

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

(First External Review Draft)

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

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

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PREFACE

Legislative Requirements

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

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

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

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

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

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

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

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

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

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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 ₃ CH(O)OONO ₂	peroxyacetyl nitrate
CH ₃ CN	acetonitrile
CH ₃ C(O)O	peroxyacetyl radical
CH ₂ I ₂	diiodomethane

CH ₃ -S-CH ₃	dimethylsulfide, DMS
CH ₃ -S-H	methyl mercaptan
CH ₃ SO ₃ H	methanesulfonic acid
CH ₃ -S-S-CH ₃	dimethyl disulfide
Cl	chlorine
Cl ⁻	chlorine 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 Administration
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 ₂ O ₂	hydrogen peroxide
HOCl	hypochlorous acid
HOX	hypohalous acid
H ₂ S	hydrogen sulfide
H ₂ SO ₄	sulfuric acid
hν	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 ₄ NO ₃	ammonium nitrate
NH ₄ HSO ₄	ammonium bisulfate
(NH ₄) ₂ SO 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 ₂ O	nitrous oxide
N ₂ O 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 peroxy
RONO ₂	organic nitrate
RO ₂ NO ₂	peroxy nitrate
S	sulfur
SAV	submerged aquatic vegetation
SCAQCS	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 ₂ O	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 ≥ 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 quantities as individuals farther up the food chain ingest matter containing those elements.

Biodiversity

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

Buffering capacity

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

Carbon sequestration

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

Catchment

An area that collects and drains rainwater.

Climate

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

Critical load

A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

Denitrification

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

Dry deposition

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

Ecological community

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

Ecosystem services

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

Ecosystem

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

Eutrophication

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

Eutrophy

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

Evapotranspiration

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

Fen

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

Freshet

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

Greenhouse gas

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

Gross primary production

The total carbon fixed by plant through *photosynthesis*.

Heathland

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

Hypoxic events

Events that lead to a deficiency of oxygen.

Integrated science assessment

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

Invasive species and invasive alien species

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

Leaching

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

Lowland

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

Net ecosystem production (NEP)

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

Net primary production (NPP)

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

Nitrification

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

Nitrogen mineralization

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

Nitrogen-retention capacity

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

Nitrogen saturation

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

Occult deposition

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

Ombrotrophic bog

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

pH

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

Phytoplankton

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

Primary Production

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

Semi-arid regions

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

Sensitivity

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

Streamflow

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

Surface runoff

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

Throughfall

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

Trophic level

The position that an organism occupies in a food chain.

Tundra

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

Upland terrestrial ecosystem

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

Valuation

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

Vulnerability

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

Welfare effects

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

Wet deposition

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

Wetland

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

Zooplankton

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

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 N₂O 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 (NO₂) and Sulfur Dioxide (SO₂) (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 NO₂

1 (0.053 parts per million [ppm], annual average) and the current secondary NAAQS for SO₂
2 (0.5 ppm, 3-h average) should be retained or revised. The scope of this draft ISA is to evaluate
3 newly available scientific evidence to best inform consideration of these framing questions,
4 including the following:

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

23
24

25 **1.1 BRIEF LEGISLATIVE BACKGROUND FOR NO_x AND SO_x: THE** 26 **RATIONALE FOR A COMBINED REVIEW**

27

28 **1.1.2 Brief Legislative Background of NO_x**

29 In 1971, the first AQCD for NO_x was issued by the National Air Pollution Control
30 Association (NAPCA), one of the Environmental Protection Agency's (EPA's) predecessor
31 agencies (U.S. Environmental Protection Agency, 1971). After reviewing the relevant science
32 on the public health and welfare effects associated with oxides of nitrogen, EPA promulgated
33 identical primary and secondary NAAQS for NO₂ on April 30, 1971. Under section 109 of the
34 CAA, these standards were set at 0.053 ppm as an annual average (36 FR 8186).

35 In 1982, EPA published the NO_x AQCD (U.S. Environmental Protection Agency,
36 1982a), which updated the scientific criteria upon which the initial standards were based. On
37 February 23, 1984, EPA proposed to retain these standards (49 FR 6866). After taking into

1 account public comments, EPA published the final decision to retain these standards on June 19,
2 1985 (50 FR 25532).

3 In November 1991, EPA released an updated draft AQCD for Clean Air Scientific
4 Advisory Committee (CASAC) and public review and comment (56 FR 59285). CASAC
5 reviewed the document at a meeting held on July 1, 1993 and concluded in a closure letter to the
6 Administrator that the document “provides a scientifically balanced and defensible summary of
7 current knowledge of the effects of this pollutant and provides an adequate basis for EPA to
8 make a decision as to the appropriate NAAQS for NO₂” (Wolff, 1993). The EPA also prepared a
9 draft Staff Paper that summarized and integrated the key studies and scientific evidence
10 contained in the revised AQCD and identified the critical elements to be considered in the review
11 of the NO₂ NAAQS. In September 1995, EPA finalized the Staff Paper, “Review of the National
12 Ambient Air Quality Standards for Nitrogen Dioxide: Assessment of Scientific and Technical
13 Information,” (U.S. Environmental Protection Agency, 1995a). The Administrator made a final
14 determination that revisions to neither the primary nor the secondary NAAQS for NO₂ were
15 appropriate at that time (61 FR 52852, October 8, 1996). The level for both the existing primary
16 and secondary NAAQS for NO₂ remains 0.053 ppm (equivalent to 100 micrograms per cubic
17 meter of air [$\mu\text{g}/\text{m}^3$]) in annual arithmetic average, calculated as the arithmetic mean of the 1-h
18 NO₂ concentrations.

19

20 **1.1.3 Brief Legislative Background of SO_x**

21 Based on the 1970 SO_x AQCD (DHEW, 1970), EPA promulgated primary and
22 secondary NAAQS for SO₂, under section 109 of the CAA on April 30, 1971 (36 FR 8186). The
23 secondary standards included a standard at 0.02 ppm in an annual arithmetic mean and a 3-h
24 average of 0.5 ppm, not to be exceeded more than once per year. These secondary standards
25 were established solely on the basis of vegetation effects evidence. In 1973, revisions made to
26 Chapter 5 “Effects of Sulfur Oxide in the Atmosphere on Vegetation” of the SO_x AQCD (U.S.
27 Environmental Protection Agency, 1973), indicated that it could not properly be concluded that
28 the reported vegetation injury resulted from the average SO₂ exposure over the growing season,
29 rather than from short-term peak concentrations. EPA, therefore, proposed (38 FR 11355) and
30 then finalized a revocation of the annual mean secondary standard (38 FR 25678).

1 In 1979, EPA announced that it was revising the SO_x AQCD concurrently with that for
2 PM and would produce a combined PM-SO_x AQCD. Following its review of a draft revised
3 criteria document in August 1980, CASAC concluded that acidic deposition was a topic of
4 extreme scientific complexity because of the difficulty in establishing firm quantitative
5 relationships among (1) emissions of relevant pollutants (e.g., SO₂ and NO_x); (2) formation of
6 acidic wet and dry deposition products; and (3) effects on terrestrial and aquatic ecosystems.
7 CASAC also noted that acidic deposition involves, at a minimum, several different criteria
8 pollutants (i.e., SO_x, NO_x, and the fine particulate fraction of suspended particles). The
9 Committee felt that any document on this subject should address both wet and dry deposition, as
10 dry deposition was believed to account for at least one half of the total acid deposition problem.

11 For these reasons, CASAC recommended that a separate, comprehensive document on
12 acidic deposition be prepared prior to any consideration of using the NAAQS as a regulatory
13 mechanism for the control of acidic deposition. CASAC also suggested that a discussion of
14 acidic deposition be included in the AQCDs for both NO_x and PM-SO_x. Following CASAC
15 closure on the criteria document for SO₂ in December 1981, EPA's Office of Air Quality
16 Planning and Standards (OAQPS) published a Staff Paper in November 1982 (U.S.
17 Environmental Protection Agency, 1982b). The issue of acidic deposition was not, however,
18 assessed directly in this Staff Paper; EPA followed CASAC guidance and subsequently prepared
19 the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical*
20 *Assessment Review Papers, Volumes I and II* (U.S. Environmental Protection Agency, 1984a,b),
21 and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (U.S.
22 Environmental Protection Agency, 1985). These documents, though they were not considered
23 criteria documents and did not undergo CASAC review, represented the most comprehensive
24 summary of relevant scientific information completed by the EPA at that point.

25 On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and
26 secondary standards. This proposal regarding the secondary SO₂ NAAQS was due to the
27 Administrators conclusions that (1) based upon the then-current scientific understanding of the
28 acidic deposition problem, it would be premature and unwise to prescribe any regulatory control
29 program at that time, and (2) when the fundamental scientific uncertainties had been reduced
30 through ongoing research efforts, EPA would draft and support an appropriate set of control
31 measures.

1 **1.1.4 History of the Current Review**

2 EPA's National Center for Environmental Assessment in Research Triangle Park, NC
3 (NCEA-RTP) announced the official initiation of the current periodic review of air quality
4 criteria for NO_x on December 9, 2005, and for SO_x on May 15, 2006. For each of these reviews,
5 the Agency began by announcing in the Federal Register (70 FR 73236 and 71 FR 28023) the
6 formal commencement of the review and a call for information. With these reviews underway, a
7 workshop addressing the separate, joint review of just the secondary standards for these two
8 pollutants was announced in the Federal Register on June 20, 2007 (72 FR 11960). The review
9 of the NAAQS for NO₂ and SO₂ is under a court-ordered schedule, and that schedule includes a
10 deadline for completion of the final ISA for the review of the secondary NAAQS for NO₂ and
11 SO₂ by December 12, 2008.

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

17 18 19 **1.2 DOCUMENT DEVELOPMENT**

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

30 Emphasis has been placed on studies that evaluate effects at realistic ambient levels and
31 studies that consider NO_x and SO_x as components of a complex mixture of air pollutants.
32 Studies conducted in any country that contribute significantly to the knowledge base have been

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

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

21
22

23 **1.3 ORGANIZATION OF THE DOCUMENT**

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

1 and structures damage, and GHG emissions of N₂O. Finally, Chapter 5 articulates findings and
2 conclusions.

3 In addition, a series of 10 supplemental Annexes provide additional details of the
4 information discussed in the ISA. Annex 1 presents evidence related to the physical and
5 chemical processes in the atmosphere, including both oxidized and reduced chemical species. In
6 Annex 2, we present evidence related to emissions, air monitoring, and deposition processes of
7 atmospherically derived NO_x and SO_x. Annex 3 presents the major ecosystem monitoring
8 networks and models available for analysis of NO_x and SO_x effects on ecosystems. Annex 4
9 examines the effects of acidification on terrestrial and aquatic ecosystems, a process driven by
10 the combined deposition of NO_x and SO_x. Annex 5 examines the non-acidification effects of
11 NO_x on terrestrial and aquatic ecosystems and includes a broader discussion of the NO_x acting
12 in combination with total reactive nitrogen. Annex 6 evaluates the non-acidification effects of S
13 deposition, including interactions between SO_x deposition and mercury methylation in
14 ecosystems. In Annex 7, a preliminary discussion of the interactions between climate variables
15 and NO_x effects on the environment is presented. The concept and application of critical loads
16 are presented in Annex 8. In Annex 9, we present the effects of NO_x and SO_x deposition on
17 acid-driven erosion of man-made materials and structures. Finally, Annex 10 presents evidence
18 on the valuation of environmental effects of NO_x and SO_x on ecosystems as one of a number of
19 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

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

1 formation of ozone (O_3), particulate matter (PM), and other elements of photochemical smog.
2 Moreover, NO_2 is an oxidant, reacting to form other photochemical oxidants including organic
3 nitrates ($RONO_2$) like the peroxyacyl nitrates (PANs), and can react with toxic compounds like
4 the polycyclic aromatic hydrocarbons (PAHs) to form nitro-PAHs, some of which demonstrate
5 greater toxicity than either reactant alone. NO_2 and SO_2 can be also be further oxidized to the
6 strong mineral acids nitric acid (HNO_3) and sulfuric acid (H_2SO_4), respectively, thereby
7 contributing to the acidity of cloud, fog, and rain water and ambient particles.

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

16
17

18 **2.2 NITROGEN OXIDES IN THE TROPOSPHERE**

19

20 **2.2.1 Gas-Phase Chemistry**

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

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

1 the surface, NO_x emissions from elevated sources will tend to be transformed to the more
2 oxidized NO_z products before they reach the surface at some distance from the source.

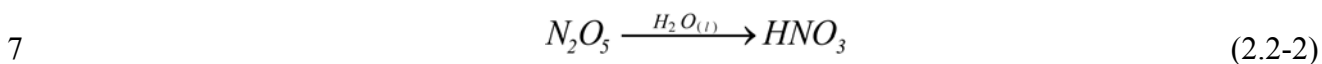
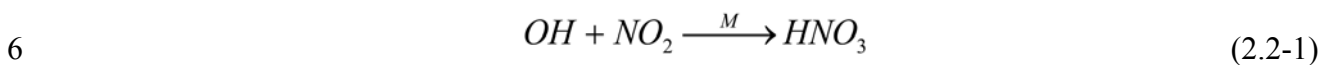
3 The concentrations ($[]$) and atmospheric lifetimes (τ) of inorganic and organic products
4 from reactions of NO_x vary widely in space and time. Inorganic reaction products include
5 nitrous acid (HNO₂), HNO₃, pernitric acid (HNO₄), and particulate nitrate (pNO₃). While a
6 broad range of organic N compounds are emitted by combustion sources (e.g. nitrosamines and
7 nitro-PAHs), they are also formed in the atmosphere from reactions of NO and NO₂. These
8 include PAN and isoprene nitrates, other nitro-PAHs, and the more-recently identified nitrated
9 quinones. By far the largest mass fractions of NO_z products shown in the outer box of Figure
10 2.2-1 are in the form of PAN and HNO₃, although other RONO₂, e.g., isoprene nitrates and
11 specific biogenic PANs can be important at locations nearer to biogenic sources (Horowitz et al.,
12 2007; Singh et al., 2007).

13 The role of NO_x in O₃ formation was exhaustively reviewed in Chapter 2, Section 2.2 of
14 the most recently published AQCD for O₃ (U.S. Environmental Protection Agency, 2006) and
15 has been presented in numerous texts (e.g., Seinfeld and Pandis, 1998; Jacob, 1999; Jacobson,
16 2002). The mechanisms for transporting the NO_x O₃ precursors, the factors controlling the
17 efficiency of O₃ production (P(O₃)) from NO_x, methods for calculating O₃ from its precursors,
18 and the methods for measuring NO_y were all reviewed in Section 2.6 of the 2006 O₃ AQCD.
19 Here we present only the salient points from that 2006 O₃ AQCD, updated where appropriate to
20 reflect new data relevant for NO_x and its ecological effects.

21 Because O₃ changes are strongly nonlinear in the concentrations of its precursors VOC
22 and NO_x, O₃ is unlike other secondarily formed atmospheric species whose rates of formation
23 vary directly with their precursor emissions. At the low [NO_x] usually found in environments
24 ranging from remote continental areas to rural and suburban areas downwind of urban centers,
25 the net P(O₃) increases with increasing [NO_x]. At the high [NO_x] found in downtown
26 metropolitan areas and especially near busy streets and roadways and in power plant plumes,
27 excess NO titrates O₃, and excess hydroxyl radicals (OH) combine with NO₂ removing them
28 from the P(O₃) chain. In this high [NO_x] regime, NO₂ scavenges OH radicals that would
29 otherwise oxidize VOCs to produce peroxy radicals (RO₂), which would in turn oxidize NO to
30 NO₂. In the low [NO_x] regime, oxidation of VOCs generates excess free radicals; hence, P(O₃)
31 varies more nearly monotonically with changes in [NO_x] there. Between these two regimes lies

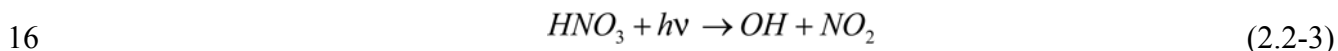
1 a transition zone in which P(O₃) and O₃ accumulation show only weak dependence on [NO_x].
2 Further explanation of these relationships appears in Annex 1.

3 The tropospheric chemical removal processes for NO_x include reaction of NO₂ with the
4 OH radical as described above and hydrolysis of dinitrogen pentoxide (N₂O₅) in aqueous aerosol
5 solutions, both producing HNO₃



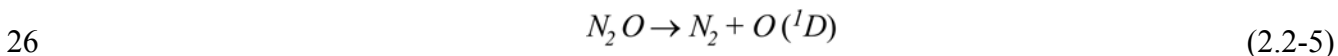
8 The gas-phase reaction of OH with NO₂ in Reaction 2.2-1 is a major removal process for NO_x in
9 the troposphere. The timescale for conversion of NO_x to HNO₃ in the planetary boundary layer
10 (PBL) at 40° N latitude ranges from ~4 h in July to ~16 h in January; at 25° N latitude, the
11 timescale is 4 to 5 h; and at 50° N latitude, from 4 to 20 h (Martin et al., 2003). Reaction 2.2-2
12 limits NO_x τ to a range of hours to days.

13 Gas-phase HNO₃ formed by Reaction 2.2-2 undergoes wet and dry deposition to the
14 surface, and uptake by ambient aerosol particles. In addition, HNO₃ photolyzes and reacts with
15 OH radicals



18 The HNO₃ τ with respect to these two reactions is long enough for HNO₃ to act as a minor
19 reservoir species for NO_x during long-range pollutant transport, contributing in this way to
20 [NO₂] after photolysis returns NO₂ as in Reaction 2.2-3, and hence to P(O₃) in areas remote from
21 the source of the NO_x that formed the original HNO₃.

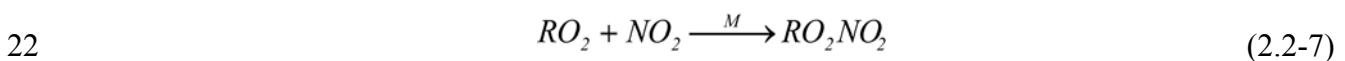
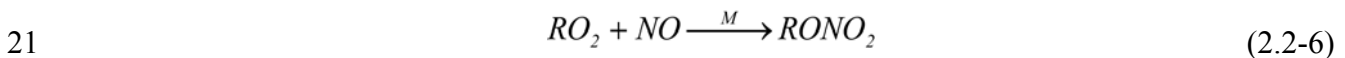
22 N₂O is another gas-phase oxide of nitrogen and has a τ of ~114 years. This long lifetime
23 results from N₂O having effectively no chemistry in the lower troposphere on urban and regional
24 scales. The chief N₂O loss pathway (with a quantum yield of ~1) is the photodissociation
25 process



1 driven by short wavelength UV present in the stratosphere. Although there are no tropospheric
2 reactions to consider, N₂O is a greenhouse gas (GHG) with a global warming potential (GWP)
3 on the conventional 100-year time horizon of ~296 – i.e., N₂O is nearly 300 times more effective
4 for trapping heat in the atmosphere than carbon dioxide (CO₂) over a 100-year period (IPCC,
5 2001a); its sources and role in the total budget of U.S. GHG are described with the emissions
6 sources of other nitrogen oxides in Chapter 3 and in Annexes 1 and 2.

7 Because N₂O has extremely low reactivity and hence a long τ in the troposphere, its
8 radiative forcing climate effects in the stratosphere can be both direct and indirect. By
9 comparison, the primary climate effects of NO and NO₂ are indirect and result from their role in
10 promoting P(O₃) in the troposphere and, to a lesser degree, lower stratosphere, where NO_x has
11 positive radiative forcing effects. Additionally, NO_x emissions from high-altitude aircraft are
12 also likely to decrease methane (CH₄) concentrations, thereby having a negative radiative forcing
13 (IPCC, 1996). EPA does not compute GWPs for NO_x, SO_x, PM, or CO because there is no
14 agreed method to estimate the contributions from these gases that are short-lived in the
15 atmosphere, have strong spatial variability, or have only indirect effects on radiative forcing
16 (IPCC, 1996).

17 A broad range of organic N compounds can be directly emitted by combustion sources or
18 formed in the atmosphere from NO_x emissions. Oxidation of VOCs produces RO₂ as discussed
19 in the O₃ AQCD (U.S. Environmental Protection Agency, 2006a). Reaction of RO₂ radicals with
20 NO and NO₂ produces RONO₂ and peroxy nitrates (RO₂NO₂)



23 Thus, formation of PANs is favored at conditions of the high ratios of NO₂ to NO most typically
24 found under low total [NO_x] conditions. The PANs are thermally labile and will photolyze back
25 to their reactants on timescales of a few hours during warm sunlit conditions, having a τ with
26 respect to thermal decomposition ranging from ~1 h at 298 K to ~2.5 days at 273 K, to several
27 weeks at 250 K. Thus, they can provide an effective sink for NO_x at cold temperatures and high
28 solar zenith angles, allowing release of NO₂ as air masses warm, in particular by subsidence.
29 The PANs are also removed by uptake to vegetation (Sparks et al., 2003; Teklemariam and
30 Sparks, 2004). To a lesser extent, HNO₃ will act in a similar way, but its high solubility and fast

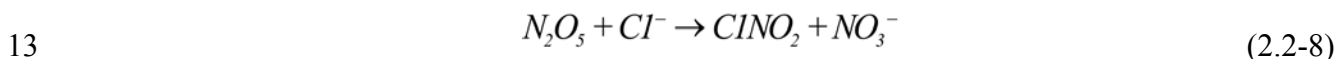
1 deposition velocity (V_d) mean that it is removed from the atmosphere by uptake onto aqueous
2 aerosols and into cloud droplets or to the surface faster than is PAN.

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

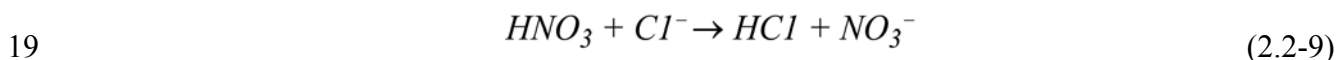
7 The RO_2NO_2 produced by Reaction 2.2-7 are unstable, with τ on the order of a few
8 minutes, owing to thermal decomposition back to the original reactants. Thus, they, too, are
9 ineffective NO_x transport vehicles or sinks.

10 11 **2.2.2 Heterogeneous-Phase Chemistry**

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

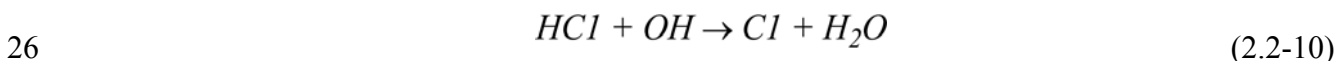


14 can also be important (Finlayson-Pitts et al., 1989; Behnke et al., 1997; Erickson et al., 1999).
15 Diatomic bromine (Br_2), bromium chloride (BrCl), diatomic chloride (Cl_2), and nitryl chloride
16 (ClNO_2) volatilize and photolyze in sunlight to produce atomic Br and Cl. The acidification of
17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

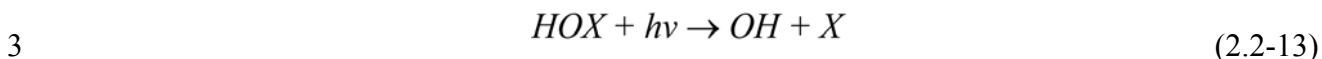
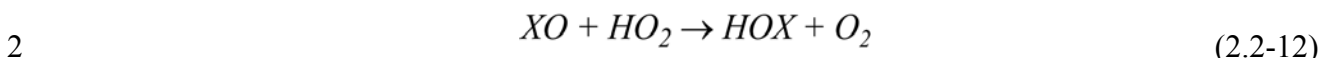
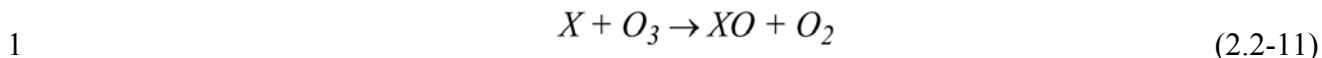


20 and the corresponding shift in phase partitioning can accelerate the deposition flux to the surface
21 of total NO_3 (Russell et al., 2003; Fischer et al., 2006). However, Pryor and Sorensen (2000)
22 have shown that the dominant phase form of NO_3 deposition is a complex function of wind
23 speed.

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



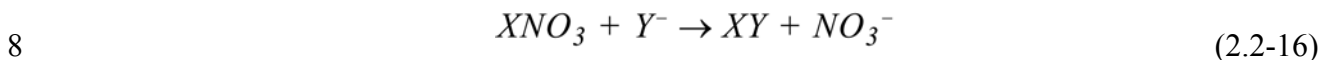
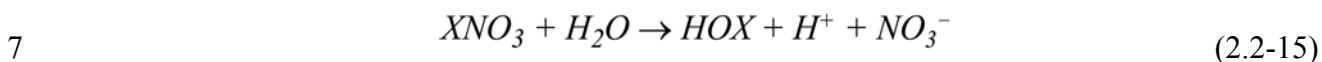
27 (Singh and Kasting, 1988; Keene et al., 2007). The Br and Cl atoms so produced then
28 catalytically destroy O_3 via



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



6 and the subsequent reaction of XNO₃ with sea salt and sulfate aerosols via



9 (where Y = Cl, Br, or I). This reaction cascade accelerates conversion of NO_x to pNO₃ and
10 thereby contributes directly to increased [pNO₃] (Sander et al., 1999; Vogt et al., 1999; Pszenny
11 et al., 2004).

12 The majority of XNO₃ reacts via Reaction 2.2-16 on sea salt while Reaction 2.2-15 is
13 more significant for particulate SO₄²⁻ (pSO₄). Product NO₃ from both reactions partitions with
14 the gas-phase HNO₃ following Henry's Law. Because most aerosol size fractions in the MBL
15 are near equilibrium with respect to HNO₃ (Erickson et al., 1999; Keene et al., 2004), both SO₄²⁻
16 and sea salt aerosol can sustain the catalytic removal of NO_x and re-activation of Cl and Br with
17 no detectable change in composition. The photolytic reduction of NO₃⁻ in sea salt aerosol
18 solutions then also recycles NO_x back to the gas phase (Pszenny et al., 2004).

19 An autocatalytic cycle involving multiphase iodine (I) chemistry also operates in the MBL
20 (Alicke et al., 1999; Vogt et al., 1999; McFiggans et al., 2000; Ashworth et al., 2002). In this
21 case, the primary source of I is believed to be either photolysis of diiodomethane (CH₂I₂), other
22 I-containing gases (Carpenter et al., 1999; Carpenter, 2003), and/or perhaps diatomic iodine (I₂)
23 (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; McFiggans, 2005) emitted by micro- and
24 macro-flora. Sea salt and pSO₄ provide substrates for multiphase reactions that sustain the
25 catalytic I-IO cycle. The iodine oxide (IO) radical has been measured by long-path and/or multi-
26 axis differential optical absorption spectroscopy (MAX-DOAS) at Mace Head, Ireland; Tenerife,

1 Canary Islands; Cape Grim, Tasmania; and coastal New England, USA. Average daytime
2 mixing ratios are on the order of 1 part per trillion (ppt) with maxima up to 7 ppt (e.g., Allan
3 et al., 2000; Pikel'naya et al., 2005). The reaction of IO with NO₂ followed by uptake of nitric
4 iodine (INO₃) into aerosols in a reaction cascade analogous to that shown in Reactions 2.2-11
5 through 2.2-16 accelerates the conversion of NO_x to pNO₃. The reaction IO + NO → I + NO₂
6 also influences NO_x cycling.

7 The studies described above considered halogen-radical chemistry and related influences
8 on NO_x cycling in coastal and urban air. However, available evidence suggests that similar
9 chemical transformations can proceed in other halogen-rich tropospheric air masses (see, e.g.,
10 Hebestreit et al., 1999; Stutz et al., 1999, 2002; Zingler and Platt, 2005; Wagner et al., 2001;
11 Hollwedel et al., 2004). The primary source of reactive halogens in these regions is thought to
12 be due to activation along the lines of Reactions 2.2-8 through 2.2-10. High concentrations of
13 bromium oxide (BrO) have also been measured in volcanic plumes (Bobrowski et al., 2003;
14 Gerlach, 2004). Although very little is known about it, the substantial emissions of inorganic
15 halogens during biomass burning (Lobert et al., 1999; Keene et al., 2006) and in association with
16 crustal dust (Keene et al., 1999; Sander et al., 2003) may also support active halogen-radical
17 chemistry and related transformations involving NO_x downwind of sources. Recent aircraft and
18 satellite observations confirm that BrO is present in the free troposphere at levels sufficient to
19 influence photochemistry significantly (see, e.g., von Glasow et al., 2004).

20
21

22 **2.3 SULFUR OXIDES IN THE TROPOSPHERE**

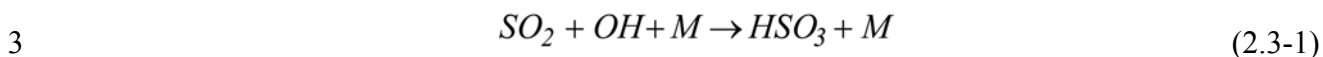
23

24 **2.3.1 General Sulfur Chemistry**

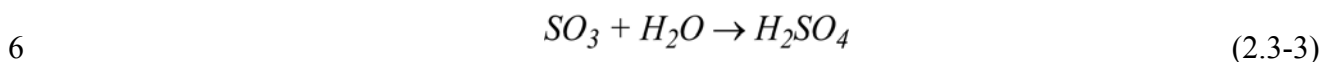
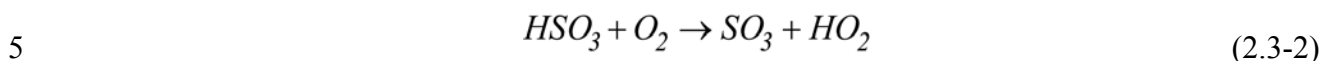
25 The four known monomeric sulfur oxides are SO, SO₂, SO₃, and S₂O. SO is formed by
26 photolysis of SO₂ at wavelengths <220 nm and so is found only in the middle and upper
27 stratosphere (Pinto et al., 1989). SO₃ can be emitted from the stacks of power plants and
28 industrial facilities; however,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

31 SO₂ can be oxidized either in the gas phase through OH attack, or, owing to its high
32 solubility, in the aqueous phase in cloud droplets; this aqueous-phase oxidation dominates

1 P(SO₄²⁻) at a ratio of ~80% (Warneck, 1999). Gas-phase oxidation of SO₂ proceeds through the
2 reaction



4 followed by



7 But because H₂SO₄ is highly soluble, it will be removed rapidly by transfer to the
8 aqueous phase of aerosol particles and cloud droplets; see the discussion in Section 2.4 below.
9 Other pathways for SO₂ oxidation, such as reaction with HO₂ or NO₃⁻ have very low rate
10 constants (JPL, 2003) and so are insignificant on urban and regional scales.

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

18 Because tropospheric OCS is relatively long-lived, it can be transported up into the
19 stratosphere. Crutzen (1976) proposed that its oxidation serves as the major source of SO₄²⁻ in
20 the stratospheric aerosol layer, sometimes called the “Junge layer” (Junge et al., 1961), during
21 periods when volcanic plumes do not reach the stratosphere. By contrast, Myhre et al. (2004)
22 proposed that SO₂ transported upwards from the troposphere is the most likely source since the
23 up-flux of OCS is too small to sustain the observed SO₄²⁻ loadings in the Junge layer. Moreover,
24 in situ measurements of the isotopic composition of S do not match those of OCS (Leung et al.,
25 2002). Reaction with NO₃ at night is the most likely major loss process for DMS and CH₃-S-H.

26 Mechanisms of the oxidation of DMS are still incompletely understood. Excess SO₄²⁻ in
27 marine aerosol is related mainly to production of SO₂ from oxidation of DMS. Initial attack by
28 NO₃⁻ and OH involves H⁺ abstraction, with a smaller branch leading to OH addition to the S

1 atom; the yield from this latter branch varies inversely with temperature and is the major
2 pathway at temperatures <285 K (Ravish Ankara et al., 1997). The adduct formed may then
3 either decompose to form methane sulfuric acid (MSA), or undergo further reactions in the main
4 pathway to yield DMS (Barnes et al., 1994). Following H+ atom abstraction from DMS, the
5 main reaction products include MSA and SO₂. The ratio of MSA to SO₂ is strongly temperature-
6 dependent, varying from ~0.1 in tropical waters to ~0.4 in Antarctic waters (Seinfeld and Pandis,
7 1998). Transformations among atmospheric S compounds are summarized in Figure 2.3-1,
8 where S(IV) represents SO₂·H₂O, HSO₃⁻, and SO₃²⁻, and S(VI) represents gas-phase SO₃ and
9 H₂SO₄ or aqueous-phase HSO₄⁻ and SO₄²⁻.

10

11 **2.3.2 Heterogeneous-Phase Production and Loss Processes**

12 Chemical transformations involving inorganic halogenated compounds effect changes in
13 the multiphase cycling of sulfur oxides in ways analogous to their effects on NO_x. Oxidation of
14 DMS by BrO produces dimethylsulfoxide (DMSO; (CH₃)₂SO) (Barnes et al., 1991; Toumi,
15 1994), and oxidation by atomic Cl leads to formation of SO₂ (Keene et al., 1996). DMSO and
16 SO₂ are precursors for methanesulfonic acid (CH₃SO₃H) and H₂SO₄. In the MBL, virtually all
17 H₂SO₄ and CH₃SO₃H vapor condenses onto existing aerosols or cloud droplets that subsequently
18 evaporate, contributing to aerosol growth and acidification. Unlike CH₃SO₃H, H₂SO₄ also has
19 the potential to produce new particles (Korhonen et al., 1999; Kumala et al., 2000); in marine air
20 masses, these are thought to be present mainly in the free troposphere. Saiz-Lopez et al. (2004)
21 estimated that observed levels of BrO at Mace Head would oxidize (CH₃)₂S ~6 times faster than
22 OH and thereby substantially increase production rates of H₂SO₄ and other condensable S
23 species in the MBL.

24 SO₂ is also scavenged by deliquesced aerosols and oxidized to H₂SO₄ in the aqueous
25 phase by several strongly pH-dependent pathways (Chameides and Stelson, 1992; Vogt et al.,
26 1996; Keene et al., 1998). Model calculations indicate that oxidation of S(IV) by O₃ dominates
27 in fresh, alkaline sea salt aerosols, whereas oxidation by hypohalous acids (primarily HOCl)
28 dominates in moderately acidic solutions. Additional non-sea salt (nss) pSO₄ is generated by
29 SO₂ oxidation in cloud droplets (Clegg and Toumi, 1998). Ion-balance calculations indicate that
30 most nss pSO₄ in short-lived sea salt size fractions (on the order of 2 to 48 h) accumulates in

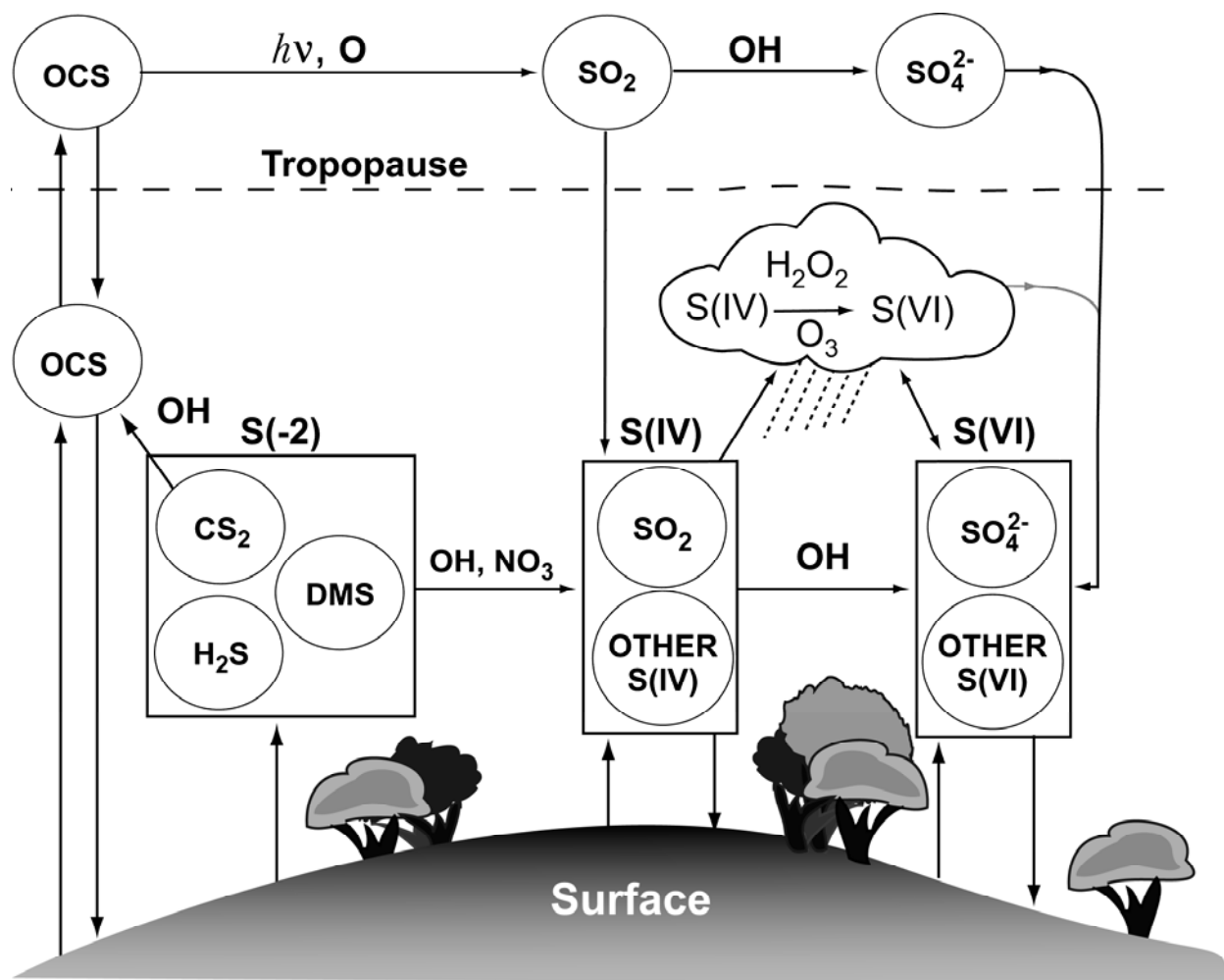


Figure 2.3-1. Transformations of sulfur compounds in the atmosphere.

Source: Adapted from Berresheim (1995).

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

3 The production, cycling, and associated radiative effects of S-containing aerosols in
4 marine and coastal air are regulated in part by chemical transformations involving inorganic
5 halogens as described above; see Glasow et al., 2002b. These transformations include:
6 dry-deposition fluxes of nss pSO₄ in marine air dominated by sea salt size fractions (Huebert
7 et al., 1996; Turekian, 2001); HCl phase partitioning that regulates sea salt pH and associated
8 pH-dependent pathways for S(IV) oxidation (Keene et al., 2002; Pszenny et al., 2004); and
9 potentially important oxidative reactions with reactive halogens for DMS and S(IV). However,

1 the absolute magnitudes and relative importance of these S cycling processes in the MBL are
2 poorly known.

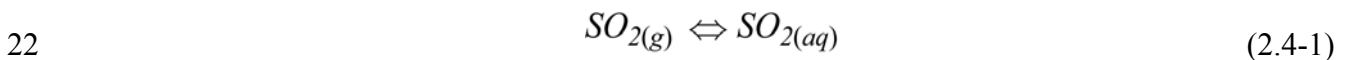
3 Iodine chemistry has been linked to ultrafine particle bursts at Mace Head (O'Dowd
4 et al., 1999, 2002). Observed bursts coincide with the elevated concentrations of IO and
5 are characterized by particle concentrations increasing from background levels to up to
6 $300,000 \text{ cm}^{-3}$ on a time scale of seconds to minutes. This newly identified source of marine
7 aerosol would provide additional aerosol surface area for condensation of SO_x and thereby
8 presumably diminish the potential for nucleation pathways involving H_2SO_4 . However, a
9 subsequent investigation in polluted air along the New England, USA, coast found no correlation
10 between periods of nanoparticle growth and corresponding concentrations of I oxides (Russell
11 et al., 2006). Thus, the potential importance of I chemistry in aerosol nucleation and its
12 associated influence on S cycling remain highly uncertain.

13
14

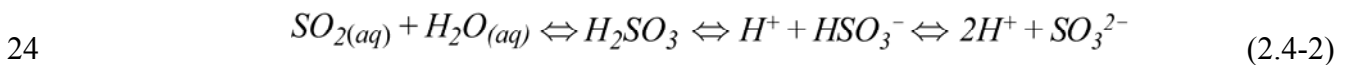
15 **2.4 AQUEOUS-PHASE FORMATION OF SULFATES AND NITRATES**

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

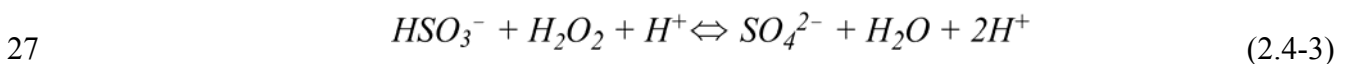
19 The basic mechanism of aqueous-phase SO_2 oxidation has long been known and is found
20 in numerous texts (see, e.g., Seinfeld and Pandis, 1998; Jacob, 2000; and Jacobson, 2002):
21 dissolution of SO_2



23 followed by formation and dissociation of H_2SO_3



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



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

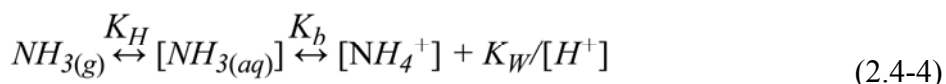
1 These major pathways for aqueous-phase oxidation of S(IV) to S(VI) as a function of pH
2 are shown in Figure 2.4-1. For pH up to ~5.3, H₂O₂ is the dominant oxidant; above 5.3, O₃ and
3 Fe(III) dominate. Marine aerosols are expected to have higher pH; however, in marine aerosols
4 the Cl-catalyzed oxidation of S(IV) may be the more significant process (Zhang and Millero,
5 1991; Hoppel and Caffrey, 2005).

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

8 NO₂ can also be taken up in cloud droplets and oxidized there to NO₃⁻; although because
9 NO₂ is much less soluble than SO₂, this pathway is of minor importance. Instead, the uptake of
10 the highly soluble N-containing acids like HNO₃ initiates the aqueous-phase chemistry of NO₃⁻
11 formation.

12 13 **2.4.1 Heterogeneous Processes and NH₃**

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



17 where K_H and K_b are the temperature-dependent Henry's Law and dissociation constants
18 for NH₃, 62 M atm⁻¹ and 1.8 × 10⁻⁵ M, respectively; and K_w is the ion product of water,
19 1.0 × 10⁻¹⁴ M (Chameides, 1984). Reaction 2.4-4 shows that for any [NH_x] in the system,
20 increasing aqueous concentrations of particulate H⁺ will shift the partitioning of NH₃ towards the
21 condensed phase. Consequently, under the more-polluted conditions characterized by higher
22 concentrations of acidic pSO₄, the ratios of gas-phase NH₃ to pNH₄ decrease (Smith et al., 2007).
23 Thus, in marine air, where aerosol acidity varies substantially as a function of particle size, NH₃
24 partitions preferentially to the more acidic sub-μm size fractions (e.g., Keene et al., 2004; Smith
25 et al., 2007).

26 Because the V_d of gas-phase NH₃ to the surface is substantially greater than that for the
27 sub-μm size fraction of pSO₄ with which most pNH₄ is associated, dry-deposition fluxes of total
28 NH₃ are dominated by the gas-phase fraction (Russell et al., 2003; Smith et al., 2007).
29 Consequently, this partitioning with highly acidic pSO₄ effectively increases the τ of total NH₃

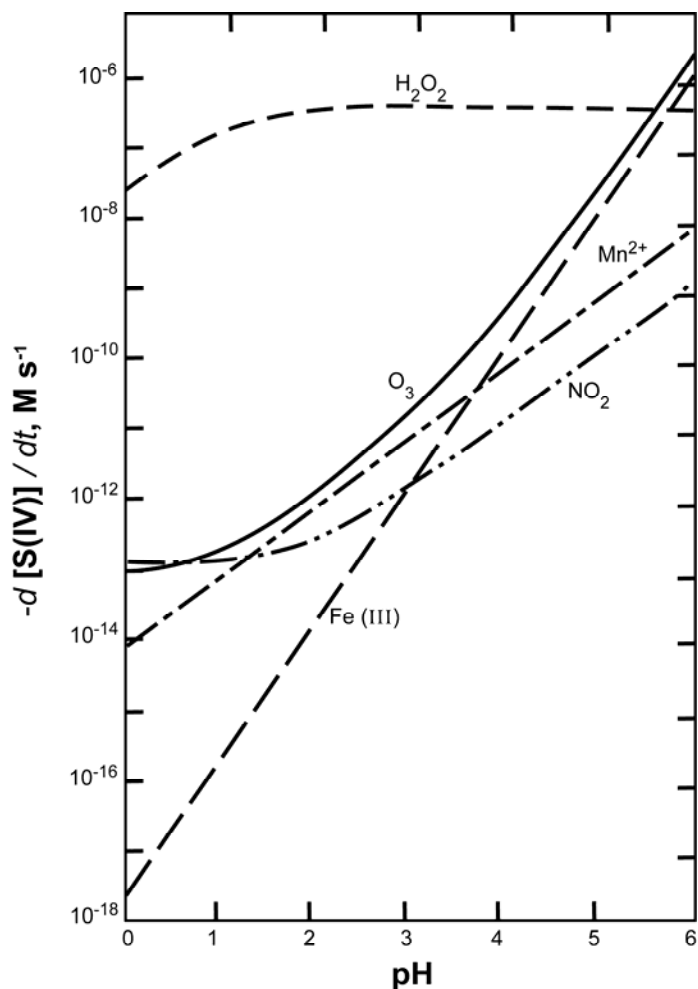


Figure 2.4-1. Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) is shown as a function of pH. Conditions assumed are: $[\text{SO}_{2(\text{g})}] = 5 \text{ ppb}$; $[\text{NO}_{2(\text{g})}] = 1 \text{ ppb}$; $[\text{H}_2\text{O}_{2(\text{g})}] = 1 \text{ ppb}$; $[\text{O}_{3(\text{g})}] = 50 \text{ ppb}$; $[\text{Fe(III)}_{(\text{aq})}] = 0.3 \text{ }\mu\text{M}$; $[\text{Mn(II)}_{(\text{aq})}] = 0.3 \text{ }\mu\text{M}$.

Source: Seinfeld and Pandis (1998).

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

3 In coastal New England during summer, for example, air transported from rural eastern
 4 Canada contains relatively low concentrations of nss pSO_4 and total NH_3 (Smith et al., 2007).
 5 Under these conditions, the roughly equal partitioning of total NH_3 between gas and aerosol
 6 phases sustains dry-deposition fluxes of total NH_3 to coastal ocean waters with a median value of
 7 $10.7 \text{ }\mu\text{mol m}^{-2} \text{ day}^{-1}$. By contrast, heavily polluted air transported from the industrialized

1 midwestern United States contains nss $[\text{SO}_4^{2-}]$ and total $[\text{NH}_3]$ that are approximately a factor of
2 3 greater than those in clean air, based on median values. Under polluted conditions, >85% of
3 total NH_3 partitions to the highly acidic pSO_4 ; consequently, the median dry-deposition flux of
4 total NH_3 is 30% lower than that under the cleaner flow regime. The relatively larger τ of total
5 NH_3 against dry deposition under more polluted conditions implies that, on average, total NH_3
6 would accumulate to higher atmospheric concentrations under these conditions and hence be
7 subject to atmospheric transport over longer distances. Consequently, the importance of NH_x
8 removal via wet deposition would also increase. Given the inherently sporadic character of
9 precipitation, greater heterogeneity in NH_3 deposition fields and in any potential responses by
10 sensitive ecosystems downwind of major S emission regions could be expected.

11
12

13 **2.5 ATMOSPHERIC TRANSPORT OF NO_x AND SO_x**

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

26 Because NO and NO_2 are only slightly soluble, they can be transported over longer
27 distances in the gas phase than can more soluble species like SO_2 which are depleted by
28 deposition to moist surfaces or taken up more readily on aqueous surfaces of particles. During
29 transport, NO and NO_2 can be transformed into the longer-lived reservoir species HNO_3 and the
30 PANs as described above. These species can then contribute to local NO_x concentrations and
31 deposition in remote areas as it is now well established that PAN decomposition provides a
32 major source of NO_2 in the remote troposphere (Staudt et al., 2003). The decomposition of PAN

1 in subsiding air masses from Asia over the eastern Pacific may also make an important
2 contribution to enhanced O₃ and NO_x concentrations in the United States (Kotchenruther et al.,
3 2001; Hudman et al., 2004). Further details about mechanisms for transporting NO_x and SO_x
4 are described Annex 1.

5 6 7 **2.6 SAMPLING AND ANALYSIS FOR NO_x AND SO_x**

8 9 **2.6.1 NO_x Measurement Methods and Associated Issues**

10 Separate sections in Annexes 1 and 2 on field-deployed measurement techniques focus on
11 current methods and promising new technologies so no attempt is made here to cover the
12 extensive development of these methods or of methods no longer in widespread use. Rather, the
13 descriptions in this chapter concern chiefly the Federal Reference Methods and Federal
14 Equivalent Methods (FRM and FEM, respectively). More detailed discussions of the FRM,
15 FEM, and other, newer methods including issues about their field use is found in U.S.
16 Environmental Protection Agency (1993a, 1996), McClenny (2000), Parrish and Fehsenfeld
17 (2000), and Clemitshaw (2004).

18 19 **2.6.1.1 NO and NO₂**

20 NO is routinely measured using the principle of gas-phase chemiluminescence induced
21 by the reaction of NO with O₃ at low pressure. However, Cardelino and Chameides (2000)
22 reported that measured [NO] during the afternoon was frequently at or below the operational
23 limit of detection (LOD), ~1 ppb, of the regulatory NO_x instruments even in large metropolitan
24 regions such as Washington, DC, Houston, TX, and New York, NY, where [NO_x] from mobile
25 sources would be high. The FRM for NO₂ also makes use of this NO detection technique using a
26 prerequisite step to reduce NO₂ to NO on the surface of a molybdenum oxide (MoO_x) substrate
27 heated to ~340 °C. Because the FRM monitor cannot detect NO₂ directly, the [NO₂] is
28 determined as the difference between the sample passed over the heated MoO_x substrate (the
29 nitrogen oxides total) and the sample not so reduced (the NO alone). However, reduction of NO₂
30 to NO on the MoO_x substrate is not specific for NO₂; hence, chemiluminescence monitors are all
31 subject to unknown and varying interferants in the sample from other oxidized N compounds,
32 i.e., species of NO_z; see the outer box elements in Figure 2.2-1 above.

1 Interference by NO_Z compounds has long been known (Fehsenfeld et al., 1987; Rodgers
2 and Davis, 1989; U.S. Environmental Protection Agency, 1993a, 2006; Crosley, 1996;
3 Nunnermacker et al., 1998; Parrish and Fehsenfeld, 2000; McClenny et al., 2002; Dunlea et al.,
4 2007). The sensitivity of the MoO_X instrument to interference from multiple NO_Z compounds is
5 highly variable and dependent in part on instrument inlet design, on the temperature of the
6 reducing substrate, and on the interactions of species with MoO_X. Because of losses on inlet
7 surfaces and differences in the efficiency of reduction of NO_Z compounds on the heated MoO_X
8 substrate, NO_X as reported from these instruments cannot be considered as a universal surrogate
9 for NO_Y. However, in settings close to relatively high-concentration fresh emissions like those
10 in urban areas during rush hour, most of the NO_Y is present as NO_X. Additional details on this
11 interference and descriptions of methods other than chemiluminescence are given in Annex 1.

12

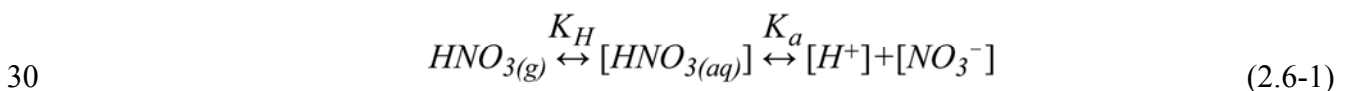
13 **2.6.2 Total and Speciated NO_Y**

14 Gold-catalyzed CO or H₂ reduction or conversion on heated MoO_X have been used to
15 reduce total NO_Y to NO before detection by chemiluminescence (Fehsenfeld et al., 1987;
16 Crosley, 1996). Both techniques offer generally reliable measurements, with response times on
17 the order of 60 s and a linear dynamic range demonstrated in field intercomparisons from ~10
18 ppt to 10s of ppb. Under some conditions, hydrogen cyanide (HCN), NH₃, alkyl nitrates
19 (RNO₂), and acetonitrile (CH₃CN) can be converted to NO; but at normal concentrations and
20 humidity, these are minor interferants. Thermal decomposition followed by laser-induced
21 fluorescence (LIF) has also been used for NO_Y detection, and this is described in more detail in
22 Annex 1. In field comparisons, instruments based on these two principles generally showed
23 good agreement (Day et al., 2002) with experimental uncertainty estimated to be on the order of
24 15 to 30%.

25

26 **2.6.2.1 HNO₃**

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



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

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

18 Methods used widely for measuring HNO_3 include standard filterpacks configured with
19 nylon or alkaline-impregnated filters (see, e.g., Goldan et al., 1983; Bardwell et al., 1990),
20 annular denuders like EPA method IP-9, and standard mist chambers (see Talbot et al., 1990).
21 Samples from these instruments are typically analyzed by ion chromatography.
22 Intercomparisons of these measurement techniques by Hering et al. (1988), Tanner et al. (1989),
23 and Talbot et al. (1990) reported differences on the order of a factor of 2 or more. In part, this
24 variance is due to nonsystematic sampling error. When chemically distinct aerosols with
25 different pHs, for example, sea salt and pSO_4 , mix together on a bulk filter, the acidity of the
26 bulk mixture will be greater than that of the less-acidic aerosols with which most of the NO_3^- is
27 associated. This change in pH may cause the bulk mix to be supersaturated with respect to
28 HNO_3 leading to volatilization and, thus, to a positive measurement bias in HNO_3 sampled
29 downstream. Alternatively, when undersaturated super- μm size fractions like sea salt
30 accumulate on a bulk filter and chemically interact over time with HNO_3 in the sample air
31 stream, scavenging may lead to a negative bias in the HNO_3 sampled downstream. Because the

1 magnitude of both effects will vary as functions of the overall composition and thermodynamic
2 state of the multiphase systems, the combined influence can cause net positive or net negative
3 measurement bias in data with unknown frequencies. Pressure drops across particle filters can
4 also lead to artifact volatilization and associated positive bias in $[\text{HNO}_3]$ measured downstream.

5 Recently, sensitive HNO_3 measurements based on the principle of chemical ionization
6 mass spectroscopy (CIMS) have been reported; see, e.g., Huey et al. (1998), Mauldin et al.
7 (1998), Furutani and Akimoto (2002), and Neuman et al. (2002). The CIMS relies on selective
8 formation of ions such as $\text{SiF}_5^- \cdot \text{HNO}_3$ or $\text{HSO}_4^- \cdot \text{HNO}_3$ followed by detection via mass
9 spectroscopy. Two CIMS techniques and a filter pack technique were intercompared in Boulder,
10 CO (Fehsenfeld et al., 1998). Results indicated agreement to within 15% between the two CIMS
11 instruments and between the CIMS and filterpack methods under relatively clean conditions with
12 HNO_3 mixing ratios between 50 and 400 ppt. In more polluted air, the filterpack technique
13 generally yielded higher values than the CIMS, suggesting that interactions between chemically
14 distinct particles on bulk filters is a more important source of bias in polluted continental air.
15 Differences were also greater at lower temperature when pNO_3 corresponded to relatively greater
16 fractions of total NO_3 .

17 A recent large field intercomparison of different techniques for HNO_3 measurement was
18 conducted in Tampa, FL in 2003 (Arnold et al., 2007) using the annular denuder + filter pack
19 time-integrated method and three semi-continuous techniques: two different implementations of
20 the $\text{NO}_Y - \text{NO}_Y^*$ denuder difference technique (Joseph and Spicer, 1978); the parallel plate wet
21 diffusion scrubber + online ion chromatography method (Boring et al., 2002); and the CIMS
22 (Huey et al., 1998). Results for 10 min aggregates computed from the various higher sampling
23 frequencies of each semi-continuous instrument showed good agreement ($R^2 > 0.7$) for afternoon
24 periods of highest production and accumulation of HNO_3 . Further, agreement was within $\pm 30\%$
25 even at $[\text{HNO}_3] < 0.30$ ppb, although the 12-h and 24-h time-integrated denuder + filterpack
26 measurements were substantially in error. This study also confirmed the importance of sample
27 inlet height for HNO_3 monitoring through comparison to previous field work at this and other
28 sites where inlet height ranged from 1.5 to 10 m, producing systematic discrepancies in measured
29 $[\text{HNO}_3]$ of more than a factor of 2 correlated with height. The correlation of this concentration
30 discrepancy with inlet height is governed by HNO_3 's very fast V_d , which is essentially at the
31 limit of aerodynamic resistance.

1 **2.6.2.2 Other Nitrates**

2 Methods for sampling and analysis of RONO₂ in the atmosphere have been reviewed
3 by Parrish and Fehsenfeld (2000). PAN, PPN, and MPAN are typically measured using a gas
4 chromatograph followed by electron capture detectors (GC-ECD) (see, e.g., Gaffney et al.,
5 1998), although other techniques such as Fourier Transform InfraRed (FTIR) analysis can
6 also be used. Field measurements made using GC-ECD have reported a total uncertainty of
7 ±5 ppt + 15% (Roberts et al., 1998).

8 In the two most extensive networks in the United States, the Interagency Monitoring of
9 Protected Visual Environments (IMPROVE) and the Speciation Trends Network (STN) – see
10 additional description of these networks in Chapter 3 and Annex 2 – pNO₃ in the ≤2.5 μm
11 (PM_{2.5}) size fraction is typically collected on nylon filters downstream of annular denuders
12 coated with a basic solution to remove acidic gases such as HNO₃, HNO₂, and H₂SO₄. Filter
13 extracts are then analyzed by ion chromatography (IC) for NO₃⁻, SO₄²⁻, and Cl⁻. NO₂⁻ ions are
14 also measured by this technique but their concentrations are almost always below operation
15 LODs. However, both networks measure NO₃⁻ only in the PM_{2.5} fraction. Because of
16 interactions with more highly acidic components on filter surfaces, there can be volatilization of
17 NO₃⁻ in PM₁₀ samples. These effects are minimized if separate aerosol size fractions are
18 collected; i.e., by separating the more acidic PM_{2.5} and the more alkaline PM_{10-2.5} as is done in a
19 dichotomous sampler or multistage impactor.

20

21 **2.6.2.3 Remote Sensing of Tropospheric NO₂ Columns**

22 The paucity of in situ NO₂ measurements motivates development of new techniques to
23 infer surface [NO₂] from satellite measurements of tropospheric total column [NO₂]. These total
24 column [NO₂] have been shown to have a strong correlation with in situ [NO₂] when evaluated in
25 northern Italy (Ordonez et al., 2006). Table 2.6-1 contains an overview of the three satellite
26 instruments used to retrieve total column [NO₂] from measurements of solar backscatter.

27 Figure 2.6-1 shows total column [NO₂] retrieved from the Scanning Imaging
28 Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument on the
29 European ENVISAT satellite. Pronounced [NO₂] enhancements are evident in Figure 2.6-1 over
30 major urban and industrial emission centers. The high degree of spatial heterogeneity over the
31 southwestern United States provides empirical evidence that most of the total column [NO₂] is

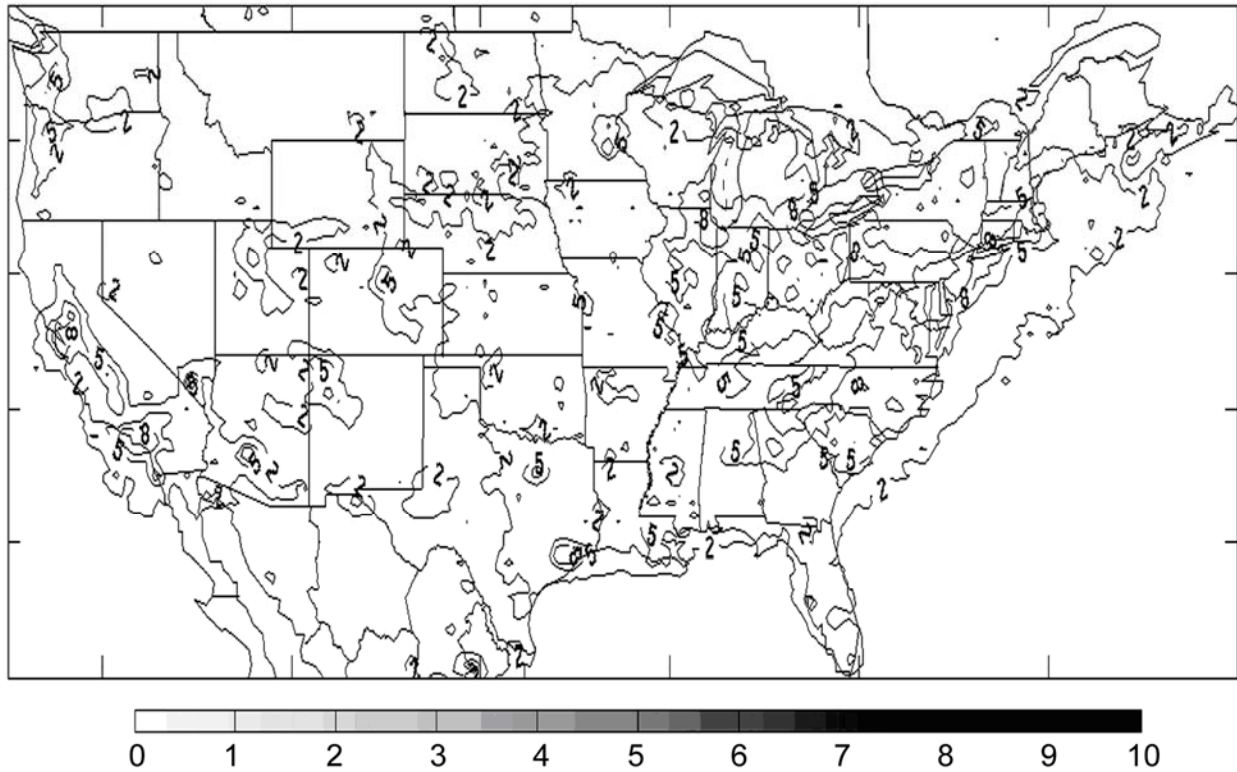


Figure 2.6-1. Tropospheric total column [NO₂] (molecules NO₂ cm⁻²) retrieved from the SCIAMACHY satellite instrument for 2004-2005.

Source: Martin et al. (2006).

1 concentrated in the lower troposphere. These total column [NO₂] are more sensitive to NO_x in
 2 the lower troposphere than in the upper troposphere (Martin et al., 2002) because the NO₂/NO
 3 ratio is lower by a factor of 25 aloft relative to the surface, a difference driven by the temperature
 4 dependence of the NO + O₃ reaction. Martin et al. (2004a) integrated in situ airborne
 5 measurements of NO₂ and found that during summer the lower mixed layer contains 75% of the
 6 total column [NO₂] over Houston and Nashville. However, it should be noted that while
 7 certainly useful, the satellite measurements are very sensitive to surface albedo and aerosol
 8 loading and have considerable restrictions on timing and location.

9

10 **2.6.3 SO_x Measurement Methods and Associated Issues**

11 Currently, ambient SO₂ is measured using instruments based on pulsed UV fluorescence.
 12 The UV fluorescence monitoring method for atmospheric SO₂ was developed to improve upon

1 the flame photometric detection (FPD) method, which in turn had displaced the pararosaniline
2 wet chemical method. Although the pararosaniline method remains the EPA FRM for
3 atmospheric SO₂, it is rarely used because of its complexity and slow response, even in its
4 automated forms. Both the UV fluorescence and FPD methods are designated as FEMs by EPA,
5 but UV fluorescence has largely supplanted the FPD approach because of the UV method's
6 inherent linearity and sensitivity, and the need for consumable hydrogen gas for the FPD method.

7 The LOD for a non-trace-level SO₂ analyzer is 10 ppb (CFR, 2006). However, most
8 commercial analyzers report operational detection limits of ~3 ppb. This concentration is very
9 near the current ambient annual average [SO₂] of ~4 ppb; see the fuller description of
10 concentrations and variations in Chapter 3. The EPA-sponsored National Core Monitoring
11 Network (NCore) is intended to operate newer, trace-level SO₂ instruments to increase the
12 accuracy and precision of measurements at the much lower ambient levels currently encountered
13 in most of the United States.

14 15 **2.6.3.1 Sources of Interference**

16 The most common interferants for the UV fluorescence method for SO₂ are other gases
17 that fluoresce like SO₂. Luke (1997) reported the positive artifacts of a modified pulsed
18 fluorescence detector generated by the coexistence of NO, CS₂, and a number of highly
19 fluorescent aromatic hydrocarbons such as benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene,
20 *m*-ethyltoluene, ethylbenzene, and 1,2,4-trimethylbenzene. Consequently, any such
21 hydrocarbons in the sample in the optical chamber can act as a positive interferant. To remove
22 this source of interference, high-sensitivity SO₂ analyzers like those to be used in the NCore
23 network have hydrocarbon scrubbers to remove these compounds from the sample stream before
24 the sample air enters the optical chamber.

25 Nonradiative deactivation (quenching) of excited SO₂ molecules can occur from
26 collisions with common molecules in air, including N₂, O₂, and H₂O. During collisional
27 quenching, the excited SO₂ molecule transfers energy, kinetically allowing the SO₂ molecule to
28 return to the original lower energy state without emitting a photon. Collisional quenching results
29 in a decrease in the SO₂ fluorescence and, hence, an underestimation of [SO₂]. Of particular
30 concern is the variable water vapor content of air. Luke (1997) reported that the response of the
31 detector could be reduced by ~7 and 15% at water vapor mixing ratios of 1 and 1.5 mole percent,
32 respectively.

1 Other techniques for SO₂ and other issues in their field deployment are described in
2 Annex 1.

3 4 **2.6.4 Sampling and Analysis for SO₄²⁻, NO₃⁻, and NH₄⁺**

5 SO₄²⁻, NO₃⁻, and NH₄⁺ are commonly present in PM_{2.5}. The common techniques for
6 sampling for these compounds uses air drawn through the sample filter at a controlled flow rate
7 by a pump located downstream of the sample filter. The systems generally have two critical
8 flow-rate components for the capture of fine particulate: (1) the flow of air through the sampler
9 must be at a flow rate that ensures the 2.5 μm size cut; and (2) the flow rate must be optimized to
10 capture the desired amount of particulate loading with respect to the analytical method LODs.

11 When using the technique described above to collect pSO₄, pNO₃, and pNH₄, sampling
12 artifacts can occur principally for two reasons similar to those described for HNO₃ above:
13 (1) positive sampling artifacts for all three species due to chemical reactions on the filter face;
14 and (2) negative sampling artifacts for NO₃ and NH₄⁺ due to decomposition and evaporation
15 after capture on the filter.

16 17 **2.6.4.1 Denuder + Filter-Based Techniques**

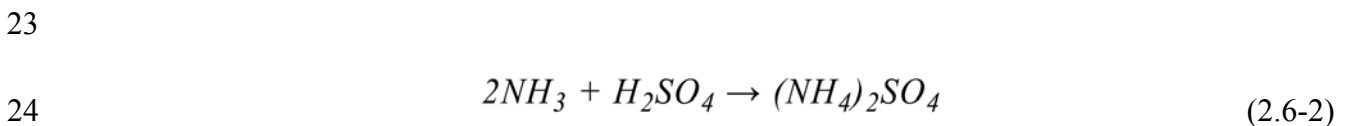
18 The STN and IMPROVE networks implement this general technique with somewhat
19 different instruments and protocols. Current STN samplers include three filters: (1) Teflon for
20 equilibrated mass and elemental analysis including elemental S; (2) a HNO₃-denuded nylon filter
21 for ion analysis including NO₃⁻ and SO₄²⁻; and (3) a quartz-fiber filter for elemental and organic
22 carbon (EC and OC, respectively), analyzed using the thermal-optical reflectance (TOR) method.
23 The IMPROVE sampler, which collects two 24-h samples each week, simultaneously collects
24 one sample of particulate matter ≤ 10 μm (PM₁₀) on a Teflon filter, and three samples of PM_{2.5} on
25 Teflon, nylon, and quartz filters as STN does. In each network, total mass concentrations of
26 PM_{2.5} are determined gravimetrically from the PM_{2.5} Teflon filter samples, which are also used
27 to determine concentrations of selected individual elements. The STN and IMPROVE networks
28 represent a major advance in the measurement of pNO₃, because the combination of a denuder
29 coated with either sodium carbonate (Na₂CO₃) or magnesium oxide (MgO) to remove HNO₃
30 vapor and a nylon filter to adsorb HNO₃ vapor volatilizing from the collected NH₄NO₃ particles
31 overcomes the loss of NO₃⁻ from Teflon filters.

1 In a side-by-side comparison of two of the chief aerosol monitoring techniques, PM_{2.5}
2 mass and major contributing species were well correlated among the different methods with
3 $r > 0.8$ (Hains et al., 2007). Agreement was good for total mass, SO₄²⁻, OC, total carbon (TC),
4 and NH₄⁺, while NO₃⁻ and black carbon (BC) showed less-good fits. Based on reported
5 uncertainties, however, even daily concentrations of PM_{2.5} mass and major contributing species
6 were often significantly different at the 95% confidence level. The STN methods reported
7 generally higher values of PM_{2.5} total mass and of individual species than did the IMPROVE-like
8 ones. Since these differences can only be partially accounted for by known random errors, the
9 authors concluded that the current uncertainty estimates used in the STN network may
10 underestimate the actual uncertainty.

11
12 **2.6.4.1.1 Sampling Artifacts**

13 The reaction of SO₂ and other acid gases with basic sites on glass fiber filters or with
14 basic coarse particles on the filter leads to the formation of nonvolatile pSO₄, pNO₃, and Cl salts.
15 These positive artifacts lead to the overestimates of the concentrations of PM total mass and
16 SO₄²⁻ and likely NO₃⁻ as well. These problems were largely overcome by changing to quartz
17 fiber or Teflon filters and by the separate collection of the PM_{2.5} fraction. However, the possible
18 reaction of acidic gases with basic coarse particles remains a possibility, especially with PM₁₀
19 and PM_{10-2.5} measurements. These positive artifacts could be effectively eliminated by
20 removing acidic gases in the sampling line with denuders coated with NaCl or Na₂CO₃.

21 Positive sampling artifacts also occur during measurement of pNH₄. The reaction of NH₃
22 with acidic particles, as for example



25 either during sampling or during transportation, storage, and equilibration could lead to an
26 overestimation of pNH₄ concentrations. Techniques have been developed to overcome this
27 problem, including using a denuder coated with hydrofluoric, citric, or phosphoric acid to remove
28 NH₃ during sampling and to protect the collected PM from NH₃ (Suh et al., 1992, 1994; Brauer
29 et al., 1991; Koutrakis et al., 1988a,b; Keck and Wittmaack, 2006; Possanzini et al., 1999;
30 Winberry et al., 1999). Positive artifacts for pNH₄ can also develop during sample handling due
31 to contamination. NH₃ emitted directly from human sweat, breath, and tobacco smoking will

1 react with acidic aerosols on the filter to form $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and NH_4NO_3 if the filter is
2 improperly handled (Sutton et al., 2000).

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

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

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

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

3 Negative sampling artifacts due to decomposition and volatilization are also significant
4 for pNH₄. Ammonium particles are very sensitive to environmental factors such as temperature,
5 relative humidity, acidity of aerosols, as well as to filter type (Spurny, 1999; Keck and
6 Wittmaack, 2005). Any change in these parameters during the sampling period influences the
7 position of the equilibrium between the particle and gas phases. Keck and Wittmaack (2005)
8 observed that at temperatures below 0 °C, acetate-nitrate, quartz fiber, and Teflon filters could
9 properly collect pNH₄, NH₃, and Cl; but at temperatures > 0 °C, the salts were lost from quartz
10 fiber and Teflon filters, more so at higher temperatures and with no significant difference
11 between quartz fiber and Teflon filters. The salts were lost completely from denuded quartz
12 fiber filters at temperatures above ~20 °C, and from non-undened quartz fiber and Teflon
13 filters at temperatures above ~25 °C. It is anticipated that current sampling techniques
14 underestimate [pNH₄] due to volatilization, but fine particle mass contains many acidic
15 compounds, and, as consequence, a fraction of volatilized NH₄⁺ in the form of NH₃ can be
16 retained on the Teflon filter by reactions with them. Therefore, it is reasonable to assume that
17 the magnitude of pNH₄ loss, while uncertain because of these positive and negative effects, will
18 be somewhat less than that for total pNO₃ loss. Techniques have been applied to pNH₄ sampling
19 to correct its concentrations due to evaporation using a backup filter coated with hydrofluoric
20 acids, citric acid, or phosphorous acids to absorb the evaporated NH₄ as NH₃; total [NH₄] then is
21 the sum of the pNH₄ collected on the Teflon filter and [NH₃] collected on the backup filter.

22
23

24 **2.7 SUMMARY**

25

26 **2.7.1 Significant Chemical Species**

27 NO_x is the category label for oxides of nitrogen that includes a range of chemical species,
28 chief among which are NO, NO₂, HNO₃, and PAN in the gas phase, and particulate nitrate pNO₃
29 in the particulate phase. Some of these species are directly emitted; others are formed as
30 secondary products from the emitted species.

1 SO_x is the category label for oxides of sulfur including SO, SO₂, SO₃, and S₂O, though
2 only SO₂ is present in concentrations relevant for atmospheric chemistry and ecological
3 exposures.

4 Aqueous oxidation dominates production of SO₄²⁻ from SO₂; gas-phase oxidation is
5 responsible for only ~20% of the SO₄²⁻ total. By contrast, there is little aqueous-phase oxidation
6 of NO₂ to NO₃⁻ owing to its low solubility.

7 NH₃ and NH₄⁺ (the category label is NH_x) play significant roles in controlling SO₂
8 oxidation by neutralizing acidity on particles and in cloud, fog, and rain water, and in
9 determining the range and extent of N deposition both in themselves as reduced N and through
10 combining to form NH₄NO₃.

11 Oxidation of NH₃ is a minor source of total NO_x.

12 Excess NH₃ is an actor alone and with NO_x in the N cascade leading to nitrification in
13 aquatic and terrestrial ecosystems.

14 N₂O is a constituent oxide of nitrogen having effectively no chemical or ecological
15 effects in the troposphere, thus giving it an atmospheric lifetime of ~114 yr. N₂O is also a GHG
16 with a GWP on the standard 100-year basis of ~296 times that of CO₂.

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

20 21 **2.7.2 Field Sampling and Analysis**

22 Techniques for routine regulatory monitoring of gas-phase NO_x and SO₂ are adequate but
23 have important limitations. Routine NO₂ measurements by chemiluminescence (the FRM) are
24 contaminated by unknown and varying concentrations of NO_z. SO₂ measurements by the FRM
25 in the standard regulatory network are now mostly at or below the instrument's operating LOD
26 (~4 ppb), producing irresolvable uncertainty in these data.

27 Routine field sampling techniques for NH₃ are at present limited to integrated values over
28 periods from several days to one week because higher frequency semi-continuous methods are
29 not yet sufficiently robust to deploy widely.

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

4 Despite the aforementioned limitations, for the purposes of identifying and quantifying
 5 the atmospheric concentrations and deposition totals causing ecological effects, these
 6 measurement techniques and sampling frequencies are fully adequate. Nevertheless, the
 7 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

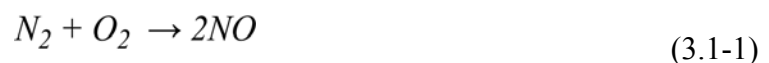
Estimated annual emissions of nitrogen oxides (NO_x), sulfur oxides (SO_x), and ammonia (NH₃) for 2002 (U.S. Environmental Protection Agency, 2006a) are given in Annex Table AX2-1; methods for estimating these emissions, quality assurance procedures, and examples of calculated emissions are given in 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 NH₃ and ammonium (NH₄⁺). (The category label for NH₃ and NH₄⁺ 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

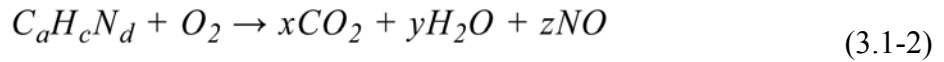
3.1.1 Anthropogenic Sources of NO and NO₂

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 N₂



Below this temperature NO can be formed from fuel N by



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 (HO₂), and molecular oxygen (O₂).

3.1.2 Biogenic Sources of NO and NO₂

3.1.2.1 Soils

The pathways for nitrification and denitrification include two gas-phase intermediates, nitric oxide (NO) and nitrous oxide (N₂O) that can evolve from soil microbes before reaching the reaction endpoint, N₂. NO from soil metabolism is the dominant, but not exclusive, source of atmospheric NO_x from the biosphere. As noted below, present understanding of NO₂ exchange with vegetation suggests that there should be emission of NO₂ from foliage when ambient concentrations are less than the compensation point of ~1 part per billion (ppb). However, Lerdaу 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 NO₂ emission were important when atmospheric concentrations were below that compensation point.

Temperature, soil moisture, and [O₂] control the rates of reaction and, more importantly, the partitioning between NO and N₂O. In flooded soils where oxygen levels are low, N₂O is typically the dominant soil N gas; as soils dry, allowing more O₂ 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 Kinglerlee, 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, N₂O, N₂, have different chemical reactivities in different regions of the atmosphere. NO is a key precursor for formation of ozone (O₃) in the troposphere. Although N₂ is not reactive in the troposphere, N₂O is a greenhouse gas (GHG) with a significant global warming potential (GWP) from its direct radiative forcing and from its

1 role in production and destruction of O₃ in the stratosphere. Additional details on these
2 reactivities are given in Chapter 2 and in Annex 1.

3 Emission rates of NO from cultivated soils depend chiefly on fertilization levels and soil
4 temperature. Production of NO from agriculture results from both the oxidation of NH₃ emitted
5 by livestock and from soils after fertilization with ammonium nitrate (NH₄NO₃) and other
6 exogenous sources of N. Estimates of these biogenic N emissions are less certain than those for
7 anthropogenic sources. On a global scale, the contribution of soil emissions to the NO_x budget
8 is on the order of 10% (van Aardenne et al., 2001; Finlayson-Pitts and Pitts, 2000; Seinfeld and
9 Pandis, 1998). On finer, more regional scales, however, NO_x emissions from fertilized fields
10 can demonstrate wide variation around this value.

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

19

20 **3.1.2.2 Biomass Burning**

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

1 **3.1.2.3 Lightning**

2 Annual global production of NO by lightning is the most uncertain source of reactive N.
3 In the last decade, literature values of the global average production rate range from 2 to 20 Tg N
4 per year. However, most recent estimates are in the range of 3 to 8 Tg N per year. Estimates of
5 the [NO] produced per flash have been made from theoretical considerations (e.g., Price et al.,
6 1997); laboratory (e.g., Wang et al., 1998) and field experiments (e.g., Stith et al., 1999;
7 Huntrieser et al., 2002); and through a combination of cloud-resolving model simulations,
8 observed lightning flash rates, and measurements of [NO] in cloud anvils (e.g., DeCaria et al.,
9 2000, 2005; Ott et al., 2007). The last method was used by Pickering et al. (1998), to show that
10 only ~5 to 20% of the total [NO] produced by lightning in a given storm exists in the planetary
11 boundary layer (PBL) at the end of a thunderstorm, thereby reducing its importance as an
12 emissions source on regional or smaller scales.

13 **3.1.3 Anthropogenic and Biogenic Sources of N₂O**

14 N₂O, a gas-phase oxide of nitrogen with an atmospheric lifetime (τ) of ~114 years, is a
15 small contributor to the total U.S. GHG budget, accounting for 6.5% of total GHG (on a Tg
16 carbon dioxide (CO₂) equivalents basis) in 2005 (U.S. Environmental Protection Agency,
17 2007b). CO₂, for comparison, accounted for 83.9% in the same year and methane (CH₄) for
18 7.4% (U.S. Environmental Protection Agency, 2007b). Together with N₂O, these are the three
19 largest GHG emissions components in the United States. Although the atmospheric [N₂O] has
20 increased globally by ~18% to its current value of ~315 ppb owing to Western industrialization
21 since 1750 (IPCC, 2001a; Hofmann, 2004), there is considerable interannual variation in N₂O
22 emissions and this remains largely unexplained (IPCC, 2001b). N₂O emissions in the United
23 States, for example, decreased by 2.8% or 13.4 Tg CO₂ equivalents over the years 1990-2005
24 (U.S. Environmental Protection Agency, 2007b).

