N_2O

N_2O is a GHG with a global warming potential (GWP) on the conventional 100-year time horizon of ~296 (i.e., N_2O is nearly 300 times more effective for trapping heat in the atmosphere than CO_2 over a 100-year period) (IPCC, 2007). The largest U.S. emissions of GHGs are from CO_2, followed by CH_4 and N_2O (83.3%, 7.4%, and 6.5% of total GHG emissions from the United States on a Tg CO_2 equivalents basis, respectively) in 2005 (U.S. Environmental Protection Agency, 2007b). GHGs work together to force global climate change. A rigorous assessment of this process is provided by the International Panel on Climate Change (IPCC, 2007), and the adverse effects of climate change on welfare in North America are assessed in chapter fourteen of the IPCC working group II assessment (Field et al., 2007).

5.7 CONCLUSIONS

In the review of the scientific literature for oxides of nitrogen and oxides of sulfur, evidence from the various disciplines of atmospheric sciences, environmental exposure, ecology, biogeochemistry, plant sciences, animal toxicology, limnology, and marine science were integrated and collectively considered in formulating conclusions. This draft ISA focused on scientific information that has become available since the last reviews and reflects the current state of knowledge on the most relevant issues pertinent to the review of the secondary NAAQS for NO_X and SO_X. Currently, the secondary NAAQS for sulfur oxides uses SO_2 as the chemical indicator and has an annual 3-h maximum average of 0.5 ppm. The secondary NAAQS for nitrogen oxides has NO_2 as the chemical indicator and is set same as the primary with an annual average of 0.053ppm. These secondary NAAQS were set to protect against direct gas-phase damage to vegetation. In the years since the current oxides of nitrogen and sulfur NAAQSs were set, there is little new evidence on the direct gas-phase effects on vegetation; however evidence describing and quantifying the effects of N and S deposition has grown substantially. Overall, we conclude that there is a *causal* relationship between current levels of N and S deposition and numerous biologically adverse effects on ecosystems across the United States. The chemical and biological effects are listed in Table 5.7-1. The main effects may be broadly categorized as acidification and nitrogen enrichment/eutrophication.

It is important to note that the regulatory networks that monitor N and S deposition are inadequate to characterize regional heterogeneity and hotspots. Hotspots have been identified at specific research sites where deposition rates exceed the value of the nearest regulatory monitor by as much as a factor of seven (cite). Adverse ecosystem effects are directly linked to deposition hotspots.

Acidification of ecosystems is caused by both NO_X and SO_X deposition. SO_X deposition is considered the main cause of chronic acidification. Decreases in sulfur deposition have lead to recovery with over one quarter to one third of lakes and streams that were chronically acidic in the 1980s, but were no longer acidic in the year 2000. However, a number of lakes and streams remain acidic at current ambient deposition levels. NO_X deposition is the leading cause of episodic acidification, which despite its short duration has been shown to cause long-term adverse effects on biota. Vulnerability of a given ecosystem to acidification occurs at the intersection of current loading, accumulation of NO_X and SO_X from past loading and the inherent ecosystem sensitivity, which is predominantly governed by the underlying geologic composition that serves as soil parent material. Regions where vulnerable ecosystems occur in the United States include New England, the Appalachian Mountains, and the Upper Midwest and high elevation areas of the East. The ISA focuses on two case studies for which to provide more detail: The Adirondacks (NY) and Shenandoah National Park. In the Adirondacks, the current rates of NO_X and SO_X deposition exceed the level that would allow recovery of the most acid sensitive lakes. In the Shenandoah, sulfate has accumulated in the soil from past deposition making this region sensitive to current loading. The accumulated sulfur is slowly leaching from the soil into stream water, where it causes acidification. Modeling results suggest the number of acidic streams will increase under the current deposition levels and re-acidification may be prevented if deposition is kept between 9-15 kg N ha^{-1} yr^{-1} and 0-6 kg S ha^{-1} yr^{-1}.

