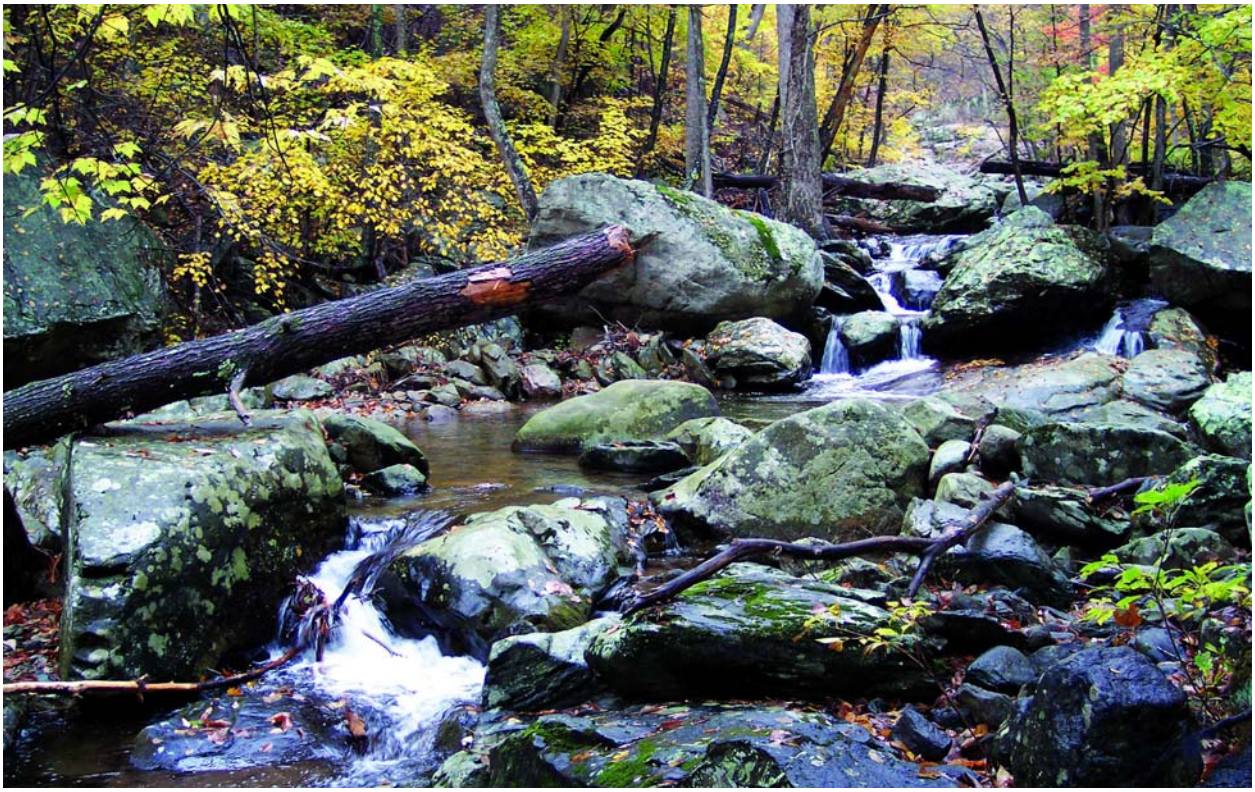
Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur

Final

Main Content



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U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Health and Environmental Impacts Division
Research Triangle Park, NC

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ACRONYMS AND ABBREVIATIONS

Al	aluminum$^{2+,3+}$
AM	arbuscular mycorrhizae
AN	acid anions (NO_3^- and SO_4^{2-})
ANC	acid neutralizing capacity
AQCD	Air Quality Criteria Document
ASSETS EI	Assessment of Estuarine Trophic Status eutrophication index
Bc	base cation ($Ca^{2+} + K^+ + Mg^{2+}$)
BC	base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$)
Bc_u	base cation ($Ca^{2+} + K^+ + Mg^{2+}$) uptake
Bc_w	base cation ($Ca^{2+} + K^+ + Mg^{2+}$) weathering
BC_w	base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$) weathering
Bc/Al	base cation to aluminum ratio
$(Bc/Al)_{crit}$	base cation to aluminum ratio (indicator)
C	carbon
Ca^{2+}	calcium
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAF	Coastal Assessment Framework
CAFO	confined animal feeding operation
CAIR	Clean Air Interstate Rule
CAL FIRE	California Department of Forestry and Fire Protection
CASAC	Clean Air Scientific Advisory Committee
CASTNET	Clean Air Status and Trends Network
CH_4	methane
Cl^-	chloride
CLF	critical load function
cm	centimeter
CMAQ	Community Multiscale Air Quality
CO_2	carbon dioxide
CS_2	carbon disulfide
CSS	coastal sage scrub
DFO	Determined Future Outlook
DIN	dissolved inorganic nitrogen
DL	depositional load
DO	dissolved oxygen
DOC	dissolved organic carbon
DOI	U.S. Department of the Interior
EC	ecosystem carbon content
EES	Ecological Effects Subcommittee
EGU	electric generating unit
EMAP	Environmental Monitoring and Assessment Program
EPA	U.S. Environmental Protection Agency
ESRI	Environmental Systems Research Institute, Inc.

FASOMGHG	Forest and Agriculture Sector Optimization Model – Greenhouse Gas version
FHWAR	Fishing, Hunting, and Wildlife-Associated Recreation
FIA	Forest Inventory and Analysis
GHG	greenhouse gas
GIS	geographic information systems
GPP	gross primary productivity
H^+	hydrogen ion
H_2O	water
H_2S	hydrogen sulfide
H_2SO_4	sulfuric acid
ha	hectare
HAB	harmful algal bloom
HBEF	Hubbard Brook Experimental Forest
HFC	hydrofluorocarbon
Hg^{2+}	divalent mercury
Hg^0	elemental mercury
HNO_3	nitric acid
HONO	nitrous acid
HUC	hydrologic unit code
ICP	International Cooperative Programme
IDW	inverse distance weighted
IPCC	Intergovernmental Panel on Climate Change
IPM	Integrated Planning Model
ISA	Integrated Science Assessment
K^+	potassium
KEF	Kane Experimental Forest
kg	kilogram
kg/ha/yr	kilograms per hectare per year
K_{gibb}	gibbsite equilibrium constant
km	kilometers
LTER	Long-Term Ecological Research
LTM	Long-Term Monitoring
m	meters
MAGIC	Model of Acidification of Groundwater in Catchments
MAHA	Mid-Atlantic Highlands Assessment
MCF	mixed conifer forest
MCIP	Meteorology-Chemistry Interface Processor
MEA	Millennium Ecosystem Assessment
mg/L	milligrams per liter
Mg^{2+}	magnesium
MSA	metropolitan statistical area
N	nitrogen
N_{de}	denitrification
N_i	nitrogen immobilization
N_r	total reactive nitrogen

N_{ret}	retention of nitrogen
N_u	nitrogen uptake
N_2	nitrogen gas
N_2O	nitrous oxide
N_2O_3	nitrogen trioxide
N_2O_4	nitrogen tetroxide
N_2O_5	dinitrogen pentoxide
Na^+	sodium
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NAWQA	National Water Quality Assessment
NEE	net ecosystem exchange
NEEA	National Estuarine Eutrophication Assessment
NEI	National Emissions Inventory
NEP	net ecosystem productivity
NH_3	ammonia
NH_4^+	ammonium
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NH_x	reduced nitrogen
NLCD	National Land Cover Data
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	nitrite
NO_3^-	nitrate
NO_x	nitrogen oxides
NO_y	total oxidized nitrogen
NOAA	National Oceanic and Atmospheric Administration
NPP	net primary productivity
NRC	National Research Council
NSRE	National Survey on Recreation and the Environment
NSWS	National Surface Water Survey
NTN	National Trends Network
NTR	organic nitrate
O_2	oxygen
O_3	ozone
OAQPS	Office of Air Quality Planning and Standards
OEC	Overall Eutrophic Condition
OH^-	hydroxide
OHI	Influencing Factors/Overall Human Influence
ORD	Office of Research and Development
PAN	peroxyacetyl nitrates
PFC	perfluorocarbons
PM	particulate matter
$PM_{2.5}$	fine particulate matter less than 2.5 microns in size

ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
REMAP	Regional Environmental Monitoring and Assessment Program
RFNRP	Regional Forest Nutrition Research Project
RSM	response-surface model
S	sulfur
S_{ret}	retention of sulfur
S_2O	disulfur monoxide
$S_2O_3^{2-}$	thiosulfate
$S_2O_7^{2-}$	sulfur heptoxide
SAB	Science Advisory Board
SAV	submerged aquatic vegetation
SF_6	sulfur hexafluoride
Si	silicon
SMB	Simple Mass Balance
SO	sulfur monoxide
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_4^{2-}	sulfate
SO_x	sulfur oxides
SOM	soil organic matter
SPARROW	SPAtially Referenced Regression on Watershed Attributes
SRB	sulfate-reducing bacteria
SSURGO	Soil Survey Geographic Database
STORET	STORage and RETrieval
TIME	Temporally Integrated Monitoring of Ecosystems
TN	total nitrogen
TN_{atm}	total nitrogen atmospheric loading
TN_s	instream total nitrogen concentration
TP	total phosphorus
U.S. EPA	U.S. Environmental Protection Agency
USFS	United States Forest Service
USGS	U.S. Geological Survey
VIF	variance inflation factor
VOC	volatile organic carbon
WTP	willingness to pay
μeq/L	microequivalent per liter
μg/g	microgram per gram
$\mu g/m_3$	microgram per cubic meter
μM	micromolar

KEY TERMS

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, such as underlying geology, base cation concentrations, and weathering rates.

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

Adverse Effect: The response or component of an ecosystem that is deemed harmful in its function.

Air Quality Indicator: The substance or set of substances (e.g., fine particulate matter [$PM_{2.5}$], nitrogen dioxide [NO_2], sulfur dioxide [SO_2]) occurring in the ambient air for which the National Ambient Air Quality Standards (NAAQS) set a standard level and monitoring occurs.

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.

Arid Region: A land region of low rainfall, where "low" is widely accepted to be less than 250 millimeters (mm) of precipitation per year.

Assessment Endpoint: An ecological entity and its attributes that are considered welfare effects, as defined in Clean Air Act Section 302(h), and that are analyzed in the assessment.

ASSETS Rating: Assessment of Estuarine Trophic Status that builds on the U.S. National Estuarine Eutrophication Assessment developed by National Oceanic and Atmospheric Administration. The Overall Eutrophic Condition, Overall Human Influence, and Determination of Future Outlook are combined to provide a single eutrophication assessment rating for an estuary in one of five categories: high, good, moderate, poor, or

bad. These categories provide a scale for setting eutrophication-related reference conditions for different types of transitional waters.

ASSETS rating *High*: Low pressure from influencing factors, low overall eutrophic condition OEC, and any expected improvement or no future change in eutrophic condition.

ASSETS rating *Good*: Low to moderate pressure, low to moderate-low eutrophic condition, and any expected future change in condition.

ASSETS rating *Moderate*: Any pressure, moderate-low to moderate-high eutrophic condition, and any expected future change in eutrophic condition.

ASSETS rating *Poor*: Moderate-low to high pressure, moderate to moderate-high eutrophic condition, and any expected future change in condition.

ASSETS rating *Bad*: Moderate to high pressure, moderate-high to high eutrophic condition, and any expected future change in eutrophic condition.

ASSETS rating *Unknown*: Insufficient data for analysis.

Atmospheric Deposition Transformation Function: Process by which ambient atmospheric concentrations of NO_x and So_x are translated into a nitrogen and sulfur deposition metric.

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 acidic. There is a threshold whereby soils with base saturations less than 20% (especially between 10% and 20%) are extremely sensitive to change.

Biologically Relevant Indicator: A physical, chemical, or biological entity/feature that demonstrates a consistent degree of response to a given level of stressor exposure and that is easily measured/quantified to make it a useful predictor of biological, environmental, or ecological risk.

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 nitrogen oxides (NO_x; e.g., nitrate or nitrite) to gaseous nitrogen (e.g., nitrous oxide [N_2O] or gaseous nitrogen [N_2]) by denitrifying bacteria.

Determined Future Outlook: This index provides an assessment of the susceptibility of the system (in terms of the capacity of a system to dilute and/or flush nutrients) and a categorical indicator of foreseeable changes in nutrient loads. Predictions of nutrient loading (i.e., increase, decrease, unchanged) are based on expected population increase, planned management actions, and expected changes in watershed uses, and as such, are heuristically determined. A matrix is used for the final definition of the Determined Future Outlook index and shows that, conceptually, systems with slower flushing (i.e., higher susceptibility) are expected to improve at a slower rate than those of lower susceptibility if nutrient inputs are decreased in the future.

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

Ecological Dose: The concentration of a toxicant that causes an effect (i.e., morbidity or mortality) in an organism. This measure may be acute or chronic and may have an effect over a period of time.

Ecological Effect Function: Process by which deposition of nitrogen and sulfur is related to a given ecological indicator.

Ecological Exposure: The exposure of a nonhuman organism to an environmental stressor.

Ecological Risk: The likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (U.S. EPA, 1992).

Ecological Risk Assessment: A process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (U.S. EPA, 1992).

Ecosystem: The interactive system formed from all living organisms and their abiotic (i.e., 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.

Ecosystem Benefit: The value, expressed qualitatively, quantitatively, and/or in economic terms, where possible, associated with changes in ecosystem services that result either directly or indirectly in improved public welfare. Examples of ecosystem benefits that derive from improved air quality include improvements in habitats for sport fish species, the quality of drinking water and recreational areas, and visibility.

Ecosystem Function: The processes and interactions that operate within an ecosystem. Such processes include but are not limited to nutrient flow, energy flow, water dynamics, and the flux of trace gases.

Ecosystem Services: The ecological processes or functions having monetary or nonmonetary value to individuals or society at large. These are (1) supporting services, such as productivity or biodiversity maintenance; (2) provisioning services, such as food, fiber, or fish; (3) regulating services, such as climate regulation or carbon sequestration; and (4) cultural services, such as tourism or spiritual and aesthetic appreciation.

Ecosystem Structure: Refers to species' composition, stratification, and interactions with some abiotic attributes of the environment and with each other as they vary through space and time.

Elasticity: The percentage of change in the response variable for a 1% change in the input physical or meteorological characteristic.

Eutrophication: The process by which nitrogen additions stimulate the growth of autotrophic biota, usually resulting in the depletion of dissolved oxygen.

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 vapor (H_2O), carbon dioxide (CO_2), N_2O, methane (CH_4), and ozone (O_3) are the primary greenhouse gases in the earth's atmosphere. In addition to CO_2, N_2O, and CH_4, the Kyoto Protocol deals with the greenhouse gases sulfur hexafluoride (SF_6), hydrofluorocarbons, and perfluorocarbons.

Key Elements of Secondary National Ambient Air Quality Standards:

(a) Indicators

(1) Air Quality Indicator (for secondary NAAQS): The air pollutant(s) whose concentration(s) in the ambient air is (are) measured for purposes of determining compliance with the NAAQS. An indicator may either be the actual criteria air pollutant listed in the Clean Air Act or an appropriate surrogate. For example, NO_2 is the current indicator for the primary and secondary NO_x NAAQS and represents all NO_x, while the current indicator for the primary and secondary sulfur oxides (SO_x) NAAQS is SO_2, representing all SO_x.

(2) Ecological Indicator: A characteristic of an ecosystem that can provide quantitative information on its ecological condition. An indicator can be or contribute to a measure of integrity and sustainability. For example, one indicator of increasing acidification effects in an aquatic ecosystem is a decrease in acid neutralizing capacity (ANC). A decrease in ANC can lead to acidification of stream water, and thereby, to changes to fish community structure, a good indicator of overall stream health.

(b) Level (of secondary NAAQS): The specified value of the indicator or metric (see definition below) that is judged requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of the criteria pollutant in ambient air. The current level of the secondary NO_2 NAAQS indicator is 0.053 parts per million (ppm) (same as primary). The current level of the secondary SO_2 NAAQS

indicator is 0.5 ppm. The level of the W126 metric proposed in the 2007 O_3 secondary NAAQS proposal was 21 ppm-hrs.

(c) Averaging Time (for secondary NAAQS): The period of time over which exposure to metric values at or above the level of the standard is considered relevant. Over that time period, concentrations are averaged or cumulated to determine whether the level of the standard has been met. Examples include 3-hour, 8-hour, 24-hour, seasonal, or annual averages. The current averaging time for the secondary NO_2 NAAQS is a year. The current averaging time for the secondary SO_2 NAAQS is 3 hours.

(d) Form (of secondary NAAQS): The statistical characteristics of a standard that determine the stringency, stability, and robustness of that standard when implemented. For example, the current secondary O_3 standard is set at the level of 0.075 ppm, averaged over an 8-hour period. To attain this standard, however, only the 3-year average of the fourth-highest daily maximum (rather than the maximum itself) 8-hour average O_3 concentrations measured at each monitor within an area over each year is compared to the level of the standard and must not exceed 0.075 ppm. The current form of the secondary NO_2 NAAQS is the annual arithmetic mean. The current form of the secondary SO_2 NAAQS is not to be exceeded more than once per year.

Maximum Depositional Load: The maximum amount of nitrogen and/or sulfur deposition that a given ecosystem can receive without the degradation of the ecological indicator for a targeted effect.

Nitrogen Saturation: The point at which nitrogen inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem; a level beyond nutrient enrichment.

Nutrient Enrichment: The process by which a terrestrial system becomes enhanced by nutrient additions to a degree that stimulates the growth of plant or other terrestrial biota, usually resulting in an increase in productivity.

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

Overall Eutrophic Condition: An ASSETS index meaning an estimate of current eutrophic conditions derived from data for five symptoms known to be linked to eutrophication.

Overall Human Influence: An ASSETS index meaning physical, hydrologic, and anthropogenic factors that characterize the susceptibility of the estuary to the influences of nutrient inputs (also quantified as part of the index) and eutrophication.

Semi-arid Regions: Regions of moderately low rainfall that are not highly productive and are usually classified as rangelands. "Moderately low" is widely accepted as between 250 and 500 mm of 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, nutrient enrichment). The effect may be direct (e.g., a change in growth in response to a change in the mean, range, or variability of nitrogen deposition) or indirect (e.g., changes in growth due to the direct effect of nitrogen consequently altering competitive dynamics between species and decreased biodiversity).

Target Load: A policy-based metric that takes into consideration such factors as economic costs and time frame for emissions reduction. The target load can be lower than the critical load if a very sensitive area is to be protected in the short term, especially if deposition rates exceed critical loads.

Total Reactive Nitrogen: All biologically, chemically, and radiatively active nitrogen compounds in the atmosphere and biosphere, such as ammonia gas (NH_3), ammonium ion (NH_4^+), nitric oxide (NO), nitrite (NO_2^-), nitric acid (HNO_3), N_2O, nitrate (NO_3^-), and organic compounds (e.g., urea, amines, nucleic acids).

Uncertainty: A measure of the knowledge of the magnitude of a parameter. Uncertainty can be reduced by research (i.e., the parameter value can be refined). Uncertainty is quantified as a distribution. For example, the volume of a lake may be estimated from its surface area and an average depth. This estimate can be refined by measurement (Webster and MacKay, 2003).

Valuation: The economic or noneconomic 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.

Variability: The degree to which values in a distribution differ from each other. Variability can be measured as range, mean, variance and standard deviation.

Variable Factors: Influences that, by themselves or in combination with other factors, may alter the effects of an air pollutant on public welfare [Clean Air Act Section 108 (a)(2)].

(a) Atmospheric Factors: Atmospheric conditions, such as precipitation, relative humidity, oxidation state, and co-pollutants present in the atmosphere, that may influence transformation, conversion, transport, and deposition, and thereby, the effects of an air pollutant on public welfare.

(b) Ecological Factors: Ecological conditions that may influence the effects of an air pollutant on public welfare once it is introduced into an ecosystem, such as soil base saturation, soil thickness, runoff rate, land use conditions, bedrock geology, and weathering rates.

Vulnerability: The degree to which a system is susceptible to and unable to cope with the adverse effects of NO_x and/or SO_x air pollution.

Welfare Effects: The effects on soils, water, crops, vegetation, manmade 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. [Clean Air Act Section 302(h)].

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

REFERENCES

U.S. Environmental Protection Agency (EPA). 1992. Framework for ecological risk assessment. Washington, DC: Risk Assessment Forum, U.S. Environmental Protection Agency. EPA/630/R-92/001.

Webster, E., and D. MacKay. 2003. *Defining Uncertainty and Variability in Environmental Fate Models*. CEMC Report No. 200301. Canadian Environmental Modelling Centre, Trent University, Peterborough, ON, Canada.

RISK AND EXPOSURE ASSESSMENT FOR REVIEW OF THE SECONDARY NATIONAL AMBIENT AIR QUALITY STANDARDS FOR OXIDES OF NITROGEN AND OXIDES OF SULFUR

EXECUTIVE SUMMARY

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is conducting a joint review of the existing secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for nitrogen oxides (NO_x) and sulfur oxides (SO_x).[1] A joint secondary review of these pollutants is being conducted because the atmospheric chemistry and environmental effects of NO_x, SO_x, and their associated transformation products are linked, and because the National Research Council (NRC) has recommended that EPA consider multiple pollutants, as appropriate, in forming the scientific basis for the NAAQS. This is the first time since the NAAQS were established in 1971 that a joint review of NO_x, SO_x, as well as of total reactive nitrogen, has been conducted.

OVERVIEW OF NITROGEN AND SULFUR IN THE ENVIRONMENT

Under Section 108 of the Clean Air Act, the secondary standard is to specify an acceptable level of the criteria pollutant(s) in the ambient air that is protective of known or anticipated adverse effects to public welfare. For this review, the relevant atmospheric indicators are ambient NO_x and SO_x concentrations that can be linked to levels of deposition for which there are known or anticipated adverse ecological effects. The ecological effects of nitrogen and sulfur are caused both by the gas-phase and atmospheric deposition of the

> The sum of mono-nitrogen oxides, nitrogen dioxide (NO_2), and nitric oxide (NO) are typically referred to as nitrogen oxides (NO_x) in the atmospheric science community. More formally, the family of NO_x includes any gaseous combination of nitrogen and oxygen (e.g., NO_2, NO, nitrous oxide [N_2O], nitrogen trioxide [N_2O_3], nitrogen tetroxide [N_2O_4], and dinitrogen pentoxide [N_2O_5]).
>
> Sulfur dioxide (SO_2) is one of a group of substances known as oxides of sulfur, or SO_x, which include multiple gaseous substances (e.g., SO_2, sulfur monoxide [SO], sulfur trioxide [SO_3], thiosulfate [S_2O_3], and heptoxide [S_2O_7], as well as particulate species, such as ammonium sulfate [$(NH_4)_2SO_4$]).

[1] EPA is also conducting independent reviews of the primary (health-based) NAAQS for NO_x and SO_x. For documents related to this review, see http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html.

pollutants. The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase NO_x or SO_x, such as foliar injury, decreased photosynthesis, and decreased growth.

Deposition of nitrogen- and sulfur-containing compounds that are derived from NO_x and SO_x may be wet (e.g., rain, snow), cloud and fog deposition, or dry (e.g., gases and particles) and can affect ecosystem biogeochemistry, structure, and function. Nitrogen and sulfur interactions in the environment are highly complex. Both are essential nutrients, and nitrogen can sometimes be limiting for productivity. Excess nitrogen (both oxidized and reduced forms) or sulfur can lead to acidification, and excess nitrogen can lead to nutrient enrichment and eutrophication. Acidification causes a cascade of effects that alter both terrestrial and aquatic ecosystems. When fully developed, acidification effects include lower biomass production rates, the injury and/or death of forest vegetation, and localized loss and extinction of fish and other aquatic species. In addition to contributing to acidification, NO_x acts with other forms of reactive nitrogen (including reduced nitrogen) to increase the total amount of available nitrogen in ecosystems.