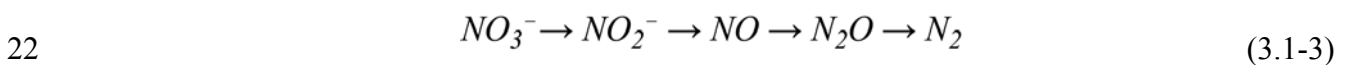
25 N₂O is produced by biological processes occurring in the soil and water as described
26 above and by a variety of anthropogenic activities in the agricultural, energy, industrial, and
27 waste management sectors. The chief anthropogenic activities producing N₂O in the United
28 States are agricultural soil management, fuel combustion in motor vehicles, manure
29 management, production of adipic acid (nylon) and nitric acid (HNO₃), wastewater treatment,
30

1 and stationary fuel combustion. N₂O emissions from these anthropogenic activities in the United
2 States were 468.7 Tg CO₂ equivalent in 2005 (U.S. Environmental Protection Agency, 2007b).

3 In 2005, N₂O emissions from mobile sources were 38.0 Tg CO₂ equivalents, or ~8% of
4 the U.S. N₂O emissions total (U.S. Environmental Protection Agency, 2007). From 1990 to
5 2005, N₂O emissions from mobile sources decreased by 13%; however, emissions increased by
6 10% in the period 1990-1998 due to control technologies that reduced on-road vehicle NO_x
7 emissions at the expense of increasing N₂O emissions. Since 1998, newer controls have led to a
8 steady decline in N₂O from mobile sources.

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

14 Biogenic N₂O emissions are predominately the result of incomplete bacterial
15 denitrification and nitrification processes that occur in soils, sediments, and water.
16 Denitrification is a reduction process performed by particular groups of heterotrophic bacteria
17 having the ability to use nitrate (NO₃⁻) as an electron acceptor during anaerobic respiration,
18 thereby converting NO₃⁻ in soils and water to gas-phase N forms (Firestone and Davidson,
19 1989). At low [O₂], these microbial communities may use NO₃⁻, nitrite (NO₂⁻), or N₂O as
20 alternative electron acceptors to O₂, with molecular N₂ as the final product in this reaction
21 sequence (Davidson and Schimel, 1995).



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

28 Emissions of NO and N₂O can be increased by agricultural practices and activities,
29 including use of synthetic and organic fertilizers, production of N-fixing crops, cultivation of
30 soils with high organic content, and the application of livestock manure to croplands and pasture.

1 All of these practices directly add N to soils, of which a portion may then be converted to N₂O
2 on the pathway to full conversion to N₂ as in Reaction 3.1-3. Indirect additions of N to soils can
3 also result in N₂O emissions from agricultural and non-agricultural systems. Indirect additions
4 include processes by which atmospheric NO_x is deposited directly to a region, or N from applied
5 fertilizer or manure volatilizes into NH₃ and NO_x, and then is ultimately re-deposited onto the
6 soil in the form of NH₄NO₃, HNO₃, and NO_x (U.S. Environmental Protection Agency, 2006a).

7 Aquatic sources of N₂O may also be stimulated by environmental conditions. In some
8 ocean areas, large areas of surface water can become depleted in O₂, allowing active
9 denitrification in open water. Oceanic N₂O can also arise from denitrification in marine
10 sediments, particularly in nutrient-rich areas like estuaries.

11 12 13 **3.2 SO_x EMISSIONS**

14 Emissions of sulfur dioxide ((SO₂), the chief component of SO_x; see the full description
15 in Chapter 2) are due mainly to the combustion of fossil fuels by electrical utilities and other
16 industries; transportation-related sources make only a very minor contribution (see Annex Table
17 AX2-1). As a result, most SO₂ emissions originate from elevated point sources. Since S is a
18 volatile component of fuels, it is released almost quantitatively during combustion; thus,
19 emissions can be calculated on the basis of the S content of fuels to greater accuracy than they
20 can be for other pollutants such as NO_x or primary particulate matter (PM), for example.

21 SO₂ data collected from the State and Local Air Monitoring Stations (SLAMS) and
22 National Air Monitoring Stations (NAMS) networks show that the decline in SO₂ emissions
23 following controls placed on electric generating utilities in the previous 15 years has improved
24 air quality. There has not been a single monitored exceedance of the SO₂ annual ambient air
25 quality standard in the United States since 2000, according to the EPA Acid Rain Program
26 (ARP) 2005 Progress Report (U.S. Environmental Protection Agency, 2006b). EPA's trends
27 data (www.epa.gov/airtrends) reveal that the national composite average SO₂ annual mean
28 ambient concentration decreased by ~48% from 1990 to 2005, with the largest single-year
29 reduction coming in 1994-1995, the ARP's first operating year (U.S. Environmental Protection
30 Agency, 2006b). Figure 3.2-1 depicts data for SO₂ emissions in the continental United States
31 (CONUS) in these years that reflect this reduction using individual state-level totals.

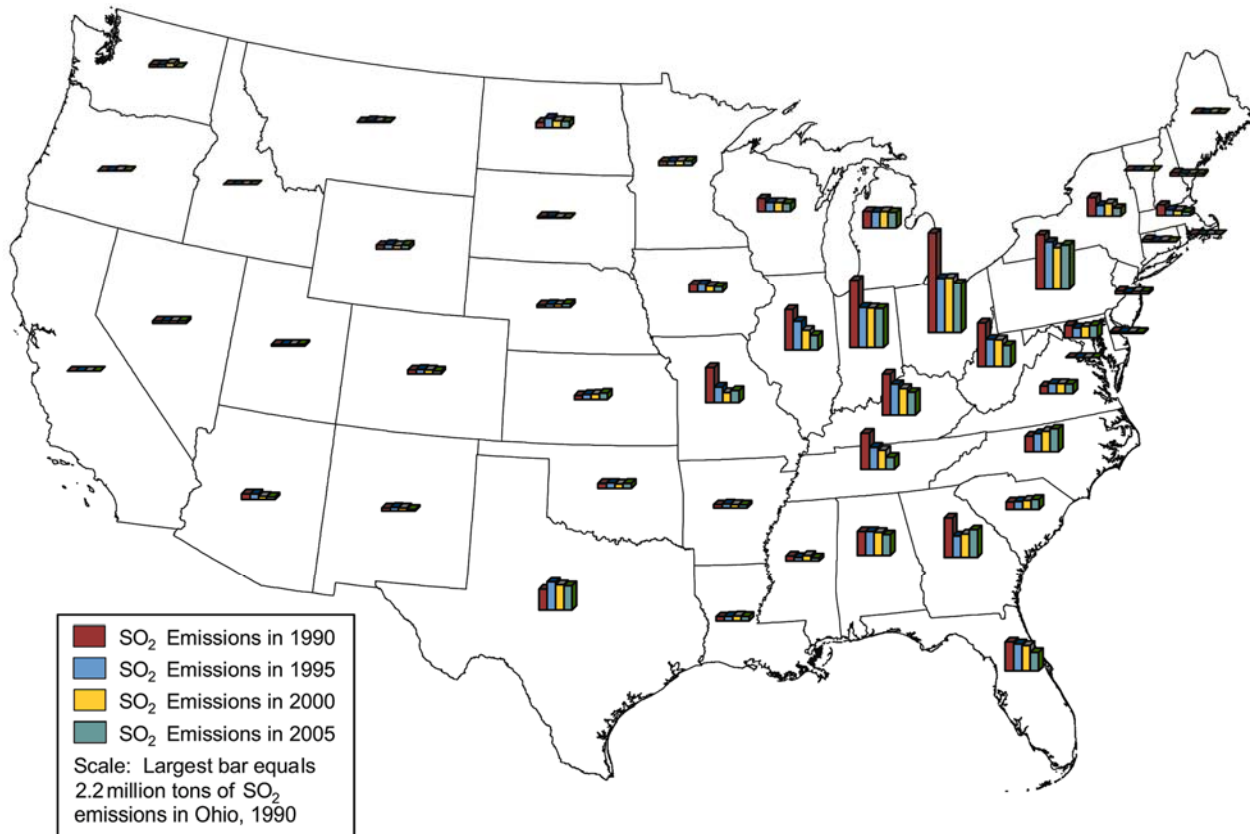


Figure 3.2-1. State-level SO₂ emissions, 1990-2005.

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

1 These trends in emissions data are consistent with the trends in the observed ambient
 2 concentrations from the Clean Air Status and Trends Network (CASTNET). Following
 3 implementation of the Phase I controls on ARP sources between 1995 and 2000, significant
 4 reductions in [SO₂] and ambient sulfate concentrations ([SO₄²⁻]) were observed at CASTNET
 5 sites throughout the eastern United States.

6 Figure 3.2-2 depicts for the CONUS the magnitude and spatial distribution of SO₂
 7 emissions in 2006 from sources in the ARP. This depiction shows clearly the continuing over-
 8 representation of SO₂ sources in the United States east of the Mississippi River as compared to
 9 west of it, an over-representation that is strongest in the central Ohio River Valley.

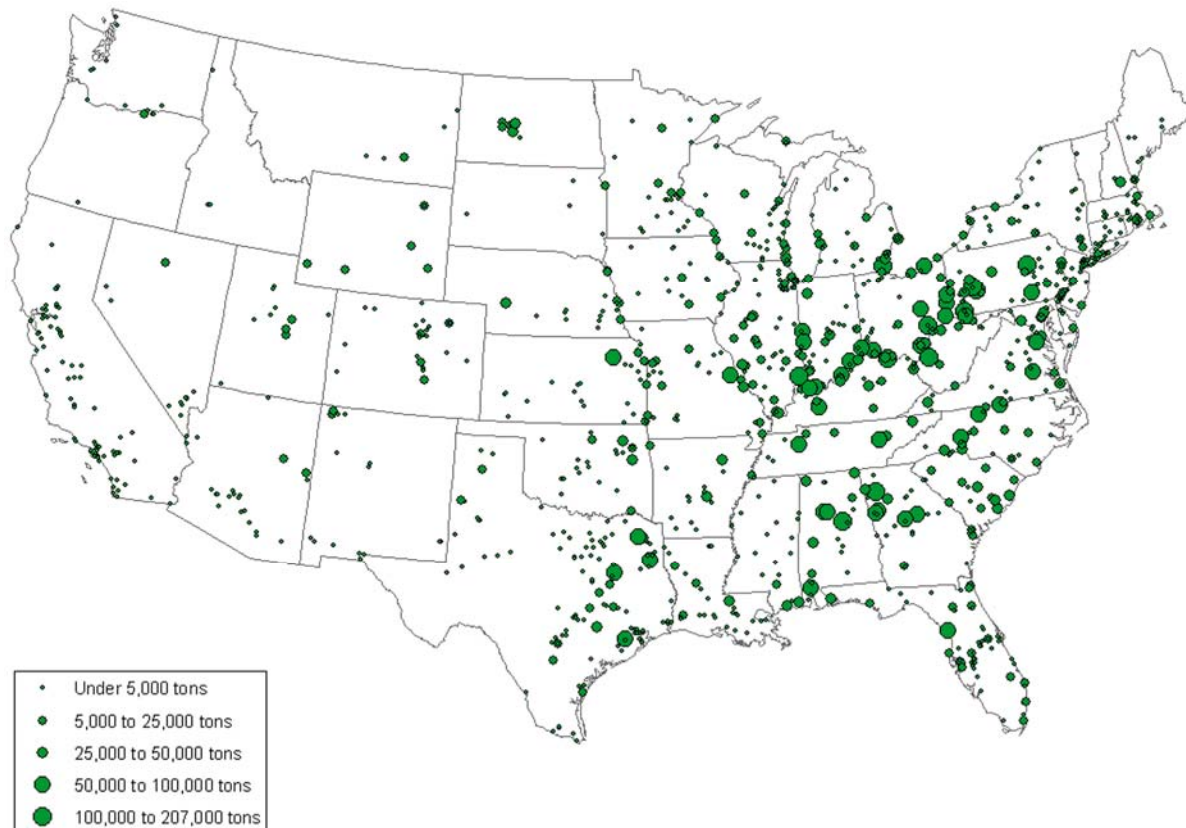


Figure 3.2-2. Annual SO₂ emissions in 2006 for acid rain program cooperating facilities.

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

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

6 Emissions of SO₂ from burning vegetation are generally in the range of 1 to 2% of the
 7 biomass burned (e.g., Levine et al., 1999). S is bound in amino acids in vegetation and this
 8 organically bound S is released during combustion. However, unlike N, approximately one-half
 9 of the [S] initially present in vegetation is found in the ash (Delmas, 1982). Gas-phase emissions
 10 are mainly in the form of SO₂ with much smaller amounts of H₂S and carbonyl sulfide (OCS).
 11 The ratio of gas-phase N to S emissions is ~14, very close to the ratio in plant tissue (Andreae,

1 1991). The ratio of reduced N and S species such as NH₃ and H₂S to their more oxidized forms,
2 such as NO and SO₂, increases as fire conditions go from the flaming to the smoldering phases of
3 combustion because emissions of reduced species are favored by lower temperatures and reduced
4 O₂ availability.

5 Emissions of reduced S species are associated typically with marine organisms living
6 either in pelagic or coastal zones and with anaerobic bacteria in marshes and estuaries.
7 Emissions of DMS from marine plankton represent the largest single source of reduced S species
8 to the atmosphere (e.g., Berresheim et al., 1995). Other sources such as wetlands and terrestrial
9 plants and soils probably account for less than 5% of the DMS global flux, with most of this
10 coming from wetlands. The coastal and wetland sources of DMS have a dormant period in fall
11 and winter from senescence of plant growth. Marshes die back in fall and winter, so DMS
12 emissions from them are lower, and reduced light levels in winter at mid-to-high latitudes reduce
13 phytoplankton growth also tending to reduce DMS emissions. Transport of SO₂ from regions of
14 biomass burning seems to be limited by heterogeneous losses that accompany convective
15 processes that ventilate the surface layer and the lower boundary layer (Thornton et al., 1996).

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

20
21

22 **3.3 NH₃ EMISSIONS**

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

29 The initial step in the oxidation of atmospheric NH₃ to NO is reaction with OH radicals.
30 However, the τ of NH₃ from this pathway is sufficiently long (1 to 2 months at typical OH values
31 of 1 to 2 × 10⁶ cm⁻³) so that it is a small sink compared to the uptake of NH₃ by cloud droplets
32 and aerosols and loss to dry deposition. Thus, gas-phase oxidation of NH₃ makes a very small

1 contribution as a source of NO. Holland et al. (2005) estimated wet and dry deposition of NH_x,
2 based on measurements over the CONUS, and found that emissions of NH₃ in the 1999 National
3 Emissions Inventory (NEI) were underestimated by approximately a factor of 2 or 3. Possible
4 reasons for this error include under-representation of deposition monitoring sites in populated
5 areas and the neglect of offshore transport in the NEI estimate. The use of fixed deposition
6 velocities (V_d) that do not reflect local conditions at the time of measurement introduces
7 additional uncertainty into estimates of dry deposition to which NH₃ is particularly sensitive.

8 9 10 **3.4 EVALUATING EMISSIONS INVENTORIES**

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

17 Results from some more recent emissions evaluation studies have been mixed, with some
18 studies showing agreement to within ±50% (Trainer et al., 2000; Parrish et al., 1998; Parrish and
19 Fehsenfeld, 2000; U.S. Environmental Protection Agency, 2000). However, Pokharel et al.
20 (2002) employed remotely sensed emissions from on-road vehicles and fuel use data to estimate
21 emissions in Denver, and their calculations indicate a continual decrease in CO, hydrocarbon
22 (HC), and NO emissions from mobile sources over the 6-year study period, 1996 through 2001.
23 Inventories based on the ambient data were 30 to 70% lower for CO, 40% higher for HC, and 40
24 to 80% lower for NO than those predicted by the MOBILE6 on-road mobile source emissions
25 model.

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

1 **3.5 ECOLOGICAL SINKS**

2 Several reactive N species are deposited to vegetation, among them, HNO₃, NO₂,
3 peroxyacyl nitrates (PAN and its higher analogs), and other organic nitrates (RONO₂).

4 **3.5.1 HNO₃**

6 Field observations based on concentration gradients of HNO₃ and using eddy covariance
7 techniques demonstrate rapid deposition that approaches the aerodynamic limit (as constrained
8 by atmospheric turbulence) in the Wesely (1989) formulation based on analogy to resistance.
9 Surface resistance to HNO₃ uptake by vegetation is negligible. Deposition rates are independent
10 of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the
11 leaf cuticle as well as leaf surfaces. The HNO₃ V_d typically exceeds 1 cm s⁻¹ and exhibits a diel
12 pattern controlled by turbulence characteristics of midday maxima and lower values at night in
13 the more-stable boundary layer.

14 **3.5.2 NO₂**

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

1 Two approaches to modeling NO₂ uptake by vegetation are the resistance-in-series
2 analogy which considers flux (F) as the product of concentration (C) and V_d , related to the sum
3 of aerodynamic, boundary layer, and internal resistances (R_a , R_b , and R_c , respectively); positive
4 fluxes are from atmosphere to foliage

$$5 \quad F = CV_d \quad (3.5-1)$$

$$6 \quad V_d = (R_a + R_b + R_c)^{-1} \quad (3.5-2)$$

7 The terms R_a and R_b are controlled by turbulence in the mixed layer; R_c is dependent on
8 characteristics of the foliage and soil and may be viewed as a combination of resistance internal
9 to the foliage and external on the cuticle, soils, and bark. This approach is very similar to the
10 method most often used to predict deposition with regional air quality models (Wesely, 1989).
11 Typically, the NO₂ V_d is less than that for O₃ due to the surface's generally higher resistance to
12 NO₂ uptake, consistent with NO₂'s lower reactivity.

13 Alternatively, NO₂ exchange with foliage can be modeled from a physiological
14 standpoint where the flux from the leaf (J) is related to the stomatal conductance (g_s) and a
15 concentration gradient between the ambient air and interstitial air in the leaf ($C_a - C_i$). This
16 approach best describes results for exchange with individual foliage elements, and is expressed
17 per unit leaf or needle area. While this approach provides linkage to leaf physiology, it is not
18 straightforward to scale up from the leaf to the ecosystem

$$19 \quad J = g_s(C_a - C_i) \quad (3.5-3)$$

20 This model implicitly associates the compensation point with a finite internal
21 concentration. Typically observed compensation points are ~1 ppb; values of internal [NO₂] are
22 consistent with metabolic pathways that include NO_x. In this formulation, the uptake will be
23 linear with [NO₂], which is typically measured in foliar chamber studies.

24 Several studies have shown the UV dependence of NO₂ emissions, which implies some
25 photo-induced surface reactions to release NO₂. Rather than model this as a UV-dependent
26 internal concentration, it would be more realistic to add an additional term to account for
27 emission that is dependent on light levels and other surface characteristics

$$J = g_s(C_a - C_i) = J_s(UV) \quad (3.5-4)$$

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; Schrimpf et al., 1996) and from leaf chamber studies (Teklemariam and Sparks, 2004) have indicated that uptake of PAN is slower than that of O₃; however, recent work in coniferous canopies with direct eddy covariance PAN flux measurements indicated a V_d more similar to that of O₃. 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 RONO₂

The biosphere also interacts with NO_x through HC emissions and their subsequent reactions to form multi-functional RONO₂. 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 NO₂ when it is present to form HNO₃.

Isoprene nitrates are an important class of RONO₂. Isoprene reacts with OH to form a radical that adds NO₂ 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, NO₂ and PAN, which is attributed to the RONO₂ (Horii et al., 2006; Munger et al., 1998). Furthermore, the total NO_y flux exceeds the sum of HNO₃, NO_x, and PAN, which implies that the RONO₂ are a substantial fraction of the total N deposition. Other observations showing evidence of hydroxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

3.5.5 HNO₂

HNO₂ formation on vegetative surfaces at night has long been observed based on measurements of positive gradients (Harrison and Kitto, 1994). Surface reactions of NO₂ enhanced by moisture were proposed to explain these results. Production was evident at sites with high ambient NO₂; at low concentration, uptake of HNO₂ exceeded the source. Daytime observations of HNO₂ when rapid photolysis is expected to deplete ambient concentrations to very low levels implies a substantial source of photo-induced HNO₂ 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

1 Air Quality Standards (NAAQS) reviews and National Academy of Sciences (NAS)
 2 recommendations resulting in periodic step enhancements to these routine networks. Examples
 3 include CASTNET and the National Atmospheric Deposition Program (NADP) addressing
 4 acidification; the Photochemical Assessment Monitoring Stations (PAMS) in response to
 5 persistent O₃ pollution and to monitor O₃ precursors including NO_x; and the particulate matter
 6 ≤2.5 μm (PM_{2.5}) network to monitor aerosol- and solid-phase pollutants that can act in concert
 7 with NO_x and SO_x. Annex Table AX2.5-1 lists the networks, sponsoring agencies, site
 8 densities, dates of operation, locations, and measurement parameters.

9 The relatively wide geographic distribution and persistence of exceedances of the O₃ and
 10 PM NAAQS (see Figure 3.6-1) have led to these pollutants dominating the national monitoring
 11 networks. These sites remain relevant for characterizing ambient concentrations and deposition
 12 of NO_x and SO_x because those species are often measured at the same locations and because of
 13 the role of NO_x in the formation and destruction of O₃, and because of PM's role in NO_x and
 14 SO_x deposition. Additional details about the homogeneous- and heterogeneous-phase
 15 atmospheric chemistry of NO_x and SO_x are given in Chapter 2 and in Annex 1.

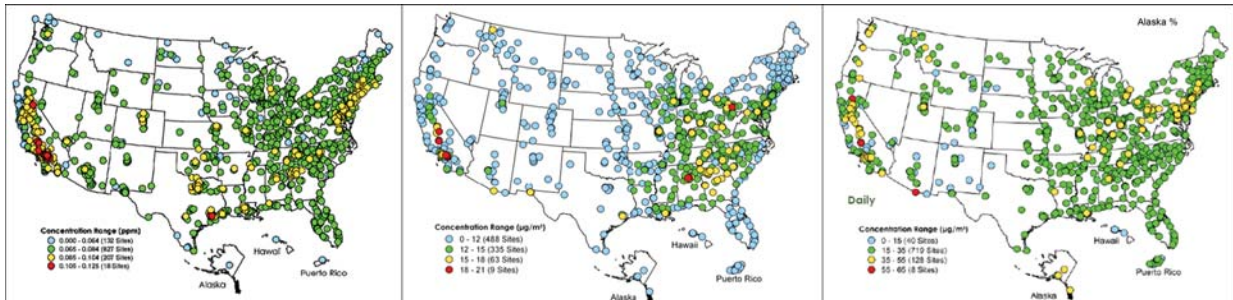


Figure 3.6-1. 2006 air quality summaries for O₃, annual average PM_{2.5}, and daily PM_{2.5}. Yellow and red sites indicate values exceeding NAAQS levels.

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

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

Ambient Air Monitoring Stations in the United States

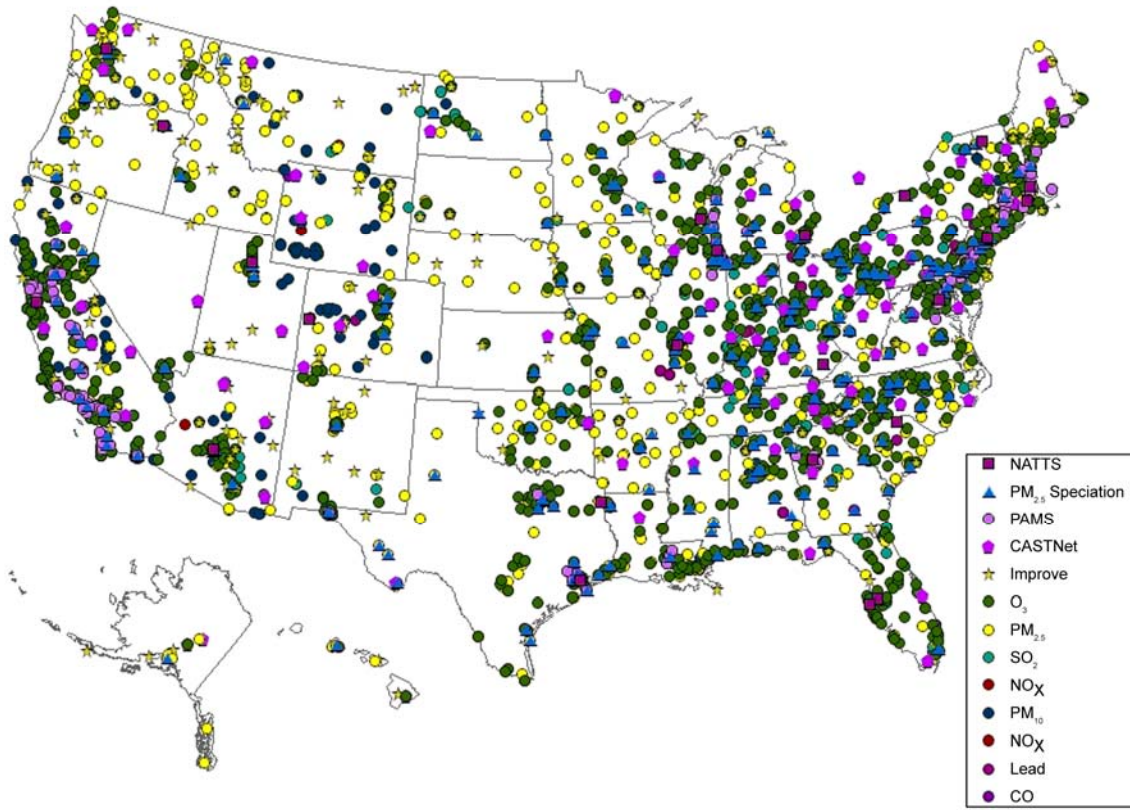


Figure 3.6-2. Aggregate map of the majority routine U.S. monitoring stations.

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

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

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

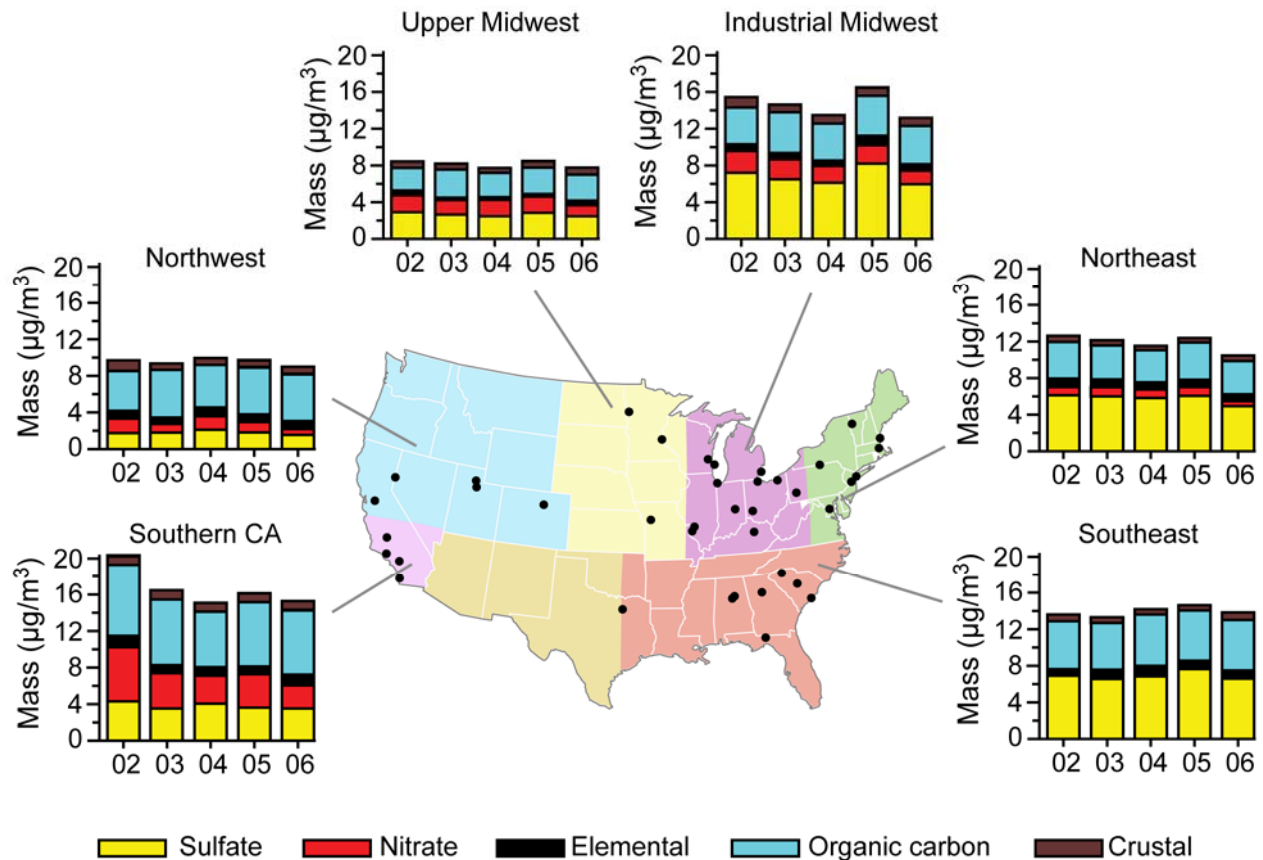


Figure 3.6-3. Regional chemical composition of PM_{2.5} aerosols based on urban speciation sites and averaged over the entire 2006 sampling period.

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

1 A new multipollutant monitoring network, the National Core Monitoring Network
 2 (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
 3 “Level 2” sites (see Figure 3.6-4) in most major urban areas and in the important transportation
 4 corridors and at background locations.
 5

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

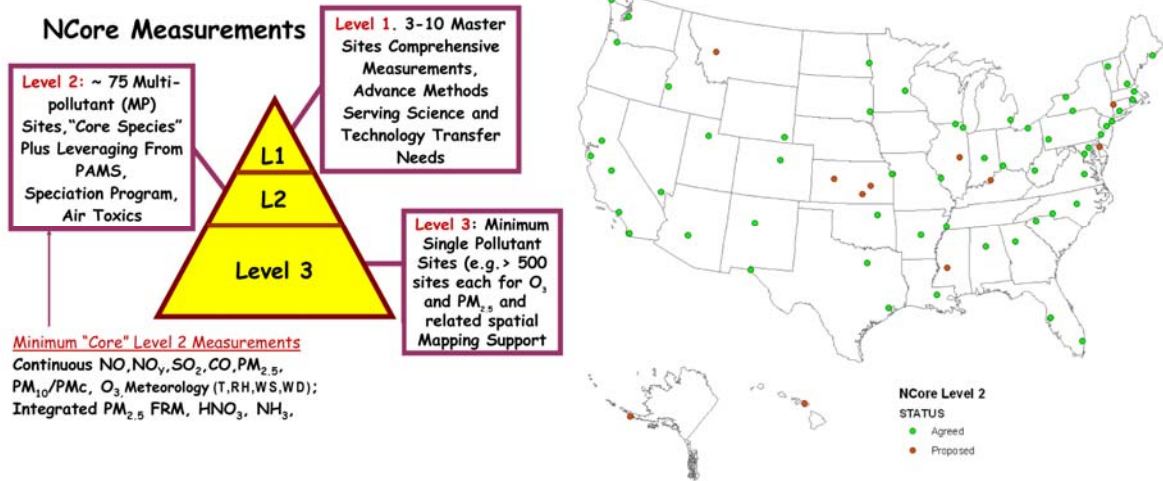


Figure 3.6-4. Planned 3-tiered NCore design (left) and proposed site locations for Level 2 multiple pollutant sites.

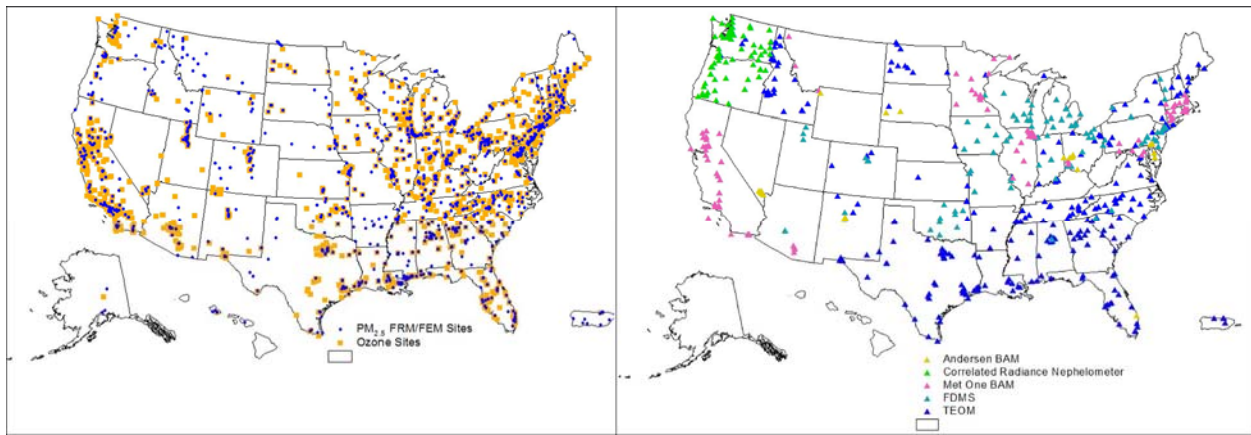


Figure 3.6-5. Maps illustrating breadth of $PM_{2.5}$ FRM and FEM and O_3 networks (left); and $PM_{2.5}$ continuous samplers (right).

- 1 comparison across sites and geographic areas with different operational characteristics. In
- 2 recognition of potential geographic differences, EPA has developed monitoring policy (U.S.
- 3 Environmental Protection Agency, 2006b) for regionally approved methods to lead to

1 equivalency status (Federal Equivalent Method, (FEM)) from the Federal Reference Method
2 (FRM) for the continuous PM_{2.5} samplers and compliance applications.

3 The IMPROVE network has provided a nearly 20-year record of the chief components
4 (SO₄²⁻, NO₃⁻, organic and elemental carbon fractions (OC and EC, respectively) and trace
5 metals) of PM_{2.5} aerosols mostly in pristine areas of the United States in and around National
6 Parks. More than 300 additional speciation sites were added between 2000 and 2002 in urban
7 areas of the United States to assist assessment efforts related to the PM_{2.5} NAAQS. This total
8 cross-network coverage (see Figure 3.6-6) is now a widely used resource across disciplines from
9 exposure and epidemiology and atmospheric sciences over spatial scales of interest ranging from
10 long-range hemispheric transport to near-source analysis.

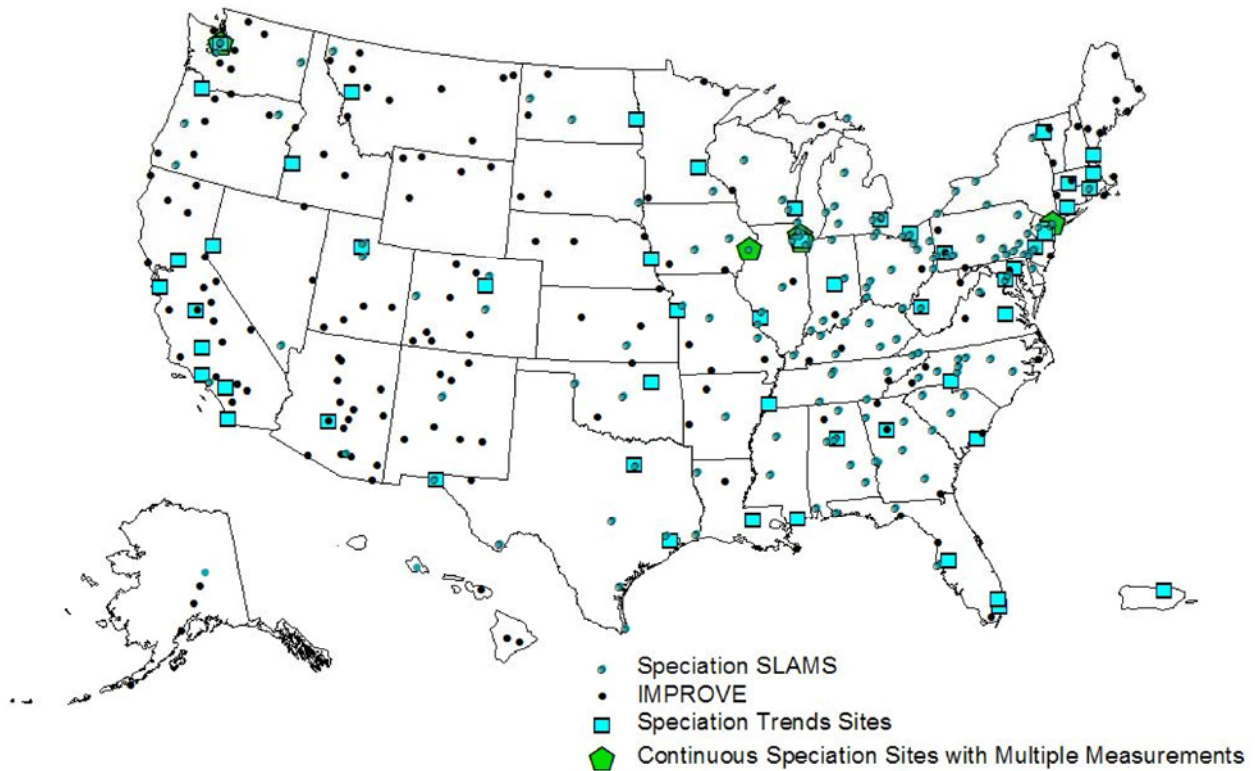


Figure 3.6-6. Locations of chemical speciation sites delineated by program type.

11 The speciation networks typically collect a 24-h sample once every 3 or 6 days.
12 CASTNET provides weekly averaged measurements of major ions (SO₄²⁻, NO₃⁻, calcium (Ca²⁺),

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

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

13 14 **3.6.1.2 Precipitation-based Networks and Sites**

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

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

27 28 **3.6.3 Intensive Field Campaigns**

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

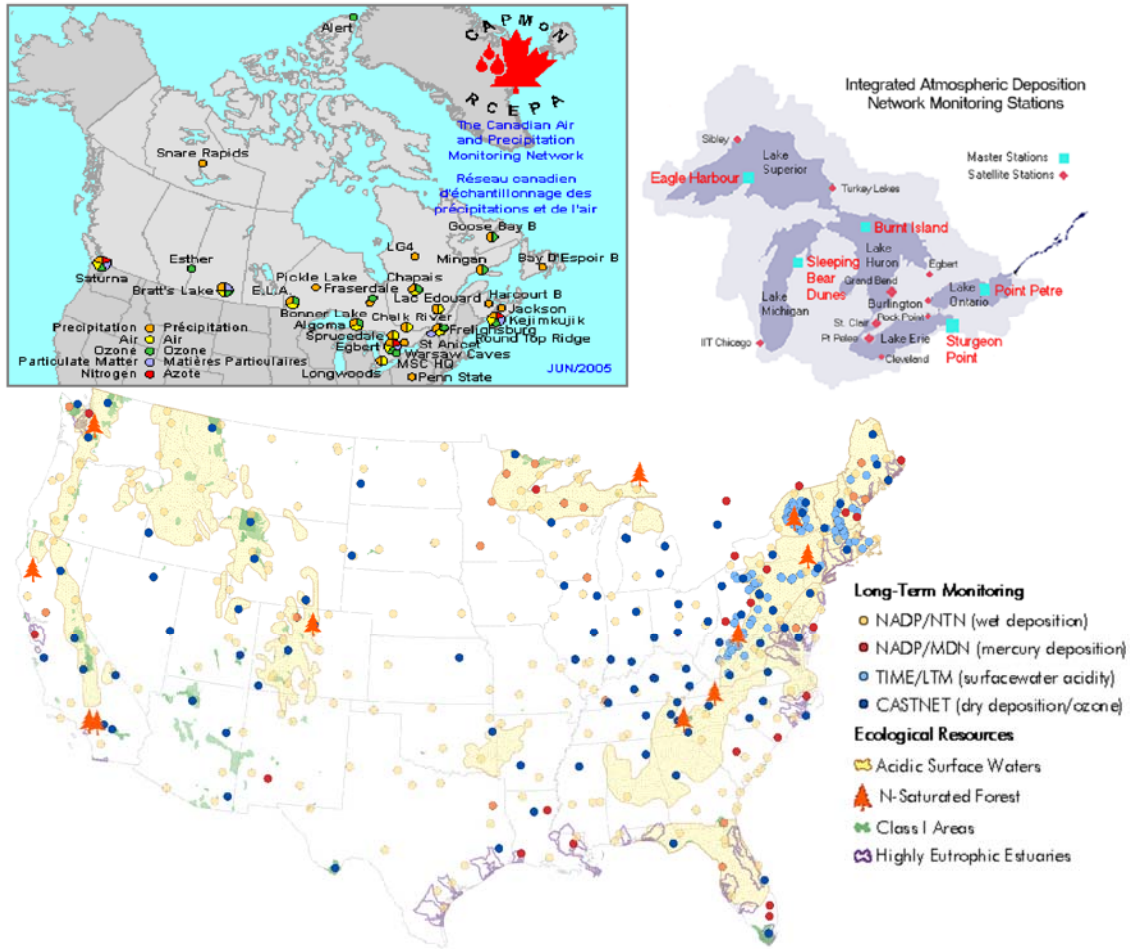


Figure 3.6-7. Routinely operating North American precipitation and surface water networks: Upper left, Canadian Air and Precipitation Monitoring Network (CAPMoN); upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); bottom, National Atmospheric Deposition Program (NADP) with TIME/LTM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

- 1 use some combination of aircraft studies, high time-resolved instrumentation, and advanced in-
- 2 situ and laboratory analytical methods, all complementing routine ground-based measurements.
- 3 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

1 Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) in
2 the United States and the European Space Agency (ESA). A suite of satellites including Aqua,
3 Aura, CALIPSO, OCO, Glory, as well as NOAA-17, NOAA-18, and NPOESS, have either been
4 launched since roughly 2000 or have near-term proposed launch dates. Collectively, the remote
5 sensing techniques for measuring total atmospheric columns and/or profiles exist for aerosol
6 optical depth (AOD), O₃, carbon monoxide (CO), formaldehyde (HCHO), carbon dioxide (CO₂),
7 CH₄, SO₂, NO₂, and chlorinated fluorocarbons (CFCs) among other pollutants, and for such
8 atmospheric parameters as temperature and total H₂O content. Satellites with a near-polar orbit
9 can make two passes each day over a given location. When taken together, a group of six
10 satellites (Aqua, Aura, CALIPSO, OCO, as well as CloudSat and PARASOL; category label is
11 “A-Train”) is being configured to fly in a formation that crosses the equator a few minutes apart
12 at around 1330 local time to give a comprehensive picture of Earth’s weather, climate, and
13 atmospheric conditions.

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

19 20 **3.6.5 Monitoring Networks in Europe**

21 Extensive air monitoring networks have also been implemented in Europe, many served
22 by centralized organization structures linked to international efforts like the Convention on Long
23 Range Transport of Air Pollution ((LRTAP); <http://www.unece.org/env/lrtap/>) and the
24 underlying technical assessment body, the Co-operative Programme for Monitoring and
25 Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). The Global
26 Atmospheric Watch program ((GAW); <http://www.wmo.int>) under the World Meteorological
27 Organization (WMO) provides quality assurance guidelines and data to an important body of air
28 quality measurements relevant to assessing intercontinental pollution transport and climate
29 forcing phenomena. The Norwegian Institute for Air Research ((NILU), <http://www.nilu.no>),
30 maintains a database for many of the European based networks. Annex Table AX2.5-5 includes
31 combined contributions from several European countries ranging from a few sites to tens of sites

1 in a country, some with data records extending more than 30 years. Measurements for a variety
2 of air pollutants are addressed including O₃, metals, persistent organic pollutants (POPs), PM,
3 VOCs, and acidifying and eutrophying N and S compounds.

4 5 6 **3.7 AMBIENT CONCENTRATIONS**

7 8 **3.7.1 NO_x and NO_y**

9 Figure 3.7-1 shows ambient [NO₂] measured at all monitoring sites located within
10 Metropolitan Statistical Areas (MSAs) in the United States from 2003 through 2005. Mean
11 [NO₂] are ~15 ppb for averaging periods ranging from a day to a year, with an interquartile range
12 (IQR) of 10 to 15 ppb. However, the average daily maximum 1-h [NO₂] are ~30 ppb, roughly a
13 factor of 2 greater than the 24-h averages. The single highest maximum 1-h concentration of
14 ~200 ppb in this period (measured at one monitor in southern California) was more than a factor
15 of 10 greater than the mean 1-h or 24-h concentrations.

16 Data for concentrations of other oxidized N species in urban areas in the United States
17 are sparse. The most comprehensive set of data was obtained for HNO₃, for example, as part of
18 the Children's Health Study for which gas-phase HNO₃ was measured at 12 sites in Southern
19 California from 1994 through 2001 (Alcorn and Lurmann, 2004). Levels ranged from <1 ppb to
20 >10 ppb. In general, the highest [HNO₃] and the highest ratio of [HNO₃]-to-[NO₂] were found
21 downwind of central Los Angeles in the San Bernardino Valley during summer, as one would
22 expect for this more-oxidized N product.

23 Measurements of HNO₂ in urban areas are still very limited; however, data from Stutz
24 et al. (2004) indicate that [HNO₂] are <1 ppb even under heavily polluted conditions, with the
25 highest levels at night and just after dawn and lowest values in the afternoon because of rapid
26 photolysis; see the fuller descriptions in Chapter 2. Several field studies such as Hayden et al.
27 (2003) in rural Quebec, Williams et al. (1987) near Boulder, CO, and Singh et al. (2007) in
28 aircraft flights over eastern North America have also found much higher levels of HNO₃ and of
29 other, further oxidized N compounds in relatively unpolluted rural air.

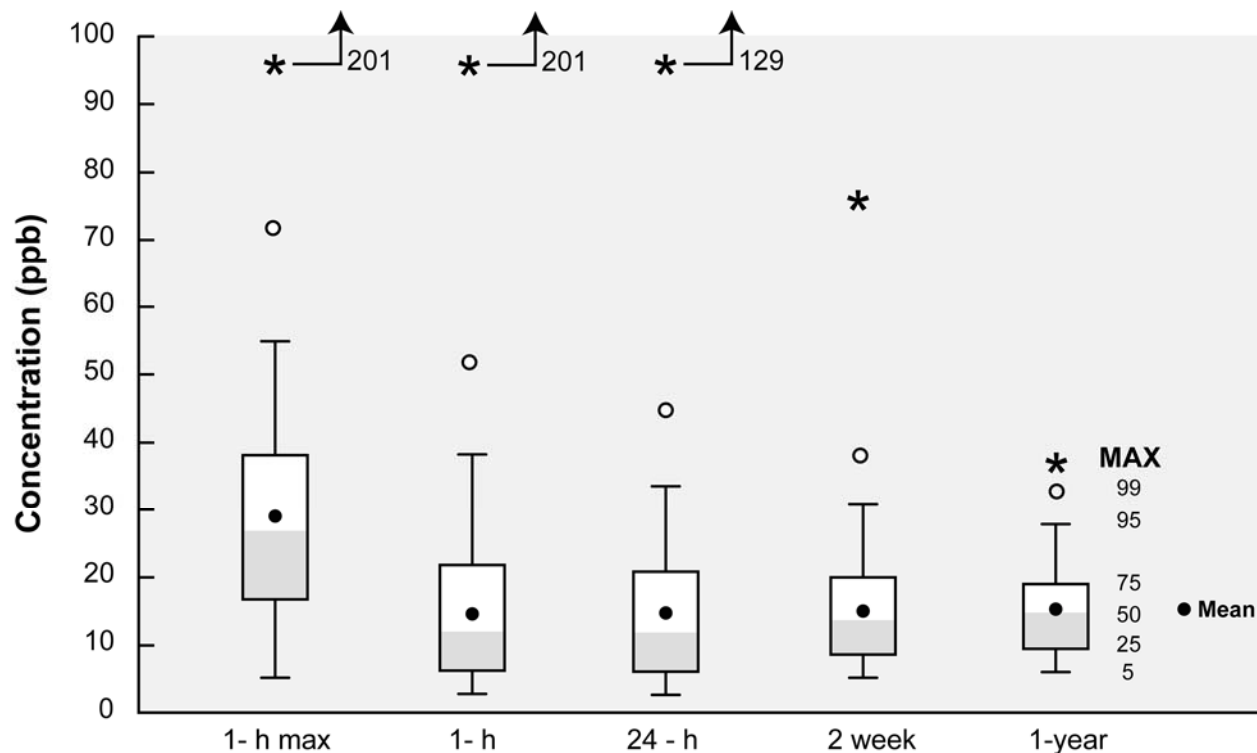


Figure 3.7-1. Ambient concentrations of NO₂ measured at all monitoring sites located within Metropolitan Statistical Areas in the United States from 2003 through 2005.

1 Calculations with EPA’s Community Multiscale Air Quality (CMAQ) modeling system
 2 for the Mid-Atlantic region in a domain from Virginia to southern New Jersey showed that the
 3 highest [HNO₃] and [RONO₂] occur during mid-afternoon, consistent with their formation by
 4 photochemical processes also producing O₃. Model simulations of an O₃ episode in July 2002
 5 made for the Maryland State O₃ Implementation Plan (SIP) showed episode averages of the ratio
 6 of the further-oxidized N species like HNO₃ to NO₂ ranging from 0.26 to 3.6 in rural Virginia,
 7 with the highest ratios in rural areas and lowest ratios in urban centers nearer the sources of fresh
 8 NO_x emissions.

9
 10 **3.7.2 SO_x**

11 The mean annual [SO₂] and [SO₄²⁻] from CASTNET’s long-term monitoring sites can be
 12 compared using two 3-year periods (1989 through 1991, and 2003 through 2005) shown in
 13 Figure 3.7-2 for SO₂, and Figure 3.7-3 for SO₄²⁻.

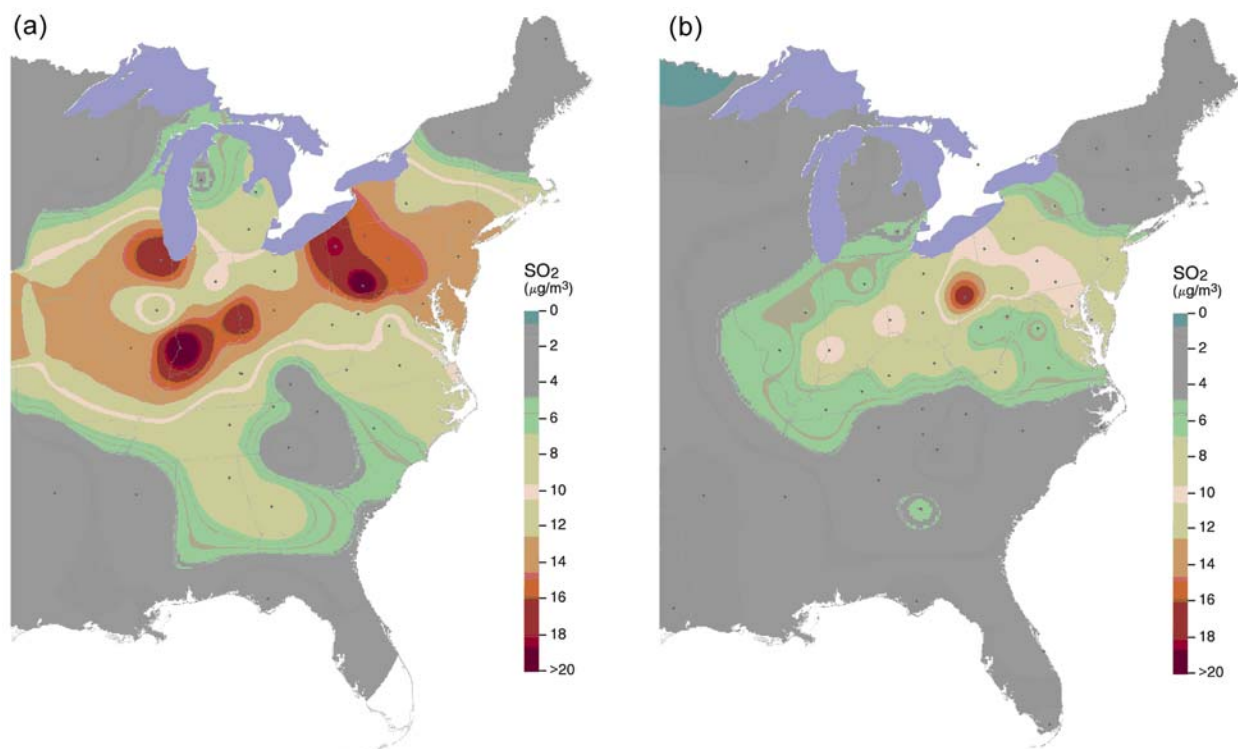


Figure 3.7-2. Annual mean ambient SO₂ concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

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

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

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

7 SO₂ concentrations have been falling throughout all regions of the United States as
 8 demonstrated by the CASTNET data depicted in Figure 3.7-2. In and around most individual
 9 CMSAs, the trends are also toward lower [SO₂]. Many annual and even 1-h mean concentrations
 10 for the years 2003 through 2005 were consistently at or below the operating LOD of ~3 ppb for
 11 the standard SO₂ monitor deployed in the networks, while the aggregate mean value over all

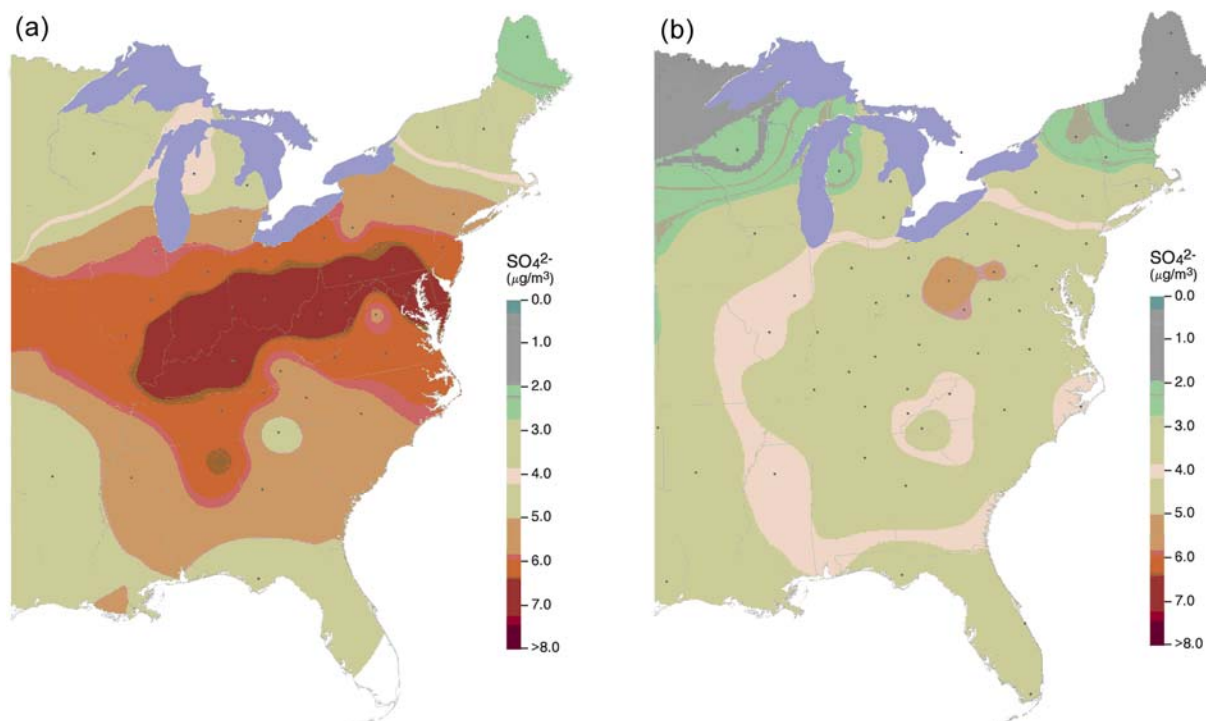


Figure 3.7-3. Annual mean ambient SO_4^{2-} Concentration, (a) 1989 through 1991, and (b) 2003 through 2005.

* 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/).

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

3 Figure 3.7-4 shows the composite diel variation in hourly $[\text{SO}_2]$ from all monitors
 4 reporting data to the Air Quality System (AQS) database. (The AQS contains measurements of
 5 air pollutant concentrations in the 50 states, plus the District of Columbia, Puerto Rico, and the
 6 Virgin Islands for the six criteria air pollutants (SO_2 , NO_2 , PM, CO, Pb, O_3) and some hazardous
 7 air pollutants.) As can be seen from Figure 3.7-4, concentrations beneath the 95th percentile
 8 level are indistinguishable from each other, but are typically in the range of a few ppb. However,
 9 the peaks in the distribution at any hour of the day can be a factor of 10 or more higher than
 10 values in the bulk of the distribution. Overall, there is some indication that the highest values are
 11 reached either at midday or during the middle of the night. Daytime peaks could result from

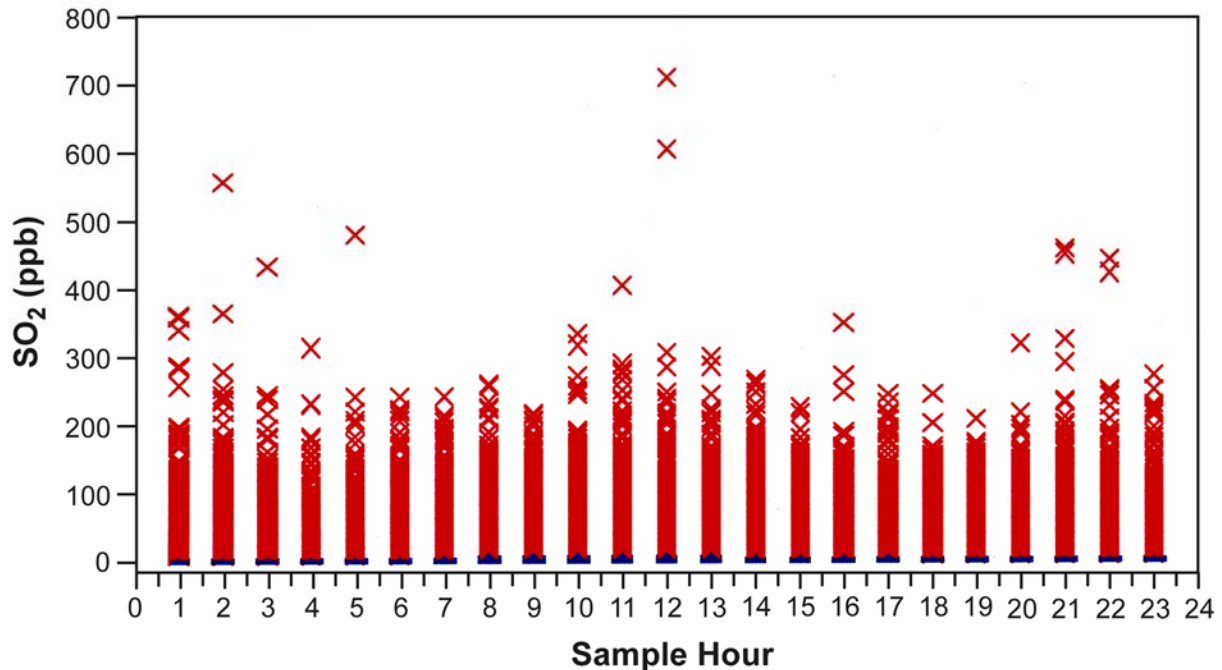


Figure 3.7-4. Boxplot of hourly SO₂ concentrations across all cities in focus.

1 down-mixing of air aloft due to convective activity since SO₂ is emitted mainly by elevated
 2 sources. Nighttime peaks are more likely due to trapping of local emissions beneath a shallow
 3 stable nocturnal boundary layer.

4 To be sure, the maximum 1-h concentration observed at some sites in and around some
 5 CMSAs did still exceed the mean by a large margin, with maximum 1-h values of >600 ppb.
 6 However, the 50th percentile maximum value outside CMSAs, 5 ppb, was only slightly greater
 7 than the 1-h, 24-h, and annual mean values of 4 ppb. The 50th percentile maximum value inside
 8 CMSAs, 7 ppb, was 75% greater than these longer-term averages, reflecting heterogeneity in
 9 source strength and monitor location. In addition, even with 1-h maximum values of >600 ppb,
 10 the maximum annualized mean value for all CMSAs was still <16 ppb, and, hence, below the
 11 current annual primary SO₂ 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 SO₂ 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 NH₃ 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

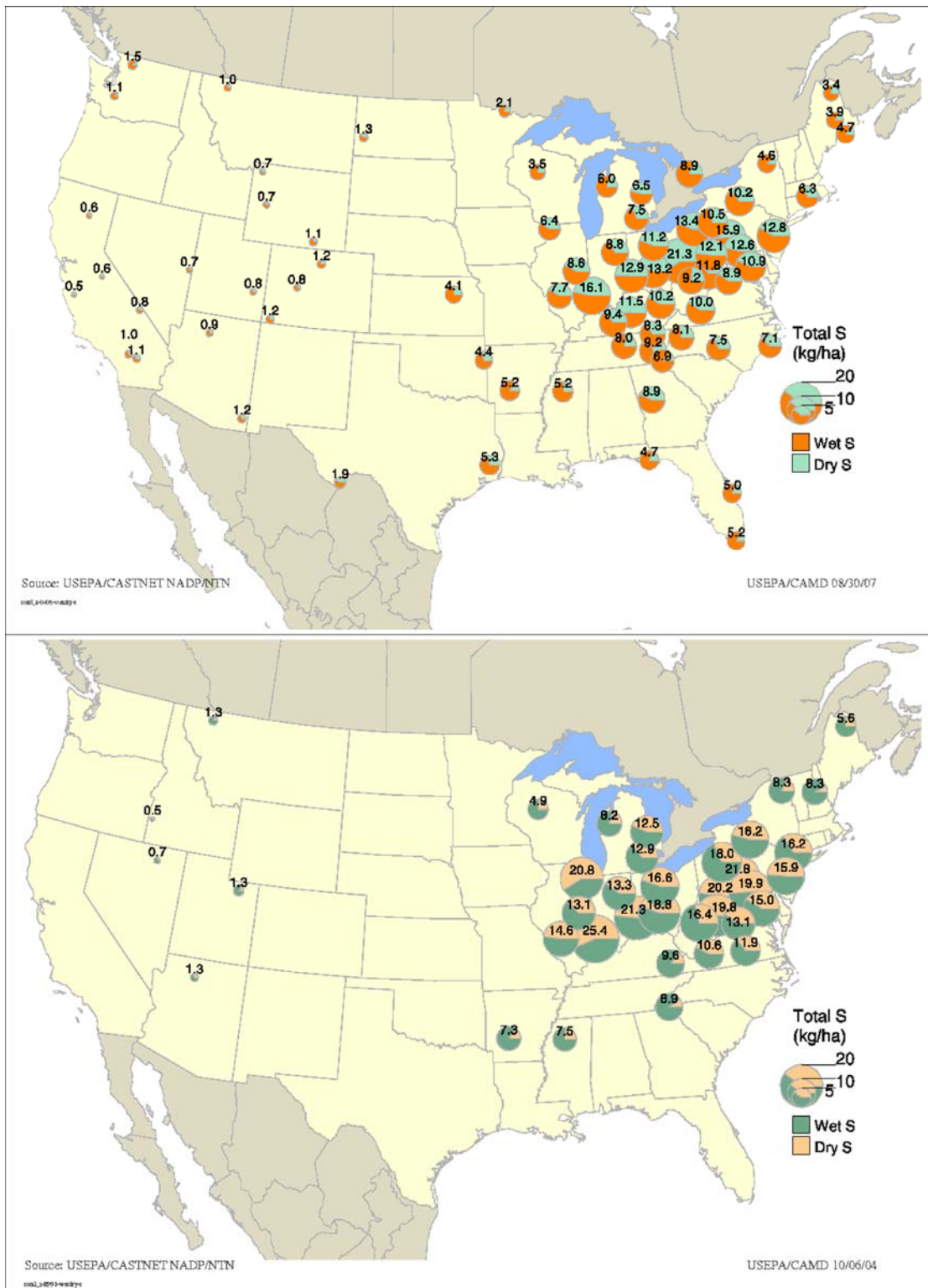


Figure 3.8-1. Total average yearly wet and dry sulfur deposition for 2004-2006 (top) and 1989-1991 (bottom).

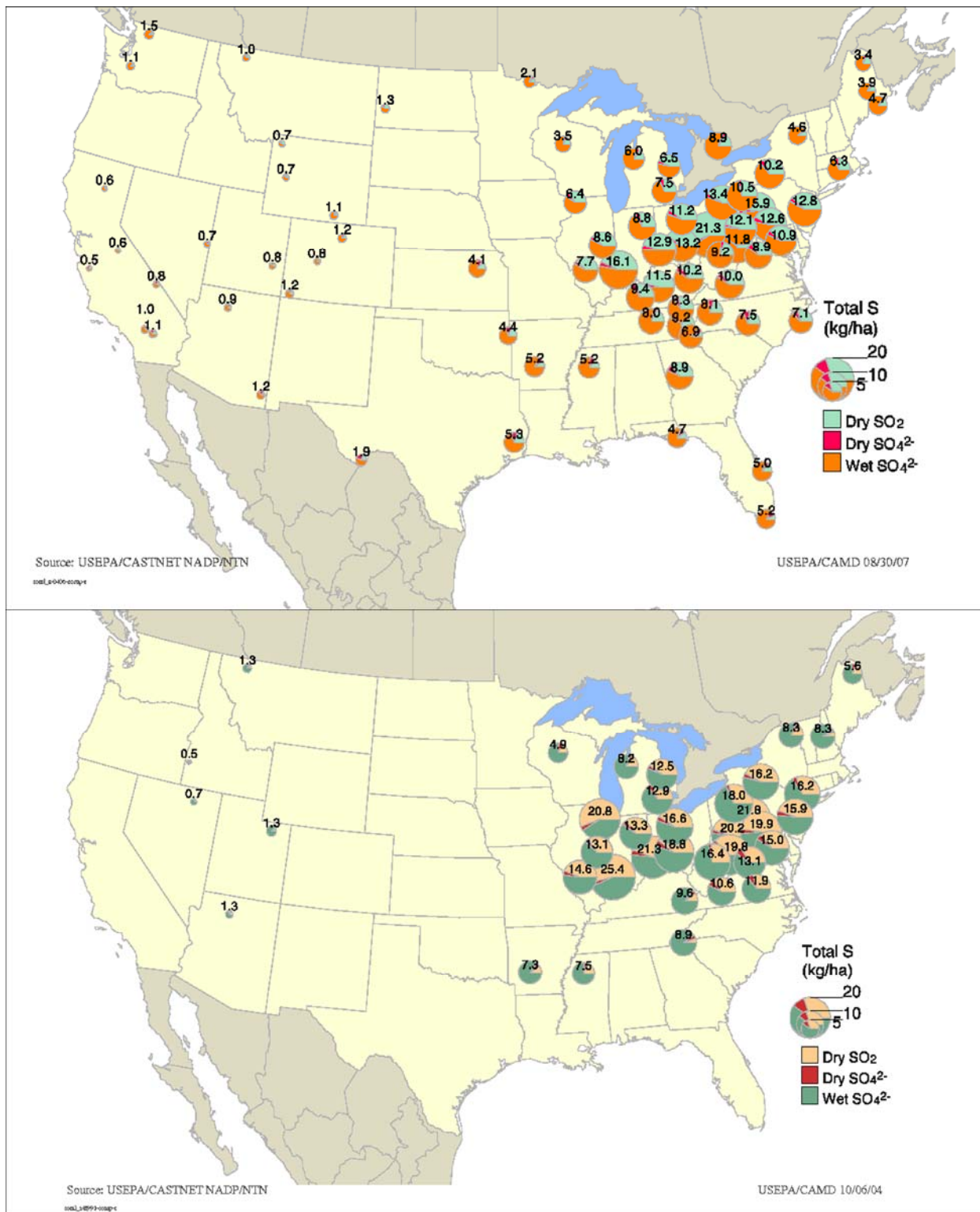


Figure 3.8-2. Total average yearly sulfur deposition by species for 2004-2006 (top) and 1989-1991 (bottom).

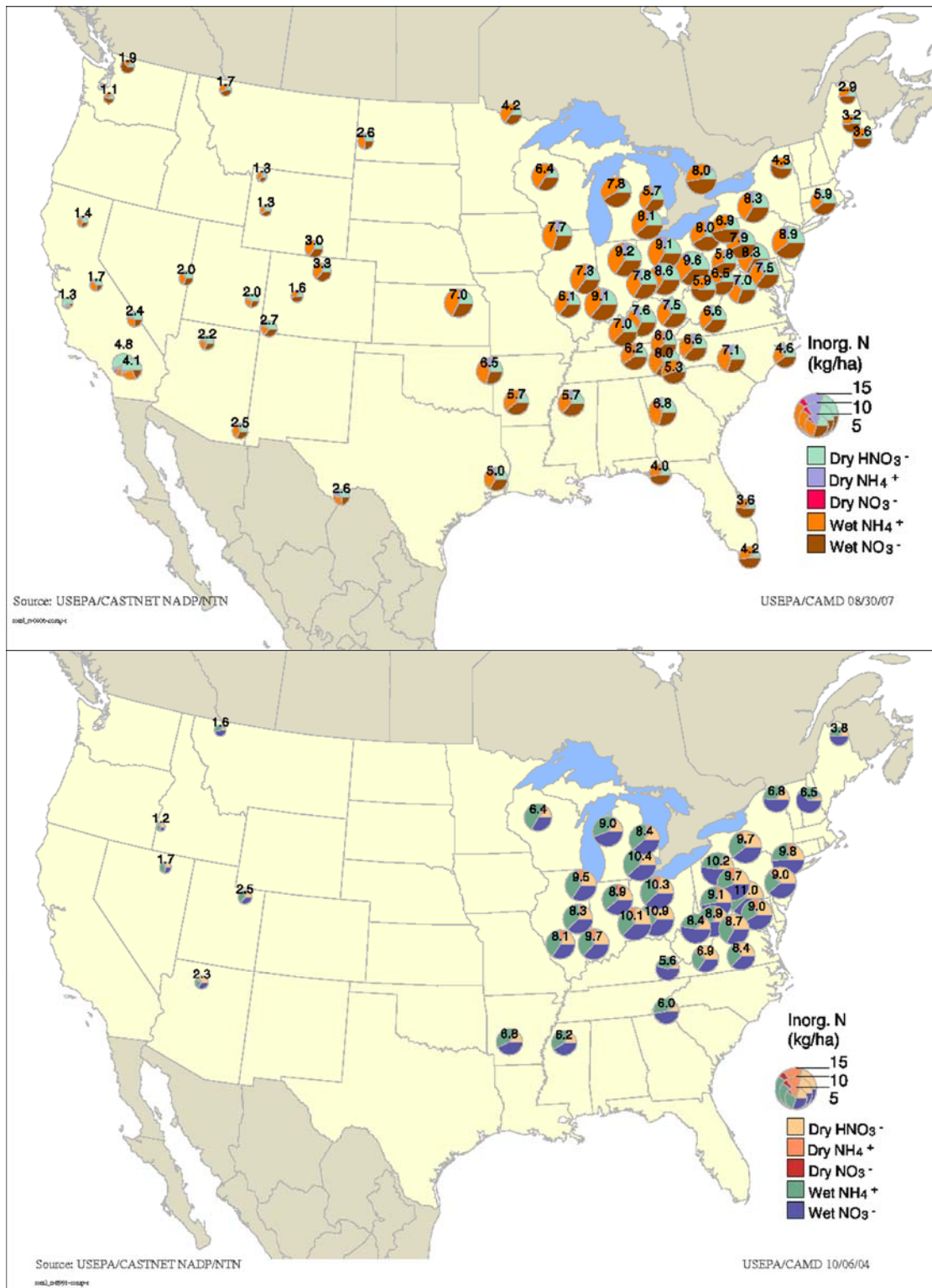


Figure 3.8-4. Total average yearly inorganic nitrogen deposition by species for 2004-2006 (top) and 1989-1991 (bottom).

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

7 Because NO_x emissions decreased by ~25% between 1990 and 2005, recent N deposition
8 is lower compared with average deposition for the years 1989 to 1991. For 1989 to 1991, several
9 recording stations in the Ohio River basin reported average annual deposition rates in excess of
10 10 kg ha⁻¹ yr⁻¹. Data are lacking, however, for much of the central and western United States
11 and little can be said for changes between the two reporting periods in these areas for the reasons
12 given above. The greatest mass of N deposition primarily occurred as wet NO₃⁻ and NH₄⁺,
13 followed in importance by dry HNO₃, dry NH₄⁺, and dry NO₃⁻. Although most deposition for
14 both reporting periods occurred as wet deposition, there were some exceptions, including parts of
15 California where N deposition was primarily dry.

16

17 **3.8.2 Sulfur**

18 For the most recent 3-year reporting period available (2004 to 2006), mean S deposition
19 was greatest in the eastern United States east of the Mississippi River, with the highest
20 deposition of 21.3 kg ha⁻¹ yr⁻¹ in the Ohio River basin. Most recording stations throughout the
21 Ohio River basin report 3-year total S deposition averages >10 kg ha⁻¹ yr⁻¹ and many other
22 stations in the East report deposition >5 kg ha⁻¹ yr⁻¹. Data are sparse for the central and west
23 United States, but, where available, indicate lower values than in most of the East, ranging from
24 4.1 to 5.3 kg ha⁻¹ yr⁻¹. Total S deposition in the United States west of the 100th meridian is
25 lower, with all recording stations reporting <2 kg ha⁻¹ yr⁻¹ and many reporting <1.0 kg ha⁻¹ yr⁻¹.

26 Station-by-station comparisons between averaging periods are difficult because some
27 stations do not have sufficient data to report a mean for the sampling period. There are,
28 however, clear regional decreases in S deposition across the country. S deposition for the years
29 1989 through 1991 (the earliest 3-year reporting period available) is almost uniformly greater
30 than for the years 2004 through 2006. Deposition since the period 1989 through 1991 has
31 declined throughout the Ohio River basin from a previous high of 25.4 kg ha⁻¹ yr⁻¹; and in New

1 England and the Mid-Atlantic states, deposition is consistent with the ~48% decrease in SO₂
2 emissions nationwide between 1990 and 2005. Very little coverage for the western and central
3 United States was available for the 1989 through 2001 reporting period, but sites with data show
4 a similar decrease. For both the 1989 through 1991 and 2004 through 2006 reporting periods, S
5 was primarily deposited as wet SO₄²⁻, followed by a smaller proportion of dry SO₂, and a much
6 smaller proportion of deposition as dry SO₄²⁻.

7 8 9 **3.9 EXAMPLE NO₂ AND HNO₃ FLUX DATA FROM HARVARD** 10 **FOREST**

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

14 An intensive study in 2000 used a Tunable Diode Laser Absorption Spectrometer
15 (TDLAS) to measure [NO₂] and [HNO₃]. The TDLAS has an inherently fast response, and for
16 species such as NO₂ and HNO₃ with well-characterized spectra it provides an absolute and
17 specific measurement. Absolute concentrations of HNO₃ were measured, and the flux inferred
18 based on the dry deposition inferential method that uses momentum flux measurements to
19 compute a V_d and derive an inferred flux along the suggestions of Wesely and Hicks (1977) and
20 Hicks et al. (1987); see the descriptions around Equations 3.5-1 and 3.5-2 above. Direct eddy
21 covariance calculations for HNO₃ were not possible because the atmospheric variations were
22 attenuated by interaction with the inlet walls despite very short residence time and use of
23 fluorinated silane coatings to make the inlet walls more hydrophobic. NO response was
24 adequate to allow both concentration and eddy covariance flux determination. Simultaneously,
25 NO and NO_y eddy covariance fluxes were determined with two separate O₃ chemiluminescence
26 detectors, one equipped with a H₂-Au catalyst at the inlet to convert all reactive N compounds to
27 NO. (A full description of this technique appears in Chapter 2.) Additionally, the measurements
28 included concentration gradients for NO, NO₂, and O₃ over several annual cycles to examine
29 their vertical profiles in the forest canopy.

30 Overall, the results show typical [NO₂] of 1 ppb under clean-air conditions and mean
31 concentrations up to 3 ppb at night and 1 ppb during daytime for polluted conditions. Net
32 positive fluxes (emission) of NO₂ were evident in the daytime and negative fluxes (deposition)

1 were observed at night as Figure 3.9-1 shows. NO fluxes were negative during the daytime and
 2 near 0 at night.

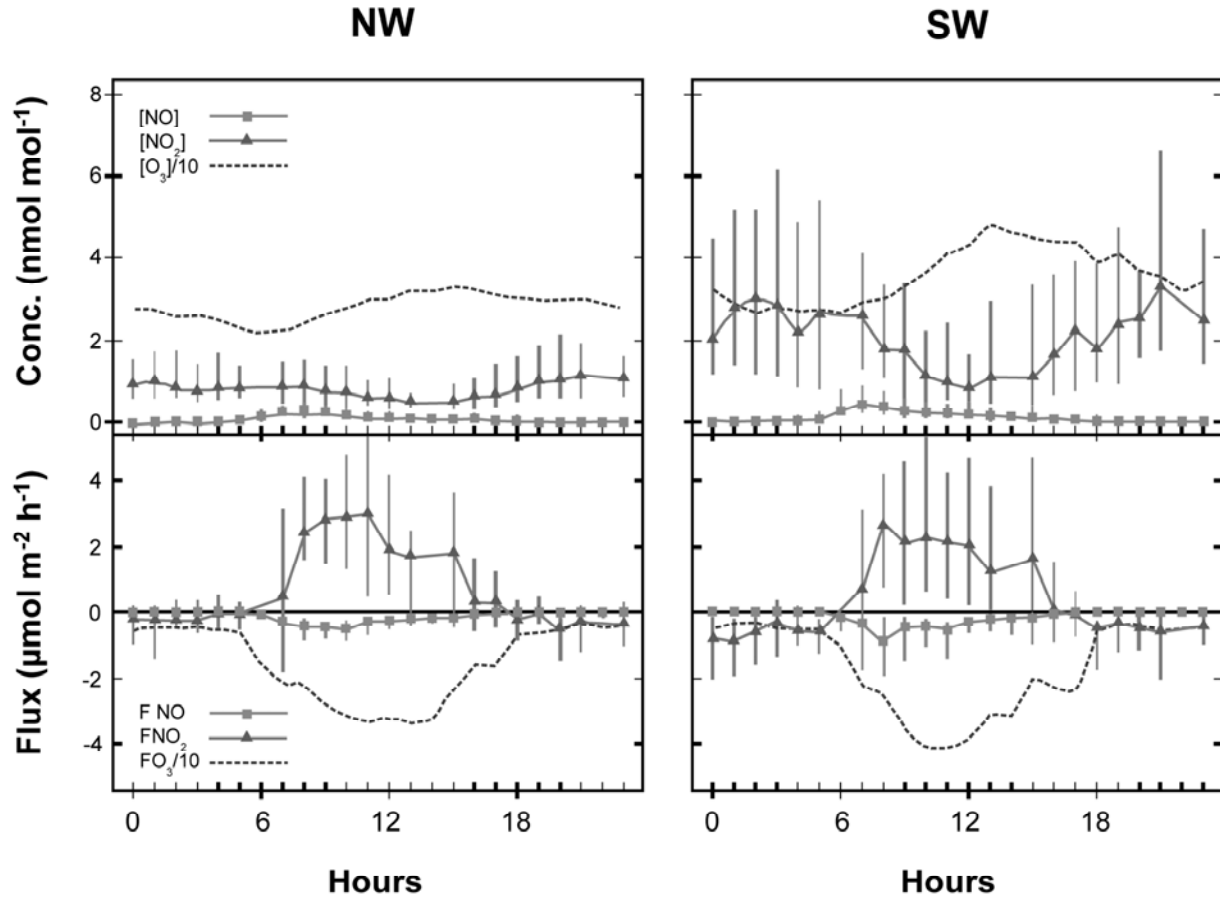


Figure 3.9-1. Diel cycles of median concentrations (upper panels) and fluxes (lower panels) for the Northwest clean sector, left panels) and Southwest (polluted sector, right panels) wind sectors at Harvard Forest, April-November, 2000, for NO, NO₂, and O₃/10. NO and O₃ were sampled at a height of 29 m, and NO₂ at 22 m. Vertical bars indicate 25th and 27th quartiles for NO and NO₂ measurements. NO₂ concentration and nighttime deposition are enhanced under southwesterly conditions, as are O₃ and the morning NO maximum.

Source: Horii et al. (2004).

3 In part, the opposite NO and NO₂ fluxes are simply consequences of variable NO and
 4 NO₂ distributions responding to vertical gradients in light intensity and [O₃], which resulted in
 5 no net NO_x flux (Gao et al., 1993). In the Harvard Forest situation, the NO and NO₂

1 measurements were not at the same height above the canopy, and the resulting differences come
2 at least in part from the gradient in flux magnitude between the two inlets; see Figure 3.9-2. At
3 night, when [NO] are near 0 owing to titration by ambient O₃, there is no flux of NO to offset
4 NO₂ fluxes. Nighttime data consistently show NO₂ deposition as seen in Figure 3.8-3, and these
5 increase with increasing [NO₂]. Concentrations > 10 ppb were rare at this site, but the few high
6 [NO₂] suggest a nonlinear dependence on concentration. The data fit a model with V_d of -0.08
7 plus an enhancement term that is second order in [NO₂]. The second-order term implies that
8 NO₂ deposition rates to vegetation in polluted urban sites would be considerably larger than what
9 was observed at this rural site.