Ecosystem nitrogen enrichment is caused by atmospheric NO_X and NH_X deposition in combination with all other forms of reactive Nitrogen loading in ecosystems. Additions of N promote growth in some ecosystems and causes significant biologically adverse effects in others. For example, low-level chronic nitrogen deposition can act as a fertilizer and increase productivity of some forests, but cause the mortality of other organisms in that occur in the same forests, such as lichens. In general, ecosystems adapted to low nitrogen availability or those that are N limited are most sensitive to the effects of nitrogen deposition (e.g. Alpine ecosystems, CA coastal sage scrub, ombrotrophic wetlands and estuaries). Excess nitrogen to vulnerable ecosystems can cause “nitrogen pollution”, resulting in a suite of terrestrial and aquatic ecological problems including species mortality, biodiversity losses, altered community species composition and biochemical function, eutrophication and harmful algal blooms. Deposition levels of approximately 2 kg N ha^{-1} yr^{-1} are reported to cause alterations in algal communities of freshwater lakes (Colorado), changes in foliar N concentration (Colorado), and increased CO_2 emissions from peat bog wetlands (Europe). Mortality of lichen species occurs at 3 kg N ha^{-1} yr^{-1} (Wet coast). Deposition levels of 5 kg N ha^{-1} yr^{-1} correlate to the onset of declining biodiversity within grasslands in the UK. At approximately 8 kg N ha^{-1} yr^{-1} many forest ecosystems begin to leach nitrate into stream and ground water.

Eutrophication of estuaries is a particularly detrimental ecological problem to which atmospheric deposition of NO_X and NH_X contribute. In highly eutrophic estuaries the contribution of atmospheric deposition to total loads can be greater than 40%. Eutrophication causes water quality deterioration, resulting in numerous adverse effects including (but not limited to): hypoxic zones, species mortality, and harmful algal bloom. The Chesapeake Bay is an example of a large well-studied estuary that receives 21-30% of its total N load from the atmosphere.

TABLE 5.4-1. CHEMICAL INDICATORS OF ACIDIFICATION TO TERRESTRIAL ECOSYSTEMS

Soil Base Saturation	
Reuss (1983)	If base saturation is less than 15-20%, exchange ion chemistry is dominated by inorganic Al.
Cronan and Grigal (1995)	Base saturations below about 15% in the soil B-horizon could lead to impacts from Al stress.
Lawrence et al. (2005)	Base saturation declines from 30% to 20% in the upper soil B-horizon showed decreases in diameter growth of Norway spruce.
Bailey et al. (2004)	At Ca saturation less than 2% and Mg saturation less than 0.5% in the upper soil B-horizon, found sugar maple mortality.
Aluminum Concentrations	
Johnson et al. (1991); Joslin and Wolfe (1992); Eagar et al. (1996)	In soils with base saturation below about 20%, base cations reserves are so low that Al exchange dominates.
Cronan and Grigal (1995)	50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. 100% risk for adverse effects on growth at molar ratio value below 0.2.
Johnson et al. (1994a,b)	Ca:Al ratios above 1.0 through 4 years were found in a foreststand experiencing high mortality.
DeWitt et al. (2001)	Ca:Al ratios of Norway spruce stand below 0.5 showed reduced Mg concentrations in needles in third year.
C:N Ratio	
Aber et al. (2003) Ross et al. (2004)	Increased effects of nitrification occur only in soil with C:N ratio below about 20-25.