Nitrogen deposition alone can alter numerous biogeochemical indicators, including primary productivity that leads to changes in community composition and eutrophication. In aquatic ecosystems, alterations in freshwater lake diatom communities and impaired water quality in the western United States have been observed. In estuarine ecosystems, additional nitrogen from anthropogenic atmospheric sources contributes to the total nitrogen loading and to increased phytoplankton and algal productivity, which leads to eutrophication.

In terrestrial ecosystems, nitrate leaching is a well-documented phenomenon indicating that an ecosystem is receiving nitrogen in excess of biotic nutritional needs. Nitrogen deposition affects primary productivity, thereby altering terrestrial carbon cycling. This may result in shifts in population dynamics, species composition, community structure, and in extreme instances, ecosystem type. Lichens are the most nitrogen-sensitive terrestrial taxa, with documented adverse effects in the Pacific Northwest and in Southern California. Declining biodiversity within grasslands due to nitrogen deposition has also been observed in the central United States, along with changes in biodiversity in other ecosystems such as coastal sage scrub (CSS), mixed conifer forest (MCF) in California, and alpine ecosystems in the Rocky Mountains.

A summary illustration of NO_x and SO_x effects on the environment is presented in **Figure ES-1**.

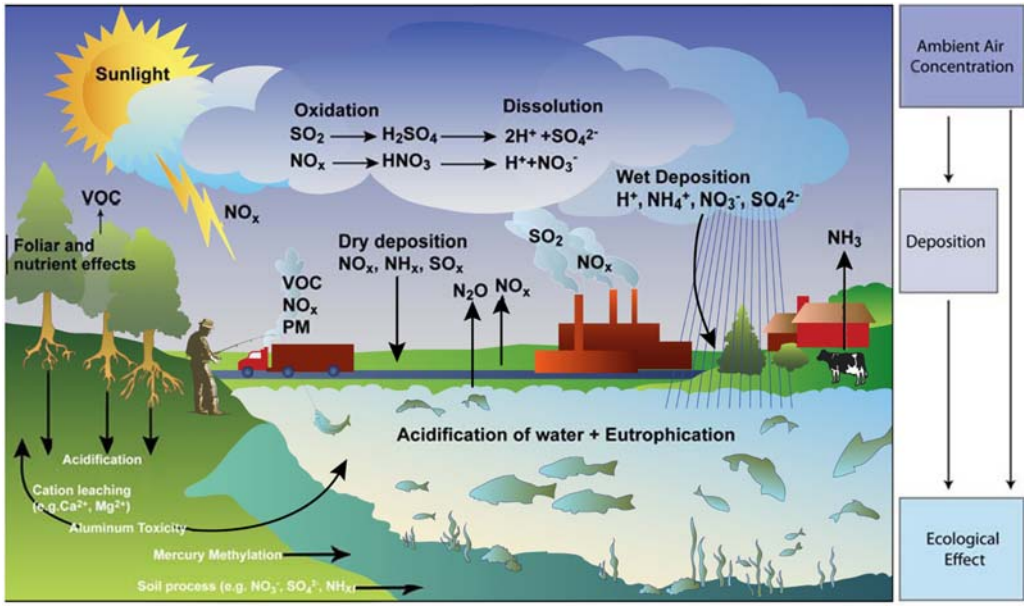


Figure ES-1. Nitrogen and sulfur cycling, and interactions in the environment.

RISK AND EXPOSURE ASSESSMENT APPROACH

Figure ES-2 shows the conceptual model framing this review describing a possible structure for establishing secondary standards based on meaningful ecological indicators that provides for protection against the range of potentially adverse ecological effects that are associated with the deposition of NO_x, NH_x, and SO_x. In creating this framework, consideration has been given as to how the basic elements of NAAQS standards—indicator, averaging time, form, and level—would be reflected in such a structure.

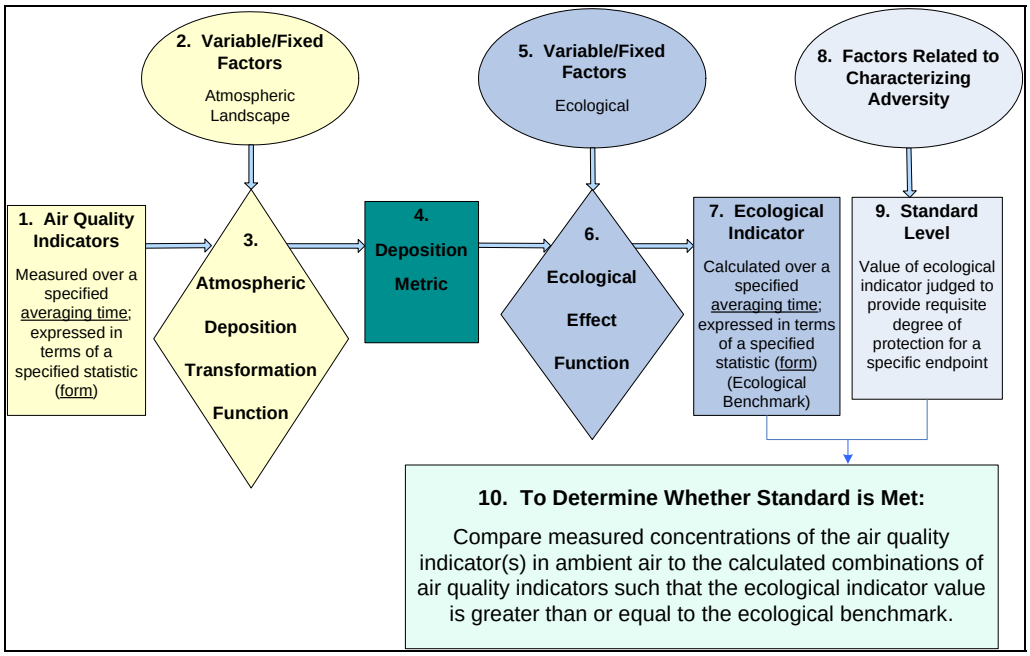


Figure ES-2. Possible structure of a secondary NAAQS for NO_x and SO_x based on an ecological indicator.

The framework shown in **Figure ES-2** provides an example of how an ecologically meaningful secondary NAAQS might be structured. This example presents a system of linked functions that translate an air quality indicator (e.g., concentrations of NO_x and SO_x) into an ecological indicator that expresses either the potential for deposition of nitrogen and sulfur to acidify an ecosystem, or for nitrogen to over-enrich an ecosystem. This system encompasses the linkages between ambient air concentrations and resulting deposition metrics, as well as between the deposition metric and the ecological indicator of concern. For example, the atmospheric deposition transformation function (see box 3, **Figure ES-2**) translates ambient air concentrations of NO_x and SO_x to nitrogen and sulfur deposition metrics, while the ecological effect function (see box 6, **Figure ES-2**) relates the deposition metric into the ecological indicator. These two functions are very difficult to derive, taking into account geographical and seasonal variability of the relationship between concentrations and deposition, as well as uncertainty associated with measurements and model predictions.

The amounts of NO_x and SO_x in the ambient air can be used to derive a deposition metric (via the atmospheric deposition transformation function), which can then be used to derive a level of an ecological indicator (through the ecological effect function) that falls within the range defined as acceptable by the standard; by definition, the levels of NO_x and SO_x will be

considered to meet that standard of protection. The atmospheric levels of NO_x and SO_x that satisfy a particular level of ecosystem protection are those levels that result in an amount of deposition that is less than the amount of deposition a given ecosystem can accept without degradation of the ecological indicator for a targeted ecosystem effect.

Because ecosystems differ in biota, climate, geochemistry, and hydrology, response to pollutant exposures can vary greatly between ecosystems. This Risk and Exposure Assessment addresses four main ecosystem effects identified in the 2008 *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)*(ISA):

- Aquatic acidification due to nitrogen and sulfur
- Terrestrial acidification due to nitrogen and sulfur
- Aquatic nitrogen enrichment, including eutrophication
- Terrestrial nitrogen enrichment.

Since these ecosystem effects are not evenly distributed across the United States, case studies have been developed for these analyses based on ecosystems identified as sensitive to nitrogen and/or sulfur deposition effects. This assessment builds upon the scientific information presented in the ISA, and ecological indicator(s) and case study locations were selected based on this information. The case study areas that were identified and analyzed for the Risk and Exposure Assessment are described in **Table ES-1,** along with a summary of the ecosystem characteristics, indicators, and ecosystem service information regarding these areas. A map highlighting each of the case study areas is shown in **Figure ES-3**.

Table ES-1. Summary of Sensitive Characteristics, Indicators, Effects, and Impacted Ecosystem Services Analyzed for Each Case Study Evaluated in This Review

Targeted Ecosystem Effect	Characteristics of Sensitivity (Variable Ecological Factors)	Biological/Chemical Indicator	Ecological Endpoint	Ecological Effects	Ecosystem Services Impacted	Case Study Areas
Aquatic Acidification	Geology, surface water flow, soil depth, weathering rates	Al pH ANC	Species richness, abundance, composition, ANC	Species losses of fish, phytoplankton, and zooplankton; changed community composition, ecosystem structure, and function	Subsistence fishing, recreational fishing, other recreational activities	Adirondack Mountains, NY (referred to as Adirondack) Shenandoah National Park, VA (referred to as Shenandoah)
Terrestrial Acidification	Geology, surface water flow, soil depth, weathering rates	Soil base saturation Al Ca C:N ratio	Tree health of red spruce and sugar maple, ANC, Bc:Al ratio	Decreased tree growth, increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure, and function	Provision of food and wood products, recreational activities, natural habitat, soil stabilization, erosion control, water regulation, climate regulation	Kane Experimental Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)
Aquatic Nutrient Enrichment	Nitrogen-limited systems, presence of nitrogen in surface water, eutrophication status, nutrient criteria	Chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, submerged aquatic vegetation (SAV)	Changes in Eutrophication Index (EI)	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Commercial and recreational fishing, other recreational activities, aesthetic value, nonuse value flood and erosion control	Potomac River Basin, Chesapeake Bay (referred to as Potomac River/Potomac Estuary) Neuse River Basin, Pamlico Sound (referred to as Neuse River/Neuse River Estuary)
Terrestrial Nutrient Enrichment	Presence of acidophytic lichens, anthropogenic land cover	Cation exchange capacity, C:N ratios, Ca:Al ratios, NO_3^- leaching and export	Species composition, lichen presence/absence, soil root mass changes, NO_3 breakthrough to water, biomass	Species changes, nutrient enrichment of soil, changes in fire regime, changes in nutrient cycling	Recreation, aesthetic value, nonuse value, fire regulation, loss of habitat, loss of biodiversity, water quality	Coastal Sage Scrub (southern, coastal California) and Mixed Conifer Forest (San Bernardino Mountains of the Transverse Range and Sierra Nevada Mountain Ranges, California); Rocky Mountain National Park (a supplemental study area)

Note: ANC = acid neutralizing capacity, SAV = submerged aquatic vegetation, EI = eutrophication index.

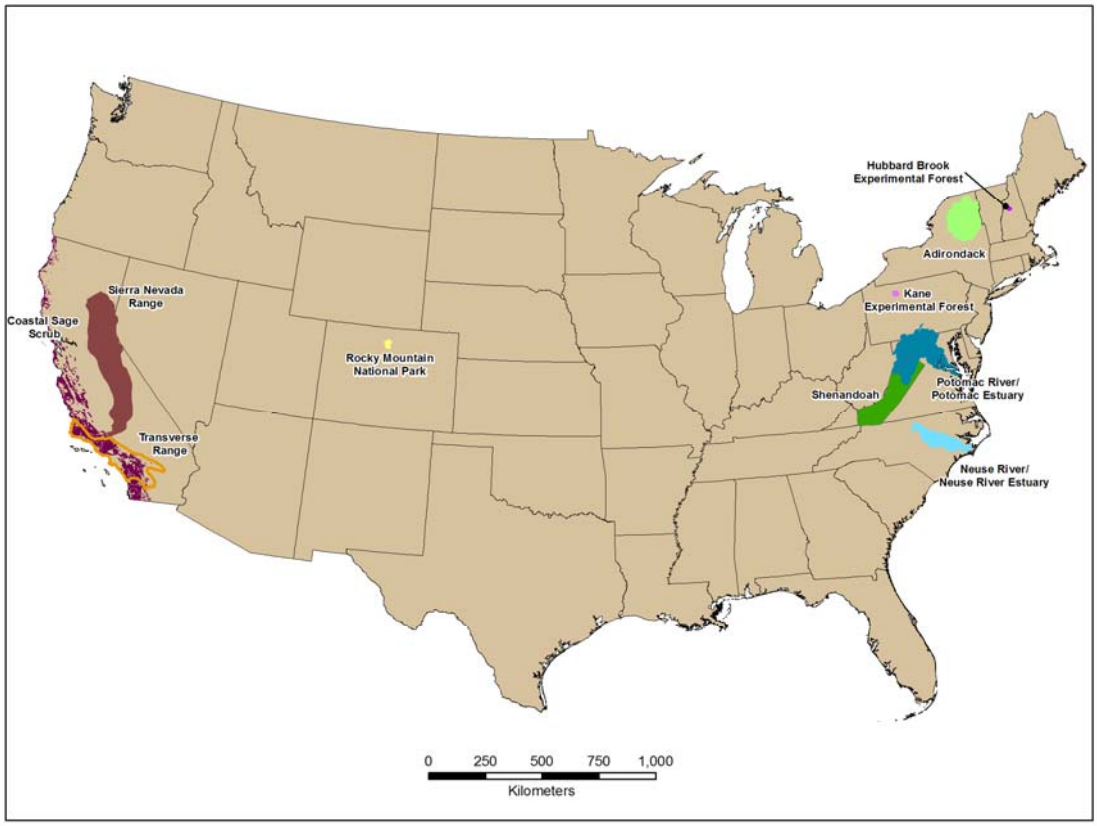


Figure ES-3. National map highlighting the 8 case study areas and the Rocky Mountain National Park (a supplemental study area) evaluated in the Risk and Exposure Assessment.

For assessing this set of secondary NAAQS, in addition to assessing the degree of scientific impairment of ecological systems relating to inputs of NO_x and SO_x, this Risk and Environmental Assessment presents an overview of the concept of ecosystem services. The analysis of the effects on ecosystem services will help link what is considered to be a biologically adverse effect with a known or anticipated adverse effect to public welfare. In this Risk and Exposure Assessment, ecosystem services is used to show the impacts of ecological effects on public welfare and to help explain how these effects are viewed by the public. The ability to inform decisions on the level of a secondary NAAQS will require the development of clear linkages between biologically adverse effects and effects that are known or anticipated to be adverse to public welfare. The concept of adversity to public welfare does not require the use of ecosystem services, yet it is envisioned as a beneficial tool for this review that may provide more information on the linkages between changes in ecological effects and known or anticipated adverse public welfare effects.

As described in the EPA's *Ecological Benefits Assessment Strategic Plan*, it is necessary to recognize that in the analysis of the environmental responses associated with any particular policy or environmental management action, some of the ecosystem services likely to be affected are readily identified, while others will remain unquantified. Of those ecosystem services that are identified, some changes can be quantified, whereas others will remain unidentified. Within those services whose changes are quantified, only a few will likely be monetized, and many will remain unmonetized. Similar to health effects, only a portion of the ecosystem services affected by a policy can be monetized. A conceptual model integrating the role of ecosystem services in characterizing known or anticipated adverse effects to public welfare is shown in **Figure ES-4**.

Knowledge about the relationships linking ambient concentrations and ecosystem services can be used to inform a policy judgment on a known or anticipated adverse public welfare effect. The conceptual model outlined for aquatic acidification in **Figure ES-4** can be modified for any targeted effect area where sufficient data and models are available. This information can then be used to characterize known or anticipated adverse effects to public welfare and to inform a policy based on welfare effects.

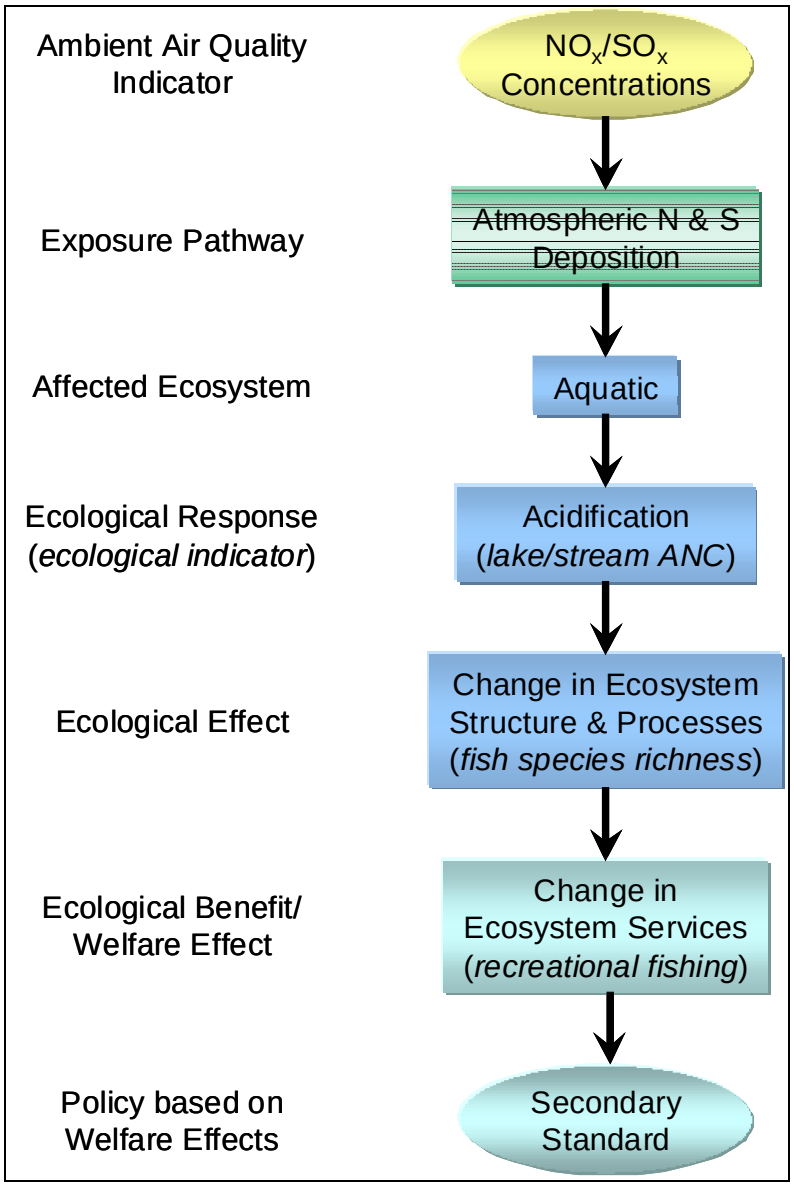


Figure ES-4. Conceptual model showing the relationships among ambient air quality indicators and exposure pathways and the resulting impacts on ecosystems, ecological responses, ecological effects, and finally, on the quality of a particular activity (e.g., recreational fishing) known to influence public welfare.

KEY FINDINGS

The case study analyses in this Risk and Exposure Assessment have shown that, from a scientific perspective, there is confidence that known or anticipated adverse ecological effects are occurring under current ambient loadings of nitrogen and sulfur in sensitive ecosystems across the United States. Key findings from the air quality analyses, acidification and nutrient

enrichment case studies, as well as general conclusions from evaluating additional welfare effects, are presented below.

AIR QUALITY ANALYSES

The air quality analyses for this review encompass the current emissions sources of nitrogen and sulfur, as well as atmospheric concentrations, estimates of deposition of total nitrogen, policy-relevant background, and nonambient loadings of nitrogen and sulfur to ecosystems, both nationwide and in the case study areas. Spatial fields of deposition were created using wet deposition measurements from the National Atmospheric Deposition Program (NADP) National Trends Network and dry deposition predictions from the 2002 Community Multi-Scale Air Quality (CMAQ) model simulation.

- Total reactive nitrogen deposition and sulfur deposition are much greater in the East compared to most areas of the West.
- These regional differences in deposition correspond to the regional differences in NO_x and SO_2 concentrations and emissions, which are also higher in the East.
- NO_x emissions are much greater and generally more widespread than NH_3 emissions nationwide; high NH_3 emissions tend to be more local (e.g., eastern North Carolina) or sub-regional (e.g., the upper Midwest and Plains states).
- The relative amounts of oxidized versus reduced nitrogen deposition are consistent with the relative amounts of NO_x and NH_3 emissions.
  - Oxidized nitrogen deposition exceeds reduced nitrogen deposition in most of the case study areas; the major exception being the Neuse River/Neuse River Estuary Case Study Area.
  - Reduced nitrogen deposition exceeds oxidized nitrogen deposition in the vicinity of local sources of NH_3.
- There can be relatively large spatial variations in both total reactive nitrogen deposition and sulfur deposition within a case study area; this occurs particularly in those areas that contain or are near a high emissions source of NO_x, NH_3, and/or SO_2.
- The seasonal patterns in deposition differ between the case study areas.
  - For the case study areas in the East, the season with the greatest amounts of total reactive nitrogen deposition correspond to the season with the greatest amounts of

sulfur deposition. Deposition peaks in spring in the Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas, and it peaks in summer in the Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas.

- For the case study areas in the West, there is less consistency in the seasons with greatest total reactive nitrogen and sulfur deposition in a given area. In general, both nitrogen and/or sulfur deposition peaks in spring or summer. The exception to this is the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, in which sulfur deposition is greatest in winter.

ACIDIFICATION

Aquatic

The role of aquatic acidification in two eastern United States areas—northeastern New York's Adirondack area and the Shenandoah area in Virginia—was analyzed to assess surface water trends in $SO_4^{2-}$and NO_3^-concentrations and acid neutralizing capacity (ANC) levels and to affirm the understanding that reductions in deposition could influence the risk of acidification. Monitoring data from the EPA-administered Temporally Integrated Monitoring of Ecosystems (TIME)/Long-Term Monitoring (LTM) programs and the Environmental Monitoring and Assessment Program (EMAP) were assessed for the years 1990 to 2006, and past, present, and future water quality levels were estimated using both steady-state and dynamic biogeochemical models. A summary of findings follows:

Although wet deposition rates for SO_2 and NO_x in the Adirondack Case Study Area have reduced since the mid-1990s, current concentrations in are still well above preacidification (1860) conditions. Model of Acidification of Groundwater in Catchments (MAGIC) modeling predicts NO_3^- and SO_4^{2-} are 17- and 5-fold higher today, respectively. The estimated average ANC for 44 lakes in the Adirondack Case Study Area is 62.1 microequivalents per liter (μeq/L) (± 15.7 μeq/L); 78 % of all monitored lakes in the Adirondack Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 78%, 31% experience episodic acidification, and 18% are chronically acidic today.

- Based on the steady-state critical load model for the year 2002, 18%, 28%, 44%, and 58% of 169 modeled lakes received combined total sulfur and nitrogen deposition that exceeded their critical load, with critical ANC limits of 0, 20, 50, and 100 μeq/L, respectively.
- Based on a deposition scenario that maintains current emission levels to 2020 and 2050, the simulation forecast indicates no improvement in water quality in the Adirondack Case Study Area. The percentage of lakes within the *Elevated* to *Acute Concern* classes remains the same in 2020 and 2050.
- Since the mid-1990s, streams in the Shenandoah Case Study Area have shown slight declines in NO_3^- and SO_4^{2-} concentrations in surface waters. ANC levels increased from about 50 μeq/L in the early 1990 to >75 μeq/L until 2002, when ANC levels declined back to 1991–1992 levels. Current concentrations are still above preacidification (1860) conditions. MAGIC modeling predicts surface water concentrations of NO_3^- and SO_4^{2-} are 10- and 32-fold higher today, respectively. The estimated average ANC for 60 streams in the Shenandoah Case Study Area is 57.9 μeq/L (± 4.5 μeq/L). 55% of all monitored streams in the Shenandoah Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 55%, 18% experience episodic acidification, and 18% are chronically acidic today.
- Based on the steady-state critical load model for the year 2002, 52%, 72%, 85%, and 93% of 60 modeled streams received combined total sulfur and nitrogen deposition that exceeded their critical load, with critical ANC limits of 0, 20, 50, and 100 μeq/L, respectively.
- Based on a deposition scenario that maintains current emission levels to 2020 and 2050, the simulation forecast indicates that a large number of streams still have *Elevated* to *Acute* problems with acidity. In fact, from 2006 to 2050, the percentage of streams with *Acute Concern* increases by 5%, while the percentage of streams in *Moderate Concern* decreases by 5%.