10 After accounting for the time of the NO-NO₂ null cycle during the measurement
11 sampling period, the net NO_x flux can be derived. Overall, there was a net deposition of NO_x
12 during the night and essentially 0 flux in the day with large variability in the magnitude and sign
13 of individual flux observations. For the periods with [NO₂] > 2 ppb, deposition was always
14 observed. These canopy-scale field observations are consistent with a finite compensation point
15 for NO₂ in the canopy that offsets foliar uptake or even reverses it when concentrations are
16 especially low. At concentrations above the compensation point, NO_x is absorbed by the
17 canopy. Examination of concentration profiles corroborates the flux measurements as shown in
18 Figure 3.9-4. During daytime low [NO_x] conditions, there is a local maximum in the
19 concentration profile near the top of the canopy where O₃ has a local minimum, consistent with
20 foliar emission or light-dependent production of NO_x in the upper canopy. Depletion is evident
21 for both NO_x and O₃ near the forest floor. Air reaching the ground has passed through the
22 canopy where uptake is efficient and the vertical exchange rates near the ground are slow. At
23 night, the profiles generally decrease with decreasing height above the ground, leaving only the
24 uptake process. At higher concentrations, daytime [NO_x] are nearly constant through the
25 canopy; no emission is evident from the sunlit leaves.

26 Figure 3.9-5 compares observed fluxes of all the sampled species described here. The
27 measured NO_x and estimated PAN fluxes are small relative to the observed total NO_y flux. In
28 clean air, HNO₃ accounts for nearly all the NO_y flux and the sum of all measured species is
29 roughly equal to [NO_y]. However, under polluted conditions, unmeasured species can be up to
30 25% of total [NO_y], and HNO₃ fluxes cannot account for all of the observed NO_y flux. Likely

Simple Model

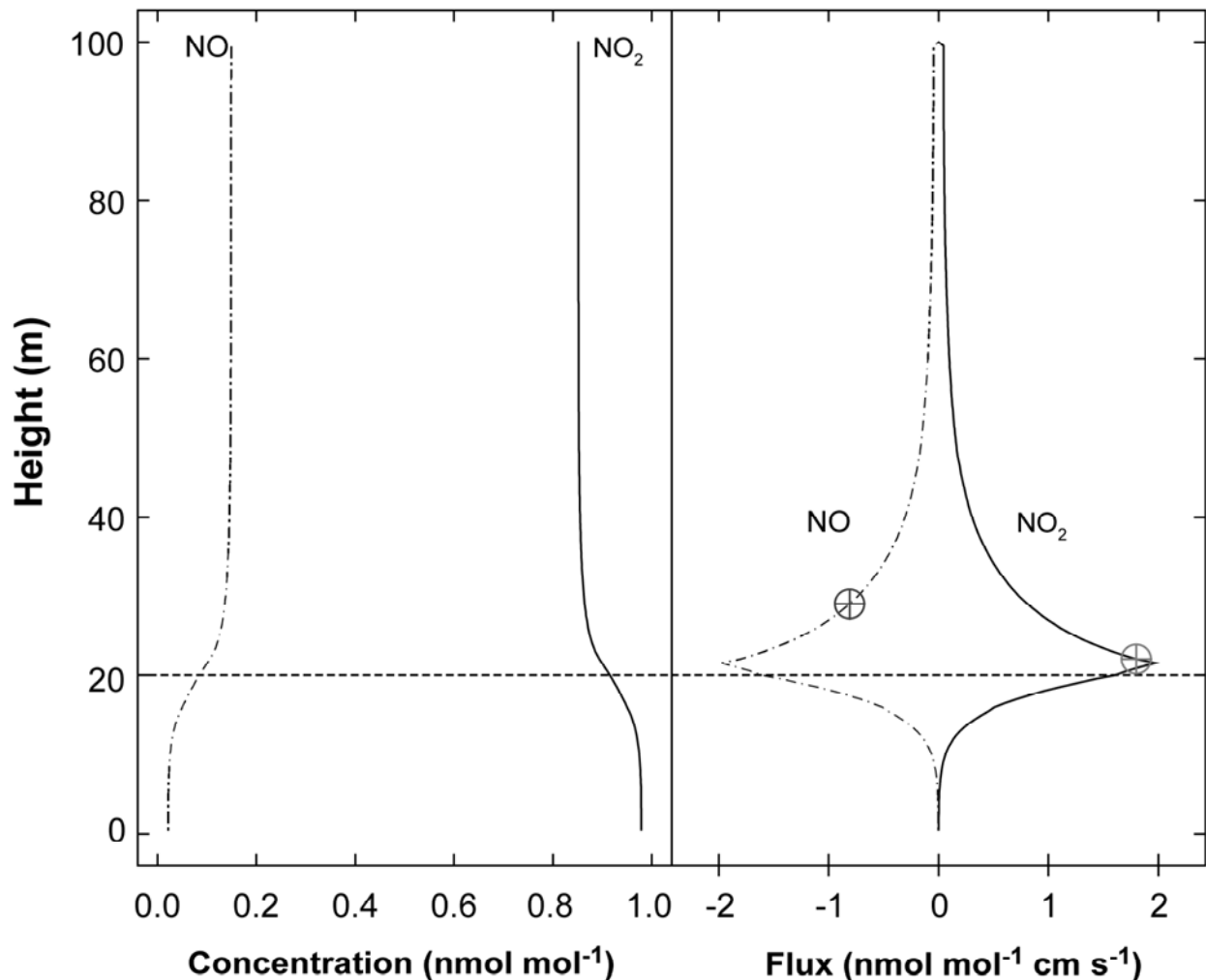


Figure 3.9-2. Simple NO_x photochemical canopy model outputs. Left panel, concentrations of NO (dashed) and NO₂ (solid); right, fluxes of NO (dashed) and NO₂ (solid). Symbols indicate measurement heights for NO (29m) and NO₂ (22m) at Harvard Forest. The model solves the continuity equation for NO concentration at 200 levels, $d/dz(-Kc(dNO/dz)) = PNO - LNO$, where $PNO = [NO]/t1$, $LNO = [NO]/t2$, and zero net deposition or emission of NO_x is allowed. NO_x is normalized to 1ppb. $t1 = 70s$ in this example. Due to the measurement height difference, observed upward NO₂ flux due to photochemical cycling alone should be substantially larger than observed downward NO flux attributable to the same process.

Source: Horii (2002).

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

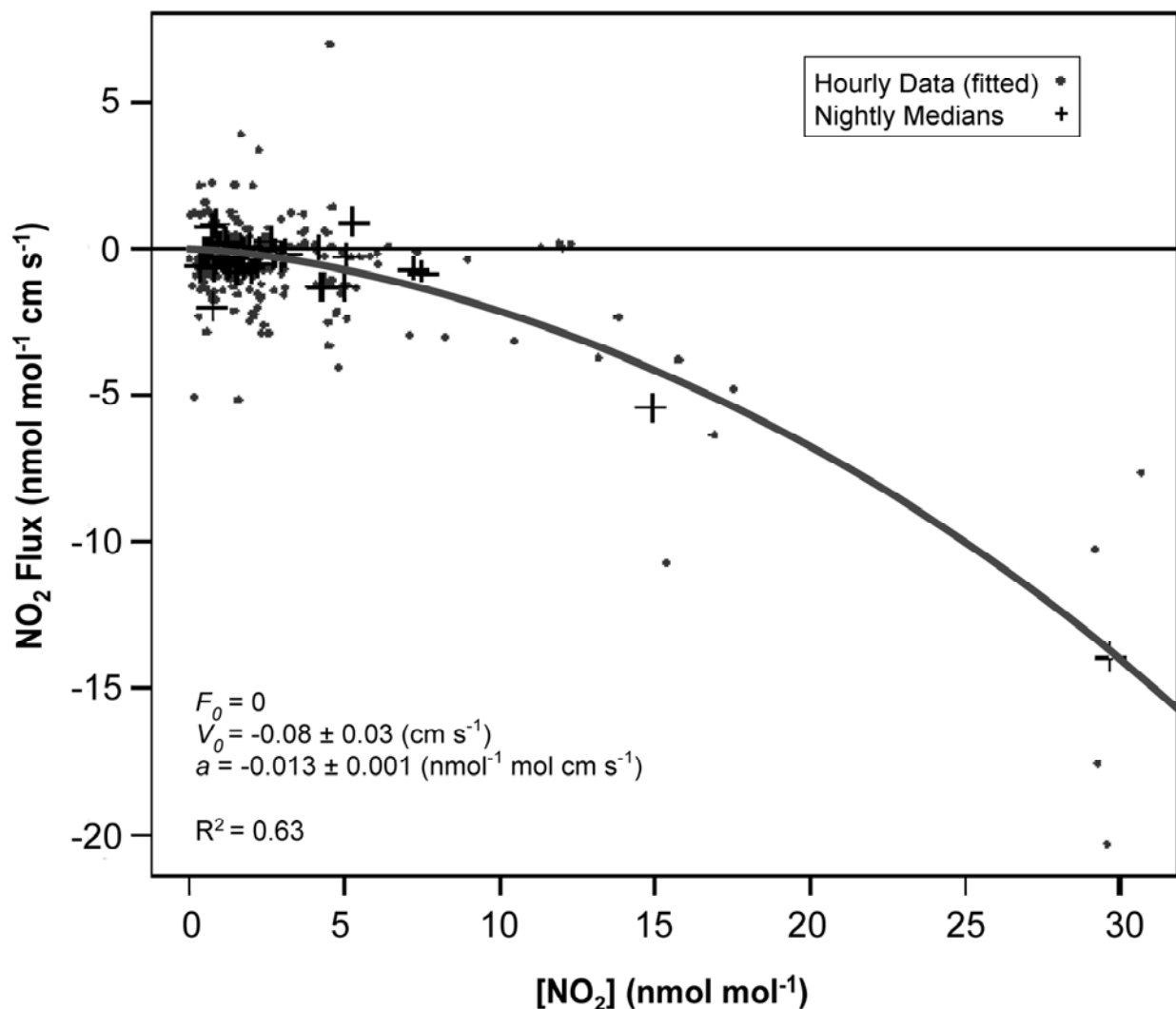


Figure 3.9-3. Hourly (dots) and median nightly (pluses) NO₂ flux vs. concentration, with results of least-squares fit on the hourly data (curve). The flux is expressed in units of concentration times velocity (nmol mol⁻¹ cm s⁻¹) in order to simplify the interpretation of the coefficients in the least-squares fit. Pressure and temperature corrections have been taken into account in the conversion from density to mixing ratio.

Source: Horii et al. (2004).

NO_x PROFILES

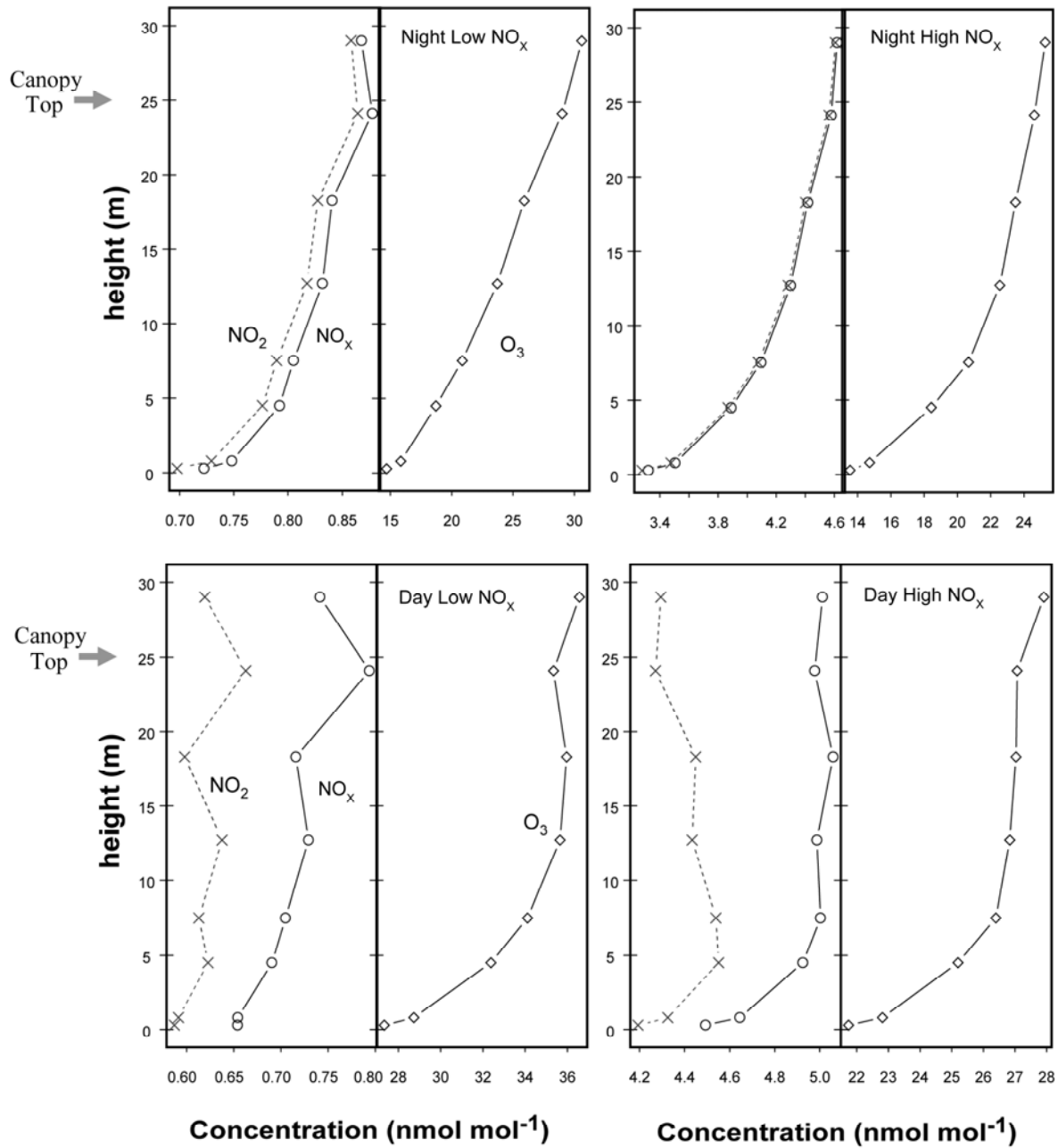


Figure 3.9-4. Averaged profiles at Harvard Forest give some evidence of some NO₂ input near the canopy top from light-mediated ambient reactions, or emission from open stomates.

Source: Horii et al. (2004).

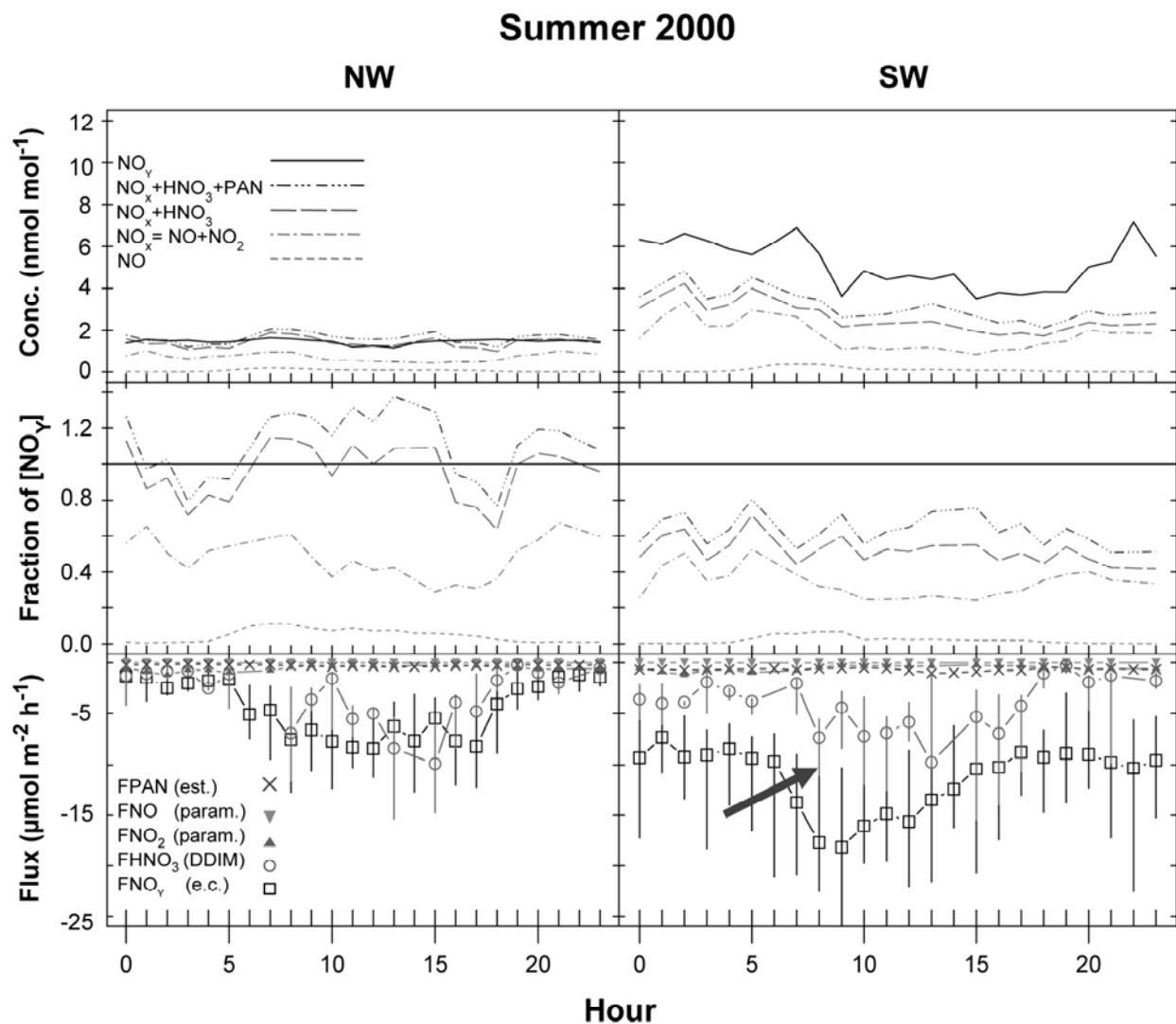


Figure 3.9-5. Summer (June-August) 2000 median concentrations (upper panels), fractions of NO_Y (middle panels), and fluxes (lower panels) of NO_Y and component species separated by wind direction (Northwest on the left and Southwest on the right). Vertical lines in the flux panels show 25th and 75th quartiles of F(NO_Y) and F(HNO₃); negative fluxes represent deposition; F(NO_X) is derived from eddy covariance F(NO) and F(NO₂) measurements (corrected for photochemical cycling), F(HNO₃) is inferred, and F(NO_Y) was measured by eddy covariance. The sum of NO_X, HNO₃, 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).

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

3 Although NO₂ uptake may be important to the plant, because it is an input directly to the
4 interior of foliage that can be used immediately in plant metabolism, it is evidently not a
5 significant part of overall N deposition to rural sites.

6 The deposition of HNO₃ and multifunctional RONO₂ are the largest elements of the N
7 dry deposition budget. Two key areas of remaining uncertainty are the production of HNO₂ over
8 vegetation and the role of the very reactive biogenic VOCs. HNO₂ is important both because its
9 photolysis is a source of OH radicals and because its formation may represent an unrecognized
10 mechanism to regenerate photochemically active NO_X from NO_X that had been considered
11 terminally removed from the atmosphere.

12
13

14 **3.10 METHODS TO COMPUTE NO_X AND SO_X CONCENTRATIONS** 15 **AND CHEMISTRY**

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

25 Emissions of precursor compounds can be divided into anthropogenic and natural source
26 categories, and natural sources can be further divided into biotic (vegetation, microbes, animals)
27 and abiotic (biomass burning, lightning) categories as presented above. However, the distinction
28 between natural sources and anthropogenic sources is often difficult to make, as human activities
29 affect directly or indirectly emissions from what would have been considered natural sources
30 during the preindustrial era. Thus, emissions from plants and animals used in agriculture have
31 been referred to as anthropogenic or natural in different applications. Wildfire emissions may be

1 considered to be natural, except that forest management practices may have led to the buildup of
2 fuels on the forest floor, thereby altering the frequency and severity of forest fires.

3 4 **3.10.1 CTMs**

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

13 Global-scale CTMs are used to address issues associated with climate change and
14 stratospheric O₃ depletion, and to provide boundary conditions for the regional-scale models.
15 The CTMs include simplified mathematical descriptions of atmospheric transport, the transfer of
16 solar radiation through the atmosphere, chemical reactions, and removal to the surface by
17 turbulent motions and precipitation for pollutants emitted into the model domain. The upper
18 boundaries of the CTMs extend anywhere from the top of the mixed layer to the mesopause at
19 ~80 km in order to obtain more realistic boundary conditions for problems involving
20 stratospheric dynamics.

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

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

9 10 **3.10.1.1 Regional-Scale CTMs**

11 Most major modeling efforts within EPA use CMAQ (Byun and Ching, 1999; Byun and
12 Schere, 2006). A number of other modeling platforms using Lagrangian and Eulerian
13 frameworks were reviewed in the 1996 Air Quality Criteria Document (AQCD) for O₃ (U.S.
14 Environmental Protection Agency, 1997), and in Russell and Dennis (2000). The capabilities of
15 a number of CTMs designed to study local- and regional-scale air pollution problems were also
16 summarized by Russell and Dennis (2000). Recent evaluations of CMAQ performance are given
17 in Arnold et al. (2003), Eder and Yu (2005), Appel et al. (2005), and Fuentes and Raftery (2005).
18 More details are available in Annex 2.

19 20 **3.10.1.2 Global-Scale CTMs**

21 The importance of the global transport of pollutant precursors and secondary products
22 and their contribution to regional pollutant levels in the United States is now apparent. There are
23 at present ~25 3-dimensional global models developed to address problems in tropospheric
24 physics and chemistry. These models resolve synoptic meteorology, O₃-NO_x-CO-HC
25 photochemistry, have parameterizations for wet and dry deposition, and parameterize sub-grid
26 scale vertical mixing processes like convection. Global models have proved useful for testing
27 and advancing scientific understanding beyond what is possible with observations alone. For
28 example, they can calculate quantities of interest that cannot be measured directly, such as the
29 export of pollution from one continent to the global atmosphere or the response of the
30 atmosphere to future perturbations to anthropogenic emissions. Additional details are available
31 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.

Wesely 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 $\pm 30\%$ (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 $p\text{NO}_3$ and $p\text{SO}_4$ 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

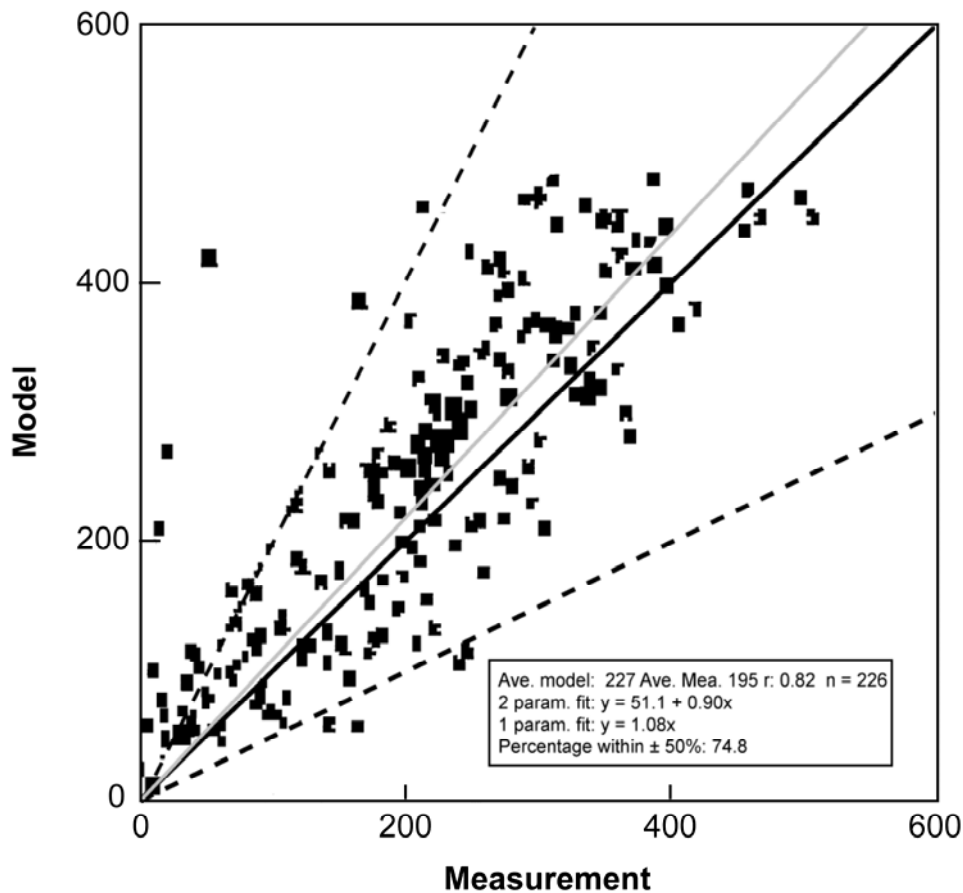


Figure 3.10-1. Scatter plot of total nitrate (HNO_3 plus aerosol nitrate) wet deposition ($\text{mg(N)m}^{-2}\text{yr}^{-1}$) of the mean model versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression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

Source: Dentener et al. (2006b).

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

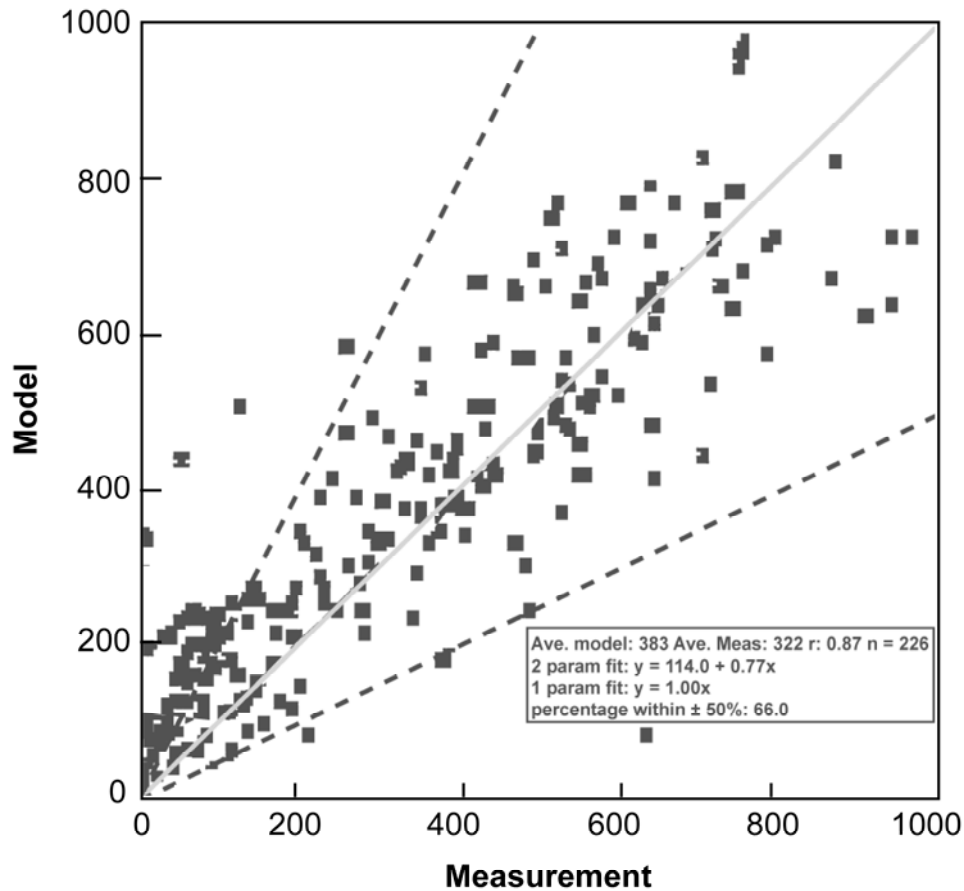


Figure 3.10-2. Same as Figure 3.10-1 but for sulfate wet deposition ($\text{mg(S)m}^{-2}\text{yr}^{-1}$).

Source: Dentener et al. (2006b).

1 **3.10.3 CTM Evaluation**

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

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

11 The evaluation of urban- and regional-scale models is also limited by the availability of
12 data. Measured [NO] and some speciated [VOC] are available through the EPA AQS, but
13 questions have been raised about the accuracy of some of those measurements; see the fuller
14 descriptions of measurement techniques relevant for NO_x and SO_x in Chapter 2. Evaluation of
15 urban- and regional-scale models against measurements has generally relied on results from a
16 limited number of field studies in the United States. Short-term, research-grade measurements
17 for species relevant to O₃ formation, including VOCs, NO_x, PANs, HNO₃, and hydrogen
18 peroxide (H₂O₂) are also sometimes available during focused campaigns at selected rural and
19 remote sites. See the descriptions in Daum et al. (1990 and 1996); Martin et al. (1997); Young
20 et al. (1997); Thompson et al. (2000); Hoell et al. (1997 and 1999); Fehsenfeld et al. (1996a);
21 Emmons et al. (2000); Hess (2001); and Carroll et al. (2001) for examples. The equivalent
22 measurements are available for some polluted rural sites in the eastern United States, but only for
23 a few urban locations as described in Meagher et al. (1998); Hübler et al. (1998); Kleinman et al.
24 (2000 and 2001); and Fast et al. (2002). Extensive measurements have also been made in
25 Vancouver (Steyn et al., 1997) and in several European cities (Staffelbach et al., 1997; Prévôt
26 et al., 1997, Dommen et al., 1999; Geyer et al., 2001; Thielman et al., 2001; Martilli et al., 2002;
27 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 estuarine 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

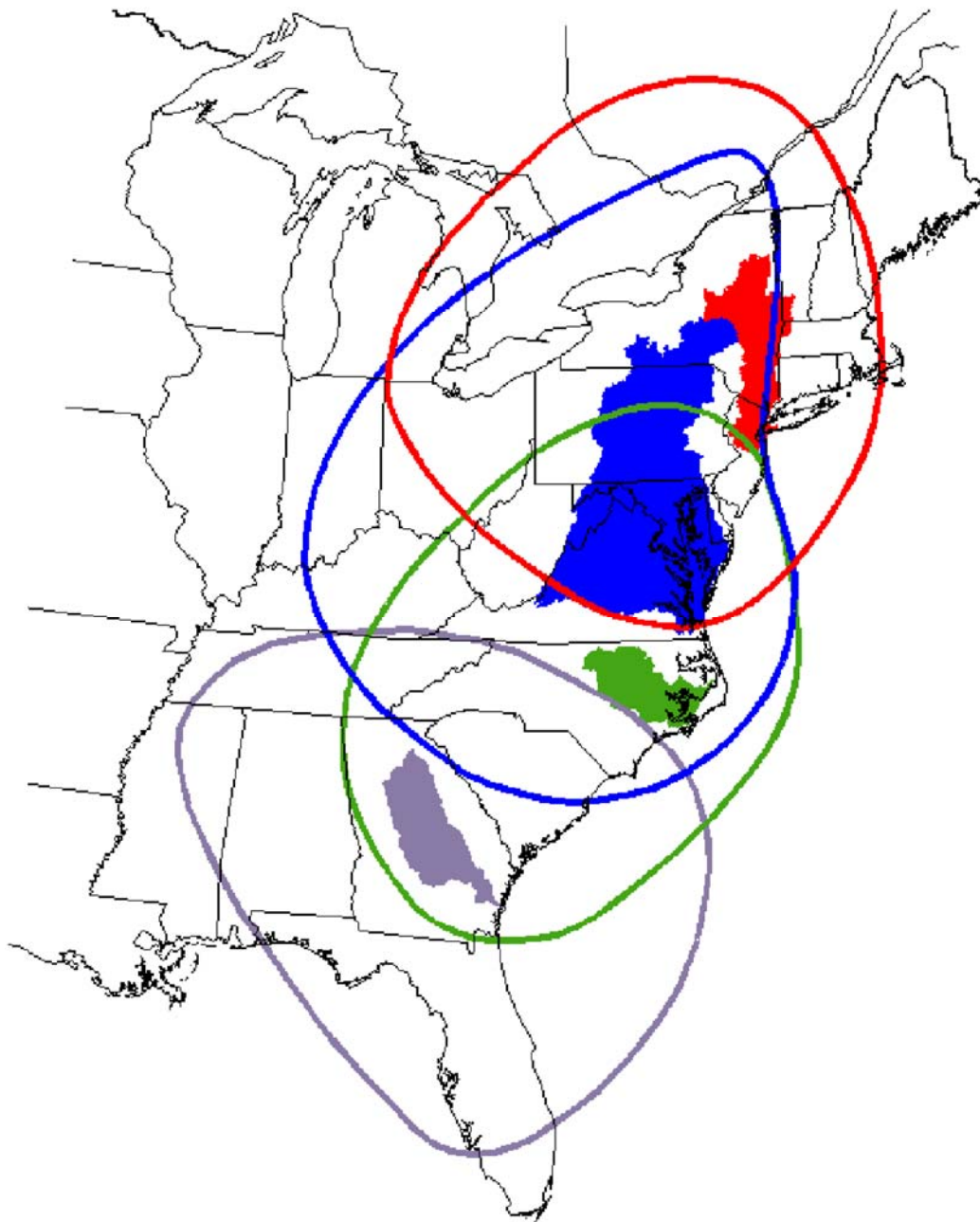


Figure 3.11-1. Principal airsheds and watersheds for oxides of nitrogen for these estuaries: Hudson/Raritan Bay; Chesapeake Bay; Pamlico Sound; and Altamaha Sound (listed from North to South). Airshed extents developed by R. Dennis, NOAA-ARL.

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

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

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

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

26 Considerable uncertainty attaches to estimates of the third form of atmospherically
27 derived N, organic N, in part because convenient methods for measurement and analysis are not
28 widely available; see Table 3.11-2. Intensive studies at individual sites have shown, however,
29 that for the North Carolina coast, for example, 30% of rain water N and deposition consisted of
30 organic N, 20-30% of which was then available to primary producers on time scales of hours to
31 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 NO₂ and SO₂ 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 [NO₂] and [SO₂] in surface air is considered. Figure 3.12-1 shows the annual mean [NO₂] 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 [NO₂] (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 [NO₂] are highest, PRB contributes <1% to the total concentrations.

The spatial pattern of present-day [SO₂] over the CONUS is similar to that of NO₂, with highest concentrations of >5 ppb along the Ohio River valley; see the upper panel Figure 3.12-2.

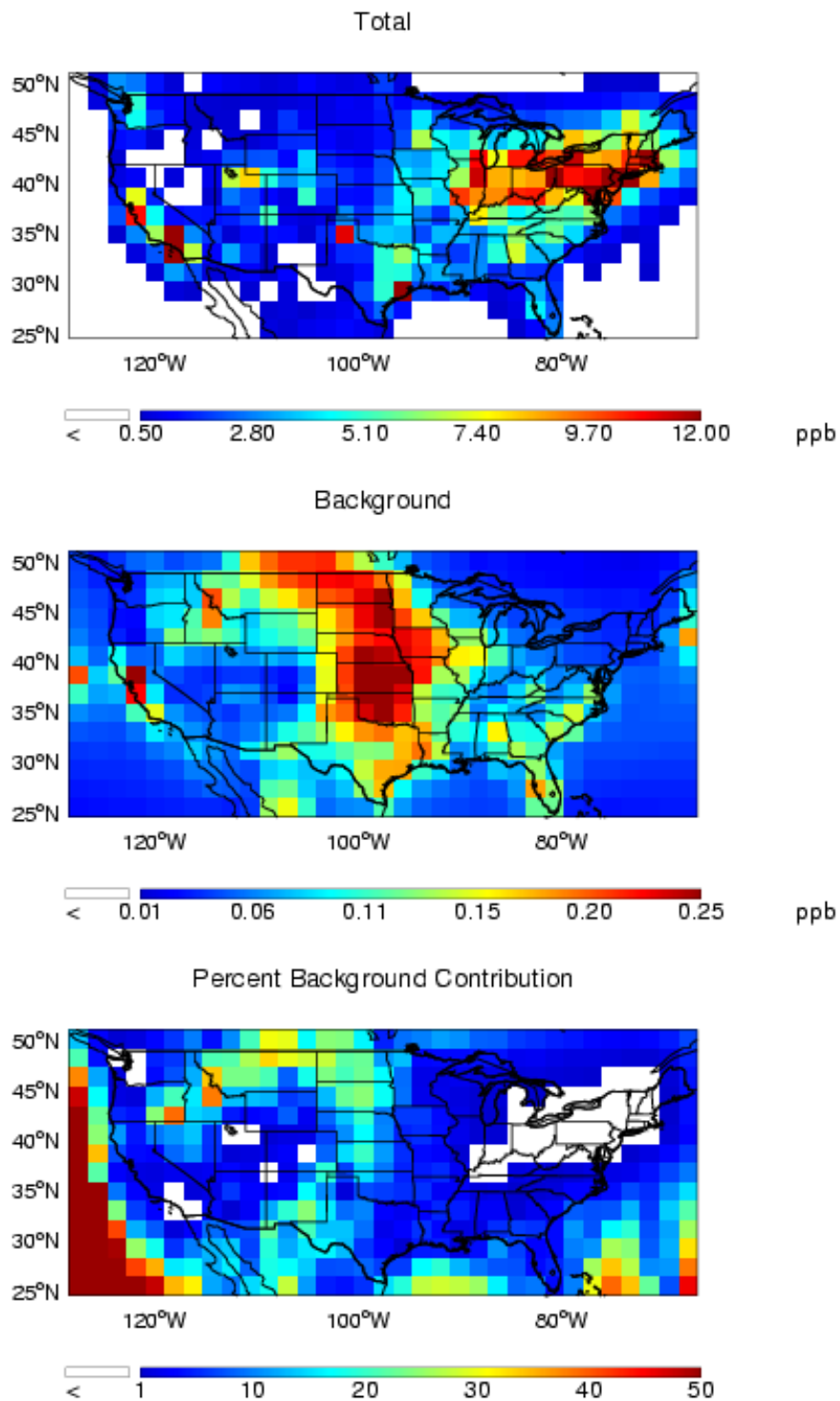


Figure 3.12-1. Annual mean concentrations of NO₂ (ppbv) in surface air over the United States in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations. Please see text for details.

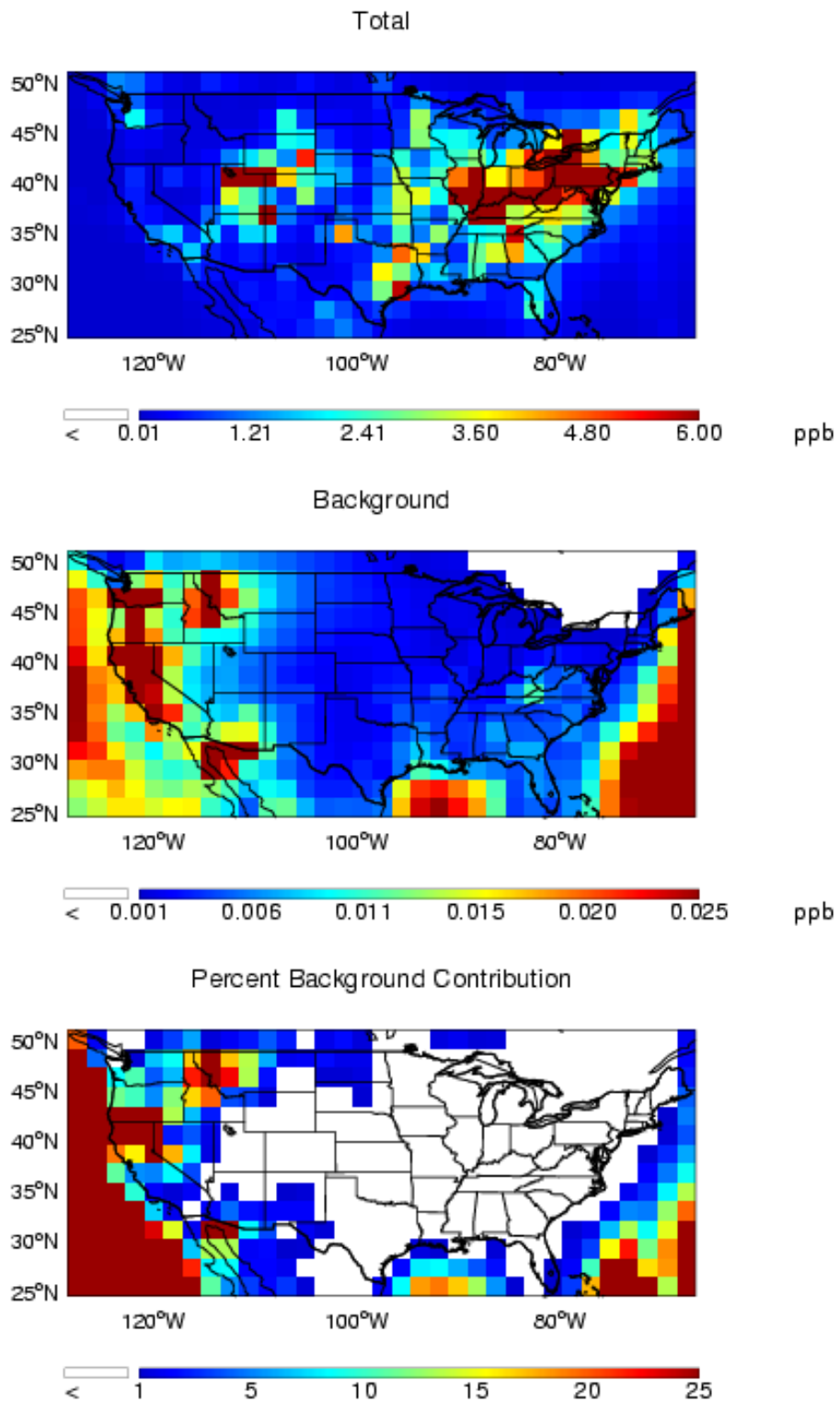


Figure 3.12-2. Same as Figure 3.12-1 but for SO₂ concentrations.

1 Background [SO₂] are orders of magnitude smaller, <10 ppt over much of the CONUS as shown
2 in the middle panel of Figure 3.12-2. Maximum PRB [SO₂] are 30 ppt. In the Northwest where
3 there are geothermal sources of SO₂, the contribution of PRB to total SO₂ is 70 to 80%.
4 However, excepting this, PRB contributes <1% to present-day [SO₂] in surface air as shown in
5 the bottom panel Figure 3.12-2.

6 The spatial pattern of NO_y (defined in the model as HNO₃ + NH₄NO₃ + NO_x + HO₂NO₂
7 + RONO₂) in wet and dry deposition is shown in Figure 3.12-3. Figure 3.12-3 (upper panel)
8 shows that highest values are found in the eastern United States in and downwind of the Ohio
9 River Valley. The pattern of N deposition in the PRB simulation shown in the Figure 3.12-3
10 middle panel, however, shows maximum deposition centered over Texas and in the Gulf Coast
11 region, reflecting a combination of N emissions from lightning in the Gulf region, biomass
12 burning in the Southeast, and from microbial activity in soils with maxima in central Texas and
13 Oklahoma. The bottom panel of Figure 3.12-3 shows that the PRB contribution to N deposition
14 is <20% over the eastern United States, and typically <50% in the western United States where
15 NO_y deposition is already lower at 25 to 50 mg N m⁻² yr⁻¹.

16 Present-day deposition of SO₂ and pSO₄ is largest in the Ohio River Valley, due to coal-
17 burning power plants in that region, while background deposition is typically at least an order of
18 magnitude smaller; see Figure 3.12-4. Over the eastern United States, the background
19 contribution to SO_x deposition is <10%, and it is even smaller, <1%, where present-day SO_x
20 deposition is highest. The contribution of PRB to S deposition is highest in the western United
21 States at >20% because of the geothermal sources of SO₂ and oxidation of DMS in the surface of
22 the eastern Pacific.

23 Figure 3.12-5 shows results from MOZART-2 discussed above as compared with those
24 from another tropospheric chemistry model, GEOS-Chem (Bey et al., 2001), which was
25 previously used to diagnose PRB [O₃] (Fiore et al., 2003; U.S. Environmental Protection
26 Agency, 2006a). In both models, the surface PRB [NO_x] tend to mirror the distribution of soil
27 NO emissions, which are highest in the Midwest. The NO emissions in GEOS-Chem are greater
28 than those in MOZART-2 by nearly a factor of 2 reflecting different assumptions regarding the
29 contribution to soil NO emissions largely through fertilizer, since GEOS-Chem total soil NO
30 emissions are actually higher than MOZART-2 at 0.07 versus 0.11 Tg N over the United States

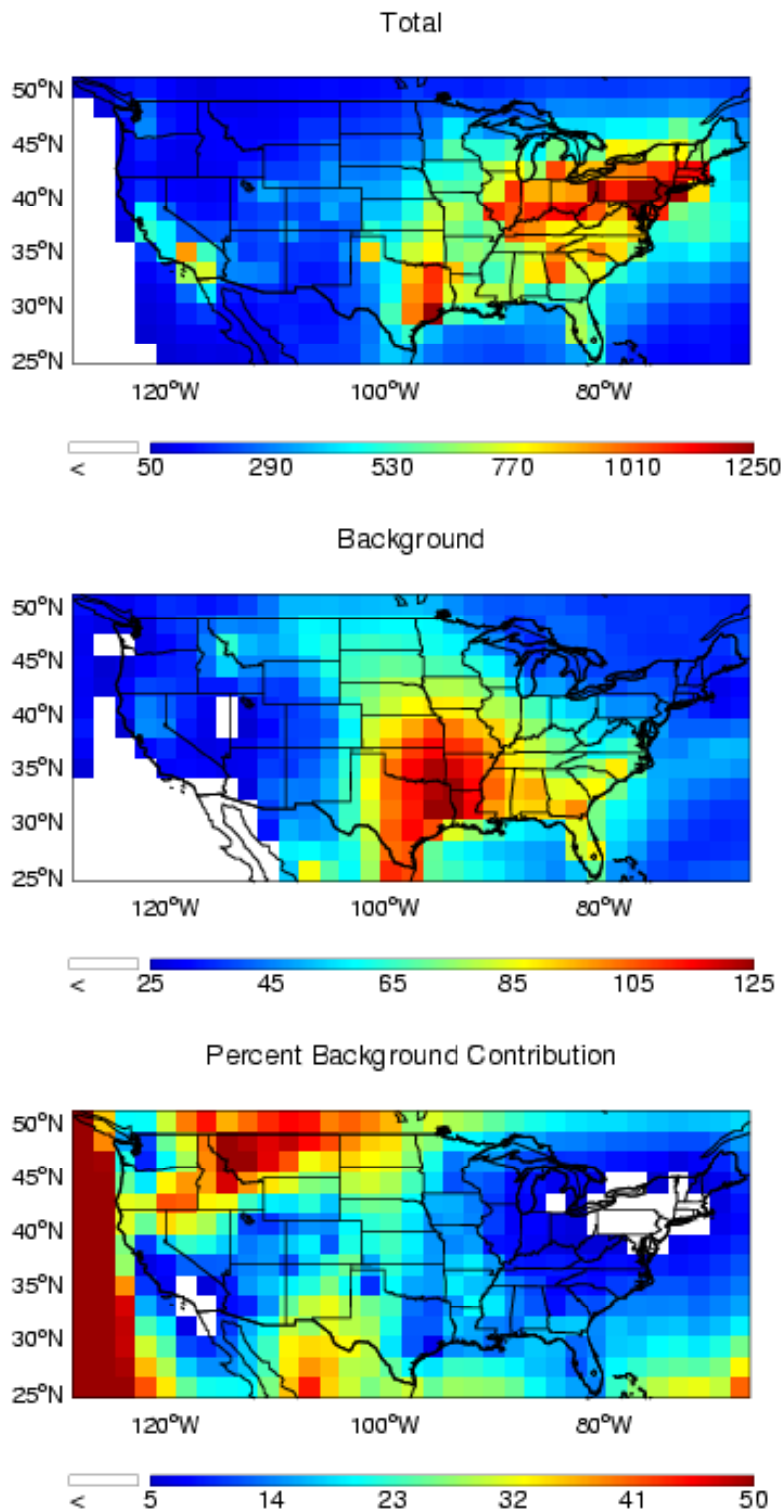


Figure 3.12-3. Same as for Figure 3.12-1 but for wet and dry deposition of HNO_3 , NH_4NO_3 , NO_x , HO_2NO_2 , and organic nitrates ($\text{mg N m}^{-2}\text{y}^{-1}$).

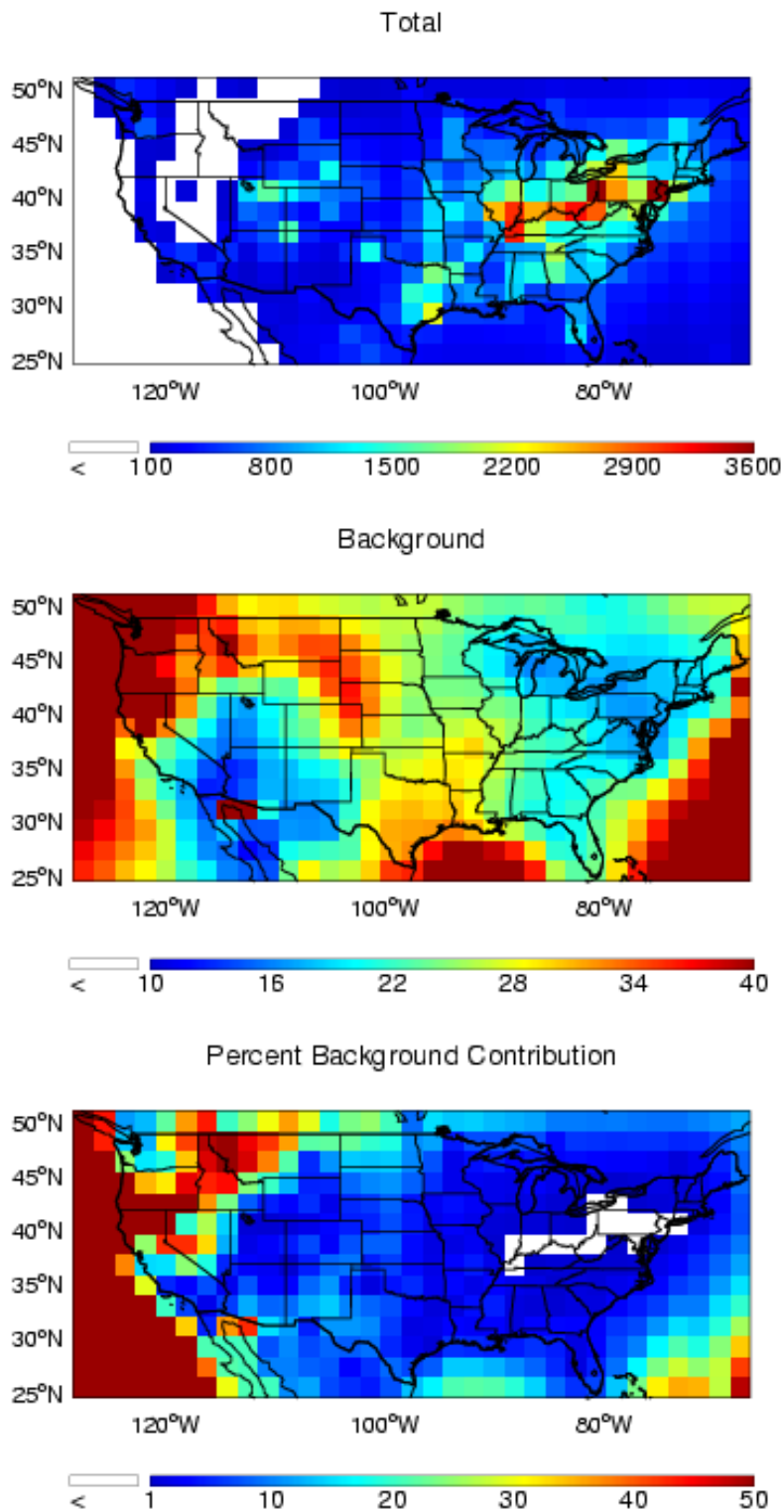


Figure 3.12-4. Same as Figure 3.12-1 but for SO_x deposition (SO₂ + pSO₄) (mg S m⁻²y⁻¹).

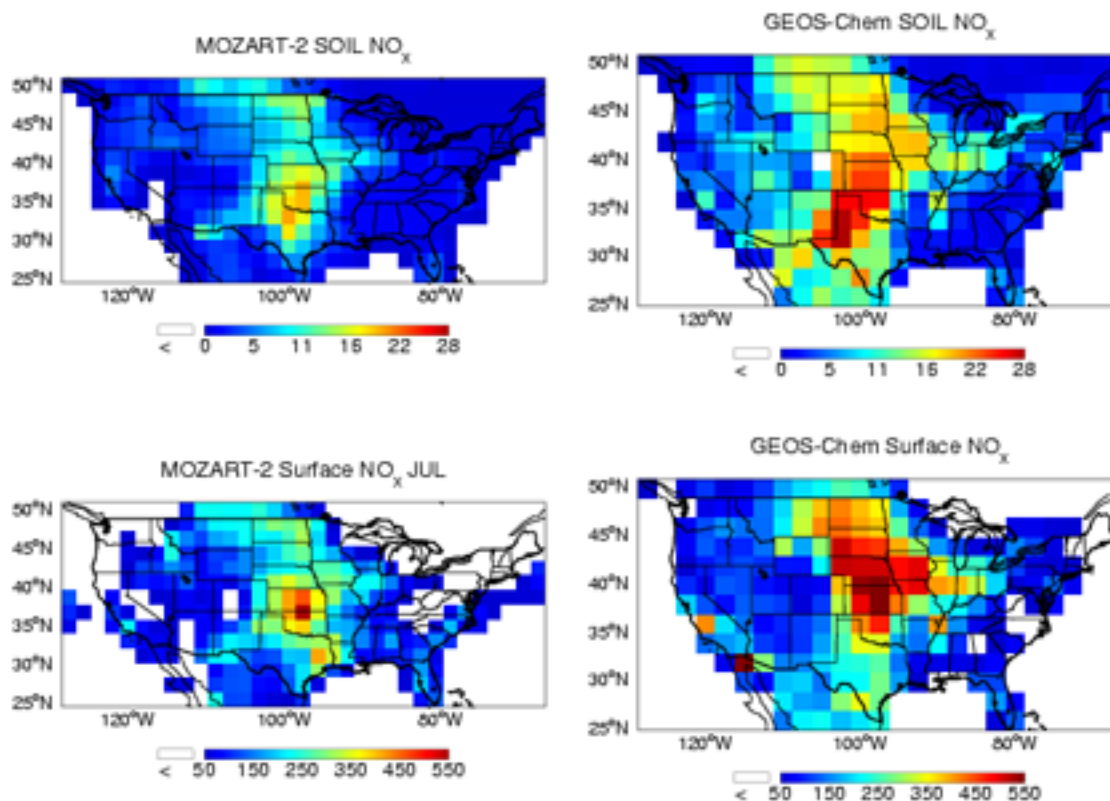


Figure 3.12-5. July mean soil NO emissions (upper panels; 1×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$) and surface PRB NO_x concentrations (lower panels; pptv) over the United States from MOZART-2 (left) and GEOS-Chem (right) model simulations in which anthropogenic O₃ precursor emissions were set to zero in North America.

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

3 It is also instructive to consider measurements of SO₂ at relatively remote monitoring
 4 sites, i.e., ones located in sparsely populated areas not subject to obvious local sources of
 5 pollution. Berresheim et al. (1993) used a type of atmospheric pressure ionization mass
 6 spectrometer (APIMS) at Cheeka Peak, WA (48.30N, 124.62W, 480 m asl), in April 1991 during
 7 a field study for DMS oxidation products: [SO₂] there ranged from 20 to 40 ppt. Thornton et al.
 8 (2002) have also used an APIMS with an isotopically labeled internal standard to determine
 9 background [SO₂] and found 25 to 40 ppt in northwestern Nebraska in October 1999 at 150 m

1 above ground using the NCAR C-130. These values are comparable to remote central south
2 Pacific convective boundary layer [SO₂] (Thornton et al., 1999).

3 Volcanic sources of SO₂ in the United States are limited to the Pacific Northwest, Alaska,
4 and Hawaii. Since 1980 the Mt. St. Helens volcano in Washington Cascade Range (46.20 N,
5 122.18 W, summit 2549 m asl) has been a variable source of SO₂. Its major effects came in the
6 explosive eruptions of 1980, which primarily affected the northern part of the mountainous west
7 of the United States. The Augustine volcano near the mouth of the Cook Inlet in southwestern
8 Alaska (59.363 N, 153.43 W, summit 1252 m asl) has had SO₂ emissions of varying extents
9 since its last major eruptions in 1986. Volcanoes in the Kamchatka peninsula of the eastern
10 region of Siberian Russia do not especially affect surface concentrations in northwestern North
11 America. The most serious effects in the United States from volcanic SO₂ occurs on the island
12 of Hawaii. Nearly continuous venting of SO₂ from Mauna Loa and Kilauea produce SO₂ in such
13 large amounts that >100 km downwind of the island, [SO₂] can be >30 ppb (Thornton and
14 Bandy, 1993). Depending on wind direction, the Kona region of the Hawaiian west coast has
15 had significant effects from SO₂ and pSO₄ for the past decade. Indeed, [SO₂] in Volcanoes
16 National Park, HI were in excess of the 3-h and the 24-h NAAQS in the 2004 to 2005 reporting
17 period.

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

20
21

22 **3.13 SUMMARY**

23

24 **3.13.1 Emissions and Atmospheric Concentrations of NO_x and SO_x**

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

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

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

1 NO and N₂O can be emitted from soils as intermediate products from denitrification,
2 either naturally; or as stimulated by addition of N containing fertilizers to crops and other soil
3 management practices.

4 N₂O is a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO₂-equivalent
5 basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there
6 remains considerable interannual variation in this number.

7 PRB [NO₂] are <300 ppt over most of the CONUS and <100 ppt in the eastern United
8 States on an annual average basis. The 24-h ambient [NO₂] in CMSAs where most monitors are
9 located were, on average, <20 ppb with a 99%ile value <50 ppb for the years 2003–2005.
10 Annual-average [NO₂] over the CONUS are calculated to be <5 ppb for nearly all urban and
11 rural and remote sites.

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

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

16 Annual-average policy-relevant background [SO₂] are <10 ppt over most of the CONUS,
17 or <1% of observed [SO₂] everywhere except areas in the Pacific Northwest where geogenic SO₂
18 sources are particularly strong.

19 NH₃ emissions are chiefly from livestock and from soils as stimulated by addition of N-
20 containing fertilizers to crops and other soil management practices.

21 **3.13.2 Deposition of Nitrogen and Sulfur**

22 Increasing trends in urbanization, agricultural intensity, and industrial expansion during
23 the previous 100 years have produced a nearly 10-fold increase in N deposited from the
24 atmosphere. NO_x, chiefly from fossil fuel combustion, often dominates total N pollution in the
25 United States and comprises ~50 to 75% of the total N atmospheric deposition.
26

27 Confined animal feeding operations and other intensified agricultural production methods
28 over a period of many decades have resulted in greatly increased volumes of animal wastes that
29 are high in N, of which 30% to 70% may be emitted as NH₃. This increase in NH₃ emissions,
30 and consequent increase in NH₄⁺ deposition, correlates well with the local and regional increases
31 in agricultural intensity.

1 For the period 2004–2006, the routine monitoring networks report the mean N deposition
2 in the United States was greatest in the Ohio River valley, specifically in the states of Indiana
3 and Ohio, with values as high as 9.2 and 9.6 kg ha⁻¹ yr⁻¹, respectively. N deposition was lower
4 in other parts of the East, including the Southeast and in northern New England. In the central
5 United States, Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg ha⁻¹ yr⁻¹,
6 respectively. Deposition primarily occurred as wet NO₃ and NH₄, followed by dry HNO₃, dry
7 NH₄, and dry NO₃. Although deposition in most areas of the United States occurred in wet form,
8 there were some exceptions, including parts of California where N deposition was primarily dry.
9 Data are very sparse for the central United States between the 100th meridian and the Mississippi
10 River; but, where available, N deposition values there are lower than most of the eastern United
11 States, ranging from 4.1 to 5.3 kg ha⁻¹ yr⁻¹.

12 For the period 2004–2006, mean S deposition in the United States was greatest east of
13 the Mississippi River with the highest deposition amount, 21.3 kg ha⁻¹ yr⁻¹, in the Ohio River
14 valley where most recording stations reported three-year averages >10 kg ha⁻¹ yr⁻¹. Numerous
15 other stations in the East reported S deposition >5 kg ha⁻¹ yr⁻¹. Total S deposition in the United
16 States west of the 100th meridian is relatively low, with all recording stations reporting less than
17 2 kg ha⁻¹ yr⁻¹ and many reporting less than 1.0 kg ha⁻¹ yr⁻¹. S was primarily deposited as wet
18 SO₄ followed by a smaller proportion of dry SO₂ and a much smaller proportion of deposition as
19 dry SO₄. However, these S data in the western United States, like those for N deposition, are
20 very thinly spread over the landscape there.

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

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

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

4 At Chesapeake Bay, where N and S deposition and ecological effects have been
5 extensively studied, total atmospheric deposition of atmospheric NO₃ is estimated to contribute
6 from 20 to 30% of total N and 14% of the NH₄ 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 ₂ O (air, land, water) Dust and aerosols generated by storms Microbially mediated volatilization
Organic Nitrogen (Dissolved and Particulate)	Agricultural Dust and volatilization of wastes ?? Urban and Rural (non-agricultural) Dust or aerosols ?? Natural Atmospheric photochemical and lighting Biological production in oceans ??

?? = possible, but little known about sources

Source: Swackhamer et al. (2004).

TABLE 3.11-3. CHARACTERISTICS OF OXIDIZED-NITROGEN AIRSHEDS

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

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

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 (N₂O) 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,

1 nutrient uptake, respiration, translocation carbon (C) allocation, and biosynthesis are directly
2 related to functions of energy flow and nutrient recycling. The energy accumulated and stored
3 by vegetation (via photosynthetic C capture) is available to other organisms. Energy moves from
4 one organism to another through the food chain in one direction, until it is ultimately released as
5 heat. Nutrients and water can be recycled. Air pollution alters the function of ecosystems when
6 nutrient cycle or the energy flow is altered.

7 8 **4.1.2 Ecosystem Services**

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

15 i. Supporting services are necessary for the production of all other ecosystem
16 services. Some examples include biomass production, production of atmospheric
17 oxygen, soil formation and retention, nutrient cycling, water cycling, and
18 provisioning of habitat. Biodiversity is a supporting service that is increasingly
19 recognized to sustain many of the goods and services that humans enjoy from
20 ecosystems. These provide a basis for three higher-level categories of services.

21
22 ii. Provisioning services, such as products (cf. Gitay et al., 2001), i.e., food (including
23 game, roots, seeds, nuts and other fruit, spices, fodder), fiber (including wood,
24 textiles), and medicinal and cosmetic products (including aromatic plants, pigments).

25
26 iii. Regulating services, which are of paramount importance for human society such
27 as (a) C sequestration, (b) climate and water regulation, (c) protection from natural
28 hazards such as floods, avalanches, or rock-fall, (d) water and air purification, and (e)
29 disease and pest regulation.

30
31 iv. Cultural services, which satisfy human spiritual and aesthetic appreciation of
32 ecosystems and their components.

33 34 **4.1.3 Quantifying Adverse Effects of Anthropogenic Pollution**

35 Quantifying adverse effects of pollution to ecosystems has been a challenge to the
36 secondary National Ambient Air Quality Standards (NAAQS) process from the onset (Tingey

1 et al., 1990). The following section discusses critical loads as a conceptual approach for
2 quantifying adversity. A second approach for quantifying adversity is valuation, this method is
3 discussed in more detail in Annex 10.

4 5 **4.1.3.1 Critical Loads**

6 Critical loads are used to express the amount of deposition of an atmospheric pollutant
7 (a “load”) that can be tolerated by natural or man-made systems without significant harm or
8 change occurring in those systems. The generally accepted definition of a critical load of
9 atmospheric pollutant deposition emerged from a pair of international workshops held in the late
10 1980s (Nilsson, 1986; Nilsson and Grennfelt, 1988). The workshop participants defined a
11 critical load as:

12 “A quantitative estimate of an exposure to one or more pollutants below which
13 significant harmful effects on specified sensitive elements of the environment do
14 not occur according to present knowledge.”

15 In North America, critical loads studies have been undertaken in Canada, partly to
16 support efforts to design emission reduction programs (RMCC, 1990; Jeffries and Lam, 1993).
17 Critical loads modeling was included in the 1997 Canadian Acid Rain Assessment (Jeffries,
18 1997) for several regions in eastern Canada. More recently, critical loads have been determined
19 and mapped for waters and forest soils for a number of regions in eastern Canada and acid-
20 sensitive lakes on the Canadian pre-Cambrian shield.

21 The Conference of New England Governors and Eastern Canadian Premiers (NEG/ECP)
22 has undertaken a program to “estimate sustainable acidic deposition rates and exceedences for
23 upland forests representative of the New England States and the Eastern Canadian Provinces...”
24 (NEG/ECP Forest Mapping Group, 2001). The Forest Mapping Working Group within the
25 NEG/ECP conducts regional assessments of the sensitivity of northeastern North American
26 forests to current and projected S and N emissions levels. The NEG/ECP have also provided
27 estimates of critical loads for surface waters in northeastern North America (cf. Dupont et al.,
28 2005).

29 Aside from the NEG/ECP studies and the national mapping effort of McNulty et al.
30 (2007), most critical loads studies on N and S in the United States have focused on smaller sub-
31 regional areas or individual sites. Critical loads studies for forests in the United States have been
32 centered in the Northeast and have usually used a catchment-based approach (cf. Pardo and

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

10 The development of a quantitative critical load estimate requires a number of steps
 11 (Figure 4.1-1). Eight general steps must be taken to define the basic critical load question in any
 12 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 1. Identify the *ecosystem disturbance* that is occurring (e.g., acidification,
2 eutrophication). Not all disturbances will occur in all regions or at all sites, and the
3 degree of disturbance may vary across landscape areas within a given region or site.
- 4 2. Identify the *landscape receptors* subjected to the disturbance (e.g., forests, surface
5 waters, crops). Receptor sensitivity may vary locally and/or regionally, and the hierarchy
6 of which receptors are most sensitive to what kind of disturbance may vary as well.
- 7 3. Identify the *biological indicators* within each receptor that are affected by
8 atmospheric deposition (i.e., individual organism, species, population, or community
9 characteristics). Indicators will vary geographically and perhaps locally within a given
10 receptor type.
- 11 4. Establish the *critical biological responses* that define “significant harm” to the
12 biological indicators (e.g., presence/absence, loss of condition, reduced productivity,
13 species shifts). Significant harm may be defined differently for biological indicators that
14 are already at risk from other stressors, or for indicators that are perceived as “more
15 valued.”
- 16 5. Identify the *chemical indicators* or variables that produce or are otherwise associated
17 with the harmful responses of the biological indicators (e.g., streamwater pH, lake
18 aluminum (Al) concentration, soil base saturation). In some cases, the use of relatively
19 easily measured chemical indicators (e.g., surface water pH or acid neutralizing capacity
20 [ANC]) may be used as a surrogate for chemical indicators that are more difficult to
21 measure (e.g., Al concentration).
- 22 6. Determine the *critical chemical limits* for the chemical indicators at which the
23 harmful responses to the biological indicators occur (e.g., pH < 5, base saturation <5%,
24 inorganic Al concentration greater than 2 μM). Critical limits may be thresholds for
25 indicator responses such as presence/absence, or may take on a continuous range of
26 values for continuous indicator responses such as productivity or species richness.
27 Critical limits may vary regionally or locally depending on factors such as temperature,
28 existence of refugia, or compensatory factors (e.g., high calcium (Ca) concentration
29 mitigates the toxicity of Al to fish and plant roots).
- 30 7. Identify the *atmospheric pollutants* that control (affect) the pertinent chemical
31 indicators (e.g., deposition of sulfate [SO₄⁺], nitrate [NO₃⁻], ammonium [NH₄⁺], nitric
32 acid [HNO₃]). Multiple pollutants can affect the same chemical variable. The relative
33 importance of each pollutant in producing a given chemical response can vary spatially
34 and temporally.
- 35 8. Determine the *critical pollutant loads* (e.g., kg ha⁻¹ yr⁻¹ total deposition of S or
36 nitrate-N) at which the chemical indicators reach their critical limits. Critical pollutant
37 loads usually include both wet and dry forms of pollutant deposition. The critical
38 pollutant load may vary regionally within a receptor or locally within a site (as factors
39 such as elevation or soil depth vary) and may vary temporally at the same location (as
40 accumulated deposition alters chemical responses).

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

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

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

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

30 Finally, there is the inescapable heterogeneity of all natural environments. Consider
31 soils, for instance. The high spatial variability of soils almost guarantees that for any reasonably

1 sized soil-based “receptor” that might be defined in a critical load analysis, there will be a
2 continuum of critical load values for any indicator chosen. The range of this continuum of
3 values may be narrow enough to be ignored; nevertheless, there is an a priori expectation in any
4 critical load analysis that multiple values (or a range of values) will result from the analysis.
5 Given the policy requirements for establishing critical loads and the heterogeneity of ecosystem
6 impacted by acidic deposition, we have not attempted to define critical loads for the United
7 States in this ISA.

8 9 10 **4.2 ECOLOGIC EFFECTS OF ACIDIFICATION**

11 **4.2.1 Effects on Major Biogeochemical Processes**

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

22 23 **4.2.1.1 Soil Acidification**

24 Soil acidification is the buildup of hydrogen cations (H^+), also called protons, in the soil.
25 This happens when a proton donor is added to the soil. Soil acidification can be a natural
26 process. However, the donor can also be a mineral acid, such as HNO_3 and sulfuric acid
27 (H_2SO_4), the common components of acid rain that result from NO_x and SO_x air pollution.
28 Decreases in soil pH attributable to acidic deposition have been documented in the United States.
29 Effects in the eastern United States appear to have been limited mainly to the Northeast and
30 portions of the Appalachian Mountains in both hardwood and coniferous forests. Soil
31 acidification has also probably occurred in localized areas of mixed conifer forest and chaparral

1 vegetation in, and near, the Los Angeles Basin, in response to locally high levels of atmospheric
2 dry N deposition.

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

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

18 Several studies document declines in soil pH within the Oa/A horizons and the upper B
19 horizon in sensitive regions of the United States over the past several decades (Johnson et al.,
20 1994a,b; Drohan and Sharpe, 1997; Bailey et al., 2005). These declines have been attributed at
21 least partly to acidic deposition (Bailey et al., 2005).

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

27

28 **4.2.1.2 Sulfur Accumulation and SO_4^+ Leaching**

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

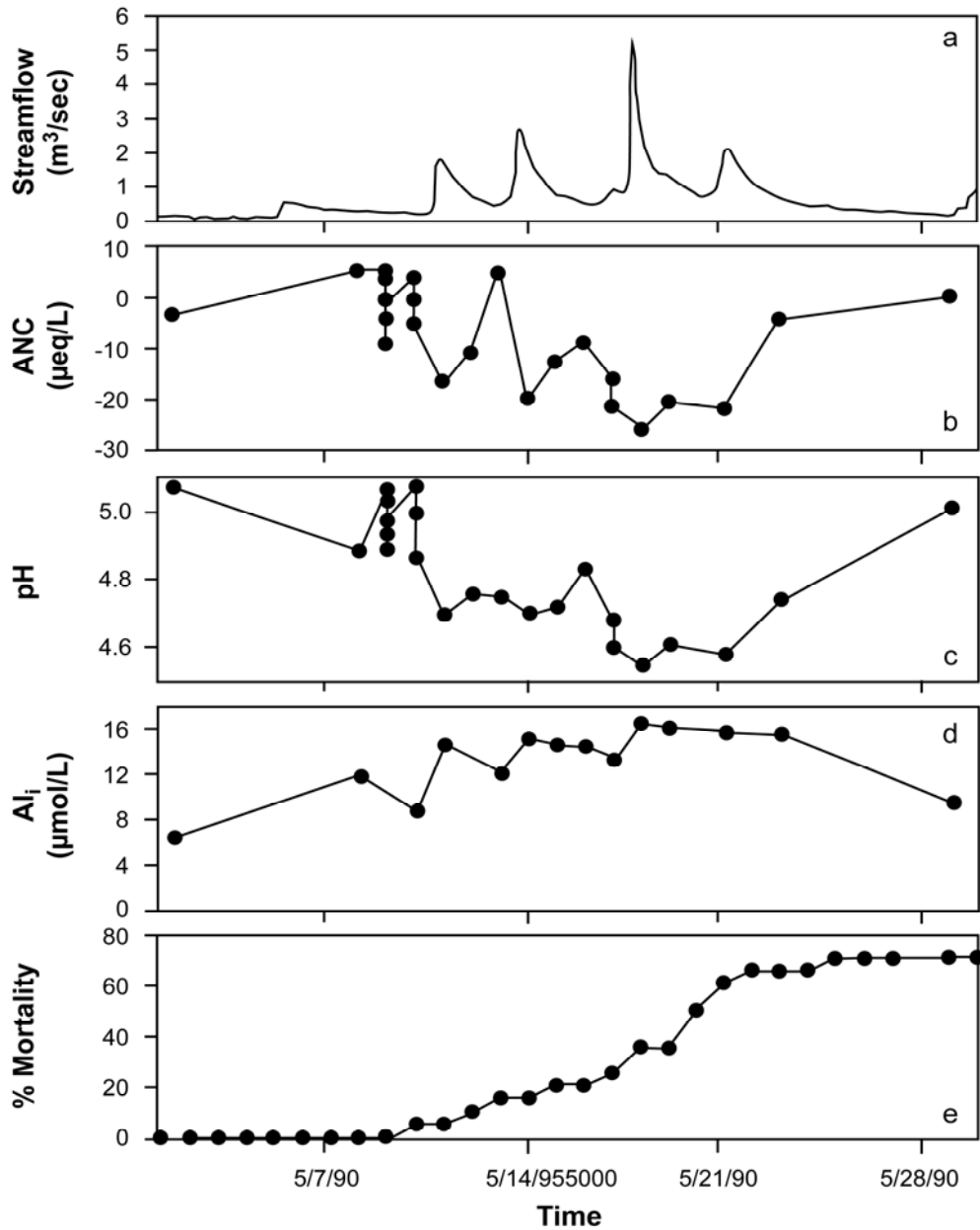


Figure 4.2-1. Diagram illustrates “ideal” soil horizons to which many soils conform. Each main horizon is denoted by a capital letter: **O) Organic matter**: Litter layer of plant residues in relatively undecomposed form. **A) Surface soil**: Layer of mineral soil with most organic matter accumulation 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).

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

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

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

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

23
24 *Southeast*

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

32

1 *Northeast*

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

8 Uncertainties in estimates of ecosystem S fluxes, such as weathering and dry deposition,
9 and complications in discerning the effects of S desorption from mineralization make it difficult
10 to predict when S outputs in the northeastern United States will no longer exceed inputs. Recent
11 research results, based on experimental reduction of S inputs, suggest that this process will occur
12 on a decadal timescale (Martinson et al., 2005; Mörth et al., 2005). The long-term role of C-
13 bonded S adds further uncertainty because enhancement of S mineralization by a warming
14 climate could also affect S retention and release from soil (Knights et al., 2000; Driscoll et al.,
15 2001b).

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

23
24 **4.2.1.3 Nitrogen Accumulation and NO_3^- Leaching**

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

31

1 *Nitrification and Accumulation*

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

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

25
26 *Leaching*

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

1 (Stoddard, 1994; U.S. Environmental Protection Agency, 2004). In general, atmospheric
2 deposition of 8 to 10 kg ha⁻¹ yr⁻¹ of N or more, results in NO₃⁻ leaching to surface waters in the
3 eastern United States. Lower N deposition levels (less than 5 kg N ha⁻¹ yr⁻¹) may lead to NO₃⁻
4 leaching in the mountainous West because of colder temperatures, shorter growing season, little
5 soil development, extensive exposed bedrock, and rapid melting of large snowpacks (Baron
6 et al., 1994; Williams et al., 1996a).

7 NO₃⁻ leaching usually contributes to the leaching of base cations from soils to surface
8 waters. Although there is typically less NO₃⁻ than SO₄⁺ leaching in most ecosystems in the
9 United States, concentrations of NO₃⁻ in some streams are high enough to suggest a substantial
10 role for NO₃⁻ in base cation loss from soil, particularly during periods of high soil-water NO₃⁻
11 flux during the nongrowing season (Van Miegroet et al., 1992; Cook et al., 1994).

12 The relationship between atmospheric N deposition and NO₃⁻ leaching from terrestrial
13 ecosystems is often modified by land-use history, current land-use, and climate. The N retention
14 capacity of soils is highly dependent on land-use history. For example, the removal of trees
15 reduces the amount of N in the watershed and enhances the demand of vegetative regrowth for
16 added N. This effect results in little or no NO₃⁻ leaching and can last for decades to more than a
17 century (Goodale et al., 2000). NO₃⁻ leaching is also affected by current land use. In the
18 northeastern United States, concentrations of N in streams of upland forested watersheds tend to
19 be considerably lower than in streams draining watersheds with other land uses. Perhaps the
20 most noteworthy affect of urban land use on processes of nutrient enrichment from N deposition
21 concerns the transport of NO₃⁻ to N-limited estuarine and near-coastal waters. This topic is
22 discussed in Section 4.3.2.2. In agricultural, and especially in forested areas it is generally
23 expected that most atmospherically deposited N is taken up by terrestrial vegetation. This is
24 usually not the case in urban landscapes, although it is sometimes possible. Due to the relatively
25 large impervious surface area in the urban landscape (e.g., buildings, roads, parking lots), a
26 higher percentage of precipitation is routed directly to surface waters, with little opportunity for
27 vegetative uptake of deposited N.

28 Climatic factors also play an important role in determining the extent of NO₃⁻ leaching.
29 In particular, temperature and moisture have large effects on N cycling and NO₃⁻ leaching.
30 Murdoch et al. (1998) found that, for at least one site, annual mean NO₃⁻ concentrations in
31 stream water were not related to annual wet N deposition, but rather were positively correlated

1 with mean annual air temperature. This was likely due partly to the fact that microbial processes
2 responsible for NO_3^- production are very sensitive to temperature. Fluctuations in microbial
3 immobilization and mineralization in response to climatic variability affect NO_3^- losses to
4 drainage waters.

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

15 16 **4.2.1.4 Base-Cation Leaching**

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

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

1 In the 1990s, data were published supporting the occurrence of base cation depletion
2 from soils in the United States, although decreases in exchangeable Ca concentrations had earlier
3 been identified in European soils through repeated sampling. Recent data reveal that decreases
4 in concentrations of exchangeable base cations and base saturation in the Oa and B soil horizons
5 have occurred over the past several decades in the eastern United States and most studies
6 attribute this change to the effects of acidic deposition. For example, the most thorough soil re-
7 sampling study in the United States was conducted in northwestern Pennsylvania by Bailey et al.
8 (2005). This study showed that between 1967 and 1997 pronounced decreases, attributed largely
9 to acidic deposition, were measured in exchangeable Ca and Mg concentrations in Oa/A horizons
10 and throughout the B horizon. Similarly, Sullivan et al. (2006a,b) documented base saturation of
11 B-horizon soils in the Adirondack Mountains between the mid-1980s and 2003. The depletion
12 of base cations contributes to soil acidification and influences the ability of watershed soils to
13 support acid-sensitive vegetation and to neutralize acidity in future acidic deposition.

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

25

26 **4.2.1.5 Aluminum Leaching**

27 If soil base saturation is 20 to 25%, or lower, acidic deposition can mobilize inorganic Al,
28 which can lead to the leaching of this toxic form of Al into soil waters and surface waters (Reuss
29 and Johnson, 1985). This is an extremely important effect of acidic deposition because inorganic
30 Al is toxic to tree roots, fish, algae, and aquatic invertebrates (see Section 4.2.3). In fact, fish
31 mortality in response to surface water acidification is usually attributable to Al toxicity.
32 Increases in the concentration of exchangeable Al in soil over the past several decades have been

1 documented at several locations in North America and Europe. Increased amounts of
2 exchangeable inorganic Al in the mineral soil have been identified through repeated soil
3 sampling over periods ranging from 17 years to 41 years (see discussion in Annex 4). In areas of
4 Europe with very high acidic deposition levels, evidence of inorganic Al depletion in the mineral
5 soil has also been found. Al depletion has not been documented in the United States.

6 Acidic deposition is an important cause of increased mobilization of inorganic Al from
7 soils to streams and lakes. Acidic deposition introduces mineral acidity associated with anions
8 that are more mobile than those from organic matter. If the release of base cations from the soil
9 is insufficient to neutralize the inputs of sulfuric and HNO₃, then Al that had previously been
10 deposited by normal soil development in the upper mineral soil is mobilized. Al may also be
11 mobilized by organic acids. However, acidic deposition, mobilizes Al in inorganic forms, and in
12 doing so increases the amount of exchangeable inorganic Al within the B horizon and results in
13 transport of inorganic Al into soil waters and surface waters. Inorganic Al is minimally soluble
14 at pH about 6.0. Solubility increases steeply at pH values below about 5.5. This distinction
15 between organic and inorganic forms of Al is important because organic Al is not toxic, whereas
16 inorganic Al is toxic to a variety of plants and aquatic organisms (Section 4.2.3.1.6).