TABLE 5.4-2. STUDIES ON CHEMICAL INDICATORS OF ACIDIFICATION IN SURFACE WATER

Sulfate	
Driscoll et al. (2001a)	Acidic deposition at Hubbard Brook Experimental Forest in New Hampshire contributed to a nearly four-fold increase in stream SO_4^{2-} concentration between 1850 and 1970.
Stoddard et al. (2003)	Widespread decreasing trends in SO_4^{2-} concentrations were documented by EPA during the period 1990-2000 in the eastern United States including New England lakes (1.77 µeq L^{-1} yr^{-1}), Adirondack lakes (2.26 µeq L^{-1} yr^{-1}), Appalachian streams (2.27 µeq L^{-1} yr^{-1}), and Upper Midwest lakes (3.36 µeq L^{-1} yr^{-1}).
Nitrate	
Driscoll and Newton (1985)	NO_3^- concentrations in 20 Adirondack lakes in the early 1980 averaged 12% of SO_4^{2-} concentrations.
Lovett et al. (2000)	Baseflow NO_3^- concentrations in 1994-97 were an average of 37% of SO_4^{2-} concentrations in 39 Catskill streams.
Murdoch and Stoddard (1993)	During high-flows in Catskill streams concentrations periodically equaled or exceeded SO_4^{2-} concentrations.
Webb et al. (2004)	Average concentrations of NO_3^- in most southeastern streams also tend to be considerably less than SO_4^{2-} concentrations.
Cook et al. (1994)	Very high NO_3^- concentrations in streamwater documented at high elevations in the Great Smoky Mountains in North Carolina.
Base Cations	
Likens et al. (1996)	Approximately linear increasing relationship between concentrations of base cations and $[SO_4^{2-} + NO_3^-]$ in Hubbard Brook streams from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994.
Lawrence et al. (1999)	Decreasing concentrations of base cations at a rate that exceeded decreases in $[SO_4^{2-} + NO_3^-]$ in Catskill Mountain streams from 1984 to 1997.
Acid Neutralizing Capacity	
Sullivan et al. (2006)	Model simulations suggest that none of the lakes in the Adirondack target lake population were chronically acidic or had ANC less than 20 µeq/L under preindustrial conditions. By 1980, there were hundreds of such lakes.
Stoddard et al. (2003)	Tendencies during the 1990s toward increasing surface water Gran ANC in all glaciated regions of the eastern United States (i.e., New England, Adirondacks, Northern Appalachian Plateau) and Upper Midwest; and decreasing Gran ANC in the Ridge/Blue Ridge province.

TABLE 5.4-2 (cont'd). STUDIES ON CHEMICAL INDICATORS OF ACIDIFICATION IN SURFACE WATER

Surface Water Aluminum	
Gensemer and Playle (1999)	Found that organically complexed aluminum (*organic Al*) can occur in surface waters as a result of natural soil and hydrologic processes, but this form of Al is not harmful to aquatic life.
Gensemer and Playle (1999)	Demonstrated that *inorganic Al* has been found to be toxic to plant and animal species throughout the food web.
Baldigo et al. (2007)	Documented 20% mortality of brook trout young-of-the yr *in situ* during a 30-day period with a median inorganic Al concentration of 2 µmol/L. 90% mortality occurs over 30 days with a median inorganic Al concentration of 4.0 µmol/L.
Lawrence et al. (2007)	49 of 195 streams (25%) in the western Adirondack region had inorganic Al concentrations above 2.0 µM during Aug. base flow.
pH	
Haines and Baker (1986); Baker et al. (1990a)	Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms. Common reference values for pH are 5.0, 5.5, and 6.0.
Charles et al. (1989); Sullivan et al. (1990); Cumming et al. (1992, 1994)	25 to 35% of the Adirondack lakes that are larger than 4 ha have acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had ambient pH less than 5.2 in the mid-1980s were inferred to have experienced large declines in pH and ANC since the previous century. About 30 to 45% of the lakes with ambient pH between 5.2 and 6.0 have also acidified.
Gbondo-Tugbawa et al. (2002)	PnET-BGC modeling at Hubbard Brook estimated that past stream pH (circa 1850) was probably about 6.3, compared with just above 5.0 in 2000.
Stoddard et al. (2003)	Reported an increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq L^{-1} yr^{-1}) and Upper Midwest lakes (0.01 µeq L^{-1} yr^{-1}). No trends were found in New England lakes or Appalachian streams in this study.

TABLE 5.5-1. NITROGEN FLUXES FROM WETLANDS CLASSIFIED ACCORDING TO THE IMPORTANCE OF ATMOSPHERIC DEPOSITION TO THE TOTAL NITROGEN BUDGETS

	Precipitation Increasing in Importance		
	Intertidal Fresh and Salt Water Mashes ($g\ N\ m^{-2}\ yr^{-1}$)	**Fens ($g\ N\ m^{-2}\ yr^{-1}$)**	**Wet Heathland and Bog ($g\ N\ m^{-2}\ yr^{-1}$)**
Wet deposition	0.8-1.1	4.2-4.4	0.7-0.9
Total N inputs	57.6-74.4	5.3-7.6	0.9-1.0
Total N exports	54.6-79.7	4.9-8.8	0.4

Source: Morris (1991).