Terrestrial

The role of terrestrial acidification was examined using a critical load analysis for sugar maple and red spruce forests in the eastern United States by using the base cation to aluminum (Bc/Al) ratio in acidified forest soils as an indicator to assess the impact of nitrogen and sulfur

deposition on tree health. These are the two most commonly studied species in North America for impacts of acidification. At a Bc/Al ratio of 1.2, red spruce growth can be reduced by 20%. Sugar maple growth can be reduced by 20% at a Bc/Al ratio of 0.6. Key findings of the case study are summarized below.

- Case study results suggest that the health of at least a portion of the sugar maple and red spruce growing in the United States may have been compromised with acidifying total nitrogen and sulfur deposition in 2002:
  - 2002 CMAQ/NADP total nitrogen and sulfur deposition levels exceeded three selected critical loads in 3% to 75% of all sugar maple plots across 24 states. The three critical loads ranged from 107 to 6,008 eq/ha/yr for the Bc/Al ratios of 0.6, 1.2, and 10.0 (increasing levels of tree protection).
  - 2002 CMAQ/NADP total nitrogen and sulfur deposition levels exceeded three selected critical loads in 3% to 36% of all red spruce plots across 8 states. The three critical loads ranged from 180 to 4,278 eq/ha/yr for the Bc/Al ratios of 0.6, 1.2, and 10.0 (increasing levels of tree protection).
- The Simple Mass Balance model assumptions made for base cation weathering (Bcw) and forest soil ANC input parameters are the main sources of uncertainty since these parameters are rarely measured and require researchers to use default values. Bcw contributed 49% to the total variability in the critical load estimates, and forest soil ANC contributed 46% to the total variability.
- The pattern of case study results suggests that nitrogen and sulfur acidifying deposition in the sugar maple and red spruce forest areas studied were very close to, if not greater than, the critical loads for those areas, and both ecosystems are likely to be sensitive to any future changes in the levels of deposition.

NUTRIENT ENRISHMENT

Aquatic

The role of nitrogen deposition in two mainstem rivers feeding their respective estuaries was analyzed to determine if decreases in deposition could influence the risk of eutrophication as predicted using the Assessment of Estuarine Trophic Status eutrophication index (ASSETS EI) scoring system in tandem with SPAtially Referenced Regression on Watershed Attributes

(SPARROW) modeling. This modeling approach provides a transferrable, intermediate-level analysis of the linkages between atmospheric deposition and receiving waters, while providing results on which conclusions could be drawn. Future application of the methods to case study areas where atmospheric deposition plays a larger role in the nitrogen loading to an estuary will likely provide more tangible results. A summary of findings follows:

- 2002 CMAQ/NADP results showed that an estimated 40,770,000 kg of total nitrogen was deposited in the Potomac River watershed. SPARROW modeling predicted that 7,380,000 kg N/yr of the deposited nitrogen reached the estuary (20% of the total load to the estuary). The overall ASSETS EI for the Potomac River and Potomac Estuary was *Bad*.
- To improve the Potomac River and Potomac Estuary ASSETS EI score from *Bad* to *Poor*, there is a slim chance that a decrease of at least 78% in the 2002 total nitrogen atmospheric deposition load to the watershed would be required.
- 2002 CMAQ/NADP results showed that an estimated 18,340,000 kg of total nitrogen was deposited in the Neuse River watershed. SPARROW modeling predicted that 1,150,000 kg N/yr of the deposited nitrogen reached the estuary (26% of the total load to the estuary). The overall ASSETS EI for the Neuse River/Neuse River Estuary was *Bad*.
- It was found that the Neuse River/Neuse River Estuary ASSETS EI score could not be improved from *Bad* to *Poor* with decreases only in the 2002 atmospheric deposition load to the watershed. Additional reductions would be required from other nitrogen sources within the watershed.

The small effect of decreasing atmospheric deposition in the Neuse River watershed is because the other nitrogen sources within the watershed are more influential than atmospheric deposition to the total nitrogen loadings to the Neuse River Estuary as estimated with the SPARROW model. A waterbody's response to nutrient loading depends on the magnitude (e.g., agricultural sources have a high influence in the Neuse), spatial distribution, and other characteristics of the sources within the watershed.

Terrestrial

California CSS and MCF were the focus of the Terrestrial Nutrient Enrichment Case Study. Geographic information systems (GIS) analysis supported a qualitative review of past field research to identify ecological benchmarks associated with CSS and mycorrhizal

communities, as well as MCF's nutrient-sensitive acidophyte lichen communities, fine-root biomass in Ponderosa pine, and leached nitrate in receiving waters. These benchmarks, ranging from 3.1 to 17 kg N/ha/yr, were compared to 2002 CMAQ/NADP data to discern any associations between atmospheric deposition and changing communities. Evidence supports the finding that nitrogen alters CSS and MCF. Key findings include the following:

- 2002 CMAQ/NADP nitrogen deposition data show that the 3.3 kg N/ha/yr benchmark has been exceeded in more than 93% of CSS areas (654,048 ha). These deposition levels are a driving force in the degradation of CSS communities. Although CSS decline has been observed in the absence of fire, the contributions of deposition and fire to the CSS decline require further research. CSS is fragmented into many small parcels, and the 2002 CMAQ/NADP 12-km grid data are not fine enough to fully validate the relationship between CSS distribution, nitrogen deposition, and fire.
- 2002 CMAQ/NADP nitrogen deposition data exceeds the 3.1 kg N/ha/yr benchmark in more than 38% (1,099,133 ha) of MCF areas, and nitrate leaching has been observed in surface waters. Ozone effects confound nitrogen effects on MCF acidophyte lichen, and the interrelationship between fire and nitrogen cycling requires additional research.

ADDITIONAL EFFECTS

Ecological effects have also been documented across the United States where elevated nitrogen deposition has been observed, including the eastern slope of the Rocky Mountains where shifts in dominant algal species in alpine lakes have occurred where wet nitrogen deposition was only about 1.5 kg N/ha/yr. High alpine terrestrial communities have a low capacity to sequester nitrogen deposition, and monitored deposition exceeding 3 to 4 kg N/ha/yr could lead to community-level changes in plant species, lichens, and mycorrhizae.

Additional welfare effects that are documented, but examined less extensively, in this Risk and Exposure Assessment include the following:

- **Visibility and materials damage, such as corrosion, erosion, and soiling of paint and buildings.** Both effects are being addressed in the particulate matter (PM) NAAQS review currently underway.
- **The causal relationship between sulfur deposition (as sulfate, SO_4^{2-}) and increased mercury methylation in wetlands and aquatic environments.** Decreases in sulfate

deposition will likely result in decreases in methyl mercury concentration; however, spatial and biogeochemical variations nationally hinder establishing large scale dose-response relationships.

- **Nitrous oxide (N_2O).** A potent GHG, it is most appropriate to analyze the role of N_2O in the context of all of the GHGs rather than as part of this Risk and Exposure Assessment.
- **Nitrogen deposition and its correlation with the rate of photosynthesis and net primary productivity.** Nitrogen addition ranging from 15.4 to 300 kg N/ha/yr is documented as increasing wetland N_2O production by an average of 207%. Nitrogen addition ranging from 30 to 240 kg N/ha/y increased CH_4 emissions by 115%, averaged across all ecosystems, and methane uptake was reduced by 38% when nitrogen addition ranged from 10 to 560 kg N/ha/yr, but reductions were only significant for coniferous and deciduous forests. The heterogeneity of ecosystems across the United States, however, introduces variations into dose-response relationships.
- **Phytotoxic effects on vegetation.** A unique secondary NAAQS exists for SO_2, and concentrations of NO, NO_2, and peroxyacetyl nitrates (PAN) are rarely high enough to have phtyotoxic effects on vegetation. Although relatively little is known about the direct effects of nitric acid (HNO_3) vapor on vegetation in California's Transverse Range MCF, HNO_3 has been estimated to provide 60% of all dry deposited nitrogen and has been suspected as the cause of a dramatic decline in lichen species.

SYNTHESIS AND INTEGRATION OF CASE STUDY RESULTS

The case study analyses associated with each targeted effect area were synthesized by identifying the strengths, limitations, and uncertainties associated with the available data, modeling approach, and the relationship between the selected ecological indicator and atmospheric deposition as described by the ecological effect function. The level of confidence associated with each parameter, as well as the known data gaps and research needs associated with each targeted effect area, were identified. This information is summarized below.

AQUATIC ACIDIFICATION

- The available data used for the targeted effect of aquatic acidification are robust and considered *high quality*. There is a *high confidence* about the use of these data and their value for extrapolating to a larger regional population of lakes.
- There is *fairly high confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for aquatic acidification.
- There is *high confidence* associated with the ecological effect function developed for aquatic acidification.

Data Gaps and Research Needs

- Developing relationships between critical loads for aquatic acidity and effects on ecosystem services, especially due to incremental changes in an ecological indicator such as ANC
- Developing nationwide weathering rates, or weathering rates for aquatic ecosystems sensitive to acidification
- Developing a better understanding of the uncertainty in critical loads for acidity and exceedance values
- Developing methods for calculating critical loads for surface water acidity when data are absent or of poor quality
- Evaluating ways to combine multiple critical load estimates for surface waters and soils on a national scale
- Estimating ways to determine critical load parameters across different media (e.g., surface waters, soils).

TERRESTRIAL ACIDIFICATION

- The available data used to quantify the targeted effect of terrestrial acidification are robust and considered *high quality*. There is *high confidence* about the use of these data and their value for extrapolating to a larger regional population of forests.
- There is *high confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for terrestrial acidification.

- There is *fairly high confidence* associated with the ecological effect function developed for terrestrial acidification.

Data Gaps and Research Needs

- Determining the most appropriate and accurate base cation weathering model to estimate terrestrial critical acid loads nationwide
- Expanding analyses to examine the relationships between tree growth and (1) critical load exceedance and (2) nitrogen deposition (i.e., further refine analyses of sugar maple and red spruce, and expand analyses to include more tree species and a larger geographical area) to establish additional evidence of the connection between nitrogen and sulfur deposition and biological end points
- Exploring field-based tree growth as a tool to determine the most suitable Bc/Al soil solution indicator ratio
- Developing relationships between critical loads for terrestrial acidity and effects on ecosystem services.

AQUATIC NUTRIENT ENRICHMENT

- The available data used for the targeted effect of aquatic nitrogen enrichment are considered *medium quality*. There is *intermediate confidence* about the use of these data and their value for extrapolating to a larger regional area.
- There is *intermediate confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for excess aquatic nitrogen enrichment.
- There is *low confidence* associated with the ecological effect function developed for excess aquatic nitrogen enrichment.

Data Gaps and Research Needs

- Refining development of adequate indicators of effects of nitrogen enrichment
- Enhancing relationships between ecological indicators of nitrogen enrichment and atmospheric deposition used in this study
- Applying the methods used in this study to an atmospheric deposition-dominated estuarine system

- Reducing model and data uncertainty
- Expanding relationships between ecological indicators of nitrogen enrichment and ecosystem services associated with them
- Exploring alternative relationships between ecological indicators and atmospheric deposition other than what was used in this study giving consideration to methods that can be extrapolated outside of the case study area
- Improving knowledge of how individual chemical species of nitrogen contribute to eutrophication effects.

TERRESTRIAL NUTRIENT ENRICHMENT

- The available data used for the targeted effect of terrestrial nitrogen enrichment are considered *high quality*; however, there is a limited ability to extrapolate these data to a larger regional area.
- No quantitative modeling was conducted for terrestrial nitrogen enrichment.
- No ecological effect function was developed for excess terrestrial nitrogen enrichment.

Data Gaps and Research Needs

- Elucidating the interactions among elevated levels of atmospheric nitrogen, fire intensity and frequency, and invasive grasses for CSS and elevated nitrogen and fire for MCF
- Increasing the understanding of CSS and MCF communities long-term response to elevated nitrogen and how benchmarks may change
- Developing indicators of CSS ecosystem health
- Using modeled data with a higher spatial resolution
- Increasing the understanding of the interactions between ozone, climate change, and nitrogen deposition on CSS and MCF communities.

CONCLUSIONS

Although it is recognized that while there will always be inherent variability in ecological data and uncertainties associated with modeling approaches, there is a high level of confidence from a scientific perspective that known or anticipated adverse ecological effects are occurring

under current ambient loadings of nitrogen and sulfur in sensitive ecosystems across the United States.

For aquatic and terrestrial acidification effects, a similar conceptual approach was used (critical loads) to evaluate the impacts of multiple pollutants on an ecological endpoint, whereas the approaches used for aquatic and terrestrial nutrient enrichment were fundamentally distinct. Although the ecological indicators for aquatic and terrestrial acidification (i.e., ANC and Bc/Al) are very different, both ecological indicators are well-correlated with effects such as reduced biodiversity and growth. While aquatic acidification is clearly the targeted effect area with the highest level of confidence, the relationship between atmospheric deposition and an ecological indicator is also quite strong for terrestrial acidification. The main drawback with the understanding of terrestrial acidification is that the data are based on laboratory responses rather than field measurements. Other stressors that are present in the field but that are not present in the laboratory may confound this relationship.

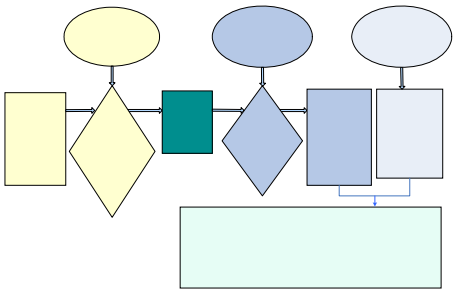
The ecological indicator chosen for aquatic nutrient enrichment, the ASSETS EI, seems to be inadequate to relate atmospheric deposition to the targeted ecological effect, likely due to the many other confounding factors. Further, there is far less confidence associated with the understanding of aquatic nutrient enrichment because of the large contributions from non-atmospheric sources of nitrogen and the influence of both oxidized and reduced forms of nitrogen, particularly in large watersheds and coastal areas. However, a strong relationship exists between atmospheric deposition of nitrogen and ecological effects in high alpine lakes in the Rocky Mountains because atmospheric deposition is the only source of nitrogen to these systems. There is also a strong weight-of-evidence regarding the relationships between ecological effects attributable to terrestrial nitrogen nutrient enrichment; however, ozone and climate change may be confounding factors. In addition, the response for other species or species in other regions of the United States has not been quantified.

A summary of the information presented by this Risk and Exposure Assessment that may be useful for characterizing known or anticipated adverse effects to public welfare is shown in **Table ES-2**. This information may be useful to inform decision makers about what levels of protection might be appropriate to protect public welfare from known or anticipated adverse impacts on ecosystems. Characterizing known or anticipated adverse effects to public welfare from a policy perspective will be addressed in the policy assessment for this review.

Table ES-2. Summary of Information Assessed in the Risk and Exposure Assessment to Aid in Informing Policy Based on Welfare Effects.

Exposure Pathway (Current Deposition Levels) (NADP/CMAQ, 2002)	Affected Ecosystem (Case Study Areas)	Ecological Response (Targeted Effect)	Ecological Indicator	Ecological Effect	Ecosystem Service Affected
Adirondack Case Study Area: 10 kg N/ha/yr 9 kg S/ha/yr Shenandoah Case Study Area: 11 kg N/ha/yr 11 kg S/ha/yr	Adirondack Mountains, NY Blue Ridge Mountains and Shenandoah National Park, VA	Acidification in lakes and streams	Fish species richness, abundance, composition, ANC	Species losses of fish, phytoplankton, zooplankton; changed community composition, ecosystem structure, and function	Annual recreational freshwater fishing in New York State = more than 13 million days Approximately $66.4 million in implied value to NY anglers from a zero-out of nitrogen and sulfur deposition
Kane Experimental Forest Case Study Area: 14 kg N/ha/yr 210 kg S/ha/yr Hubbard Brook Experimental Forest Case Study Area: 8 kg N/ha/yr 7 kg S/ha/yr	Kane Experimental Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)	Acidification of forest soils	Tree health Red spruce, sugar maple Bc/Al ratio	Decreased tree growth Increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure, and function	Provision of wood products (sugar maple) 900 million board feet timber production

Exposure Pathway (Current Deposition Levels) (NADP/CMAQ, 2002)	Affected Ecosystem (Case Study Areas)	Ecological Response (Targeted Effect)	Ecological Indicator	Ecological Effect	Ecosystem Service Affected
Potomac River/Potomac Estuary Case Study Area: 13 kg N/ha/yr Neuse River/Neuse River Estuary Case Study Area: 14 Kg N/ha/yr	Potomac River Basin, Chesapeake Bay Neuse River Basin, Pamlico Sound	Nutrient enrichment in main stem river of an estuary	ASSETS EI	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Current saltwater recreational fishing 26.1 million activity days (North Carolina-Massachusetts)
Coastal Sage Scrub: from 3 to 10 kg N/ha/yr Mixed Conifer Forest (San Bernardino Mountains and Sierra Nevada Range): from 3 to 10 kg N/ha/yr	Southern California Coastal Sage Scrub Mixed Conifer Forest (San Bernardino Mountains and Sierra Nevada Mountains, CA)	Nutrient enrichment in terrestrial ecosystems	Species composition	Species changes, nutrient enrichment of soil, changes in fire regime, changes in nutrient cycling	Annual benefits to California residents hunting, fishing, and wildlife viewing = approximately $4.6 billion; state expenditures for fire suppression = $300 million (2008)



1.0 INTRODUCTION

1.1 RATIONALE AND BACKGROUND FOR JOINT REVIEW

The U.S. Environmental Protection Agency (EPA or the Agency) is conducting a joint review of the existing secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for nitrogen oxides (NO_x) and sulfur oxides (SO_x), which are currently defined in terms of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), respectively.[1] Sections 108 and 109 of the Clean Air Act (CAA or the Act) govern the establishment and periodic review of the NAAQS and of the air quality criteria upon which the standards are based. The NAAQS are established for pollutants that may reasonably be anticipated to endanger public health or welfare and whose presence in the ambient air results from numerous or diverse mobile or stationary sources. The NAAQS are based on air quality criteria that reflect the latest scientific knowledge, which is useful in indicating the kind and extent of identifiable effects on public health or welfare that may be expected from the presence of the pollutant in ambient air. Based on periodic reviews of the air quality criteria and standards, EPA makes revisions to the criteria and standards and promulgates any new standards as may be appropriate. The Act also requires that an independent scientific review committee advise the Administrator as part of this NAAQS review process, a function now performed by the Clean Air Scientific Advisory Committee (CASAC).

In conducting this periodic review of the NO_2 and SO_2 secondary NAAQS, EPA has decided to jointly assess the scientific information, associated risks, and standards relevant to protecting the public welfare from adverse effects associated with NO_x and SO_x. As noted in Section 1.2 of this report, EPA has historically defined the NAAQS for these pollutants in terms

[1] EPA is also conducting independent reviews of the primary (health-based) NAAQS for NO_x and SO_x.

of the specific compounds NO_2 and SO_2, which serve as indicators of the broader set of compounds that comprise NO_x and SO_x, respectively. The chemical species of nitrogen and sulfur compounds and the types of related ecological effects that are being considered within the scope of this review are discussed in Section 1.3 of this report. A joint secondary review of these pollutants is being conducted because the atmospheric chemistry and environmental effects of NO_x, SO_x, and their associated transformation products are linked and because the National Research Council (NRC) has recommended that EPA consider multiple pollutants, as appropriate, in forming the scientific basis for the NAAQS (NRC, 2004). This is the first time since the NAAQS were established in 1971 that a joint review of NO_x, SO_x, as well as total reactive nitrogen, has been conducted. There is a strong basis for considering these pollutants together, building upon EPA's and CASAC's past recognition of the interactions of these pollutants and on the growing body of scientific information that is now available related to these interactions and associated ecological effects. A series of framing questions that help to shape this review are presented in Section 1.4 of this report, together with an overview of how secondary NAAQS for NO_x and SO_x might be structured to reflect the complex interactions among relevant species of these pollutants that are ecologically meaningful. As discussed in the CAA [Section 109(b)(2)], the purpose of a secondary NAAQS is to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutants in the ambient air.

This joint review is organized according to EPA's current NAAQS review process, which consists of four major components and related documents: an *Integrated Review Plan* (U.S. EPA, 2007), the *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008), the Risk and Exposure Assessment, and a policy assessment and rulemaking notices. The *Integrated Review Plan* provides the framework and schedule for this review and identifies policy-relevant questions to be addressed in the other components of the review. The ISA, released on December 12, 2008, provides an integrative assessment of the relevant scientific information and forms the scientific basis for the assessments presented in this Risk and Exposure Assessment, which describes the progress to date on the assessments being conducted as part of the third component of the review process. To view related documents developed as part of the planning and science assessment phases of this

review (e.g., *Integrated Review Plan*, the ISA), go to http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html.

When complete, the Risk and Exposure Assessment will evaluate the exposures of ecological receptors to both ambient and deposited species of NO_x and SO_x, as well as their transformation products (including reduced forms of ambient nitrogen), and assess, both quantitatively and qualitatively, the risks associated with these exposures. Where possible, the contributions of various sources and forms of atmospheric nitrogen to these risks are characterized. The following bullets outline the organization of this final draft report, which, to the degree possible, reflects the components of the Risk and Exposure Assessment:

- **Chapter 1** provides an overview of this review; a history of past reviews and other relevant scientific assessments and EPA actions; a discussion of the scope of this joint NO_x and SOx review; and a series of framing questions, together with an overview of how secondary NAAQS for NO_x and SO_x might be structured.
- **Chapter 2** provides an overview of the Risk and Exposure Assessment, including the scope and approach to assessing current conditions for a targeted effect, a summary of the case study areas, a discussion of the identification and selection of ecosystem services, and a discussion on addressing uncertainty throughout the review.
- **Chapter 3** addresses the relevant air quality issues associated with this review, including the sources, emissions, and deposition of total reactive nitrogen and sulfur and their current contributions to ambient conditions. Both spatial and temporal characterizations of ambient concentrations of nitrogen and sulfur and the contributions of ambient concentrations of nitrogen and sulfur to deposition are explored in select case study areas. In addition, there is a discussion on the relationship between atmospheric concentrations and deposition and how the Atmospheric Deposition Transformation Function might be structured (see **Figure 1.4-1**).
- **Chapter 4** focuses on acidification, with an overview of the relevant science and progress on case study analyses and developing the associated ecological effect functions (see **Figure 1.4-1**) for both aquatic and terrestrial acidification.
- **Chapter 5** focuses on nitrogen nutrient enrichment, with an overview of the relevant science and progress on case study analyses and developing the associated ecological

effect functions (see **Figure 1.4-1**) for both aquatic and terrestrial nitrogen nutrient enrichment (commonly referred to as nutrient enrichment).

- **Chapter 6** qualitatively addresses additional effects, including visibility, climate, and materials. There is a discussion on the interactions between sulfur and methylmercury production, nitrous oxide (N_2O) effects on climate, nitrogen addition effects on primary productivity and biogenic greenhouse gas fluxes, and phytotoxic effects on plants.
- **Chapter 7** synthesizes the case study analyses associated with each targeted effect area by identifying the strengths, limitations, and uncertainties associated with the available data, modeling approach, and relationship between the selected ecological indicator and atmospheric deposition as described by the ecological effect function. The level of confidence associated with each parameter, as well as the known data gaps and research needs associated with each targeted effect area, is identified.