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

27 In summary, the natural downward movement and deposition of Al within the upper soil
28 profile is altered by acidic deposition if the release of base cations is insufficient to buffer
29 atmospheric inputs of acidity. Rather than be deposited as an alumino-organic complex, Al
30 mobilized by acidic deposition tends to stay in solution in an inorganic form that can be
31 transported out of the soil and into surface waters. Depletion of exchangeable base cations

1 precedes the mobilization of inorganic Al. Therefore, as base cation concentrations in drainage
2 water decrease, inorganic Al concentrations increase. Increases in concentrations of inorganic Al
3 have been documented at several locations in base-cation depleted soils in the United States and
4 Europe. In soils with base saturation values less than about 15 to 20%, the ratio of exchangeable
5 Ca to Al is typically low in upper mineral soils (Lawrence et al., 2005).

6 7 **4.2.1.6 Short-Term Changes in Surface Water Chemistry: Episodic Acidification**

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

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

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

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

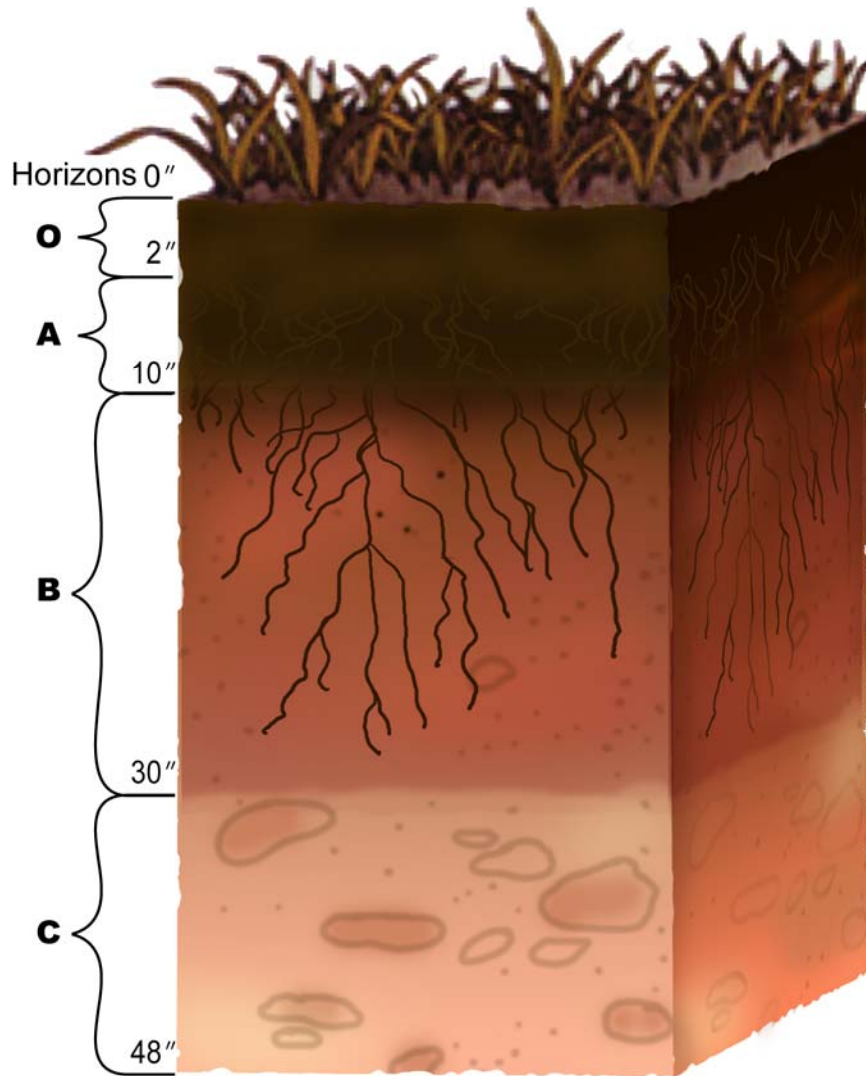


Figure 4.2-2. Results of an in situ bioassay during a period of episodic acidification in Buck Creek, Adirondack Mountains, in spring 1990: (a) discharge, (b) acid neutralizing capacity, (c) pH, (d) concentration of inorganic monomeric aluminum, and (e) cumulative percentage of mortality of brook trout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

Source: Driscoll et al. (2001b).

- 1 surface waters. The ERP also clearly showed that the episodic chemical response that has the
- 2 greatest effect on aquatic biota is increased inorganic Al concentration (Wigington et al., 1996).
- 3 Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in
- 4 inorganic Al in waters having low Ca concentration. Baker et al. (1990a) concluded that

1 episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above
2 5.5 and minimum pH during the episode of less than 5.0. The most thorough characterization of
3 episodic variation in stream chemistry in the United States was conducted through the ERP, in
4 which 13 low-order streams (watershed areas less than 24 km²) in the Adirondack and Catskill
5 regions of New York, and the Appalachian Plateau in Pennsylvania were monitored from 1988
6 to 1990 (Wigington et al., 1996). About 10% of the acid episodes involved decreases in ANC of
7 up to 200 µeq/L, decreases in pH of up to one unit, and increases in concentrations of inorganic
8 Al of up to 15 µM (Wigington et al., 1996). Results showed that acid episodes reduced the size
9 of fish populations and eliminated acid-sensitive species if median high-flow pH was less than
10 5.2 and inorganic Al concentration exceeded 3.7 µM, despite the relatively short duration of
11 episodes (Baker et al., 1996).

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

16 In general, the most severe acidification of surface waters generally occurs during spring
17 snowmelt (Charles, 1991) in many regions. Stoddard et al. (2003) found that, on average, spring
18 ANC values in New England, the Adirondacks, and the Northern Appalachian Plateau were
19 about 30 µeq/L lower than summer values during the period 1990 to 2000 (Figure 4.2-3). This
20 implies that lakes and streams in these regions would need to recover to chronic ANC values
21 above 30 µeq/L before they could be expected to not experience acidic episodes (Stoddard et al.,
22 2003). However, the estimate of 30 µeq/L is certain to be low because the comparison was made
23 with non-episodic sampling in spring, expressed as average spring ANC. Episodic ANC during
24 spring would be expected to be lower than average ANC during spring.

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

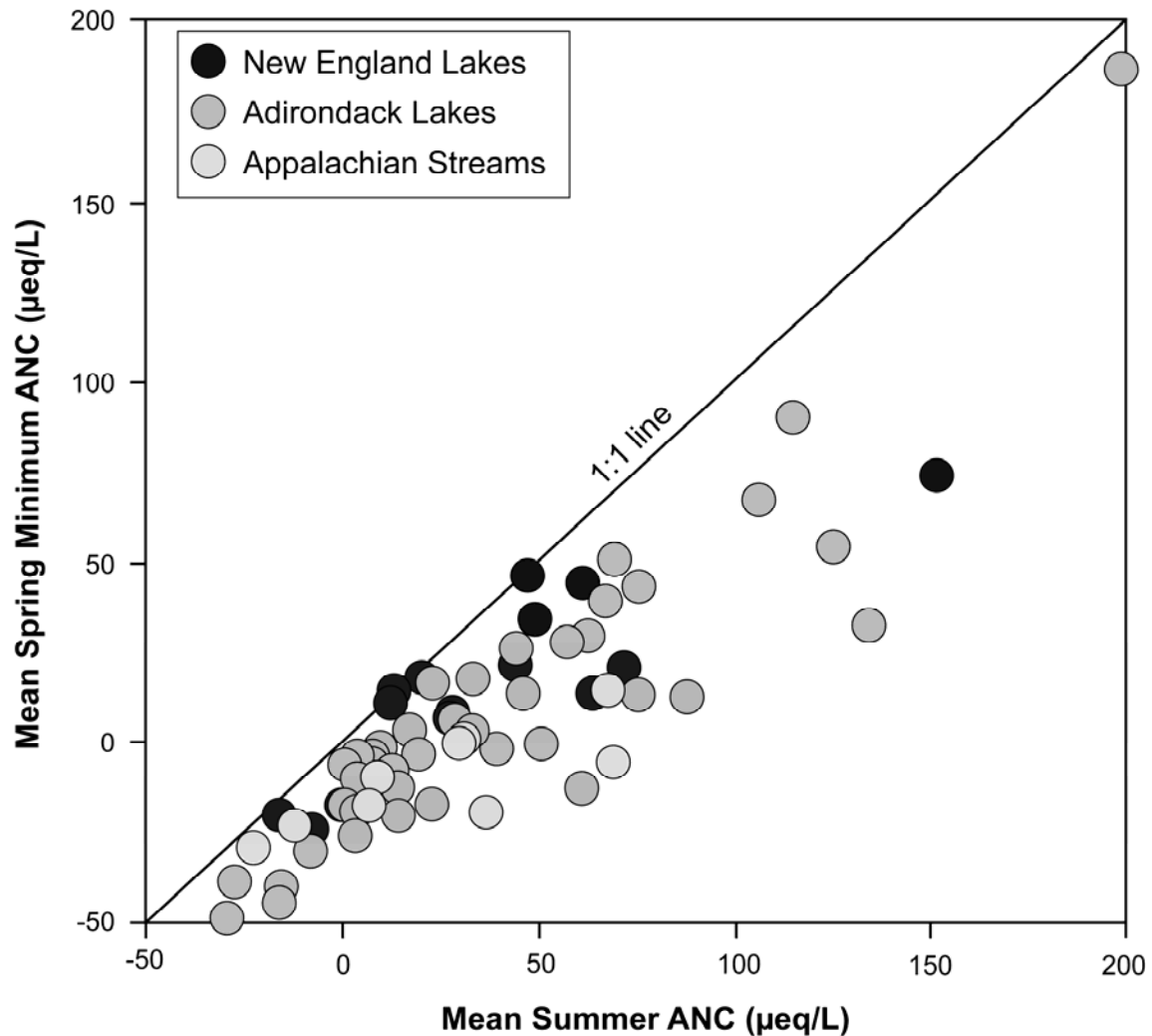


Figure 4.2-3. Relationship between mean summer ANC and the mean of minimum spring ANC values at long-term monitoring lake and stream sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

Source: Stoddard et al. (2003).

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

6 Streams having acidic episodes show significantly higher fish mortality and other aquatic
 7 community changes as compared with streams in which ANC remains above zero. Results from

1 in situ bioassay studies from across the eastern United States show that acidic episodes (with
2 associated low pH and elevated inorganic Al concentrations, and high streamwater discharge)
3 induced rapid fish mortality under some conditions (Baker et al., 1996; Bulger et al., 1999;
4 Driscoll et al., 2001b). For example, streams with suitable conditions during low flow, but
5 moderate-to-severe episodic acidification during high flow, had higher fish mortality in
6 bioassays, higher net downstream movement of brook trout during events, and lower brook trout
7 abundance and biomass compared to streams that did not experience appreciable episodic
8 acidification. These episodically impacted streams lacked the more acid-sensitive fish species
9 (blacknose dace and sculpin). Movement of trout into refugia (areas with higher pH and lower
10 inorganic Al) during episodes only partially mitigated the adverse effects of episodes (Baker
11 et al., 1996).

12 Consideration of episodic acidification greatly increases the extent and degree of
13 estimated impacts for acidic deposition on surface waters. In the Northeast, inclusion of
14 episodically acidified water bodies in regional assessments substantially increases estimates of
15 the extent of surface water acidification. For example, baseflow samples collected from 1991 to
16 1994 through the EPA Temporally Integrated Monitoring of Ecosystems (TIME) Program
17 indicated that 10% of the 1,812 lakes larger than 1 ha surface area in the Adirondack region
18 could be considered chronically acidic (ANC values less than 0 $\mu\text{eq/L}$), but that an additional
19 31% of these lakes had baseflow ANC values less than 50 $\mu\text{eq/L}$ and were, therefore, estimated
20 to be susceptible to episodic acidification (Driscoll et al., 2001b).

21 Lawrence (2002) estimated the extent of episodically acidified stream reaches in a
22 Catskill, NY watershed (area = 85 km^2) using an index site at the base of the watershed that
23 became episodically acidified at high flows. Upstream sites with a lower base flow ANC than
24 the index site at the same date and time were found to have a high likelihood of becoming
25 episodically acidified. Base flow sampling of 122 upstream sites indicated that approximately
26 16% of the total upstream reaches had chronic ANC less than 10 $\mu\text{eq/L}$, but that 66% of the
27 stream reaches had episodic ANC less than 10 $\mu\text{eq/L}$.

28 In the Southeast, a recent study by Deviney et al. (2006) within Shenandoah National
29 Park, Virginia used hourly ANC predictions over short time periods to compute recurrence
30 intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They
31 extrapolated the results to the rest of the Shenandoah National Park catchments using catchment

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

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

25 There have been no studies in the United States to determine if either the severity or
26 frequency of episodic acidification has lessened in response to recent decreases in acidic
27 deposition over the past three decades. In a study of two streams in Nova Scotia (Laudon et al.,
28 2002), trends in ANC during four phases of storm hydrographs from 1983 to 1998 were not
29 detected other than during the peak-flow phase of one stream (an increase of 0.87 $\mu\text{eq/L}$).

30 In summary, the vast majority of water chemistry data for acid-sensitive lakes and
31 streams in the United States have been collected under low-flow conditions. It is well known,

1 however, that water chemistry changes with season and with weather. Water chemistry is most
2 stressful to aquatic biota (lowest pH and ANC; highest inorganic Al concentration) during high
3 flow episodes that are associated with snowmelt and rainstorms. During such conditions, stream
4 chemistry can be toxic to species that thrive under chemical conditions more typical of base
5 flow. The EPA's ERP and other more localized studies have quantified the effects of episodes
6 on fish. Episodes are driven by hydrological processes, but the acidification that occurs is
7 largely a result of acidic deposition, especially in cases where inorganic Al has been mobilized.
8 Consideration of such variability in water chemistry is critical for accurate assessment of the
9 extent, magnitude, and biological effects of surface water acidification. The biological effects of
10 changes in surface water chemistry are discussed in greater detail in Section 4.2.3.2.

11 12 **4.2.2 Terrestrial Ecosystems**

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

21 22 **4.2.2.1 Chemical Effects**

23 There are several chemical indicators that provide useful information about the acid-base
24 status of soils. These include (1) soil base saturation, (2) Ca:Al ratio, and (3) C:N ratio (Table
25 4.2-1). Each chemical indicator provides insight into the degree to which the ecosystem has
26 acidified and may be susceptible to associated biological effects. These chemical indicators may
27 also be used to monitor the extent of acidification or recovery that occurs in forest ecosystems as
28 deposition rates of S and N change. As such, several chemical indicators and possible impact
29 thresholds have been developed and applied in conjunction with efforts to estimate critical loads.
30 The critical load refers to a quantitative estimate of deposition below which significant harmful
31 effects on the environment do not occur according to present knowledge (Nilsson and Grennfelt,
32 1988). The critical loads approach is discussed in more detail in Section 4.1.2

1 **4.2.2.1.1 Soil Base Saturation**

2 Soil base saturation expresses the concentration of exchangeable bases (Ca, Mg,
3 potassium [K]), sodium [Na]) as a percent of the total cation exchange capacity (which includes
4 exchangeable hydrogen ion and inorganic Al). In soils with a base saturation less than about 15
5 to 20%, exchange ion chemistry is dominated by Al (Reuss, 1983). Under this condition,
6 responses to sulfuric and HNO₃ inputs largely involve the release and mobilization of inorganic
7 Al through cation exchange. This is the form of Al that interferes with uptake of Ca by plant
8 roots and is also toxic to many forms of aquatic biota.

9 The soil O horizon tends to have a much higher base saturation than the B horizon,
10 despite having lower pH due to organic acidity. The base saturation of the B horizon is more
11 sensitive than that of the O horizon to base cation depletion from leaching by SO₄⁺ and NO₃⁻,
12 and is therefore particularly useful for assessing base status with regard to acidic deposition.
13 Little direct work has been done to relate soil base saturation to forest health, but Cronan and
14 Grigal (1995) determined that base saturation values below about 15% in the B horizon could
15 lead to impacts from Al stress. Lawrence et al. (2005) also observed pronounced decreases in
16 diameter growth of Norway spruce in northwestern Russia, where base saturation decreased from
17 30% to 20% in the upper 10 cm of the B horizon over a period of 37 years.

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

28
29 **4.2.2.1.2 Aluminum Concentration in Soil Solution: Calcium to Aluminum Ratio**

30 Al is toxic to tree roots. Plants affected by high Al concentration in soil solution often
31 have reduced root growth, which restricts the ability of the plant to take up water and nutrients,
32 especially Ca (Parker et al., 1989). Ca is well known as an ameliorant for Al toxicity to roots in

1 soil solution, as well as to fish in a stream. However, because inorganic Al does not become
2 mobilized until after soil Ca is depleted, elevated concentrations of inorganic Al tend to occur
3 with low levels of Ca in surface waters. Mg, and to a lesser extent Na and K, have also been
4 associated with reduced Al toxicity.

5 Dissolved Al concentrations in soil solution at spruce-fir study sites in the southern
6 Appalachian Mountains frequently exceed 50 μM and sometimes exceed 100 μM (Johnson et al.,
7 1991; Joslin and Wolfe, 1992; Eagar et al., 1996). All studies reviewed by Eagar et al. (1996)
8 showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution.
9 They surmised that the occurrence of periodic large pulses of NO_3^- in solution were important in
10 determining Al chemistry in the soils of spruce-fir forests.

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

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

25 The information available to define levels of risk for the Ca:Al ratio is complicated by
26 differences in natural soil conditions. As a result of these complications, the risk levels for the
27 ratio defined in laboratory experiments have not necessarily been successfully applied to field
28 conditions. For example, Johnson et al. (1994a,b) reported Ca:Al ratios above 1.0 through most
29 of 4 years in the Oa and B horizons of a high-elevation red spruce stand experiencing high
30 mortality. In the 3-year study of DeWitt et al. (2001), Al additions lowered molar Ca to
31 inorganic Al ratios in soil solutions of a Norway spruce stand below 0.5, but the authors found

1 no response other than reduced Mg concentrations in needles in the third year, which was a
2 possible precursor to damage.

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

11
12 **4.2.2.1.3 Soil Nitrogen: Calcium to Nitrogen Ratio**

13 Mechanisms of retention and release of N in forest ecosystems are not fully understood,
14 but the adverse effects of nitrification and associated acidification and cation leaching have been
15 consistently shown to occur only in soils with a C:N ratio below about 20 to 25 (Aber et al.,
16 2003; Ross et al., 2004). This observation makes the C:N ratio especially useful because
17 N mineralization and nitrification rates cannot be measured directly under natural conditions.
18 All available measurement approaches disturb the soil and often cause artificially high rates.
19 Therefore, field measurement provides a relative index rather than a realistic quantitative rate
20 (Ross et al., 2004). Approaches for measuring N mineralization and nitrification also are subject
21 to high degrees of variability, both temporally (hourly to seasonal) and spatially (down to the sub
22 meter level). Measurements of total OC and N however, are less variable in space and time and
23 are therefore more straightforward to document than N mineralization and nitrification rates.
24 Also, ratios of C to N in the forest floor are inversely related to acidic deposition levels, although
25 the relation is stronger for hardwood stands than conifer stands (Aber et al., 2003). In sum, these
26 factors make the C:N ratio a reliable and relatively straightforward measure for identifying forest
27 ecosystems that may be experiencing soil acidification and base leaching as a result of N input
28 and increased nitrification.

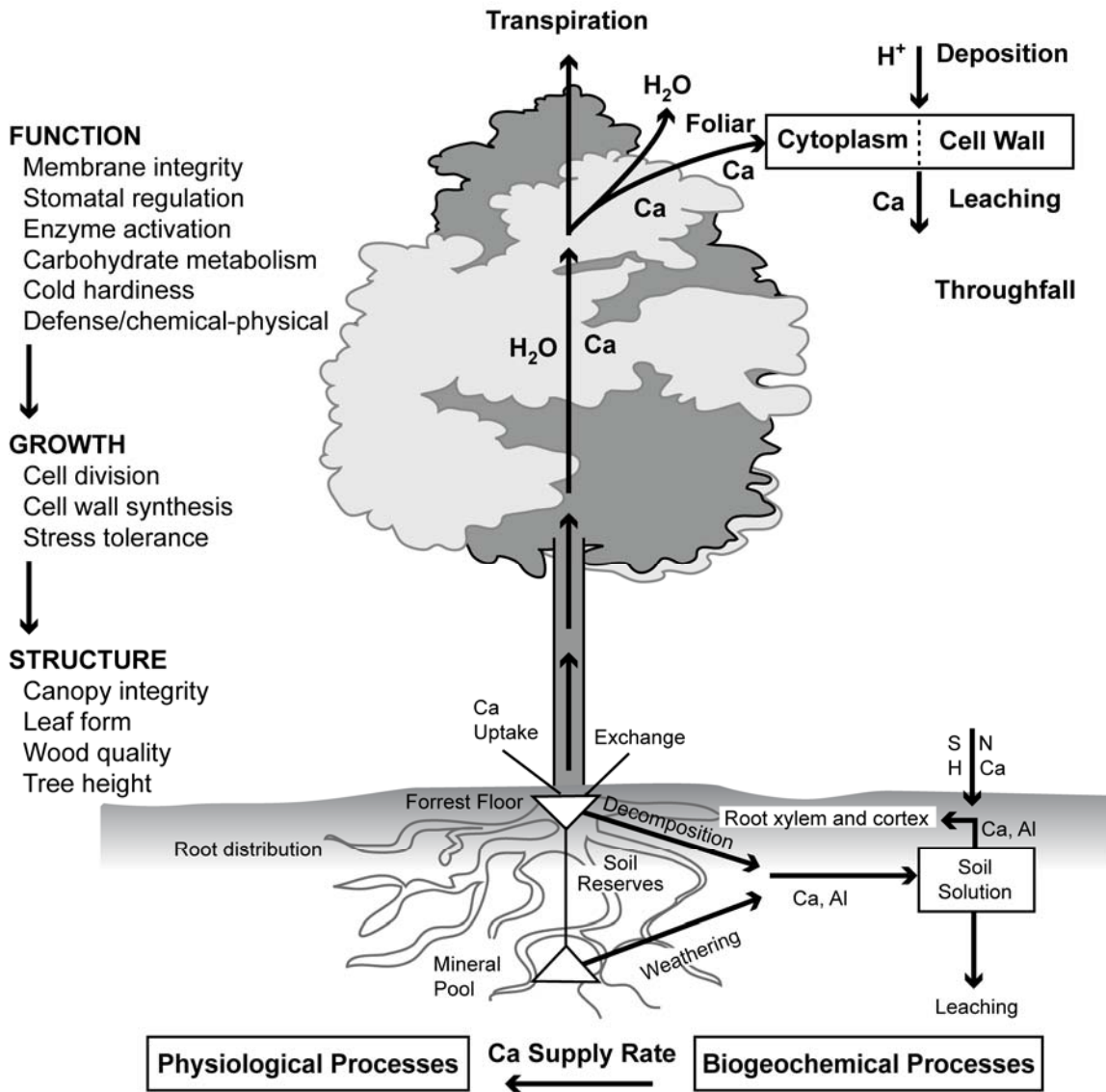


Figure 4.2-4. Diagram based on Fenn et al. (2006) shows indicators of forest physiological function, growth and structure that are lined to biogeochemical cycles through processes that control rates of Ca supply. Calcium effects plant physiological processes that influence growth rates and the capacity 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 Al, 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.

1 **4.2.2.2 Biological Effects**

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

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

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

22

23 **4.2.2.2.1 Health, Vigor, and Reproduction of Tree Species in Forests**

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

32

1 *Red Spruce*

2 Red spruce (*Picea rubens*) is a conifer that occurs mainly in the northeastern United
3 States and at scattered high-elevation sites in the Appalachian Mountains (Figure 4.2-5). Red
4 spruce dieback or decline has been observed across high elevation landscapes of both the
5 northeastern and southeastern United States. At high elevations in the Adirondack and Green
6 Mountains, more than 50% of the canopy red spruce trees died during the 1970s and 1980s. In
7 the White Mountains, about 25% of the canopy spruce died during that same period. Dieback of
8 red spruce has also been observed in mixed hardwood-conifer stands at relatively low elevations
9 in the western Adirondack Mountains, an area that receives high inputs of acidic deposition
10 (Shortle et al., 1997). Acidic deposition has been implicated as a causal factor (DeHayes et al.,
11 1999). The frequency of freezing injury to red spruce needles has increased over the past
12 40 years, a period that coincided with increased emissions of S and N oxides and increased
13 acidic deposition (DeHayes et al., 1999).

14 From the 1940s to 1970s, red spruce growth also declined in the southeastern United
15 States, as emissions of both nitrogen oxides and sulfur dioxide (SO₂) increased to maxima of
16 about 25 and 30 million tons/yr, respectively. The growth decline started earlier at higher
17 elevations (around the 1940s and 1950s) and was steeper, while the growth decline developed at
18 lower elevation sites 20 years later. After the 1980s, red spruce growth increased substantially at
19 both the higher- and lower-elevation sites, corresponding to a decrease in SO₂ emissions in the
20 United States (to about 20 million tons/yr by 2000), while nitrogen oxide emissions held fairly
21 steady (at about 25 million tons/yr). Annual emissions of S plus nitrogen oxides explained about
22 43% of the variability in red spruce tree ring growth between 1940 and 1998. Climatic
23 variability accounted for about 8% of the growth variation for that period. At low elevation,
24 changes in radial growth could be explained by climatic variables only, and there was no
25 correlation with national S plus nitrogen oxide emissions trends. Recent reductions in S oxide
26 emissions may have changed growth trajectories (Webster et al., 2004).

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

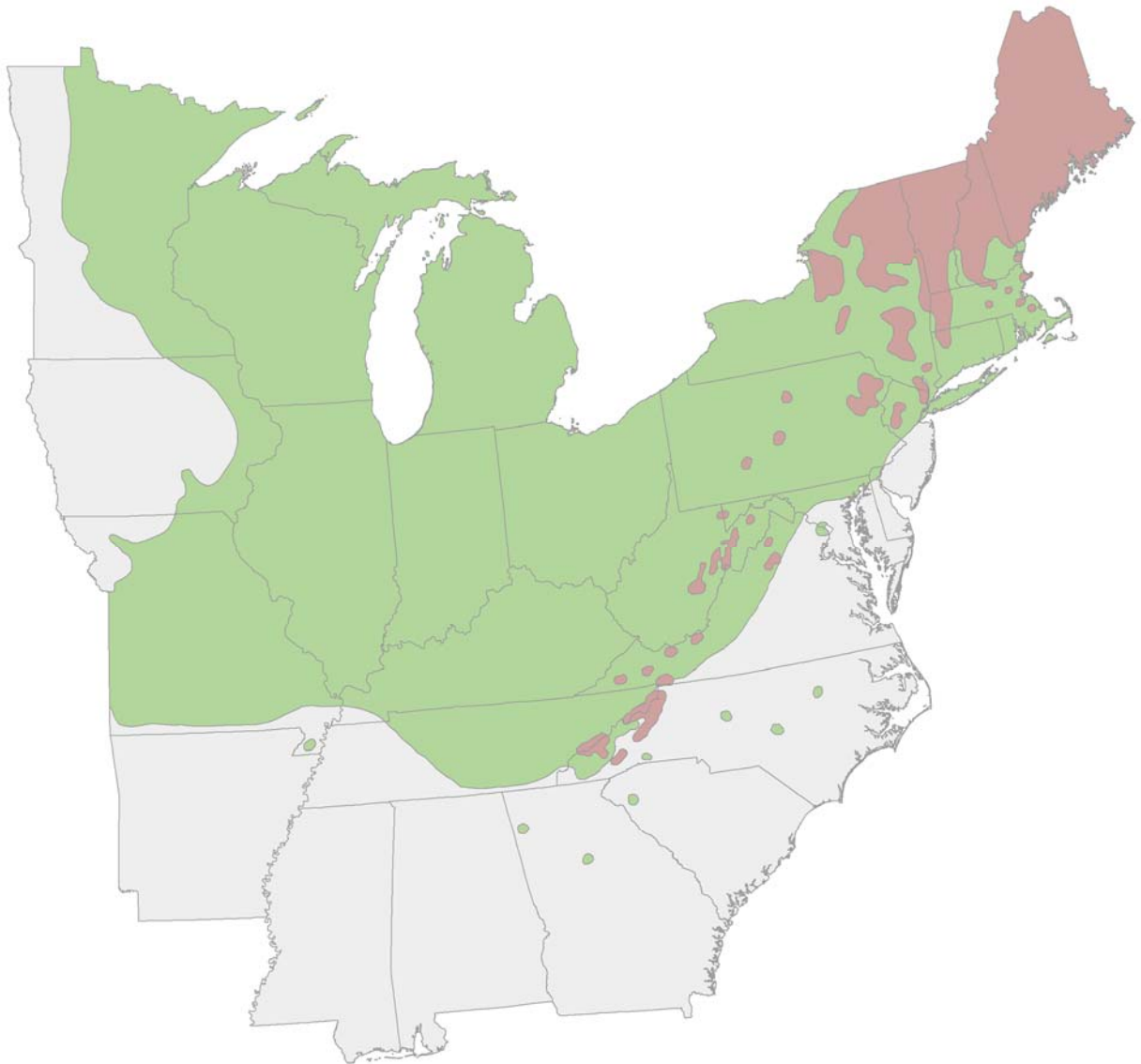


Figure 4.2-5. Distribution of red spruce (rose) and sugar maple (green) in the eastern United States. These two tree species have experienced adverse effects in portions of their ranges that have been attributed to acidification from acidic deposition. Tree distribution data were obtained from Little's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

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

- 1 3 to 10 °C (DeHayes et al., 1999). There is a significant positive association between cold
- 2 tolerance and foliar Ca in trees that exhibit foliar Ca deficiency. The membrane-associated pool
- 3 of Ca, although a relatively small fraction of the total foliar Ca pool, strongly influences the

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

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

18 19 *Sugar Maple*

20 Sugar maple (*Acer saccharum*) is the deciduous tree species of the northeastern United
21 States that is most commonly associated with adverse acidification-related effects of S and
22 N deposition, though other base cation accumulating hardwoods may also be at risk (Driscoll
23 et al., 2001b). Sugar maple is distributed throughout the northeastern United States and central
24 Appalachian Mountain region as a component of the northern hardwood forest (Figure 4.2-5).
25 Figure 4.2-7 provides a conceptual view of the interactions of acidic deposition and other
26 stressors in sugar maple decline. Several studies, mainly in Pennsylvania, have indicated that
27 sugar maple decline is linked to the occurrence of relatively high levels of acidic deposition and
28 base-poor soils (Horsley et al., 2000; Bailey et al., 2004; Hallett et al., 2006; Moore and Ouimet,
29 2006).

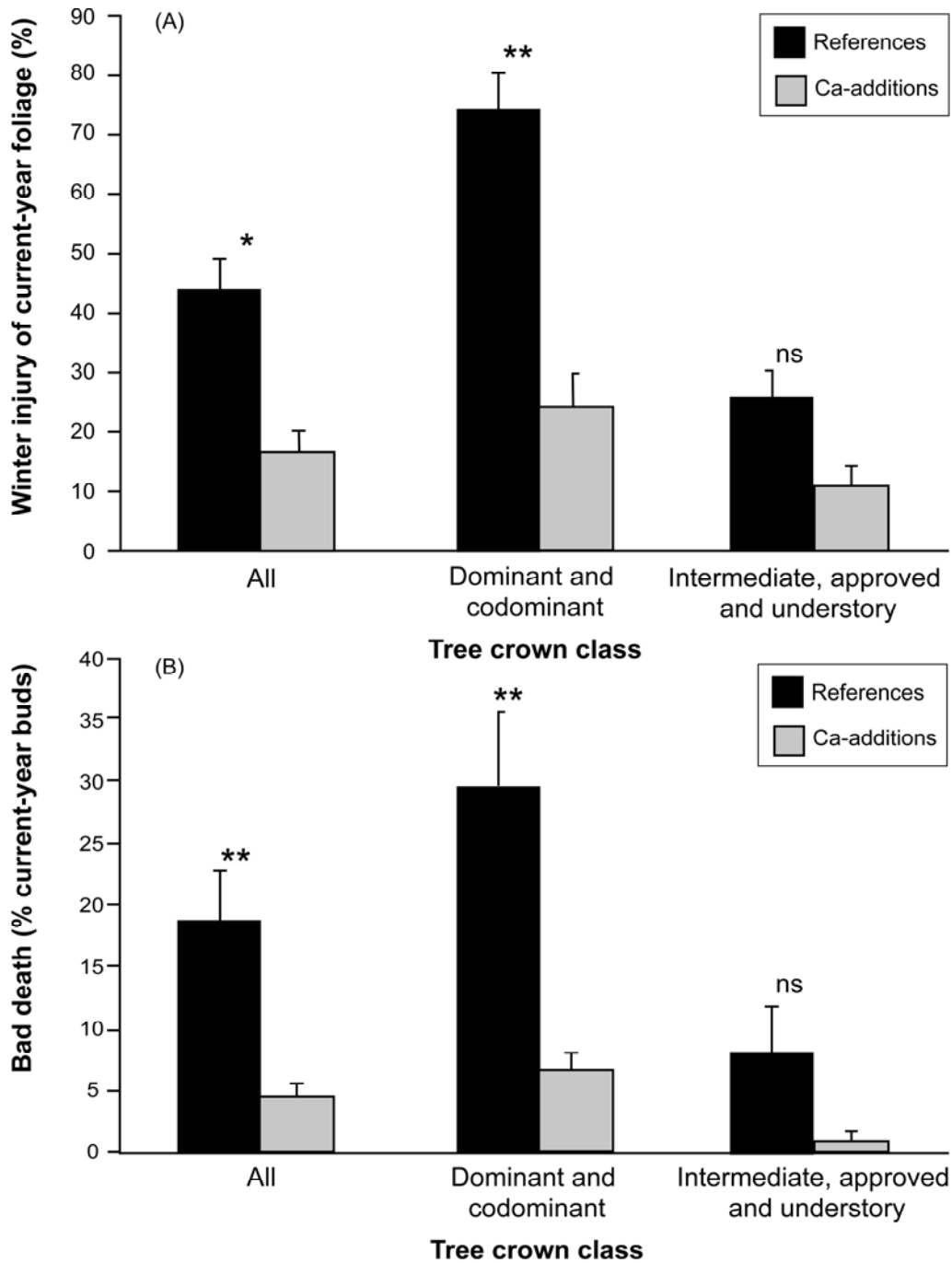


Figure 4.2-6. Mean (\pm standard error) of current-year red spruce winter injury in reference and calcium-addition watersheds and among crown classes, expressed as foliar injury (A) and bud mortality (B). Watershed means were either not significantly different (ns) or statistically different at $p <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

Source: Hawley et al. (2006).

1 Acidic deposition may be contributing to episodic dieback of sugar maple in the
2 Northeast through depletion of nutrient cations from marginal soils (Figure 4.2-7). Horsley et al.
3 (2000) found that dieback at 19 sites in northwestern and northcentral Pennsylvania and
4 southwestern New York was correlated with combined stress from defoliation and soil
5 deficiencies of Mg and Ca. Dieback occurred predominately on ridgetops and on upper slopes,
6 where soil base cation availability was much lower than on middle and lower slopes (Bailey
7 et al., 2004). A long-term decrease in soil pH since 1960 (0.78 pH unit decrease in the O
8 horizon, and 0.23 pH unit decrease in the A horizon) in Pennsylvania hardwood forests has been
9 documented, along with decreases in soil Ca and Mg concentrations. Declining sugar maples
10 were shown to be deficient in foliar Ca and Mg (Drohan and Sharpe, 1997). More recent
11 research has strengthened understanding of the role of cation nutrition in sugar maple health at a
12 regional scale across a broad range of conditions (Hallett et al., 2006).

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

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

26 27 *Other Forest Ecosystems*

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

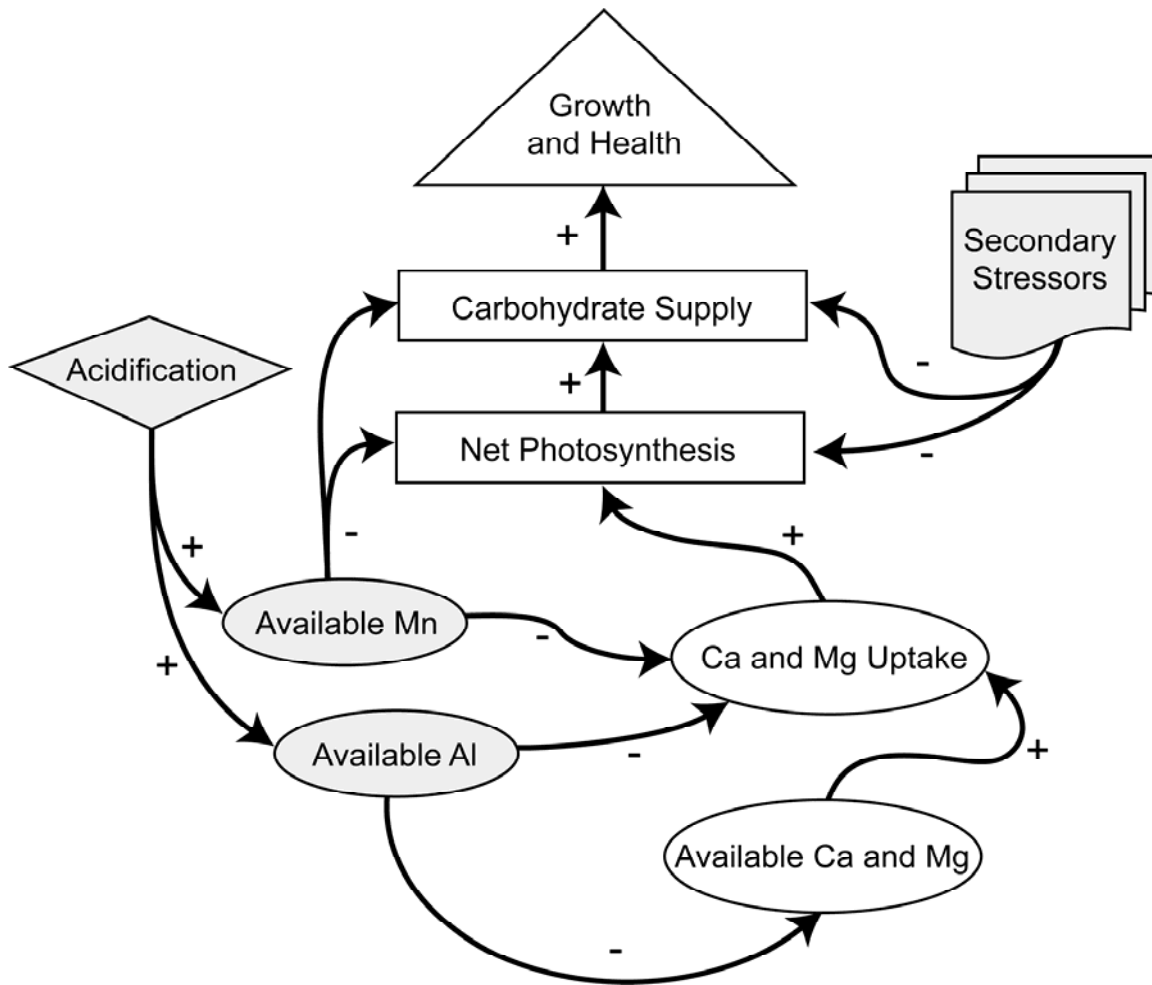


Figure 4.2-7. Conceptual diagram outlining the current understanding of sugar maple decline. Positive and negative signs indicate the nature of the correlative relationship between variables.

Source: Hallett et al. (2006).

- 1 4.4, 3.5 of 1:1 $\text{NH}_3\text{:H}_2\text{SO}_4$) showed no significant changes in growth (Temple et al., 1992).
- 2 Fenn et al. (2003a) reported that deposition levels of 20 to 35 $\text{kg N ha}^{-1} \text{yr}^{-1}$ contributed to
- 3 increased NO_3^- leaching and soil acidity and decreased base cation saturation in southern
- 4 California forest ecosystems, but they did not report quantitative measures of growth. Baron
- 5 et al. (2000) showed that small differences in the N deposition regime between the east (3 to 5 kg
- 6 $\text{N ha}^{-1} \text{yr}^{-1}$) and the west (1 to 2 $\text{kg N ha}^{-1} \text{yr}^{-1}$) side of the Rocky Mountains were associated
- 7 with significant declines in foliar Mg levels and increased foliar N:Mg and N:Ca ratios in old-

1 growth stands of Engelmann spruce (*Picea engelmannii*). It is not known whether such changes
2 in nutrient ratios affect the health or growth of these forests.

4 **4.2.2.2 Biodiversity of Forests**

5 Despite the evidence for impacts of acidic deposition on the health and vigor of some
6 terrestrial plant communities, we found a lack of scientific literature directly documenting
7 species loss, reduced biodiversity, or adverse effects on threatened and endangered species. A
8 notable exception is the impact of acidic deposition on lichen abundance and diversity within
9 forest communities (Lichens are discussed in Section 4.2.2.3). In eastern North America and
10 central Europe, areas that receive relatively high levels of acidic deposition have experienced
11 noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees
12 (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely
13 (McCune, 1988; Van Haluwyn and Van Herk, 2002). In London, epiphyte diversity, including a
14 majority of the lichen taxa, declined in areas where NO exceeded 40 $\mu\text{g}/\text{m}^3$ and total N oxides
15 exceeded 70 $\mu\text{g}/\text{m}^3$. It is also possible that effects of acidification on plant biodiversity may be
16 more widespread than those documented for lichens.

17 **4.2.2.3 Health and Biodiversity of Other Plant Communities**

19 *Shrubs*

20
21 Forest trees are not the only vascular plants that are potentially sensitive to acidic
22 deposition. Available data suggest that it is possible, or perhaps likely, that a variety of shrub
23 and herbaceous species are sensitive to base cation depletion and/or Al toxicity. However,
24 conclusive evidence is generally lacking.

25 Westman et al. (1985) reported a decrease in the number of inflorescences for different
26 shrubs fumigated with SO₂ over 10 weeks, at 0, 0.05, 0.20, and 0.50 ppm. Decreased
27 inflorescences were observed at 0.05-ppm SO₂ for black sage (*Salvia mellifera*), and at 0.20 ppm
28 SO₂ for California sagebrush (*Artemisia californica*), Eastern Mojave buckwheat (*Eriogonum*
29 *fasciculatum*), and California brittlebush (*Encelia californica*), with progressive declines as SO₂
30 concentration increased. This suggests impact of exposure to SO₂ on the reproduction of a
31 species rather than solely through impacts on the health of individual plants. We have found no

1 documentation of effects of S deposition, rather than atmospheric exposure, on plant
2 reproduction.

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

10
11 *Lichens*

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

20 Effects of SO₂ exposure on lichens includes reduced photosynthesis and respiration,
21 damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation,
22 reduced K absorption, and structural changes (Fields, 1988; Farmer et al., 1992). In response to
23 reductions after the 1970s in SO₂ exposure and acidic deposition in London, lichen diversity
24 increased dramatically (Hawksworth, 2002). However, the recovery of lichens in response to
25 reduced S and N inputs is inconsistent. Improvement for bryophytes has been reported to occur
26 in 1 year by Power et al., (2006) and Mitchell et al., (2004), 5 years by Gordon et al., (2001), and
27 49 years by Strengbom et al., (2001).

28 Scott (1989a,b) concluded that the S:N exposure ratio was as important as pH in causing
29 toxic effects on lichens, based on experiments on *Cladina rangiferina* and *C. stellaris*. Thus, it is
30 not clear to what extent acidity may be the principal stressor under high levels of air pollution
31 exposure. The toxicity of SO₂ to several lichen species is greater under acidic conditions than

1 under neutral conditions. The impacts of excess N deposition to lichen communities is discussed
2 in Section 4.3.3.1.5.

3
4 *Grasslands*

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

11
12 *Arctic and Alpine Tundra*

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

26
27 **4.2.3 Aquatic Ecosystems**

28
29 **4.2.3.1 Chemical Effects**

30 The changes in major biogeochemical processes and soil conditions caused by acidic
31 deposition have significant ramifications for the water chemistry and biological functioning of
32 associated surface waters. Surface water chemistry indicates the adverse effects of acidification
33 on the biotic integrity of fresh water ecosystems. Because surface water chemistry integrates the

1 sum of soil and water processes that occur upstream within a watershed, it also reflects the
2 results of watershed-scale terrestrial effects, including N saturation, forest decline, and soil
3 acidification (Stoddard et al., 2003). Thus, water chemistry integrates and reflects changes in
4 soil and vegetative properties and biogeochemical processes.

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

21 22 **4.2.3.1.1 Surface Water SO_4^+**

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

1 naturally derived organic anions represented an average of 71% of total negative charge in the
2 17% of lakes in which organic anions predominated (Driscoll et al., 2001b).

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

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

16 As emissions and deposition of S have declined over approximately the last 30 years,
17 surface water concentrations of SO_4^+ have decreased in most regions in the eastern United States.
18 For example, Stoddard et al. (2003) found that surface waters monitored in EPA Long-Term
19 Monitoring program showed consistent decreases in SO_4^+ concentrations from 1990 to 2000 in
20 New England lakes (1.77 $\mu\text{eq/L/yr}$), Adirondack lakes (2.26 $\mu\text{eq/L/yr}$), Appalachian streams
21 (2.27 $\mu\text{eq/L/yr}$) and Upper Midwest lakes (3.36 $\mu\text{eq/L/yr}$). The only exception to the pattern of
22 decreasing SO_4^+ concentration in surface waters during this period was for streams in the Blue
23 Ridge Mountain region of Virginia, which showed a significant increase in SO_4^+ concentrations
24 (0.29 $\mu\text{eq/L/yr}$) during this period. The increasing trend in Virginia streams is presumably
25 the result of decreased S adsorption and net desorption in the soil in response to decreased
26 S deposition.

27 In summary, available data indicate a pattern of increasing concentrations of SO_4^+ in
28 surface waters before the year of peak S emissions in 1973, followed by widespread decreasing
29 trends in SO_4^+ concentrations after the peak (with the only exception being the Blue Ridge
30 Mountain region in Virginia). On this basis, continued decreases in S emissions would be
31 expected to result in further decreases in SO_4^+ concentrations in surface waters, although the rate

1 of response is variable and some model results suggest that recovery may be delayed as
2 accumulated S leaches from watersheds, even as emissions and deposition decline.

3 4 **4.2.3.1.2 Surface Water NO_3^-**

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

11 Release of NO_3^- from soil to surface waters may affect nutrient relationships and
12 biological neutralization processes in aquatic ecosystems to a greater extent than SO_4^+ (Kelly
13 et al., 1987; Bukaveckas and Shaw, 1998; Momen et al., 2006). The importance of NO_3^- as an
14 agent of acidification varies by region. Driscoll and Newton, (1985) found that NO_3^-
15 concentrations in 20 lakes in the early 1980s in the Adirondack region of New York averaged
16 12% of SO_4^+ concentrations, whereas Lovett et al. (2000) found that baseflow NO_3^-
17 concentrations in 1994—97 were an average of 37% of SO_4^+ concentrations in 39 streams in the
18 Catskill region of New York. Murdoch and Stoddard (1993) demonstrated the importance of
19 NO_3^- during high-flow conditions in Catskill streams in which concentrations periodically
20 equaled or exceeded SO_4^+ concentrations. Average concentrations of NO_3^- in most southeastern
21 streams also tend to be considerably less than SO_4^+ concentrations (Webb et al., 2004).
22 However, Cook et al. (1994) documented very high NO_3^- concentrations in stream water at high
23 elevation in the Great Smoky Mountains in North Carolina.

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

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

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

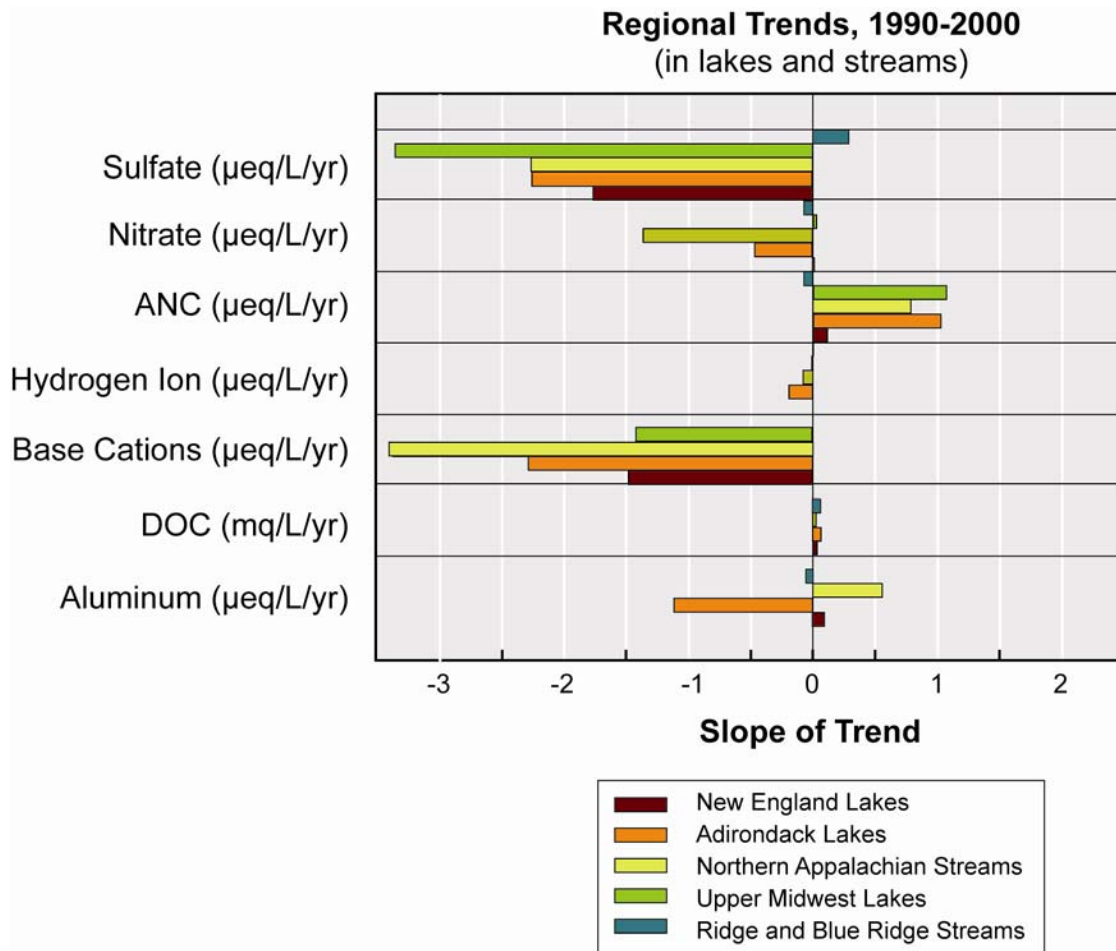


Figure 4.2-8. Summary of regional trends in surface water chemistry from 1990 to 2000 in regions covered by the Stoddard et al. (2003) report.

Source: Stoddard et al. (2003).

1 Processes within lakes may have also played a role in the measured trends in Adirondack
 2 lakes. In a study of 30 of the 48 long-term monitoring lakes investigated by Driscoll et al.
 3 (2003c; 2007a) and Momen et al. (2006) found that concentrations of dissolved NO_3^- were
 4 inversely correlated with concentrations of chlorophyll *a* in 11 lakes, and that chlorophyll *a* was
 5 increasing in concentration in 9 lakes. The increase in pH observed in most of these lakes may
 6 have stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

7 In summary, NO_3^- contributes to the acidity of many lakes and streams in the eastern
 8 United States that have been impacted by acidic deposition, especially during spring months and

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

12

13 **4.2.3.1.3** *Surface Water Base Cations*

14 The results from several studies in the eastern United States suggest that base cation
15 concentrations in surface waters increased during the initial phases of acidification into the
16 1970s. This trend reversed and base cations decreased in response to decreasing SO_4^+ and NO_3^-
17 concentrations. For example, the study of Likens et al. (1996) evaluated trends in base cation
18 concentrations in stream water in relation to long-term trends in SO_4^+ plus NO_3^- for the Hubbard
19 Brook Experimental Forest. This record showed an approximately linear increasing relationship
20 between concentrations of base cations and SO_4^+ plus NO_3^- from 1964 to 1969, then a reversal in
21 1970 and a decreasing trend up to 1994. The slope of the phase with increasing anion
22 concentrations was steeper than the slope for the phase with decreasing anion concentrations.
23 Regional declines in base cation concentrations were measured in the Long-Term Monitoring
24 project from 1990 to 2000 for lakes in New England, the Adirondack Mountains, and the Upper
25 Midwest (Figure 4.2-8). The study of Lawrence et al. (1999) showed decreased concentrations
26 of base cations at a rate that exceeded decreases in (SO_4^+ plus NO_3^-) in Catskill Mountain
27 streams from 1984 to 1997. In streams within western Virginia and in Shenandoah National
28 Park, concentrations of base cations did not exhibit significant trends from 1988 to 2001, perhaps
29 due to the influence of S adsorption to soil on stream water SO_4^+ concentrations.

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

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

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

22 23 **4.2.3.1.4 Surface Water pH**

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

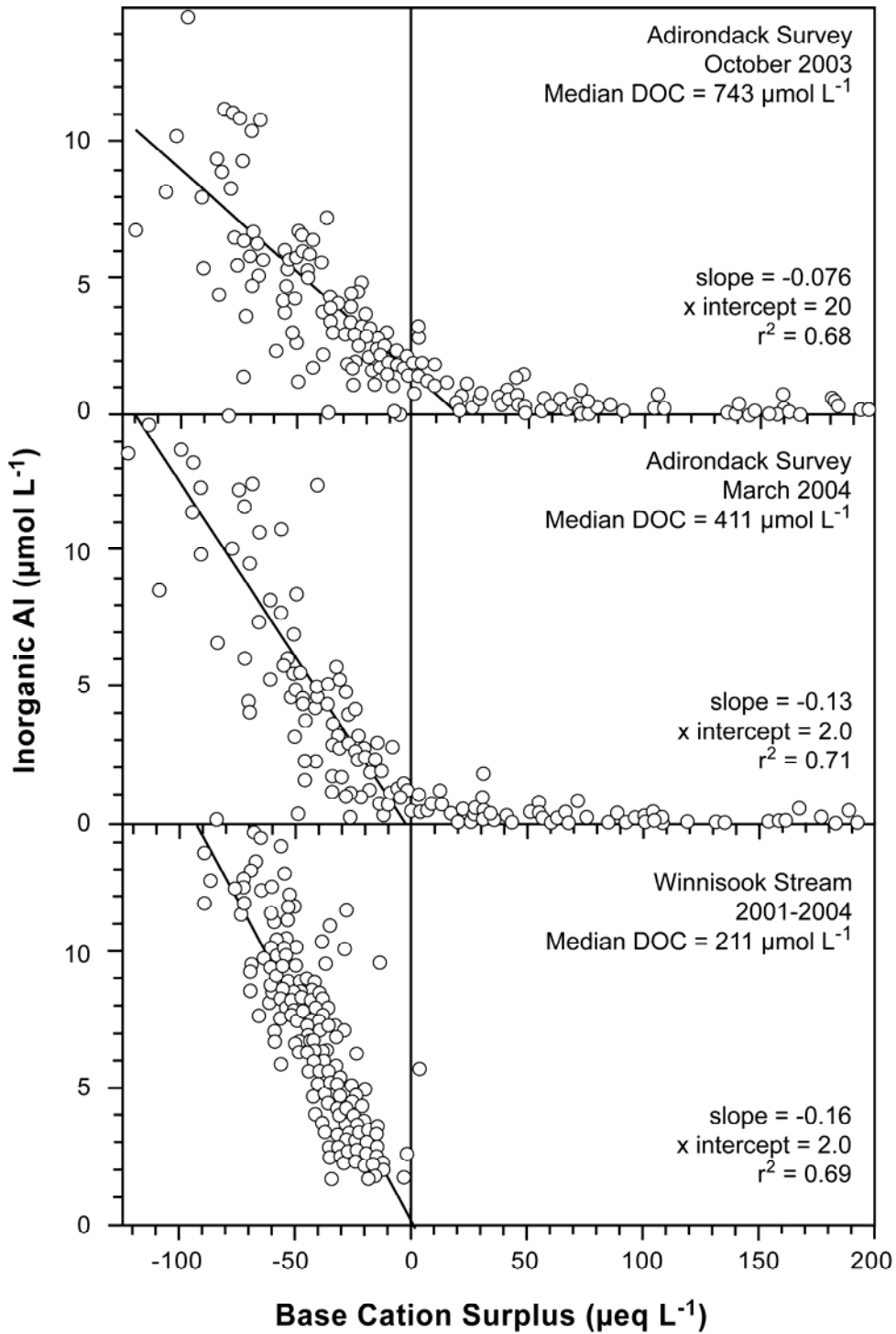


Figure 4.2-9. Concentration of inorganic Al in Adirondack streams as a function of the calculated base cation surplus.

Source: Lawrence et al. (2007).

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

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

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

18 In recent decades, measurements of pH have been routinely collected in surface waters in
19 the United States where effects of acidic deposition have been monitored, but a long-standing
20 reliance on titrated ANC rather than pH as the primary chemical measurement has limited the
21 amount of pH data published. Overall, between 1980 and 2000 most studies reported slight
22 increases in surface water pH, including lakes in the Adirondack Mountains (rate variable)
23 (Driscoll et al., 2007a) and southern New England (0.002 pH units per year) (Warby et al.,
24 2005), and streams in the Catskill/Poconos region of New York and Pennsylvania (0.008 pH
25 units per year) (Warby et al., 2005).

26 Through frequent interval monitoring from 1990 to 2000, Stoddard et al. (2003) found a
27 decrease in hydrogen ion ($0.19 \mu\text{eq/L/yr}$) that was similar to the rate of change observed in the
28 same Adirondack lakes by Driscoll et al. (2007a) from 1992 to 2004 ($0.18 \mu\text{eq/L}$). Stoddard
29 et al. (2003) also reported an increase in the hydrogen ion concentration of Appalachian streams
30 ($0.08 \mu\text{eq/L/yr}$) and Upper Midwest lakes ($0.01 \mu\text{eq/L/yr}$). No trends were found in New
31 England lakes or Appalachian streams in this study (Figure 4.2-8).

1 In summary, increasing trends in pH (decreasing hydrogen ion concentration) in surface
2 waters in the northeastern United States were common through the 1990s up to 2004, but many
3 exceptions occur, and overall, the rates of change have been small. Driscoll et al. (2001a,b;
4 2007c) attributed the limited pH recovery of lakes in acid-sensitive regions to three factors.
5 (1) The levels of acid-neutralizing base cations in surface waters have decreased markedly
6 because of the depletion of available base cations from the soil, and to a lesser extent, a reduction
7 in atmospheric inputs of base cations. (2) As forests mature, their requirements for N decrease,
8 and they are expected to exhibit increasing losses of NO_3^- as forests develop. (3) Sulfur has
9 accumulated in the soil under previous conditions of high atmospheric S deposition and is now
10 being gradually released to surface water as SO_4^+ , even though S deposition has decreased.

11 12 **4.2.3.1.5 *Surface Water ANC***

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

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

24 Baker et al. (1990c) used ANC cutoffs of 0, 50, and 200 $\mu\text{eq/L}$ for reporting on national
25 lake and stream population estimates. ANC less than 0 $\mu\text{eq/L}$ is of significance because waters
26 at or below this level have no capacity to neutralize acid inputs. Surface waters with ANC
27 < 50 $\mu\text{eq/L}$ have been termed “extremely acid sensitive” (Schindler, 1988), are prone to episodic
28 acidification in some regions (DeWalle et al., 1987; Eshleman, 1988), and may be susceptible to
29 future chronic acidification at current or increased rates of acidic deposition. Bulger et al. (1999)
30 defined ANC response categories for brook trout in Virginia as less than zero (chronic damage

1 likely), 0 to 20 $\mu\text{eq/L}$ (episodic damage likely), 20 to 50 $\mu\text{eq/L}$ (likelihood of damage not
2 determined), and greater than 50 $\mu\text{eq/L}$ (brook trout not sensitive).

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

11 Some of the most detailed studies of ANC have been conducted in the Adirondack
12 Mountains. Model simulations suggested that none of the lakes in the Adirondack target lake
13 population identified by EPA's Environmental Monitoring and Assessment Program (EMAP)
14 were chronically acidic or had ANC less than 20 $\mu\text{eq/L}$ under preindustrial conditions, but that
15 by 1980 there were hundreds of such lakes (Table 4.2-4). Many lakes were estimated to have
16 had preindustrial ANC below 50 $\mu\text{eq/L}$, but this estimate more than doubled by 1990. Based on
17 Model of Acidification of Groundwater in Catchments (MAGIC) model outputs extrapolated to
18 the regional population of Adirondack lakes larger than 1 ha that currently have ANC below
19 200 $\mu\text{eq/L}$, maximum past acidification occurred by about 1980 or 1990, with median ANC of
20 the lake population of about 61 $\mu\text{eq/L}$ (reduced from a median of 92 $\mu\text{eq/L}$ estimated for the
21 preindustrial period). Changes in ANC produced an increase in not only the percentage of lakes
22 that were chronically acidic, but also in those that were deemed likely to experience episodic
23 acidification and its associated short-term changes in water chemistry (Sullivan et al., in press).

24 In other regions, responses to reduced levels of acidic deposition required by the Clean
25 Air Act (CAA) and other emissions control legislation were reported by Stoddard et al. (2003).
26 They found tendencies during the 1990s toward increasing surface water Gran ANC in all of the
27 glaciated regions of the eastern United States (i.e., New England, Adirondacks, and Northern
28 Appalachian Plateau) and Upper Midwest, and decreasing Gran ANC in the Ridge/Blue Ridge
29 province. Changes in ANC were relatively modest compared with observed reductions in SO_4^+
30 concentrations in surface waters. The regional increases in the Adirondacks, Northern
31 Appalachian Plateau, and Upper Midwest were statistically significant (Table 4.2-5). Median

1 increases of about +1 $\mu\text{eq/L/yr}$ in the Northern Appalachian Plateau, Adirondacks, and Upper
2 Midwest represent significant movement towards ecological recovery from acidification
3 (Stoddard et al., 2003). Estimated change in the number of acidic surface waters decreased
4 during the 1990s in all regions investigated by Stoddard et al. (2003), except the Ridge and Blue
5 Ridge Provinces in the mid-Appalachian Mountains (Table 4.2-4). For other regions, the change
6 in number of acidic systems ranged from -2% in New England to -68% in the Upper Midwest.

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

16

17 **4.2.3.1.6 Surface Water Aluminum**

18 The concentration of inorganic Al in surface waters is an especially useful indicator of
19 acidic deposition effects because (1) it is widely toxic, and (2) it generally does not leach from
20 the terrestrial soils to surface waters in the absence of acidic deposition (Lawrence et al., 2007),
21 with exceptions such as acid mine drainage and relatively rare geologic deposits. Lawrence et al.
22 (2005) showed that strong organic acid anions can contribute to the mobilization of inorganic Al
23 in combination with SO_4^+ and NO_3^- , but that, in the absence of geologic S, the presence of
24 inorganic Al in surface waters is an ambiguous indication of acidic deposition effects.

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

1 Earlier studies demonstrated reduced growth and survival of various species of fish
2 (Baker and Schofield, 1982; Baker et al., 1996) at inorganic Al concentrations between
3 approximately 2 and 7.5 $\mu\text{mol/L}$. Most recently, 20% mortality of brook trout young-of-the year
4 was documented in situ during a 30-day period with a median inorganic Al concentration of
5 2 $\mu\text{mol/L}$ (Baldigo et al., 2007). This same study estimated that 90% mortality would occur over
6 30 days with a median inorganic Al concentration of 4.0 $\mu\text{mol/L}$.

7 The development of methods to fractionate Al into organic and inorganic forms (Driscoll,
8 1984; Sullivan et al., 1986) resulted in collection of a considerable amount of data on Al
9 concentrations in surface waters in the 1980s, but most of this sampling was done either once or
10 for a limited period of time (Driscoll and Newton, 1985; Driscoll et al., 1987a; Lawrence et al.,
11 1987; Cronan et al., 1990). Available long-term trend information for inorganic Al is limited. In
12 Adirondack lakes, inorganic Al concentrations decreased slightly (e.g., by 0.02 $\mu\text{M/yr}$ to
13 0.18 $\mu\text{M/yr}$; Driscoll et al., 2007a) or remained unchanged between 1982 and 2004 (Stoddard
14 et al., 2003; Driscoll et al., 2007a). There was no trend in inorganic Al for this period in New
15 England lakes, Appalachian streams, or Midwest lakes. Monthly stream chemistry monitoring at
16 the Hubbard Brook Experimental Forest showed decreases in inorganic Al concentrations at four
17 locations along the reference stream for the experimental forest from 1982 to 2000, but no trends
18 at two other locations along this stream (Palmer et al., 2004).

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

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

31

1 **4.2.3.2 Biological Effects**

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

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

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

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

24 25 **4.2.3.2.1 Measures of Health, Vigor, and Reproductive Success**

26 There are few measures of the effects of acidification on the health, vigor, and
27 reproductive success of aquatic species. Condition factor is one measure of sublethal
28 acidification stress that has been used to quantify effects of acidification on an individual fish.
29 Condition factor is an index to describe the relationship between fish weight and length.
30 Expressed as fish weight/length³, multiplied by a scaling constant, this index reflects potential
31 depletion of stored energy reserves (Everhart and Youngs, 1981; Goede and Barton, 1990;
32 Dennis and Bulger, 1995). Condition factor is interpreted as depletion of energy resources such

1 as stored liver glycogen and body fat in response to increased stress at sublethal levels (Goede
2 and Barton, 1990). Fish with higher condition factor are more robust than fish having low
3 condition factor. Field studies have shown lower condition factor in fish found in more acidic
4 streams (Dennis and Bulger, 1995).

5 6 **4.2.3.2.2 *Measures of Biodiversity***

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

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

20 Taxonomic richness is a metric that is commonly used to quantify the effects of an
21 environmental stress on biota. It can be applied at various taxonomic levels. For example, the
22 number of fish species present in a lake or stream can be used as an index of acidification (cf.
23 Bulger et al., 1999). Similarly, acidification effects on aquatic insects can be evaluated on the
24 basis of the number of families or genera of mayflies (order Ephemeroptera) (Sullivan et al.,
25 2003). In the latter cases, the mayfly order was selected for study because it includes a number
26 of genera and species having varying degrees of sensitivity to acidification.

27 Decreases in ANC and pH and increases in inorganic Al concentration have been shown
28 to contribute to declines in species richness and abundance of zooplankton, macroinvertebrates,
29 and fish (Schindler et al., 1985; Keller and Gunn, 1995). Species richness is positively
30 correlated with pH and ANC (Rago and Wiener, 1986; Baker et al., 1990b) primarily because of
31 the elimination of acid-sensitive species at lower values of pH and ANC (Schindler et al., 1985).
32 Interpretation of species richness can be complicated by the observation that more species tend to

1 occur in larger lakes and streams as compared with smaller ones, irrespective of acidity (Sullivan
2 et al. 2003). Nevertheless, decreases in species richness have been observed for all major trophic
3 groups of aquatic organisms (Baker et al., 1990a), even after adjusting for lake size (Harvey and
4 Lee, 1982; Frenette et al., 1986; Rago and Wiener, 1986; Schofield and Driscoll, 1987; Matuszek
5 and Beggs, 1988).

6 7 **4.2.3.2.3 Health, Vigor, and Reproductive Success of Fish**

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

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

24 There exists marked variability among species, and among life stages within species, in
25 the specific levels of pH and inorganic Al that produce measurable responses. In general, early
26 life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and
27 adults (Baker and Schofield, 1985; Johnson et al., 1987; Baker et al., 1990a). Also, small fish,
28 especially swim-up fry, are probably less mobile and less able to avoid exposure to adverse
29 chemical conditions than the relatively larger adults (Baker et al., 1996). Here effects are
30 described by life stage. Several studies have shown that the earliest reproductive stages are
31 highly sensitive to low pH. The processes of oogenesis and fertilization in fish are especially
32 sensitive (Muniz, 1991; Havas et al., 1995), most likely due to adverse effects on the female

1 spawner. For instance, Beamish (1976) reported that reduced serum and plasma Ca in female
2 fish in acidified Canadian lakes caused a higher probability of failure in producing viable eggs.
3 A depletion of Ca from bone and increased numbers of females with unshed eggs have also been
4 linked to sensitivity at this life stage (cf. Rosseland, 1986; Muniz, 1991).

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

21 Emergent alevins show susceptibility to the adverse effects of inorganic Al and hydrogen
22 ion that increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland
23 (1986) indicated that this increasing sensitivity results from changes that take place in the
24 respiratory system. Shortly after hatching, alevins still respire through their skin but gradually
25 gills become the primary organ of gas and ion exchange. Gills are the locus for interference of
26 hydrogen ion and inorganic Al with iono-regulatory exchange.

27 Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus clarki*) from the Snake
28 River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory and found that
29 reductions in pH from 6.5 to 6.0 in low-Ca water (70 µeq/L) did not affect survival, but did
30 reduce growth of swim-up larvae. The eggs, alevin, and swim-up larval stages showed
31 significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher at pH 5.0 than

1 at pH 6.5, but only statistically higher for eggs. The authors concluded that the threshold for
2 effects of acidity on greenback cutthroat trout in the absence of inorganic Al was pH 5.0
3 (Woodward, 1991).

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

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

19 The cumulative sublethal effects of physiological impacts can be expressed by changes in
20 condition factor. Condition factor has been developed and applied mainly for blacknose dace.
21 This fish species is widely distributed in Appalachian Mountain streams and is moderately
22 tolerant of low pH and ANC, relative to other fish species in the region. However, the condition
23 factor concept is probably applicable to other species as well. Condition factor may be a useful
24 metric for many species in aquatic ecosystems that are only marginally affected by acidification.
25 Bulger et al. (1999) observed a positive relationship between dace condition factor and pH in
26 streams in Shenandoah National Park. Dennis and Bulger (1995) found a reduction in the
27 condition factor for blacknose dace in waters near pH 6.0. The four populations with the lowest
28 condition factor had mean habitat pH values within or below the range of critical pH values at
29 which Baker and Christensen (1991) estimated that negative population effects are likely for the
30 species. The mean condition factor of fish from the study stream with the lowest ANC was
31 about 20% lower than that of the fish in best condition. In addition to effects on blacknose dace

1 condition factor, reduced growth rates have been also attributed to acid stress in a number of
2 other fish species, including Atlantic salmon (*Salmo salar*), chinook salmon (*Oncorhynchus*
3 *tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook
4 trout, brown trout (*Salmo trutta*), and arctic char (*Salvelinus alpines*) (Baker et al., 1990a).

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

11 **4.2.3.2.4 Fish Biodiversity**

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

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

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

1 5.2 to 5.5. Bioassay experiments using brook trout eggs and fry have demonstrated greater
2 mortality in chronically acidic stream water as compared to water having higher ANC.

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

9 Fish species richness is an important indicator of acidification response, in part because
10 the public tends to place relatively high value on fisheries resources. As discussed in the
11 previous section, lakes and streams having pH below about 5.0 or ANC below about 0 generally
12 do not support fish. There is often a positive relationship between pH and number of fish
13 species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and
14 50 to 100 $\mu\text{eq/L}$ (Bulger et al., 1999; Cosby et al., 2006; Sullivan et al., 2006a). Such observed
15 relationships are complicated, however, by the tendency for smaller lakes and streams, having
16 smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This
17 pattern may be due to a decrease in the number of available niches as stream or lake size
18 decreases. Nevertheless, fish species richness is relatively easily determined and is one of the
19 most useful indicators of biological effects of surface water acidification.

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

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

1 National Park streams spanning a range of pH and ANC conditions. There was a highly
2 significant ($p < 0.0001$) relationship between stream acid-base status (during the 7-year period of
3 record) and fish species richness among the 13 streams. The streams with the lowest ANC
4 hosted the fewest species (Figure 4.2-10). The 3-year FISH study of stream acidification
5 demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al.,
6 1999). Bulger et al. (1999) concluded that the most important cause of the observed decline in
7 species richness with decreasing ANC was acid stress associated with acidification. However,
8 an additional causal factor may have been a decrease in the number of available aquatic niches
9 when moving from downstream locations (which are seldom low in pH and ANC) to upstream
10 locations (which are often low in pH and ANC in this region; Sullivan et al., 2003).

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

18 Dynamic water chemistry model projections have been combined with biological dose-
19 response relationships to estimate declines in fish species richness with acidification. A
20 relationship derived from the Shenandoah National Park data was used by Sullivan et al. (2003),
21 along with stream ANC values predicted by the MAGIC model to provide estimates of the
22 expected number of fish species in each of the modeled streams for the past, present and future
23 chemical conditions simulated for each stream. Results suggest that historical loss of species had
24 been greatest in the streams located on the most sensitive geological class (siliciclastic bedrock;
25 1.6 species lost), with fewer lost species on granitic bedrock and basaltic bedrock (average of
26 0.4 species lost).

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

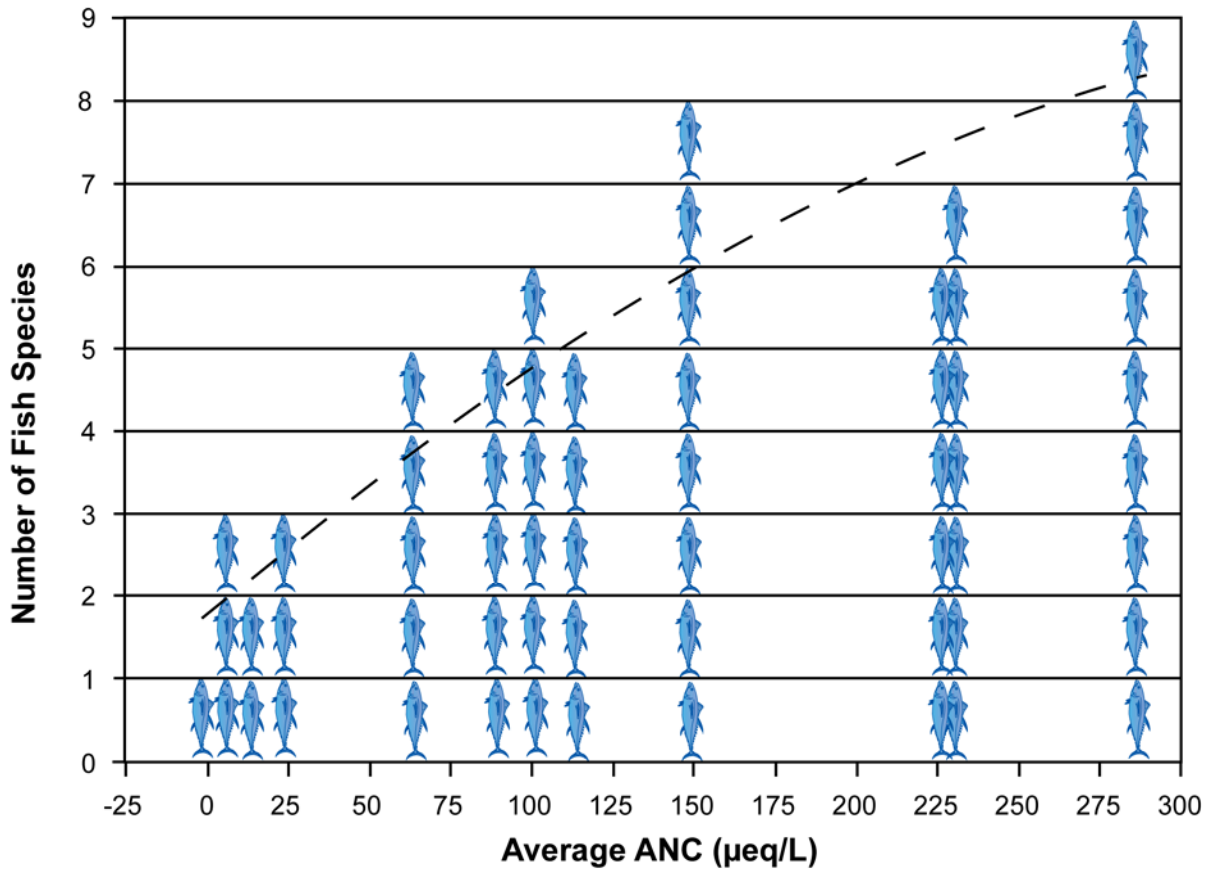


Figure 4.2-10. Number of fish species as a function of mean stream ANC among 13 streams in Shenandoah National Park, Virginia. Values of ANC are means based on quarterly measurements, 1987-1994. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream ANC and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

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

- 1 by the Adirondack Lakes Survey Corporation, about half (26 species) were absent from lakes
- 2 with pH below 6.0. Among the absent species were several important recreational species
- 3 (Baker et al., 1990b), plus ecologically important minnows that serve as forage for sport fish.
- 4 Fully 346 of 1,469 lakes surveyed supported no fish at all at the time of the survey. These lakes
- 5 were significantly lower in pH, dissolved Ca, and ANC, and had higher concentrations of
- 6 inorganic Al than lakes hosting one or more species of fish (Gallagher and Baker, 1990). Among
- 7 lakes with fish, there was an unambiguous relationship between the number of fish species and

1 lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six
2 species per lake for lakes having pH higher than 6.5 (Baker et al., 1990b; Driscoll et al., 2001a).

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

9 Sullivan et al. (2006a) developed a relationship between fish species richness and ANC
10 class for Adirondack lakes. Under chronically acidic conditions (summer index or annual
11 average ANC < 0 $\mu\text{eq/L}$), Adirondack lakes are generally without fish. There was a marked
12 increase in mean species richness with increases in ANC up to values of approximately 50 to
13 100 $\mu\text{eq/L}$ (Figure 4.2-11). The asymptote for the fish species equation was 5.7 species. This
14 analysis suggests that there could be loss of fish species with decreases in ANC below
15 approximately 50 to 100 $\mu\text{eq/L}$.

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

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

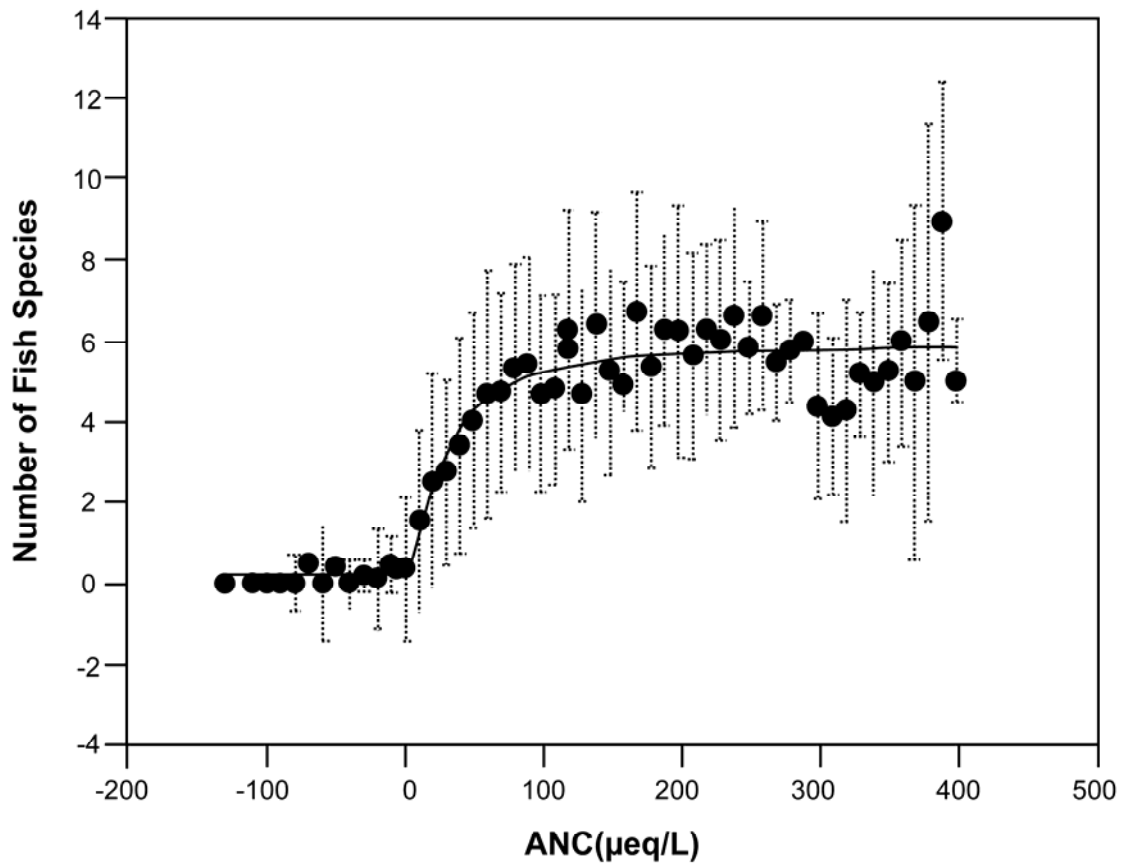


Figure 4.2-11. Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 $\mu\text{eq/L}$ ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

Source: Sullivan et al. (2006a).