TABLE 5.5-2. CHESAPEAKE BAY VALUATION STUDY

Author	Measure	Findings
Bockstael et al. (1989)	Aggregate willingness-to-pay for 20% water quality improvement.	\$34.7 million, \$4.7 million, and \$1.4 million for beach use, boating, and sport fishing.
Morgan and Owens (2001)	Lower bound aggregate benefits of 60% water quality improvement.	\$288.8 million, \$6.7 million, and \$288.8 million for beach use, boating, and sport fishing.
Lipton (2004)	Willingness-to-pay for one unit water quality improvements.	\$7.3 million per yr with a \$146 million present value.

TABLE 5.7-1. SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Acidification							
Forest	7-10		increased NO_3^- leaching		Northeastern U.S.		Aber et al. (2003)
Forest	25-35		1) increased NO_3^- leaching and soil acidity; 2) decreased base cation saturation		Southern California		Fenn et al. (2003a)
Forest		25-35.5	increased NO_3^- concentrations in soil water and stream water		Maine and West Virginia	hardwood	Kahl et al. (1993); Peterjohn et al. (1996).
Meadow (alpine)	5	20-60	increased NO_3^- leaching and NO_3^- concentration in soil water	1) caused changes of plant species composition within 3 yrs of the initiation of the experiment; 2) net nitrification were detectable at levels above 20 kg N/ha/yr	Colorado Front Range		Bowman et al. (2006)
Surface waters	<5		increased NO_3^- leaching		Western U.S.		Baron et al. (1994); Williams et al. (1996a)
Surface waters	5.6		increased NO_3^- leaching		Northeastern U.S.		Driscoll et al. (1989); Stoddard et al. (1994)
Surface waters	8-10		increased NO_3^- leaching		Eastern U.S.		Stoddard et al. (1994)

TABLE 5.7-1 (cont'd). SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Nitrogen enrichment							
Forest	1-2			decreased foliar Mg concentration and increased foliar N:Mg and N:Ca	Western slope of Rocky Mtns.	Engelmann Spruce	Baron et al. (2000)
Forest	1-5			decreased soil organic horizon C/N and foliar C/N, and increased foliar N concentration, foliar N/Mg, foliar N/P and potential net mineralization	Continental Divide, Colorado	spruce	Rueth and Baron (2002)
Forest	2.0	25		increased N concentration in foliar and organic soil horizon	Fraser Experimental Forest, Colorado	spruce	Rueth et al. (2003)
Forest	3-5			decreased foliar Mg concentration and increased foliar N:Mg and N:Ca	Eastern slope of Rocky Mtns.	Engelmann Spruce	Baron et al. (2000)
Forest (boreal)	3-12			decreased the abundance and cover of ericaceous shrubs	Sweden		Gilliam (2006)
Forest	4-5	25		doubled N mineralization rates and stimulated nitrification	Loch Vale watershed, Colorado	old-growth spruce	Rueth et al. (2003)
Forest	5			increased rates of nitrification	Colorado	old-growth forests	Rueth and Baron (2002)
Forest	5-10			decreased the abundance of lichens containing cyanobacteria	Northern Europe	lichens	Bobbink et al. (1998)
Forest	5.4	25		triggered net nitrification	Vermont	spruce	McNulty et al. (1996)

TABLE 5.7-1 (cont'd). SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Nitrogen enrichment (cont'd)							
Forest	6-20			species shifts towards nitrophilous and more acid-tolerant plant species	Sweden	oak	Gilliam (2006)
Forest	9.8			stimulated productivity of forests in high latitudes in the Northern Hemisphere	Northern Hemisphere		Holland et al. (2005)
Forest		14-28		decreased herbaceous cover under hardwoods	Adirondack Park, New York	hardwood	Gilliam (2006)
Forest		25		basal area increment of sugar maple was enhanced 13 to 104%, whereas red spruce was not significantly affected	Bear Brook, Maine	sugar maple; red spruce	Elvir et al. (2003)
Forest		30		stimulate stemwood production	Northern Sweden	Scots pine	Högberg et al. (2006)
Forest		35		enhanced growth of black cherry and yellow poplar during the first 7 yrs, but reduced growth of these species in years 9 to 12, with no change in red maple or sweet birch	Fernow Experimental Forest, West Virginia		DeWalle et al. (2006)
Forest		35		no significant impact on the herbaceous layer under hardwoods	Fernow Experimental Forest, West Virginia	hardwood	Gilliam et al. (2006)