1.2 HISTORY

1.2.1 History of the Secondary NO_2 NAAQS

On April 30, 1971, EPA promulgated identical primary and secondary NAAQS for NO_2 under Section 109 of the CAA. The standards were set at 0.053 parts per million (ppm), annual average (36 FR 8186). In 1982, EPA published the air quality criteria document (AQCD) *Air Quality Criteria for Oxides of Nitrogen* (U.S. EPA, 1982), which updated the scientific criteria for NO_x, upon which the initial NO_2 standards were based. On February 23, 1984, EPA proposed to retain these standards (49 FR 6866). After taking into account public comments, EPA published the final decision to retain these standards on June 19, 1985 (50 FR 25532).

On July 22, 1987, EPA announced that it was undertaking plans to revise the 1982 NO_x AQCD (52 FR 27580), and in November 1991, EPA released an updated draft AQCD for CASAC and public review and comment (56 FR 59285). This latter draft document provided a comprehensive assessment of the available scientific and technical information on health and welfare effects associated with NO_2 and other NO_x. CASAC reviewed the draft document at a meeting held on July 1, 1993, and concluded in a closure letter to the Administrator that the document "provides a scientifically balanced and defensible summary of current knowledge of the effects of this pollutant and provides an adequate basis for EPA to make a decision as to the

appropriate NAAQS for NO_2" (Wolff, 1993). The AQCD *Air Quality Criteria for Oxides of Nitrogen* was then finalized (U.S. EPA, 1993).

EPA also prepared a Staff Paper that summarized an air quality assessment for NO_2 conducted by the Agency (McCurdy, 1994). This Staff Paper summarized and integrated the key studies and scientific evidence contained in the revised NO_x AQCD and identified the critical elements to be considered in the review of the NO_2 NAAQS. CASAC reviewed two drafts of the Staff Paper and concluded in a closure letter to the Administrator that the document provided a "scientifically adequate basis for regulatory decisions on nitrogen dioxide" (Wolff, 1995). In September 1995, EPA finalized the Staff Paper, entitled *Review of the National Ambient Air Quality Standards for Nitrogen Dioxide: Assessment of Scientific and Technical Information* (U.S. EPA, 1995a).

In October 1995, the Administrator announced her proposed decision not to revise either the primary or secondary NAAQS for NO_2 (60 FR 52874; October 11, 1995). A year later, the Administrator made a final determination not to revise the NAAQS for NO_2 after careful evaluation of the comments received on the proposal (61 FR 52852; October 8, 1996). The level for both the existing primary and secondary NAAQS for NO_2 is 0.053 ppm (100 micrograms per cubic meter [$\mu g/m^3$] of air), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO_2 concentrations.

1.2.2 History of the Secondary SO_2 NAAQS

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

At that time, EPA was aware that SO_x has other public welfare effects, including effects on materials, visibility, soils, and water; however, the available data were considered insufficient to establish a quantitative relationship between specific atmospheric SO_x concentrations and effects needed for setting a standard (38 FR 25679).

In 1979, EPA announced that it was revising the 1973 SO_x AQCD concurrently with that for particulate matter (PM) and would produce a combined PM and SO_x criteria document. Following its review of a draft revised criteria document in August 1980, CASAC concluded that acidifying deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (1) emissions of relevant pollutants (e.g., SO_2, NO_x), (2) formation of acidifying wet and dry deposition products, and (3) effects on terrestrial and aquatic ecosystems. CASAC also noted that acidifying deposition involves, at a minimum, several different criteria pollutants: SO_x, NO_x, and the fine particulate fraction of suspended particles. CASAC felt that any document on this subject should address both wet and dry deposition because dry deposition was believed to account for at least one-half of the total acidifying deposition problem.

For these reasons, CASAC recommended that a separate, comprehensive document on acidifying deposition be prepared prior to any consideration of using the NAAQS as a regulatory mechanism for the control of acidifying deposition. CASAC also suggested that a discussion of acidifying deposition be included in the AQCD for NO_x, PM, and SO_x. Following CASAC closure on the criteria document for SO_2 in December 1981, EPA's Office of Air Quality Planning and Standards (OAQPS) published a Staff Paper in November 1982, but the paper did not directly assess the issue of acidifying deposition. Instead, EPA subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (U.S. EPA, 1984a, b) and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (U.S. EPA, 1985) (53 FR 14935-14936). Though these documents were not considered criteria documents and did not undergo CASAC review, they represented the most comprehensive summary of relevant scientific information completed by EPA to that point.

On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and secondary standards. This proposal regarding the secondary SO_2 NAAQS was due to the Administrator's conclusions that (1) based upon the then-current scientific understanding of the

acidifying deposition problem, it would be premature and unwise to prescribe any regulatory control program at that time, and (2) when the fundamental scientific uncertainties had been reduced through ongoing research efforts, EPA would draft and support an appropriate set of control measures.

1.2.3 History of Related Assessments and Agency Actions

In 1980, Congress created the National Acid Precipitation Assessment Program (NAPAP) in response to growing public concern about acidifying deposition. The NAPAP was given a broad 10-year mandate to examine the causes and effects of acidifying deposition and to explore alternative control options to alleviate acidifying deposition and its effects. During the course of the program, the NAPAP issued a series of publicly available interim reports prior to the completion of a final report in 1990 (NAPAP, 1990).

In spite of the complexities and significant remaining uncertainties associated with the acidifying deposition problem, it soon became clear that a program to address acidifying deposition was needed. The Amendments to the CAA passed by Congress and signed into law by the president on November 15, 1990, included numerous separate provisions related to the acidifying deposition problem that reflect the comprehensive approach envisioned by Congress. The primary and most important of the provisions, Title IV of the CAA Amendments, established the Acid Rain Program to reduce SO_2 emissions by 10 million tons and NO_x emissions by 2 million tons from 1980 emission levels to achieve reductions over broad geographic regions. In this provision, Congress included a statement of findings that led them to take action, concluding that (1) the presence of acid compounds and their precursors in the atmosphere and in deposition from the atmosphere represents a threat to natural resources, ecosystems, materials, visibility, and public health; (2) the problem of acidifying deposition is of national and international significance; and (3) current and future generations of Americans will be adversely affected by delaying measures to remedy the problem.

Second, Congress authorized the continuation of the NAPAP to assure that the research and monitoring efforts already undertaken would continue to be coordinated and would provide the basis for an impartial assessment of the effectiveness of the Title IV program.

Third, Congress—clearly envisioning that further action might be necessary in the long term to address any problems remaining after implementation of the Title IV program and

reserving judgment on the form that action could take—included Section 404 of the 1990 Amendments (CAA Amendments of 1990, Pub. L. 101-549, § 404), requiring EPA to conduct a study on the feasibility and effectiveness of an acidifying deposition standard or standards to protect "sensitive and critically sensitive aquatic and terrestrial resources." At the conclusion of the study, EPA was to submit a report to Congress. Five years later, in fulfillment of this requirement, EPA submitted its report, entitled *Acid Deposition Standard Feasibility Study: Report to Congress* (U.S. EPA, 1995b). The report concluded that establishing acidifying deposition standards for sulfur and nitrogen deposition may at some point in the future be technically feasible, although appropriate deposition loads for these acidifying chemicals could not be defined with reasonable certainty at the time of the report (1995).

Fourth, the 1990 Amendments also added new language to sections of the CAA pertaining to the scope and application of the secondary NAAQS designed to protect the public welfare. Specifically, the definition of "public welfare" in Section 302(h) was expanded to state that the welfare effects identified should be protected from adverse effects associated with criteria air pollutants "…whether caused by transformation, conversion, or combination with other air pollutants." This change has particular relevance to the current review because the transformation products of NO_x and SO_x are associated with environmental impacts.

In 1999, seven northeastern states cited this amended language in Section 302(h) in a petition asking EPA to use its authority under the NAAQS program to promulgate secondary NAAQS for the criteria pollutants associated with the formation of acid rain. The petition stated that this language "clearly references the transformation of pollutants resulting in the inevitable formation of sulfate and nitrate aerosols and/or their ultimate environmental impacts as wet and dry deposition, clearly signaling Congressional intent that the welfare damage occasioned by sulfur and nitrogen oxides be addressed through the secondary standard provisions of Section 109 of the Act." The petition further stated that "recent federal studies, including the NAPAP Biennial Report to Congress: An Integrated Assessment, document the continued-and increasing-damage being inflicted by acid deposition to the lakes and forests of New York, New England and other parts of our nation, demonstrating that the Title IV program had proven insufficient." The petition also listed other adverse welfare effects associated with the transformation of these criteria pollutants, including impaired visibility, eutrophication of coastal estuaries, global warming, and depletion of tropospheric ozone and stratospheric ozone.

In a related matter, the Office of the Secretary of the U.S. Department of Interior (DOI) requested in 2000 that EPA initiate a rulemaking proceeding to enhance the air quality in national parks and wilderness areas to protect resources and values that are being adversely affected by air pollution. Included among the effects of concern identified in the request were the acidification of streams, surface waters, and/or soils; eutrophication of coastal waters; impairment of visibility; and foliar injury from ozone.

In a *Federal Register* notice in 2001, EPA announced receipt of this request and asked for comments on the issues raised. EPA stated that it would consider any relevant comments and information submitted, along with the information provided by the petitioners and DOI, before making any decision concerning a response to this request for rulemaking (65 FR 48699).

The 2005 NAPAP report states that "… scientific studies indicate that the emission reductions achieved by Title IV are not sufficient to allow recovery of acid-sensitive ecosystems. Estimates from the literature of the scope of additional emission reductions that are necessary in order to protect acid-sensitive ecosystems range from approximately 40-80% beyond full implementation of Title IV.… The results of the modeling presented in this Report to Congress indicate that broader recovery is not predicted without additional emission reductions" (NAPAP, 2005).

Given the state of the science as described in the ISA and in other recent reports, such as the 2005 NAPAP report, EPA believes it is appropriate, in the context of evaluating the adequacy of the current NO_2 and SO_2 secondary standards in this review, to revisit the question of the appropriateness and the feasibility of setting a secondary NAAQS to address remaining known or anticipated adverse public welfare effects resulting from the acidifying and nutrient deposition of these criteria pollutants and their transformation products. This document comprises the Risk and Exposure Assessment portion of the review.

1.3 SCOPE OF THE RISK AND EXPOSURE ASSESSMENT FOR THE CURRENT REVIEW

1.3.1 Species of Nitrogen Included in the Analyses

The sum of mono-nitrogen oxides—nitrogen dioxide (NO_2) and nitric oxide (NO)—typically is referred to as nitrogen oxides (NO_x) in the atmospheric science community. More formally, the family of NO_x includes any gaseous combination of nitrogen and oxygen (e.g.,

NO_2, NO, N_2O, nitrogen trioxide [N_2O_3], nitrogen tetroxide [N_2O_4], and dinitrogen pentoxide [N_2O_5]).

With regard to NO_x, it is also necessary in this review to distinguish between the definition of "nitrogen oxides" as it appears in the enabling legislation related to the NAAQS and the definition commonly used in the air pollution research and management community. In this document, the term "oxides of nitrogen" and "nitrogen oxides" refer to all forms of oxidized nitrogen compounds, including NO, NO_2, and all other oxidized nitrogen-containing compounds transformed from NO and NO_2. This definition is supported by Section 108(c) of the CAA, which states that "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 term used by the scientific community to represent the complete set of oxidized nitrogen compounds, including those listed in CAA Section 108(c), is total oxidized nitrogen (NO_y). NO_y includes all nitrogen oxides, including gaseous nitrate species such as nitric acid (HNO_3) and peroxyacyl nitrates (PAN).

In addition to oxidized forms of nitrogen, reduced forms of nitrogen also contribute to the atmospheric chemistry that leads to the deposition of ambient nitrogen species to the environment. Reduced atmospheric nitrogen species include ammonia (NH_3) and ammonium ion (NH_4^+), the sum of which is referred to as reduced nitrogen (NH_x). Total reactive nitrogen is recognized as the combination of both oxidized and reduced forms of nitrogen that are biologically available (i.e., forms other than the stable form of gaseous nitrogen [N_2]). Atmospheric nitrogen deposition often is delineated further as dry (e.g., gas and particulate phases) or as wet (e.g., precipitation-derived ion phase) (see **Figure 1.3-1**).

Organic nitrogen compounds include the PANs, nitrosamines, nitro-polycyclic aromatic hydrocarbons (PAHs), and the more recently identified nitrated quinones. Oxidation of volatile organic compounds (VOCs) produces organic peroxy radicals (RO_2). Reaction of RO_2 radicals with NO and NO_2 produces $RONO_2$ and peroxynitrates (RO_2NO_2). Considerable uncertainty attaches to estimates of the third form of atmospherically derived nitrogen (i.e., organic nitrogen) in part because convenient methods for measurement and analysis are not widely available; see ISA Table 2-11. Intensive studies at individual sites have shown, however, that for the North Carolina coast, for example, 30% of rainwater nitrogen and deposition consisted of organic

nitrogen, 20% to 30% of which was then available to primary producers on time scales of hours to days.

Important compounds, reactions, and cycles are schematized in **Figure 1.3-1**. **Figure 1.3-1** also illustrates that NO_2, itself an oxidant, can react to form other photochemical oxidants, including organic nitrates ($RONO_2$) like the PANs and can react with toxic compounds like the PAHs to form nitro-PAHs, some of which demonstrate greater toxicity than either reactant alone. NO_2 can also be further transformed to HNO_3 and can contribute in that form to the acidity of cloud, fog, and rain water.

In many areas, multiple forms of nitrogen from a variety of atmospheric and other sources enter ecosystems. The scientific community has long recognized that the effects from atmospheric deposition of nitrogen to ecosystems are due to both oxidized and reduced forms, rather than to one form alone. As a result, much of the published research on ecological response to nitrogen does not differentiate between the various sources of nitrogen, but instead reports only total nitrogen inputs to the ecosystem.

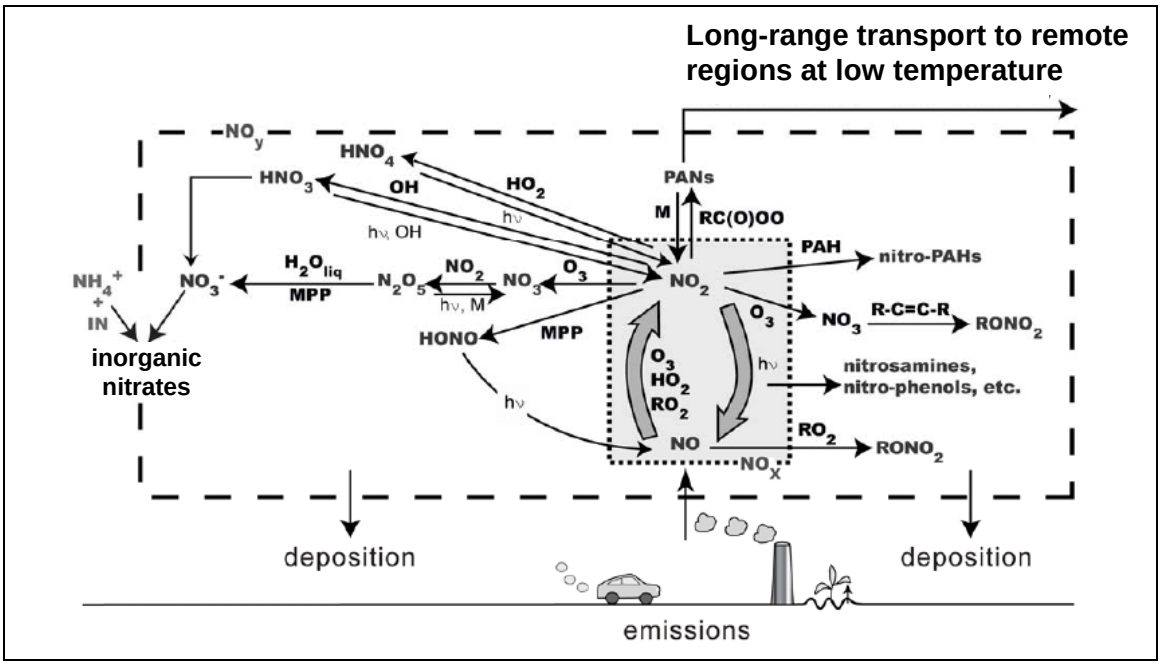


Figure 1.3-1. Schematic diagram of the cycle of reactive, oxidized nitrogen species in the atmosphere. Particulate-phase organic nitrates are also formed from the species on the right side of the figure (U.S. EPA, 2008).

Note: IN = inorganic particulate species (e.g., sodium [Na+], calcium [Ca^{2+}]), MPP = multiphase processes, PAN = peroxyacetyl nitrates, PAH = polycyclic aromatic hydrocarbon, hν = a solar photon, R = an organic radical.

1.3.2 Species of Sulfur Included in the Analyses

SO_2 is one of a group of substances known as "oxides of sulfur", or SO_x, which include multiple gaseous species (e.g., SO_2, sulfur monoxide [SO], sulfur trioxide [SO_3], thiosulfate [S_2O_3], sulfur heptoxide [S_2O_7]) and particulates (e.g., ammonium sulfate [$(NH_4)_2SO_4$]) (**Figure 1.3-2**). SO_2 is chiefly, but not exclusively, primary in origin; it is also produced by the photochemical oxidation of reduced and organic sulfur compounds, such as dimethyl sulfide (DMS), hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (OCS), and methyl mercaptan, which are all mainly biogenic in origin. Acidification can result from the atmospheric deposition of SO_x and NO_x; in acidifying deposition, these species combine with water in the atmosphere to form sulfuric acid (H_2SO_4) and HNO_3. Due to known acute effects on plants, SO_2 served as the chemical indicator for SO_x species in previous NAAQS reviews.

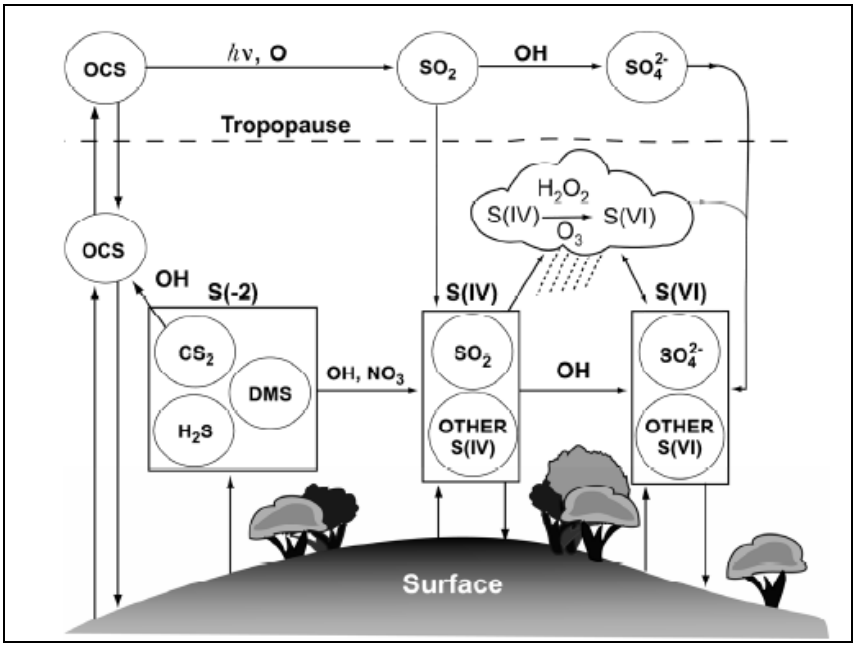


Figure 1.3-2. Schematic diagram of the cycle of sulfur species in the atmosphere (adapted from Berresheim et al. (1995); used with permission).

Note: OCS = carbonyl sulfide, DMS = dimethyl sulfide, S(IV) = S^{+4}, S(VI) = S^{+6}.

1.3.3 Overview of Nitrogen- and Sulfur-Related Ecological Effects

The ecological effects of nitrogen and sulfur are caused both by the gas-phase and atmospheric deposition of the pollutants. The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase NO_x or SO_x. Acute and chronic exposures to SO_2 can have phytotoxic effects on vegetation, such as foliar injury, decreased

photosynthesis, and decreased growth. Similarly, exposure to sufficient concentrations of NO_2, NO, PAN, and HNO_3 can cause foliar injury, decreased photosynthesis, and decreased growth (U.S. EPA 2008).

With respect to direct gas-phase effects, the ISA for the secondary NAAQS review determined the following:

The evidence is sufficient to infer a causal relationship between exposure to SO_2, NO, NO_2, PAN, and HNO_3 and injury to vegetation.

Even though these gas-phase chemicals will cause phytotoxicity, the evidence indicates there is little new evidence that current concentrations of gas-phase sulfur or nitrogen oxides are not sufficiently high to cause phytotoxic effects. One exception is that some studies indicate that current HNO_3 concentrations may be contributing to the decline of lichen species in the Los Angeles basin. (U.S. EPA, 2008).

Deposition of nitrogen-containing and sulfur-containing compounds that are derived from NO_x and SO_x may be wet (e.g., rain and snow), occult (e.g., cloud and fog), and dry (e.g., gases and particles) and can affect ecosystem biogeochemistry, structure, and function. Nitrogen and sulfur interactions in the environment are highly complex. Both are essential elements for vegetation growth and development and are needed for growth and productivity. However, excess nitrogen (both oxidized and reduced forms) or sulfur can lead to acidification, nitrogen nutrient enrichment, eutrophication, and sulfur-mediated mercury methylation. Acidification causes a cascade of effects that alter both terrestrial and aquatic ecosystems. These effects include slower biotic growth, the injury or death of forest vegetation, and the localized extinction of fish and other aquatic species.

With respect to acidification, the ISA determined the following:

The evidence is sufficient to infer a causal relationship between acidifying deposition and effects on

(1) biogeochemistry related to terrestrial and aquatic ecosystems;

(2) biota in terrestrial and aquatic ecosystems.

The ISA highlights evidence from two well-studied areas to provide more detail on how acidification affects ecosystems: the Adirondack Case Study Area (New York) and the Shenandoah Case Study Area (Virginia) (U.S., EPA, 2008, Section 3.2). In the Adirondack Case Study Area, the current rates of nitrogen and sulfur deposition exceed the amount that would

allow recovery of the most acid-sensitive lakes. In the Shenandoah Case Study Area, legacy sulfate has accumulated in the soil and is slowly released from the soil into stream water, where it causes acidification and makes this region sensitive to current loading. Models for the latter study area suggest that the number of acidic streams will increase under the current deposition rates (U.S. EPA, 2008, Section 3.2). The ISA highlights forests in the Adirondack Case Study Area of New York, Green Mountains of Vermont, White Mountains of New Hampshire, and the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians as the regions most sensitive to terrestrial acidification effects from atmospheric deposition (U.S. EPA, 2008, Section 3.2). In this Risk and Exposure Assessment, these areas are targeted for the air quality modeling presented in Chapter 3 and the case study analyses presented in Chapter 4 of this report.

In addition to acidification, NO_x acts with other forms of total reactive nitrogen (including reduced nitrogen) to increase the total amount of available nitrogen in ecosystems. The contribution of nitrogen deposition to total nitrogen load varies among ecosystems. Atmospheric nitrogen deposition is the main anthropogenic source of new nitrogen to most headwater streams, high-elevation lakes, and low-order streams. Atmospheric nitrogen deposition contributes to the total nitrogen load in terrestrial, wetland, freshwater, and estuarine ecosystems that receive nitrogen through multiple pathways (i.e., biological nitrogen-fixation, agricultural land runoff, and wastewater effluent discharges) (U.S. EPA, 2008, Section 3.3). Nitrogen deposition alters numerous biogeochemical indicators, including primary productivity that may lead to changes in community composition and eutrophication.