1 concentrations, contribute to loss of the most acid-sensitive fish species. Species richness is a
 2 common indicator used to reflect the effects of water acidification on aquatic biota. This index is
 3 most often applied to fish. Few or no fish species are found in lakes and streams that have low
 4 ANC (near zero) and low pH (near 5.0). The number of fish species generally increases at
 5 higher ANC and pH values. This relationship is complicated to some extent by the tendency of
 6 smaller lakes and streams (which are more likely to have low ANC and pH) to host fewer fish

1 species, regardless of acid-base chemistry. Nevertheless, available data suggest that acid stress is
2 a major factor governing the observed relationship between fish species richness and surface
3 water acidity.

4 5 **4.2.4 Characterization of Most Sensitive and Most Affected Ecosystems** 6 **and Regions**

7 8 **4.2.4.1 Characteristics of Sensitive Ecosystems**

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

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

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

1 acidification were those with low weathering rates and thus limited buffering capacity
2 (Moncoulon et al., 2004).

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

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

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

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

30

1 **4.2.4.2 Extent and Distribution of Sensitive Ecosystems**

2

3 **4.2.4.2.1 Surface Waters**

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

16 Several national assessments have been conducted to estimate the distribution and extent
17 of surface water acidity in the United States. During summer baseflow of 2004, the EPA
18 conducted a National Wadeable Stream Assessment (WSA) survey of 1,392 randomly selected
19 sites across the conterminous 48 United States to assess the ecological condition of wadeable
20 streams (U.S. Environmental Protection Agency, 2006c). Because this sampling was conducted
21 during baseflow in the summer, which exhibits the least acidic conditions of the year, only the
22 most chronically acidified streams were identified as acidic. Therefore, the extent of potential
23 seasonal acidification was underestimated by this approach (Lawrence et al., in review).
24 Overall, less than 1% of the 1,020,000 km of stream in the target population (based on the
25 1:100,000-scale U.S. Geological Survey (USGS) map blue line network) was acidic due to acidic
26 deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper
27 Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams
28 attributable to acidic deposition were found in the Northern Appalachians (2.8% of 96,100 km of
29 stream), and the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0-25 µeq/L)
30 streams likely exposed to episodic acidification were found in the Northern Appalachians (2.7%
31 of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West
32 (0.6% of 204,000 km).

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

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

23 Overall, out of the estimated 57,000 stream reaches in the NSS, after excluding streams
24 acidic due to acid mine drainage, 6.2% of the upstream and 2.3% of the downstream reach ends
25 were acidic during spring baseflow (Kaufmann et al., 1991). After interpolation, this
26 corresponded to 2.7% of the 201,000 km of stream in the study region. In acidic and low-ANC
27 NSS reaches, ANC usually increased with downstream distance. Acidic ($ANC \leq 0$) streams were
28 located in the highlands of the Mid-Atlantic Region (southern New York to southern Virginia,
29 2320 km), in coastal lowlands of the Mid-Atlantic (2530 km), and in Florida (461 km). Acidic
30 streams were rare (less than 1%) in the highlands of the Southeast and Piedmont. Inorganic
31 monomeric Al concentrations were highest in acidic streams of the Mid-Atlantic Highlands,

1 where over 70% of the acidic streams had inorganic Al greater than 3.7 μM (100 $\mu\text{g/L}$), a
2 concentration above which deleterious biological effects have frequently been reported.

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

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

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

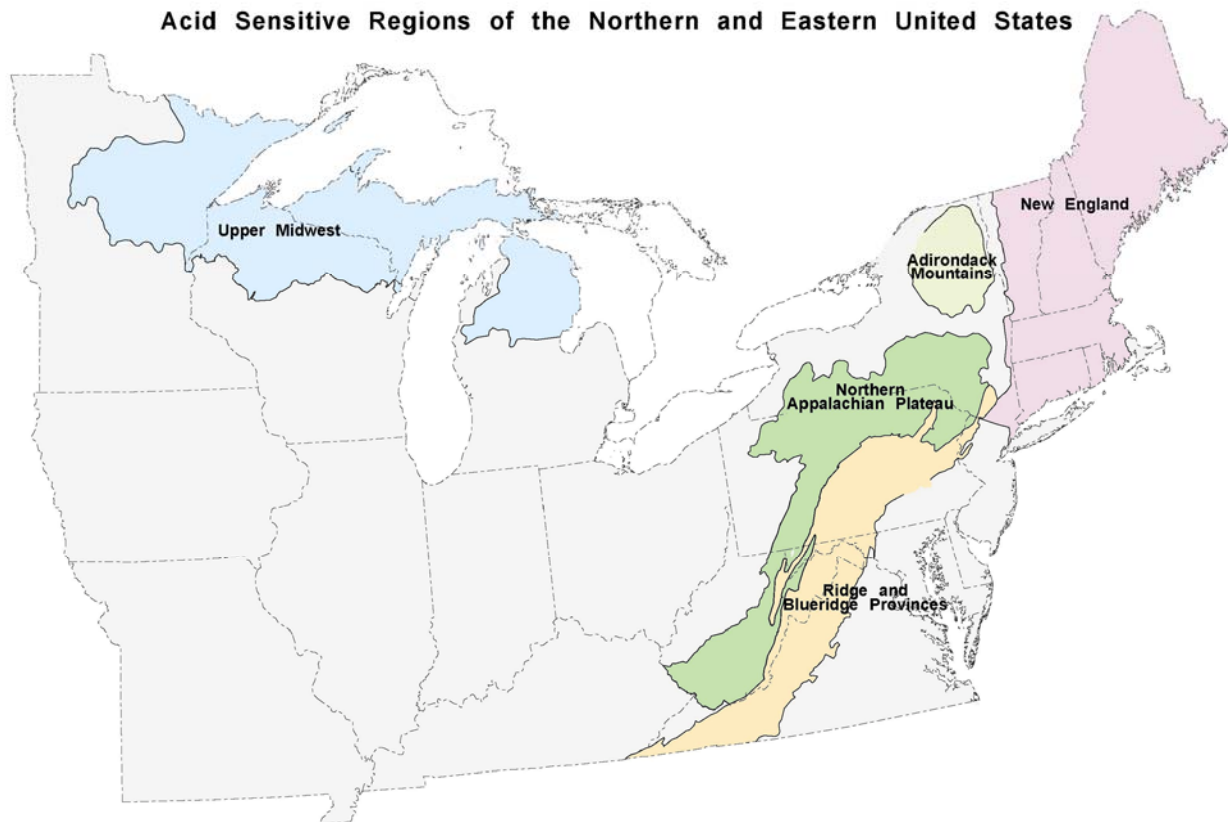


Figure 4.2-12. Regions of the eastern United States that contain appreciable numbers of lakes and streams that are sensitive to acidification from acidic deposition.

Source: Stoddard et al. (2003).

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

3
 4 *New England*

5 For the New England region, results from EPA's TIME program indicate that 5.6% of the
 6 regional lake population (386 lakes) in New England exhibited $ANC < 0 \mu\text{eq/L}$ during the period
 7 1991 to 1994. This result is similar to the Environmental Monitoring and Assessment Program
 8 (EMAP) findings, which indicate that 5% of lakes in New England had ANC values less than
 9 $0 \mu\text{eq/L}$. The EMAP survey was a probability based survey representative of lakes with surface
 10 area greater than 1 ha (1,812 lakes). The survey was conducted during low-flow summer

1 conditions, and the results therefore likely reflect the highest ANC values for the year. The
2 EMAP analysis also estimated that an additional 10% of the population had low ANC values,
3 between 0 and 50 $\mu\text{eq/L}$, and were probably sensitive to episodic acidification (Driscoll et al.,
4 2001b).

5
6 *Adirondacks*

7 A study by Driscoll et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the
8 extent of acidic lakes in the Adirondacks for that period. Results from the survey indicate that
9 10% of the population of Adirondack lakes were chronically acidic (ANC values of less than 0)
10 and 31% were sensitive to episodic acidification (ANC values between 0 and 50) during the
11 study period (Driscoll et al., 2001b).

12 The Adirondack Lake Survey Corporation conducted a comprehensive survey of
13 Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al.,
14 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were
15 chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic
16 acidification (ANC between 0 and 50; Driscoll et al., 2007a).

17
18 *Mid-Appalachian Region*

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

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

1 conditions in the park for the preindustrial past, current conditions, and anticipated future
2 conditions.

3
4 *Florida Panhandle*

5 According to the EPA's Eastern Lakes Survey conducted in 1984, 75% of the Florida
6 Panhandle lakes were acidic at that time, as were 26% of the lakes in the northern peninsula.
7 Most of the acidic lakes were clear water (dissolved OC < 400 μ M) seepage lakes in which the
8 dominant acid anions were chloride and SO_4^+ . Most of the acidic and low-ANC lakes were
9 located in the Panhandle and northcentral lake districts. Acidic streams were located in the
10 Panhandle and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-
11 corrected sum of base cations (mean 21 μ eq/L) and sea salt-corrected SO_4^+ concentrations (mean
12 16 μ eq/L). One-fourth of these acidic Panhandle streams were organic-dominated but the
13 remaining sites all had dissolved OC < 2 mg/L. Inorganic monomeric Al concentrations in these
14 acidic streams were very low (mean 11 μ g/L). In these low dissolved OC, low ANC Panhandle
15 streams, it was suggested that the degree of SO_4^+ and NO_3^- retention in soil was an important
16 control on streamwater ANC (Baker et al., 1990c).

17
18 *Upper Midwest*

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

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

31

1 *West*

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

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

13 Along the eastern edge of the Continental Divide in Colorado and southeastern
14 Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in
15 the mountainous areas that are exposed to relatively high (by western standards) deposition of N.
16 A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed
17 bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically
18 acidic ($ANC < 0$), although several had $ANC < 10 \mu\text{eq/L}$, and more than 10% of the lakes had
19 $ANC < 50 \mu\text{eq/L}$.

20
21 *Forest Ecosystems*

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

29 One national and a few regional efforts have been undertaken to characterize forest
30 sensitivity to acidic deposition using a critical loads approach. In this context, acid-sensitive
31 soils are those which contain low levels of exchangeable base cations and low base saturation.
32 On a broad national scale, McNulty et al. (2007) used a simple mass balance equation and

1 available national databases to estimate forest soil critical acidic loads (for wet and dry
2 deposition of S and N) and exceedences for forest soils. Exceedences are pollutant loads that are
3 greater than the estimated critical load. They found that approximately 15% of forest soils in the
4 United States exceed the estimated critical load of wet and dry deposition of S and N by more
5 than 250 eq ha⁻¹ yr⁻¹ (McNulty et al., 2007). The areas where exceedences reach this level could
6 be considered to represent those areas that are likely most sensitive to continued high levels of
7 acidic deposition. Thus, there is not a national survey of soil sensitivity to acidification, but
8 there are approaches available with which to identify areas likely to include sensitive soils.

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

28 Another approach to identification of sensitive forest lands is to map the distribution of
29 tree species thought be most sensitive to adverse impacts. The effects of acidic deposition are
30 particularly well documented for red spruce trees that occur in the northeastern United States and
31 southern Appalachian Mountains (Figure 4.2-5 shows the distribution). In the Northeast, red

1 spruce grows at elevations from near sea level to about 4500 feet. In the Appalachian
2 Mountains, spruce-fir forests are generally found at relatively high elevation, for example above
3 about 1400 m in the southern Appalachian Mountains (SAMAB, 1996). Northern hardwood
4 forests have also been identified as forest resources experiencing air pollution impacts. Impacts
5 are best documented for sugar maple trees which are broadly distributed across the northern
6 hardwood forests in the northeastern United States (Figure 4.2-5 shows the distribution). The
7 areas where sugar maple appears to be at greatest risk are along ridges and where it occurs on
8 nutrient-poor soils.

9 10 **4.2.4.3 Levels of Deposition at Which Effects are Manifested**

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

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

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

1 The effects of N addition on forests have been shown to be wide-ranging. Additions of
2 25 kg N ha⁻¹ yr⁻¹ to spruce plots in Vermont (ambient bulk deposition 5.4 kg N ha⁻¹ yr⁻¹), in
3 which net nitrification did not occur prior to treatment, triggered net nitrification in the second
4 year of treatment (McNulty et al., 1996). Similar results were seen in Colorado, where additions
5 of 25 kg N ha⁻¹ yr⁻¹ to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition
6 4 to 5 kg N ha⁻¹ yr⁻¹) doubled N mineralization rates and stimulated nitrification. In marked
7 contrast to these results, concentrations of NO₃⁻ plus NH₄⁺ were not detected until the seventh
8 year in hardwood plots in Harvard Forest, Massachusetts, which received additions of 150 kg
9 N ha⁻¹ yr⁻¹ (Magill et al., 2004). Concentrations of NO₃⁻ plus NH₄⁺ in hardwood plots receiving
10 50 kg N ha⁻¹ yr⁻¹ were not yet detectable in the 15th year of treatment.

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

14 15 **4.2.4.3.1 Critical Loads and Timeframes of Response**

16 Critical loads one way one way to express the amount of deposition of an atmospheric
17 pollutant (a “load”) or the concentration of an airborne pollutant that can be tolerated by natural
18 or synthetic systems without significant harm or change occurring in those systems. The
19 generally accepted definition of a critical load of atmospheric pollutant deposition emerged from
20 a pair of international workshops held in the late 1980s (Nilsson, 1986; Nilsson and Grennfelt,
21 1988). The workshop participants defined a critical load as:

22 “a quantitative estimate of an exposure to one or more pollutants below which
23 significant harmful effects on specified sensitive elements of the environment do
24 not occur according to present knowledge.”

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

28 It is important to note that critical loads developed to date in the United States have
29 largely been at sub-regional scales or for individual sites and usually used a catchment-based
30 approach. The definitions of adversity and harm in critical load applications are specific to the
31 resource under consideration. Therefore, there is no single “definitive” critical load for a natural
32 resource. Rather, there is a range of values, each of which is applicable to a particular sensitive

1 resource element. The chemical indicators and linkages to biological receptors articulated
2 through the critical loads process can provide a framework for documenting ecosystem responses
3 to changing emissions and deposition. For example, surface water monitoring data collected
4 from 1990 to the present provide information on the extent to which lakes and streams are
5 responding to reductions in SO₂ emissions. This information is then used in models to estimate
6 how ecosystems may respond in the future. The response of surface waters since the 1990s and
7 projected future responses in terrestrial and aquatic ecosystems in sensitive regions are
8 summarized below using many of the indicators identified through the various critical loads
9 initiatives.

10

11 **4.2.4.3.2 Chemical Response**

12

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

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- SO₄⁺ 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 SO₄⁺ 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 SO₄⁺ 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

1 limited the increase in ANC and pH that occurred in response to lower SO_4^+ concentrations.
2 Overall, improvements in lakewater acid-base chemistry since 1990 have been measurable but
3 modest. Similar patterns have been observed in most other regions. There are currently no data
4 in the United States that indicate increases in soil pH associated with recent declines in acidic
5 deposition levels.

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

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

30 The results for the portion of the region south of Virginia and West Virginia suggest that
31 the percentages of streams having ANC below zero and below 20 $\mu\text{eq/L}$ will actually increase

1 through the year 2040 under all except the most restrictive emissions control strategies (Sullivan
2 et al., 2005). Most simulated changes in stream water ANC from 1995 to 2040 were rather
3 modest, given the very large estimates of future decrease in S deposition. Few modeled streams
4 showed projected change in ANC of more than about 20 $\mu\text{eq/L}$ (Sullivan et al., 2005). Some of
5 the largest changes were simulated for some of the streams that were most acidic in 1995. For
6 such streams, however, even relatively large increases in ANC would still result in stream water
7 having negative ANC, and therefore little biological improvements would be expected from the
8 simulated improvement in chemistry (Sullivan et al., 2005).

9 Similarly, Bulger et al. (2000) developed model-based projections using the MAGIC
10 model to evaluate the potential effect of reductions in total S deposition of 40% and 70% from
11 1991 levels S. Bulger et al. (2000) estimated that 1991 ambient stream chemistry was marginal
12 or unsuitable for brook trout in half of the streams in western Virginia that were considered in
13 the study. The model projections suggest that neither the 40% nor the 70% reductions in
14 S deposition would be expected to increase the number of streams that were suitable for brook
15 trout above the ambient 50% (Bulger et al., 2000). In fact, the results suggest that a 70%
16 reduction in deposition would be needed in the long term just to maintain the number of streams
17 that were considered suitable for brook trout (Bulger et al., 2000). Because of the length of time
18 required to restore buffering capacity in watershed soils (typically more than 100 years), most of
19 the marginal or unsuitable streams were expected to remain marginal or unsuitable for the
20 foreseeable future.

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

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

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

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

24 25 **4.2.4.3.3 Biological Response**

26 Biological recovery can occur only if chemical recovery is sufficient to allow survival
27 and reproduction of acid-sensitive plants and animals. The time required for biological recovery
28 is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored
29 because of the long life of many plant species and the complex interactions of soil, roots,
30 microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate

1 populations may recover relatively rapidly (within approximately 3 years), whereas lake
2 populations of zooplankton recover more slowly (Gunn and Mills, 1998).

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

12 The Sudbury region of Ontario, Canada has been important for studying both the
13 chemical and biological effects of S deposition. Mining and smelting of copper-nickel ore began
14 in the 1880s. By the 1950s and 1960s, SO₂ emissions from the mining and smelting operations
15 peaked at over 5,000 tons/day and extensive acidification of nearby surface waters was
16 documented (Beamish and Harvey, 1972). Emissions of SO₂ then decreased during the 1970s to
17 less than one-third of the peak values. S emission reductions resulted in improved water quality
18 in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries recovery was
19 also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and Keller (1992)
20 found changes in the occurrence and abundance of benthic invertebrates that were consistent
21 with a direct effect of reduced lakewater acidity. A more recent assessment of recovery of
22 ecosystems in Canada provided further evidence of biological recovery, but also showed that the
23 spatial extent of recovery was limited to lakes that had been severely acidified by the Sudbury
24 smelter (Jeffries et al., 2003). Research at Sudbury clearly documented that chemical recovery
25 of lakes was possible upon reduced emissions and deposition of S, and also that biological
26 recovery, involving multiple trophic levels, could follow. Major findings of the research at
27 Sudbury and elsewhere are summarized below.

28
29 *Phytoplankton*

30 Studies of phytoplankton recovery from experimental acidification indicate that there is
31 an increase in phytoplankton species richness and diversity as pH increases. In Lake 223 in the
32 Experimental Lakes area of Ontario, there was little increase in phytoplankton diversity as pH

1 changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian,
2 1996). In Lake 302S, profound change began at pH 5.5; phytoplankton assemblages at pH below
3 5.5 resembled acidified lakes.

4 5 *Zooplankton*

6 Zooplankton recovery in response to experimental de-acidification has been reported for
7 lakes in Ontario, Canada and Minnesota. Zooplankton recovery in experimentally acidified Lake
8 223 as pH returned back to 6.1 was reported by Malley and Chang (1995). Species diversity that
9 had been reduced during the acidification phase had partially returned to pre-acidification levels.
10 Rotifers had recovered less than crustaceans.

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

17 18 *Benthic Invertebrates*

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

28 29 *Fish*

30 Fish populations have recovered in acidified lakes when the pH and ANC have been
31 raised through liming or reduction of acidic deposition (Hultberg and Andersson, 1982; Beggs
32 and Gunn, 1986; Dillon et al., 1986; Keller and Pitblado, 1986; Raddum et al., 1986; Gunn et al.,

1 1988; Kelso and Jeffries, 1988). The timing of fish recovery is uncertain and probably depends
2 heavily on dispersal opportunities. Stocking could accelerate fish population recovery (Driscoll
3 et al., 2001b). Limitations on dispersal and recolonization can hamper biological recovery from
4 acidification.

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

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

23 24 *Waterfowl*

25 Few studies have been conducted on the recovery of higher trophic level organisms such
26 as waterfowl. However, breeding distribution for the common goldeneye (*Bucephala clangula*),
27 an insectivorous duck, may be impacted by changes in acidic deposition (Longcore and Gill,
28 1993). Similarly, reduced prey diversity and quantity have been observed to create feeding
29 problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

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

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

10 11 **4.2.4.4 Acidification Case Study #1: Adirondack Region of New York**

12 13 **4.2.4.4.1 General Description of Region**

14 The Adirondack Mountains region is situated in northeastern New York State. It is
15 characterized by dense forest cover and abundant surface waters, with 46 peaks that extend up to
16 1600 m in elevation. The Adirondack Park has long been a nationally important recreation area
17 for fishing, hiking, boating, and other outdoor activities.

18 The Adirondack region, and the southwestern Adirondacks in particular, is sensitive to
19 acidic deposition because it receives high precipitation, has shallow base-poor soils, and is
20 underlain by igneous bedrock with low weathering rates and buffering capacity (Driscoll et al.,
21 1991; Sullivan et al., 2006b). The Adirondack region is among the most severely acid-impacted
22 regions in North America (Landers et al., 1988; Driscoll et al., 2003b). It has long been used as
23 an indicator of the response of forest and aquatic ecosystems to United States policy on
24 atmospheric emissions of SO₂ and N oxides (U.S. Environmental Protection Agency, 1995b;
25 NAPAP, 1998; GAO, 2000).

26 27 **4.2.4.4.2 Levels of Acidic Deposition**

28 Current rates of wet deposition of S and N in the western Adirondacks remain among the
29 highest in the nation. Spatial patterns in wet deposition of S and N from 1988 to 1999 were
30 developed by Ito et al. (2002), using data from 24 precipitation and 4 wet deposition monitoring
31 stations. Results from this effort suggest that wet S deposition ranged from 2.3 to 12.9 kg S ha⁻¹
32 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)

1 (Figure 4.2-13). In general, deposition rates are highest in the southwestern Adirondacks and
2 decrease to the northeast. Rates of dry deposition are less well known, but probably constitute
3 25% to 50% or more of total wet deposition.

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

11 **4.2.4.4.3 Soil Retention and Leaching of Sulfur and Nitrogen**

12 As discussed in Section 4.2.4.4, acidic deposition has resulted in the accumulation of S
13 and N in Adirondack soils. Although input-output budgets for S developed in the 1980s
14 suggested that the amount of S exported was approximately equal to the S inputs from
15 atmospheric deposition, more recent studies show that watershed loss of SO_4^+ now exceeds
16 atmospheric S deposition inputs (Driscoll et al., 1998). This pattern suggests that decades of
17 atmospheric S deposition have resulted in the accumulation of S in forest soils. With recent
18 declines in atmospheric S deposition and a possible warming-induced enhancement of S
19 mineralization from soil organic matter, previously retained S is gradually being released to
20 surface waters (Driscoll et al., 1998). This release of SO_4^+ from soils could contribute to a delay
21 in the recovery of surface waters in response to SO_2 emissions controls.
22

23 N dynamics are quite different from those of S. Since N is a growth-limiting nutrient for
24 many forest plants, retention in forest ecosystems under low levels of air pollution is generally
25 high and NO_3^- loss to streams is relatively low. However, recent research suggests that N has
26 accumulated in soils over time in the Adirondacks and that some forests have exhibited declining
27 retention of N inputs. The result has been increased leaching of NO_3^- to surface waters. The
28 extent and degree of leaching appear to be linked to climatic variation, land-use history, and
29 vegetation type (see Section 4.2.1.3).
30

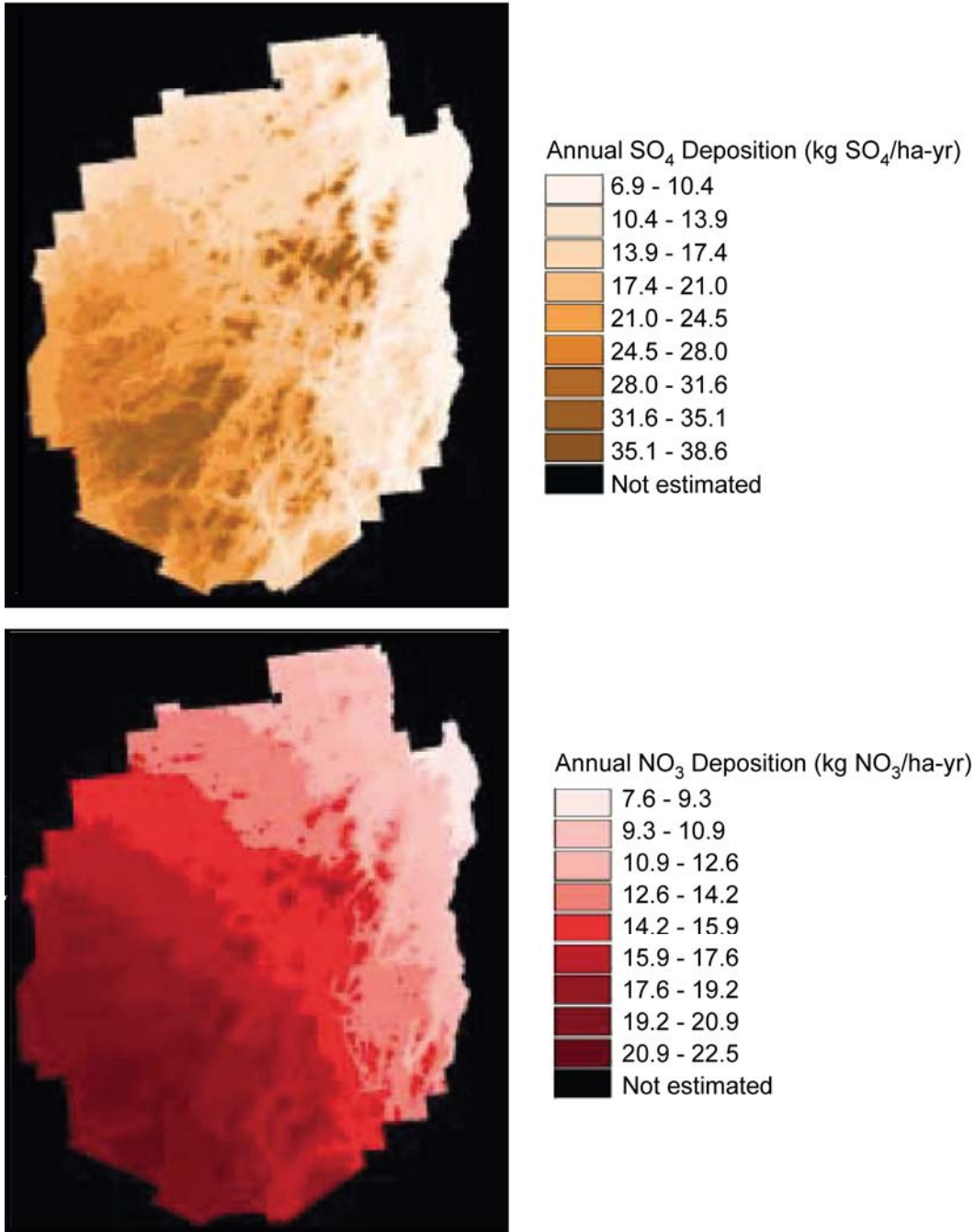


Figure 4.2-13. Spatial patterns in predicted wet sulfate and nitrate deposition in the Adirondack Park during the period 1988 to 1999.

Source: Ito et al. (2002).

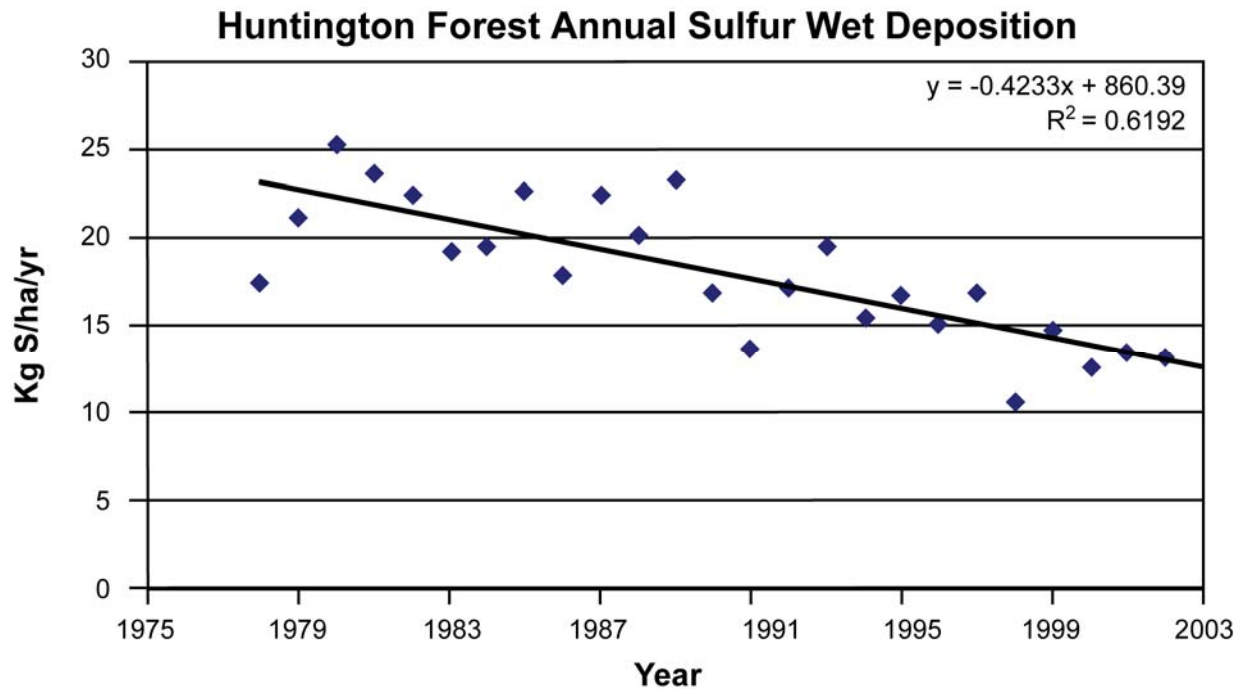


Figure 4.2-14. Measured wet deposition of sulfur and inorganic nitrogen at the Huntington Forest NADP/NTN monitoring station.

Source: Sullivan et al. (2006a).

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

4
 5 **4.2.4.4.4 Soil Acidification and Base Cation Depletion**

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

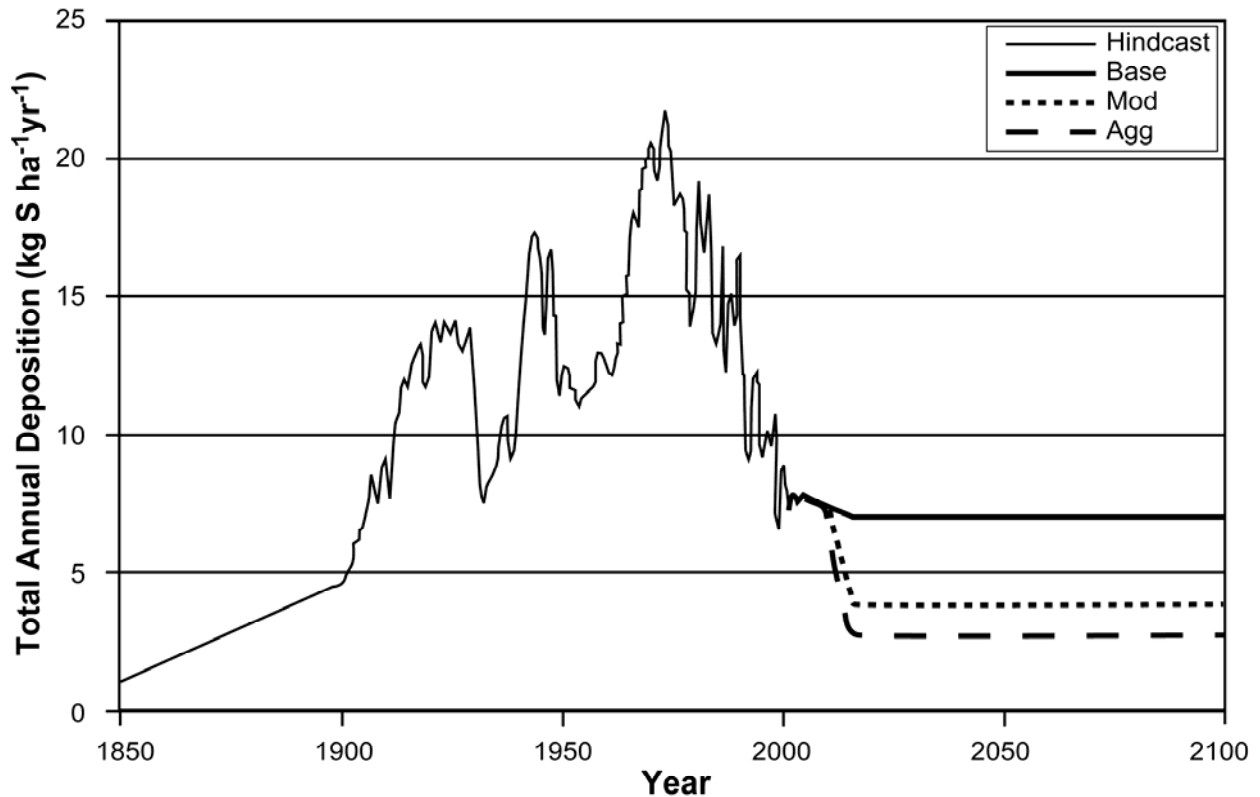


Figure 4.2-15. Estimated time series of S deposition at one example watershed in the southwestern Adirondack Mountains used by Sullivan et al. (2006b) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidic deposition. Future deposition estimates 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).

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

4 In a regional assessment of changes in soil-exchange chemistry, Sullivan et al. (2006a)
 5 found that base saturation and exchangeable Ca concentrations in the Adirondack region
 6 appeared to have decreased in the B horizon between the mid 1980s and 2003 in watersheds of
 7 lakes with acid-neutralizing capacity less than 200 $\mu\text{eq/L}$. Although this study did not involve
 8 repeated sampling of the same sites, the comparison could be made on a regional basis because

1 the sampling locations were selected randomly in both the mid 1980s and in 2003, and a large
2 and similar number of sites were included in both samplings.

3
4 **4.2.4.4.5 *Effects of Acidic Deposition on Adirondack Surface Water Chemistry***

5 The Adirondack Lake Survey Corporation conducted a comprehensive survey of
6 Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al.,
7 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were
8 chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic
9 acidification (ANC between 0 and 50; Driscoll et al., 2007a).

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

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

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

29 The PIRLA results are generally consistent with projections from model hindcasts.
30 Sullivan et al. (2006a) modeled past changes in the acid-base chemistry of 70 Adirondack lake
31 watersheds, including 44 that were statistically selected to be representative of the approximately
32 1,320 Adirondack lake watersheds that have lakes larger than 1 ha and deeper than 1 m and that

1 have ANC ≤ 200 $\mu\text{eq/L}$. Model hindcasts were constructed using both the MAGIC and PnET-
2 BGC models. Based on MAGIC model outputs, maximum past acidification occurred by about
3 1980 or 1990, with a median ANC for the study population of about 61 $\mu\text{eq/L}$ (reduced from a
4 median of 92 $\mu\text{eq/L}$ estimated for the preindustrial period). By 1990, 10% of the population
5 target lakes had decreased in ANC to below -16 $\mu\text{eq/L}$ and 25% had ANC < 28 $\mu\text{eq/L}$. The
6 model simulations suggest that none of the target lakes were chronically acidic (had ANC
7 < 0 $\mu\text{eq/L}$) under preindustrial conditions, but that by 1980 there were about 204 chronically
8 acidic Adirondack lakes.

9 PnET-BGC model simulations generated output that was generally similar to results
10 provided by MAGIC model simulations. Results from PnET-BGC suggest that none of the lakes
11 in the Adirondack population had preindustrial ANC below 20 $\mu\text{eq/L}$. By 1990, there were
12 289 lakes having ANC < 20 $\mu\text{eq/L}$ and 217 chronically acidic (ANC ≤ 0 $\mu\text{eq/L}$) lakes according
13 to PnET-BGC simulations. There were 202 lakes in the population simulated to have had
14 preindustrial ANC below 50 $\mu\text{eq/L}$, and this number increased 2.8 times by 1980 under the
15 PnET-BGC simulations.

16 Zhai et al. (2007) reported PnET-BGC hindcasts for the 44 EMAP lakes. They
17 report that simulated median values of pH, ANC, and soil percent base saturation were 6.63,
18 67.7 $\mu\text{eq/L}$, and 12.3%, respectively, in 1850 compared to current measured values of 5.95,
19 27.8 $\mu\text{eq/L}$, and 7.9%. They also calculated F factors for the PnET-BGC model projections of
20 historical acidification. The F-factor (Henriksen, 1984; Husar et al., 1991) reflects the
21 proportion of the increase in lakewater SO_4^+ plus NO_3^- concentration that is charge balanced by
22 an equivalent increase in base cation concentrations. The remaining proportion (1-F) is
23 attributed to increase in the potentially toxic cations, hydrogen and inorganic Al. Based on
24 PnET-BGC hindcast simulations, F-factors for the EMAP lakes ranged from 0.3 to slightly over
25 1.0, with a mean value of 0.7 (Figure 4.2-16). The F-factor increased with ambient lakewater
26 ANC. These results are in close agreement with paleolimnological analyses reported by Sullivan
27 et al. (1990), which showed historic F-factors ranging from about 0.5 to above 1.0.

28 29 **4.2.4.4.6 Biological Effects**

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

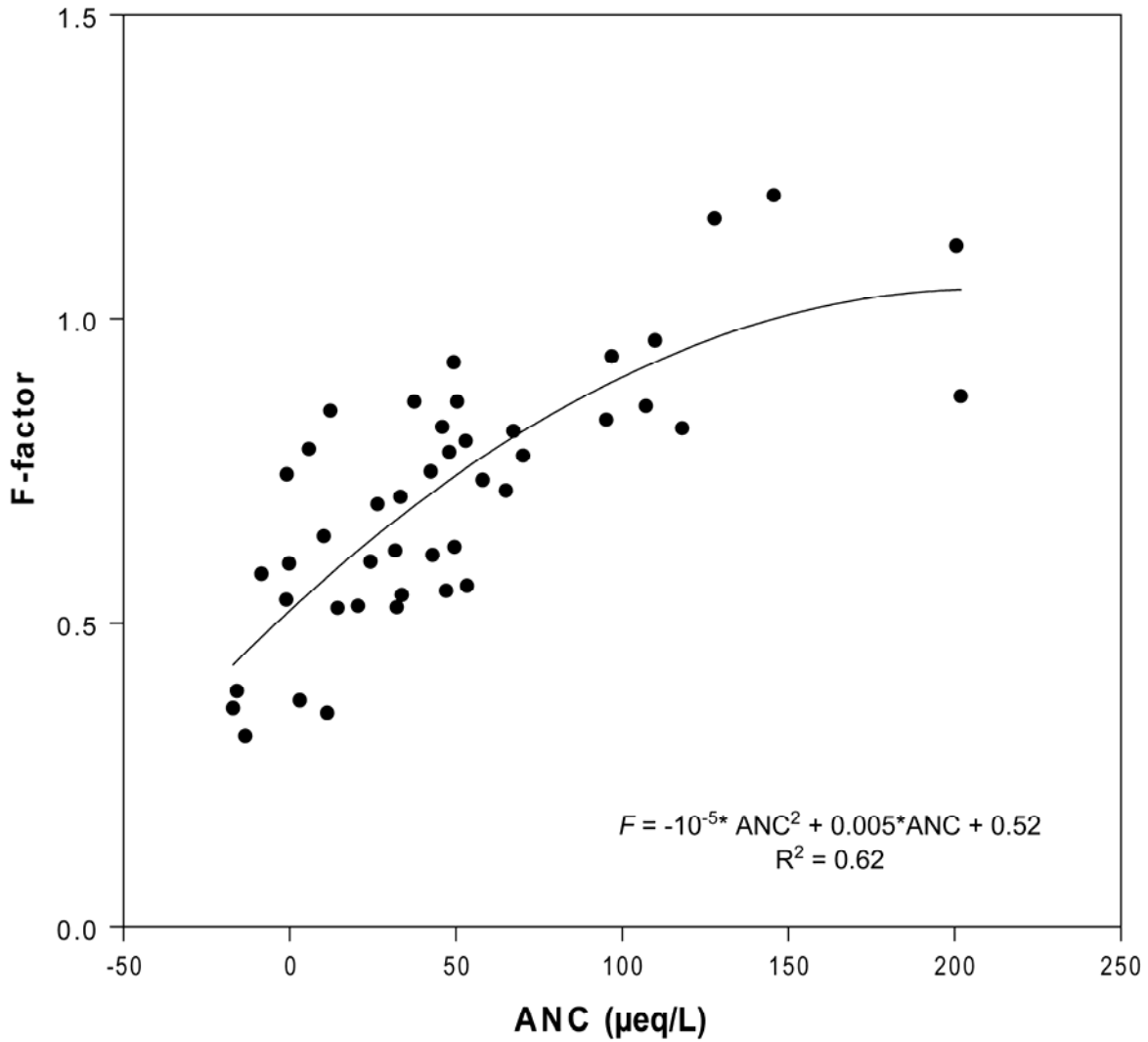


Figure 4.2-16. F-factors ($\Delta\text{SBC}/\Delta[\text{SO}_4 + \text{NO}_3]$, where SBC is the sum of the base cation concentrations, with all units in $\mu\text{eq/L}$) calculated from model results for the period 1850 to 1980 as a function of simulated ANC in 1980 for 44 statistically selected EMAP lakes in the Adirondack region of New York.

Source: Zhai (2007).

- 1 general, there tends to be a negative relationship in Adirondack lakes between pH, ANC, and
- 2 inorganic Al chemical variables and the diversity and abundance of fish (Baker and Laflen,
- 3 1983; Baker et al., 1990c; Havens et al., 1993), phytoplankton, and zooplankton (Confer et al.,
- 4 1983; Siegfried et al., 1989).

1 Through the Adirondack Lakes Survey, 1,469 lakes were sampled between 1984 and
2 1987, representing 80% of the estimated population of Adirondack lakes larger than 1 ha in area
3 (Whittier et al., 2002). The goal of the survey was to characterize the biological, physical, and
4 chemical characteristics of the lakes and evaluate the relationships between fish communities and
5 water chemistry. The major results were reported by Baker et al. (1990b). The key findings are
6 summarized in the bullet list below and accompanying figures.

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

19 Researchers in the Adirondacks were among the first in the United States to demonstrate
20 that fish mortality increases during acid episodes, which are common to lakes and streams in the
21 Adirondacks during spring runoff. Driscoll et al. (1987a) documented surface water chemistry
22 changes associated with periods of high flow. They found that pH and ANC dropped
23 substantially during hydrological episodes and inorganic Al concentrations commonly exceeded
24 thresholds harmful to fish. These relationships were further documented by the Episodic
25 Response Project as shown in the example for Bald Mountain Brook in the Adirondacks
26 (Wigington et al., 1996). Subsequent work by Van Sickle et al. (1996) and others linked these
27 chemical changes to fish mortality in small streams. They determined that blacknose dace were
28 highly sensitive to low pH and could not tolerate inorganic Al concentrations above about
29 3.7 μM for extended periods of time. After 6 days of exposure to high inorganic Al, dace
30 mortality increased rapidly to nearly 100% (Van Sickle et al., 1996). Brook trout were less
31 sensitive, but still showed high mortality during many acid episodes.

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

11
12 **4.2.4.4.7 *Recent Trends in Surface Water Chemistry and Projections of Future Change***

13 Several studies have been conducted to analyze trends in lake chemistry in the
14 Adirondacks. Driscoll et al. (2003c) evaluated changes from 1982 to 2000 in 16 LTM lakes and
15 from 1992 to 2000 in an additional 48 LTM lakes that had been more recently added to the
16 monitoring program. They found that nearly all study lakes showed marked decreases in SO_4^+
17 concentration over the period of record and several lakes showed declines in NO_3^- concentration.
18 Data for one example monitoring lake are given in Figure 4.2-17. They found that 7 of the 16
19 original monitoring lakes showed a statistically significant increase in ANC (Figure 4.2-18), with
20 a mean rate of increase of $0.78 \mu\text{eq/L/yr}$ (Driscoll et al., 2003c). Twenty-nine of the group of 48
21 lakes showed increasing ANC trends from 1992 to 2000 with a mean rate of increase of
22 $1.60 \mu\text{eq/L/yr}$ (Driscoll et al., 2003b). The authors attributed this recent increase in ANC to
23 declines in both SO_4^+ and NO_3^- concentrations (Driscoll et al., 2003b).

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

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

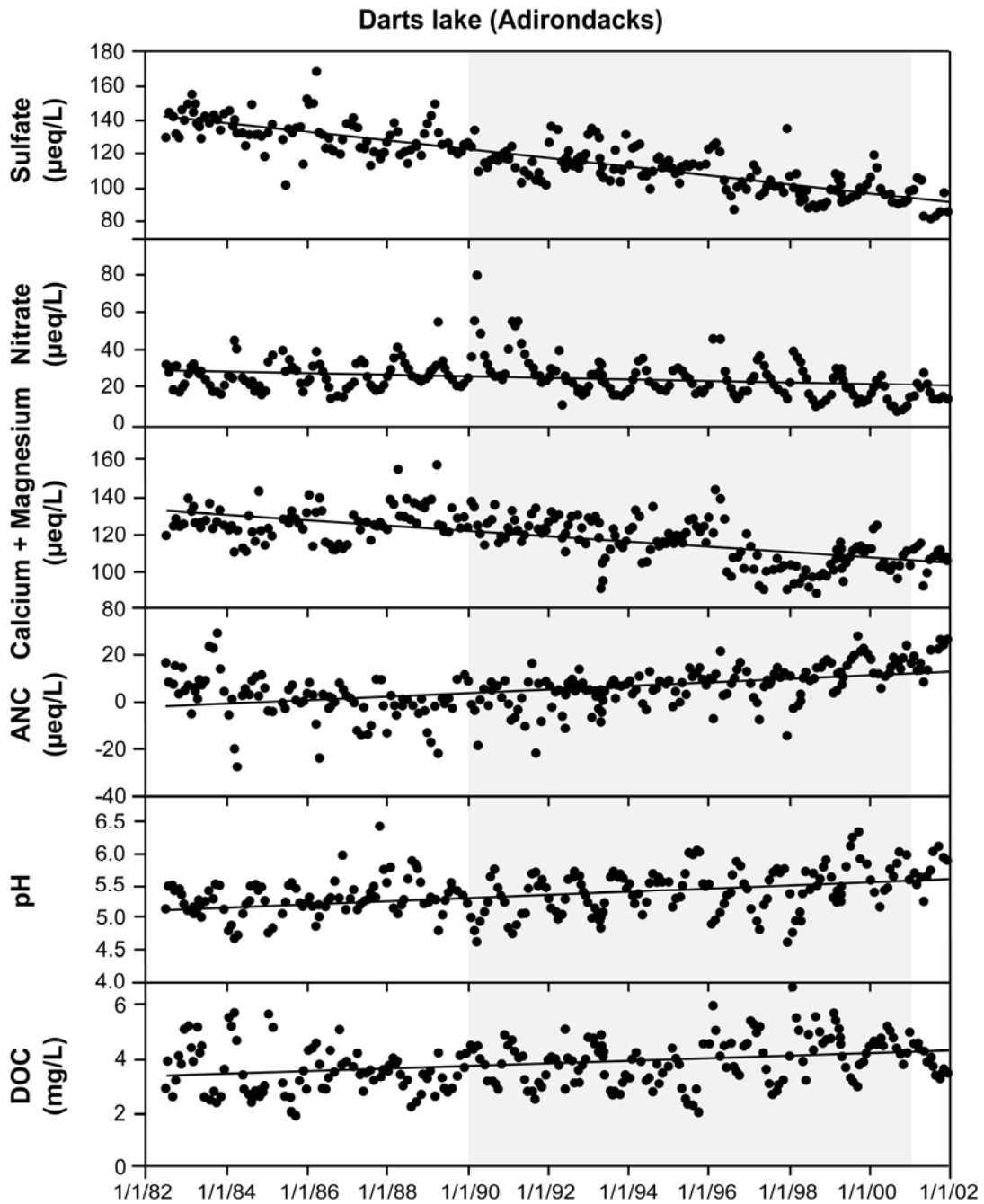


Figure 4.2-17. Time series data for sulfate, nitrate, base cations [Ca plus Mg], Gran ANC, pH, and dissolved organic carbon in one example Long-Term Monitoring Lake in the Adirondack Park. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Source: Stoddard et al. (2003).

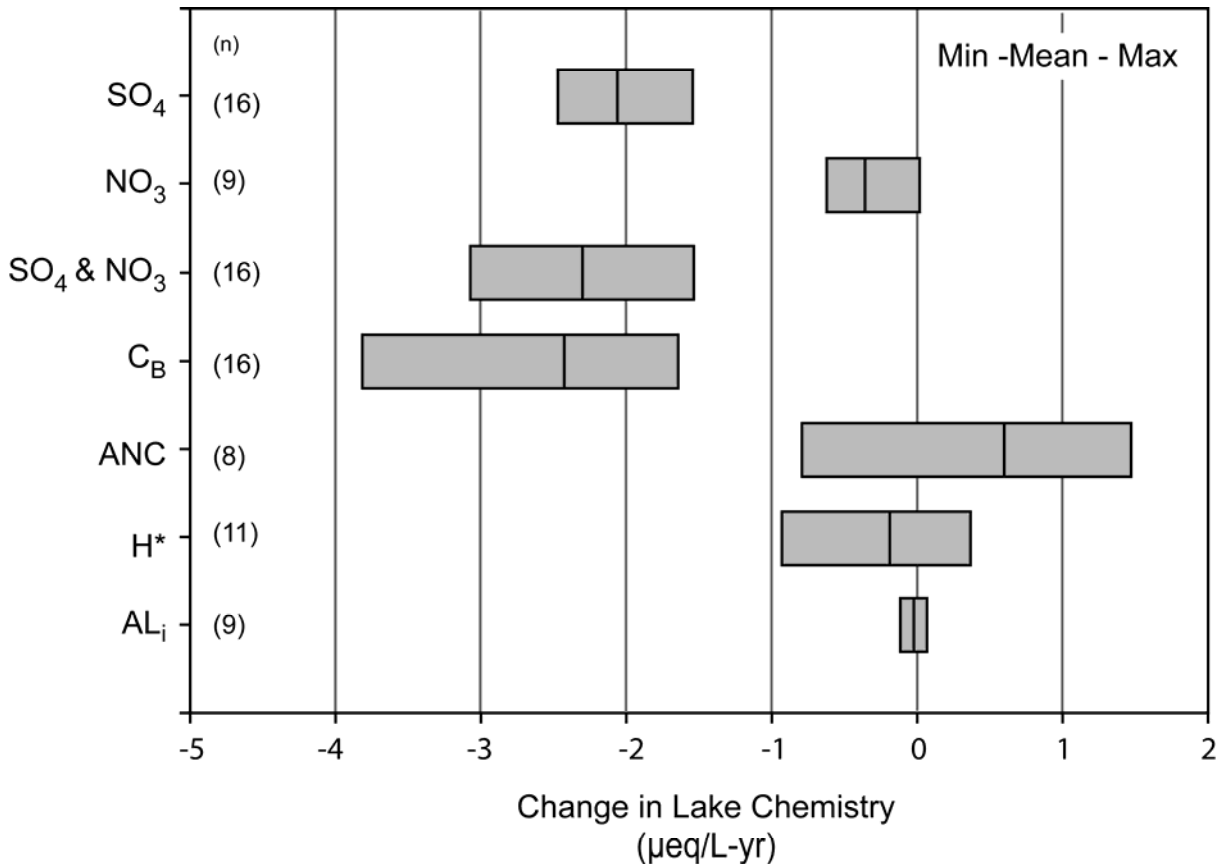


Figure 4.2-18. Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in $\mu\text{eq/L/yr}$, except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

Source: Driscoll et al. (2001b).

1 (2006b) to evaluate the extent to which lakes might be expected to continue to increase in ANC
 2 in the future. Estimated levels of S deposition at one representative watershed are shown in
 3 Figure 4.2-15 for the hindcast period and in the future under the three emissions control
 4 scenarios. Model simulations for 44 statistically selected Adirondack lakes using the MAGIC
 5 and PnET-BGC models were extrapolated to the regional lake population. Cumulative
 6 distribution frequencies of ANC response projected by MAGIC are shown in Figure 4.2-19 for
 7 the past (1850), peak acidification period (approximately 1990), and future (2100). Results for
 8 the future are given for each of the scenarios.

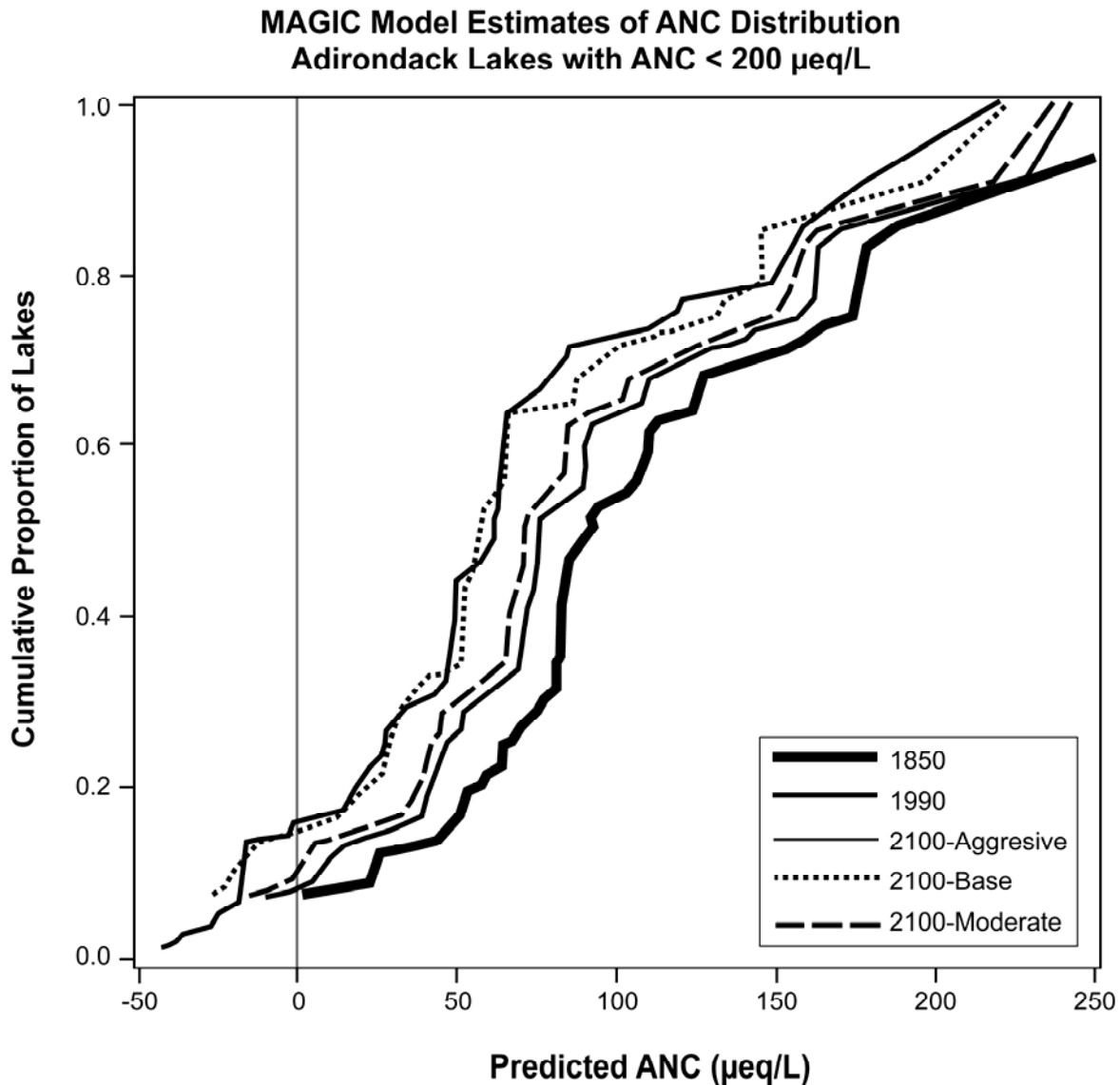


Figure 4.2-19. Simulated cumulative frequency distributions of lakewater ANC at three points in time for the population of Adirondack lakes, based on MAGIC model simulations reported by Sullivan et al., 2006. Conditions for the year 2100 are presented for three emissions control scenarios: Base Case,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

Source: Sullivan et al. (2006b).

- 1 Forecasting results suggested that the ongoing trend of increasing lakewater ANC for the
- 2 most acid-sensitive lakes would not continue under future emissions and deposition levels
- 3 anticipated as of 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC

1 below 20 and below 50 $\mu\text{eq/L}$ were projected to increase between 2000 and 2100 under that
2 scenario, and the number of chronically acidic Adirondack lakes (i.e., ANC less than 0) was
3 projected to stabilize at the level reached in 2000. This projected partial reversal of chemical
4 recovery of acid-sensitive lakes was due to a continuing decline in the simulated pool of
5 exchangeable base cations in watershed soils. Simulations suggested that re-acidification might
6 be prevented with further reductions in emissions and deposition.

7 Chen and Driscoll (2004) applied the PnET-BGC model to 44 EMAP lake watersheds in
8 the Adirondacks. The model was applied to three future emissions scenarios: base case,
9 moderate emissions reductions, and aggressive emissions reductions. A case study for Indian
10 Lake in the Adirondacks illustrated that larger reductions in deposition caused greater decreases
11 in SO_4^+ and base cation concentrations in lake water and greater recovery in pH and ANC.
12 Within the full population of lake-watersheds, some showed decreasing ANC and pH values
13 from 1990 to 2050 even under the moderate and aggressive reduction scenarios. By 2050 to
14 2100, however, nearly all lakes were simulated to experience increasing ANC and pH. The
15 modeled soil base saturation increased very slowly over the modeled time period compared to
16 changes in surface water chemistry. For 95% of the lake-watersheds studied, simulated soil base
17 saturation remained below 20% in 2100 under all emissions scenarios.

18 19 **4.2.4.4.8 *Multipollutant Interaction: Biological Mercury Hotspots in the Adirondacks***

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

1 4.2.4.5 Acidification Case Study #2: Shenandoah National Park, Virginia

2 Shenandoah National Park is located along the crest of the Blue Ridge Mountains in
3 Virginia. Air pollution within Shenandoah National Park, including S and N deposition and O₃
4 concentration, is higher than in most other national parks in the United States. Measured wet
5 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
6 S ha⁻¹ yr⁻¹ since 2000 (Figure 4.2-20). Dry S deposition may be nearly as high as wet deposition
7 (Sullivan et al., 2003). Most acidification effects in the park have been linked with S deposition.

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

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

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

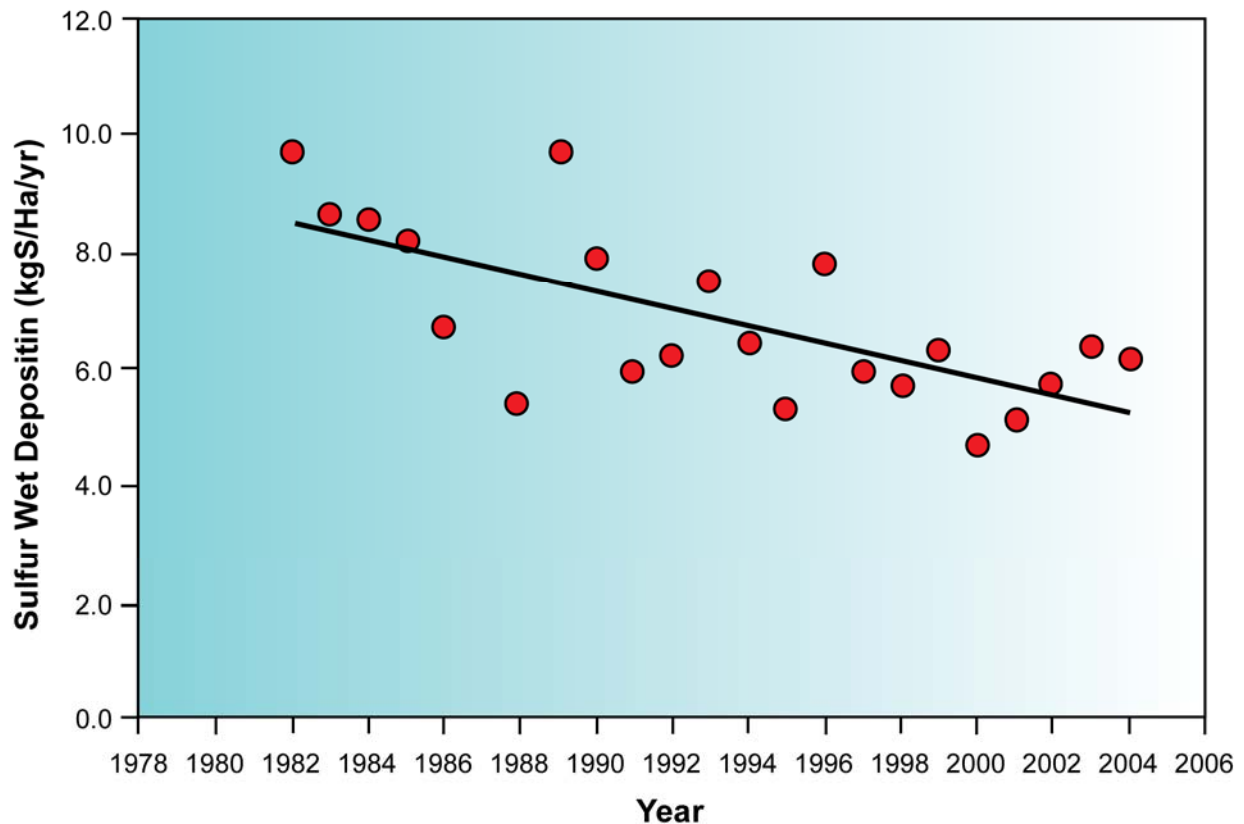


Figure 4.2-20. Wet sulfur deposition for the period of record at the Big Meadows NADP/NTN monitoring station in Shenandoah National Park.

Source: Sullivan et al. (2003).

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

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

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

5 6 **4.2.4.5.1 Episodic Acidification**

7 A number of studies of episodic acidification have been conducted in streams within
8 Shenandoah National Park. Eshleman and Hyer (2000) estimated the contribution of each major
9 ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during
10 a 3-year period. During the study, 33 discrete storm events were sampled and water chemistry
11 values were compared between antecedent baseflow and the point of minimum measured ANC
12 (near peak discharge). The relative contribution of each ion to the ANC depressions was
13 estimated using the method of Molot et al. (1989), which normalized the change in ion
14 concentration by the overall change in ANC during the episode. At the low-ANC (~0) Paine
15 Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^+ , and to a lesser extent organic acid
16 anions, were the primary causes of episodic acidification. Base cations tended to compensate for
17 most of the increases in acid anion concentration. ANC declined by 3 to 21 $\mu\text{eq/L}$ (median
18 7 $\mu\text{eq/L}$) during the episodes studied.

19 At the intermediate-ANC (~60 to 120 $\mu\text{eq/L}$) Staunton River site on granitic bedrock,
20 increases in SO_4^+ and organic acid anions, and to a lesser extent NO_3^- , were the primary causes
21 of episodic acidification. Base cation increases compensated these changes to a large degree,
22 and ANC declined by 2 to 68 $\mu\text{eq/L}$ during the episodes (median decrease in ANC was
23 21 $\mu\text{eq/L}$).

24 At the high-ANC (~150 to 200 $\mu\text{eq/L}$) Piney River site on basaltic (69%) and granitic
25 (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other
26 two sites where base cation concentrations increased). SO_4^+ and NO_3^- usually increased. The
27 change in ANC during the episodes studied ranged from 9 to 163 $\mu\text{eq/L}$ (median 57 $\mu\text{eq/L}$)
28 (Eshleman and Hyer, 2000). Changes in base cation concentrations during episodes contributed
29 to the ANC of Paine Run, had little effect in Staunton River, and consumed ANC in Piney River.

30 The most acidic conditions in Shenandoah National Park streams occur during high-flow
31 periods, in conjunction with storm or snowmelt runoff. There are several different mechanisms

1 of episodic acidification in operation in these streams, depending at least in part on the bedrock
2 geology of the stream watershed. The relative importance of the major processes that contribute
3 to episodic acidification varies among the streams, in part as a function of bedrock geology and
4 baseflow streamwater ANC. S-driven acidification was an important contributor to episodic loss
5 of ANC at all three study sites, probably because S adsorption by soils occurs to a lesser extent
6 during high-flow periods. This is due, at least in part, to diminished contact between drainage
7 water and potentially adsorbing soil surfaces. Dilution of base cation concentrations during
8 episodes was most important at the high-ANC site.

9 Thus, episodic acidification of streams in Shenandoah National Park can be attributed to
10 a number of causes, including dilution of base cations and increased concentrations of sulfuric,
11 nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-
12 episode ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can
13 have adverse effects on fish populations. However, not all of the causes of episodic acidification
14 are related to acidic deposition. Base-cation dilution and increase in organic acid anions during
15 high-flow conditions are natural processes. The contribution of HNO₃, indicated by increased
16 NO₃⁻ concentrations, has evidently been (at least for streams in the park) related to forest
17 defoliation by the gypsy moth (Webb et al., 1995; Eshleman et al., 1998). Significant
18 contributions of H₂SO₄, indicated by increased SO₄⁺ concentrations during episodes in some
19 streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils
20 (Eshleman and Hyer, 2000).

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

1 smaller catchments are more vulnerable to episodic acidification than larger catchments
2 underlain by the same bedrock. Catchments with similar topography and size are more
3 vulnerable if underlain by less basaltic and carbonate bedrock.

4 5 **4.2.4.5.2 Biological Effects of Acidification**

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

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

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

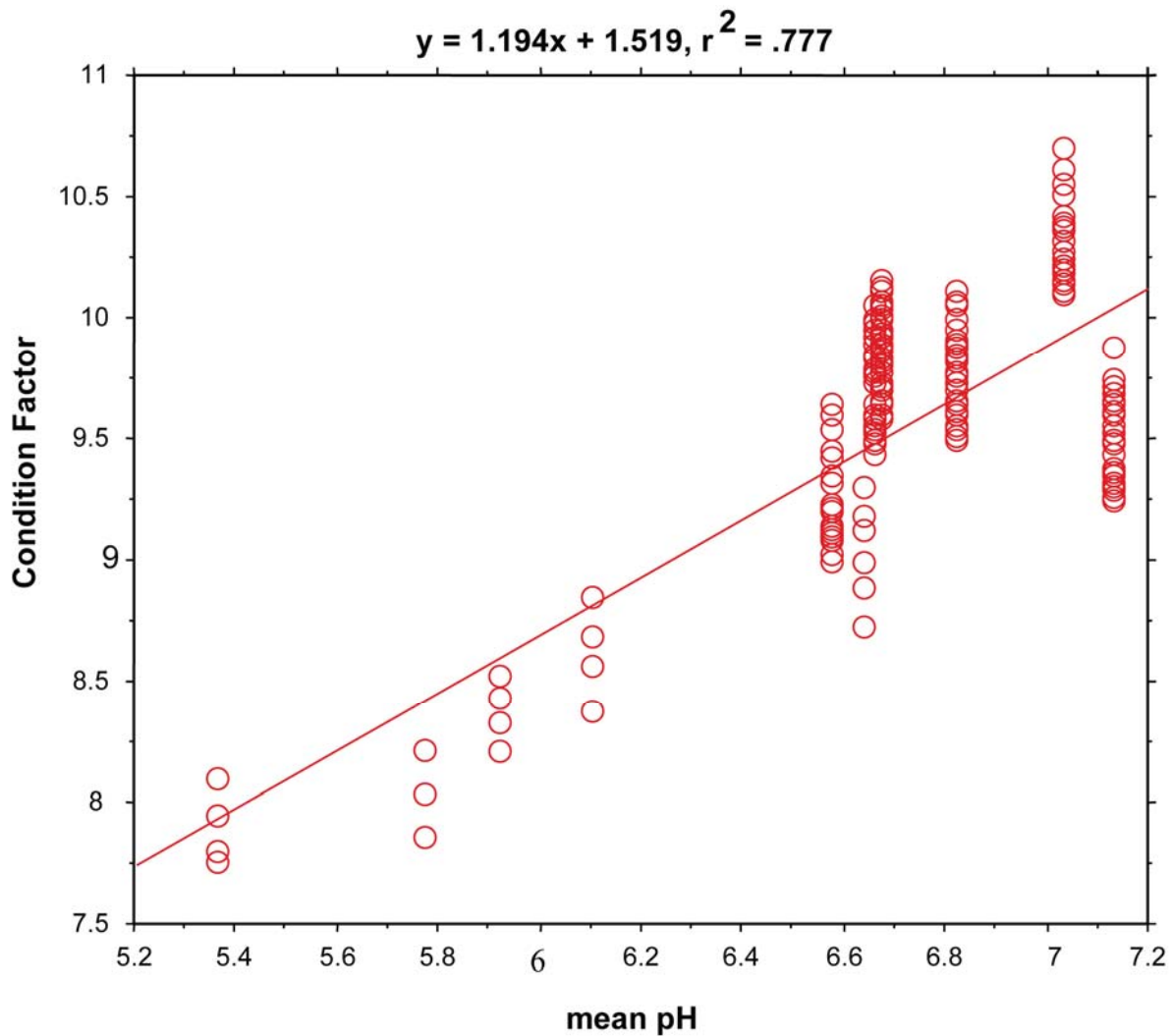


Figure 4.2-21. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The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

- 1 in mid- and higher-ANC reference streams. Acidic episodes, with associated low pH and
- 2 elevated inorganic Al concentrations and high streamwater discharge, induced rapid fish

1 mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger
2 et al., 1999).

3
4 **4.2.4.5.3 *Modeling of Acidification, Recovery, and Critical Loads***

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

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

25 MAGIC model simulations for streams in Shenandoah National Park by Sullivan et al.
26 (2003) also suggested that acidic deposition would have to be decreased substantially in order to
27 improve and maintain acid-sensitive streams at levels of ANC that would be expected to protect
28 against ecological harm. In addition, it took a long time for these streams to acidify in the past;
29 because of complexities related to soil conditions, it will take even longer for them to recover in
30 the future. In order to protect against chronic acidity in the year 2100, with associated probable
31 lethal effects on brook trout, S deposition to the most sensitive Si-based watersheds in the park
32 will have to be kept below about 9 kg per hectare per year for the next 100 years (Sullivan et al.,

1 2007a). Prior to the industrial revolution, most streamwater in the park had ANC higher than
2 about 50 $\mu\text{eq/L}$. In order to promote ANC recovery to 50 $\mu\text{eq/L}$ in the future, to protect against
3 general ecological harm, S deposition to Si-based watersheds in the park will have to be kept
4 below about 6 kg per hectare per year. Some watersheds will likely not recover streamwater
5 ANC to values above 50 $\mu\text{eq/L}$ over the next century even if S deposition is reduced to zero
6 (Sullivan et al., 2007a).

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

20 Simulation and mapping of watershed responses to predicted future changes in acidic
21 deposition by (Cosby et al., 2006) were developed following EPA methods for preparation of
22 emissions inventory inputs into air quality modeling for policy analysis and rule making
23 purposes. These alternate emissions scenarios were based on existing emission control
24 regulations and several proposed alternatives. The model output suggested that the responses of
25 soil conditions to changes in S deposition are expected to be relatively slow. In the short term
26 (by the year 2020), neither improvement nor further deterioration is likely to be observed in soil
27 condition regardless of the future deposition scenario considered. However, model results
28 suggested that constant deposition at 1990 levels would produce worsening soil conditions in the
29 park by the year 2100 with the development of areas of “acute concern” (average percent soil
30 base saturation below 5%) in the southern district. Although the scenarios of possible reduced

1 future deposition did not produce worsening soil conditions, neither did they indicate any
2 improvement in soil condition, even in the long term.

3 Simulated responses of stream conditions were more rapid than those of soils. In the
4 short term (by the year 2020), constant deposition at 1990 levels would likely produce further
5 deterioration in stream condition. The scenarios of future deposition reductions failed to reverse
6 the deterioration of stream condition that has occurred during the last century. In the long term
7 (by year 2100), the effects of the deposition reduction scenarios begin to diverge. The moderate
8 S deposition reduction scenario (69% reduction from 1990 values) did not produce improvement
9 in stream chemistry relative to current conditions. The larger deposition reduction scenario
10 (75%), by contrast, produced modest improvements in stream chemistry by 2100. However,
11 even the relatively large S deposition reductions of this scenario did not result in a simulated
12 return of stream conditions to the preindustrial state.

13 To develop projections of probable past and future responses of aquatic biota to changing
14 S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al.
15 (2003) with several empirical models that linked biological response to past and future model
16 projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the
17 biological effects estimates were based on observed empirical relationships rooted in correlation
18 and expressed as linear relationships. Correlation does not necessarily imply causality, but an
19 observed pattern of covariation between variables does provide a quantitative context for
20 extrapolation. In this case, the projections did not require extrapolation beyond the observed
21 ranges of observations, and therefore the projections were statistically robust. To the extent that
22 the observed empirical relationships used in the coupled models do in fact reflect the effects of
23 acid stress on aquatic biota, the projections were also biologically robust.

24 Dynamic water chemistry model projections were combined with biological dose-
25 response relationships to estimate declines in fish species richness with acidification. A
26 relationship derived from the data in Figure 4.2-10 was used by Sullivan et al. (2003) with
27 stream ANC values predicted by the MAGIC model to provide estimates of the expected number
28 of fish species in each of the modeled streams for the past, present, and future chemical
29 conditions simulated for each stream. The coupled geochemical and biological model
30 predictions were evaluated by comparing the predicted species richness in each of the 13 streams
31 with the observed number of species that occur in each stream. The agreement between

1 predicted and observed species numbers was good, with a root mean squared error in predicted
2 number of species across the 13 streams of 1.2 species. The average error was 0.3 species,
3 indicating that the coupled models were unbiased in their predictions. Model reconstructions of
4 past species richness in the streams suggested that historical loss of species had been greatest in
5 the streams located on the most sensitive geological class (siliciclastic). The average number of
6 species lost from streams on the three bedrock types examined were estimated as 1.6 species on
7 siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4 species on basaltic bedrock. In the
8 case of the siliciclastic streams, the projected past changes were much larger than the average
9 error and root mean squared error of the coupled models, suggesting that the projections were
10 reasonably robust.

11
12

13 **4.3 NITROGEN NUTRIENT ADDITION**

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

25 Once in a reactive form, N is transported easily between air, water and soils in what is
26 known as the N cascade (See Section 4.3.1). A single N-containing molecule can have a series
27 of impacts on the environment because it can move so easily from the atmosphere, into soils and
28 onto other surfaces, into waterways, and back again. Atmospheric deposition, generates a series
29 of effects contributing to both acidification (see Section 4.2) and N pollution, the latter, by
30 causing inadvertent fertilization of trees and grasslands, creating unnatural growth rates, nutrient
31 imbalances, and ultimately decreasing ecosystem health and biodiversity. Leaching out of the
32 soil, reactive N can pollute groundwater and surface water, rendering it unfit for human

1 consumption. Reactive N also promotes eutrophication in coastal ecosystems, ultimately
2 reducing biodiversity due to a lack of oxygen needed for the survival of many species of aquatic
3 plants and animals. The cascade is interrupted only when reactive N is stored in inaccessible
4 places or converted back to N₂ gas through denitrification. Even where denitrification occurs,
5 not all the reactive N is always converted to unreactive N₂. Instead a portion is often converted
6 by denitrifying bacteria to the intermediate product, nitrous oxide, which contributes to both the
7 greenhouse effect and to stratospheric O₃ depletion. The following sections begin with a
8 discussion of the N cascade, which is the foundation from which to discuss the effects of N_r on
9 terrestrial, transitional, and aquatic ecosystems within the United States.

10 11 **4.3.1 Reactive Nitrogen and the Nitrogen Cascade**

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

23 An increase in global reactive N has occurred over the past century, largely due to three
24 main causes: (1) widespread cultivation of legumes, rice, and other crops that promote
25 conversion of N₂ gas to organic N through biological N fixation; (2) combustion of fossil fuels,
26 which converts both atmospheric N₂ and fossil N to reactive NO_x; and (3) synthetic N fertilizer
27 production via the Haber-Bosch process, which converts nonreactive N₂ to N_r to sustain food
28 production and some industrial activities (Galloway and Cowling, 2002; Galloway et al., 2003).
29 Food production accounts for much of the conversion from N₂ to N_r, and accounts for geographic
30 redistribution of N as food is shipped to meet population demands.

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

9 The results of the N cascade and the various transformations in the N cycle can be both
10 beneficial and detrimental to humans and to ecosystems (Galloway and Cowling, 2002;
11 Galloway et al., 2003). Among the most adverse effects of chronic N deposition are changes in
12 terrestrial plant biodiversity, aquatic eutrophication, disruptions in nutrient cycling, increased
13 soil emissions of nitrous oxide (a potent GHG), accumulation of N compounds in the soil with
14 enhanced availability of NO₃⁻ or NH₄⁺, soil-mediated effects of acidification, and increased
15 susceptibility of plants to stress factors (Aber et al., 1989, 1998; Bobbink et al., 1998; Fenn et al.,
16 1998; Driscoll et al., 2003a). Important ecological effects known or suspected to occur in the
17 western United States are summarized in Table 4.3-1.

18 19 **4.3.2 Biogeochemical Processes and Chemical Effects Indicators**

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

25 **4.3.2.1 Terrestrial Ecosystems**

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

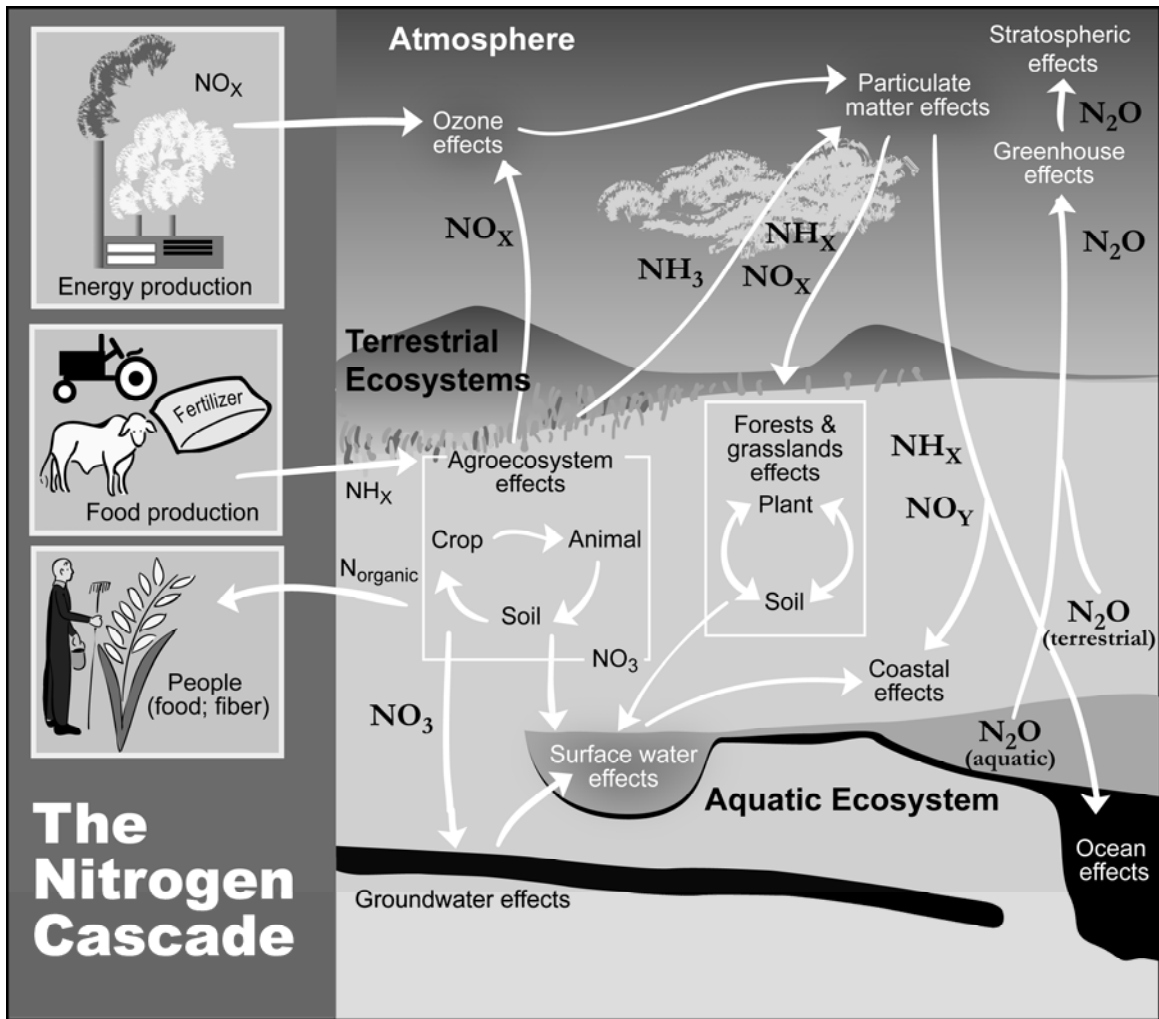


Figure 4.3-1. Illustration of the nitrogen cascade showing the movement of the human-produced reactive nitrogen (N_r) as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and aquatic ecosystems.