TABLE 5.7-1 (cont'd). SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Nitrogen enrichment (cont'd)							
Forest		50	concentrations of NH_4^+ plus NO_3^- were not detected in soil water until the 15th yr		Harvard Forest	hardwood	Magill et al. (2004)
Forest		50-150	elevated NH_4^+ plus NO_3^- in soil water were detected after 1 yr of 150 kg N/ha/yr doses, and after 5 yrs of 50 kg N/ha/yr doses		Harvard Forest	red pine	Magill et al. (2004)
Forest		90		decreased stem volume growth	Northern Sweden	Scots pine	Högberg et al. (2006)
Forest (alpine)		100-200		marginally increased plant foliage productivity but reduced species richness	Niwot Ridge, Colorado		Seastedt and Vaccaro (2001)
Forest		150	concentrations of NH_4^+ plus NO_3^- were not detected in soil water until the 7th yr		Harvard Forest	hardwood	Magill et al. (2004)
Oak savanna		54-170		decreased ectomycorrhizal fungal diversity and changed species composition	Minnesota	ectomycorrhizal fungi	Avis et al. (2003)
Coastal sage shrub	2-57			caused a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity	California		Egerton-Warburton and Allen (2000)

TABLE 5.7-1 (cont'd). SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Nitrogen enrichment (cont'd)							
Costal sage shrub	30			native shrub and forb seedlings replaced by the grasses, especially following disturbances such as fire	Southern California		Eliason and Allen (1997); Yoshida and Allen (2001)
Coastal sage shrub	30			1) decreased the diversity of native plants; 2) increased exotic grass biomass; 3) changed the biodiversity of microbial communities	Los Angeles Air Basin		Bytnerowicz and Fenn (1996)
Grassland	5-30			increased non-native grass biomass at sites that received 30 kg N/ha/yr, but not at the sites that received 5 kg N/ha/yr	Joshua Tree National Park, California		Allen et al. (2007)
Grassland	10-15			decreased populations of the bay checkerspot butterfly	California	checkerspot butterfly	Weiss (1999)
Grassland	10-15			displaced native grass species by exotic nitrophilous grasses	San Francisco Bay area, California		Fenn et al. (2003a)
Grassland		0-100		1) increased growth; 2) native species did not consistently grow better at low nitrogen levels than the exotic species	Greenhouse study		Lowe et al. (2002)
Grassland		70		decreased forb production concomitant with increased grass productivity	Jasper Ridge Biological Preserve, California		Zavaleta et al. (2003)

TABLE 5.7-1 (cont'd). SUMMARY OF NITROGEN DEPOSITION LEVELS AND THE CORRESPONDING EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEMS

Type of Ecosystem	Ambient N Deposition (kg N/ha^{-1}/yr^{-1})	N Additions (kg N/ha^{-1}/yr^{-1})	Chemical Effects	Biological Effects	Study Site	Study Species	Citation
Nitrogen enrichment (cont'd)							
Meadow	5	20-60		increased plant biomass and tissue N concentration	Niwot Ridge, Colorado		Seastedt and Vaccaro (2001)
Meadow		25		1) caused a community shift towards greater dominance of hairgrass in wet alpine meadows, 2) increased in plant biomass	Niwot Ridge, Colorado		Bowman et al. (1995); Burns (2004)
Desert		32		increased biomass of non-native plants by 54%, decreased native species biomass by about 39%	Mojave desert		Brooks (2003)
Desert		100		increased the cover of warm season grasses and decreased the cover of legumes	Chihuahuan Desert		Baez et al. (2007)
Wetland		30	increased CH_4 emissions		Eastern Finland		Saarnio et al. (2003)
Wetland		240	increased CH_4 emissions	increased abundance of *Deyeucia angustifolia*	Northeast China		Zhang et al. (2007)
Lake	1.3-2.2			increased lake algal productivity	Sweden		Bergström et al. (2005)
Lake	1.5			caused a shift in algae community composition	Beartooth Mountains, Wyoming	algae	Saros et al. (2003)
Lake	<2			observed diatom shifts in alpine lakes	Rocky Mountain, Colorado	diatom	Interlandi and Kilham (1998)

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