With respect to nitrogen nutrient enrichment, the ISA determined the following:

The evidence is sufficient to infer a causal relationship between nitrogen deposition, to which NO_x and NH_x contribute, and the alteration of the following:

(1) Biogeochemical cycling of nitrogen and carbon in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems

(2) Biogenic flux of methane and nitrous oxide in terrestrial and wetland ecosystems

(3) Species richness, species composition, and biodiversity in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems.

In aquatic ecosystems, wet deposition loads of approximately 1.5 to 2 kg N/ha/yr are reported to cause alterations in diatom communities of freshwater lakes and to impair water

quality in the western United States, a region especially sensitive to increased nitrogen atmospheric inputs (U.S. EPA, 2008, Section 3.3). In estuarine ecosystems, additional nitrogen from anthropogenic atmospheric sources contributes to the total nitrogen loading and to increased phytoplankton and algal productivity, which may lead to eutrophication. Estuary eutrophication is a detrimental ecological problem indicated by water quality deterioration, resulting in numerous adverse effects, including hypoxic zones, species mortality, and harmful algal blooms. The ISA indicates that the contribution of atmospheric deposition to total nitrogen loads can be >40% in some eutrophic estuaries. The Chesapeake Bay is an example of a large, well-studied estuary that receives as much as 30% of its total nitrogen load from the atmosphere (U.S. EPA, 2008, Section 3.3).

In terrestrial ecosystems, there are multiple chemical indicators that the biogeochemical cycling of nitrogen has been altered by the deposition of total reactive nitrogen. Nitrate leaching from terrestrial ecosystems is a well-documented effect that indicates the ecosystem is receiving more nitrogen than it uses; the atmospheric deposition threshold for nitrate leaching is calculated to be between 8 and 10 kg/ha/yr for eastern forests (U.S. EPA, 2008, Section 3.3). Nitrogen deposition can cause ecological effects prior to the onset of nitrate leaching. For example, nitrogen deposition affects primary productivity, thereby altering terrestrial carbon cycling. This may result in shifts in population dynamics, species composition, community structure, and, in extreme instances, ecosystem type. Lichen are the most sensitive terrestrial taxa, with documented adverse effects occurring at atmospheric inputs as low as 3 kg N/ha/yr (Pacific Northwest and Southern California); 5 kg N/ha/yr correlates to the onset of declining biodiversity within grasslands (Minnesota and the European Union); and 10 kg N/ha/yr causes changes in community composition of Alpine ecosystems and forest encroachment into temperate grasslands (U.S. EPA, 2008, Section 3.3). Some of the aquatic and terrestrial ecosystems highlighted in the ISA are targeted for the air quality modeling presented in Chapter 3 and the case study analyses presented in Chapter 5 of this Risk and Exposure Assessment.

There is increasing evidence on the relationship between sulfur deposition and increased methylation of mercury in aquatic environments; this effect occurs only where other factors are present at levels within a range to allow methylation. The production of methylmercury requires the presence of sulfate and mercury, but the amount of methylmercury produced varies with oxygen content, temperature, pH, and supply of labile organic carbon (U.S. EPA, 2008, Section

3.4). In watersheds where changes in sulfate deposition did not result in changes in methylmercury generation, one or several of those interacting factors were not in the range required for substantial methylation to occur (U.S. EPA, 2008, Section 3.4). Watersheds with conditions known to be conducive to mercury methylation can be found in the northeastern United States and southeastern Canada, but can occur elsewhere. The relationship between sulfur and methylmercury production is addressed qualitatively in Chapter 6 of this report.

With respect to sulfur deposition and mercury methylation, the ISA determined the following:

The evidence is sufficient to infer a causal relationship between sulfur deposition and increased mercury methylation in wetlands and aquatic environments.

In terrestrial and wetland ecosystems, total reactive nitrogen deposition alters biogenic sources and sinks of N_2O and methane—two potent greenhouse gases—resulting in a higher emission to the atmosphere of these gases. Terrestrial soil is the largest source of N_2O, accounting for 60% of global emissions. Total reactive nitrogen deposition increases the flux of N_2O in coniferous forests, deciduous forests, grasslands, and wetlands. Nitrogen deposition significantly reduces methane uptake in coniferous and deciduous forests, with a reduction of 28% and 45%, respectively. In wetlands, nitrogen addition increases methane production, but has no significant effect on methane uptake (U.S. EPA, 2008, Section 3.4). These effects are also addressed qualitatively in Chapter 6 of this report.

A summary illustration of NO_x and SO_x effects on the environment is presented in **Figure 1.3-3**.

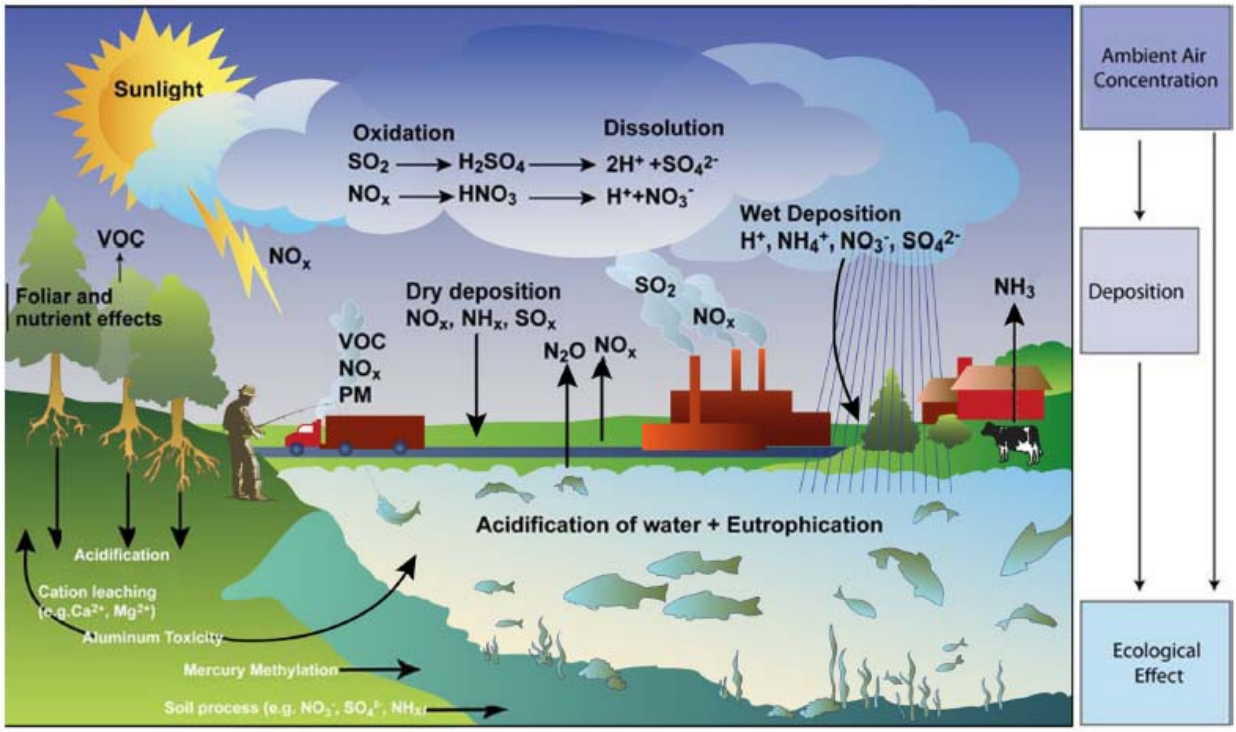


Figure 1.3-3. Nitrogen and sulfur cycling and interactions in the environment.

1.4 FRAMING QUESTIONS FOR THE RISK AND EXPOSURE ASSESSMENT

As many years of research have clearly demonstrated, the ecological effects associated with acidification (due to both nitrogen and sulfur) and excess nitrogen nutrient enrichment derive from both oxidized and reduced nitrogen, not NO_x alone, which is the current listed criteria pollutant. The questions framing this review recognize that the effects of NO_x occur as part of the overall effects of total reactive nitrogen and address the need to understand the role of NO_x relative to other sources of reactive nitrogen that contribute to adverse public welfare effects. Throughout the ISA and the Risk and Exposure Assessment, public welfare effects due to total reactive nitrogen are examined, and where possible, the contributions to these effects from oxidized and reduced forms of nitrogen are assessed. For this secondary NO_x/SO_x NAAQS review, the main questions directing the Risk and Exposure Assessment include the following:

Overall Framing Questions:

- What are the known or anticipated welfare effects influenced by ambient NO_x, an important component of total reactive nitrogen, and SO_x, and for which effects is there

sufficient information available to be useful as a basis for considering distinct secondary standard(s)?

- To what extent do the current standards provide protection from the known or anticipated welfare effects associated with NO_x and SO_x?
- To what extent does the current NO_x standard provide protection against known or anticipated adverse effects associated with total reactive nitrogen?
- For which ecological effects being considered is a joint NO_x/SO_x standard most appropriate, and for which ecological effects would separate standards be more appropriate?
- Taking into consideration factors related to determining when the various detrimental ecological effects under consideration occur, what range of levels, averaging times, and forms of alternative ecological indicators are supported by the information and what are the uncertainties and limitations in that information?
- To what extent do specific levels, averaging times, and forms of alternative ecological indicators reduce detrimental impacts attributable to NO_x/SO_x relative to current conditions, and what are the uncertainties in the estimated reductions?

Air Quality Framing Questions:

- Does the available information provide support for considering different air quality indicators for NO_x and SO_x?
- Given that dry deposition can contribute significantly to total deposition, to what extent do receptor surfaces influence the deposition of gases and particles (i.e., dry deposition)?
- Does the available information provide support for the development of appropriate atmospheric deposition transformation functions, and what atmospheric and environmental factors (e.g., co-pollutants, land use) are most appropriate to account for in such a function?

Ecological Framing Questions:

- What are the nature and magnitude of ecosystem responses to total reactive nitrogen, to which NO_x contributes, and SO_x that are understood to have known or anticipated detrimental public welfare effects, and what is the variability associated with those responses (e.g., ecosystem type, climatic conditions, interactions with other environmental factors, pollutants)?

- Does the available information provide support for the development of appropriate ecological effect functions that meaningfully relate to the ecological endpoints being considered, and what ecological factors (e.g., reduced forms of nitrogen, bedrock type, weathering rates) are most relevant for such functions?
- To what extent can ecological effects due to NO_x be distinguished from effects due to total reactive nitrogen?
- Which ecological indicators adequately capture the relationships between ecosystem exposures and responses for the known or anticipated adverse welfare effects that are trying to be protected against?
- Does the available information provide a basis for identifying relevant ecological indicators for the range of ecological endpoints being considered in the review?
- Is there enough information to determine when ecological effects become adverse?

In order to answer these questions, the relevant scientific and policy issues that need to be addressed in the science, risk and exposure, and policy assessment portions of this review include the following:

- Identifying important nitrogen and sulfur chemical species in the atmosphere
- Identifying the atmospheric pathways that govern the chemical transformation, transport, and deposition of total reactive nitrogen and SO_x to the environment
- Identifying the attributes of ecosystem receptors that govern their susceptibility to effects from deposition of nitrogen and sulfur compounds
- Identifying the relationships between ambient air quality indicators and ecological indicators of effects (through deposition)
- Identifying relationships between ecosystem services and ecological indicators
- Evaluating alternative approaches to assess the adversity of effects on ecosystem services, including, but not limited to, economic valuation
- Evaluating environmental impacts and sensitivities to varying meteorological scenarios and climate conditions
- Evaluating the relationship between NO_x and deposition of total reactive nitrogen, and between NO_x and total nitrogen loadings that are related to ecological effects.

To the extent the evidence suggests that the current standards do not provide appropriate protection from known or anticipated adverse public welfare effects associated with the criteria

pollutants NO_x and SO_x, ecologically meaningful revisions to the current standards will be considered. Recognizing the high degree of complexity that exists in relationships between ambient air concentrations of NO_x and SO_x, deposition of nitrogen and sulfur into sensitive aquatic and terrestrial ecosystems, and associated potential adverse ecological effects, it is anticipated that ecologically meaningful NAAQS need to be structured to take into account such complexity. To provide some context for addressing the key framing questions that are salient in this review, a possible structure for secondary standards based on meaningful ecological indicators that provides for protection against the range of potentially adverse ecological effects associated with the deposition of NO_x, NH_x, and SO_x has been developed and is shown in **Figure 1.4-1**. In so doing, it was considered how the basic elements of NAAQS standards—indicator, averaging time, form, and level—would be reflected in such a structure.

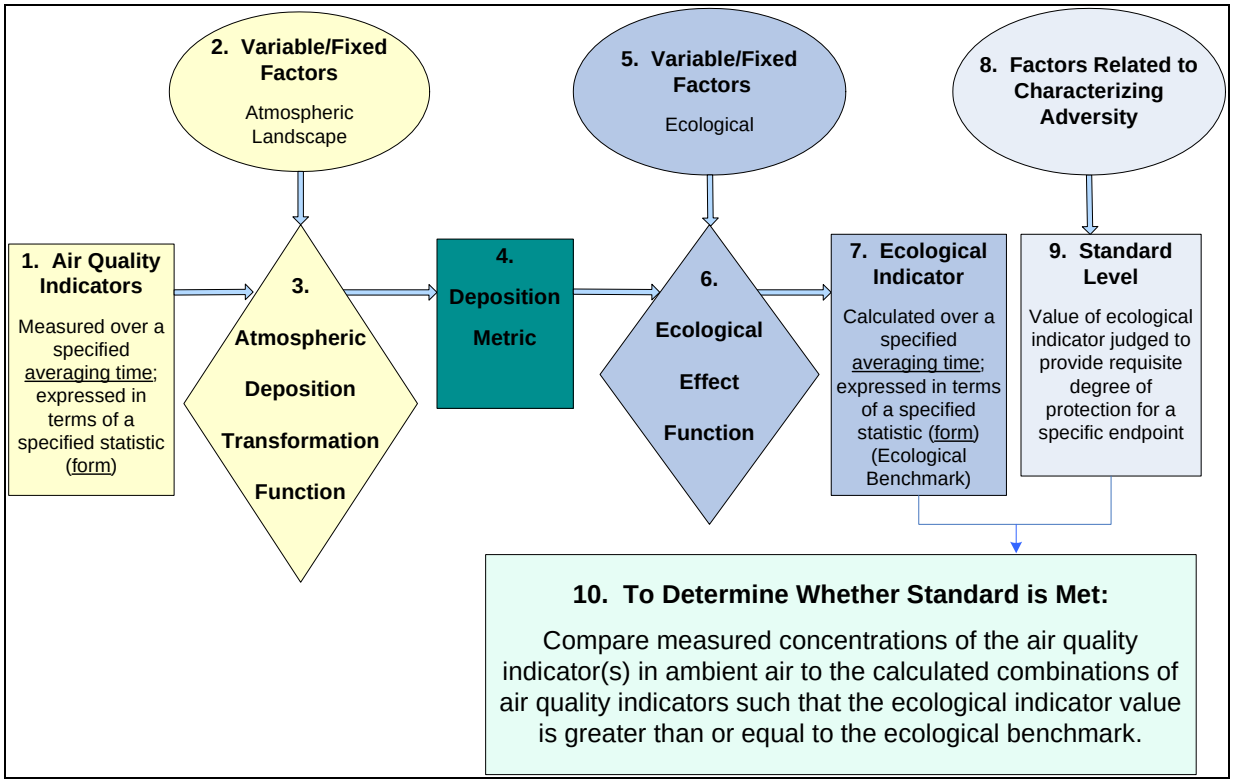


Figure 1.4-1. Possible structure of a secondary NAAQS for NO_x and SO_x based on an ecological indicator.

Figure 1.4-1 illustrates the working structure for an ecological effect-based secondary NAAQS for NO_x and SO_x, together with the combination of various elements that would serve to define such a standard. The subsequent chapters of this report will address each component of this structure. Starting from the left side of **Figure 1.4-1**, Chapter 3 of this report addresses the

atmospheric analyses covered in this review, including sources, emissions, concentrations, and deposition and characterization of the spatial and temporal patterns of concentration and deposition in the case study areas (boxes 1 to 4). The Atmospheric Deposition Transformation Function that quantifies the relationship between atmospheric concentrations and deposition of NO_x and SO_x (box 3), while taking atmospheric and landscape factors into account (i.e., deposition velocities, land use, co-pollutants), are addressed in Chapter 3 and Appendices 1–3 of this report. Chapters 4 and 5 and their associated appendices (Appendices 4–7) focus on the ecological effects of acidification and nutrient enrichment, respectively, and discuss the selection of ecological indicators, ecosystem services, the case study areas and their representativeness, and the evaluation of current conditions in these areas (boxes 4 to 7). For each targeted effect, the ecological effect functions are derived and described in Chapters 4 and 5 and Appendices 4–7 (box 6), and the role of ecosystem services in defining adversity is discussed in Chapters 2, 4 or 5, and 7 (box 8). Chapter 7 of this report synthesizes the case study analyses by evaluating the relative confidence level associated with the available data, modeling approach, and the relationship between the selected ecological indicator and atmospheric deposition as described by the ecological effect function (boxes 5 to 7). All of the components of **Figure 1.4-1** will be evaluated in the policy assessment associated with this review, which will consider the structure of a secondary NAAQS from a statutory standpoint and characterize the atmospheric and ecological inputs discussed throughout the Risk and Exposure Assessment. In addition, the policy assessment will highlight boxes 8, 9, and 10 in **Figure 1.4-1** in a discussion of the risks associated with alternative levels of ecological indicators for each targeted effect area.

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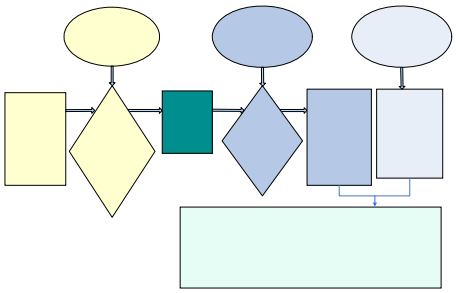

2.0 OVERVIEW OF RISK AND EXPOSURE ASSESSMENT

2.1 INTRODUCTION

The Risk and Exposure Assessment focuses on ecosystem welfare effects that result from the deposition of total reactive nitrogen and sulfur. Because ecosystems are diverse in biota, climate, geochemistry, and hydrology, response to pollutant exposures can vary greatly between ecosystems. In addition, these diverse ecosystems are not distributed evenly across the United States. To target nitrogen and sulfur acidification and nitrogen and sulfur enrichment, the Risk and Exposure Assessment addresses four main targeted ecosystem effects on terrestrial and aquatic systems identified by the *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA; U.S. EPA, 2008a):

- Aquatic acidification due to nitrogen and sulfur
- Terrestrial acidification due to nitrogen and sulfur
- Aquatic nutrient enrichment, including eutrophication
- Terrestrial nutrient enrichment.

In addition to these four targeted ecosystem effects, this assessment qualitatively addresses the influence of sulfur oxides (SO_x) deposition on methylmercury production; nitrous oxide (N_2O) effects on climate; nitrogen effects on primary productivity and biogenic greenhouse gas fluxes; and phytotoxic effects on plants.

Because the targeted ecosystem effects outlined above are not evenly distributed across the United States, the Risk and Exposure Assessment identified case studies for the analyses based on ecosystems identified as sensitive to nitrogen and/or sulfur deposition effects. This Risk and Exposure Assessment builds upon the scientific information presented in the ISA, with ecological indicator(s) and case study areas selected based on the information presented (U.S.

EPA, 2008a). Eight case study areas and two supplemental study areas (Rocky Mountain National Park and Little Rock Lake, WI) are summarized in **Table 2.1-1** based on ecosystem characteristics, indicators, and ecosystem service information developed for this Risk and Exposure Assessment. Detailed explanations of this information are presented in Chapters 4 and 5 of this report (i.e., *Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur*), and a map highlighting each of the eight case study areas and the Rocky Mountain National Park is shown in **Figure 2.1-1**.

Table 2.1-1. Summary of Sensitive Characteristics, Indicators, Effects, and Impacted Ecosystem Services Analyzed for Each Case Study Evaluated in This Review

Targeted Ecosystem Effect	Characteristics of Sensitivity (Variable Ecological Factors)	Biological/ Chemical Indicator	Ecological Endpoint	Ecological Effects	Ecosystem Services Impacted	Case Study Areas
Aquatic Acidification	Geology, surface water flow, soil depth, weathering rates	Al pH ANC	Species richness, abundance, composition, ANC	Species losses of fish, phytoplankton, and zooplankton; changed community composition, ecosystem structure, and function	Subsistence fishing, recreational fishing, other recreational activities	Adirondack Mountains, NY (referred to as Adirondack) Shenandoah National Park, VA (referred to as Shenandoah)
Terrestrial Acidification	Geology, surface water flow, soil depth, weathering rates	Soil base saturation Al Ca C:N ratio	Tree health of red spruce and sugar maple, ANC, base cation :Al ratio	Decreased tree growth, increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure, and function	Provision of food and wood products, recreational activities, natural habitat, soil stabilization, erosion control, water regulation, climate regulation	Kane Experimental Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)
Aquatic Nutrient Enrichment	nitrogen-limited systems, presence of nitrogen in surface water, eutrophication status, nutrient criteria	Chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, submerged aquatic vegetation (SAV)	Changes in Eutrophication Index (EI)	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Commercial and recreational fishing, other recreational activities, aesthetic value, nonuse value flood and erosion control	Potomac River Basin, Chesapeake Bay (referred to as Potomac River/Potomac Estuary) Neuse River Basin, Pamlico Sound (referred to as Neuse River/Neuse River Estuary)

Targeted Ecosystem Effect	Characteristics of Sensitivity (Variable Ecological Factors)	Biological/ Chemical Indicator	Ecological Endpoint	Ecological Effects	Ecosystem Services Impacted	Case Study Areas
Terrestrial Nutrient Enrichment	Presence of acidophytic lichens, anthropogenic land cover	Cation exchange capacity, C:N ratios, Ca:Al ratios, NO_3^- leaching and export	Species composition, lichen presence/absence, soil root mass changes, NO_3 breakthrough to water, biomass	Species changes, nutrient enrichment of soil, changes in fire regime, changes in nutrient cycling	Recreation, aesthetic value, nonuse value, fire regulation, loss of habitat, loss of biodiversity, water quality	Coastal Sage Scrub (southern, coastal California) and Mixed Conifer Forest (San Bernardino Mountains of the Transverse Range and Sierra Nevada Mountain Ranges, California); Rocky Mountain National Park (a supplemental study area)

Note: ANC = acid neutralizing capacity, SAV = submerged aquatic vegetation, EI = eutrophication index.