Source: Galloway et al. (2003).

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

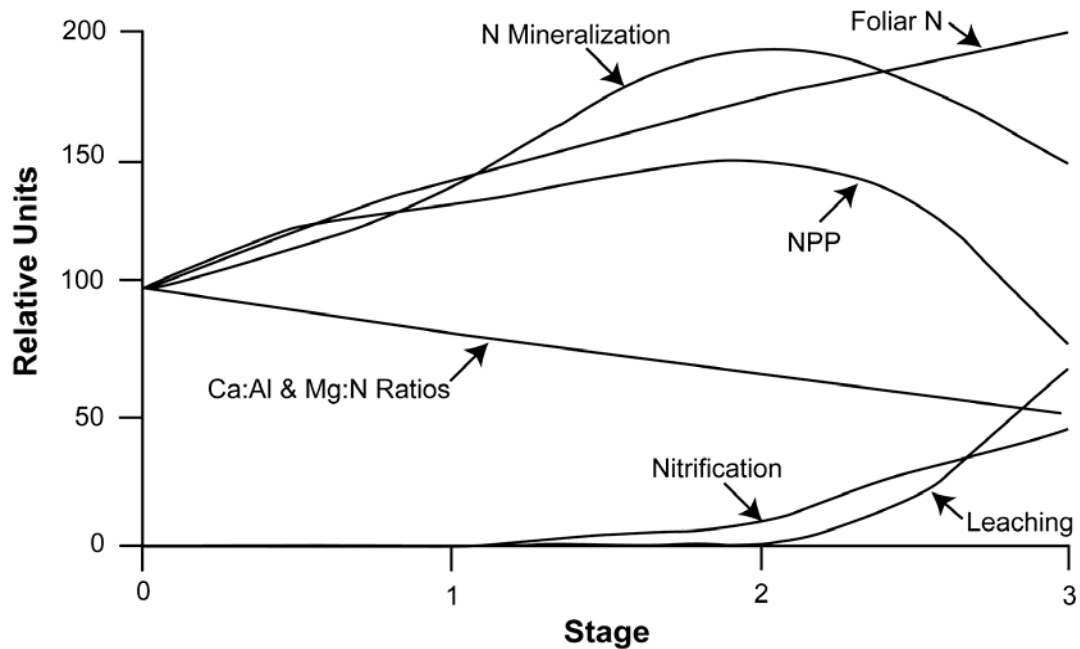


Figure 4.3-2. Schematic illustration of the response of temperate forest ecosystems to long-term, chronic N additions. Changes from initial hypotheses of Aber et al. (1989) include the reduction in N mineralization in stage 3 and the addition of foliar Ca:Al and Mg:N ratios.

Source: Aber et al. (1998).

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

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

1 Experimental additions of N to plots and watersheds demonstrate that rates of leaching
2 and nitrification associated with N saturation vary among terrestrial ecosystems. Additions of
3 N to hardwood watersheds in Maine ($25 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) and West Virginia ($35.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$),
4 which were releasing NO_3^- to surface waters prior to the additions, resulted in substantial
5 increases in NO_3^- concentrations in soil water and stream water within the first treatment year
6 (Kahl et al., 1993; Peterjohn et al., 1996). Additions of $25 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ to spruce plots in
7 Vermont (ambient bulk deposition $5.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), in which net nitrification did not occur
8 prior to treatment, triggered net nitrification in the second year of treatment, whereas nitrification
9 was not triggered until the third year in plots receiving $19.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (McNulty et al.,
10 1996). Similar results were seen in two studies from Colorado. Additions of $25 \text{ kg N ha}^{-1} \text{ yr}^{-1}$
11 to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition $\sim 4\text{-}5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$)
12 doubled N mineralization rates and stimulated nitrification, while the addition of the same
13 amount to plots receiving ambient bulk deposition of $\sim 2.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in Fraser Experimental
14 Forest elicited no microbial response but significantly increased foliar and organic soil horizon N
15 (Rueth et al., 2003). A comparison study of old-growth spruce plots across a depositional
16 gradient in Colorado found mineralization rates to be higher where N deposition ranged from 3
17 to $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ than where N deposition ranged from 1 to $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, with measurable
18 nitrification rates at sites with the highest deposition amounts (Rueth and Baron, 2002). In
19 marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the
20 seventh year in hardwood plots in Harvard Forest, which received additions of 150 kg N ha^{-1}
21 yr^{-1} (Magill et al., 2004). Concentrations of (NO_3^- plus NH_4^+) in hardwood plots receiving
22 $50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ were not yet detectable in the 15th year of treatment. The same treatments
23 were applied to red pine (*Pinus resinosa*) plots, which exhibited elevated concentrations of
24 (NO_3^- plus NH_4^+) in soil water after 1 year of $150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ doses, and after 5 years of 50
25 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ doses.

26 Severe symptoms of N saturation have been observed (1) in the northern hardwood
27 watersheds at Fernow Experimental Forest near Parsons, West Virginia (Peterjohn, 1996), (2) in
28 high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains (Cook, 1994),
29 (3) throughout the northeastern United States (Aber, 1989, 1998). Mixed conifer forests and
30 chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated

1 and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North
2 America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998).

3 There are examples of N saturation in lower-elevation eastern forests, especially in West
4 Virginia. For example, progressive increases in streamwater NO_3^- and Ca concentrations were
5 measured at the Fernow Experimental Forest in the 1970s and 1980s (Edwards and Helvey,
6 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000). This watershed has received higher
7 N deposition (average throughfall input of $22 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of N in the 1980s) than is typical for
8 low-elevation areas of the eastern United States, however (Eagar et al., 1996), and this may help
9 to explain the observed N saturation.

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

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

24 The varying degree of N assimilation, leaching and microbial transformation illustrated
25 by the following examples often reflect differences in N status of the treatment sites. These
26 variations have most often been attributed to disturbance history, dating back a century or more
27 (Goodale and Aber, 2001). Sites which have undergone disturbances that cause loss of soil N,
28 such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and
29 experimental inputs of N. N retention capability often decreases with stand age, which suggests
30 that older forests are more susceptible than younger forests to becoming N-saturated (Hedin

1 et al., 1995). Aber et al. (1998) surmised that land use history may be more important than
2 cumulative atmospheric deposition of N in determining the N status of a forest ecosystem.

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

18 19 **4.3.2.2 Transitional Ecosystems**

20 N dynamics in wetland ecosystems are variable in time and with type of wetland and
21 environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as
22 a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these
23 functions can vary with season and with hydrological conditions. Vegetation type,
24 physiography, local hydrology, and climate all play significant roles in determining source/sink
25 N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren,
26 1994; Mitchell et al., 1996).

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

1 Broderick et al., 1988; Cooper, 1990). This process increases the contribution of nitrous dioxide
2 (a GHG) and NO (a precursor to O₃) to the atmosphere, but limits NO₃⁻ levels in soils and
3 leaching into drainage waters and the associated environmental effects. However, increased
4 N inputs to wetland systems would only be expected to stimulate denitrification if there is an
5 adequate C supply (Groffman, 1994). Although denitrification has been observed to increase
6 with N addition, N mineralization has also been shown to increase, and this can cause an increase
7 in wetland N export to adjacent surface water (Groffman, 1994). Denitrification appears to be
8 negligible in wetland environments that are typically nutrient (including N) poor, such as some
9 bogs and fens (Morris, 1991).

10 Denitrification is also a major factor governing the loss of N from estuarine and marine
11 ecosystems. Previously, it was believed that denitrification was responsible for virtually all of
12 the transfer of N_r in the ocean to the atmosphere as N₂ gas. It now appears that anaerobic NH₄⁺
13 oxidation (anammox) may account for up to 50% of the N₂ production in the oceans (Devol,
14 2003; Ward, 2003; Dalsgaard et al., 2005; Kuypers et al., 2005).

15 Increased N loading to transitional ecosystems can affect both methane (CH₄)-producing
16 and CH₄-oxidizing microbial activity. The difference between the CH₄ production and oxidation
17 determines the magnitude of CH₄ emission from soils. NO₃⁻ can decrease CH₄ production by
18 acting as a redox buffer during organic decomposition in anaerobic sediments. NH₄⁺ compounds
19 are generally considered to reduce CH₄ oxidation (Steudler et al., 1989; King and Schnell, 1994;
20 Gullledge et al., 1997), but have also been observed to increase methanotropic bacterial activity
21 (Bodelier et al., 2000).

22 CH₄ emissions from saturated soils have been observed to increase with N addition
23 (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). The prevailing hypothesis for
24 explaining this effect is that increased vegetative cover increases C availability through root
25 exudates, which in turn stimulates methanogenic bacteria and CH₄ emissions (Granberg et al.,
26 2001; Saarnio et al., 2003; Zhang et al., 2007). Saarnio et al. (2003) observed moderate
27 increases in CH₄ emissions from boreal wetland soils with N fertilization rates of 30 kg N ha⁻¹
28 yr⁻¹ as NH₄NO₃. Comparable N application rates and effects on CH₄ emissions were also
29 observed by Granberg et al. (2001) in a similar ecosystem type. Zhang et al. (2007) observed
30 elevated CH₄ emissions from freshwater wetland soils with experimental N additions of 240 kg
31 N ha⁻¹ yr⁻¹. They postulated that additional N increased abundance of *Deyeucia angustifolia*

1 which increased CH₄ emissions by supplying methanogenic bacteria with additional substrate in
2 the form of root exudates. Other studies have shown that N addition had little or no effect on
3 CH₄ emissions across a variety of ecosystem types (Saarnio et al., 2000; Silvola et al., 2003;
4 Ambus and Robertson, 2006).

5 It is important to note that the N enrichment rates employed in all of the above reported
6 studies related to N effects on soil CH₄ emissions were much greater (30 to 240 kg N ha⁻¹ yr⁻¹)
7 than atmospheric N inputs in most areas of the United States that are heavily impacted by
8 elevated atmospheric N deposition. Nevertheless, an increase in CH₄ emissions from wetland
9 soils in response to N loading is important, especially because CH₄ is an effective GHG
10 contributing to global warming (Saarnio et al., 2000). Changes in the C cycle in wetlands,
11 especially within the geographically extensive boreal zone, could have an important influence on
12 climate. The reason(s) for the observed difference in response are not known.

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

27 28 **4.3.2.3 Aquatic Ecosystems**

29 Anthropogenic sources of N to freshwater and coastal ecosystems are varied and include
30 atmospheric deposition, wastewater discharge, agricultural runoff, and urban runoff. A large
31 fraction of atmospheric N deposition is retained in most forests. Nevertheless, the fraction that

1 does leach to streams can make a substantial contribution to total N inputs to downstream large
2 rivers and estuaries, especially in the eastern United States. Direct atmospheric N deposition to
3 the estuary surface constitutes an additional important N source, especially to estuaries which
4 have a large surface area relative to their watershed area. N deposition effects on the nutrient
5 dynamics of aquatic ecosystems are described by the process of eutrophication, whereby a body
6 of water becomes over-enriched in nutrients, resulting in increased productivity (of algae or
7 aquatic plants) and sometimes also decreased dissolved oxygen levels. The following sections
8 discuss the biogeochemical processes associated with N loading in freshwater and estuarine
9 ecosystems.

10 11 **4.3.2.3.1 Freshwater Aquatic Ecosystems**

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

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

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

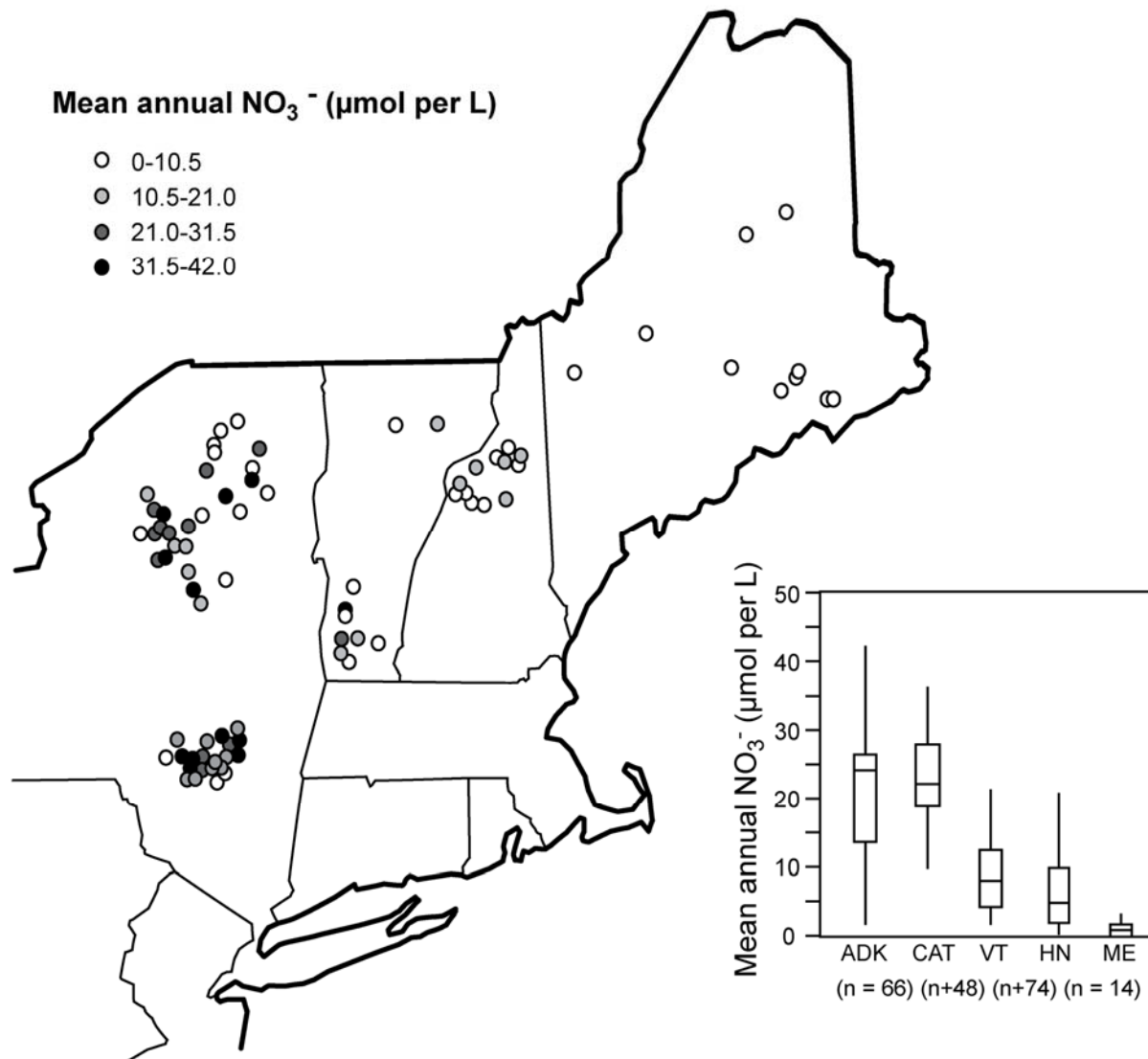


Figure 4.3-3. Mean annual nitrate (NO_3^-) concentrations in 230 lakes and streams across the northeastern United States. Inset indicates the median, quartile, and 90% range of mean annual NO_3^- in the Adirondacks (ADK), the Catskills (CAT), Vermont (VT), New Hampshire (NH), and Maine (ME).

Source: Aber et al. (2003).

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

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

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

20 In the Uinta Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of
21 the lakes included within the Western Lakes Survey had NO_3^- concentrations greater than
22 10 $\mu\text{eq/L}$. This suggests that N deposition in these areas may have exceeded the capability of
23 these lakes to assimilate N. It is unknown if these concentrations of NO_3^- represent effects from
24 anthropogenic sources or if this constituted a natural condition associated with inhibited NO_3^-
25 assimilation in cold alpine environments.

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

31

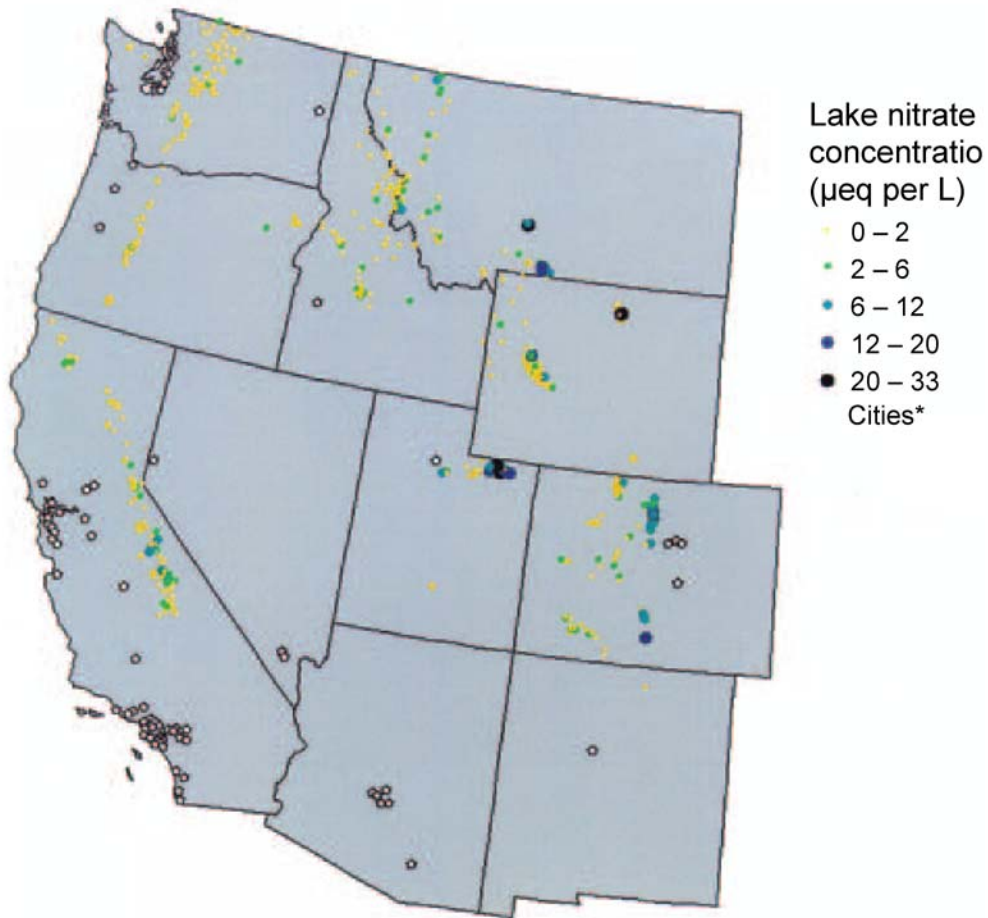


Figure 4.3-4. Nitrate concentrations in high-elevation lakes in western North America. Stars represent cities with a population greater than 100,000.

Source: Fenn et al. (2003a).

1 **4.3.2.3.2 Estuarine and Coastal Marine Ecosystems**

2 Estuarine and coastal marine ecosystems experience a range of ecological problems
 3 associated with nutrient enrichment. Because the productivity of estuarine and nearshore marine
 4 ecosystems is generally limited by the availability of N_r , excessive contribution of N_r from
 5 sources of water and air pollution can contribute to eutrophication. Some of the most important
 6 environmental effects include increased algal blooms, depletion of dissolved oxygen in bottom
 7 waters, and reduction in fisheries and sea grass habitats (Valiela and Costa, 1988; Valiela et al.,

1 1990; Boynton et al., 1995; Paerl, 1995, 1997; Howarth et al., 1996). The general process of
 2 estuarine eutrophication is depicted in Figure 4.3-5.

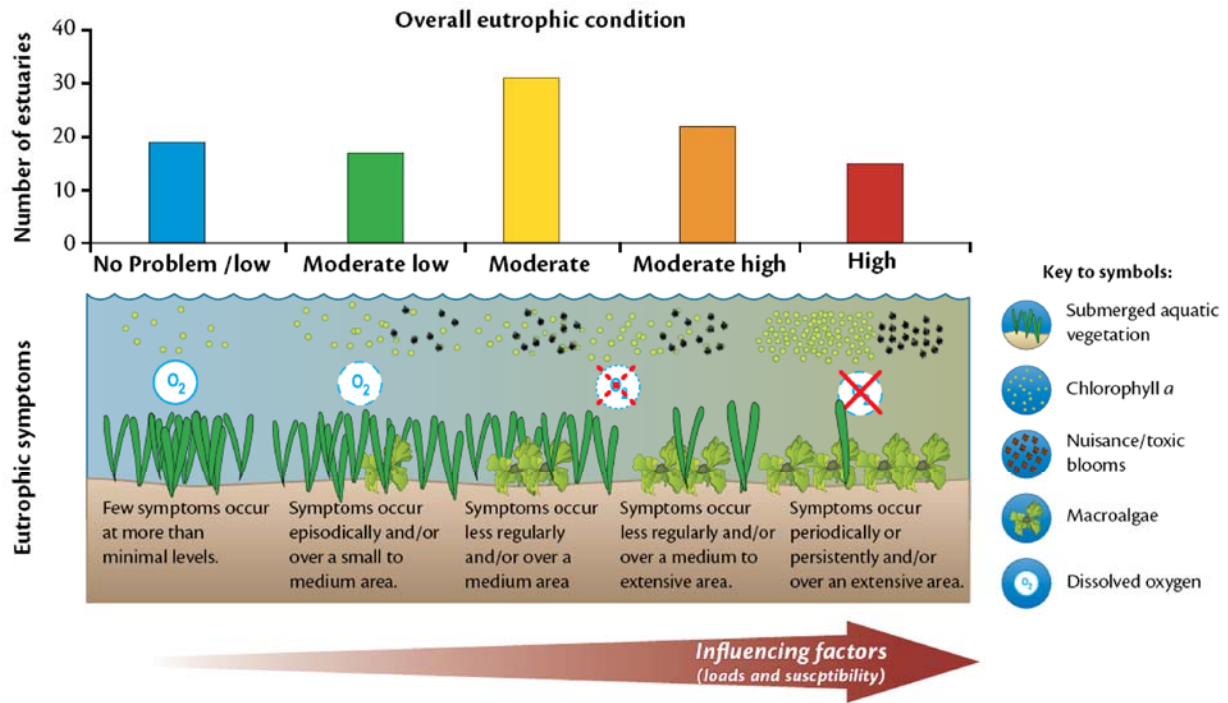


Figure 4.3-5. A conceptualization of the relationship between overall eutrophic conditions, associated eutrophic symptoms, and influencing factors (N loads and susceptibility). Overall eutrophic condition was assessed for estuaries throughout the United States. (See also Figure 4.3-10.)

Source: Bricker et al. (2007).

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

1 those that received the greatest N loads from all sources, including atmospheric and land-based
2 sources (Bricker et al., 2007).

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

16 Atmospheric N deposition has been estimated to account for only a few percent to more
17 than 40% of total external N loading to estuaries in North America and Europe. Valigura et al.
18 (2000) estimated that direct atmospheric deposition to the estuary surface generally constitutes at
19 least 20% of the total N load for estuaries that occupy more than 20% of their watershed. U.S.
20 Environmental Protection Agency (1999b) estimated that between 10% and 40% of the total
21 N input to estuaries in the United States is typically derived from atmospheric deposition. NRC
22 (2000) judged that U.S. Environmental Protection Agency (1999a) underestimated the
23 importance of atmospheric deposition as a contributor to the total N load.

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

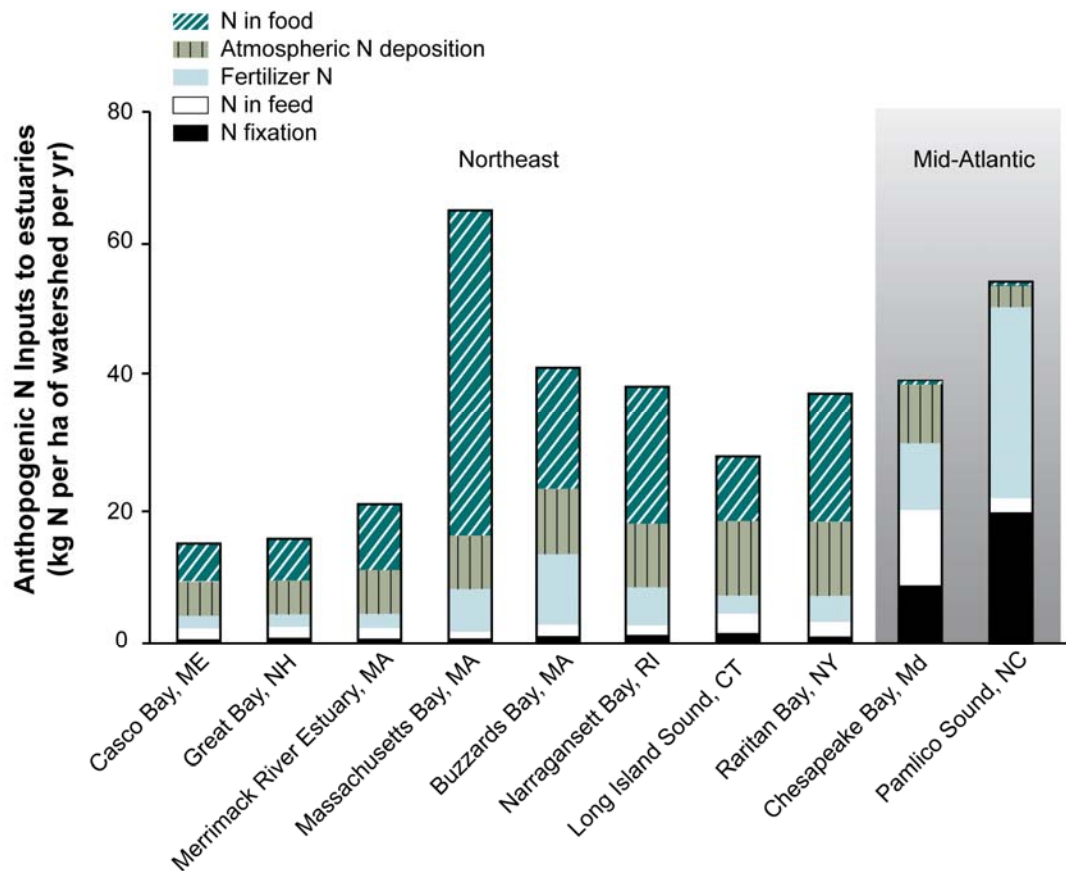


Figure 4.3-6. Estimated anthropogenic nitrogen inputs to the estuaries of the northeastern United States, in kg ha⁻¹ yr⁻¹.

Source: Driscoll et al. (2001b).

1 the northeastern United States is probably higher. For the watersheds that export more than
 2 10 kg N ha⁻¹ yr⁻¹, Smith et al. (1997) concluded that fertilizer was the largest source of N (48%),
 3 followed by atmospheric deposition (18%) and livestock wastes (15%). In this analysis,
 4 fertilizer used for human food production was considered to be the ultimate source of
 5 N contributed to waterways through waste water treatment plants. If the analysis of N sources to
 6 estuarine water is restricted to only nonpoint sources of N, atmospheric deposition is often
 7 considered to be the largest individual source (Howarth et al., 1996; Jaworski et al., 1997; Smith
 8 et al., 1997; NRC, 2000; Howarth, 2007).

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

10 11 **4.3.3 Biological Effects**

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

21 22 **4.3.3.1 Terrestrial Ecosystems**

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

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

3
4 **4.3.3.1.1 Forests**

5 Over 50% of plant N is used for photosynthetic enzymes. Because N is so crucial to
6 photosynthesis, rates of photosynthesis and net primary productivity is typically correlate with
7 metrics of N availability such as leaf N content and net N mineralization rate (Field and Mooney,
8 1986; Reich et al., 1997a,b; Smith et al., 2002). Because N availability often limits rates of net
9 primary productivity, many modeling analyses expect atmospherically deposited N to increase
10 growth of vegetation (e.g., Townsend et al., 1996; Holland et al., 1997; Ollinger et al., 2002).

11 In order to understand the effects of added N to forest ecosystems, it is helpful to
12 examine the results of modeling projects and experimental N additions. Experimental
13 N additions to forest ecosystems have elicited positive growth responses in some, but certainly
14 not all, organisms (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006).
15 Forest growth enhancement, to the extent that it occurs, can potentially exacerbate other nutrient
16 deficiencies, such as Ca, Mg, or K, thereby causing problems with forest health. Multiple long-
17 term experiments have demonstrated transient growth increases followed by increased mortality,
18 especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al.,
19 2005; Högberg et al., 2006).

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

27 It is expected that low to moderate levels of N deposition should result in increased forest
28 growth (Aber et al., 1998). However, there is little direct evidence for regional increases in
29 overall forest productivity in the United States in response to atmospheric deposition of N.
30 Evaluation of tree growth rates in five states (Minnesota, Michigan, Virginia, North Carolina,
31 and Florida) found little evidence for growth enhancement due to any factor examined, including
32 N deposition, carbon dioxide (CO₂) fertilization, or climate change (Caspersen et al., 2000).

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

12 In Europe, forest biomass is accumulating, largely in response to increases in forest area
13 and improved management, but other possible mechanisms of growth enhancement cannot be
14 ruled out (Kauppi et al., 1992; Spiecker et al., 1996). One of the most comprehensive analyses
15 of regional forest growth trends was an analysis of tree increment cores from more than
16 31,000 plots in Norway. In this study, growth increased during the 1960s and 1970s and then
17 declined in the 1990s, especially in southern regions exposed to the highest rates of N deposition
18 (Figure 4.3-7) (Nellemann and Thomsen, 2001).

19 Conifer forests that receive high inputs of reactive N appear to exhibit decreases in
20 productivity and increases in mortality (Fenn et al., 1998). Multiple long-term experiments have
21 demonstrated transient growth increases followed by increased mortality, especially at higher
22 rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al.,
23 2006).

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

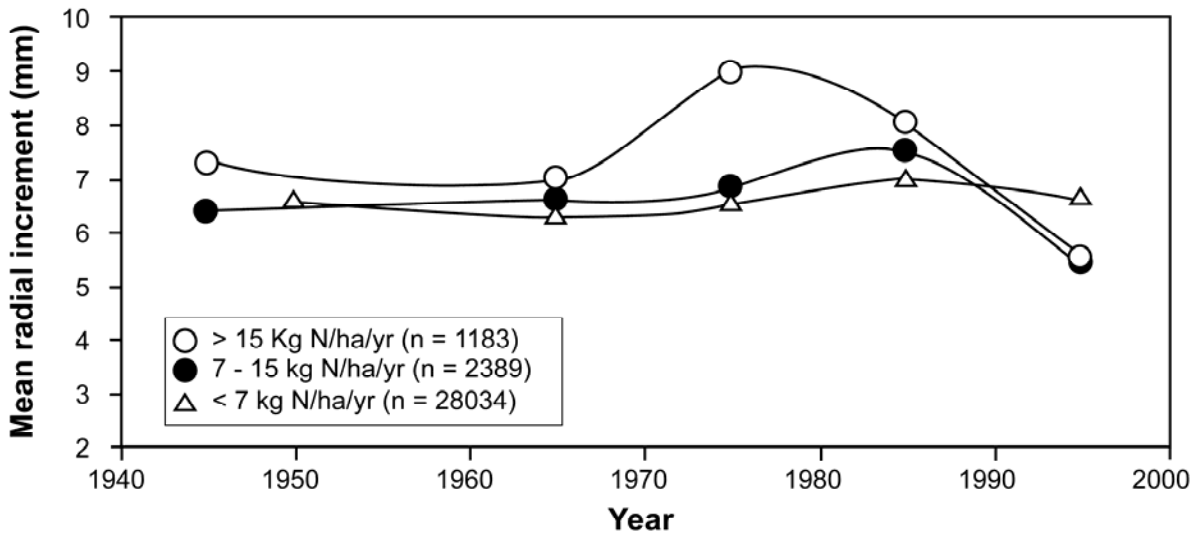


Figure 4.3-7. Mean 5-y radial increment from 31,606 core samples from *Picea abies* during the period 1945 to 1996 for three atmospheric N deposition zones (high, medium, and low wet N-deposition in 1990), respectively. Note that the decline in radial increment after 1975 corresponds with the peak in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

1 At the Bear Brook, Maine, acidification study, basal area increment of sugar maple was
 2 enhanced 13 to 104% by addition of 25 kg N ha⁻¹ yr⁻¹ as ammonium sulfate ((NH₄)₂SO₄),
 3 whereas red spruce was not significantly affected (Elvir et al., 2003). In a comparable
 4 experiment at the Fernow Experimental Forest, WV, application of 35 kg N ha⁻¹ yr⁻¹ as
 5 (NH₄)₂SO₄ enhanced growth of black cherry and yellow poplar during the first 7 years, but led to
 6 reduced growth of these species relative to control trees in years 9 through 12, with no change in
 7 red maple or sweet birch (DeWalle et al., 2006). Chronic fertilization combined with drought led
 8 to significant mortality in a 70-year old red pine stand at Harvard Forest, Massachusetts (Magill
 9 et al., 2004). As red pine has died, striped maple, black cherry, and black birch have increased
 10 their contributions to annual litterfall production. At the same site, N fertilization of a 50-year-

1 old red-oak/red maple stand largely stimulated productivity, although the drought in 1995
2 induced significant mortality in fertilized small red maple trees (Magill, 2004).

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

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

19 Disturbance can affect N cycling and the response of forest ecosystems to N deposition.
20 Disturbance can be human-caused (e.g., timber harvesting, road-building, agricultural
21 development) or natural (e.g., wind storm, wildfire, drought). The extent to which disturbance
22 influences leaching of NO_3^- and base cations from soils to drainage waters depends on rates of
23 primary productivity, nutrient uptake by plants and microorganisms within the terrestrial
24 ecosystem, and hydrological pathways for transferring nutrients to drainage water. Historical
25 land use also influences N leaching from currently forested watersheds that receive moderate to
26 high levels of atmospheric N deposition. The severity of effect and length of the recovery period
27 probably vary according to the nature of the past disturbance. Past logging and agricultural
28 cultivation appear to have considerable and long-lasting effects on nutrient cycling.

29 There is very little information on the effect of N deposition on the biodiversity of
30 overstory trees in the United States. However, some effects have been documented on other

1 plant communities and on understory species, lichens, mycorrhizae, and microbial diversity
2 within forests. See the sections below for explanations of these effects.

3 4 **4.3.3.1.2 Grasslands**

5 Grasslands are well known to respond to increased N availability through changes in
6 growth rates of both native and exotic species. Under high N supply, exotic grasses often out-
7 compete other species, and cause changes in plant community composition. Lowe et al. (2002)
8 tested the response of two native (blue grama and western wheatgrass) and four exotic
9 (cheatgrass, leafy spurge, Canada thistle, and Russian knapweed) grassland species to increased
10 N availability (0, 10, 40, 70, or 100 kg N ha⁻¹ yr⁻¹) in a 75-day greenhouse experiment. They
11 found that all of the grass species exhibited increased growth with increased N availability.
12 Native species did not consistently grow better at low N levels than the exotic species. Two of
13 the exotic grasses exhibited the greatest increase in growth, while another of the exotics
14 exhibited the smallest increase in growth.

15 From studies of N additions in tallgrass prairie (0.1, 1, 3 mmol N addition for 80 days),
16 Lane and BassiriRad (2002) suggested that increasing N deposition levels could cause species-
17 specific growth and plant tissue quality changes, which in turn could lead to changes in
18 ecosystem dynamics and community structure. In interior coastal grasslands at Jasper Ridge
19 Biological Preserve in California, additions of 70 kg N ha⁻¹ yr⁻¹ over three years led to decreased
20 forb production concomitant with increased grass productivity (Zavaleta et al., 2003).

21 In a European study involving 15 herb and 13 grass species, Falkengren-Grerup (1998)
22 found that, in general, grasses grew better than herbs in response to experimental addition of N.
23 At the highest experimental N deposition rates, growth was limited for most species by the
24 supply of nutrients other than N.

25 Several grassland studies have demonstrated that increased N availability can lead to an
26 overall decrease in plant species richness and an increase in exotic nitrophilous grasses that
27 displace native grass and forb species. Change in species composition in response to
28 N deposition have been observed regardless of soil type in European grasslands. Such effects
29 have been found in calcareous, neutral, and acidic environments, species-rich heaths, and
30 montane-subalpine grasslands (Stevens et al., 2004; Bobbink et al., 1992, 1998; Bobbink, 1998).

1 Wedin and Tilman (1996) conducted studies of N enrichment over a 12-year period on
2 Minnesota grasslands and found that plots initially dominated by native warm-season grasses
3 shifted to low-diversity mixes of species dominated by cool-season grasses at all but the lowest
4 rates of N addition. Grasslands with high N retention and C storage rates were the most
5 vulnerable to loss of species and major shifts in N cycling in response to experimental
6 N enrichment.

7 From a study of interior coastal grasslands in California, Zavaleta et al. (2003) found
8 increased N deposition led to a decline in total species richness. After three years of N additions
9 ($70 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), species diversity decreased by 5% and all three N-fixing forbs disappeared.

10 In the San Francisco Bay area of California, which receives N deposition levels of 10 to
11 $15 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, exotic nitrophilous grasses have been reported to have displaced native grass
12 species, likely due to greater N availability from deposition and from the cessation of grazing,
13 which previously exported N out of the system (Fenn et al., 2003a).

14 Not all studies have shown an effect of N addition on species richness or diversity. In old
15 agricultural fields in Michigan, increased N deposition changed neither the successional timing
16 nor the gain or loss of species numbers (Huberty et al., 1998). A lack of response in species
17 richness may have been due to application of mid-growing season fertilization in the
18 experimental design. Huberty and colleagues (1998) suggested that N additions may change the
19 dominance structure of these successional old-field communities. Other studies in Michigan also
20 indicated that successional grasslands were not N-saturated (Ambus and Robertson, 2006) and
21 showed no response to N application of $1 \text{ g N/m}^2/\text{yr}$, equivalent to about 2.5 times ambient
22 deposition rates.

23 24 **4.3.3.1.3 *Arid and Semi-Arid Land Ecosystems***

25 Some arid, semi-arid, and desert ecosystems in the southwestern United States are
26 considered sensitive to N enrichment effects and receive high levels of atmospheric
27 N deposition. However, water is generally more limiting than N in these systems. Nevertheless,
28 enhanced N could play a role in the observed invasion of some exotic plant species and
29 associated changes in ecosystem function, especially where water supply is adequate.

30 In semi-arid ecosystems, results from several N fertilization experiments showed (1)
31 increased biomass of nonnative plant species over native species, (2) decreased soil moisture

1 under some conditions, and (3) increased fire risk where dense mats of grasses replaced shrub
2 cover (Eliason and Allen, 1997; Yoshida and Allen, 2001). For example, in the coastal sage
3 shrub community of southern California, dry N deposition is above $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in some
4 places. Native shrub and forb seedlings in this plant community are unable to compete with
5 dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially
6 following disturbances such as fire (Eliason and Allen, 1997; Yoshida and Allen, 2001; Cione
7 et al., 2002). The coastal sage shrub community in California has been declining in land area
8 and in shrub density over about the past 60 years and is being replaced in many areas by
9 Mediterranean annual grasses (Allen et al., 1998; Padgett and Allen, 1999; Padgett et al., 1999).
10 N deposition is considered a possible cause or contributor to this ecosystem alteration. More
11 than $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ of atmospheric N is deposited to this ecosystem in portions of the Los
12 Angeles Air Basin (Bytnerowicz and Fenn, 1996). Decreases in the diversity of native plants
13 paralleled increases in exotic grass biomass. Biodiversity impacts have also been documented
14 for microbial communities in coastal sage scrub ecosystems. It has been hypothesized that the
15 decline in coastal sage shrub species could be linked to the decline of the arbuscular mycorrhizal
16 community (Egerton-Warburton and Allen, 2000). Refer to Section 4.3.3.1.6 for more on
17 mycorrhizae.

18 Similar responses to N fertilization have been reported in other arid land ecosystems.
19 Fertilization experiments in the Mojave Desert showed that increased levels of N deposition
20 could favor the establishment of nonnative species where the nonnatives are already prevalent
21 (Brooks, 2003). At application rates of $32 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ over two years, biomass of nonnative
22 plants increased 54%, while native species biomass declined by about 39%. A fertilization
23 experiment in the Chihuahuan Desert, with inputs of $100 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ over about a decade,
24 resulted in a 30% increase in cover of warm season grasses and a 52% reduction in cover of
25 legumes (Baez et al., 2007). The effect on legumes may be attributable to the fact that legumes,
26 which are N fixers, often compete better under low N supply.

27 Another fertilization experiment in an arid grassland on the Colorado Plateau
28 demonstrated a large difference in the response of native and nonnative plants. The increased
29 N application hastened the onset of water stress and a nonnative species, Russian thistle (*Salsola*
30 *iberica*), showed a rapid growth response to the highest fertilization rate in the first summer,
31 when rainfall was above average. In Joshua Tree National Park, California, which receives

1 moderate levels of air pollution from the Los Angeles Basin, N fertilizer was applied at levels of
2 5 and 30 kg N ha⁻¹ yr⁻¹ at four sites over a two-year period. Nonnative grass biomass increased
3 significantly at three of four treatment sites that received 30 kg N ha⁻¹ yr⁻¹, but not at the sites
4 that received 5 kg N ha⁻¹ yr⁻¹ (Allen et al., 2007).

5 Vegetative changes stimulated by nutrient enrichment from N deposition may affect the
6 frequency and severity of subsequent disturbance. Several lines of evidence suggest that
7 N deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of
8 ecosystem types. Invasive grasses, which can be favored by high N deposition, promote a rapid
9 fire cycle in many locations (Fenn et al., 2003a).

10 In summary, N fertilization experiments in arid and semi-arid plant communities have
11 shown that changes in plant biomass associated with increased N deposition tend to alter species
12 composition, with negative impacts on biodiversity. Such plant community changes resulting
13 from experimental fertilization have been reported in the Chihuahuan Desert, Colorado Plateau,
14 Mojave Desert, and Joshua Tree National Park in California.

15 16 **4.3.3.1.4 Herbaceous Plants and Shrubs**

17 The negative effects of increasing N deposition on herbaceous plants was reviewed by
18 Gilliam (2006). Reported effects include (a) species shifts towards nitrophilous and more acid-
19 tolerant plant species along a deposition gradient from 6 to 20 kg N ha⁻¹ yr⁻¹ in Swedish oak
20 forests; (b) a decline in abundance and cover of ericaceous shrubs along a deposition gradient
21 from <3 to >12 kg N ha⁻¹ yr⁻¹ in the boreal forest in Sweden; and (c) a decline in herbaceous
22 cover under hardwoods following 3 years of N additions applied as (NH₄)₂SO₄ at rates ranging
23 from 14 to 28 kg N ha⁻¹ yr⁻¹. The decline in herbaceous cover in the latter study was attributed
24 to increased shading by ferns, and the effect was more pronounced at sites that experienced
25 lower ambient atmospheric N inputs.

26 Mixed results have been reported in other studies. Research at Fernow Experimental
27 Forest, West Virginia, indicated that application of 35 kg N ha⁻¹ yr⁻¹ applied as (NH₄)₂SO₄ for
28 6 years had no significant impact on the herbaceous layer in an Appalachian hardwood forest
29 (Gilliam et al., 2006). Fernow has been the recipient of high levels of N deposition for decades,
30 raising the possibility that the herbaceous layer responded long ago to changes in N availability.

1 Brunet et al. (1998) and Falkengren-Grerup (1998) reported the effects of excessive
2 N deposition on mixed-oak forest vegetation along a depositional gradient. Results of this study
3 suggest that N deposition had affected nonwoody vegetation directly by increased N availability
4 and, indirectly, by accelerating soil acidity. Time series studies indicated that 20 of the 30
5 nonwoody plant species that were associated most closely with high N deposition had increased
6 in abundance in those areas in Europe that received high N deposition.

7 8 **4.3.3.1.5 Lichens**

9 Lichens are frequently used as indicators of air pollution and atmospheric deposition
10 levels. In addition to being good subjects for biomonitoring, they constitute important
11 components of the forest ecosystem by contributing to biodiversity, regulating nutrient and
12 hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997).

13 Epiphytic macro lichens (those that grow attached to trees or other plants) exhibit
14 different sensitivities to atmospheric pollutants, with some species being adversely impacted at
15 air pollution levels that may not be considered high relative to other sensitive receptors.
16 Particularly sensitive genera include *Alectoria*, *Bryoria*, *Ramalina*, *Lobaria*, *Pseudocyphellaria*,
17 *Nephroma*, and *Usnea* (McCune and Geiser, 1997; Blett et al., 2003).

18 Lichens that include a cyanobacterium as the photobiont are adversely affected by
19 N deposition as well as acidity. In contrast, those that include a green algal photobiont tend to be
20 only sensitive to acidity. The decline of lichens containing cyanobacteria in parts of northern
21 Europe has been associated with N deposition in the range of 5 to 10 kg N ha⁻¹ yr⁻¹ (Bobbink
22 et al., 1998). In fact, epiphytic cyanobacteria-containing lichens may be among the most
23 sensitive species in humid forested ecosystems to atmospheric N deposition (Hallingbäck, 1991;
24 Bobbink et al., 1998).

25 Community composition of epiphytic lichens in the United States can be altered by
26 relatively small increases in N deposition (Fenn et al., 2003a). Most epiphytic lichens meet their
27 nutritional requirements from atmospheric deposition and can store N in excess of their
28 nutritional needs (van Herk, 1999). In the San Bernardino Mountains, California, up to 50% of
29 lichen species that occurred in the region in the early 1900s have disappeared, with a
30 disproportionate number of locally extinct species being epiphytic cyanolichens (Nash and Sigal,
31 1999; Fenn et al., 2003a).

1 The Pacific Northwest retains widespread populations of pollution-sensitive lichens
2 (Fenn et al., 2003a). However, in urban areas, intensive agricultural zones, and downwind of
3 major urban and industrial centers in the Pacific Northwest, there are few air pollution-sensitive
4 lichen species, such as epiphytic cyanolichens, and high N concentrations have been measured in
5 lichen tissue (Fenn et al., 2003a). With N enrichment, especially around urban and agricultural
6 areas, there is a shift towards weedy, nitrophilous lichen species (Fenn et al., 2003a).
7 Replacement of sensitive lichens by nitrophilous species has undesirable ecological
8 consequences. In late-successional, naturally N-limited forests of the Coast Range and western
9 Cascade Mountains, for example, epiphytic cyanolichens make important contributions to
10 mineral cycling and soil fertility (Pike, 1978; Sollins et al., 1980; Antoine, 2001), and together
11 with other large, pollution-sensitive macrolichens, are an integral part of the food web for
12 mammals, insects, and birds (McCune and Geiser, 1997). Sensitive lichen species appear to be
13 negatively affected by N inputs as low as 3 to 8 kg N ha⁻¹ yr⁻¹ (Fenn et al., 2003a).

14 15 **4.3.3.1.6 *Mycorrhizal and Microbial Diversity***

16 Mycorrhizal and microbial biodiversity can also be affected by N enrichment.
17 Interactions between atmospherically deposited N and terrestrial vegetation frequently occur in
18 the rhizosphere. The rhizosphere includes the soil that surrounds and is influenced by plant roots
19 (Wall and Moore, 1999). Relationships among plant roots, mycorrhizal fungi, and microbes are
20 critical for N cycling and for the growth and health of plants. Mycorrhizal fungal diversity has
21 been shown to be associated with above-ground plant biodiversity and ecosystem productivity
22 (Wall and Moore, 1999) and to be adversely affected by increased N availability (Egerton-
23 Warburton and Allen, 2000). The loss of mycorrhizal function has been hypothesized as a key
24 process contributing to reduced N uptake by vegetation and increased NO₃⁻ mobility from soil
25 into drainage water under conditions of high N supply (U.S. Environmental Protection Agency,
26 2004).

27 It has been hypothesized that the decline in coastal sage shrub species in California could
28 be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton and
29 Allen, 2000). They discerned a shift in arbuscular mycorrhizal community composition with
30 decreased species richness and diversity along a deposition gradient (2 to 57 µg N/g as soil
31 NO₃⁻). These shifts in mycorrhizal fungal communities may facilitate replacement of native

1 plant communities by Mediterranean annual grasslands. Larger-spored fungal species
2 (*Scutellospora* and *Gigaspora*) have decreased in number due to a failure to sporulate, with a
3 concomitant proliferation of small-spored species. This suggests selective pressure favoring the
4 smaller spored species of fungi (Egerton-Warburton and Allen, 2000), and that N enrichment of
5 the soil might alter the arbuscular mycorrhizal species composition and diversity.

6 Progressive decline in ectomycorrhizal fungal species richness in Alaskan coniferous
7 forest (white spruce [*Picea glauca*] dominant) occurred along a local N deposition gradient, from
8 1 to 20 kg N ha⁻¹ yr⁻¹, downwind from an industrial complex (Lilleskov et al., 2002).

9 Ectomycorrhizal fungal communities are important in tree nutrition, and ectomycorrhizal fungal
10 trees tend to be dominant in N-limited forest ecosystems. A shift in ectomycorrhizal fungal
11 community structure could result in a shift in dominant tree species and in nutrition.

12 N fertilization at rates of 54 and 170 kg N ha⁻¹ yr⁻¹ (as NH₄NO₃) led to a decline in
13 ectomycorrhizal fungal diversity and species composition in an oak savanna at Cedar Creek
14 Natural History Area in Minnesota (Avis et al., 2003). In the control plots, five species
15 collectively accounted for more than 40% cover versus four plant species in the lower N addition
16 plots. In the higher N addition plots, a single plant species accounted for more than 40% cover.

17 Compton et al. (2004) investigated the effects of 11 years of experimental N addition on
18 forest soil microbial ecology. Experimental N addition decreased the C content of microbial
19 biomass in the O horizon of both experimental forest stands, based on chloroform fumigation-
20 extraction. In addition, the use of N-containing substrates by microbes appeared to be reduced
21 by N addition in the pine stand, but not in the hardwood stand.

22 23 **4.3.3.2 Transitional Ecosystems**

24 Ombrotrophic bogs, peatlands, and coastal marshes are the transitional ecosystems that
25 appear to be most sensitive to the effects of excess N deposition. Many bogs receive the
26 majority of their nutrients, including N, from atmospheric deposition. If atmospheric N loading
27 increases substantially to a bog ecosystem, it is expected that productivity will increase and may
28 be accompanied by changes in species composition to favor those species that are adapted to
29 higher nutrient levels. U.S. Environmental Protection Agency (1993b) reviewed field
30 experiments involving N fertilization of wetlands. Results of those experiments confirmed the
31 belief that wetland vegetation is commonly limited by N availability.

1 Most of the documented impacts of elevated N on wetlands relate to changes in species
2 diversity. Especially important is the effect of elevated nutrient concentrations on the
3 distribution and biomass of nonnative and invasive species.

4 The sensitivity of wetlands to N enrichment is particularly important given that they
5 contain a disproportionately high number of rare plant species (Figure 5-10; Moore et al., 1989).
6 EPA reported that, of the 130 plant species from the conterminous United States that were listed
7 as threatened or endangered in 1987, 14% occurred principally in wetlands (U.S. Environmental
8 Protection Agency, 1993b). Bedford and Godwin (2003) indicated that a disproportionately high
9 number of rare plant species occur in fens relative to their percent land cover (Table 5-2; Bedford
10 and Godwin, 2003).

11 Marler et al. (2001) evaluated the potential impacts of experimentally elevated stream
12 water nutrient concentrations on three riparian wetland tree species: Fremont cottonwood
13 (*Populus fremontii*), Goodding willow (*Salix gooddingii*), and exotic saltcedar (*Tamarix*
14 *ramosissima*) in the riparian zone of the Salt River near Phoenix, Arizona. The results from this
15 43-day experiment showed that growth of all three riparian plant species responded positively to
16 increased nutrient supply (treatment 3 and 4) (Marler et al., 2001). The exotic and invasive
17 saltcedar showed the greatest increases in biomass at high nutrient supply. Other studies have
18 also found that exotic plant species often respond more rapidly than native vegetation to
19 increased nutrient supply (Milberg et al., 1999; Paschke et al., 2000). This experiment was
20 conducted to simulate impacts of wastewater effluent on riparian zones, and N additions were
21 therefore very large. Elevated nutrient supply to riparian systems via atmospheric N deposition
22 in the United States is more typically in the range of treatments in this experiment that showed
23 minimal response to N addition.

24 The form of added N may partially regulate wetland response to N deposition.
25 Experimental applications of NO_3^- may have been less effective at stimulating wetland plant
26 productivity than applications of NH_4^+ (U.S. Environmental Protection Agency, 1993b). This
27 may reflect higher rates of denitrification in response to the added NO_3^- , suggesting the
28 importance of competition between plants and microbes for bioavailable N. Plants appear to
29 compete more successfully for NH_4^+ and microbes to compete more successfully for NO_3^- . An
30 important caveat expressed by EPA (1993), however, was that the results of relatively short-term

1 N fertilization experiments are not necessarily good predictors of long-term wetland community
2 responses to increased N inputs.

3 In wet heathlands in Europe, changes in plant species composition have been attributed to
4 elevated atmospheric N deposition (Roem and Berendse, 2000). Diverse plant communities
5 consisting of *Erica tetralix*, *Calluna vulgaris*, *Gentiana pneumonanthe*, *Drosera intermedia*, and
6 *Lycopodium inundatum* have been replaced by monospecific stands of the grass *Molina caerulea*
7 or *Deschampsia flexuosa* in Dutch wet heathlands (Aerts and Berendse, 1988; Houdijk et al.,
8 1993).

9 In other studies, wetland species such as *Calluna vulgaris* can successfully compete with
10 grasses even at relatively high rates of N deposition, as long as the vegetative canopies are closed
11 (Aerts et al., 1990). However, N deposition causes nutrient imbalances, and increased plant
12 shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost
13 stress, and attack by insect pests (Heil and Diemont, 1983). These can result in gaps in the
14 canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in
15 using the additional N and therefore gain a competitive advantage (Krupa, 2003).

16 17 *Biodiversity*

18 Increased N availability in nutrient-poor wetland environments may lead to a decrease in
19 species diversity and increased risk of extinction for some of the more sensitive and rare species
20 (Moore et al., 1989). Peatlands and bogs are among the most vulnerable transitional ecosystems
21 to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland
22 *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse
23 et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to
24 be negatively affected by experimentally elevated atmospheric N and S inputs in Europe
25 (Kooijman and Bakker, 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to
26 elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and
27 broadly distributed across, the United States and is federally listed as endangered in Illinois and
28 Iowa, threatened in Tennessee, and vulnerable in New York.

29 For two ombrotrophic bogs in the northeastern United States (Vermont and
30 Massachusetts) model estimates of extinction risk for the northern pitcher plant (*Sarracenia*
31 *purpurea*) were calculated under varying N deposition scenarios (Gotelli and Ellison, 2002).
32 Modeled extinction risk within the next 100 years was relatively low under precipitation

1 N concentrations equivalent to those at the time of the study (0.391 to 0.477 mg N/l/yr).
2 However, model estimates showed increased extinction risk under elevated N deposition
3 scenarios (Gotelli and Ellison, 2002).

4 5 **4.3.3.3 Freshwater Ecosystems**

6 There are a variety of potential eutrophication effects of excess N deposition to the
7 watersheds of lakes, streams, rivers, and estuaries. Primary productivity in many coastal waters
8 and some freshwaters can be increased with the addition of even very low amounts of N. Effects
9 on freshwater ecosystems are discussed here; effects on estuarine and marine ecosystems are
10 discussed in Section 4.3.3.4.

11 Eutrophication typically increases algal biomass, alters algal species assemblages, and
12 may affect aquatic biota at all trophic levels. Biological changes in freshwater ecosystems
13 attributed to nutrient enrichment from atmospheric N deposition are likely to be most
14 pronounced in high-elevation aquatic ecosystems in the western United States. Important effects
15 can include changes in biomass, species composition, and diversity of algae, especially diatoms.

16 In freshwater ecosystems, excess contribution of N to N-limited systems can stimulate
17 ecosystem productivity and contribute to eutrophication. Gradient studies of undisturbed
18 northern temperate, mountain, or boreal lakes that receive low levels of atmospheric
19 N deposition showed strong correlations between N limitation and productivity where
20 N deposition was low. P (or N plus P) limitations occurred where N deposition was higher (Fenn
21 et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006). Paleolimnological studies
22 provide additional evidence suggesting N-limitation or N and P co-limitation of some high-
23 elevation oligotrophic lakes in the western United States (Saros et al., 2005; Wolfe et al., 2006).
24 A recent meta-analysis of 990 freshwater field experiments to determine patterns of autotrophic
25 nutrient limitation found that N limitation of stream benthos, lake benthos, and phytoplankton
26 was as common as P limitation from sites in all biomes worldwide (Elser et al., 2007).

27 28 **4.3.3.3.1 Chlorophyll a**

29 The most widely used index of biological change in response to nutrient addition is
30 measurement of chlorophyll *a* concentration in water. Surveys and fertilization experiments
31 show increased inorganic N concentration and aquatic ecosystem productivity (as indicated by
32 chlorophyll *a* concentration) to be strongly related. For example, a series of in situ meso- and

1 microcosm N amendment experiments more than 30 years ago showed increases in lake algal
2 productivity. Lake 226S in Ontario's Experimental Lake District (ELD) showed doubling of
3 average epilimnetic chlorophyll *a* over five years of fertilization. However, because the response
4 to P fertilization was much greater, the effects of N received less attention (Schindler, 1980).
5 Other ELD lakes that had relatively low N to P concentration ratios experienced 3 to 10 times
6 greater increases in chlorophyll *a* than Lake 226S (Schindler, 1980). Similar experiments at
7 Castle Lake, California, the Snowy Range of southern Wyoming, and Alaskan arctic
8 foothill lakes yielded measurable increases in chlorophyll *a* and primary productivity with
9 N amendments (Axler and Reuter, 1996; Levine and Whalen, 2001; Nydick et al., 2003, 2004a;
10 Lafrancois et al., 2004). Long-term data from 28 years of study in Lake Tahoe, California
11 showed that primary productivity doubled during that period, while water clarity associated with
12 chlorophyll *a* concentration declined, mostly as a result of atmospheric N deposition (Goldman,
13 1988; Jassby et al., 1994).

14 15 **4.3.3.3.2 *Phytoplankton Biomass***

16 Studies have shown an increase in lake phytoplankton biomass with increasing
17 N deposition in several regions, including the Snowy Range in Wyoming (Lafrancois et al.,
18 2003), the Sierra Nevada Mountains in California (Sickman et al., 2003), throughout Sweden
19 (Bergström et al., 2005), and across Europe (Bergström and Jansson, 2006).

20 Chemical data from 3,907 lakes and phytoplankton biomass from 225 lakes from
21 Swedish monitoring programs were used to identify clear north-south gradients of increasing
22 lake algal productivity related to the pattern of increasing N deposition input (Bergström et al.,
23 2005). The lowest productivity was found at sites where wet inorganic N deposition was about
24 $1.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; higher productivity occurred at N deposition levels above $2.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$
25 (Bergström et al., 2005). Although these lakes are all in Sweden, the sheer number of them used
26 to derive a strong correlation between productivity and atmospheric deposition makes the results
27 of interest to North American audiences.

28 Experiments conducted with mesocosms in lakes where NO_3^- was below the detection
29 level found a strong response in phytoplankton biomass with additions of N (bringing
30 concentrations to $\sim 1.0 \text{ mg N/L}$) and even stronger responses to additions of N plus P, but not P
31 alone (Lafrancois et al., 2004). The reverse was also found in Colorado Front Range lakes with

1 ambient NO_3^- concentrations of ~1.0 mg/L: productivity increased with additions of N plus P or
2 P only, but not NO_3^- alone (Lafrancois et al., 2004).

3 A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America,
4 including many of the studies described above, found algal growth enhancement from
5 N amendments to be common in slightly less than half the studies (Elser et al., 1990). There was
6 a mean increase in phytoplankton biomass of 79% in response to N enrichment (average of
7 46.3 $\mu\text{eq/L N}$) (Elser et al., 1990).

8 9 **4.3.3.3 Periphyton Biomass**

10 N effects have been observed in periphyton which grow on rocks or sediment in lakes
11 and streams where there is sufficient light for photosynthesis. Several studies found stimulated
12 growth with N amendments from ecosystems throughout the United States, including streams in
13 Alaska, Arizona, Iowa, Texas, Minnesota, Missouri, and lakes in California, Colorado, and
14 Massachusetts. Growth stimulation occurred with N additions ranging from 8 to 50 $\mu\text{M/L}$, or
15 with exposure to 0.5 M N concentrations on agar substrate (e.g., Bushong and Bachmann, 1989;
16 Allen and Hershey, 1996; Wold and Hershey, 1999; Smith and Lee, 2006). Additional lake
17 bioassay experiments that enriched the water column down into the sediments found
18 enhancement of periphyton growth on bioassay container walls in experiments in California,
19 Wyoming, and Massachusetts (Axler and Reuter, 1996; Nydick et al., 2004b; Smith and Lee,
20 2006).

21 The implications of these studies are that the productivity of many freshwater ecosystems
22 is currently limited by the availability of N, European and North American lakes may have been
23 N-limited before human-caused disturbance, and remote lakes may have remained N-limited
24 until slight increases in atmospheric N deposition brought about an increase in phytoplankton
25 and periphyton biomass and induced P limitation. Increases in algal biomass are associated with
26 changes in algal assemblages that favor certain species over others. These effects are described
27 below in the discussion of biodiversity.

28 29 **4.3.3.4 NO_3^- Toxicity**

30 In addition to the biological effects described above, NO_3^- in freshwater at extremely
31 high concentrations can have direct adverse effects on many life stages of fish, as well as on
32 invertebrates and amphibians. These effects occur at levels that are typically more than 30 times

1 higher than those that would commonly be attributable to atmospheric deposition, and therefore
2 NO_3^- concentration has not been defined as a primary biological indicator. Nevertheless, these
3 effects are described in Annex 5.

4 5 **4.3.3.3.5 Biodiversity**

6 Some freshwater algae are particularly sensitive to the effects of added nutrient N and
7 experience shifts in community composition and biodiversity with increased N deposition. For
8 example, two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate
9 the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have
10 occurred in Lake Tahoe (Interlandi and Kilham, 1998; Baron et al., 2000; Wolfe et al., 2001,
11 2003; Saros et al., 2003, 2005). The timing of this shift has varied, with changes beginning in
12 the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky
13 Mountains (Figure 4.3-8). These species are opportunistic algae that have been observed to
14 respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

15 Further evidence for the relationship between N enrichment and algal changes has been
16 provided by N addition studies. For example, the growth of *A. formosa* has been stimulated with
17 N amendments during in situ mesocosm incubations (6.4 to 1616 μM N, McKnight et al., 1990;
18 76 μM N/L, Lafrancois et al., 2004; 18 μM N, Saros et al., 2005). In situ incubations in large
19 lakes of Yellowstone National Park, Wyoming also stimulated *F. crotonensis* (Interlandi and
20 Kilham, 1998), although this publication did not reveal how much N was added to the
21 incubations. The N requirements for *A. formosa* and *F. crotonensis* were determined to be 0.041
22 μM and 0.006 μM , respectively, and higher concentrations stimulated growth (Michel et al.,
23 2006). *A. formosa* and *F. crotonensis* have extremely low P requirements, enabling them to
24 outcompete other algae under relatively low P conditions.

25 Differences in resource requirements allow some species to gain competitive advantage
26 over others upon nutrient addition, causing changes in species composition (Wolfe et al., 2001,
27 2003; Lafrancois et al., 2004; Saros et al., 2005). This is in keeping with findings of Interlandi
28 and Kilham (2001), who demonstrated that maximum species diversity was maintained when
29 N levels were low ($<3 \mu\text{M}$) in lakes in the Yellowstone National Park region.

30 The implication of this research is that species diversity declines with increasing
31 availability of N. In studies of lake sediment diatom remains, typical oligotrophic species such

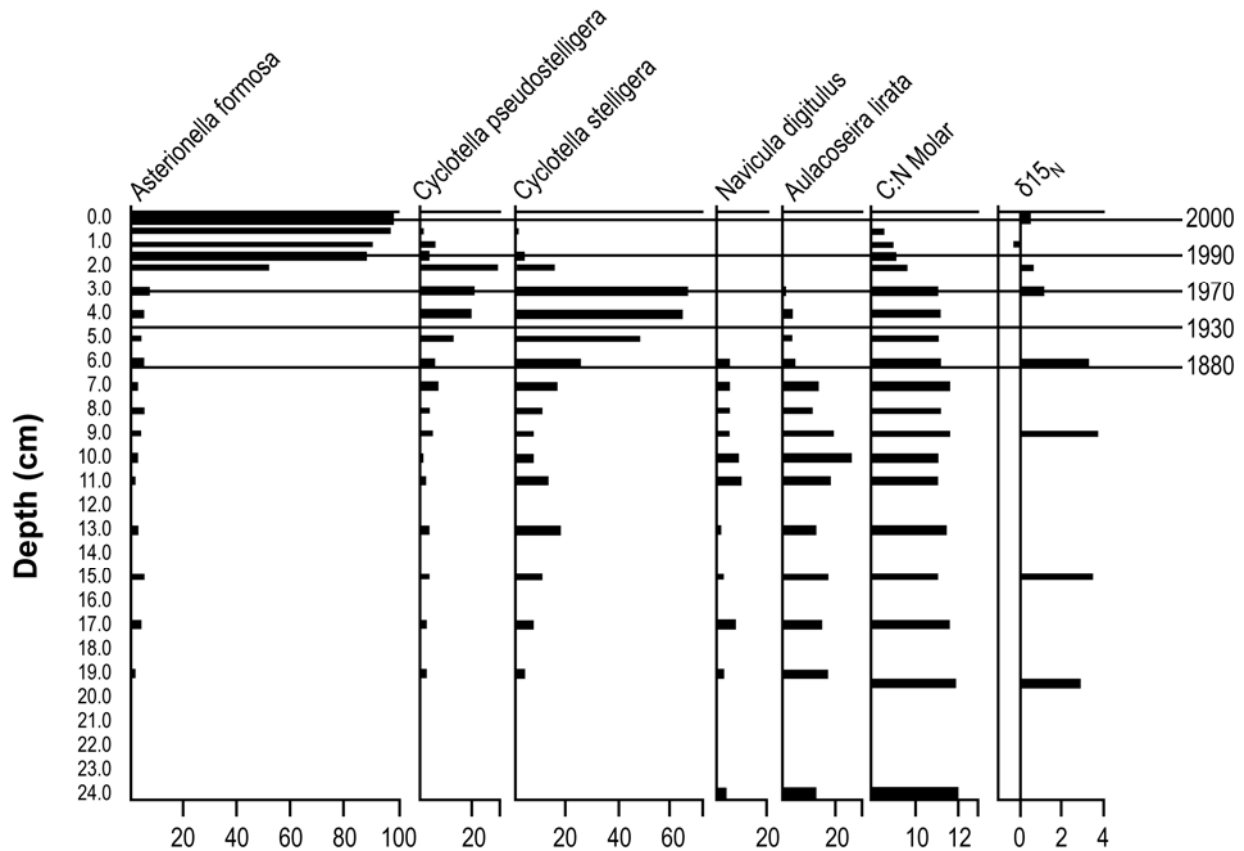


Figure 4.3-8. Diatom assemblage sediment patterns in Emerald Lake, WY.

Source: Saros et al. (2003).

1 as *Aulacoseria perglabra*, *Cyclotella steligera*, and *Achnanthes* spp. declined coincident with the
 2 rise in dominance of *A. formosa* and *F. crotonensis* (Wolfe et al., 2001, 2003).

3 Community shifts in phytoplankton other than diatoms have also been observed under
 4 conditions of elevated N availability. Mesocosm experiments in oligotrophic Snowy Range,
 5 Wyoming lakes illustrated a shift away from a general dominance by chrysophyte species to
 6 dominance primarily by large chlorophytes and the dinoflagellate *Gymnodinium* (Lafrancois
 7 et al., 2004). A similar positive correlation between the proportion of the phytoplankton
 8 comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of
 9 15 Snowy Range lakes (Lafrancois et al., 2003). Chlorophytes, like the two diatom species
 10 identified above, generally have a preference for high concentrations of N and are able to rapidly

1 dominate the flora when N concentrations increase (Findlay et al., 1999). This occurs in both
2 circumneutral and acidified waters (Wilcox and Decosta, 1982; Findlay et al., 1999).

3 Available data suggest that the increases in total N deposition do not have to be large in
4 order to elicit an ecological effect; a model hindcasting exercise determined that the change in
5 Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated
6 with an increase in wet N deposition that was only about $1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Baron, 2006).
7 Similar changes inferred from lake sediment cores in the Beartooth Mountains of Wyoming also
8 occurred at about $1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ deposition (Saros et al., 2003). Preindustrial inorganic
9 N deposition in the western United States was estimated by Holland et al. (1999) to range from
10 about 0.4 to $0.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

11 In summary, survey data and fertilization experiments demonstrate that increase in algal
12 productivity, as well as species changes and reductions in biodiversity, have occurred at sensitive
13 high elevation lakes in the western United States in response to increased availability of N.

14 15 **4.3.3.4 Estuarine and Marine Ecosystems**

16 N is an essential nutrient for estuarine and marine ecosystem fertility, and is often the
17 algal growth limiting nutrient. Excessive N contributions can cause habitat degradation, algal
18 blooms, toxicity, hypoxia (reduced dissolved oxygen), anoxia (absence of dissolved oxygen),
19 fish kills, and decrease in biodiversity (Paerl, 2002). In order to evaluate these impacts, five
20 biological indicators were used in the recent national assessment of estuary trophic condition:
21 chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and submerged
22 aquatic vegetation (SAV) (Bricker et al., 2007) (Figure 4.3-9). Each of these indicators is
23 discussed below regarding its relationship with the health and vigor of aquatic species and
24 ecosystem biodiversity.

25 26 **4.3.3.4.1 Chlorophyll *a***

27 Chlorophyll *a* concentration in estuarine or marine water is an indicator of total
28 phytoplankton biomass. It can signal an early stage of water quality degradation related to
29 nutrient loading. High concentration of chlorophyll *a* suggests that algal biomass is sufficiently
30 high that it might contribute to low dissolved oxygen concentration due to increased
31 decomposition of dead algae. In the national estuary condition assessment, high chlorophyll *a*






Primary symptoms		Description
	Chlorophyll <i>a</i> (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).

1 concentration was the most widespread documented symptom of eutrophication (Bricker et al.,
2 2007) (Figure 4.3-10). Half of the estuaries for which there were available data exhibited high
3 chlorophyll *a* concentration (Bricker et al., 2007). San Francisco Bay, California is an example
4 of an estuary that has experienced considerable increases in chlorophyll *a* concentrations in
5 recent years. Phytoplankton biomass in much of the bay has increased by more than 5% per year
6 from 1993 to 2004. During this time, modeled primary production has doubled and nutrient
7 loading is identified as one of eight possible causes (Cloern et al., 2006).

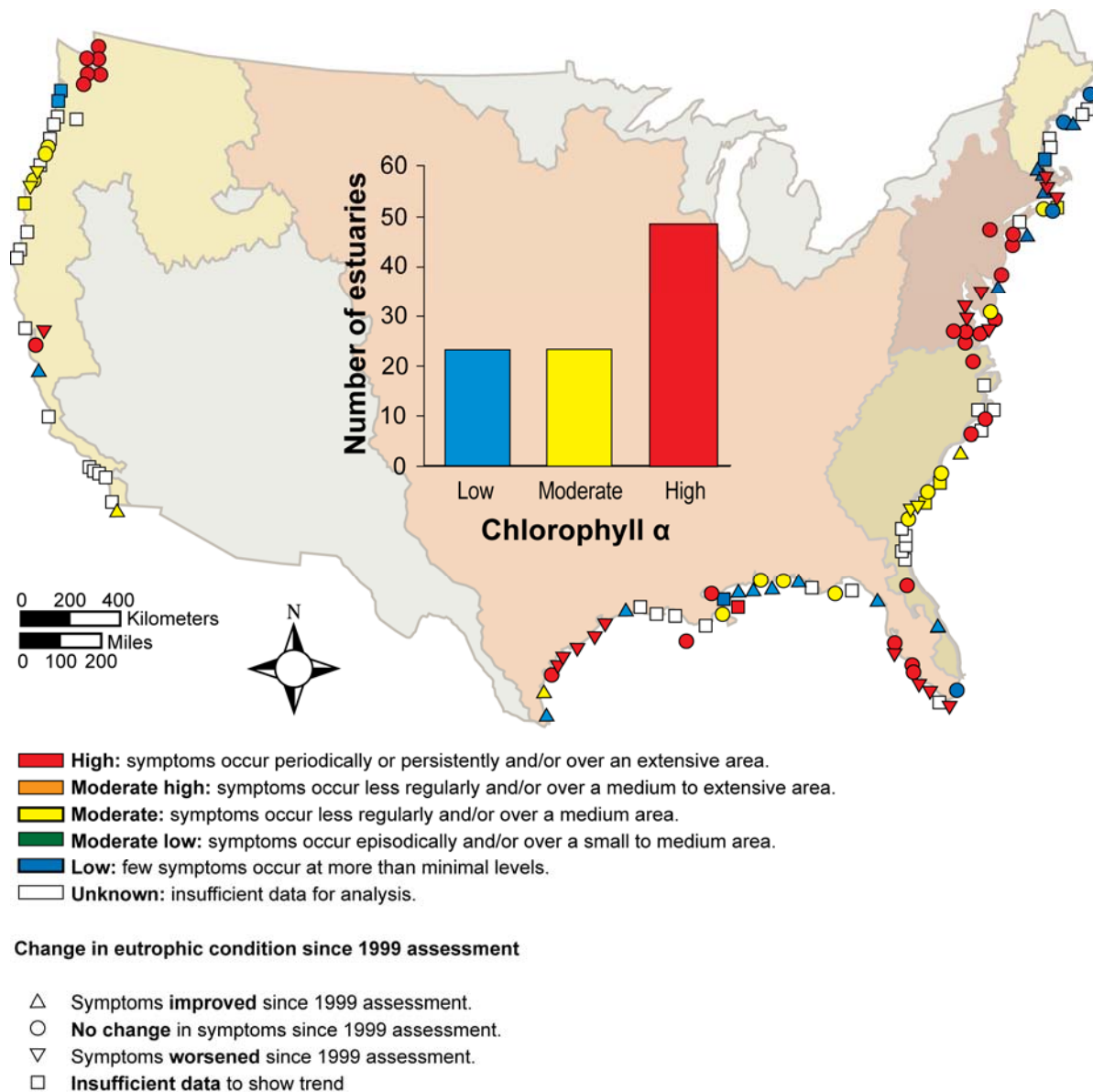


Figure 4.3-10. A high chlorophyll a rating was observed in a large number of the nation's estuaries. White squares indicate that data were not available for a particular estuary.

Source: Bricker et al. (2007).

1 **4.3.3.4.2 *Macroalgal Abundance***

2 Macroalgae are generally referred to collectively as seaweed. Macroalgal blooms can
 3 contribute to loss of important SAV by blocking the penetration of sunlight into the water

1 column. Although macroalgal data for estuaries in the United States were generally sparse, the
2 national estuary condition assessment reported that conditions were moderate or high for 33 of
3 the estuaries evaluated (Bricker et al., 2007).

4 5 **4.3.3.4.3 Dissolved O₂**

6 The decomposition of organic matter associated with increased algal abundance
7 consumes dissolved oxygen and can reduce dissolved oxygen concentrations in eutrophic waters
8 to levels that cannot support aquatic life. Decreased dissolved oxygen can lead to development
9 of hypoxic or anoxic zones that are inhospitable to fish and other life forms. Perhaps the most
10 important environmental effect of N input to coastal waters is the development of hypoxia. The
11 largest zone of hypoxic coastal water in the United States has been documented in the northern
12 Gulf of Mexico on the Louisiana-Texas continental shelf. During midsummer, this hypoxic zone
13 has regularly been larger than 16,000 km² (Rabalais, 1998). The timing, duration, and spatial
14 extent of hypoxia in this case are related mostly to the nutrient flux from the Mississippi River
15 (Justic et al., 1993, 1997; Rabalais et al., 1996; Lohrenz et al., 1997; Paerl et al., 2001).

16 Although impacts on dissolved oxygen can be quite severe in the areas where they are
17 manifested, the national assessment reports that the severity of dissolved oxygen impacts related
18 to eutrophication are relatively limited in many of the systems assessed (Bricker et al., 2007). In
19 the shallow estuary of Long Island Sound, the existence of extended periods of low dissolved
20 oxygen is a notable problem, and atmospheric deposition is considered to comprise a significant
21 fraction of the total N loading. Dissolved oxygen levels below 3 mg/L are common, and levels
22 below 2 mg/L also occur. During some years, portions of the Long Island Sound bottom waters
23 become anoxic (<1 mg/L; Figure 4.3-11) (Bricker et al., 2007).

24 25 **4.3.3.4.4 Nuisance/Toxic Algal Blooms**

26 Nuisance or toxic algal blooms reflect the proliferation of a toxic or nuisance algal
27 species that negatively affects natural resources or humans. Such blooms can release toxins that
28 kill fish and shellfish and pose a risk to human health. Unlike the other indicators of estuarine
29 eutrophication, the role of nutrients in stimulating toxic algal blooms is less clear. Of the
30 81 estuary systems for which data were available, 26 exhibited a moderate or high symptom
31 expression for nuisance or toxic algae (Bricker et al., 2007).

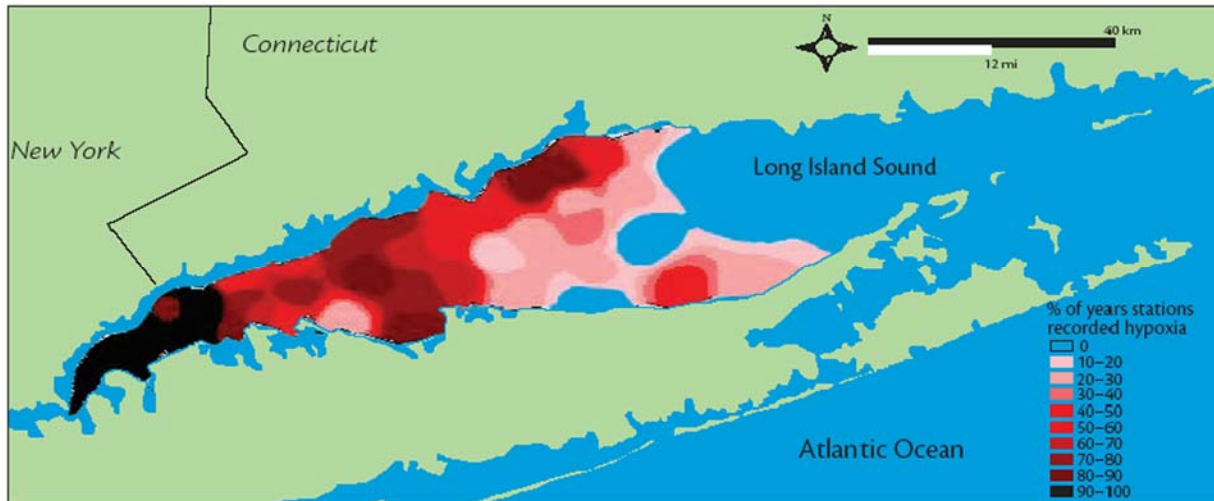


Figure 4.3-11. Frequency of hypoxia in Long Island Sound, 1994 to 2002.

Source: Bricker et al. (2007).

1 **4.3.3.4.5 Biodiversity**

2
3 *Phytoplankton*

4 In addition to causing increased phytoplankton biomass, as indicated by chlorophyll *a*
5 measurements, excess N can contribute to changes in phytoplankton species composition.
6 N enrichment of marine and estuarine waters can alter the ratios among nutrients and affect
7 overall nutrient limitation. For example, excessive N loading to Chesapeake Bay and its
8 tributaries during spring high runoff periods contributes to periods of P limitation and co-
9 limitation (Boynton et al., 1995). The ecosystem then returns to N limitation during low flow
10 summer months (Paerl, 2002). High loadings of N and P can also increase the potential for Si
11 limitation, with associated changes in diatoms. Such changes to the phytoplankton community
12 can also affect higher trophic levels. For example, Officer and Ryther (1980) and Turner et al.
13 (1998) suggested that a shift in the Si-to-N atomic ratio to less than 1 would alter the marine food
14 web. Specifically, the diatom-to-zooplankton-to-higher trophic level ratios would decrease,
15 whereas flagellated algae (including those that often contribute to hypoxia) would increase (Paerl
16 et al., 2001).

1 Phytoplankton production and community composition in estuarine and marine
2 environments also respond to differences in the form of atmospheric N input. Atmospheric
3 deposition of reduced N has increased relative to oxidized N in the eastern United States, and
4 this trend is expected to continue in the future under existing emissions controls. Such patterns
5 can influence marine eutrophication responses. Large diatoms tend to dominate coastal waters
6 when NO_3^- is supplied (Stolte et al., 1994; Paerl et al., 2001), whereas smaller diatom species
7 have a greater preference for NH_4^+ uptake. Thus, ongoing trends of decreasing NO_3^- deposition
8 and increasing NH_4^+ deposition might lead to changes in species distributions and size
9 distributions of estuarine phytoplankton, with cascading effects on trophic structure and
10 biogeochemical cycling (Paerl et al., 2001).

11 Changes in phytoplankton species abundances and diversity have been further
12 documented through in situ bioassay experiments such as the results reported by Paerl et al.
13 (2003) for the Neuse River Estuary in North Carolina. Effects were species-specific and varied
14 dramatically depending on whether, and in what form, N was added. The findings illustrate the
15 potential impacts of N additions on phytoplankton community structure (Figure 4.3-12).

16 Changing phytoplankton community composition has numerous potential ecological
17 ramifications, including modifications to the ecosystem food web and nutrient dynamics. For
18 example, if the nutrient mix favors species that are not readily grazed (e.g., cyanobacteria and
19 dinoflagellates), trophic transfer will be poor and relatively large amounts of unconsumed algal
20 biomass will settle to the bottom, which could stimulate decomposition, oxygen consumption,
21 and the potential for hypoxia (Paerl et al., 2003).

22 23 *Submerged Aquatic Vegetation*

24 Submerged aquatic vegetation (SAV) provides important nursery grounds to many
25 estuarine fish. There are few data documenting the long-term response of SAV in coastal
26 ecosystems to N loading. The national assessment (Bricker et al., 2007) suggested that only a
27 small fraction of the estuary systems evaluated reported high severity of SAV loss. Most of
28 those that did report moderate or high loss were located in the Mid-Atlantic region. However,
29 where SAV loss is a problem, the results can be severe, and there is evidence suggesting a
30 correlation with increases in N loading. For example, at Waquoit Bay, Massachusetts, Driscoll

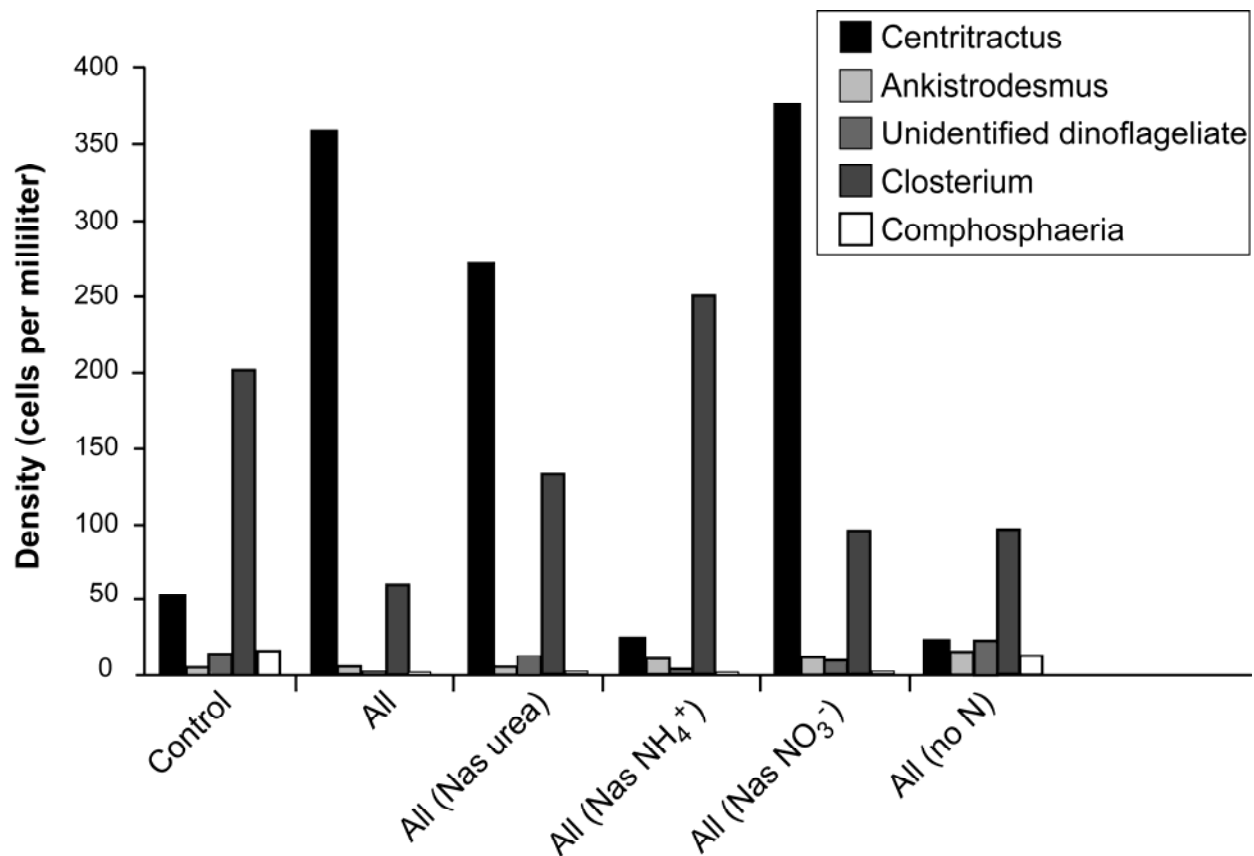


Figure 4.3-12. Microscopic counts of phytoplankton species composition in the Neuse River Estuary, NC following 36-h in situ bioassays to manipulate available forms of nitrogen (N). Treatments included a control (unamended estuarine water sample), all nutrients (N, P, vitamins, trace metals, and Si), all with urea as the N form, all with ammonium (NH₄⁺) as the N form, all with nitrate (NO₃⁻) 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).

1 et al. (2003b) reported a strong negative relationship between modeled N loading and measured
 2 eelgrass area based on measurements of eelgrass coverage from 1951 to 1992.

3
 4 **4.3.3.5 Effects on Rare and Endemic Species**

5 Changes in species composition, taxonomic richness, and species diversity are important
 6 in their own right. Of particular importance, however, is the extent to which such changes in
 7 species occurrence might impact rare species, especially those that are federally listed as

1 threatened or endangered. The coastal sage shrub community in California is of particular
2 interest because about 200 sensitive plant species and several federally listed threatened or
3 endangered animal species are found in the area (Allen et al., 1998). It is not clear to what extent
4 changes that occur in biodiversity within this community in response to N deposition may have
5 affected any of the rare species known to occupy these habitats.

6 Changes in grass species composition at ambient N deposition levels of 10 to 15 kg
7 N ha⁻¹ yr⁻¹ has been associated with the decline of the bay checkerspot butterfly (*Euphydryas*
8 *editha bayensis*), which is a federally threatened species that is native to California. Since the
9 1980s, the population of checkerspots has been in serious decline. According to the U.S. Fish
10 and Wildlife Service, the bay checkerspot butterfly historically occurred east, west, and south of
11 San Francisco Bay before the invasion of nonnative grasses. Today, their habitat is limited to
12 approximately 19,000 acres on serpentine soils.

13 The proposed plan for designating critical habitat for the bay checkerspot butterfly
14 developed by the U.S. Fish and Wildlife Service cites the impacts of N deposition as a key factor
15 in the loss of bay checkerspot butterfly habitat (Federal Register, 2007). Specifically, they note
16 that the serpentine and serpentine-like grasslands had previously supported uncommon plants
17 including the bay checkerspot butterfly's larval host plants *Plantago erecta*, *Castilleja*
18 *densiflora*, and *Castilleja exserta*. These remnant native grasslands are being invaded by
19 nonnative grass species, and this has been partially attributed to N deposition that is primarily
20 caused by air pollution (Weiss, 1999; Federal Register, 2007).

21 22 **4.3.4 Characterization of Most Sensitive and Most Affected Ecosystems** 23 **and Regions**

24 25 **4.3.4.1 Extent and Distribution of Sensitive Ecosystems**

26 The following discussion of sensitive ecosystems is organized into three ecosystem
27 categories: terrestrial, transitional, and aquatic. Table 4.3-2 gives an overview of the sensitive
28 ecosystems. Changes in terrestrial and aquatic plant or algal community composition that occur
29 in response to increased N deposition will be most obvious in ecosystems that are naturally
30 deficient in N. This is because species that are adapted to low N supply will often be more
31 readily outcompeted by species that have higher N demand when the availability of N is
32 increased (Aerts, 1990; Tilman and Wedin, 1991; Krupa, 2003). As a consequence, some native

1 species can be eliminated by N-enhanced eutrophication (Ellenberg, 1985; Falkengren-Grerup,
2 1986, 1989; Roelofs, 1986; Stevens et al., 2004).

3
4 *Terrestrial*

5 Little is known about the full extent and distribution of the terrestrial ecosystems in the
6 United States that are most sensitive to adverse impacts caused by nutrient enrichment from
7 atmospheric N deposition. Effects are most likely to occur where areas of relatively high
8 atmospheric N deposition intersect with N-limited plant communities. The factors that govern
9 the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the
10 degree of N-limitation, rates and form of N deposition, elevation, species composition, length of
11 growing season, and soil N retention capacity.

12 Alpine tundra is believed to be among the terrestrial systems most sensitive to
13 N enrichment. Factors that govern the sensitivity of alpine tundra to N deposition include low
14 rates of primary production, short growing season, low temperature, and wide variation in
15 moisture availability in the alpine environment (Bowman and Fisk, 2001). Alpine plant
16 communities have also developed under conditions of low nutrient supply, in part because soil-
17 forming processes are poorly developed, and this also contributes to their N-sensitivity (Bowman
18 et al. 2006).

19 Regions and ecosystems in the **western** United States where N enrichment effects have
20 been documented in terrestrial ecosystems are shown on Figure 4.3-13 (Fenn et al., 2003a). The
21 alpine ecosystems of the Colorado Front Range (see case study), chaparral watersheds of the
22 Sierra Nevada, lichen communities in the San Bernadino Mountains and the Pacific Northwest,
23 and the southern California coastal sage scrub community are among the most sensitive
24 terrestrial ecosystems (see Section 4.3.3.1 for description of effects).

25 In the **eastern** United States, the degree of N saturation of the terrestrial ecosystem is
26 often assessed in terms of the degree of NO_3^- leaching from watershed soils into ground water or
27 surface water. Stoddard (1994) estimated the number of surface waters at different stages of
28 saturation across several regions in the eastern United States. Of the 85 northeastern watersheds
29 examined, 40% were in N-saturation Stage 0, 52% in Stage 1, and 8% in Stage 2. Of the

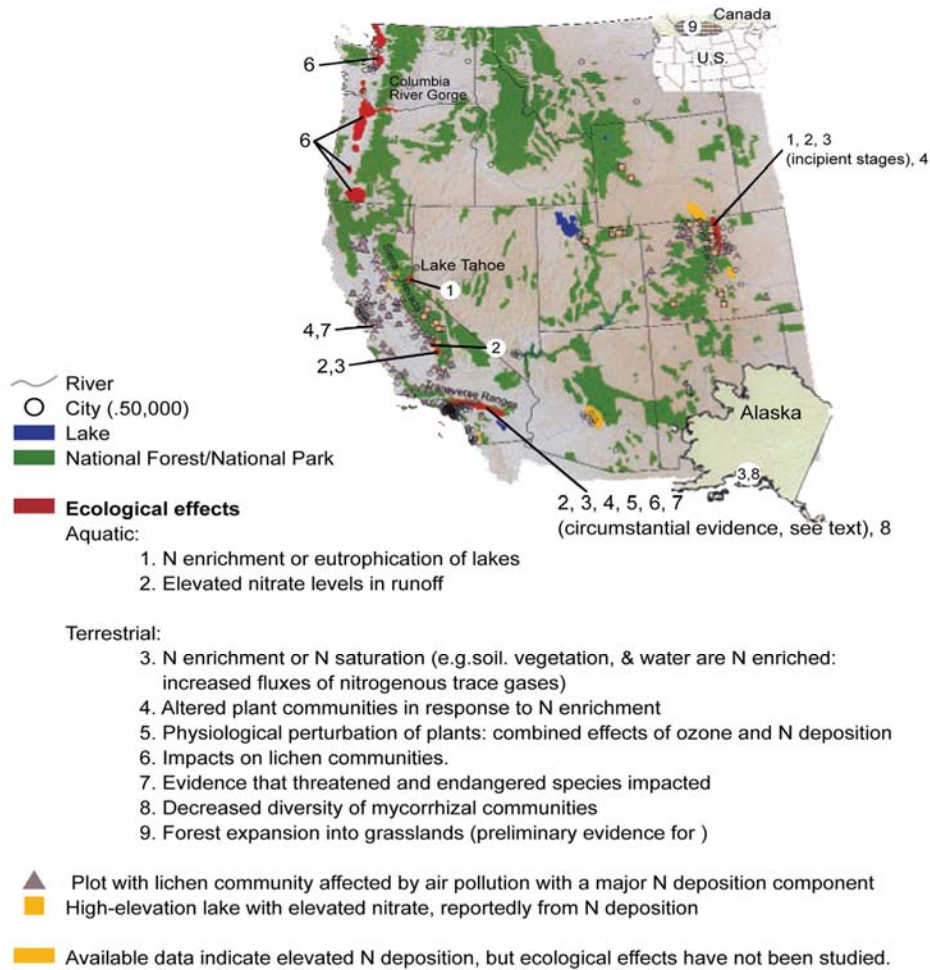


Figure 4.3-13. Map of the western United States showing the primary geographic areas where N deposition effects have been reported. Eutrophication effects are more widespread and of greater importance than acidification effects in western North America. Areas where effects of air pollution on lichen 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 $\mu\text{eq/L}$ (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).

1 northeastern sites for which adequate data were available for assessment, those in Stage 1 or 2
2 were most prevalent in the Adirondack and Catskill Mountains. Effects on individual plant
3 species have not been well studied in the United States. More is known about the sensitivity of
4 particular plant communities. Based largely on results obtained in more extensive studies
5 conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include
6 hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems.

7
8 *Transitional*

9 Wetlands considered sensitive to N deposition typically host plant species that evolved
10 under N-limited conditions. It is believed that the balance of competition among plant species in
11 some sensitive wetland ecosystems can be altered by N addition, with resulting displacement of
12 some species by others that can utilize the excess N more efficiently (U.S. Environmental
13 Protection Agency, 1993a). Data are not available with which to evaluate the extent to which
14 wetlands in the United States have been affected by nutrient enrichment from N deposition.
15 Wetlands are widely distributed, including some areas that receive moderate to high levels of
16 N deposition.

17 Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the
18 effects of N deposition. In the conterminous United States, peat-forming bogs are most common
19 in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (U.S.
20 Environmental Protection Agency, 1993a). In Alaska, these ecosystems are common in poorly
21 drained locations throughout the state. Other types of wetlands occur across broad areas of the
22 United States. It is not clear whether current levels of N deposition cause eutrophication to these
23 ecosystems.

24 Coastal marsh ecosystems, unlike bog ecosystems, often receive large N inputs in tidal
25 water, groundwater, and surface runoff. At many locations, especially along the Atlantic and
26 Gulf coasts, atmospheric N inputs probably contribute to eutrophication problems in coastal
27 marshes. Atmospheric inputs to these systems are important because any N addition has the
28 potential to contribute to eutrophication of coastal marshes and nearby marine and estuarine
29 ecosystems (Paerl, 2002; Galloway et al., 2003).

30 Nutrient concentrations in wetland waters associated with the Great Lakes suggest that
31 coastal Great Lakes wetlands are N-limited. Hill et al. (2006) found that more wetlands were N-
32 than P-limited at each of the five Laurentian Great Lakes. This result is consistent with the

1 apparent N-limitation of most North American marsh lands (Bedford et al., 1999). Nutrient
2 loading to lakeshore wetlands is a concern throughout the lower lakes (Lakes Erie, Ontario, and
3 the southern part of Lake Michigan) and in some localized areas of the upper lakes (Hill et al.,
4 2006). Both agricultural and atmospheric sources of nutrients contribute to this stress.

5
6 *Aquatic*

7 Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of
8 greatest concern in lakes and streams that have very low productivity and nutrient levels and that
9 are located in remote areas. In more productive freshwaters, nutrient enrichment from N
10 deposition usually does not stimulate productivity or community changes because P is more
11 commonly the limiting nutrient. Also, in many places with even minor levels of human
12 disturbance, nutrient enrichment with both N and P from non-atmospheric sources is common.
13 Thus, eutrophication effects from N deposition are most likely to be manifested in undisturbed,
14 low-nutrient surface waters such as those found in the higher elevation areas of the western
15 United States. The most severe eutrophication from N deposition effects are expected downwind
16 of major urban and agricultural centers.

17 High concentrations of lake or streamwater NO_3^- , indicative of ecosystem saturation,
18 have been found at a variety of locations throughout the United States, including the San
19 Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the
20 Front Range of Colorado (Baron et al., 1994; Williams et al., 1996a), the Allegheny Mountains
21 of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and
22 Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al.,
23 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994). All of these regions,
24 except Colorado, received more than about $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ atmospheric deposition of N
25 throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives up to about
26 $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ of total (wet plus dry) deposition (Sullivan et al., 2005), less than half of the
27 total N deposition received at many of these other locations.

28 High concentrations of NO_3^- in surface waters in the western United States are not
29 widespread. NO_3^- concentrations during the fall sampling season were low in most western
30 lakes sampled in the Western Lakes Survey. Only 24 sampled lakes were found to have NO_3^-

1 concentrations greater than 10 µeq/L. Of those, 19 lakes were situated at high elevation, most
2 above 3,000 m (Eilers et al., 1987).

3 There is some evidence suggesting that reductions in atmospheric N deposition could
4 decrease the extent of eutrophication in at least some of the Great Lakes. It has generally been
5 believed that the Laurentian Great Lakes are P-limited (Schelske, 1991; Downing and McCauley,
6 1992; Rose and Axler, 1998). Water quality in the open waters of these lakes has been
7 improving in recent years in response to controls on point sources of P (Nicholls et al., 2001).
8 Work by Levine et al. (1997), however, suggested a more complicated pattern of response to
9 nutrient addition for Lake Champlain. They added nutrients to in situ enclosures and measured
10 indicators of P status, including alkaline phosphatase activity and orthophosphate turnover time.
11 Although P appeared to be the principal limiting nutrient during summer, N addition also
12 resulted in algal growth stimulation. P sufficiency appeared to be as common as P deficiency.
13 During spring, phytoplankton growth was not limited by P, N, or Si, but perhaps by light or
14 temperature (Levine et al., 1997).

15 Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to
16 increased atmospheric N loading (D'Elia et al., 1986; Howarth and Marino, 2006). This is at
17 least partly because the rate of denitrification by microbes found in estuarine and marine
18 sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997).

19 The national estuary condition assessment conducted by Bricker et al. (2007) found
20 that the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the
21 lowest symptoms of eutrophication were in the North Atlantic. Other regions had mixtures of
22 low, moderate, and high degree of eutrophication (Figure 4.3-14). The estuaries with the
23 greatest extent of eutrophication corresponded with conditions related to both the degree of
24 N loading and the inherent sensitivity of the estuary, as influenced by morphology and water
25 flushing dynamics. The most eutrophic estuaries were generally those that had large watershed-
26 to-estuarine surface area, high human population density, high rainfall and runoff, low dilution,
27 and low flushing rates (Bricker et al., 2007).

28 Bricker et al. (2007) evaluated the future outlook of the nations estuaries based on
29 population growth and future management plans. They predicted that trophic conditions would
30 worsen in 48 estuaries, stay the same in 11, and improve in only 14 by the year 2020. Between
31 1999 and 2007, an equal number of estuary systems have improved their trophic status as have

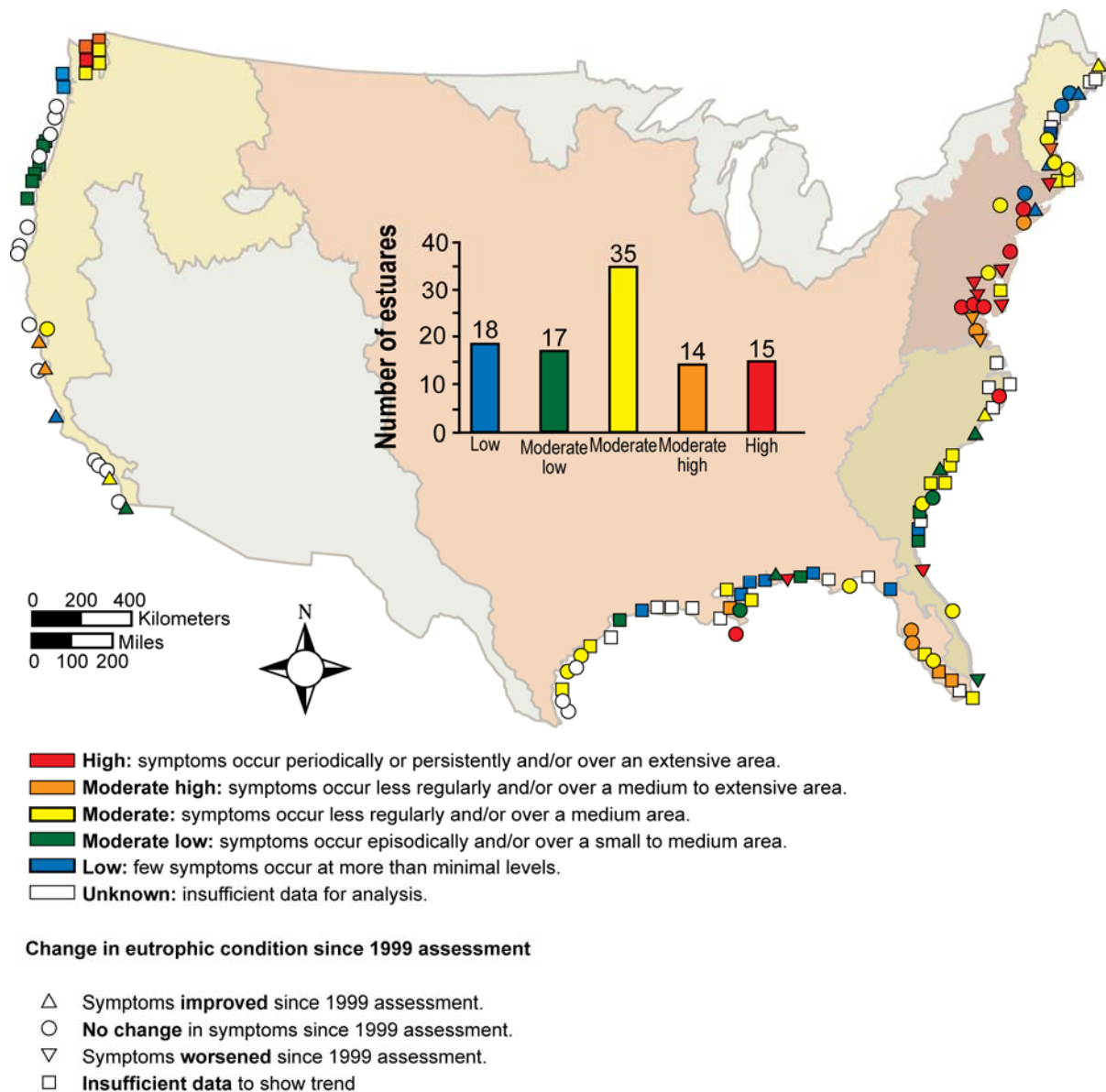


Figure 4.3-14. Overall eutrophication condition on a national scale.

Source: Bricker et al. (2007).

- 1 worsened. The assessed estuarine surface area with high to moderate/high eutrophic conditions
- 2 have stayed roughly the same, from 72% in 1999 (Bricker et al., 1999) to 78% in the recent
- 3 assessment (Bricker et al., 2007).

1 Efforts in the scientific literature to link changes in estuary nutrient status to atmospheric
2 N deposition have been limited, though it should be noted that many states are addressing
3 atmospheric inputs as part of their development of Total Maximum Daily Load plans to address
4 estuarine water quality impairments, including those associated with low dissolved oxygen. In
5 an effort to evaluate the contribution of atmospheric N deposition to the future reduction in
6 N loading to estuaries, Castro and Driscoll (2002) reported model calculations that suggested that
7 considerable reductions (more than 25%) in atmospheric N deposition will be needed to
8 significantly reduce the contribution made by atmospheric N deposition to the total N loads to
9 their study estuaries in the northeastern United States. A simulated reduction in atmospheric
10 deposition of 25% of ambient deposition rates reduced the contribution made by atmospheric
11 deposition to the total estuarine N loads by only 1% to 6% (Castro and Driscoll, 2002). In a later
12 study, Driscoll et al. (2003b) estimated that reduction of both mobile N emissions sources and
13 electric utilities would produce an estimated reduction in estuarine N loading in Casco Bay,
14 Maine of 13% (Driscoll et al., 2003). Casco Bay receives the lowest atmospheric and non-
15 atmospheric N loading per unit area of watershed ($4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) of the eight estuaries in the
16 northeastern United States evaluated by Driscoll et al. (2003) (Figure 4.3-6).

17 18 **4.3.4.2 Levels of Atmospheric Nitrogen Deposition at Which Effects are Manifested**

19 N levels at which effects are manifested in terrestrial and associated freshwater
20 ecosystems have been documented through gradient and fertilization studies. The results from
21 several major studies are summarized in Table 4.3-1. In terrestrial ecosystems, the reported
22 effect levels range from 4 to 5 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ for changes in the abundance of individual
23 sensitive alpine plant species, to 20 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ for community level changes in alpine plant
24 communities. Differences in the levels at which increased nitrification and NO_3^- leaching have
25 been observed in eastern and western watersheds. For example, Rueth (2002) observed
26 increased rates of nitrification in old-growth forests in Colorado at approximately 5 kg N ha^{-1}
27 yr^{-1} , whereas Aber et al. (2003) associated the onset of NO_3^- leaching in eastern forests with
28 deposition levels of 7 to 10 $\text{kg N ha}^{-1} \text{ yr}^{-1}$. Changes in aquatic ecosystems in the western United
29 States in response to N deposition are highlighted in Table 4.3-3.

30

1 **4.3.4.3 Critical Loads and Timeframes of Response**

2 Empirical models of critical loads for nutrient-N have been in use in Europe for some
3 time (e.g., UNECE, 2004). Within the United Nations Economic Commission for Europe
4 (UNECE) Long Range Transboundary Air Pollution (LRTAP) convention, empirical procedures
5 have been developed to set critical loads for atmospheric N deposition to protect against effects
6 caused by nutrient enrichment. Empirical critical loads of N deposition for natural and semi-
7 natural terrestrial and wetland ecosystems were first presented in a background document for the
8 1992 LRTAP workshop on critical loads held at Lökeberg, Sweden (Bobbink et al., 1992).

9 Since the identification of N deposition as one of the main drivers behind the general loss
10 of biodiversity in Europe, a number of European expert workshops have taken place in order to
11 reach agreement among specialists regarding the impacts of N deposition on various ecosystems
12 and related critical loads (Nilsson and Grennfelt, 1988; Bobbink et al., 1992; Hornung et al.,
13 1995; Bobbink et al., 1996; Achermann and Bobbink, 2003). Efforts have begun to develop
14 similar empirical relationships in the United States, particularly for western ecosystems (Baron
15 et al., 1994, 2000; Williams and Tonnessen, 2000; Fenn et al., 2003a; Burns, 2004; Nydick et al.,
16 2004b). See Section 4.1.2 for additional general information on critical loads.

17
18 **4.3.4.4 Nutrient Enrichment Case Study #1: Alpine and Subalpine Communities of the**
19 **Eastern Slope of the Rocky Mountains in Colorado**

20 Research on N enrichment effects on alpine and subalpine ecosystems in the western
21 United States has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain
22 National Park and the Niwot Ridge Long-Term Ecosystem Research site, both located east of the
23 Continental Divide in Colorado. Research has been conducted in this region on both the
24 terrestrial and aquatic effects of nutrient enrichment.

25
26 *Terrestrial Effects*

27 Changes in biomass production and NO_3^- leaching are indicative of effects on the health
28 and vigor of plants in alpine and subalpine ecosystems. Biomass production responses of alpine
29 communities to increased N deposition are dependent on moisture regimes (Fisk et al., 1998) and
30 are driven by shifts in species composition. In a fertilization experiment, the addition of 25 kg
31 $\text{N ha}^{-1} \text{ yr}^{-1}$ during summer caused a community shift towards greater dominance of hairgrass
32 (*Deschampsia sp.*) in wet alpine meadows, but the increase in plant biomass (+67%) and plant

1 N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows
2 than in forb-dominated wet meadows (+53% plant biomass, +64% standing N crop, respectively)
3 (Bowman et al., 1995; Burns, 2004).

4 Alteration of plant productivity and species richness have been observed in fertilization
5 experiments. Seastedt and Vaccaro (2001) showed that four years of N addition to alpine
6 vegetation at rates ranging between 100 and 200 kg N/ha (depending on the year) caused
7 marginal increases in plant foliage productivity but reduced species richness. In a follow-up
8 study at Niwot Ridge, additions of 20, 40, and 60 kg N ha⁻¹ yr⁻¹ (on top of ambient N deposition
9 near 5 kg N ha⁻¹ yr⁻¹) over an 8-year period to a dry alpine meadow led to an increase in plant
10 biomass, and an increase in tissue N concentration at all treatment levels within three years of
11 application. Much of the response was due to increased cover and total biomass of sedges
12 (*Carex spp.*). There was a significant decrease in Kobresia biomass with increasing N input.

13 High elevation alpine zones exhibit a relatively low capacity to sequester atmospheric
14 deposition of N because of steep slopes, shallow soils, sparse vegetation, short growing season
15 and other factors (Baron et al., 1994; Williams et al., 1996a). Results from several studies
16 suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at
17 deposition levels less than 10 kg N ha⁻¹ yr⁻¹ (Baron et al., 1994; Williams and Tonnessen, 2000).
18 The changes in plant species that occur in response to N deposition in the alpine zone can result
19 in further increased leaching of NO₃⁻ from the soils, because the plant species favored by higher
20 N supply are often associated with greater rates of N mineralization and nitrification than the
21 preexisting species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al.,
22 2006).

23 Effects of N_r deposition to alpine terrestrial ecosystems in this region include community-
24 level changes in plants, lichens, and mycorrhizae. Alpine plant communities are sensitive to
25 changes in species composition in response to added N (Bowman et al., 1995; Seastedt and
26 Vaccaro, 2001). Plant species composition likely responds at lower N input levels than those
27 that cause measurable changes in soil inorganic N content. For example, Bowman et al. (2006)
28 conducted a N-addition experiment in the Colorado Front Range with 20, 40, or 60 kg N ha⁻¹
29 yr⁻¹. Experimental sites were monitored for 8 years along with a control site that received about
30 5 kg N ha⁻¹ yr⁻¹ total ambient deposition. Changes in plant species composition associated with
31 the treatments occurred within 3 years of the initiation of the experiment, and were significant at

1 all levels of N addition (Figure 4.3-15). Using changes of individual species abundance and
2 ordination scores to evaluate critical load, the critical load for total N deposition was estimated
3 for change in individual species to be $4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and for overall community change to be
4 $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Bowman et al., 2006). In contrast, increases in NO_3^- leaching, soil solution
5 inorganic NO_3^- , and net nitrification were detectable at levels above $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Bowman
6 et al., 2006). These results indicate that changes in plant species composition may be detectable
7 at lower N deposition rates than the level at which the traditional soil indicators signal ecosystem
8 responses to N deposition. This response suggests that changes in species composition are
9 probably ongoing in alpine dry meadows of the Front Range of the Colorado Rocky Mountains
10 at current atmospheric N deposition levels. This research also demonstrated that long-term
11 experimental fertilization plots illustrate a clear response of alpine flora to N addition, including
12 shifts toward graminoid plants that shade smaller flowering species, and accompanying changes
13 in soil N cycling (Bowman et al., 2006).

14 Changes in alpine plant species composition have also been documented on Niwot Ridge,
15 where increased cover of plant species that are most responsive to N fertilization has occurred in
16 some of the long-term monitoring plots (Korb and Ranker, 2001; Fenn et al., 2003a). These
17 changes have probably developed in response to changes in N deposition. However, the
18 influences of climatic change, particularly changes in precipitation (Williams et al., 1996a), and
19 pocket gopher disturbance (Sherrod and Seastedt, 2001) could not be ruled out (Fenn et al.,
20 2003a). The altered N cycling provided the potential for replacement of some native plant
21 species by more competitive, faster growing native species (Bowman and Steltzer, 1998; Baron
22 et al., 2000; Bowman, 2000).

23 24 *Aquatic Effects*

25 Rocky Mountain National Park has been the site of research addressing the effects of
26 N deposition on algal species abundance in freshwater lakes. Wolfe et al. (2001) analyzed
27 sediments from Sky Pond and Lake Louise, two small alpine lakes located at more than 3300 m
28 elevation on the east slope of the Colorado Front Range in Rocky Mountain National Park. Prior
29 to 1900, the diatom flora was typical of oligotrophic Rocky Mountain lakes, dominated by such
30 species as *Aulacoseira distans*, *A. perglabra*, *Fragilaria pinnata*, *F. construens*, and various
31 *Achnanthes* spp. The mesotrophic planktonic species *Astrionella formosa* and *Fragilaria*

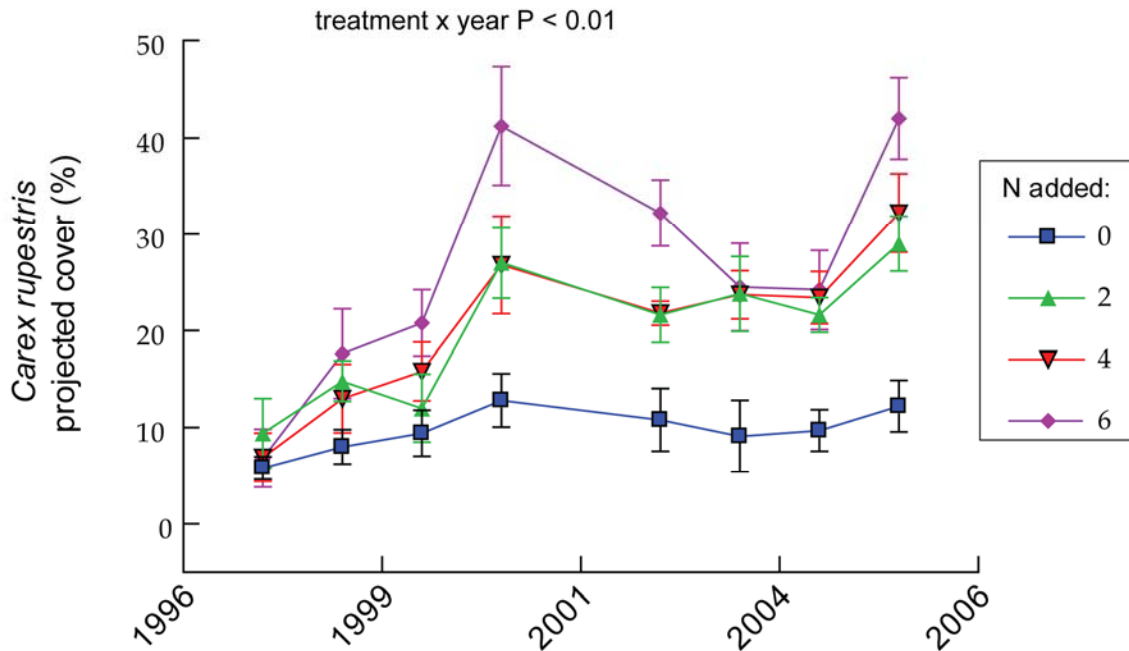


Figure 4.3-15. Changes in plant species composition associated with nitrogen addition treatments in an alpine dry meadow of the Colorado Front Range. Within 3 years of the initiation of the experiment, statistically significant changes in the cover of *Carex rupestris* occurred at all treatment levels.

Source: Bowman et al. (2006).

1 *crotonensis* were present in trace frequencies, but became common elements of the diatom flora
 2 during the 20th century. Between 1950 and 1970, *A. formosa* became the dominant taxa in both
 3 lakes. It is known from studies in other locations as an opportunistic alga that responds rapidly
 4 to disturbance and nutrient enrichment (Renberg et al., 1993; Anderson et al., 1995; Reavie and
 5 Smol, 2001). This shift in diatom species is apparently the result of environmental stimulation,
 6 rather than recent colonization, as evidenced by the presence of these mesotrophic taxa in the
 7 older sediment record.

8 Additional corroborative evidence for the linkage between atmospheric N deposition and
 9 the observed diatom shifts in these alpine lakes is provided by the results of laboratory
 10 (Interlandi and Kilham, 1998) and in-lake (McKnight et al., 1990) N addition experiments. In
 11 both sets of experiments, growth of *A. formosa* and *F. crotonensis* was accelerated by

1 experimental N addition. The post-1950 period of rapid shifts in diatom species composition in
2 Sky Pond and Lake Louise corresponded with intensification of agricultural practices, animal
3 husbandry, and population growth in adjacent regions to the east of Rocky Mountain National
4 Park (Wolfe et al., 2001). Nevertheless, N deposition at that time was estimated to be low,
5 probably less than $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Baron, 2006).

6 7 **4.3.4.5 Nutrient Enrichment Case Study #2: Chesapeake Bay**

8 Chesapeake Bay is the largest estuary in the United States and one of the most sensitive
9 to N inputs (Bricker et al., 1999; Howarth, 2007). Eutrophication effects have been pronounced
10 in Chesapeake Bay (Howarth, 2007) and it is perhaps the best known example in the United
11 States of human activities leading to accelerated estuarine eutrophication and its associated
12 negative effects. In the recent national assessment of eutrophic conditions in estuaries, the
13 Chesapeake Bay stands out as a system with both physical features and N loading levels that
14 make it particularly vulnerable to eutrophication (Bricker et al., 2007).

15 The role of atmospheric N deposition in estuary eutrophication in the United States was
16 ignored until Fisher and Oppenheimer (1991) suggested that it could constitute up to 40% of the
17 total N inputs to the Chesapeake Bay. Although their analysis was preliminary, and has been
18 updated by more conservative estimates (e.g., Boyer et al., 2002; Boyer and Howarth, 2002), it
19 served to focus attention on the role of atmospheric deposition as an important contributor to the
20 overall budget of estuaries in the eastern United States. N inputs to the Chesapeake Bay have
21 increased substantially over the last 50 to 100 years. The increase is attributed to rapid
22 acceleration of the use of chemical fertilizers in agriculture, the increasing human population
23 density and associated wastewater discharge, and rising atmospheric N emissions within the
24 airshed and consequent deposition within the Chesapeake Bay watershed. Atmospheric
25 deposition of N is currently estimated to contribute about one-fourth of the total N loading to
26 Chesapeake Bay (Boyer et al. 2002; Howarth, 2007).

27 Human activities have increased the susceptibility of the Chesapeake Bay to the effects of
28 atmospheric N deposition. For example, the filling in of wetlands and deforestation for
29 agricultural and urban development, have reduced the ability of natural ecosystem processes to
30 remove or trap nutrients, thereby further accelerating nutrient delivery to the bay. In addition,
31 diseases and over-harvesting led to a dramatic decline of the once highly abundant eastern

1 oyster, seriously reducing the natural filtering of algae and other organic matter from the water
2 column.

3 As a result of these changing conditions, eutrophic symptoms intensified in the
4 Chesapeake Bay from the mid-1950s to the mid-1980s. The most apparent symptoms were
5 (1) high production of algae, (2) increasingly turbid water, (3) major declines in SAV abundance
6 and species, and (4) increasingly worsening anoxia and hypoxia (Boesch et al., 2001). The
7 recent national estuary condition assessment (Bricker et al., 2007) reported that chlorophyll *a*,
8 dissolved oxygen, nuisance/toxic algal blooms, and SAV rated “high” in Chesapeake Bay in
9 terms of severity of effects associated with eutrophication. In addition, macroalgae and toxic
10 algal bloom conditions have worsened since the previous national assessment in 1999 (Bricker
11 et al., 1999, 2007).

12 Concentrations of chlorophyll *a* in the surface mixed layer have increased tenfold in the
13 seaward regions of the bay and one-and-one-half- to twofold elsewhere, paralleling estimates of
14 increased loading of N and P to the bay since 1945 (Harding and Perry, 1997).

15 SAV began to decline as a result of nutrient enrichment during the mid-1960s,
16 disappearing entirely from the Patuxent and lower Potomac Rivers. By 1980, many areas of the
17 bay that once contained abundant SAV beds had none or only very small remnants left (Orth and
18 Moore, 1984). Research indicated that the major driving factor in the decline of SAV was
19 nutrient enrichment, which was causing excessive growth of algae in the water column and on
20 SAV leaf blades (epiphytic algae). This algal growth decreased light availability to the
21 submerged plants to the point that they could not survive (Kemp et al., 1983; Twilley et al.,
22 1985).

23 There is an annual cycle of *oxygen depletion* in the Chesapeake Bay that begins as the
24 water starts to warm in spring, and oxygen depletion accelerates during and following the spring
25 freshet. The spring accumulation of algal biomass is more than sufficient to create conditions for
26 oxygen depletion and summer anoxia (Malone, 1991, 1992). Hypoxia (very low dissolved
27 oxygen concentration) and anoxia (absence of dissolved oxygen) generally occur from May
28 through September, with the most severe conditions observed in mid-summer. Seasonal hypoxia
29 has been a feature of the Chesapeake Bay since deforestation during the colonial period (Cooper
30 and Brush, 1991; Malone, 1991), but evidence suggests an increase in the extent of the problem
31 in recent decades (Officer et al., 1984; Malone, 1991). Estuarine eutrophication is sometimes

1 accompanied by increases in the populations of species of algae, often cyanobacteria that
2 produce toxins. Such chemicals can affect people, fish, shellfish, and other organisms. Blooms
3 of algae that produce toxins in Chesapeake Bay have become more extensive over approximately
4 the past decade (Bricker et al., 2007).

5 In 1983, EPA, District of Columbia, and states of Virginia, Maryland, and Pennsylvania
6 signed the first Chesapeake Bay Agreement, which established the Chesapeake Bay Program—a
7 voluntary government partnership that directs and manages bay cleanup efforts. Scientific
8 findings from the program led to the signing of the second Chesapeake Bay Agreement in 1987,
9 in which it was agreed to reduce by 40% the N and P entering the Chesapeake Bay by the year
10 2000. Point source reductions have been most successful, especially for P. Between 1985 and
11 1996, P point sources were reduced by 58% and N by 15%. Nonpoint source reductions have
12 been slower, largely because nonpoint sources of nutrients are more difficult to control.
13 Nonpoint sources of N and P have been reduced by only 7% and 9%, respectively (Boesch et al.,
14 2001). Effective reduction of nonpoint source nutrients will require such changes as adoption of
15 better agricultural practices, reduction of atmospheric N deposition, enhancement of wetlands
16 and other nutrient sinks, and control of urban sprawl.

17 18 19 **4.4 OTHER WELFARE EFFECTS**

20 21 **4.4.1 Nonacidification Effects of Sulfur**

22 As discussed in Section 4.2, a number of environmental effects are associated with
23 S deposition, in particular, soil and water acidification. However, S deposition also contributes
24 to nutrient enrichment, toxicity, and secondary effects on the cycling and bioavailability of Hg, a
25 highly neurotoxic contaminant. High concentrations of SO₂ can harm vegetation by causing
26 foliar injury, decreasing plant growth, and eliminating sensitive plant species, although
27 atmospheric concentrations of SO₂ are seldom high enough to cause these effects on vegetation
28 at ambient air pollution levels in the United States. The biogeochemical cycling of S is closely
29 linked with the cycling of other important elements, including C, N, P, Al, and Hg. Therefore,
30 S deposition can influence the cycling of these elements in ways that influence nutrient
31 availability or contaminant toxicity. In particular, current research suggests that S deposition
32 influences the cycling of Hg in transitional and aquatic ecosystems by stimulating SO₄⁺-reducing

1 bacteria, which are also associated with Hg methylation, a key process that increases the
2 bioavailability of Hg.

3 4 **4.4.1.1 Biological Role of Sulfur**

5 S is an essential plant nutrient. Low dosages of S serve as a fertilizer, particularly for
6 plants growing in S-deficient soil (Hogan et al., 1998). A certain level of foliar SO_4^+ is likely
7 necessary for adequate S nutrition (Johnson and Mitchell, 1998), and S deficiency has been
8 shown to occur at foliar SO_4^+ levels below 80 $\mu\text{g/g}$ (Turner and Lambert, 1980). Nevertheless,
9 the annual increment of S in vegetation is usually small compared to atmospheric deposition and
10 leaching fluxes. Plants require similar levels of S and P, but S is generally available in much
11 higher concentrations in soil. Storage of S in vegetation is of minor significance in the retention
12 or loss of S in most forests (Mitchell et al., 1992; Johnson and Mitchell, 1998).

13 Current levels of S deposition throughout much of the United States exceed the capacity
14 of most plant communities to immobilize the deposited S (Johnson, 1984; Lindberg, 1992).
15 There are few field demonstrations of foliar SO_4^+ uptake (Krupa and Legge, 1986, 1998; U.S.
16 Environmental Protection Agency, 2004). Rather, SO_4^+ in throughfall is often enriched above
17 levels in precipitation. The relative importance to this enrichment of foliar leachate versus prior
18 dry-deposited SO_4^+ particles is difficult to quantify (Cape et al., 1992).

19 S is a major component of plant proteins and, as such, is an essential plant nutrient. The
20 most important source of S to vegetation is SO_4^+ , which is taken up from the soil by plant roots
21 (Marschner, 1995). The major factor controlling the movement of S from the soil into vegetation
22 is the rate of release through microbial decomposition of S from organic to inorganic forms (May
23 et al., 1972; U.S. Environmental Protection Agency, 1982c, 1993a; Marschner, 1995). S also
24 plays a critical role in agriculture, and is an essential component of fertilizers used to increase
25 food production (Ceccotti and Messick, 1997).

26 Atmospheric deposition is an important component of the S cycle. This is true not
27 only in polluted areas where atmospheric deposition is very high, but also in areas of low
28 S deposition. Biochemical relationships between S and N are involved in plant protein synthesis
29 and metabolism. S deficiency reduces NO_3^- reductase and glutamine synthetase activity.
30 N uptake in forests, therefore, could be loosely regulated by S availability, but SO_4^+ additions in
31 excess of needs do not necessarily lead to injury (Turner and Lambert, 1980; Hogan et al., 1998).

1 S deficiency in forest soil is rare, but has been reported in remote areas that receive very
2 low levels of atmospheric S deposition and that have inherently low S levels in soil (Turner
3 et al., 1977, 1991). In such cases, atmospheric S deposition might be taken up by vegetation,
4 with little SO_4^+ leaching. Within areas of the United States influenced by acidic deposition, this
5 is not expected to be a common phenomenon. To some extent, plant uptake of S is determined
6 by the availability of N. This is because most S in plant tissue is in protein form, with a specific
7 S:N ratio (Turner et al., 1977, 1991; Johnson et al., 1982b).

8 S deposition can have direct effects on plants via nutrient enrichment pathways. S is an
9 essential nutrient for protein synthesis in plants. Adequate S supply for sustaining plant health is
10 0.01 to 0.05% in soils (Nriagu, 1978). SO_4^+ is the dominant form of bioavailable S in soils.
11 Plants can also utilize volatile S compounds such as SO_2 in the atmosphere to fulfill nutrient
12 requirements (Rennenberg, 1984). This S is directly available for diffusive uptake through the
13 leaf surface to support plant growth (Jager and Klein, 1980), and can also become bioavailable in
14 the soil for plant root uptake (Moss, 1978).

15 With the discovery of S deficiencies in some unpolluted regions (Kelly and Lambert,
16 1972; Humphreys et al., 1975; Turner et al., 1977; Schnug, 1997) and excesses associated with
17 acidic deposition in other regions (Shriner and Henderson, 1978; Meiwes and Khanna, 1981;
18 Johnson et al., 1982a), interest in S nutrition and cycling in forests has heightened (U.S.
19 Environmental Protection Agency, 2004). General reviews of S cycling in forests were written
20 by Turner and Lambert (1980), Johnson (1984), Mitchell et al. (1992), and Hogan et al. (1998).
21 The influence of atmospheric deposition on the S cycle was summarized by Johnson and
22 Mitchell (1998).

23 24 **4.4.1.2 Role of Sulfur in Methylation of Mercury**

25 A key step in the entrance of Hg into the food chain is methylation, which converts
26 inorganic Hg to organic compounds of Hg which are highly bioavailable and can accumulate in
27 fish tissue. Methylation rates are influenced by oxygen content, temperature, pH, and the
28 concentration of organic acids in solution (Nagase et al., 1982; Xun et al., 1987; Winfrey and
29 Rudd, 1990; U.S. Environmental Protection Agency, 1996). The EPA's Science Advisory Board
30 concluded that there is a large degree of scientific uncertainty and variability among water bodies
31 concerning the processes that methylate Hg (U.S. Environmental Protection Agency, 1996).
32 Experimental observations show that when SO_4^+ is added to wetlands or lakes, SO_4^+ reduction is

1 enhanced, leading to increased methylation and CH_3Hg^+ export, at least up to a point (Branfireun
2 et al., 1999; Benoit et al., 2003; Watras et al., 2006).

3 Methylating bacteria convert inorganic Hg (often Hg^{2+}) into CH_3Hg^+ , which is the form
4 that bioaccumulates in fish and other biota. SO_4^+ provides the necessary terminal electron
5 acceptor for methylating bacteria (Gilmour et al., 1992). Many studies have also illustrated an
6 association between low lake water pH and high Hg concentrations in fish (Grieb et al., 1990;
7 Suns and Hitchin, 1990; Driscoll et al., 1994; Kamman et al., 2004). Hrabik and Watras (2002)
8 found that decreases in fish Hg concentration in an experimentally de-acidified lake basin
9 exceeded those in the reference lake basin by a factor of two over a 6-year period of
10 experimental de-acidification. On the other hand, in a study of over 600 randomly selected
11 streams and rivers throughout the western United States, Peterson et al. (2007) found little
12 relationship between fish tissue Hg concentrations and surface water pH, SO_4^+ , or dissolved OC.
13 They attributed the lack of a chemical relationship to the fact that low pH (<7) and high
14 dissolved OC systems were rare in the West. The major factors controlling fish tissue Hg
15 concentrations in western streams and rivers were fish size and feeding group, not water
16 chemistry. In comparing CH_3Hg^+ levels in fish, it is necessary to control for differences in fish
17 size and trophic position because highest CH_3Hg^+ concentrations are found in large piscivorous
18 fish.

19 20 **4.4.1.2.1 Conditions Conducive to Mercury Methylation**

21 Hg in fish muscle tissue occurs mainly as CH_3Hg^+ (MeHg), (Bloom, 1992; Harris et al.,
22 2003). Hg methylation is largely attributed to SO_4^+ -reducing bacteria, which are commonly
23 found in anoxic wetland and lake bottom sediments (Compeau and Bartha, 1985; Gilmour and
24 Henry, 1991; Gilmour et al., 1992). Under increased S load, there are increases in the numbers
25 and activity of SO_4^+ -reducing bacteria. The mechanisms for Hg methylation, as mediated by
26 SO_4^+ -reducing bacteria, have been discussed by Choi et al. (1994), Ekstrom et al. (2003), and
27 Ekstrom and Morel (2004). Abiotic mechanisms responsible for Hg methylation also exist
28 (Weber, 1993; Hintelmann and Evans, 1997; Siciliano et al., 2005), but have not been shown to
29 be important.

30 Wetland environments have been shown to be significant areas of CH_3Hg^+ production
31 and sources of export to downstream receiving waters (St. Louis et al., 1994). Experimental
32 wetland studies have found that SO_4^+ addition can increase SO_4^+ -reducing bacteria activity and

1 cause increased CH_3Hg^+ production (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason
2 et al., 2006). For example, SO_4^+ additions of both 2.8 kg/ha and 28 kg/ha to a nutrient-poor fen
3 peatland in Ontario, Canada showed enhanced pore water CH_3Hg^+ production (Branfireun et al.,
4 1999). Gilmour et al. (1992) found increased CH_3Hg^+ production within anoxic sediments of a
5 reservoir located in central Massachusetts in response to SO_4^+ addition in both experimental
6 laboratory slurries and intact sediment cores. Gilmour et al. (1992) also showed that CH_3Hg^+
7 production was substantially reduced with addition of a known SO_4^+ -reducing bacteria inhibitor
8 (Na_2MoO_4). These results are in agreement with observations of Hg methylation mediated by
9 SO_4^+ -reducing bacteria in salt marsh sediments (Compeau and Bartha, 1985). SO_4^+ addition has
10 also been observed to enhance Hg methylation in freshwater wetland sediments (Branfireun
11 et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006).

12 Wetland CH_3Hg^+ production has been measured at rates 26 to 79 times higher than in
13 upland areas of a Canadian boreal forest (wetland: 1.84 to 5.55 $\text{mg ha}^{-1} \text{yr}^{-1}$; upland: 0.07 mg
14 $\text{ha}^{-1} \text{yr}^{-1}$) (St. Louis et al., 1994). Watersheds containing 14.0% to 16.3% wetland yielded 5 to
15 14 times more CH_3Hg^+ than upland catchments that lacked wetlands (St. Louis et al., 1994). In
16 the same region, St. Louis et al. (1996) found that all watersheds were net sinks for total Hg, but
17 that watersheds containing wetlands regularly exported CH_3Hg^+ (St. Louis et al., 1996).
18 However, CH_3Hg^+ export from these watersheds was not directly proportional to percent wetland
19 coverage, indicating that other variables are also involved in the major processes that regulate
20 CH_3Hg^+ production and export. In particular, the level of atmospheric Hg deposition and the
21 acid-base chemistry of drainage water may be important.

22 Branfireun et al. (1996) measured highest peat and pore water CH_3Hg^+ concentrations in
23 wetland areas that exhibited characteristics of a poor fen environment (i.e., interaction with
24 nutrient-poor ground water). St. Louis et al. (1996) observed that high water yield resulted in
25 high CH_3Hg^+ export. Thus, the proportion of upland to wetland land area within a watershed
26 was not the only control on CH_3Hg^+ export, but wetland type and annual water yield also played
27 important roles (St. Louis et al., 1996).

28 Hg methylation occurs in anoxic sediments that contain a sufficient C source to support
29 SO_4^+ -reducing bacterial activity along with an adequate supply of SO_4^+ for SO_4^+ -reducing
30 bacteria-mediated SO_4^+ reduction. These conditions are found in lake and pond bottom
31 sediments (Gilmour et al., 1992), freshwater wetland sediments (Branfireun et al., 1999; Harmon

1 et al., 2004; Jeremiason et al., 2006), and salt marsh sediments (Compeau and Bartha, 1985). Hg
2 must also be present and bioavailable to SO_4^{2-} -reducing bacteria for methylation to occur (Benoit
3 et al., 1999). Microbial SO_4^{2-} reduction can further enhance the reducing conditions in sediments
4 and bottom waters via the production of sulfide. These wetland systems that are likely to exhibit
5 high levels of Hg methylation can be found throughout the United States.

6 Several studies have shown a strong negative correlation between surface water pH and
7 Hg concentration in fish tissue, but the mechanisms responsible for this linkage are not clear. Hg
8 concentrations in fish have also been shown to be less strongly correlated with a variety of other
9 variables, including dissolved inorganic carbon (IC), Ca, Mg, dissolved OC, Na, lake area, and
10 watershed area (U.S. Environmental Protection Agency, 1996).

11 Driscoll et al. (2007b) developed indicators of Hg sensitivity using two stratified,
12 random-probability surveys of northeastern lakes combined with the survey data sets of Chen
13 et al. (2005). This analysis showed that lakes with Hg levels above the EPA criterion of $0.3 \mu\text{g/g}$
14 in yellow perch had significantly higher dissolved OC, and lower pH, ANC, and total P than
15 lakes with fish Hg concentrations below $0.3 \mu\text{g/g}$ (Driscoll et al., 2007b). Based on the
16 probability surveys, they calculated that about 20% of lakes in the region had total P
17 concentrations above $30 \mu\text{g/L}$ and yellow perch Hg concentrations below $0.3 \mu\text{g/g}$. In the
18 remaining 80% of lakes, 75% had yellow perch Hg concentrations exceeding $0.3 \mu\text{g/g}$ when
19 surface water dissolved OC levels exceeded 4.0 mg C/L , a pH of less than 6.0, or an ANC of less
20 than $100 \mu\text{eq/L}$.

21 Most Hg in the water column of freshwaters is bound to organic matter, either to
22 dissolved OC or to suspended particulate matter. Therefore, total Hg and CH_3Hg^+
23 concentrations are often positively correlated with dissolved OC in lake waters (Mierle and
24 Ingram, 1991; Driscoll et al., 1994; U.S. Environmental Protection Agency, 1996). Dissolved
25 OC, in turn, has an important influence on pH. Thus, several interrelated factors also seem to be
26 related to Hg contamination. For example, Driscoll et al. (1995) found one or more yellow perch
27 exceeding the $0.5 \mu\text{g/g}$ action level in 14 of 16 Adirondack study lakes despite wide ranges in pH
28 (to above 7) and ANC (to above $200 \mu\text{eq/L}$) (Mierle, 1990).

29 Several researchers have suggested that the export of Hg from terrestrial watersheds to
30 lakes may be controlled in large part by the nature of watershed soils and the movement of
31 naturally occurring organic acids (Mierle, 1990; Meili, 1991; Mierle and Ingram, 1991;

1 Engstrom et al., 1994). This suggestion is based partly on the fact that dissolved organic matter
2 strongly binds with Hg and partly on the observed positive correlation between Hg accumulation
3 in lake sediments and the ratio of the watershed area to the lake area in relatively undisturbed
4 watersheds ($r^2 = 0.91$; $r^2 = 0.91$) (Engstrom et al., 1994). Engstrom et al. (1994) concluded that
5 Hg export from the terrestrial watershed to lake water may be explained by factors regulating the
6 export of fulvic and humic matter and by watershed area. They based this conclusion on the
7 close correlation between Hg concentration and humic matter in surface waters, the observation
8 that peak concentrations of both Hg and dissolved organic matter tend to occur during periods of
9 high runoff, and the experimental determination that Hg transport occurs primarily in upper soil
10 horizons.

11 Driscoll et al. (1994) concluded that the most obvious factor regulating the concentration
12 and availability of both total Hg and CH_3Hg^+ in Adirondack lakes is dissolved OC. Driscoll
13 et al. (1994) found increased fish Hg concentrations with increasing dissolved OC up to
14 dissolved OC concentrations of about 8 mg/L, followed by lower concentrations in the highly
15 dystrophic Rock Pond (dissolved OC = 26 mg/L). They hypothesized that dissolved OC may
16 bind with CH_3Hg^+ at very high dissolved OC concentration, limiting the bioavailability of the
17 Hg.

18 In addition, calculations made by Driscoll et al. (1995) with the Hg Cycling Model
19 suggested that increases in dissolved OC result in increasing concentrations of Hg in biota but
20 decreases in the bioconcentration factor of Hg in fish tissue. Because the transport of Hg to
21 Adirondack lakes appeared to be linked to dissolved OC production from wetlands within the
22 watersheds of the study lakes, Driscoll et al. (1995) concluded that dissolved OC is important in
23 regulating Hg concentrations in the lakes, and ultimately the supply to fish.

24 In a recent study of biological Hg hotspots in the northeastern United States and
25 southeastern Canada, Evers et al. (2007) analyzed more than 7,300 observations of Hg levels in
26 seven species in three major taxonomic groups to quantify the spatial heterogeneity in tissue Hg
27 concentrations. Using published effect thresholds for Hg tissue concentrations, they identified
28 five known and nine possible biological Hg hotspots. They reported that two of the biological
29 hotspots, located in the Adirondack Mountains of New York and south-central Nova Scotia,
30 occur in areas with relatively low to moderate atmospheric Hg deposition and high landscape

1 sensitivity, as determined by the abundant forest and wetland cover as well as the acidic surface
2 water conditions (Evers et al., 2007).

3
4 **4.4.1.2.2 *Effects of Mercury Methylation***

5 A variety of biological effects can result from S deposition, in addition to the
6 acidification effects discussed in Section 4.2. In particular, the enhanced methylation (and
7 consequent enhanced bioavailability) of Hg that occurs in response to S addition can have
8 adverse effects on fish and on species that consume large quantities of fish. CH_3Hg^+ is a potent
9 neurotoxin to piscivorous mammals and birds (Scheuhammer et al., 2007). Thus, enhanced
10 bioavailability of Hg poses a public health risk to people who consume fish. Hg bioaccumulates
11 at higher trophic levels, and therefore fish-eating wildlife can be affected. Piscivorous birds
12 generally have higher tissue Hg concentrations than non-piscivorous birds (Boening, 2000).

13 A range of effects has been demonstrated, including behavioral, reproductive,
14 neurochemical, and hormonal effects (Scheuhammer et al., 2007). Exposure of fish and wildlife
15 to Hg occurs primarily through the diet. Top predatory, especially piscivorous, animals feeding
16 on aquatic food chains are at greatest risk for Hg accumulation and toxicity (Scheuhammer et al.,
17 2007). Wildlife living in inland lake habitats tends to accumulate higher tissue concentrations of
18 Hg than those living in coastal habitats (Frederick et al., 2002; Evers et al., 2005).

19 S deposition is most likely to result in enhanced Hg methylation in regions that receive
20 relatively high levels of atmospheric Hg and S deposition and that exhibit characteristics
21 conducive to methylation. These include low ANC and low pH surface waters, with large
22 upstream or adjoining wetlands (Scheuhammer and Blancher, 1994; Wiener et al., 2003; Chen
23 et al., 2005; Scheuhammer et al., 2007). Such sensitive ecosystems are prevalent in portions of
24 the northeastern United States and southeastern Canada. Studies of Hg concentration in feathers,
25 blood, and eggs of the common loon (*Gavia immer*) indicate decreasing concentrations from
26 west to east in this region (Evers et al., 1998, 2003). This pattern is in general agreement with
27 patterns of deposition of both Hg and S.

28 Available data suggest that numerous wild populations of fish, birds, and mammals
29 experience CH_3Hg^+ exposures that are high enough to cause substantial reproductive, behavioral
30 or health impairment. Reproduction is the component of response that appears to be most
31 affected (Scheuhammer et al., 2007).

1 CH₃Hg⁺ exposure can affect growth, reproductive ability, morphological characteristics,
2 and feeding efficiency in fish. Friedman et al. (1996) investigated the effects of low-level
3 (0.137 µg Hg/g) and high-level (0.987 µg Hg/g) dietary Hg concentrations (as CH₃Hg⁺) on
4 hatchery juvenile walleye (*Stizostedion vitreum*). These experimental Hg exposures were chosen
5 to reflect dietary Hg concentrations commonly encountered in North American lakes and
6 streams. Results showed impaired fish growth and impaired gonad development in males.

7 Fjeld et al. (1998) exposed grayling (*Thymallus thymallus*) embryos to varying
8 concentrations of CH₃Hg⁺ (0.16, 0.8, 4.0, and 20 µg Hg/L) during their first 10 days of
9 development. This exposure resulted in body tissue CH₃Hg⁺ concentrations of 0.09, 0.27, 0.63,
10 and 3.80 µg Hg/g respectively. Morphological deformities were observed in fish exposed to the
11 highest level of CH₃Hg⁺. Samson and Shenker (2000) also observed morphological disturbance
12 in zebrafish (*Danio rerio*) at embryonic CH₃Hg⁺ exposure levels of 20 and 30 µg CH₃HgCl/L.
13 Other fish such as mummichog (*Fundulus heteroclitus*) and rainbow trout (*Oncorhynchus*
14 *mykiss*) have also been observed to have teratogenic effects such as cyclopia, tail flexures,
15 cardiac malformations, jaw deformities, twinning, and axial coiling from embryonic CH₃Hg⁺
16 exposure (Samson and Shenker, 2000).

17 Fish survival and subsequent population status can be jeopardized as a result of exposure
18 to CH₃Hg⁺. Fathead minnows (*Pimephales promelas*) showed impaired feeding efficiency after
19 exposure to both 6.79 and 13.57 µg HgCl₂/L (Grippe and Heath, 2003). Reduced feeding
20 efficiency and competitive ability was also observed in grayling exposed to 0.8 to 20 µg Hg/L as
21 embryos (Fjeld et al., 1998).

22 23 **4.4.1.3 Summary**

24 The most important nonacidification effect of S deposition in areas of the United States
25 that receive high levels of S deposition concern the influence of S supply on Hg methylation.
26 The extent of methylation governs the bioavailability of Hg to biota. High concentrations of
27 CH₃Hg⁺ in fish can constitute an important health concern for people who consume large
28 quantities of fish and can affect the health and reproduction of piscivorous wildlife, including the
29 common loon, bald eagle (*Haliaeetus leucocephalus*), and river otter (*Lutra canadensis*).
30 Hg methylation occurs mostly in wetland soils and bottom sediments of lakes and ponds.
31 S deposition to these ecosystems can enhance S reduction and Hg methylation processes.
32 Although S can also be directly toxic to terrestrial vegetation, levels of S in ambient air pollution

1 and levels of S deposition commonly found in the United States are generally not high enough to
2 cause substantial direct adverse effects on plants.

3 4 **4.4.1.4 Sulfur Nutrient Enrichment Case Study: Interactive Effects of Sulfur and** 5 **Mercury in Little Rock Lake, Wisconsin**

6 Little Rock Lake is an 18-ha precipitation-dominated seepage lake located in a forested
7 and undisturbed catchment of northcentral Wisconsin. The extensive experimental work
8 conducted at Little Rock Lake was described by Hrabik and Watras (2002). The research at
9 Little Rock Lake provides considerable insight into the interactions of S and Hg in the lake, and
10 also bioaccumulation of Hg in fish in freshwater ecosystems.

11 In 1984, the lake was divided into two basins by placing an impermeable curtain across a
12 narrow lake section. One of the basins was experimentally acidified from pH 6.1 to 4.7 by
13 mixing H₂SO₄ into the surface water over a period of 6 years (Watras and Frost, 1989). The
14 other basin was left undisturbed to serve as a reference. Beginning in 1990, the treated basin was
15 left to de-acidify naturally.

16 Hg accumulation in yellow perch showed significant declines in fish in both the
17 experimental and reference basins between 1994 and 2000, commensurate with declines in
18 atmospheric deposition of Hg. Fish Hg concentrations in the experimental basin were 57%
19 higher in 1994 than in 2000, whereas concentrations were 36% higher in the reference basin
20 (Hrabik and Watras, 2002). The authors determined that half of the decrease in fish Hg
21 concentration was attributable to lakewater de-acidification and the other half was associated
22 with regional declines in atmospheric Hg deposition. In the reference basin, which had higher
23 pH and exhibited a lower rate of de-acidification, 15% of the decrease in fish Hg concentration
24 was due to de-acidification (Hrabik and Watras, 2002).

25 These findings were consistent with the hypothesis that SO₄⁺ and newly added Hg
26 synergistically contribute to enhanced bioaccumulation of Hg in fish. In subsequent analyses,
27 Watras et al. (2006) found that maximum CH₃Hg⁺ concentrations in hypolimnetic waters were
28 directly correlated with the SO₄⁺ deficit and they observed a correlation between CH₃Hg⁺ and
29 lakewater SO₄⁺ concentrations. The tracking of external loads of Hg and S, and internal loads of
30 Hg and CH₃Hg⁺ suggested a tight biogeochemical connection among atmospheric deposition,
31 SO₄⁺ reduction, and Hg methylation. However, these relationships did not fully explain the

1 observed large inter-annual variability in CH_3Hg^+ accumulation. The variability appeared to be
2 influenced by OC, terrestrial runoff and temperature.

3 The results from the Little Rock Lake acidification experiment suggest that S deposition
4 plays an important role in the accumulation and methylation of Hg in freshwater ecosystems, and
5 that acid deposition and Hg deposition have a disproportionately larger effect together than either
6 would have separately (Watras et al., 2006).

7

8 **4.4.2 Direct Phytotoxic Effects of Gaseous Nitrogen and Sulfur on** 9 **Vegetation**

10 This section is intended to be a brief overview of the exposure and phytotoxic effects of
11 gaseous N and S compounds on vegetation. This recognizes that the major focus of this review
12 is the acidic and N deposition on to vegetation and ecosystems. However, direct effects of
13 gaseous N and S could augment the effects of deposition on vegetation and there may be effects
14 of gaseous N and S that may occur in some areas.

15 The effects of major gaseous pollutants such as SO_2 , nitrogen dioxide (NO_2), and O_3 on
16 vegetation have been studied since the 1950s and 1960s. Methodologies have been developed to
17 study these effects in the lab, greenhouse, and in the field. The methodologies to study gaseous
18 pollutants effects on vegetation have been recently reviewed in the O_3 AQCD (U.S.
19 Environmental Protection Agency, 2006a). Readers are referred to the Section AX9.1 of the O_3
20 AQCD (U.S. Environmental Protection Agency, 2006a) and Section 9.2 in the 1993 NO_2 AQCD
21 (U.S. Environmental Protection Agency, 1993a) for a thorough description of all the
22 methodologies used to expose vegetation to gaseous pollutants.

23 Uptake of gaseous pollutants in a vascular plant canopy is a complex process involving
24 adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants
25 penetrate into leaves primarily in gaseous form through the stomata, although there is evidence
26 for limited pathways via the cuticle. Pollutants must travel from the bulk air to the leaf boundary
27 layer in order to get to the stomata. Although the movement of pollutants through a boundary
28 layer into the stomata region is known to be important, and even rate limiting in many cases of
29 low wind velocity, its description has been defined from aeronautical concepts and usually
30 relates to smooth surfaces that are not typical of leaf-surface morphology; however, it is nearly
31 the only treatment available (Gates, 1968). Once through the boundary layer, the gas must enter
32 the leaf through the stomata. The entry of gases into a leaf is dependent upon the physical and

1 chemical processes of gas phase and surfaces as well as the stomatal aperture. The aperture of
2 the stomata is controlled largely by the prevailing environmental conditions, such as humidity,
3 temperature, and light intensity. When the stomata are closed, as occurs under dark or drought
4 conditions, then resistance to gas uptake is very high and the plant has a very low degree of
5 susceptibility to injury (Figure 4.4-1). The stomatal control of uptake of gaseous pollutants is
6 described in more detail in AX9.2 of the O₃ AQCD (U.S. Environmental Protection Agency,
7 2006a) and Section 9.3.1.5 of the oxides of nitrogen AQCD (U.S. Environmental Protection
8 Agency, 1993a). It should be noted that unlike higher plants, mosses and lichens do not have a
9 protective cuticle barrier to gaseous pollutants, a major reason for their sensitivity to gaseous
10 S and N.

11 **4.4.2.1 Direct Phytotoxic Effects of SO₂ on Vegetation**

13 It has been known since the early 1900s that exposure of plants to SO₂ can cause damage
14 and death (Wislicenus, 1914). The large sources of SO₂ were ore smelters. Sulfides in the ore
15 were oxidized during smelting and resulted in large releases of SO₂. Emissions from large ore
16 smelters in the United States and Canada resulted in large areas denuded of vegetation
17 surrounding these facilities (Swain 1949; Thomas 1951). Much of the damage to the vegetation
18 was due to acute effects of high concentrations of SO₂. However, as early as 1923 researchers
19 recognized that SO₂ might reduce plant growth without acute symptoms of foliar injury (Stoklasa
20 1923). In the 1950s through the early 1980s, there was much research on the effects of lower
21 levels of SO₂ as well as the interaction with other pollutants such as O₃ and NO₂. Since then,
22 there has been much less research on the effects of SO₂ on vegetation, especially in the United
23 States, due to the decreasing ambient concentrations of SO₂. This section will briefly recap what
24 is known about the effect of SO₂ on vegetation and summarize some of the limited recent
25 literature.

26 Currently, SO₂ is the only Criteria Pollutant with a secondary NAAQS distinct from the
27 primary standard. This standard is to protect acute foliar injury resulting from SO₂ exposure.
28 The standard is a 3-h average of 0.50 ppm and was promulgated in 1970 to protect against acute
29 foliar injury in vegetation. The last review of the SO₂ secondary standard was completed in
30 1982 and concluded that controlled experiments and field observations supported retaining this
31 secondary standard (U.S. Environmental Protection Agency, 1982a,b). Acute foliar injury

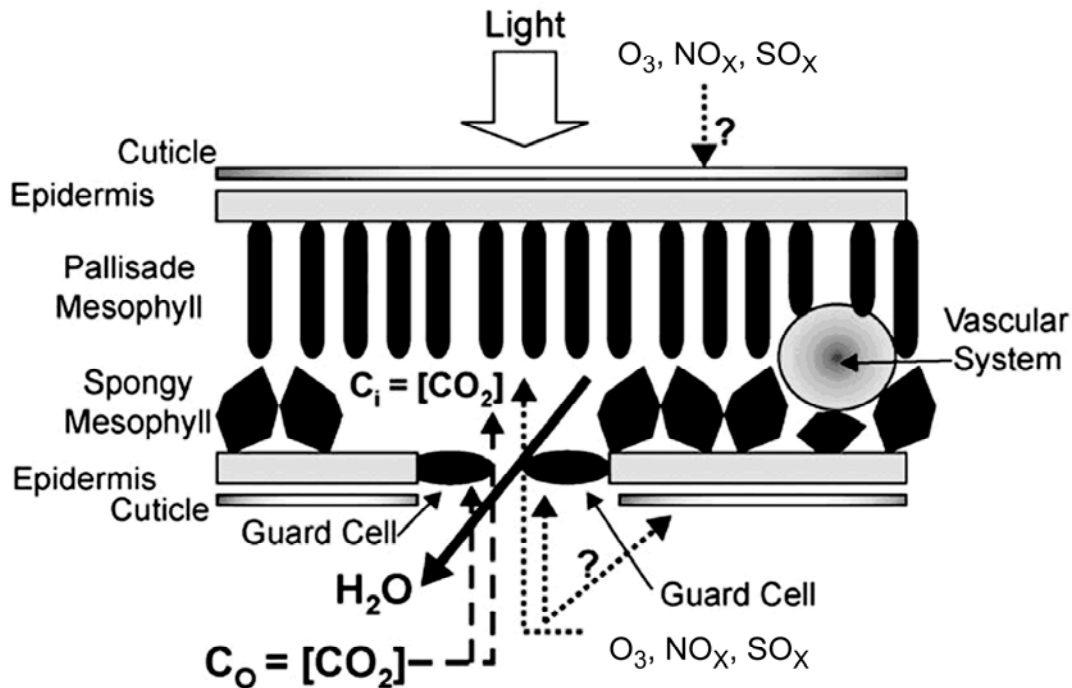


Figure 4.4-1. The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial) leaf surface. CO_2 , SO_x , NO_x , and O_3 gases generally enter through the stomata on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).

1 usually happens with hours of exposure, involves a rapid absorption of a toxic dose and involves
 2 collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and
 3 is usually a result of variable SO_2 exposures over the growing season. After entering the leaf,
 4 SO_2 is converted to sulfite and bisulfite, which may be oxidized to SO_4^+ . SO_4^+ is about 30 times
 5 less toxic than sulfite and bisulfite. The conversion of sulfite and bisulfite to SO_4^+ results in net
 6 H^+ production in the cells. Kropff (1991) proposed that the appearance of SO_2 -induced leaf
 7 injury was likely due to a disturbance of intracellular pH regulation. Kropff (1991) pointed out
 8 several studies that the pH of homogenates only shifted towards greater acidity when plants were
 9 lethally damaged from long-term SO_2 exposures (Grill 1971; Jager and Klein, 1977; Thomas
 10 et al., 1944). The appearance of foliar injury can vary significantly between species and growth

1 conditions affecting stomatal conductance. Currently there is not regular monitoring for SO₂
2 foliar injury effects in the United States.

3 Besides foliar injury, long-term lower SO₂ concentrations can result in reduced
4 photosynthesis, growth, and yield of plants. These effects are cumulative over the season and are
5 often not associated with visible foliar injury. As with foliar injury, the effects of foliar injury
6 vary among species and growing environment. The 1982 SO₂ AQCD summarized the
7 concentration-response information available at the time (U.S. Environmental Protection
8 Agency, 1982a). Effects on growth and yield of vegetation were associated with increased SO₂
9 exposure concentration and time of exposure. However, that document concluded that more
10 definitive concentration-response studies needed before useable exposure metrics could be
11 identified. Because of falling ambient SO₂ concentrations and focus on O₃ vegetation effects
12 research, few studies have emerged to better inform a metric and levels of concern for effects of
13 SO₂ growth and productivity of vegetation. Most research has been performed in areas of
14 Europe where ambient SO₂ concentrations are generally higher than in the United States.

15

16 **4.4.2.2 Direct Phytotoxic Effects of Gaseous NO₂ on Vegetation**

17

18 **4.4.2.2.1 NO and NO₂**

19 It has been well known that in sufficient concentrations nitric oxide (NO) and NO₂ have
20 the potential to have phytotoxic effects on plants through decreasing photosynthesis and
21 induction of visible foliar injury (U.S. Environmental Protection Agency, 1993a). The 1993
22 NO_x AQCD concluded that concentrations of NO₂ or NO in the atmosphere are rarely high
23 enough to have phytotoxic effects on vegetation (U.S. Environmental Protection Agency,
24 1993a). Since the 1993 AQCD, very little new research has been done on these phytotoxic
25 effects to alter this conclusion. However, it is known that these gases could be altering the N
26 cycle in some ecosystems, especially in the western United States, and contributing N saturation
27 (Fenn et al., 2003a; Bytnerowicz and Fenn, 1996). See Section 4.3 for a discussion of the
28 nutrient effects of N.

29 In general, NO and NO₂ enters leaves through stomata (Saxe, 1986). However, it has
30 also been shown that the leaf cuticle may be an important receptor for NO₂ and there is evidence
31 of transport of NO and NO₂ across isolated cuticles (Lendzian and Kerstians, 1988). After
32 entering the leaves, NO₂ dissolves in the extracellular water of the sub-stomatal cavity to form

1 HNO₂ and HNO₃, which then dissociate to form nitrite, NO₃⁻ and protons (Bytnerowicz et al.,
2 1998). Both cell and tonoplast membranes contain ATP-dependent H⁺ pumps and the tonoplast
3 pumps are strongly inhibited by NO₃⁻ (Bytnerowicz et al., 1998). If extra protons are deposited
4 in vacuoles of the plant cells during normal cellular regulation, then additional acidity will occur
5 in combination with additional NO₃⁻. This combination can cause disruptions in cellular control
6 (Taylor and MacLean, 1970). NO₃⁻ and nitrite are metabolized to amino acids and proteins
7 through a series of enzymatic reactions mainly involving NO₃⁻ and nitrite reductases (Amundson
8 and MacLean 1982). The effectiveness of plants to reduce NO₃⁻ and nitrite to amino acids and
9 proteins determines the potential of the plant to detoxify NO and NO₂ (Wellburn, 1990).
10 Reduction of NO₃⁻ takes place outside of the chloroplast while the reduction of nitrite is coupled
11 with the light reactions of photosynthesis. Therefore, when leaves are exposed to NO and NO₂
12 in the dark, highly phytotoxic levels of nitrite accumulate and may lead to greater toxicity to NO
13 and NO₂ at night (Amundson and MacLean, 1982). Exposure to NO produces both NO₃⁻ and
14 nitrite in the leaves, but the rate of NO₃⁻ accumulation is much slower than nitrite. Thus, plants
15 exposed to high NO could be at risk to elevated concentrations of nitrite (Wellburn, 1990). More
16 detailed information on the cellular effects of NO and NO₂ can be found in the 1993 NO_x
17 AQCD.

18 Necrotic lesions and excessive defoliation may occur as a result of accidental releases of
19 NO or NO₂ from point sources during relatively short periods of exposure (MacLean et al.,
20 1968). With the normal ranges of concentrations occurring in large U.S. cities, detrimental
21 effects on long-term photosynthesis and growth of plants may have the potential to occur, but
22 this effect has not been quantified or studied. Significant foliar injury due to exposure to NO or
23 NO₂ is not expected to occur.

24 25 **4.4.2.2 Peroxyacetyl Nitrate (PAN)**

26 Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant, often co-occurring
27 with O₃ during high photochemical episodes, which has been shown to cause injury to vegetation
28 (See reviews by Cape, 2003, 1997; Kleindienst, 1994; Smidt, 1994; Temple and Taylor, 1983).
29 Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a
30 glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species
31 include spinach, Swiss chard, lettuces, and tomatoes. Petunias have also been characterized as

1 sensitive to PAN exposures and have been used as bioindicators of in areas of Japan (Nouchi
2 et al., 1984). Controlled experiments have also shown significant negative effects on the net
3 photosynthesis and growth of petunia (*Petunia hybrida* L.) and kidney bean (*Phaseolus vulgaris*
4 L.) after exposure of 30 ppbV of PAN for four hours on each of three alternate days (Izuta et al.,
5 1993). As mentioned previously, it is known that oxides of N, including PAN, could be altering
6 the N cycle in some ecosystems, especially in the western United States, and contributing
7 N saturation (Fenn et al., 2003a; Bytnerowicz and Fenn, 1996). See Section 4.3 for a discussion
8 of the nutrient effects of N. Although PAN continues to persist as an important component of
9 photochemical pollutant episodes, there is little evidence in recent years suggesting that PAN
10 poses a significant risk to vegetation in the United States.