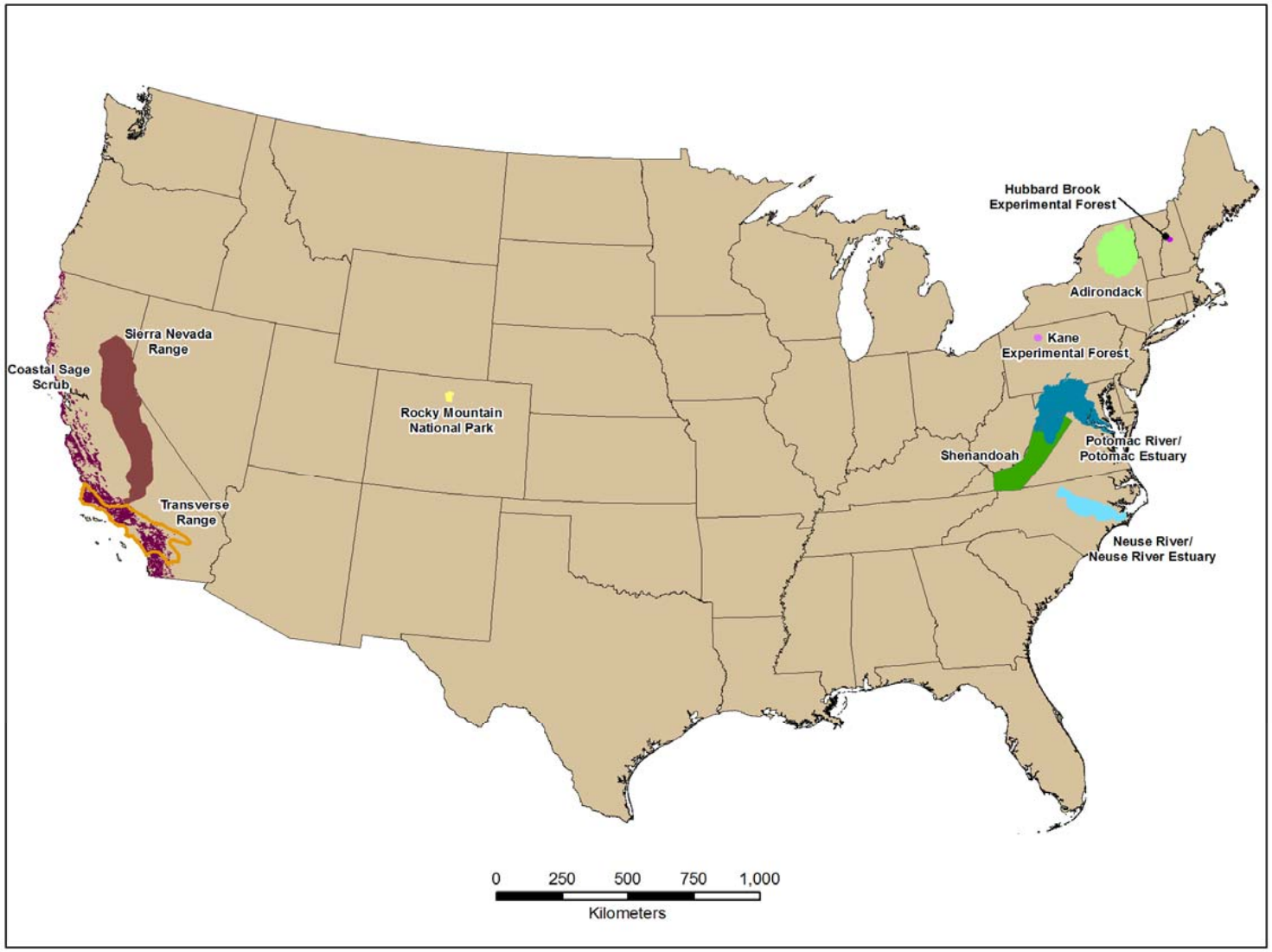

Figure 2.1-1. National map highlighting the eight case study areas and the Rocky Mountain National Park (a supplemental study area) evaluated in the Risk and Exposure Assessment.

To address the framing questions that guide the scope of this review, the Risk and Exposure Assessment evaluates the relationships between atmospheric concentrations, deposition, biologically relevant exposures, targeted ecosystem effects, and ecosystem services. To evaluate the nature and magnitude of ecosystem responses associated with adverse effects, the Risk and Exposure Assessment examines various ways to quantify the relationships between air quality indicators, deposition of biologically available forms of nitrogen and sulfur, ecologically relevant indicators relating to deposition, exposure and effects on sensitive receptors, and related effects resulting in changes in ecosystem structure and services. The intent of the Risk and Exposure Assessment is to determine the exposure metrics that incorporate the temporal considerations (i.e., biologically relevant timescales), pathways, and ecologically relevant indicators necessary to maintain the functioning of these ecosystems. To the extent feasible, this Risk and Exposure Assessment evaluates the overall load to the system for nitrogen and sulfur, as well as the variability in ecosystem responses to these pollutants. In addition, this Risk and Exposure Assessment evaluates the contributions of atmospherically deposited nitrogen and sulfur relative to the combined atmospheric loadings of both elements. Since oxidized nitrogen is the listed criteria pollutant (currently measured by the ambient air quality indicator NO_2) for the atmospheric contribution to total nitrogen, this Risk and Exposure Assessment examines the contribution of nitrogen oxides (NO_x) to total reactive nitrogen in the atmosphere, relative to the contributions of reduced forms of nitrogen (e.g., ammonia, ammonium), to ultimately assess how a meaningful secondary National Ambient Air Quality Standards (NAAQS) might be structured.

The Risk and Exposure Assessment for the secondary NAAQS review for NO_x and SO_x will aid the Administrator in judging whether the current secondary standards are requisite to protect public welfare from any known or anticipated adverse effects, or whether these standards should be retained, revised, revoked, and/or replaced with alternative standard(s) to provide the required protection.

Previous reviews of secondary NAAQS have characterized adversity according to the ecological effects associated with that pollutant. For example, in the previous ozone (O_3) secondary NAAQS review, biomass loss and foliar injury were the main effects determining adversity to public welfare on public lands, while in the particulate matter (PM) secondary NAAQS review, the loss of visibility was used. There is an important distinction between a

scientifically defined and documented adverse effect to a given ecological system or ecological endpoint and an adverse impact on public welfare from a statutory perspective. While adverse effects to ecosystems from a scientific perspective will be used to inform the Administrator's decision, the degree of change in an ecological indicator or service that corresponds to an adverse public welfare effect is ultimately decided by the Administrator.

For assessing this set of secondary NAAQS, in addition to assessing the degree of scientific impairment of ecological systems relating to inputs of NO_x and sulfur oxides (SO_x), this Risk and Exposure Assessment presents an overview of the concept of ecosystem services. The analysis of the effects on ecosystem services will help link what is considered to be a biologically adverse effect with a known or anticipated adverse effect to public welfare through ecosystem services.

In this Risk and Exposure Assessment, ecosystem services is used to show the impacts of ecological effects on public welfare and help explain how these effects are viewed by the public. Ecosystem services are addressed in more detail in Section 2.4 of this chapter, throughout the case study analyses in Chapters 4 and 5, and in the examination of the structure of an ecologically meaningful secondary standard in the policy assessment document. The ability to inform decisions on the level of a secondary NAAQS will require the development of clear linkages between biologically adverse effects and effects that are adverse to public welfare as related to ecosystem services. The concept of adversity to public welfare does not require the use of ecosystem services, yet it is envisioned as a beneficial tool for this review that may provide more information on the linkages between adverse ecological effects and adverse public welfare effects.

2.2 SEVEN-STEP APPROACH

The seven basic steps guiding the overall Risk and Exposure Assessment and the assessments for each case study area of interest are highlighted below. These steps were initially presented in the scope and methods plan for this review (U.S. EPA, 2008b) and received Clean Air Scientific Advisory Committee (CASAC) approval; therefore, this approach is being carried forward in the Risk and Exposure Assessment. The seven steps address the selection of the targeted ecosystem effects, indicators, and ecosystem services measured for exposure via atmospheric deposition of total reactive nitrogen and sulfur from ambient air. The initial step of

identifying effects, sensitive ecosystems, and potential indicators is documented in the ISA (see Chapter 3, U.S. EPA, 2008a). In addition, the ISA identifies and reviews candidate multimedia models available for fate and transport analyses of a variety of ecosystems. The science documented in the ISA provides critical inputs into the Risk and Exposure Assessment. For some of the desired case study areas, data were not abundant enough to perform a quantitative assessment for each of the steps; in those cases, some steps have been executed in a qualitative or semiquantitative fashion.

The details of the seven steps are addressed in each case study description. The steps are as follows:

- **Step 1.** Plan for assessment using documented effects, such as biological, chemical, and ecological indicators; ecological responses; and potential ecosystem services.
- **Step 2.** Map characteristics of sensitive areas that show ecological responses using research findings and geographic information systems (GIS) mapping.
- **Step 3.** Select risk and exposure case study assessment area(s) within a sensitive area.
- **Step 4.** Evaluate current loads and effects to case study assessment areas, including ecosystem services, where possible.
- **Step 5.** Evaluate representativeness of case study areas to larger sensitive areas.
- **Step 6.** Assess the current ecological conditions for those larger sensitive areas.
- **Step 7.** Develop ecological effect functions for the targeted ecosystem effects (e.g., aquatic acidification).

2.3 LINKAGES FOR STRUCTURING ECOLOGICALLY RELEVANT STANDARDS

The framework shown in **Figure 2.3-1** provides an example of how an ecologically meaningful secondary NAAQS might be structured. This example presents a system of linked functions that translate an air quality indicator (e.g., concentrations of NO_x and SO_x) into an ecological indicator that expresses either the potential for deposition of nitrogen and sulfur to acidify an ecosystem or for nitrogen to overenrich an ecosystem. This system encompasses the linkages between ambient air concentrations and resulting deposition metrics, as well as between the deposition metric and the ecological indicator of concern. For example, the atmospheric deposition transformation function (box 3) translates ambient air concentrations of NO_x and SO_x

to nitrogen and sulfur deposition metrics, while the ecological effect function (box 6) relates the deposition metric into the ecological indicator.

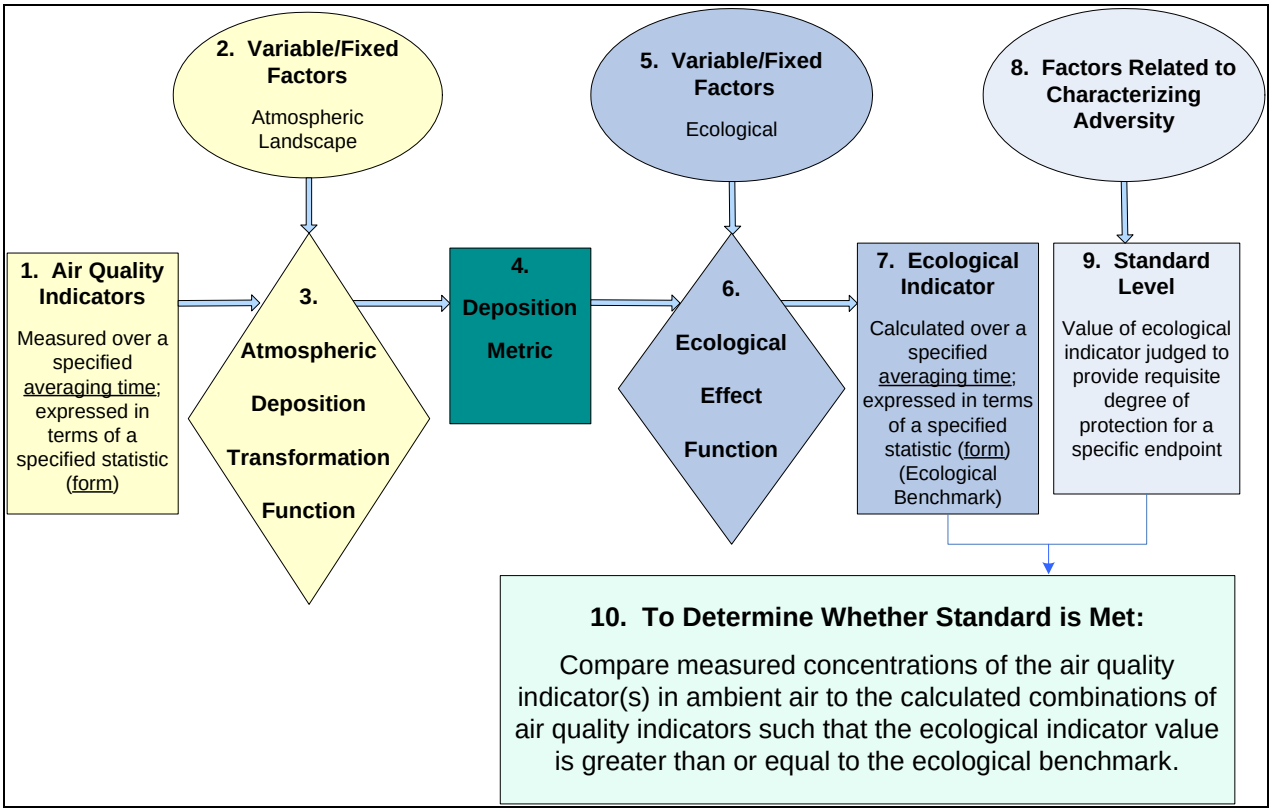

Figure 2.3-1. Possible structure of a secondary NAAQS for NO_x and SO_x based on an ecological indicator.

The amounts of NO_x and SO_x in the ambient air can be used to derive a deposition metric (via the atmospheric deposition transformation function), which can then be used to derive a level of an ecological indicator (through the ecological effect function) that falls within the range defined as acceptable by the standard; by definition, the levels of NO_x and SO_x will be considered to meet that standard of protection. The atmospheric levels of NO_x and SO_x that satisfy a particular level of ecosystem protection are those levels that result in an amount of deposition that is less than the amount of deposition a given ecosystem can accept without degradation of the ecological indicator for a targeted ecosystem effect.

Modifying factors that alter the relationship between ambient air concentrations of NO_x and SO_x and depositional loads of nitrogen and sulfur, and those that modify the relationship between depositional loads and the ecological indicator, are discussed more fully throughout the discussion of atmospheric analyses in Chapter 3 and in the review of case study analyses in

Chapters 4 and 5. The role of ecosystem services in determining an adverse effect to public welfare is introduced below (Section 2.4) and highlighted throughout the case study analyses in Chapters 4 and 5. The role of ecosystem services in informing the standard-setting process will be discussed in the policy assessment document when characterizing risks associated with the development of a standard(s).

2.4 ECOSYSTEM SERVICES

The Risk and Exposure Assessment evaluates the benefits received from the resources and processes that are supplied by ecosystems. Collectively, these benefits are known as ecosystem services and include products or provisions, such as food and fiber; processes that regulate ecosystems, such as carbon sequestration; cultural enrichment; and supportive processes for services, such as nutrient cycling. Ecosystem services are distinct from other ecosystem products and functions because there is human demand for these services.

In the Millennium Ecosystem Assessment (MEA), ecosystem services are classified into four main categories:

- **Provisioning.** Includes products obtained from ecosystems, such as the production of food and water.
- **Regulating.** Includes benefits obtained from the regulation of ecosystem processes, such as the control of climate and disease.
- **Cultural.** Includes the nonmaterial benefits that people obtain from ecosystems through spiritual enrichment, cognitive development, reflection, recreation, and aesthetic experiences.
- **Supporting.** Includes those services necessary for the production of all other ecosystem services, such as nutrient cycles and crop pollination (MEA, 2005a).

The concept of ecosystem services can be used to help define adverse effects as they pertain to NAAQS reviews. The most recent secondary NAAQS reviews have characterized known or anticipated adverse effects to public welfare by assessing changes in ecosystem structure or processes using a weight-of-evidence approach that uses both quantitative and qualitative data. For example, the previous ozone review evaluated changes in foliar injury, growth loss, and biomass reduction on trees beyond the seedling stage using field measurement

data. The presence or absence of foliar damage in counties meeting the current standard has been used as a way to evaluate the impact of current ozone air quality on plants.

Characterizing a known or anticipated adverse effect to public welfare is an important component of developing any secondary NAAQS. According to the Clean Air Act (CAA), welfare effects include the following:

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

In other words, welfare effects are those effects that are important to individuals and/or society in general. Ecosystem services can be generally defined as the benefits that individuals and organizations obtain from ecosystems. EPA has defined ecological goods and services as the "outputs of ecological functions or processes that directly or indirectly contribute to social welfare or have the potential to do so in the future. Some outputs may be bought and sold, but most are not marketed" (U.S. EPA, 2006). Conceptually, changes in ecosystem services may be used to aid in characterizing a known or anticipated adverse effect to public welfare. In the context of this review, ecosystem services may also aid in assessing the magnitude and significance of a resource and in assessing how NO_x and SO_x concentrations and deposition may impact that resource.

Figure 2.4-1 provides the World Resources Institute's schematic demonstrating the connections between the categories of ecosystem services and human well-being. The interrelatedness of these categories means that any one ecosystem may provide multiple services. Changes in these services can impact human well-being by affecting security, health, social relationships, and access to basic material goods (MEA, 2005b).

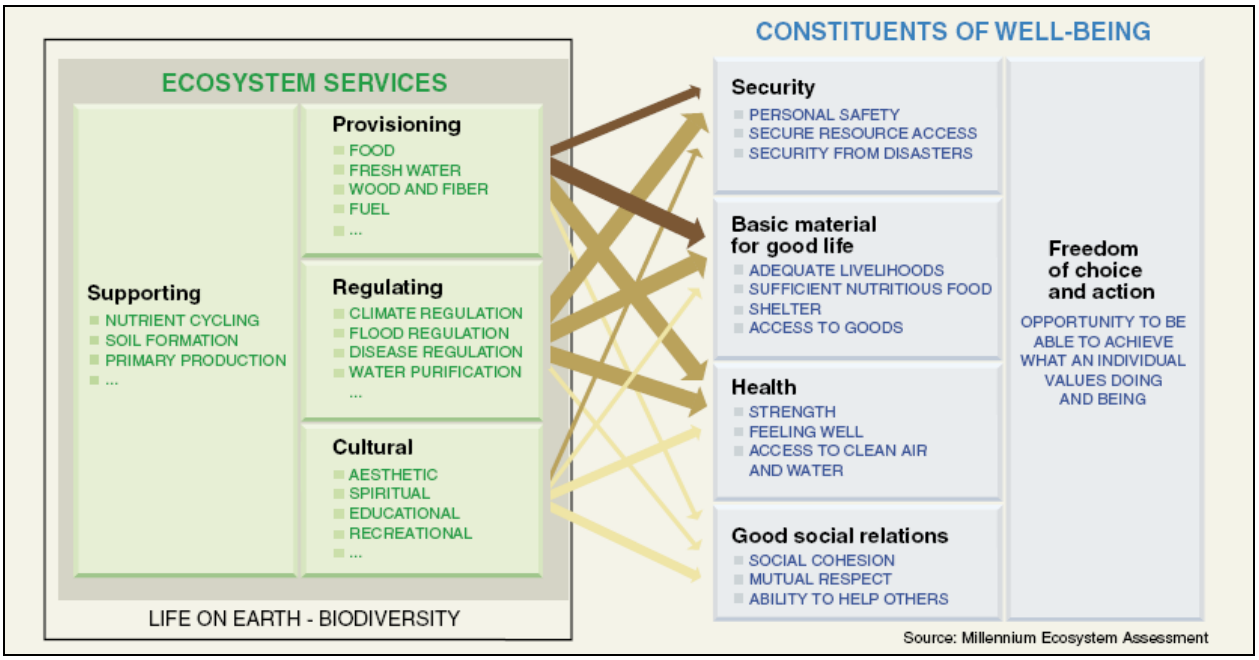

Figure 2.4-1. This figure depicts the strength of linkages between categories of ecosystem services and components of human well-being that are commonly indications of the extent to which it is possible for socioeconomic factors to mediate the linkage. (For example, if it is possible to purchase a substitute for a degraded ecosystem service, then there is a high potential for mediation.) The strength of the linkages, as indicated by arrow width, and the potential for mediation, as indicated by arrow color, differ in different ecosystems and regions (MEA, 2005a).

Historically, ecosystem services have been undervalued and overlooked; however, more recently, the degradation and destruction of ecosystems has piqued interest in assessing the value of these services. In addition, valuation may be an important step from a policy perspective because it can be used to compare the costs and benefits of altering versus maintaining an ecosystem (i.e., it may be easier to protect than repair ecosystem effects). In this Risk and Exposure Assessment, valuation is used, where possible, based on available data in the case study areas.

The economic approach to the valuation of ecosystem services is laid out as follows in EPA's *Ecological Benefits Assessment Strategic Plan*: "Economists generally attempt to estimate the value of ecological goods and services based on what people are willing to pay (WTP) to increase ecological services or by what people are willing to accept (WTA) in compensation for reductions in them" (U.S. EPA, 2006). There are three primary approaches for estimating the value of ecosystem services: market-based approaches, revealed preference methods, and stated

preference methods (U.S. EPA, 2006). Because economic valuation of ecosystem services can be difficult, nonmonetary valuation using biophysical measurements and concepts also can be used. Examples of nonmonetary valuation methods include the use of relative-value indicators (e.g., a flow chart indicating uses of a waterbody, such as boatable, fishable, swimmable); another assigns values to ecosystem goods and services through the use of the common currency of energy. Energetic valuation attempts to assess ecosystem contributions to the economy by using *one kind* of energy (e.g., solar energy) to express the value of that type of energy required to produce designated services (Odum, 1996). This energy value is then converted to monetary units. This method of valuation, however, does not account for the premise that values arise from individual or societal preferences.

Valuing ecological benefits, or the contributions to social welfare derived from ecosystems, can be challenging, as noted in EPA's *Ecological Benefits Assessment Strategic Plan* (U.S. EPA, 2006). It is necessary to recognize that in the analysis of the environmental responses associated with any particular policy or environmental management action, some of the ecosystem services likely to be affected are readily identified, whereas others will remain unidentified. Of those ecosystem services that are identified, some changes can be quantified, whereas others cannot. Within those services whose changes can be quantified, only a few will likely be monetized, and many will remain unmonetized. Similar to health effects, only a portion of the ecosystem services affected by a policy can be monetized. The stepwise concept leading up to the valuation of ecosystems services is graphically depicted in **Figure 2.4-2**.

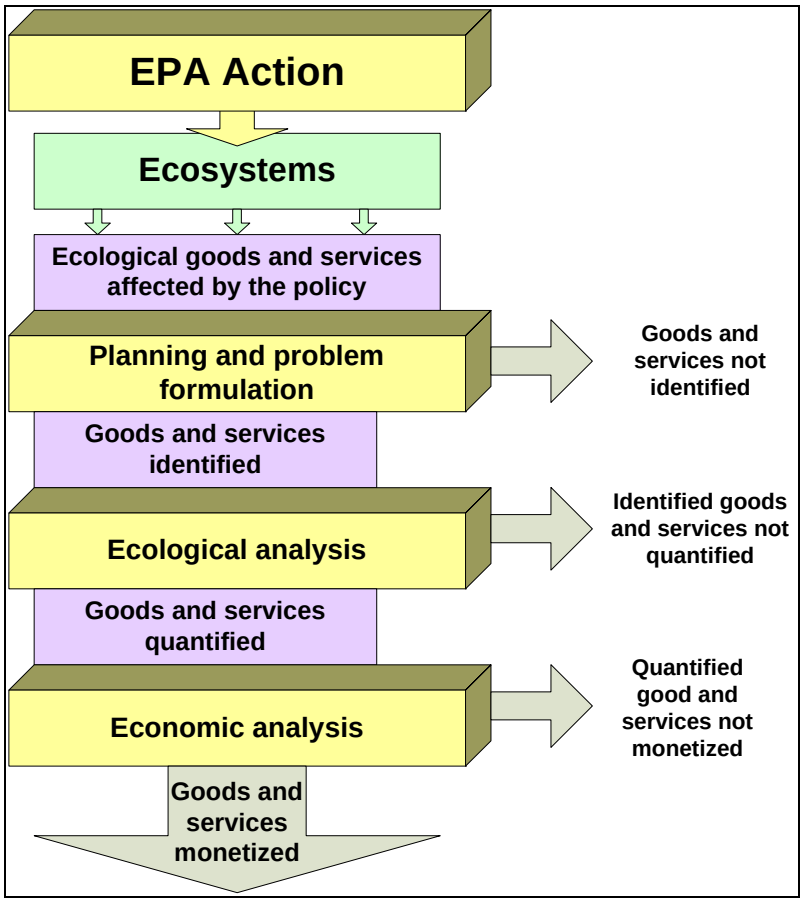

Figure 2.4-2. Representation of the benefits assessment process indicating where some ecological benefits may remain unrecognized, unquantified, or unmonetized. (Modified based on the Ecological Benefits Assessment Strategic Plan report [U.S. EPA, 2006]).

A conceptual model integrating the role of ecosystem services in characterizing known or anticipated adverse effects to public welfare is shown in **Figure 2.4-3**. Under Section 108 of the CAA, the secondary standard is to specify an acceptable level of the criteria pollutant(s) in the ambient air that is protective of public welfare. For this review, the relevant air quality indicator is interpreted as ambient NO_x and SO_x concentrations that can be linked to levels of deposition for which there are adverse ecological effects. The air quality analyses described in Chapter 3 explore the sources, emissions, and deposition of total reactive nitrogen and sulfur and their current contributions to ambient conditions. The case study analyses (described in Chapters 4 and 5) link deposition in sensitive ecosystems (e.g., the exposure pathway) to changes in a given ecological indicator (e.g., for aquatic acidification, changes in acid neutralizing capacity [ANC]) and then to changes in ecosystems and the services they provide (e.g., fish species richness and

its influence on recreational fishing). To the extent possible for each targeted effect area, ambient concentrations of nitrogen and sulfur (i.e., ambient air quality indicators) were linked to deposition in sensitive ecosystems (i.e., exposure pathways), and then deposition was linked to system response as measured by a given ecological indicator (e.g., lake and stream acidification as measured by ANC). The ecological effect (e.g., changes in fish species richness) was then, where possible, associated with changes in ecosystem services and their ecological benefits or welfare effects (e.g., recreational fishing).

Knowledge about the relationships linking ambient concentrations and ecosystem services can be used to inform a policy judgment on a known or anticipated adverse public welfare effect. The conceptual model outlined for aquatic acidification in **Figure 2.4-3** can be modified for any targeted effect area where sufficient data and models are available. For example, changes in biodiversity would be classified as an ecological effect, and the associated changes in ecosystem services—productivity, recreational viewing, and aesthetics—would be classified as ecological benefits/welfare effects. This information can then be used to characterize known or anticipated adverse effects to public welfare and inform a policy based on welfare effects.

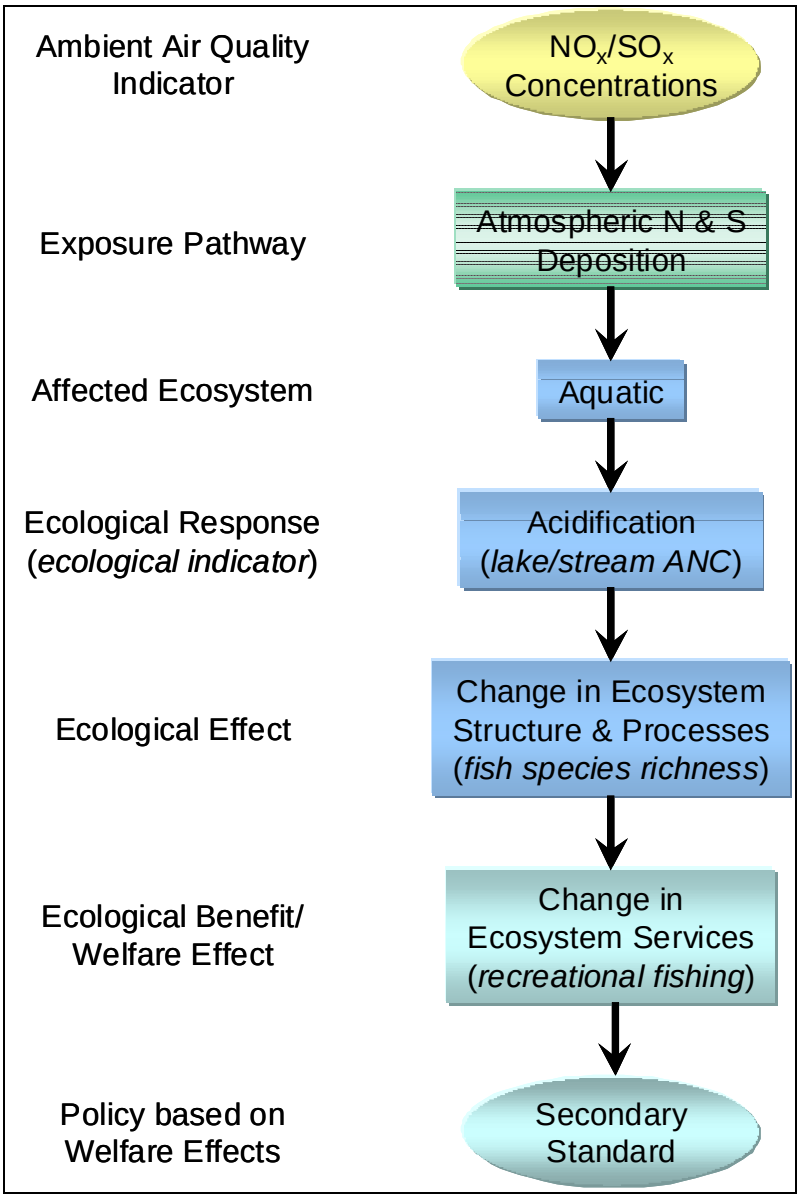

Figure 2.4-3. Conceptual model showing the relationships among ambient air quality indicators and exposure pathways and the resulting impacts on ecosystems, ecological responses, effects, and benefits to characterize known or anticipated adverse effects to public welfare.

The ecosystems of interest in this Risk and Exposure Assessment are heavily impacted by the effects of anthropogenic air pollution, which may alter the services provided by the ecosystems in question. For example, changes in forest health as a result of soil acidification from NO_x and SO_x deposition may affect supporting services such as nutrient cycling; provisioning services such as timber production; and regulating services such as climate regulation. In addition, eutrophication caused by NO_x deposition may affect supporting services

such as primary production; provisioning services such as food; and cultural services such as recreation and ecotourism.

Where possible, linkages to ecosystem services from indicators of each effect identified in Step 1 of the Risk and Exposure Assessment were developed. These linkages were based on existing literature and models, focus on the services identified in the peer-reviewed literature, and are essential to any attempt to evaluate air pollution-induced changes in the quantity and/or quality of ecosystem services provided. According to EPA's Science Advisory Board Committee on Valuing the Protection of Ecological Systems and Services, these linkages are critical elements for determining the valuation of benefits of EPA-regulated air pollutants (SAB C-VPESS, 2007). **Figure 2.4-4** provides an example pathway for nitrogen deposition in an aquatic ecosystem that links the ecological endpoints to changes in services and, finally, to valuation.

This Risk and Exposure Assessment identifies the primary ecosystem service(s) for both acidification and enrichment and for the targeted ecosystem effects under consideration in this exposure assessment (see **Table 2.1-1**). Examples of some of the linkages between impacts and each targeted ecosystem effect in relation to specific ecosystem services are summarized below and in **Table 2.4-1**.

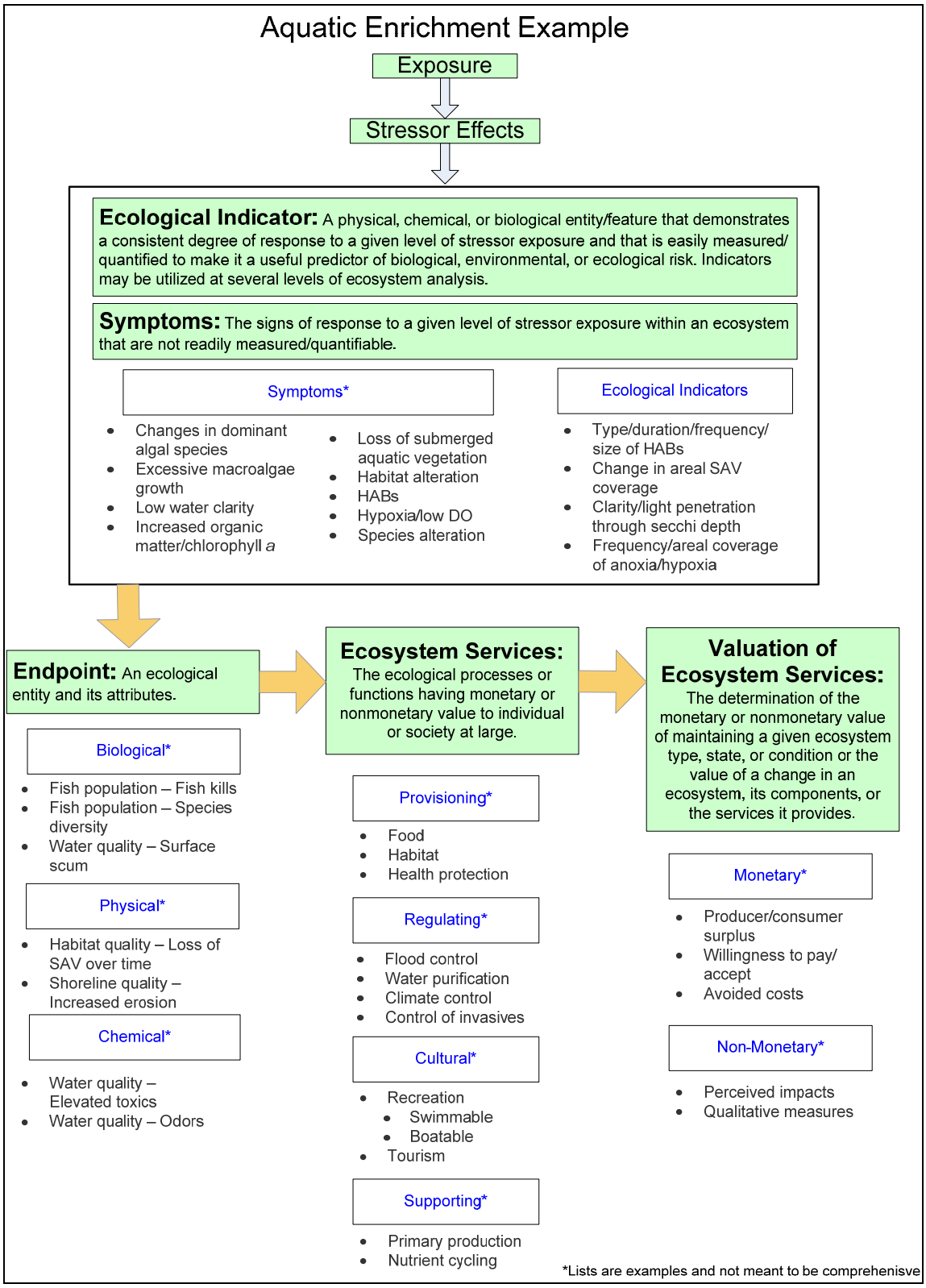

Figure 2.4-4. Pathway from nitrogen deposition to valuation for an aquatic system.

Note: HABs = harmful algal blooms, DO = dissolved oxygen, SAV = submerged aquatic vegetation.

2.4.1 Aquatic Acidification

In the current assessment, the analysis of effects on ecosystem services from aquatic acidification focused on recreational fishing. Fish abundance (decreased species richness) has been quantitatively linked to acidification through monitoring data and modeling of acid neutralizing capacity. Relevant ecosystem services were quantified, and values were estimated using a Random Utility model for fishing services and contingent valuation studies to estimate gains in total services provided by the Adirondack and New York State lakes case study area.

2.4.2 Terrestrial Acidification

The ecosystem services analysis for Terrestrial Acidification Case Study concentrated on the provision of food and wood products and on recreational activity. Sugar maple and red spruce abundance and growth (i.e., crown vigor, biomass, and geographic extent) were quantitatively linked to acidification symptoms through the Forest Inventory and Analysis National Program (FIA) database analyses. Results of the FIA database analysis were input to the Forest and Agriculture Sector Optimization Model – Green House Gas version (FASOMGHG) to estimate producer and consumer surplus gains associated with decreased acidification.

2.4.3 Aquatic Nutrient Enrichment

The ecosystem services analysis for aquatic nutrient enrichment evaluated several cultural ecosystem services, including recreational fishing, boating, and beach use. In addition, aesthetic and nonuse values were evaluated; the impacts on recreational fishing (e.g., closings, decreased species richness) to eutrophication symptoms through monitoring data were quantitatively linked; other recreational activities and aesthetic and non-use services to eutrophication symptoms were quantitatively related through user surveys and valuation literature; and the current commercial fishing markets were described. Although little data are available to link any decrease in commercial landings or subsistence fishing directly to eutrophication, it seems likely that these activities would be impacted.

2.4.4 Terrestrial Nutrient Enrichment

The ecosystem services analysis for terrestrial nutrient enrichment for the coastal sage scrub and mixed conifer forest ecosystems focused on services such as recreation, aesthetic, and

non-use services, including existence values. Given the lack of data available to develop a quantitative analysis of service impacts, the impacts on these ecosystems were addressed in a qualitative fashion.

2.4.5 Sulfur and Mercury Methylation

The major ecosystem services potentially impacted by mercury methylation are provisioning and cultural services. Fishing and shellfishing can involve both commercial operations and sport fishing, both of which provide food for human populations. For some socio-economic groups (especially low-income groups), fishing is a subsistence activity that makes a significant contribution to household food intake. Sport fishing often involves important recreational services, and for many groups (e.g., Native Americans, Alaska Native villagers), fishing and consuming local fish or shellfish is of cultural and spiritual significance. A synthesis of the ecosystem service and valuation aspects of fishing and shellfishing activities, with a focus on the mercury pollution issues affecting human health and well-being, is found in the *Regulatory Impact Analysis of the Clean Air Mercury Rule* (U.S. EPA, 2005) and in the *Mercury Study Report to Congress* (U.S. EPA, 1997).

Table 2.4-1. Ecological Impacts Associated with Acidification, Nutrient Enrichment, and Increased Mercury Methylation and Their Associated Ecosystem Services

Targeted Ecosystem Effect	Provisioning Services	Regulating Services	Cultural Services	Supporting Services
Aquatic Acidification	▪ Fishing (subsistence)	▪ Biological control	▪ Recreational fishing ▪ Nonuse	▪ Not Available
Terrestrial Acidification	▪ Food, wood products	▪ Erosion control ▪ Fire regulation ▪ Hydrologic ▪ Climate	▪ Recreational activity ▪ Aesthetic ▪ Nonuse	▪ Not Available
Aquatic Nutrient Enrichment	▪ Commercial fishing	▪ Erosion control ▪ Flood control	▪ Recreational activity ▪ Aesthetic ▪ Nonuse	▪ Nutrient cycling
Terrestrial Nutrient Enrichment				
Coastal Sage Scrub	▪ Not Available	▪ Fire regulation ▪ Hydrologic control ▪ Climate	▪ Recreational activity ▪ Aesthetic ▪ Nonuse	▪ Not Available
Mixed Conifer Forest	▪ Not Available	▪ Hydrologic control ▪ Climate	▪ Recreational activity ▪ Aesthetic ▪ Nonuse	▪ Nutrient cycling,
Sulfur and Mercury Methylation	▪ Commercial and subsistence fishing	▪ Not Available	▪ Recreational fishing ▪ Nonuse	▪ Not Available

2.5 UNCERTAINTY

The scope of this Risk and Exposure Assessment involves quantifying a number of relationships along the path of moving from ambient concentrations of NO_x, NH_x, and SO_x to their transformation products and deposition in the environment. The environmental effects of nitrogen and sulfur deposition vary widely and the extent of these effects in time and space is often uncertain in both terrestrial and aquatic ecosystems. The relationships between deposition, ecological effects, ecological indicators, and ecosystem services are also quantified. Uncertainty and variability are present at each step in this framework (as shown in **Figure 2.3-1**). In addition, extrapolating from a case study area to a larger assessment area introduces additional uncertainty and potential error into the process. Understanding the nature, sources, and importance of these uncertainties will help inform the standard setting process in the policy assessment phase of this review.

Uncertainty represents a lack of knowledge about the true value of a parameter that can result from inadequate or imperfect measurement. Uncertainty can be reduced by obtaining additional measurements, data, and information. Conceptual and numerical uncertainty can be bounded by testing a range of inputs and parameters in atmospheric and ecological numerical process models, like the ones used in this assessment. **Table 2.5.1** presents the models used in this assessment and includes model description, case study application, model type, temporal features of the model, spatial scale used in this analysis, strengths, weaknesses, supporting organization endorsements, and considerations in the application to nitrogen and sulfur deposition. An additional source of uncertainty is error due to the use of incorrect measurements, methods, data, or models. Error can be identified and addressed by thorough evaluation, review, and consultation with outside experts.

Variability in space and time is a component of all environmental systems and represents actual differences in the value of a parameter or attribute of an ecological indicator. Variability describes the natural variation in a system and cannot be reduced by taking additional measurements of a parameter, although it is possible to characterize the range of variation in a measurement or parameter. For example, there is natural variability among similar ecosystems nationwide, some of which are more sensitive to acidification and/or nutrient enrichment than

others, just as there is natural variability in the precipitation amounts that produce wet deposition loadings to these systems.

Selected terms and sources of uncertainty and variability are discussed, as appropriate, in each section of this Risk and Exposure Assessment.

Table 2.5-1. Overview of Models Used in This Assessment, Including Model Description, Case Study Application, Model Type, Temporal Features of the Model, Spatial Scale Used in This Analysis, Strengths, Weaknesses, Supporting Organization Endorsements, and Considerations in the Application to Nitrogen and Sulfur Deposition

Model	CMAQ	MAGIC	SMB	SPARROW	ASSETS
Complete Name	Community Multiscale Air Quality	Model of Acidification of Groundwater in Catchments	Simple Mass Balance	SPAtially Referenced Regression on Watershed Attributes	Assessment of Estuarine Trophic Status
Description	The CMAQ model is a comprehensive, three-dimensional grid-based Eulerian air quality model designed to simulate the formation and fate of gaseous and PM species, including ozone, oxidant precursors, and primary and secondary PM concentrations and deposition over urban, regional, and larger spatial scales. CMAQ is run for user-defined input sets of meteorological conditions and emissions.	MAGIC is a lumped-parameter model that predicts long-term effects of acidifying deposition on concentrations of the major ions in soil solution and surface waters. The model represents the catchment with aggregated, uniform soil compartments and a surface water compartment that can either be a lake or a stream. The model is calibrated using observed values of surface water and soil chemistry for a specified time period (Aherne et al., 2003).	Simple Mass Balance is a balance of system inputs of deposition and biological fixation with outputs of immobilization, uptake, adsorption, denitrification, combustion, erosion, volatilization, and leaching. It is most commonly used as a method for the analysis of the critical load of acid deposition. Its basic principle is based on identifying the long-term average sources of acidity and alkalinity to determine the maximum acid input that will balance the system at a biogeo-chemically safe limit.	SPARROW relates in-stream water quality measurements to spatially referenced characteristics of watersheds, including contaminant sources and factors influencing terrestrial and stream transport. The model empirically estimates the origin and fate of contaminants in streams.	ASSETS represents a Pressure-State-Response framework to assess the potential for eutrophication now or in the future for an estuary. It is a categorical ranking, where each of three indices results in a score that, when combined, result in a final overall score. The three indices consist of (1) Influencing Factors/ Overall Human Influence, (2) Overall Eutrophic Condition, and (3) Determined Future Outlook.
Case Study Application	All	Aquatic acidification	Terrestrial acidification	Aquatic nutrient enrichment (in tandem with ASSETS)	Aquatic nutrient enrichment (in tandem with SPARROW)
Model Type	Deterministic, process-driven model	Lumped-parameter model, which follows mass balance	Mass balance model over average conditions	Empirical/statistical model over average	Categorical, based on three numeric and

Model	CMAQ	MAGIC	SMB	SPARROW	ASSETS
		principles over time		conditions	categorical indices for average conditions
Temporal Features	Dynamic (hourly time step)	Dynamic (monthly and annual time step)	Steady-state (annual average results)	Steady-state (annual average results)	Steady-state (typically annual average results)
Spatial Scale Used in Case Study Analyses	The 2002 simulation, performed for both the eastern and western domains, used horizontal spatial resolution of approximately 12 x 12–km grid cells. The 2002 through 2005 simulations were performed for the eastern domain (12 km) and for the continental United States domain (36 x 36 km).	MAGIC is applied to 44 lakes in the Adirondack Case Study Area and 16 streams in the Shenandoah Case Study Area.	The SMB is applied to plots within the Hubbard Brook Experimental Forest and the Kane Experimental Forest. It is then applied to multiple areas (each covering 0.07 ha) within 24 states for sugar maple and in 8 states for red spruce identified from the U.S. Forest Service Forest Inventory and Analysis database.	The Potomac River and Neuse River case studies relied on the hydrology and catchments from the RF1 coverages from USGS to represent the watersheds contributing to each of the estuaries (Brakebill and Preston, 2004; Hoos et al., 2008).	ASSETS considers the tidal, mixing, and freshwater zones across a single estuary.
Strengths	▪ Is used for the continental United States. ▪ Is a process-based model, which includes chemical speciation.	▪ Has been in use for over 20 years and is widely accepted by the modeling community. ▪ Has been applied extensively in North America and Europe to both individual sites and regional networks of sites. ▪ Has been used in Asia (e.g., alpine and desert soils of China), Africa, and South America. ▪ Parameterization for new sites has much	▪ Is widely used across Europe for development of terrestrial critical loads. ▪ Is simple to apply. ▪ Model performance depends on the quality of the input data because the model is a simple balance. ▪ Considers both nitrogen and sulfur deposition.	▪ Has been published and scientifically accepted for about a decade. ▪ Has been applied on national and various regional scales. ▪ Provides estimates for different sources of nitrogen. ▪ Parameterization for new geographic domains and continuing refinement is being pursued by USGS.	▪ Has been used to assess estuarine status in all major coastal estuaries in the continental United States and at sites in Europe. ▪ Accounts for several different classes of evaluation: water quality, nitrogen loadings, physical conditions within the estuary, and future expected changes for the estuary.

Model	CMAQ	MAGIC	SMB	SPARROW	ASSETS
		background information to draw from because of the numerous applications in its 20 years of use. ▪ Has an automated built-in optimization procedure. ▪ Has versatile application (e.g., investigation of temporal chemical changes in response to changing deposition or impact analyses of emission reduction options). ▪ Simulates pH, sulfate, nitrate, ammonia, acid neutralizing capacity, and dissolved organic carbon. ▪ Directly simulates water quality response to atmospheric deposition.		▪ Model performance/ error is explicitly included (e.g., quantifies uncertainties based on model coefficient error and unexplained variability in the observed data).	▪ Provides an opportunity to link to watershed nitrogen loading models, such as SPARROW.
Weaknesses	▪ Has current minimum grid scale of 12 km.	▪ Must be parameterized for each application. ▪ Has controlled release of program.	▪ Makes it difficult to estimate reasonable input values. ▪ Does not explicitly represent environmental processes. ▪ Is not dynamic in time. ▪ Model performance depends on the quality of the input data	▪ Has empirically estimated land to water and instream delivery rates. ▪ Is not dynamic in time. ▪ Does not explicitly include deposition measurements. ▪ Cannot differentiate between nitrogen species; only	▪ Has categorical index. ▪ Is not dynamic in time. ▪ Does not explicitly include deposition measurements. ▪ Cannot differentiate between nitrogen species. ▪ Does not explicitly include uncertainty

Model	CMAQ	MAGIC	SMB	SPARROW	ASSETS
			because the model is a simple balance. ▪ Uncertainty analysis is not explicitly included. ▪ Requires assumption that nitrogen and sulfur cycles and ion exchange are all at steady-state. ▪ Assumes simple hydrology where infiltration is straight through the soil profile.	simulates total nitrogen. ▪ Can only be operated for one pollutant at a time.	analysis. ▪ Has limited extrapolation of results outside of specific estuary studied.
Supporting Organization (s)/ Agency Endorsements	U.S. EPA's Office of Research and Development	Academic, with sponsorship of Norwegian Institute for Water Research and University of Virginia. MAGIC is also cited in numerous documents by government agencies.	Utilized by multiple agencies, especially during critical load development, but not necessarily supported by any specific agency.	U.S. Geological Survey	National Oceanic and Atmospheric Administration
Nitrogen and Sulfur Deposition Considerations	The CMAQ deposition data for nitrogen and sulfur species (list provided in Appendix 1) are used to calculate oxidized and reduced wet and dry nitrogen deposition, wet and dry sulfur deposition, and total reactive nitrogen and total sulfur deposition.	Time series (annual or monthly) of deposition fluxes of ions (wet plus dry deposition).	Depending on the mass balance model used, either total nitrogen and/or sulfur or speciated nitrogen and/or sulfur atmospheric deposition rates can be incorporated.	To date, SPARROW has focused on wet deposition input data from National Atmospheric Deposition Program.	Deposition is not explicitly included in the assessment, but may be included in the watershed model used to determine loadings to the estuary (e.g., SPARROW).