11 12 **4.4.3 N₂O as a GHG and Interactions between Nitrogen Deposition and** 13 **Biogenic N₂O Emissions.**

14 15 **4.4.3.1 GHG**

16 As discussed in Chapter 2, N₂O is a GHG with a global warming potential (GWP) on the
17 conventional 100-year time horizon of ~296 (i.e., N₂O is nearly 300 times more effective for
18 trapping heat in the atmosphere than CO₂ over a 100-year period (IPCC, 2007). The largest
19 fraction of U.S. GHG emissions are from CO₂, followed by CH₄ and N₂O (83.3%, 7.4%, and
20 6.5% of total GHG emissions from the United States on a Tg CO₂ equivalents basis,
21 respectively) in 2005 (U.S. Environmental Protection Agency Inventory, 2007a). GHGs force
22 global climate change by trapping infrared radiation. A rigorous assessment of this process is
23 provided by the Intergovernmental Panel on Climate Change (IPCC, 2007). It is important to
24 note the process of climate change is projected to alter meteorological patterns that include
25 temperature extremes and patterns of precipitation, including the projected likelihood of extreme
26 precipitation events. Changes in meteorological patterns are one factor associated with climate
27 change that will alter ecosystems. In Annex 7, Table 7-1 provides a short-list of GHGs and the
28 environmental factors indicated to change because of climate change. A comprehensive
29 discussion of the adverse effects of climate change on ecosystems and other welfare effects in
30 North America are assessed in chapter fourteen of the IPCC working group II assessment (Field
31 et al., 2007).

1 In addition to directly and indirectly altering climate change, human activities may also
2 affect the biogenic production of N₂O (e.g., anthropogenic N additions to ecosystem increasing
3 the production of N₂O). The indications of a potential feedback between climate change,
4 N deposition, and N₂O emissions are discussed below.

5 6 **4.4.3.2 Interactions between Nitrogen Deposition and N₂O Production**

7 Human activities can significantly enhance the natural processes that lead to N₂O
8 formation. For example, the N nutrient loading in water bodies due to fertilization and run-off to
9 streams can enhance N₂O emissions from these natural sources.

10 11 *Terrestrial Ecosystems*

12 Numerous studies that show that N₂O emissions from soils increase upon artificial
13 N additions (Brumme and Beese, 1992; Matson et al., 1992; Klemmedtsson et al., 1997; Papen
14 et al., 2001). Regions with elevated atmospheric N-deposition due to anthropogenic activity also
15 show increased N₂O emissions (Butterbach-Bahl et al., 1998, 2002). For example, Ambus and
16 Robertson (2006) investigated study sites located in southwest Michigan consisting of old
17 growth deciduous (40-60 year old) coniferous and successional grasslands that they stimulated
18 by introducing an additional 1-3 g N m⁻² yr⁻¹ (0.84 g N m⁻² yr⁻¹ ambient). They compared the
19 field results to a second experiment conducted in a laboratory setting that simulated the field
20 conditions. The results indicate no change in N₂O emissions for conifer forest and grasslands.
21 The deciduous forest studied showed increased N mineralization, suggesting the system was
22 approaching N saturation. The additional lab study showed a significant and positive
23 relationship between N deposition and N₂O efflux with N additions up to 10 g m⁻² in both
24 coniferous and deciduous forests (Ambus and Robertson, 2006). Investigation of N₂O emissions
25 from a 145 yr old Beech tree stand in Stollig Germany that compared ambient N deposition
26 (35 kg N ha⁻¹ yr⁻¹) to elevated N deposition (145 kg N ha⁻¹ yr⁻¹) indicated elevated N deposition
27 stimulated annual N₂O emissions (5.6 to 7.8 kg N ha⁻¹ yr⁻¹, respectively [Brumme and Beese,
28 1992]). Investigation of sites with similar species composition and climate across Europe, yet
29 with differing rates of wet N deposition (measured as NH₄⁺) showed a significant and positive
30 correlations between increasing N deposition and increasing N₂O flux ($f(x) = 4.7 + 1.4x$, $r^2 =$
31 0.38, $P < 0.001$) (Butterbach-Bahl et al., 1998).

1 Other studies show N deposition to switch ecosystems from a sink to a source of biogenic
2 N₂O. For example, a study of a mixed spruce, fir and pine stand (85-125 yrs old) showed the
3 ecosystem was a sink on 7 of 9 sampling dates under ambient N deposition (10 kg N ha⁻¹ yr⁻¹).
4 However, the ecosystem was functioning as a source 6 of 9 sampling dates under elevated
5 N deposition (150 kg ha⁻¹ yr⁻¹). This switch in ecosystem function from sink to source was
6 attributed to a stimulation of nitrification rather than denitrification (Papen et al., 2001).

7 8 *Soil Moisture and Rainfall*

9 Soil moisture plays an important role affecting N₂O production. A study of mixed
10 spruce, pine and birch forest (100 yrs old) under well- and poorly drained soil moisture
11 conditions indicated poorly drained soils produced 1/3 more N₂O (118 g N₂O-N ha⁻¹ yr⁻¹).
12 When N deposition was increased in the poorly drained soil from ambient (12 kg N ha⁻¹ yr⁻¹) to
13 elevated (42 kg N ha⁻¹ yr⁻¹), N₂O emissions increased by a factor of more than 2 (254 kg N ha⁻¹
14 yr⁻¹) (Klemedtsson et al., 1997).

15 Rainfall events are an important feature controlling N₂O produced via denitrification.
16 Rainfall inhibits oxygen diffusion into the soil creating anoxic conditions, which increases rates
17 of denitrification. A study of a spruce forest under ambient and elevated N deposition (20 and
18 30 kg N ha⁻¹ yr⁻¹, respectively) revealed through most of the study period N₂O emission was
19 equivalent (Mohn et al., 2000). However, after rainfall events the maximum rate of N₂O
20 emission was much higher for the +N plots, especially when rainfall caused low soil redox
21 potential (an indicator of anoxic conditions).

22 23 *Modeling under Climate Variations*

24 The PnET-N-DNDC model is designed to simulate and predict soil C and
25 N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N₂O and NO
26 from forest soils. The model couples the PnET model (Photosynthesis-Evapotranspiration-
27 Model), the Denitrification-Decomposition (DNDC) model, and an N module that are further
28 described in Li et al. (1992, 1996, 2000), Li (2000), and Stange et al. (2000). The capacity of
29 this model to simulate N trace gas emissions from forest soils was tested by comparing model
30 results with results from field measurements at 19 different field sites across Europe and 1 site in
31 the United States (Kesik et al., 2005). Denitrification is described in the model as a series of
32 sequential reductions driven by microorganism using N oxides as electron acceptors under

1 anaerobic conditions. As intermediates of the processes, NO and N₂O are tightly controlled by
2 the kinetics of each step in the sequential reactions. Possible feedbacks of temperature change
3 on forest soil NO and N₂O emissions in Europe were investigated using PnET-N-DNDC (Kesik
4 et al., 2006). Interactions between temperature, precipitation, and forest soil NO and N₂O
5 emissions in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006), abiotic
6 parameters are summarized in Table 4.4-1. The model results indicate areas with light texture
7 soils (below 15%) that decreasing precipitation and increasing temperature resulted in decreased
8 soil moisture values; in turn, soil aeration increased while N₂O production by denitrification
9 decreases. Under these same environmental conditions, NO production by nitrification
10 increases. Most laboratory studies show increasing Temp increases N₂O production, however if
11 water filled pore space (WFPS) increases to 70-80% then N₂ rather than N₂O is the main product
12 of denitrification and N₂O emissions go down.

13

14 **4.4.4 Atmospheric Sources of NO₃⁻ in Drinking Water**

15 High-quality potable water is an ecosystem services that may be impaired by atmospheric
16 N pollution. Elevated NO₃⁻ levels in drinking water have been link to human health risks
17 (Towsend et al., 2003). Elevated NO₃⁻ in stream and groundwater raise concerns about drinking
18 water quality (Fenn et al., 1998). In regions of the United States such as southern California,
19 NO₃⁻ concentrations in stream and groundwater from montane watersheds are the highest
20 reported in North America, with concentrations reaching as much as 370 µeq/L (Fenn et al.,
21 2003a). Furthermore, ground water is elevated in these areas (Towsend et al., 2003) and these
22 watersheds serve as sources of drinking water for nearby urban areas. Similar situations may
23 exist in other areas of the United States; however, there is little information available about the
24 extent to which atmospheric N deposition contributes to NO₃⁻ levels in groundwaters used for
25 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

Region	Results of Regional Survey				Results of Monitoring during 1990s			
	Population Size	Number Acidic ¹	% Acidic ²	Time Period of Estimate	Rate of ANC change ³	Estimated Number Acidic in 2000	% Acidic in 2000	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991-94	+0.3	374 lakes	5.5%	-2%
Adirondacks	1830 lakes	238 lakes	13.0%	1991-94	+0.8	149 lakes	8.1%	-38%
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 $\mu\text{eq/L/year}$, 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

Species	Diet/ Foraging		Breeding Distribution		Reproductive Measures		Reference ^a
	Yes	No	Yes	No	Yes	No	
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

^a1 = 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)

^b The effect was beneficial.

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)

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	<p>Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.</p> <p>Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).</p>
6.0 to 5.5	<p>Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.</p> <p>Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.</p> <p>Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.</p> <p>Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.</p>
5.5 to 5.0	<p>Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.</p> <p>Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.</p> <p>Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.</p> <p>Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.</p> <p>Inhibition of nitrification.</p>

**TABLE 4.2-9 (cont'd). GENERAL SUMMARY OF BIOLOGICAL CHANGES
ANTICIPATED WITH SURFACE WATER ACIDIFICATION, EXPRESSED
AS A DECREASE IN SURFACE WATER pH**

pH Decrease	General Biological Effects
5.0 to 4.5	<p>Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass).</p> <p>Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.</p> <p>Substantial decrease in number of species of plankton and benthic invertebrates and further decline in species richness of plankton and periphyton communities; measurable decrease in total community biomass of plankton and benthic invertebrates of most waters.</p> <p>Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans.</p> <p>Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.</p>

Source: Baker et al. (1990a).

TABLE 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; NO₃⁻, nitrate; NO_x, nitrogen oxides; O₃, ozone; P, phosphorus.

Note: Summary includes the degree of uncertainty regarding the role of N deposition in each effect and the likelihood that these effects may occur elsewhere in the West.

TABLE 4.3-2. OVERVIEW OF MOST SENSITIVE AND MOST AFFECTED ECOSYSTEMS TO N DEPOSITION

Ecosystem	Type	Factors that Govern Vulnerability
Terrestrial	Forest	<ul style="list-style-type: none"> • 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	<ul style="list-style-type: none"> • Sensitive to N enrichment
	Alpine	<ul style="list-style-type: none"> • Low rates of primary production • Short growing season • Low temperature • Wide variation in moisture availability
Transitional	Peat-forming bog	<ul style="list-style-type: none"> • Typically contain plants species that have evolved under N-limited conditions
	Coastal marsh	<ul style="list-style-type: none"> • 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	<ul style="list-style-type: none"> • 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	<ul style="list-style-type: none"> • Low productivity • Low nutrient levels • Located in remote areas and/or high elevations • Downwind of major urban and agricultural centers
	Estuarine and coastal waters	<ul style="list-style-type: none"> • 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 little 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
			Oak
			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 nitrification, 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

1 present in concentrations relevant for atmospheric chemistry and ecological
2 exposures.

3 – Aqueous oxidation dominates production of sulfate ion (SO_4^{2-}) from SO_2 ; gas-
4 phase oxidation is responsible for only ~20% of the SO_4^{2-} total. By contrast,
5 there is little aqueous-phase oxidation of NO_2 to nitrate (NO_3^-) owing to its low
6 solubility.

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

11 – Oxidation of NH_3 is a minor source of total NO_x .

12 – Excess NH_3 is an actor alone and with NO_x in the N cascade leading to
13 nitrification in aquatic and terrestrial ecosystems.

14 • Nitrous oxide (N_2O) is a constituent oxide of nitrogen having effectively no chemical
15 or ecological effects in the troposphere, thus giving it an atmospheric lifetime of
16 ~114 yr. N_2O is also a greenhouse gas (GHG) with a greenhouse warming potential
17 (GWP) on the standard 100-year basis of ~296 times that of carbon dioxide (CO_2).

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

21 22 **5.2.2 Field Sampling and Analysis**

23 • Techniques for routine regulatory monitoring of gas-phase NO_x and SO_2 are adequate
24 but have important limitations.

25 – Routine NO_2 measurements by chemiluminescence (the Federal Register Method
26 [FRM]) are contaminated by unknown and varying concentrations of higher-order
27 oxidized N species (category label is NO_z).

28 – SO_2 measurements by the FRM in the standard regulatory network are now
29 mostly at or below the instrument's operating limit of detection, producing
30 irresolvable uncertainty in these data.

- 1 – Routine field sampling techniques for NH₃ are at present limited to integrated
2 values—from several days to one week—because higher frequency semi-continuous
3 methods are not yet sufficiently robust to deploy in regulatory networks.
- 4 – Routine regulatory sampling and analysis for particulate-phase NO₃⁻, SO₄²⁻, and
5 NH₄⁺ are also subject to positive and negative errors, chiefly from the loss or
6 production of constituent species on the surface of the filter used for the
7 measurement.
- 8 • Despite the aforementioned limitations, for the purposes of identifying and
9 quantifying the atmospheric concentrations and deposition totals causing ecological
10 effects, these measurement techniques and sampling frequencies are fully adequate.
11 Nevertheless, the coverage of the networks is very thin over large expanses of the
12 interior United States.

15 **5.3 EMISSIONS AND EXPOSURES**

17 **5.3.1 Emissions and Atmospheric Concentrations of NO_x and SO_x**

- 18 • Policy-relevant background concentrations of NO₂ (i.e., concentrations calculated to
19 exist without anthropogenic emissions from North America) are <300 parts per
20 trillion (ppt) over most of the conterminous United States (CONUS) and <100 ppt in
21 the eastern United States on an annual average basis.
- 22 • 24-h ambient NO₂ concentration in the consolidated metropolitan statistical areas
23 (CMSAs) where most monitors are located were, on average, <20 parts per billion
24 (ppb) with a 99%ile value <50 ppb for the years 2003–2005. Annual average NO₂
25 concentrations ([NO₂]) over the CONUS are calculated to be <5 ppb for nearly all
26 urban and rural and remote sites.
- 27 • Annual average policy-relevant background [SO₂] are <10 ppt over most of the
28 CONUS, or <1% of observed [SO₂] everywhere except areas in the Pacific Northwest
29 where geogenic SO₂ sources are particularly strong.
- 30 • Energy production at electrical generating units (EGUs) accounts for nearly all SO_x
31 emissions in the United States; very little SO_x is emitted by transportation-related and
32 other sources. Ambient annual [SO_x] has decreased ~50% over the years 1990–2005.

- 1 • Combustion at stationary sources, such as electrical utilities and industrial sites,
2 contribute roughly one-half of the total anthropogenic NO_x emissions; mobile source
3 emissions make up most of the rest. Ambient annual [NO_x] has decreased <35%
4 over the years 1990–2005.
- 5 • Biogenic NO_x sources are substantially smaller than anthropogenic ones and include
6 biomass burning, lightning, and soils. NO and N₂O can be emitted from soils as
7 intermediate products from denitrification, either naturally; or as stimulated by
8 addition of N-containing fertilizers to crops and other soil management practices.
- 9 • N₂O is a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg
10 CO₂-equivalent basis in 2005, and its U.S. emissions decreased ~3% in the years
11 1990–2005, though there remains considerable interannual variation in this number.
- 12 • NH₃ emissions are chiefly from livestock and from soils as stimulated by addition of
13 N-containing fertilizers to crops and other soil management practices.

14

15 **5.3.2 Deposition of Nitrogen and Sulfur**

- 16 • Increasing trends in urbanization, agricultural intensity, and industrial expansion
17 during the previous 100 years have produced a nearly 10-fold increase in N deposited
18 from the atmosphere.
- 19 • NO_x, chiefly from fossil fuel combustion, often dominates total N pollution in the
20 United States and comprises ~50 to 75% of the total.
- 21 • Confined animal feeding operations and other intensified agricultural production
22 methods over a period of many decades have resulted in greatly increased volumes of
23 animal wastes that are high in N, of which 30% to 70% may be emitted as NH₃. This
24 increase in NH₃ emissions, and consequent increase in NH₄⁺ deposition, correlates
25 well with the local and regional increases in agricultural intensity.
- 26 • For 2004–2006, regulatory monitoring networks report the mean N deposition was
27 greatest in the Ohio River valley, specifically in the states of Indiana and Ohio, with
28 values as high as 9.2 and 9.6 kg ha⁻¹ yr⁻¹, respectively.
 - 29 – N deposition was lower in other parts of the East, including the Southeast and in
30 northern New England. In the central United States, Kansas and Oklahoma
31 reported the highest deposition, 7.0 and 6.5 kg ha⁻¹ yr⁻¹, respectively.

- 1 – Deposition primarily occurred as wet NO_3 and NH_4 followed by dry HNO_3 , dry
2 NH_4 , and dry NO_3 . Although deposition in most areas of the United States
3 occurred as wet deposition, there were some exceptions, including parts of
4 California where N deposition was primarily dry.
- 5 • For 2004–2006, mean S deposition in the United States was greatest east of the
6 Mississippi River with the highest deposition amount ($21.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$), in the
7 Ohio River valley where most recording stations reported three-year averages
8 $>10 \text{ kg ha}^{-1} \text{ yr}^{-1}$.
 - 9 – Numerous other stations in the East reported S deposition $>5 \text{ kg ha}^{-1} \text{ yr}^{-1}$.
 - 10 – Data are sparse for the central United States between the 100th meridian and the
11 Mississippi River; but, where available, deposition values there are lower than
12 most of the eastern United States, ranging from 4.1 to $5.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$.
 - 13 – Total S deposition in the United States west of the 100th meridian is relatively
14 low, with all recording stations reporting less than $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and many
15 reporting less than $1.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$.
 - 16 – S was primarily deposited as wet SO_4 followed by a smaller proportion of dry SO_2
17 and a much smaller proportion of deposition as dry SO_4 .
 - 18 • N from atmospheric deposition is estimated to comprise 10% to 40% of the total input
19 of N to many coastal estuaries, and could be higher for some. Estimates of total N
20 loadings to estuaries, or to other large-scale elements in the landscape are then
21 computed using measurements of wet and dry N deposition where these are available
22 and interpolated with or without a set of air quality model predictions.
 - 23 – Direct atmospheric inputs (directly to the water surface) of reactive N to coastal
24 waters are essentially equal to or greater than those contained in riverine flow in
25 the absence of deposition and may contribute from 20 to $>50\%$ of external N
26 loadings to these systems: 11 , 5.6 , and 5.6 kg N ha^{-1} for the northeast Atlantic
27 coast of the United States, the southeast Atlantic coast of the United States, and
28 the U.S. eastern Gulf of Mexico, respectively.
 - 29 – Atmospheric N loads to great waters and estuaries in the United States are
30 estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to
31 $\sim 72\%$ for the Catherines-Sapelo estuary (Castro et al. 2003) on the highest.

- 1 – At Chesapeake Bay, where N and S deposition and ecological effects have been
2 extensively studied, total atmospheric deposition of atmospheric NO₃ is
3 estimated to contribute from 20% to 30% of total N and 14% of the NH₄ loadings
4 to the Bay.

7 **5.4 ECOLOGICAL EFFECTS OF ACIDIFICATION**

8 Oxides of nitrogen and sulfur act in tandem to cause acidification of ecosystems. The
9 principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification
10 from S and N deposition is geology. Geologic formations having low base cation supply
11 generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been
12 used in numerous acidification studies (e.g., Bricker and Rice, 1989; Stauffer, 1990; Stauffer and
13 Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007a). Other factors contribute to
14 the sensitivity of soils and surface waters to acidic deposition, including topography, soil
15 chemistry, land use, and hydrologic flowpath. Vulnerability of ecosystems and regions to
16 acidification lies at the intersection between the inherent sensitivity and the atmospheric loading
17 of NO_x and SO_x.

19 **5.4.1 Terrestrial**

20 In the 1982 Air Quality Criteria Document (AQCD) for SO_x, the foliar and root uptake
21 pathways for sulfur oxides were understood, as well as the role of S as a plant nutrient. Though
22 small amounts of SO₂ may be beneficial, it was understood that large amounts and high
23 frequency of SO₂ exposure and S deposition can be detrimental in the long run. At that time,
24 there were no documented observations or measurements of changes in natural terrestrial
25 ecosystems that were directly attributed to acidic precipitation. However, the AQCD authors
26 made it clear that this did not necessarily indicate that no change was occurring.

27 The 1993 NO_x AQCD indicated that there were very few documented cases in which
28 excessive atmospheric N deposition was linked to soil acidification. The process of soil
29 acidification was already well understood, whereby increased concentrations of NO₃⁻ or other
30 mineral acid anions (e.g., SO₄²⁻ or Cl⁻) in soil solution can lead to leaching of base cations from
31 soil in order to maintain charge balance in solution. Since the preparation of these assessments,

1 direct links between NO_x and SO_x deposition and many adverse affects associated with
2 ecosystem loading have been reported.

3 4 **5.4.1.2 Ecological Effects**

5 6 **5.4.1.2.1 Biogeochemistry and Chemical Effects**

7 Soil acidification occurs in response to inputs of sulfuric acid (H₂SO₄) and nitric acid
8 HNO₃; the effect can be neutralized by weathering or base cation exchange. Soil acidification
9 is a natural process, but is often exacerbated by acidic deposition. Acidic deposition has been
10 shown to be an important factor causing decreases in concentrations of exchangeable base
11 cations in soils. The limited mobility of anions associated with naturally derived acidity (organic
12 acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of
13 low atmospheric deposition of S and N. Because inputs of S and N in acidic deposition provide
14 anions that are more mobile in the soil environment than anions of naturally derived acids, these
15 mineral acid anions can accelerate natural rates of base-cation leaching.

16 The nitrification process is mediated by autotrophic bacteria that derive energy by
17 reducing NH₄⁺ to NO₃⁻. Nitrification produces acidity in the form of HNO₃ as a byproduct.
18 The HNO₃ produced contributes to the acidification of soils and surface waters.

19 There are three useful indicators of chemical changes and acidification effects on
20 terrestrial ecosystems: soil base saturation, aluminum (Al) concentration in soil water, and soil
21 carbon-to-nitrogen (C:N) ratio. In the United States, terrestrial effects of acidification are best
22 described for forested ecosystems, with supplemental information on other plant communities,
23 including shrubs and lichens. Grasslands are thought to be less sensitive to acidification than
24 woodlands.

- 25 • Soil base saturation expresses the concentration of exchangeable bases as a percent of
26 the total soil cation exchange capacity. Once base saturation decreases to a critical
27 level (approximately 15-20% see Table 5.4-1), inputs of H₂SO₄ and HNO₃ are
28 increasingly buffered by release of inorganic Al through cation exchange.
- 29 • Aluminum is toxic to tree roots. Plants affected by high Al concentrations in soil
30 solution often have reduced root growth, which restricts the ability of the plant to take
31 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 SO₂ 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.

1 **5.4.1.2.3 Regional Trends**

2 There has been no systematic national survey of terrestrial ecosystems to determine the
3 extent and distribution of terrestrial ecosystem sensitivity to the effects of acidic deposition.
4 However, one preliminary national evaluation estimated that approximately 15% of forest
5 ecosystems in the United States exceed the estimated critical load of wet and dry deposition of S
6 and N by more than 250 eq ha⁻¹ yr⁻¹.

- 7 • Forest ecosystems of the Adirondack Mountains of New York, Green Mountains of
8 Vermont, White Mountains of New Hampshire, the Allegheny Plateau of
9 Pennsylvania, and high-elevation forests in the southern Appalachians are considered
10 to be the regions most sensitive to terrestrial acidification effects from acidic
11 deposition. It is not known if terrestrial acidification effects in these areas are
12 continuing to develop, or if some recovery is occurring in response to recent
13 reductions in acidic deposition.

14
15 **5.4.2 Aquatic**

16
17 **5.4.2.1 1982 SO_x and 1993 NO_x AQCD**

18 The 1982 AQCD for SO_x (U.S. Environmental Protection Agency, 1982c) discussed the
19 growing environmental concern about acidic deposition and its role in the acidification of aquatic
20 ecosystems in the United States. As in the more recent 1993 AQCD for NO_x (U.S.
21 Environmental Protection Agency, 1993a), chronic and episodic acidification were discussed and
22 the most vulnerable regions were identified, including the Adirondack Mountains of New York.
23 The following conclusions were drawn from the 1982 AQCD regarding significant changes that
24 have occurred in aquatic ecosystems with increasing acidity, particularly as the pH drops below
25 about 5.5. Changes in community structure occur at all levels in the food web. Bacterial
26 decomposition is reduced, and fungi that feed on organic debris may become dominant in aquatic
27 communities. Consequently, organic matter accumulates rapidly, tying up nutrients and limiting
28 nutrient mineralization and cycling. Phytoplankton productivity may be reduced because of
29 changes in nutrient cycling and increased acidity. Biomass and total productivity of benthic
30 macroscopic plants and algae may increase, in part because of increased lake transparency.
31 Species diversity and total numbers of species of aquatic plants and animals (especially
32 invertebrates and fish) are reduced. Acid-tolerant species predominate.

1 The 1993 AQCD for oxides of nitrogen expanded our knowledge of the role of N
2 deposition in the acidification of aquatic ecosystems. This was especially the case with respect
3 to episodic acidification, which is far more common than chronic acidification and has been well
4 documented for streams and lakes in the eastern United States. The most prominent examples
5 exist in the Adirondack and Catskill Mountains of the Northeast as well as in the Great Smoky
6 Mountains of the Southeast. Instances of episodic acidification were also reported in the western
7 United States but to a much lesser extent than in the East.

8 9 **5.4.2.2 Ecological Effects**

10 The status of surface water chemistry can be examined and reported as chronic chemistry
11 or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often
12 represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams.
13 Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately
14 more drainage water is routed through upper soil horizons, which tend to provide less buffering
15 of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits
16 lower pH and acid neutralizing capacity (ANC) during episodes than during baseflow conditions.
17 One of the most significant impacts of acidic deposition on surface water chemistry is the short-
18 term change in chemistry that is termed “episodic acidification.” Some streams may exhibit
19 chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional
20 episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly
21 ubiquitous in drainage waters throughout the eastern United States caused partly by acidic
22 deposition and partly by natural processes.

23 24 **5.4.2.2.1 Biogeochemical Effects**

25 Surface water chemistry integrates the sum of upstream soil and water processes; and
26 reflects the results of watershed-scale terrestrial effects of S and N deposition, including N
27 saturation, forest decline, and soil acidification (Stoddard et al., 2003). In many cases, surface
28 water chemistry indicates the adverse effects of acidification on the biotic species and
29 communities found in fresh water ecosystems. Changes in surface water chemistry include
30 concentrations of SO_4^{2-} , NO_3^- , inorganic Al, and Ca, surface water pH, sum of base cations,
31 ANC, and the base cation surplus.

1 Acidification effects on aquatic life are most commonly evaluated using either Al or pH
2 as the primary chemical indicator. ANC is also used because it integrates overall acid status
3 (although ANC does not relate directly to the health of biota). The utility of the ANC criterion
4 lies in the association between ANC and the surface water constituents that directly contribute to
5 or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

6
7 *Sulfate, Nitrate, and Base Cations*

8 Changes in water chemistry in response to acidic deposition typically include changes in
9 sulfate, nitrate, and base cation concentrations. Each plays an important role in the acid-base
10 chemistry of water, but none are directly toxic at levels commonly encountered in natural waters
11 (see Table 5.4-2).

- 12 • Sulfate is the primary inorganic anion found in most acid sensitive waters. Continued
13 decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in
14 surface waters. However the rate of decrease in surface water sulfate concentrations
15 may be delayed as accumulated S leaches from watershed soils in some regions of the
16 country, especially the Blue Ridge.
- 17 • The importance of NO_3^- as an agent of acidification varies by region, but it is
18 particularly important during periods of high hydrologic flow from soils to streams
19 such as those that occur in snowmelt and rain runoff events. The relationship
20 between atmospheric N deposition and surface water NO_3^- concentration is complex
21 and involves the cycling of nitrogen and other elements in both terrestrial and aquatic
22 ecosystem compartments. NO_3^- contributes to the acidity of many lakes and streams
23 in the eastern United States, but there is no apparent relationship between recent
24 trends in N deposition and trends in NO_3^- concentrations in these surface waters (in
25 contrast to observed responses for S deposition and SO_4^{2-} concentrations). This
26 suggests that the time scales of N saturation may be longer than previously
27 considered (e.g., centuries rather than decades). Nevertheless, long-term retention of
28 N deposited in forested regions and consequent dampening of deposition effects on
29 surface waters is unlikely to continue indefinitely (Aber et al., 2003).
- 30 • Decreases in base cation concentrations in eastern U.S. surface waters over the past
31 two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-}

1 concentrations. Rates of decrease for base cations have been similar to those for
2 SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is notable exception).
3 Decreasing trends in base cation concentrations do not necessarily indicate further
4 acidification or recovery of surface waters, but may indicate either lower base cation
5 leaching rates in soils or depletion of base cations from the soil system.

6
7 *pH, Acid Neutralizing Capacity, and Aluminum*

8 Changes in pH, ANC, and inorganic aluminum concentration accompany acidification of
9 surface water. Low pH and high inorganic aluminum concentration can be directly toxic to
10 aquatic biota (see Table 5.4-2).

- 11 • The pH of freshwater streams and lakes is a common metric used to link acidification
12 to adverse effects on aquatic biota. Decreases in pH of one unit or more typically
13 result in species loss of benthic invertebrates, plankton species, and fish. A number
14 of synoptic surveys indicated loss of species diversity and absence of several fish
15 species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a
16 greater likelihood that more aquatic species could be lost without replacement,
17 resulting in decreased richness and diversity. (See the following discussion on biota).
- 18 • ANC is a variable that reflects the difference between base cations and anions of
19 strong acids in solution and is the most widely used measure of acid sensitivity,
20 acidification, and chemical recovery of surface waters in response to changes in
21 acidic deposition. Acidic waters are defined as those having ANC at or below zero.
22 Waters with ANC of $<50 \mu\text{eq/L}$ are considered “extremely acid sensitive” (Schindler,
23 1988) and are prone to episodic acidification in some regions (DeWalle et al., 1987;
24 Eshleman, 1988. Lake and stream ANC values decreased throughout much of the
25 20th century in a large number of acid-sensitive lakes and streams throughout the
26 eastern United States. Since about 1990 the ANC of many affected lakes and streams
27 has shown some increase, but such increases have been relatively small. The number
28 of acidic surface waters has decreased some areas of the Northeast, but not in the
29 mid-Appalachian Mountains.
- 30 • Dissolved inorganic Al is an important chemical indicator of the effects of acidic
31 deposition on surface water because it is toxic to aquatic life and generally does not

1 leach from soils in the absence of acidification. When pH values fall below
2 approximately 5.5, inorganic Al generally becomes the greater health risk to biota.
3 Limited data suggest that acid-sensitive regions of the northeastern United States
4 have elevated inorganic Al concentrations induced by years of acidic deposition
5 posing a threat to aquatic life. Concentrations have decreased slightly in some
6 surface waters in the northeastern United States during the last two decades in
7 response to decreased levels of acidic deposition.

8 9 **5.4.2.2.2 Biological Effects**

10 Acidification affects aquatic biota at virtually all levels of the food web in acid sensitive
11 aquatic ecosystems. Many species of phytoplankton, zooplankton, macroinvertebrates, and fish
12 are sensitive to acidification. Few studies have been conducted on the effects of acidic
13 deposition on higher trophic levels other than piscivorous birds. Acidification can result in the
14 loss of acid-sensitive species, and more species are lost with higher degrees of acidification.
15 Biological effects are linked to changes in water chemistry that include ANC, pH, and Al.
16 Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in
17 taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur
18 over both long- and short-term time scales, with further effects on biologic systems. Short-term
19 (hours or days) episodic changes in water chemistry can have the most serious biological effects,
20 including reduced fish condition factor, changes in species composition, and declines in aquatic
21 species richness across multiple taxa, ecosystems and regions.

22 23 *Species*

- 24 • Logistic regression modeling showed that the occurrence of two piscivorous birds,
25 common loons and common mergansers, are positively related to the pH of acid-
26 sensitive lakes in the Algoma region of Ontario. Model estimates suggested that the
27 number of lakes projected to be suitable for supporting breeding pairs and broods of
28 these bird species increased with increasing lake pH.
- 29 • High levels of acidification (to pH values below 5) virtually eliminate all mayflies,
30 crustaceans, and mollusks from French streams.

- 1 • In general, populations of salmonid fish are not found at pH levels less than 5.0, and
2 smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH
3 values less than 5.2 to 5.5.
- 4 • Twenty percent mortality of brook trout young-of-the year was documented during a
5 30-day period with a median inorganic Al concentration of 2 µmol/L (Baldigo et al.,
6 2007). It was estimated that 90% mortality would occur over 30 days with a median
7 inorganic Al concentration of 4.0 µmol/L.

8
9 *Community*

10 Community-level effects have been observed in the Adirondacks and Shenandoah
11 National Park where taxonomic richness is lower in lakes and streams having low ANC and pH.

- 12 • Decreases in pH and increases in inorganic Al concentrations have diminished the
13 species richness of plankton, invertebrates, and fish in acid-impacted surface waters.
- 14 • Invertebrate taxa that are most sensitive to acidification include mayflies, amphipods,
15 snails, and clams.
- 16 • In the Adirondacks, a significant positive relationship exists between the pH and
17 ANC in lakes and the number of fish species present in those lakes. A number of
18 synoptic surveys indicated suggested loss of species diversity and absence of several
19 sensitive fish species in the pH range of 5.0 to 5.5.
- 20 • In Shenandoah National Park, the number of species of fish present in streams
21 decreases with decreasing stream ANC. On average, richness is lower by one fish
22 species for every 21 µeq/L decrease in ANC.
- 23 • Short-term episodes of acidity are particularly harmful to aquatic biota. Early life
24 stages are more sensitive to acidic conditions than the young-of-the-year, yearlings,
25 and adults. Episodes are most likely to affect biota if the water had pre-episode pH
26 above 5.5 and minimum pH during the episode of less than 5.0. Episodic
27 acidification can have long-term adverse effects on fish populations.

28
29 **5.4.2.2.3 Regional Trends**

30 The effects of acidifying deposition have been assessed by several national surveys since
31 the 1980s, including: the National Surface Water Survey (NSWS) and the National Stream
32 Survey (NSS) in the mid 1980s; the Wadeable Streams Assessment (WSA) in 2004; U.S.

1 Environmental Protection Agency (EPA)'s Long-Term Monitoring (LTM) program since 1983;
2 and Temporally Integrated Monitoring of Ecosystems (TIME) probability surveys since 1991.
3 These surveys indicate that acidic deposition has acidified surface waters in the (1) southwestern
4 Adirondacks, (2) New England uplands, (3) low-silica eastern Upper Midwest, (4) forested Mid-
5 Atlantic Highlands, and (5) Mid-Atlantic Coastal Plain.

6 The Northeast and mountainous West of the United States contain many of the surface
7 waters most sensitive to potential acidification effects. Levels of acidic deposition in the West
8 are low in most areas, acidic surface waters are rare, and the extent of *chronic* surface water
9 acidification that has occurred to date has likely been very limited. Episodic acidification does
10 occur. In both the West and the Northeast, the most severe acidification of surface waters
11 generally occurs during spring snowmelt. On average, spring ANC values of acid-sensitive
12 surface waters in New England, the Adirondacks, and the northern Appalachian Plateau were
13 about 30 $\mu\text{eq/L}$ lower than summer values during the period 1990 to 2000. This implies that
14 lakes and streams in these regions would need to recover to chronic ANC values above about
15 30 $\mu\text{eq/L}$ or more before they could be expected not to experience acidic episodes (Stoddard
16 et al., 2003).

17 It is important to address whether or not surface waters recovered chemically in response
18 to reduced acidic deposition over the past few decades. The following section summarizes
19 recent regional trends in acidification recovery.

- 20 • About one-quarter to one-third of the lakes and streams that were chronically acidic
21 in the 1980s were no longer chronically acidic in the year 2000. These improvements
22 in water chemistry are largely attributed to decreases in S deposition. Throughout the
23 northeastern United States, the concentration of SO_4^{2-} in surface waters has decreased
24 substantially in response to decreased emissions and atmospheric deposition of S.
25 Decreased concentrations of SO_4^{2-} in lakes and streams of a third, or more, have been
26 commonly observed.
- 27 • EPA's LTM and TIME projects suggest that the following important changes in lake
28 and stream chemistry occurred during the 1990s in response to S and N emissions
29 reductions: (1) SO_4^{2-} concentration decreased as a percentage of total ion
30 concentration in surface waters, (2) ANC increased modestly in three of the five
31 regions included in surface water LTM efforts, (3) Dissolved organic carbon (DOC)

1 and associated natural organic acidity increased, perhaps toward more natural pre-
2 disturbance concentrations, as surface water acidity contributed from acidic
3 deposition decreased, and (4) Inorganic, and potentially toxic, Al concentrations
4 appear to have decreased slightly in some sensitive aquatic systems.

- 5 • In 2004, the EPA conducted a national WSA survey and found that, overall, less than
6 1% of the 1,020,000 km of stream in the target population was acidic due to acidic
7 deposition. No acidic streams were observed in the Mountainous West, Xeric West,
8 Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions.
9 Acidic streams attributable to acidic deposition were found in the (1) Northern
10 Appalachians (2.8% of 96,100 km of stream), and (2) the Southern Appalachians
11 (1.8% of 287,000 km). Very low ANC (0 to 25 $\mu\text{eq/L}$) streams likely exposed to
12 episodic acidification were found in (1) the Northern Appalachians (2.7% of
13 96,100 km of stream), (2) the Coastal Plain (6.3% of 119,000 km), and (3) the
14 Mountainous West (0.6% of 204,000 km).

15 16 **5.4.3 Case Studies**

17 18 **5.4.3.1 Adirondacks**

19 The Adirondack region is presented as a case study in this ISA to demonstrate a
20 geographical region that continues to experience the adverse affects of acidification due to
21 atmospheric deposition of NO_x and SO_x . This region is particularly sensitive to acidic
22 deposition because it receives high precipitation, has shallow base-poor soils, and is underlain by
23 igneous bedrock with low weathering rates and buffering capacity.

24 Hindcast modeling conducted for the Adirondack ecoregion using Paleocological
25 Investigation of Recent Lake Acidification (PIRLA) diatom reconstructions, Model of
26 Acidification of Groundwater in Catchments (MAGIC) model, and Photosynthesis and
27 EvapoTranspiration-BioGeoChemical (PnET-BGC) model simulations are useful to understand
28 changes to surface water chemistry over decadal time scales. . Maximum past acidification
29 occurred by about 1980 or 1990, with median ANC of the lake population of about 61 $\mu\text{eq/L}$
30 (reduced from a median of 92 $\mu\text{eq/L}$ estimated for the preindustrial period). Many lakes were
31 estimated to have had pre-industrial ANC below 50 $\mu\text{eq/L}$, but this estimate more than doubled
32 by 1990. During the 1990s, ANC increased in Adirondack lakes at a rate of about

1 +1 $\mu\text{eq L}^{-1} \text{yr}^{-1}$. Surface water pH also increased, and inorganic Al concentrations declined
2 slightly in many of the most acid-impacted. Overall improvements in lake water acid-base
3 chemistry have been modest. Dynamic model simulations estimate a limited chemical recovery
4 (3 to 5 $\mu\text{eq/L}$ on average) and the ongoing trend of increasing lake water ANC for the most acid-
5 sensitive Adirondack lakes would not continue under future emissions and deposition levels
6 anticipated as of 2003 (modeled as a Base Case Scenario).

7 Many acidic surface waters in this region are currently characterized by high levels of
8 inorganic Al (66% of 188 streams in 2004). Forecasting projections show that lower deposition
9 levels would lead to either stabilization of the number of chronically acidic lakes or increasing
10 levels of ANC and pH. In addition, a number of biological effects findings have been identified
11 between 1984 and 1987:

- 12 • 76% of lakes had fish; 24% (346 lakes) were fishless.
- 13 • The most common fish caught were native acid-tolerant species: brown bullhead,
14 brook trout, and white sucker.
- 15 • As pH decreases, fish richness also decreases and the number of fishless lakes
16 increases.
- 17 • After accounting for other conditions that could explain the absence of fish, 32% of
18 the fishless lakes, or 8% of all the lakes sampled were considered fishless due to the
19 inputs of acids by acidic deposition.
- 20 • Mean yellow perch mercury (Hg) conditions in the Adirondack hotspot were 1.5 to
21 2.5 times higher than the EPA and U.S. Food and Drug Administration (FDA)
22 reference dose used for fish consumption advisories, particularly due to the *combined*
23 *effects of acidic deposition and Hg deposition*.

24 25 **5.4.3.2 Shenandoah National Park, Virginia**

26 Shenandoah National Park (SNP) in Virginia received relatively high deposition of S and
27 N (and high O_3 concentrations). Measured wet S deposition ranged from 8 to 10 $\text{kg S ha}^{-1} \text{yr}^{-1}$
28 (in the early 1980s) to near 6 $\text{kg S ha}^{-1} \text{yr}^{-1}$ since 2000. Dry S deposition may be nearly as high
29 as wet deposition (Sullivan et al., 2003). Most acidification effects in the park have been linked
30 to S deposition. One third of SNP streams drain watersheds with silica (Si)-based underlying
31 geology and consequently have low ANC. These streams have probably lost much of their

1 natural ANC from the past century of acidifying deposition that came primarily from industrial
2 sources. Stream pH is now as low as 5 in many streams, versus an estimated 6 for most streams
3 prior to elevated deposition from human sources of air pollution.

4 High rates of atmospheric deposition of S, combined with naturally low contributions
5 from some rock types of Ca and other base cations (that serve to neutralize acidity), are the most
6 important causes of low stream water ANC in many park streams. In general, SNP streams do
7 not show recent recovery from acidification despite reductions in deposition. In fact, many
8 streams are expected to acidify more in the future unless deposition is further reduced. This is
9 because: (1) S adsorption on soil has decreased due to the cumulative effects of long-term S
10 deposition and (2) stored Ca and magnesium (Mg) is being depleted (due to acid deposition).

11 12 13 **5.5 ECOLOGICAL EFFECTS OF NITROGEN NUTRIENT** 14 **ENRICHMENT**

15 Terrestrial ecosystems typically respond to total reactive N loading and, with few
16 exceptions, have limited differential responses to the specific chemical species of deposited N.
17 Nitrogen compounds that are contained in atmospheric deposition, and that influence nutrient
18 dynamics, include both multiple oxidized and reduced forms of inorganic N. Excess N in
19 ecosystems causes inadvertent fertilization of trees and grasslands, creating unnatural growth
20 rates in some species and change in the competitive interactions among species, nutrient
21 imbalances, and ultimately decreasing ecosystem health and biodiversity. Reactive nitrogen (N_r)
22 can leach from the soil and pollute groundwater and surface water. Reactive nitrogen also
23 promotes eutrophication in coastal ecosystems, ultimately reducing biodiversity due in part to
24 depletion of oxygen needed for the survival of many species of aquatic plants and animals. The
25 cascade of N effects in the environment is interrupted only when N_r is stored in inaccessible
26 places or converted back to N_2 gas through denitrification. It is important to note that not all N_r
27 is converted to unreactive N_2 in the process of denitrification; a portion is often converted to the
28 intermediate products, NO and N_2O .

29 30 **5.5.1 Terrestrial**

31 The 1993 AQCD concluded that N deposition could have large impacts on terrestrial
32 systems and the impact of N deposition should consider total N in the system rather than just the

1 oxidized forms. Nitrogen deposited to an N-deficient ecosystem is generally expected to
2 increase growth. If N is deposited on an ecosystem with adequate N or saturated with N, NO_3^-
3 leaching is expected to occur. Much of the information presented in the 1993 AQCD was based
4 on results from studies of forest systems. N saturation was known to be more common in older
5 forests. Disturbances such as fire and harvesting would push ecosystems to a state of lower N
6 saturation. Forest fertilization was known to produce growth increases in N-deficient forests in
7 the short-term. However little was known about long-term effects of N fertilization and the
8 differential growth effects on various tree and herbaceous plant species. It was known that plants
9 do not necessarily benefit from added N. When N is to the point that it no longer limiting,
10 deficiencies of other nutrients can occur (Aber et al., 1989). A few studies documented the
11 deleterious affects of excessive N on tree growth and grassland biodiversity. Alpine ecosystems,
12 were identified as particularly sensitive to N deposition. The studies published since the 1993
13 AQCD generally support the conclusions of the 1993 AQCD, provide more information on the
14 long-term effects of N deposition, and expand the knowledge of effects to include more
15 ecosystems and species.

16

17 **5.5.1.2 Ecological Effects**

18 Factors that govern the sensitivity of terrestrial ecosystems to nutrient enrichment from N
19 deposition include the degree of N-limitation, rates and form of N deposition, elevation, species
20 composition, length of growing season, and soil N retention capacity. Very little is known about
21 the extent and distribution of the terrestrial ecosystems in the United States that are most
22 sensitive to adverse impacts due to nutrient enrichment from atmospheric N deposition. Based
23 largely on results obtained in more extensive studies in Europe, it is expected that the more
24 sensitive ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and
25 nutrient-poor grassland ecosystems. Effects are most likely where areas of relatively high
26 atmospheric N deposition intersect with N-limited plant communities. Table 4.3-1 summarizes
27 the ecological effects of N deposition on terrestrial ecosystems in the western United States
28 where N effects are likely to be important and have been studied in recent years.

29

30 **5.5.1.2.1 Biochemical Effects**

31 Decades of atmospheric deposition of N have increased the availability of NO_3^- and
32 NH_4^+ in some terrestrial ecosystems. It is important to note that N saturation does not need to

1 occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation
2 does occur to levels at which excess N availability results in net nitrification and associated NO_3^-
3 leaching in drainage water. Substantial leaching of NO_3^- from forest soils to streamwater can
4 acidify downstream waters (See section 5.4.2) and deplete soils of nutrient base cations,
5 especially Ca and Mg (Likens et al., 1998).

6 7 **5.5.1.2.2 Biological Effects: Plant, Lichen, and Mycorrhizae Communities**

8 Atmospheric inputs of N cause increased growth rates of some vascular and non-vascular
9 plants species. Thus, N deposition can alter competitive relationships among species, which may
10 alter species composition and diversity of plant communities. These kinds of species shifts and
11 ecosystem changes can occur even if the ecosystem does not exhibit signs of N saturation. In
12 general, the most sensitive forest ecosystems in the United States are expected to be those that
13 are naturally adapted to very low nutrient supply.

14 15 *Forest Plant Communities*

16 This section includes both woody and herbaceous vascular plants that occur in forest
17 ecosystems. In general forest ecosystems in the United States that are most impacted by nutrient
18 enrichment from nitrogen deposition are expected to be those that now receive high levels of N
19 deposition and that are naturally adapted to very low nutrient supply. Such forests are known to
20 exist in the greater Los Angeles area. Nitrogen saturation has also been found to occur in the red
21 spruce and northern hardwood forests of the northeastern United States, at high-elevation in the
22 southeastern United States, and in the unglaciated regions of the mid-Atlantic that have been
23 impacted by acidic deposition.

- 24 • In most upland forested areas in the United States, most N received in atmospheric
25 deposition is retained in soil (Nadelhoffer et al., 1999). Several different data
26 compilations indicate that 80% to 100% of N deposition is retained or denitrified
27 within terrestrial ecosystems that receive less than about $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Dise and
28 Wright, 1995; Sullivan, 2000; MacDonald et al., 2002; Aber et al., 2003; Kristensen
29 et al., 2004).
- 30 • Two of the primary indicators of N enrichment in forested watersheds are the
31 leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water,
32 especially during the growing season (Stoddard, 1994). The concentration of NO_3^- in

- 1 surface water provides an indication of the extent to which atmospherically deposited
2 (or otherwise added) N leaches from the terrestrial ecosystem. In northeastern and
3 some southeastern forests that receive atmospheric N deposition higher than about
4 $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$, elevated concentrations of NO_3^- in surface waters are common (Aber
5 et al., 2003), which suggests that their watersheds are also receiving excess N input
6 above vegetative demand.
- 7 • Experimental N additions to forest ecosystems have elicited positive growth
8 responses in some, but not all, species (Emmett, 1999; Elvir et al., 2003; DeWalle
9 et al., 2006; Högberg et al., 2006).
 - 10 • Forest growth enhancement can potentially exacerbate other nutrient deficiencies,
11 such as Ca, Mg, or K, thereby causing problems with forest health.
 - 12 • Enhanced growth generally occurs mainly above ground level. This can cause
13 changes in the shoot-to-root ratio, which can be detrimental to the plant because of
14 decreased resistance to environmental stressors, such as drought.
 - 15 • In conifer forests, multiple long-term experiments have demonstrated transient
16 growth increases (generally at deposition lower than $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) followed by
17 increased mortality, especially at higher rates of fertilization (Elvir et al., 2003;
18 Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).
 - 19 • In the western United States, atmospheric N deposition has been shown to cause
20 increased litter accumulation and carbon storage in above-ground woody biomass,
21 which in turn may lead to increased susceptibility to more severe fires (Fenn et al.,
22 2003a).
 - 23 • N deposition could be increasing growth of forest trees slightly in some regions,
24 especially in portions of the eastern United States where O_3 levels and drought
25 occurrence are low.
 - 26 • Negative effects on understory herbaceous communities of increasing N deposition
27 include species shifts towards nitrophilous and more acid-tolerant plant species along
28 a deposition gradient from 6 to $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in Swedish oak forests, decline in
29 abundance and cover of ericaceous shrubs along a deposition gradient from less than
30 3 to more than $12 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the boreal forest in Sweden, and decline in

1 herbaceous cover under hardwoods following 3 years of N additions applied as
2 $(\text{NH}_4)_2\text{SO}_4$ at rates ranging from 14 to 28 kg N ha⁻¹ yr⁻¹ (Gilliam, 2006).

3 4 *Grasslands*

5 Grasslands communities that are adapted to low nutrient supply can exhibit substantial
6 sensitivity to nutrient enrichment effects of N deposition. Several grassland studies have
7 demonstrated that increased N availability led to an overall decrease in plant species richness and
8 an increase in exotic nitrophilous grasses that displace native species.

- 9 • In the San Francisco Bay area of California, which receives N deposition levels of 10
10 to 15 kg N ha⁻¹ yr⁻¹, exotic nitrophilous grasses have displaced native grass species,
11 likely due to greater N availability from deposition and from the cessation of grazing,
12 which previously exported N out of the system (Fenn et al., 2003a).
- 13 • Change in species composition and richness in response to N deposition have been
14 observed regardless of soil type in European grasslands. Such effects have been
15 found in calcareous, neutral, and acidic environments, species-rich heaths, and
16 montane-subalpine grasslands (Stevens et al., 2004; Bobbink et al., 1992, 1998;
17 Bobbink, 1998). Stevens et al. (2004) report a linear relationship between species
18 diversity and N deposition.
- 19 • In general, data with which to quantify grassland sensitivity in the United States are
20 largely not available. Nevertheless, it is expected that increased N supply can alter
21 species composition, increase productivity, and contribute to increased herbivory
22 (Tilman and Wedin, 1991; Wedin and Tilman, 1996; Stevens et al., 2004; Throop and
23 Ler dau, 2004).

24 25 *Arid and Semi-Arid Lands*

26 Arid and semi-arid plant community changes resulting from experimental nitrogen
27 fertilization have been reported in the Chihuahuan Desert, Colorado Plateau, Mojave Desert,
28 Joshua Tree National Park in California, and the coastal sage shrub community of southern
29 California.

- 30 • In semi-arid ecosystems, results from several N fertilization experiments showed (1)
31 increased biomass of non-native plant species over native species, (2) decreased soil
32 moisture under some conditions, and (3) increased fire risk where dense grasses

1 replaced shrub cover. More than 30 kg N/ha/year of atmospheric nitrogen is
2 deposited to this ecosystem in portions of the Los Angeles Air Basin (Bytnerowicz
3 and Fenn, 1996).

- 4 • In the coastal sage shrub community of southern California, dry N deposition is very
5 high. Native shrub and forb seedlings in this plant community are unable to compete
6 with dense stands of exotic grasses, and thus are gradually replaced by the grasses,
7 especially following disturbances such as fire (Eliason and Allen, 1997; Yoshida and
8 Allen, 2001; Cione et al., 2002). The coastal sage shrub community in California has
9 been declining in land area and in shrub density over about the past 60 years and is
10 being replaced in many areas by Mediterranean annual grasses (Allen et al., 1998;
11 Padgett and Allen, 1999; Padgett et al., 1999). N deposition is considered a possible
12 cause or contributor to this ecosystem alteration.
- 13 • Several lines of evidence suggest that N deposition may be contributing to greater
14 fuel loads, thus altering the fire cycle in a variety of ecosystem types. Invasive
15 grasses, which can be favored by high N deposition, promote a rapid fire cycle in
16 many locations. The increased productivity of flammable understory grasses
17 increases the spread of fire and has been hypothesized as one mechanism for the
18 recent conversion of shrub vegetation types to grassland in southern California.

19 *Alpine Plant Communities*

20 Alpine plant communities are considered among most sensitive terrestrial communities to
21 nutrient-enrichment from atmospheric N deposition.

- 22 • Factors that govern the sensitivity of alpine tundra to N deposition include low rates
23 of primary production, short growing season, low temperature, and wide variation in
24 moisture availability in the alpine environment (Bowman and Fisk, 2001). Alpine
25 plant communities have also developed under conditions of low nutrient supply, in
26 part because soil-forming processes are poorly developed, and this also contributes to
27 their N-sensitivity.
- 28 • The western United States contains extensive land areas that receive low levels of
29 atmospheric N deposition, interspersed with hot spots of relatively higher N
30

1 deposition downwind of large metropolitan centers and agricultural areas. Some of
2 these areas of higher nitrogen deposition occur at high elevation.

- 3 • Effects of N deposition on alpine ecosystems in the western United States are thought
4 to include community-level changes in plants, lichens, and mycorrhizae. Subtle
5 effects have been shown to occur at what would be considered relatively low levels of
6 N deposition (about 3 to 5 kg N ha⁻¹ yr⁻¹).
- 7 • N deposition to the alpine tundra of Niwot Ridge in the Colorado Front Range altered
8 N cycling and provided the potential for replacement of some native plant species by
9 more competitive, faster growing species.

10 11 *Lichens*

- 12 • Sensitive lichen species appear to be negatively affected by N inputs as low as 3 to 8
13 kg ha⁻¹ yr⁻¹ (Fenn et al., 2003a).
- 14 • In the San Bernardino Mountains, California, up to 50% of lichen species that
15 occurred in the region in the early 1900s have disappeared (Nash and Sigal, 1999;
16 Fenn et al., 2003a).
- 17 • The Pacific Northwest retains widespread populations of pollution-sensitive lichens
18 (Fenn et al., 2003a). In this area, lichen communities are beginning to show evidence
19 of changes in response to increased N pollution, including decreased distribution of
20 sensitive lichen taxa, and their replacement with nitrophilous species (Geiser and
21 Neitlich, 2007).

22 23 *Mycorrhizae*

- 24 • Biodiversity impacts on microbial communities have been documented in coastal
25 sage scrub ecosystems. It has been hypothesized that the decline in coastal sage
26 shrub species could be linked to the decline of the arbuscular mycorrhizal community
27 (Egerton-Warburton and Allen, 2000).
- 28 • Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N
29 cycling and for the growth and health of plants. Changes in soil N can influence
30 mycorrhizal-plant relationships in the rhizosphere. Mycorrhizal fungal diversity has
31 been shown to be associated with above-ground plant biodiversity and ecosystem

1 productivity (Wall and Moore, 1999) and to be adversely affected by increased N
2 availability (Egerton-Warburton and Allen, 2000).

3 4 **5.5.2 Transitional**

5 Anaerobic conditions of water-logged soils in wetlands result in slow decomposition of
6 organic matter and rapid denitrification. N cycles of two types of wetland, ombrotrophic bogs
7 and coastal salt marshes, were discussed in 1993 AQCD for oxides of nitrogen. Ombrotrophic
8 bogs are generally considered the most sensitive to atmospheric N deposition because they are
9 nutrient poor, with a closed N cycle in which the predominant source of N is rainfall. The 1993
10 AQCD found that the three main ecological effects of N deposition on wetland ecosystem are:
11 (1) increasing primary production; (2) modifying microbial processes; and (3) reducing
12 biodiversity and altering ecosystem structure. The studies since 1993 support and extend the
13 conclusions in the 1993 AQCD, especially with regard to the impacts of N deposition on species
14 diversity.

15 16 **5.5.2.2 Ecological Effects**

17 18 **5.5.2.2.1 Biochemical Effects**

19 N dynamics in wetland ecosystems are variable in time and with type of wetland and
20 environmental factors, especially water availability (Howarth et al., 1996). A wetland can act as
21 a source, sink, or transformer of atmospherically deposited N (Devito et al., 1989) and these
22 functions can vary with season and with hydrological conditions. Vegetation type,
23 physiography, local hydrology, and climate all play significant roles in determining source/sink
24 N dynamics in wetlands (Devito et al., 1989; Koerselman et al., 1993; Arheimer and Wittgren,
25 1994; Mitchell et al., 1996).

26 Wetlands and other transitional ecosystems can remove NO_3^- via denitrification.
27 Previous studies suggest that elevated N inputs to wetlands will often increase the rate of
28 denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This
29 process increases the contribution of NO_2 and NO to the atmosphere, each of which can have
30 adverse consequences. However, denitrification reduces NO_3^- levels in soils and leaching into
31 drainage waters and associated environmental effects. Although denitrification has been
32 observed to increase with N addition, N mineralization has also been shown to increase, and this

1 can cause a net increase in wetland N export to adjacent surface water (Groffman, 1994).
2 Denitrification appears to be negligible in wetland environments that are typically nutrient
3 (including N) poor, such as some bogs and fens (Morris, 1991).

4 5 **5.5.2.2.2 Biological Effects**

6 7 *Ecosystem Function*

- 8 • Primary production of transitional ecosystem is commonly limited by N availability.
9 Typically, phosphorous is secondarily limiting after N. N fertilization experiments in
10 salt marsh ecosystems show biomass stimulation from 6 to 413% with application
11 rates ranging from 7 to 3120 kg N ha⁻¹ yr⁻¹, and the change of plant production is not
12 a linear function of the rate of N application (U.S. Environmental Protection Agency,
13 1993a).
- 14 • The form of N applied is shown to regulate plants and microbial responses in
15 transitional ecosystem. NH₄⁺ produces a greater stimulation of plant productivity
16 than NO₃⁻ does because plants have a preference for NH₄⁺ over NO₃⁻ as an N source.
17 Increasing soil NH₄⁺ concentration inhibits the activity of N-fixing bacteria, whereas
18 increased NO₃⁻ concentration favors N₂O production and inhibits N₂ production via
19 denitrification process.
- 20 • Elevated atmospheric N deposition stimulates leaf growth more than root growth and
21 can cause changes in plant carbon allocation, such as increase plant shoot-to-root
22 ratio. Increasing N availability can also increase N concentration in leaf tissues,
23 which has been shown to increase microbial litter decomposition activity.
- 24 • Increases in biomass linked to N deposition, have also increased evapotranspiration
25 (Howes, 1986). This changed the soil water balance of water and may influence the
26 direction of plant community succession. Model results suggest 7 kg N ha⁻¹ yr⁻¹ is
27 the threshold in which an oligotrophic bog would be influenced to become a
28 mesotrophic bog dominated by trees (conclusion from 1993 NO_x AQCD).

29 30 *Species and Community-Level*

- 31 • Wetlands considered sensitive to nitrogen deposition typically contain plant species
32 that have evolved under nitrogen-limited conditions.

- 1 • Wetlands contain a disproportionately high number of rare plant species. Excess N
2 deposition can cause shifts in wetland communities composition by altering
3 competitive relationships among species, which potentially leads to effects such as
4 decreasing biodiversity, increasing non-native species establishment and increasing
5 the risk of extinction for sensitive and rare species.
- 6 • Changes in plant species composition caused by elevated atmospheric N deposition
7 haven been demonstrated in Europe. Diverse plant communities have been converted
8 into monospecific stands dominated by *Molina caerulea* or *Deschampsia flexuosa* in
9 Dutch wet heathlands. However, it is not clear to what extent such effects occur
10 under ambient N deposition levels in the United States.
- 11 • Some wetland species, such as *Sphagnum squarrosum*, *Sphagnum fallax*, and
12 *Drosera rotundifolia*, are adapted to low-N environments. High levels of
13 atmospheric N deposition will increase the risk of decline and extinction of those
14 sensitive species.
- 15 • *Sarracenia purpurea* can be used as a biological indicator of local N deposition in
16 some locations (Ellison and Gotelli, 2002). *S. purpurea* is a perennial pitcher plant
17 native to Canada and the eastern United States that grows in nutrient-poor peatlands
18 and is sensitive to changes in N availability. Within a single growing season,
19 increasing N availability switches the plant from producing carnivorous pitchers to
20 producing more photosynthetically efficient phyllodia.

21 22 **5.5.2.2.3 Regional Trends**

- 23 • Bogs are among the most sensitive transitional ecosystems to the effects of N
24 deposition. In the CONUS, peat-forming bogs are most common in areas that were
25 glaciated, especially in portions of the Northeast and Upper Midwest (U.S.
26 Environmental Protection Agency, 1993a).
- 27 • N input and output rates of fens are intermediate between bogs and coastal marshes.
28 N deposition could drastically change species composition, increase primary
29 productivity and increase methane emission in fens (Pauli et al., 2002; Aerts and
30 de Caluwe, 1999).

- 1 • Atmospheric N inputs probably contribute to eutrophication problems in coastal
2 marshes at many locations, especially along the Atlantic and Gulf coasts.
- 3 • Table (5.5-1) compares N fluxes ($\text{g N m}^{-2} \text{yr}^{-1}$) from wetlands classified according to
4 the importance of atmospheric deposition to the total N budgets.

5 6 **5.5.3 Freshwater Aquatic**

7 General conclusions of the 1993 AQCD for oxides of nitrogen indicated that productivity
8 of fresh water is usually limited by the availability of phosphorus. However, it was noted high
9 inputs of phosphorus from anthropogenic sources could lead to N limitation occurring. The ratio
10 of dissolved organic N to total phosphorous was used as an indicator for nutrient limitation, with
11 values less than 2 indicating N limitation. The proportions of N limited lakes show wide
12 regional variation: Pacific Northwest (27.7%), Upper Midwest (19%), Northeast (5%),
13 Southeast (2.5%). All sub regions of the West contain substantial numbers of N limited lakes.

14 15 **5.5.3.2 Ecological Effects**

16 A freshwater lake or stream must be N-limited in order to be sensitive to N-mediated
17 eutrophication. Although conventional wisdom holds that most lakes and streams in the United
18 States are limited by phosphorus, recent evidence illustrates examples of lakes and streams that
19 are limited by N and show symptoms of eutrophication.

20 21 **5.5.3.2.1 Biogeochemical Effects**

22 In agreement with the 1993 AQCD, productivity of freshwater ecosystems is generally
23 limited by the availability of phosphorus. However, new information indicates many surface
24 waters in remote locations are limited by nitrogen. Such waters receive low atmospheric inputs
25 of nitrogen, and this may explain their nitrogen-limited condition.

26 27 **5.5.3.2.2 Biological Effects**

28 The following biological indicators can be used to assess the eutrophic condition of
29 aquatic ecosystems:

- 30 • Chlorophyll *a*: Increased N deposition leads to increased productivity and increased
31 chlorophyll *a*, resulting in decreased water clarity as well as decreased dissolved
32 oxygen.

- 1 • Phytoplankton Biomass: Increased N deposition leads to increased phytoplankton
2 biomass.
- 3 • Periphyton Biomass: N deposition generally stimulated periphyton biomass
4 productivity in N-limited lakes.
- 5 • Nitrate Toxicity: Extremely high NO_3^- concentrations can have direct adverse effects
6 on fish, invertebrates and amphibians, but the concentrations required to elicit such
7 effects are typically more than 30 times higher than those that would commonly be
8 attributable to atmospheric deposition. For example, mortality of rainbow trout eggs
9 and fry occurred after 30-day incubations in concentrations greater than $79 \mu\text{g N/L}$;
10 adverse effects on amphibians and insects occur at even higher concentrations.

11 Increased N deposition can cause a shift in community composition and reduce algal
12 biodiversity.

- 13 • Elevated N deposition results in changes in algal species composition, especially at
14 sensitive high elevation lakes in the western United States.
- 15 • Opportunistic algae, such as *Asterionella formosa* and *Fragilaria crotonensis*,
16 respond rapidly to nutrient enrichment and gain competitive advantage over others
17 species.

18 19 **5.5.3.2.3 Regional Trends**

20 Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of
21 greatest concern in lakes and streams that have very low productivity and nutrient levels and that
22 are located in remote areas.

- 23 • In the western United States, high-elevation lakes are considered the most sensitive
24 aquatic ecosystems to N deposition. Some examples include the Snowy Range in
25 Wyoming, the Sierra Nevada Mountains, and Lake Tahoe in California, and the
26 Colorado Front Range.
- 27 • The most severe eutrophication from N deposition effects are expected downwind of
28 major urban and agricultural centers.
- 29 • N deposition appears to have stimulated productivity and altered algal species
30 assemblages in some high-elevation lakes in the western United States at low
31 deposition rates of 1.5 to $2.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. It appears that many high-elevation

1 oligotrophic western lakes may be N limited, whereas lower elevation lakes are more
2 typically phosphorus limited.

- 3 • The change in lake algae that occurred in Rocky Mountain National Park between
4 1950 and 1964, based on the paleolimnological record, was associated with a level of
5 wet N deposition that was estimated to have been only about 1.5 kg N/ha.

6 7 **5.5.4 Estuarine Aquatic**

8 The 1993 AQCD for Oxides of Nitrogen concluded that the primary N nutrient addition
9 effect on aquatic ecosystems is eutrophication of estuarine and near-coastal marine waters, which
10 results in an increase of algal biomass and changes in community composition. Studies
11 published since 1996 generally support the conclusions of 1993 AQCD. The data for estimating
12 the contribution of N deposition to the nutrient budget of aquatic ecosystems were very sparse
13 and mainly limited to the Chesapeake Bay before 1993. The contribution of nitrogen deposition
14 to estuarine eutrophication is now better understood in the Chesapeake Bay and other estuaries.

15 16 **5.5.4.2 Ecological Effects**

17 A recent national assessment of eutrophic conditions in estuaries found that 65% of the
18 assessed systems had moderate to high overall eutrophic conditions and generally received the
19 greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al.,
20 2007). Estuarine and coastal marine ecosystems experience a range of ecological problems
21 associated with nutrient enrichment. Because the productivity of estuarine and near shore marine
22 ecosystems is generally limited by the availability of N_r , excessive contribution of N_r from
23 sources of water and air pollution can contribute to eutrophication.

24 25 **5.5.4.2.1 Biogeochemical Effects**

26 Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to
27 increased atmospheric N loading (D'Elia et al., 1986; Howarth and Marino, 2006). This is at
28 least partly because denitrification by microbes found in estuarine and marine sediments releases
29 much of the added N inputs back into the atmosphere (Vitousek et al., 1997). However, other
30 limiting factors occur in some locations and during some seasons. Levels of N limitations are
31 affected by seasonal patterns. N-deficient conditions are likely to be found during the peak of
32 annual productivity in the summer.

1 Excess N inputs will affect the Si:N ratio in water. If the Si:N ratio drops below about 1,
2 the marine food web structure would be expected to change, with decreasing diatom-to-
3 zooplankton-to-higher tropic level ratios and increasing abundance of flagellated algae.

4 5 **5.5.4.2.2 Biological Effects**

6 Increased N deposition can cause shifts in community composition reduce algale
7 biodiversity, and mortality of submerged aquatic vegetation (SAV). The form of deposited N
8 can significantly affect phytoplankton community composition in estuarine and marine
9 environments. Small diatoms are more efficient in using NO_3^- than NH_4^+ . Increasing NH_4^+
10 deposition relative to NO_3^- in the eastern United States favors small diatoms at the expense of
11 large diatoms. This alters the foundation of the food web. SAV is important to the quality of
12 estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms,
13 absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor
14 contributing to declines in SAV coverage. The Mid-Atlantic region is the most heavily impacted
15 area in terms of moderate or high loss of SAV due to eutrophication.

16 The following biological measurements can be used to assess the eutrophic condition of
17 estuarine and coastal waters:

- 18 • Chlorophyll *a*: excess N input will stimulate primary productivity. High levels of
19 chlorophyll *a* indicates a high phytoplankton biomass.
- 20 • Macroalgal Abundance: Macroalgal blooms were moderate or high for half of the
21 nation's assessed estuaries (Bricker et al., 2007). Macroalgal blooms can cause the
22 loss of important SAV by blocking sunlight.
- 23 • Dissolved Oxygen: Dissolved oxygen concentration decreases with increasing algal
24 abundance under elevated N, because microbes consume oxygen as they decompose
25 dead algae. Increased atmospheric N deposition if sufficiently high, could stimulate
26 the development of hypoxic or anoxic zones. The northern Gulf of Mexico is the
27 largest documented zone of hypoxic coastal water in United States.
- 28 • Nuisance/Toxic Algal Blooms: Excess N input can cause nuisance or toxic algal
29 blooms, which release toxins in the water that can poison aquatic animals and
30 threaten human health. About one third of the nation's assessed estuary systems

1 exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker
2 et al., 2007).

3 4 **5.5.4.2.3 Regional Trends**

5 The most eutrophic estuaries were generally those that had large watershed-to-estuarine
6 surface area, high human population density, high rainfall and runoff, low dilution, and low
7 flushing rates (Bricker et al., 2007). The national estuary condition assessment conducted by
8 Bricker et al. (2007) found the most impacted estuaries occurred in the mid-Atlantic region and
9 the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. Other
10 regions had mixtures of low, moderate, and high degree of eutrophication. The regional
11 assessment results from the report of Bricker et al. (2007) are summarized in Table 5.5-2.

12 13 **5.5.5 Case Studies**

14 15 **5.5.5.1 Chesapeake Bay**

16 The Chesapeake Bay is the largest estuary in United States. Its watershed covers 64,299
17 square miles ² and the surface area of the bay and its major tributaries is 4,479 square miles
18 (Pyzik et al., 2004). The Chesapeake Bay is perhaps the best-documented case study in the
19 United States of the effects of human activities on estuarine eutrophication. Recent studies
20 (Boyer et al., 2002; Howarth, 2007) indicated that atmospheric deposition makes a substantial
21 contribution (about 25%) to the overall N budget of Chesapeake Bay. Human disturbances, such
22 as landscape changes, have exacerbated the negative impacts of N deposition by reducing N
23 removal and retention in the upper watershed region. Anthropogenic N inputs have substantially
24 altered the trophic condition of Chesapeake Bay over the last 50 to 100 years. Symptoms of
25 eutrophication in the bay include high algal production, low biodiversity, and large hypoxia and
26 anoxia zones. SAV was once abundant in Chesapeake Bay, covering about 200,000 acres along
27 the shallows and shorelines. Increased nutrient inputs caused SAV declines since the mid-1960s
28 and the SAV community had fallen to about 38,000 acres by 1984. Eutrophication has been
29 implicated in declines and disappearance of striped bass (*Morone saxatilis*) and blue crab
30 (*Callinectes sapidus*) in Chesapeake Bay.

1 **5.5.5.2 Alpine and Subalpine Communities of the Eastern Slope of the Rocky**
2 **Mountains in Colorado**

3 Research on N enrichment effects on alpine and subalpine ecosystems in the western
4 United States has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain
5 National Park and the Niwot Ridge Long Term Ecosystem Research site, both located east of the
6 Continental Divide in Colorado. Research has been conducted in this region on both the
7 terrestrial and aquatic effects of nutrient enrichment. Some key findings are summarized below:

- 8 • Changes in plant species composition may be detectable at lower N deposition rates
9 than the level at which the traditional soil indicators signal ecosystem responses to N
10 deposition, and changes in species composition are probably ongoing in alpine dry
11 meadows of the Front Range of the Colorado Rocky Mountains at current ambient
12 atmospheric N deposition levels.
- 13 • Results from several studies suggest that the capacity of Rocky Mountain alpine
14 catchments to sequester N is exceeded at input levels less than 10 kg N ha⁻¹ yr⁻¹
15 (Baron et al., 1994; Williams and Tonnessen, 1999).
- 16 • Rocky Mountain National Park has been the site of research addressing the effects of
17 N deposition on algal species abundance in freshwater lakes. Two species of diatom,
18 *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least
19 several alpine and montane lakes, and this has been attributed to atmospheric N
20 deposition.

21
22
23 **5.6 OTHER WELFARE EFFECTS**

24
25 **5.6.1 Deposition of Sulfur Oxides Affect Mercury Methylation**

26 S deposition contributes to secondary effects on the cycling and bioavailability of Hg, a
27 highly neurotoxic contaminant. Research suggests that S deposition influences the cycling of Hg
28 in wetland and aquatic ecosystems by stimulating SO₄²⁻-reducing bacteria associated with Hg
29 methylation, a key process that increases the bioavailability of Hg. The rates of methylation are
30 influenced by oxygen content, temperature, pH, and the concentration of organic acids in
31 solution. Mercury methylation occurs in anoxic sediments that contain a sufficient carbon source
32 to support SO₄²⁻-reducing bacterial activity along with an adequate supply of SO₄²⁻. Wetland

1 environments are significant areas of methylmercury (CH₃Hg) production and sources of export
2 to downstream receiving waters (St. Louis et al., 1994). The wetland ecosystems that are likely
3 to exhibit high levels of Hg methylation can be found in the northeastern United States and
4 southeastern Canada.

5 6 *Chemical Indicators*

- 7 • Studies have shown a strong negative correlation between surface water pH and Hg
8 concentration in fish tissue, but the mechanisms responsible for this linkage are not
9 clear. Hg concentrations in fish have also been shown to be less strongly correlated
10 with a variety of other variables, including (DIC), Ca, Mg, (DOC), sodium, lake area,
11 and watershed area.
- 12 • Total Hg and CH₃Hg concentrations are often positively correlated with DOC in lake
13 waters. Dissolved organic carbon, in turn, has an important influence on pH. DOC
14 may bind with CH₃Hg at very high DOC concentration, limiting the bioavailability of
15 the Hg.
- 16 • One study showed that lakes with Hg levels above the EPA criterion of 0.3 µg/g in
17 yellow perch had significantly higher DOC, and lower pH, ANC, and total
18 phosphorus than lakes with fish Hg concentrations below 0.3 µg/g (Driscoll et al.,
19 2007b).

20 21 *Case Study*

- 22 • Little Rock Lake is an 18 ha precipitation-dominated seepage lake located in a
23 forested and undisturbed catchment of north-central Wisconsin. Results from the
24 Little Rock Lake acidification experiments suggest that S deposition plays an
25 important role in the accumulation and methylation of Hg in freshwater ecosystems.

26 27 **5.6.2 Direct Phytotoxic Effects of Gaseous Sulfur and Nitrogen on** 28 **Vegetation**

29 30 **5.6.2.1 SO₂**

31 The current secondary standard for SO₂ is a 3-h average of 0.50 ppm, which is designed
32 to protect vegetation against acute foliar injury. There has been limited research on acute foliar

1 injury since the last SO₂ AQCD and there is no clear evidence of acute foliar injury below the
2 level of the current standard.

3 Effects on growth and yield of vegetation are associated with increased SO₂ exposure
4 concentration and time of exposure. The 1982 SO₂ AQCD concluded that more definitive
5 concentration-response studies were needed before useable exposure metrics could be identified.
6 Because of falling ambient SO₂ concentrations and focus on O₃ vegetation effects research, few
7 studies have emerged to better inform a metric and levels of concern for effects of SO₂ on
8 growth and productivity of vegetation.

9
10 **5.6.2.2 NO and NO₂**

11 It has been well known that in sufficient concentrations NO and NO₂ have the potential to
12 have phytotoxic effects on plants through decreasing photosynthesis and induction of visible
13 foliar injury (U.S. Environmental Protection Agency, 1993a). The 1993 NO_x AQCD concluded
14 that concentrations of NO₂ and NO in the atmosphere are rarely high enough to have phytotoxic
15 effects on vegetation (U.S. Environmental Protection Agency, 1993a). Since the 1993 AQCD,
16 very little new research has been done on these phytotoxic effects to alter this conclusion.

17
18 **5.6.2.3 Peroxyacetyl Nitrate (PAN)**

19 Although peroxyacetyl nitrate (PAN) remains an important component of photochemical
20 pollutant episodes and negative effects on plants have been observed, there is little evidence in
21 recent years suggesting that PAN poses a significant risk to vegetation in the United States.

22
23 **5.6.3 N₂O**

24 N₂O is a GHG with a global warming potential (GWP) on the conventional 100-year time
25 horizon of ~296 (i.e., N₂O is nearly 300 times more effective for trapping heat in the atmosphere
26 than CO₂ over a 100-year period) (IPCC, 2007). The largest U.S. emissions of GHGs are from
27 CO₂, followed by CH₄ and N₂O (83.3%, 7.4%, and 6.5% of total GHG emissions from the
28 United States on a Tg CO₂ equivalents basis, respectively) in 2005 (U.S. Environmental
29 Protection Agency, 2007b). GHGs work together to force global climate change. A rigorous
30 assessment of this process is provided by the International Panel on Climate Change (IPCC,
31 2007), and the adverse effects of climate change on welfare in North America are assessed in
32 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 SO₂ as the chemical indicator and has an annual 3-h maximum average of 0.5 ppm. The secondary NAAQS for nitrogen oxides has NO₂ 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

1 ecosystem sensitivity, which is predominantly governed by the underlying geologic composition
2 that serves as soil parent material. Regions where vulnerable ecosystems occur in the United
3 States include New England, the Appalachian Mountains, and the Upper Midwest and high
4 elevation areas of the East. The ISA focuses on two case studies for which to provide more
5 detail: The Adirondacks (NY) and Shenandoah National Park. In the Adirondacks, the current
6 rates of NO_x and SO_x deposition exceed the level that would allow recovery of the most acid
7 sensitive lakes. In the Shenandoah, sulfate has accumulated in the soil from past deposition
8 making this region sensitive to current loading. The accumulated sulfur is slowly leaching from
9 the soil into stream water, where it causes acidification. Modeling results suggest the number of
10 acidic streams will increase under the current deposition levels and re-acidification may be
11 prevented if deposition is kept between $9\text{-}15 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $0\text{-}6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$.

12 Ecosystem nitrogen enrichment is caused by atmospheric NO_x and NH_x deposition in
13 combination with all other forms of reactive Nitrogen loading in ecosystems. Additions of N
14 promote growth in some ecosystems and causes significant biologically adverse effects in others.
15 For example, low-level chronic nitrogen deposition can act as a fertilizer and increase
16 productivity of some forests, but cause the mortality of other organisms in that occur in the same
17 forests, such as lichens. In general, ecosystems adapted to low nitrogen availability or those that
18 are N limited are most sensitive to the effects of nitrogen deposition (e.g. Alpine ecosystems, CA
19 coastal sage scrub, ombrotrophic wetlands and estuaries). Excess nitrogen to vulnerable
20 ecosystems can cause “nitrogen pollution”, resulting in a suite of terrestrial and aquatic
21 ecological problems including species mortality, biodiversity losses, altered community species
22 composition and biochemical function, eutrophication and harmful algal blooms. Deposition
23 levels of approximately $2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ are reported to cause alterations in algal communities of
24 freshwater lakes (Colorado), changes in foliar N concentration (Colorado), and increased CO_2
25 emissions from peat bog wetlands (Europe). Mortality of lichen species occurs at 3 kg N
26 $\text{ha}^{-1} \text{ yr}^{-1}$ (Wet coast). Deposition levels of $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ correlate to the onset of declining
27 biodiversity within grasslands in the UK. At approximately $8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ many forest
28 ecosystems begin to leach nitrate into stream and ground water.

29 Eutrophication of estuaries is a particularly detrimental ecological problem to which
30 atmospheric deposition of NO_x and NH_x contribute. In highly eutrophic estuaries the
31 contribution of atmospheric deposition to total loads can be greater than 40%. Eutrophication

1 causes water quality deterioration, resulting in numerous adverse effects including (but not
 2 limited to): hypoxic zones, species mortality, and harmful algal bloom. The Chesapeake Bay is
 3 an example of a large well-studied estuary that receives 21-30% of its total N load from the
 4 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 ($1.77 \mu\text{eq L}^{-1} \text{yr}^{-1}$), Adirondack lakes ($2.26 \mu\text{eq L}^{-1} \text{yr}^{-1}$), Appalachian streams ($2.27 \mu\text{eq L}^{-1} \text{yr}^{-1}$), and Upper Midwest lakes ($3.36 \mu\text{eq L}^{-1} \text{yr}^{-1}$).
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 $[\text{SO}_4^{2-} + \text{NO}_3^-]$ 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 $[\text{SO}_4^{2-} + \text{NO}_3^-]$ 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 $20 \mu\text{eq/L}$ 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 (<i>organic Al</i>) 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 <i>inorganic Al</i> 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 <i>in situ</i> 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 ($0.08 \mu\text{eq L}^{-1} \text{yr}^{-1}$) and Upper Midwest lakes ($0.01 \mu\text{eq L}^{-1} \text{yr}^{-1}$). 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		Wet Heathland
	Water Marshes (g N m ⁻² yr ⁻¹)	Fens (g N m ⁻² yr ⁻¹)	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 <i>Deyeucia angustifolia</i>	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)

6. REFERENCES

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