Note: PM = particulate matter, USGS = U.S. Geological Survey.

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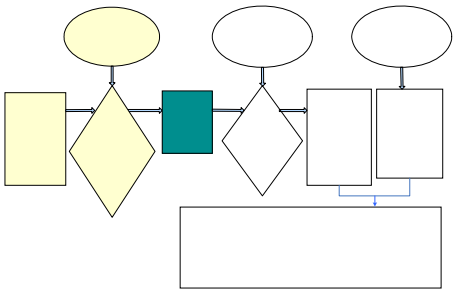

3.0 SOURCES, AMBIENT CONCENTRATIONS, AND DEPOSITION

This chapter discusses current emissions sources of nitrogen and sulfur, as well as atmospheric concentrations, estimates of deposition, policy-relevant background, and non-ambient loadings of nitrogen and sulfur to ecosystems. Both measured and modeled data are used to evaluate current contributions of nitrogen and sulfur compounds to the Risk and Exposure Assessment case study areas. The case study areas are (1) Adirondack Mountains (referred to as Adirondack); (2) Blue Ridge Mountains/Shenandoah National Park, Virginia (referred to as Shenandoah); (3) Kane Experimental Forest (KEF) on the Allegheny Plateau of Pennsylvania; (4) Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire; (5) Potomac River/Potomac Estuary; (6) Neuse River/Neuse River Estuary; (7) southern California Coastal Sage Scrub (CSS); and (8) Pacific coast states' Mixed Conifer Forest (MCF), including the Transverse (or Los Angeles) Range, which includes the San Bernardino Mountains, and the Sierra Nevada Range. The Rocky Mountain National Park (RMNP) is also highlighted as a supplemental area. A nationwide description of emissions, concentrations, and deposition is provided in Section 3.2; a detailed characterization of nitrogen and sulfur deposition in and near the case study areas[1] is presented in Section 3.3; and the relative contributions of ambient concentrations to deposition are evaluated in Section 3.4. The deposition fields described here were used as modeling input for the individual case study ecological modeling presented in Chapters 4 and 5.

[1] The eight case study areas are shown in Figure 2.1-1 and discussed in Chapters 4 and 5 and Appendices 4 through 7.

3.1 SCIENCE OVERVIEW

Prior to analyzing the effects of nitrogen and sulfur deposition to the environment, the ambient emissions, transformations, and transport of nitrogen and sulfur in the atmosphere must first be examined. As noted in Chapter 1, the terms "oxides of nitrogen" and "nitrogen oxides" (NO_x) refer to all forms of oxidized nitrogen compounds, including nitric oxide (NO), nitrogen dioxide (NO_2), and all other oxidized nitrogen-containing compounds transformed from NO and NO_2. Additionally, reduced forms of nitrogen (ammonia [NH_3] and ammonium ion [NH_4^+], collectively termed reduced nitrogen [NH_x]) can also play an important role in the emission, transformations, and deposition, and are included in this review. Much like NO_x, additional NH_x can lead to increased acidification and nutrient enrichment in ecosystems. Where possible, the analyses will separate oxidized from reduced forms of nitrogen to show the impact from each component, as well as the overall impact from total reactive nitrogen. This will be important for the policy assessment portion of this review.

Sulfur oxides (SO_x) refer to all gas-phase oxides of sulfur, including sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and disulfur monoxide (S_2O); however, only SO_2 is present in concentrations relevant for atmospheric chemistry and ecological exposures.

Deposition of nitrogen and sulfur to water and land surfaces is a function of ambient concentrations of NO_x, other forms of reactive nitrogen, NH_x, and SO_x, as well as their atmospheric transformation products, and of the earth's surface properties through complex processes involving numerous meteorological variables and dependencies. Atmospheric pollutants deposit through direct contact with the surface (i.e., dry deposition), transfer into liquid precipitation (i.e., wet deposition), and through interaction with fog or mist (i.e., occult deposition). Occult deposition is an important process in coastal and mountain areas for delivering pollutants to the ground and vegetation, as described in Chapter 2.8 of the *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008b). This Risk and Exposure Assessment review was not able to quantitatively account for occult deposition because of a lack of routine measurements and because atmospheric models do not fully account for this type of deposition. Wet and dry deposition are the two major mechanisms of deposition addressed here. The magnitude of wet and dry deposition is related to the ambient concentrations of NO_x and SO_x through the time-, location-, process-, and chemical-species–specific deposition velocity (Seinfeld and Pandis,

1998). The ambient concentrations of NO_x, NH_3, and SO_2 that contribute to nitrogen and sulfur deposition are the result of emissions of these pollutants and oxidant precursor species (e.g., volatile organic compounds) from anthropogenic and natural sources. The emissions to atmospheric-concentrations-to deposition processes involving the chemical formation and fate of gas and particle-phase total reactive nitrogen and sulfur are described in Chapter 2.6 of the ISA. **Figure 1.3-1** illustrates the cycle of reactive, oxidized nitrogen species in the atmosphere. Emissions of NO_x lead to NO and NO_2 concentrations that undergo chemical transformations to form other nitrogen-containing oxidants such as peroxyacetyl nitrates (PAN). Because NO and NO_2 are only slightly soluble, they can be transported over longer distances in the gas phase than more soluble pollutants. During transport, NO and NO_2 can be transformed into other pollutants, such as PAN, which can provide a major source of NO_x in remote areas. NO_2 can also form gas-phase nitric acid (HNO_3), which can increase the acidity of clouds, fog, and rain water and form particulate nitrate that contributes to nitrogen deposition in locations distant from the NO_x emissions source area. Emissions of SO_x contain SO_2, which is oxidized in the atmosphere through a series of reactions with hydroxide radicals (OH), hydroperoxyl radicals (HO_2), oxygen (O_2), and water (H_2O) to form sulfuric acid (H_2SO_4). H_2SO_4 is also formed from SO_3 emissions within or immediately after release into the atmosphere. H_2SO_4 is rapidly transformed to the aqueous phase of aerosol particles and cloud droplets and can participate in the formation of new particles. The transformation of sulfur compounds in the atmosphere is illustrated in **Figure 1.3-2**. Emissions of NH_3 neutralize the acidity in ambient particles and form new particles through reactions with gas-phase HNO_3 to form ammonium nitrate (NH_4NO_3) and with sulfate (SO_4^{2-}) to form ammonium sulfates, which are important components of nitrogen and sulfur deposition. Thus, NO_x, SO_x, and NH_3 emissions can not only affect atmospheric loadings of these pollutants in and near source locations, but they can also affect more distant areas through chemical transformation and transport.

3.2 NATIONWIDE SOURCES, CONCENTRATIONS, AND DEPOSITION OF NO_X, NH_3, AND SO_X

3.2.1 Sources of Nitrogen and Sulfur

The National Emissions Inventory (NEI) annual total emissions data for 2002 (U.S. EPA, 2006) are used to characterize the magnitude and spatial patterns in emissions of NO_x, NH_3, and

SO_2 nationwide[2]. The spatial resolution of these data varies by source type. Emissions from most large stationary sources are represented by individual point sources (e.g., electric generating units, industrial boilers). Sources that emit over broad areas are reported as county total emissions. The national annual 2002 emissions of NO_x, NH_3, and SO_2 by major source category are presented in Table 2-1 of the ISA (U.S. EPA, 2008b).

3.2.1.1 NO_x Emissions

The distribution of national total NO_x emissions across major source categories is provided in **Table 3.2-1.** Emissions summaries are also provided for the East[3] and West in **Tables 3.2-2a and b**, respectively, to reveal regional differences in source emissions profiles. In addition to anthropogenic sources, there are also natural sources of NO_x, including lightning, wildfires, and microbial activity in soils. Nationally, transportation-related sources (i.e., on-road, nonroad, and aircraft/locomotive/marine) account for ~60% of total anthropogenic emissions of NO_x, while stationary sources (e.g., electrical utilities and industrial boilers) account for most of the remainder (U.S. EPA, 2008b, AX2, Table 2-1). Emissions from on-road vehicles represent the major component of mobile source NO_x emissions. Approximately half the mobile source emissions are contributed by diesel engines, and half are emitted by gasoline-fueled vehicles and other sources (U.S. EPA, 2008b, AX2, Section 2.1.1 and Table 2-1). Nationwide, the nonroad, aircraft/locomotive/marine, and non-electric generating unit point emissions sectors each contribute generally similar amounts to the overall NO_x inventory. Overall, NO_x emissions are broadly split between NO and NO_2 in a ratio of 90% NO and 10% directly emitted NO_2. However, this split can vary by source category, as described in Chapter 2.2.1 of the ISA (U.S. EPA, 2008b).

Table 3.2-1. Annual National NO_x Emissions across Major Source Categories in 2002.

National Totals	NO_x	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	4.619	22%
Industrial Point Sources	2.362	11%
Stationary Area	1.529	7%

[2] For the purposes of this analysis, nationwide emissions do not include emissions from Alaska or Hawaii.

[3] In this analysis, the East is defined as all states from Texas northward to North Dakota and eastward to the East Coast of the United States. States from New Mexico northward to Montana and westward to the West Coast are considered to be part of the West.

National Totals	NO_x	
	Emissions (million tons)	**Percent of Total**
On-road	7.839	37%
Nonroad	2.219	10%
Aircraft/Locomotive/Marine	2.611	12%
Fires	0.080	< 1%
Total	21.259	

Table 3.2-2a. Annual NO_x Emissions across Major Source Categories in 2002 for the Eastern United States.

Eastern U.S.	NO_x	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	4.094	23%
Industrial Point Sources	2.031	12%
Stationary Area	1.295	7%
On-road	6.250	36%
Nonroad	1.709	10%
Aircraft/Locomotive/Marine	2.038	12%
Fires	0.028	< 1%
Total	17.445	

Table 3.2-2b. Annual NO_x Emissions across Major Source Categories in 2002 for the Western United States.

Western U.S.	NO_x	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	0.525	14%
Industrial Point Sources	0.331	9%
Stationary Area	0.234	6%
Onroad	1.589	42%
Nonroad	0.510	13%
Aircraft/Locomotive/Marine	0.573	15%
Fires	0.055	1%
Total	3.817	

In general, NO_x emissions in the East are nearly 5 times greater that NO_x emissions in the West. In both the eastern and western United States, the on-road sector is the largest contributor.

Emissions from electric generation units are the second-largest contributor to NO_x emissions in the East with 23% of the total. Emissions in the East from industrial point sources, nonroad engines, and aircraft-locomotives-marine engines each contribute in the range of 10 to 12%. In the West, the contribution to NO_x emissions from electric generation units (14%) is in the same range as the contributions from nonroad engines (13%) and aircraft-locomotives-marine engines (15%).

The spatial patterns of 2002 annual NO_x emissions across the United States are shown in **Figure 3.2-1**[4]. Emissions of NO_x are concentrated in and near urban and suburban areas and along major highways. Moderate or higher levels of NO_x emissions (>100,000 tons/yr)[5] are also evident in some rural areas at locations (i.e., grid cells) containing major point sources. The amount of NO_x emissions in and near each of the case study areas can be seen from this map. All of the case study areas contain or are near locations with NO_x emissions in excess of 100,000 tons/yr.

[4] To create this map, NO_x emissions were allocated to a 36 x 36– km grid covering the United States in order to normalize for the differences in the geographic aggregation of point- and county-based emissions. The emissions are in tons per year per 36 x 36 km (1,296 km^2).

[5] Emissions are in tons per year per 36 x 36 km (1,296 km^2).

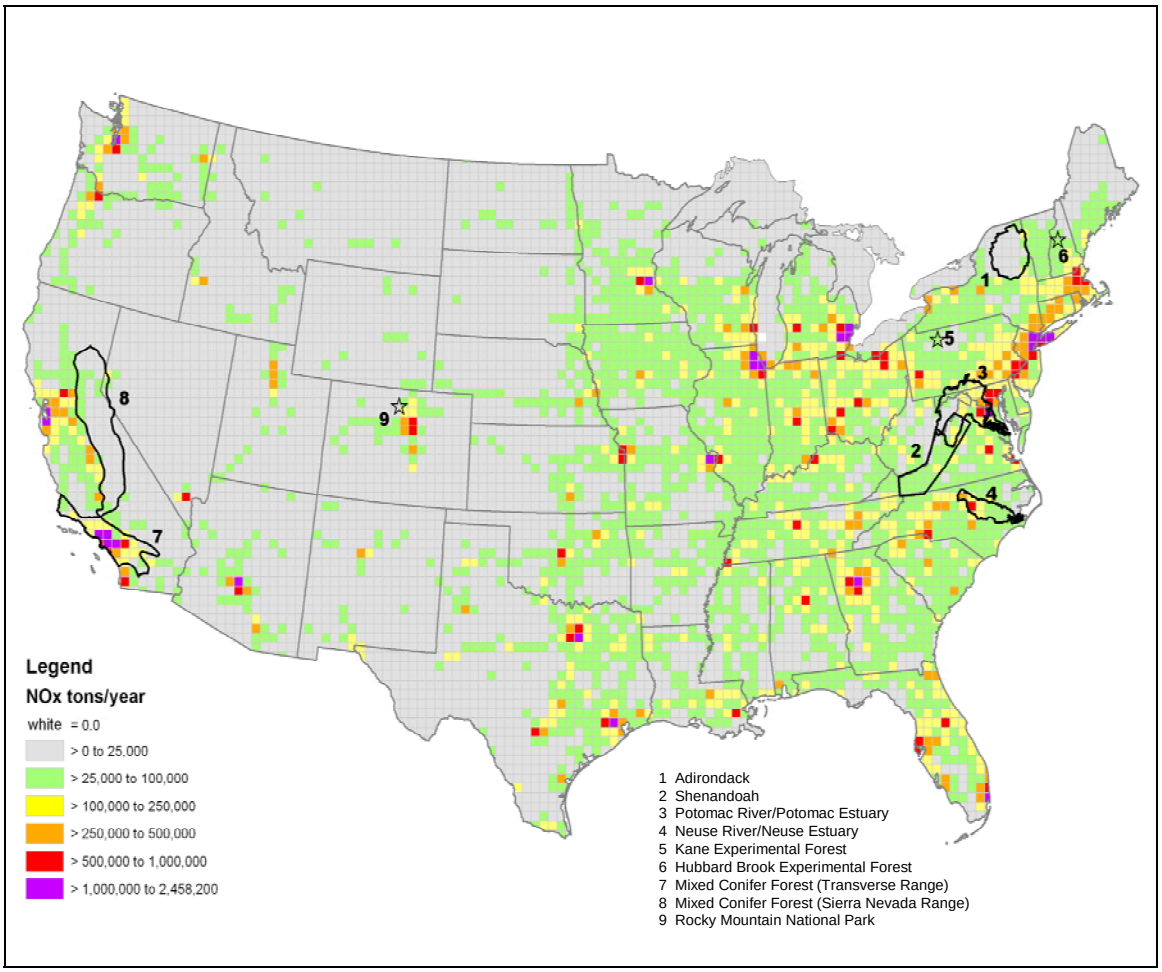

Figure 3.2-1. Spatial distribution of annual total NO_x emissions (tons/yr) for 2002.

3.2.1.2 NH_3 Emissions

The primary anthropogenic sources of NH_3 emissions are fertilized soils and livestock. Motor vehicles and stationary combustion are small emitters of NH_3. Some NH_3 is emitted as a byproduct of NO_x reduction in motor vehicle catalysts. The spatial patterns of 2002 annual NH_3 emissions are shown in **Figure 3.2-2**[6]. The highest emissions of NH_3 are generally found in areas of major livestock feeding and production facilities, many of which are in rural areas. In addition, NH_3 emissions exceeding 1,000 tons/yr are evident across broad areas that are likely associated with the application of fertilizer to crops. The patterns in NH_3 emissions are in contrast to the more urban-focused emissions of NO_x. The Potomac River/Potomac Estuary, Neuse River/Neuse River Estuary, Shenandoah, and Mixed Conifer Forest (in the Sierra Nevada Range and the Transverse Range) case study areas all have sources with NH_3 emissions

[6] Note that, because overall emissions of NH_3 are much lower than emissions of NO_x, we used a more refined set of ranges to display emissions of NH_3 compared to what was used to display emissions of NO_x.

exceeding 5,000 tons/yr. Rocky Mountain National Park is adjacent to an area with relatively high NH_3 emissions exceeding 2,500 tons/yr. The Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas are more distant from sources of NH_3 of this magnitude.

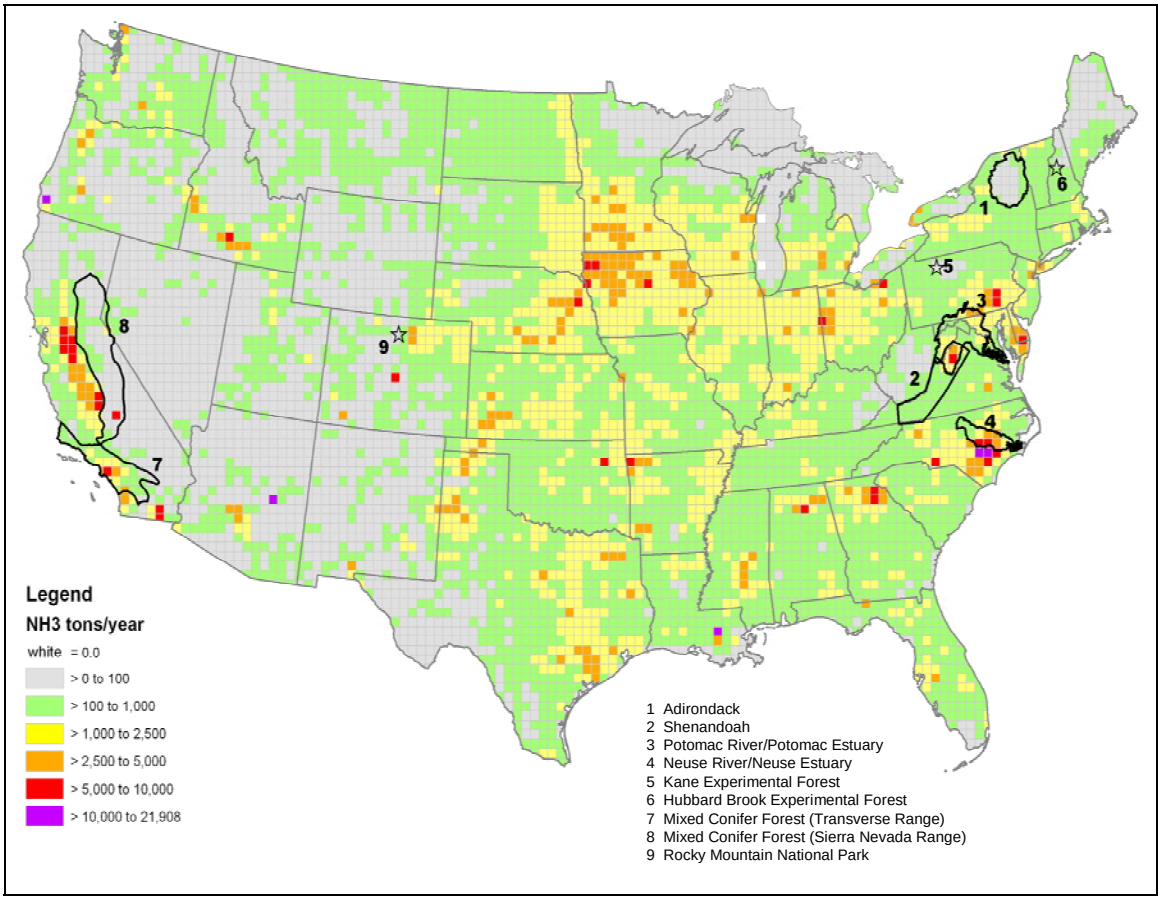

Figure 3.2-2. Spatial distribution of annual total NH_3 emissions (tons/yr) for 2002.

3.2.1.3 SO_x Emissions

The distributions of SO_2 emissions for major source categories nationally are provided in **Table 3.2-3**. Emissions of SO_2 for the East and West are presented in **Tables 3.2-4a and b**, respectively. Anthropogenic emissions of SO_2 in the United States are mainly due to combustion of fossil fuels by electrical generation units (70%) and industrial point sources (15%); transportation-related sources contribute minimally (7%). Thus, most SO_2 emissions originate from point sources. Almost all the sulfur in fuel is released as volatile components (SO_2 or SO_3) during combustion. The higher sulfur content of coal compared to other types of fossil fuels results in higher SO_2 emissions from electrical utilities using coal as fuel.

Emissions of SO_2 are more than 10 times greater in the East than in the West. Emissions from electric generation units are the largest contributor to SO_2 emissions in both the East and West, but are a much greater fraction of the inventory in the East (71%) compared to the West (44%). Stationary area sources and the aircraft-locomotive-marine engine sector have a greater relative contribution to SO_2 in the West compared to the East[7].

The largest natural sources of SO_2 are volcanoes and wildfires. Although SO_2 constitutes a relatively minor fraction (0.005% by volume) of total volcanic emissions (Holland, 1978), concentrations in volcanic plumes can be range up to tens of parts per million (ppm). Sulfur is a component of amino acids in vegetation and is released during combustion. Emissions of SO_2 from burning vegetation are generally in the range of 1% to 2% of the biomass burned (Levine et al., 1999).

Table 3.2-3. Annual National SO_2 Emissions across Major Source Categories in 2002.

National Totals	SO_2	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	10.359	70%
Industrial Point Sources	2.249	15%
Stationary Area	1.250	8%
On-road	0.242	2%
Nonroad	0.188	1%
Aircraft/Locomotive/Marine	0.533	4%
Fires	0.050	< 1%
Total	14.871	

Table 3.2-4a. Annual SO_2 Emissions across Major Source Categories in 2002 for the Eastern United States.

Eastern U.S.	SO_2	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	9.923	71%
Industrial Point Sources	2.057	15%
Stationary Area	1.116	8%
On-road	0.214	2%

[7] Note that SO_2 emissions from fires are understated in the NEI because of an error in the emissions calculations.

Eastern U.S.	SO_2	
	Emissions (million tons)	**Percent of Total**
Nonroad	0.162	1%
Aircraft/Locomotive/Marine	0.398	3%
Fires	0.011	< 1%
Total	13.881	

Table 3.2-4b. Annual SO_2 Emissions across Major Source Categories in 2002 for the Western United States.

Western U.S.	SO_2	
	Emissions (million tons)	**Percent of Total**
Electric Generation Units	0.436	44%
Industrial Point Sources	0.192	19%
Stationary Area	0.134	14%
On-road	0.029	3%
Nonroad	0.026	3%
Aircraft/Locomotive/Marine	0.136	14%
Fires	0.035	4%
Total	0.988	

The spatial patterns of 2002 annual SO_2 emissions are shown in **Figure 3.2-3**. High SO_2 emissions are scattered across the East, and there are large sources in both urban are rural locations. The greatest geographic concentration of SO_2 sources is in the Midwest, particularly along the Ohio River, where numerous electric generating units are located. As noted above, SO_2 emissions in the West are much lower than in the East, with sources concentrated in urban locations along with localized emissions in more rural areas associated with industrial sources (e.g., smelters) and gas-field operations.

The Potomac River/Potomac Estuary, Neuse River/Neuse River Estuary, Shenandoah, and Mixed Conifer Forest (Transverse Range portion) case study areas each contain numerous locations of major SO_2 emitters. The Kane Experimental Forest Case Study Area and Rocky Mountain National Park are relatively close to SO_x emission locations exceeding 5,000 tons/yr. The Adirondack, Hubbard Brook Experimental Forest, and Mixed Conifer Forest (Sierra Nevada Range portion) case study areas are more distant from SO_x sources of this magnitude.

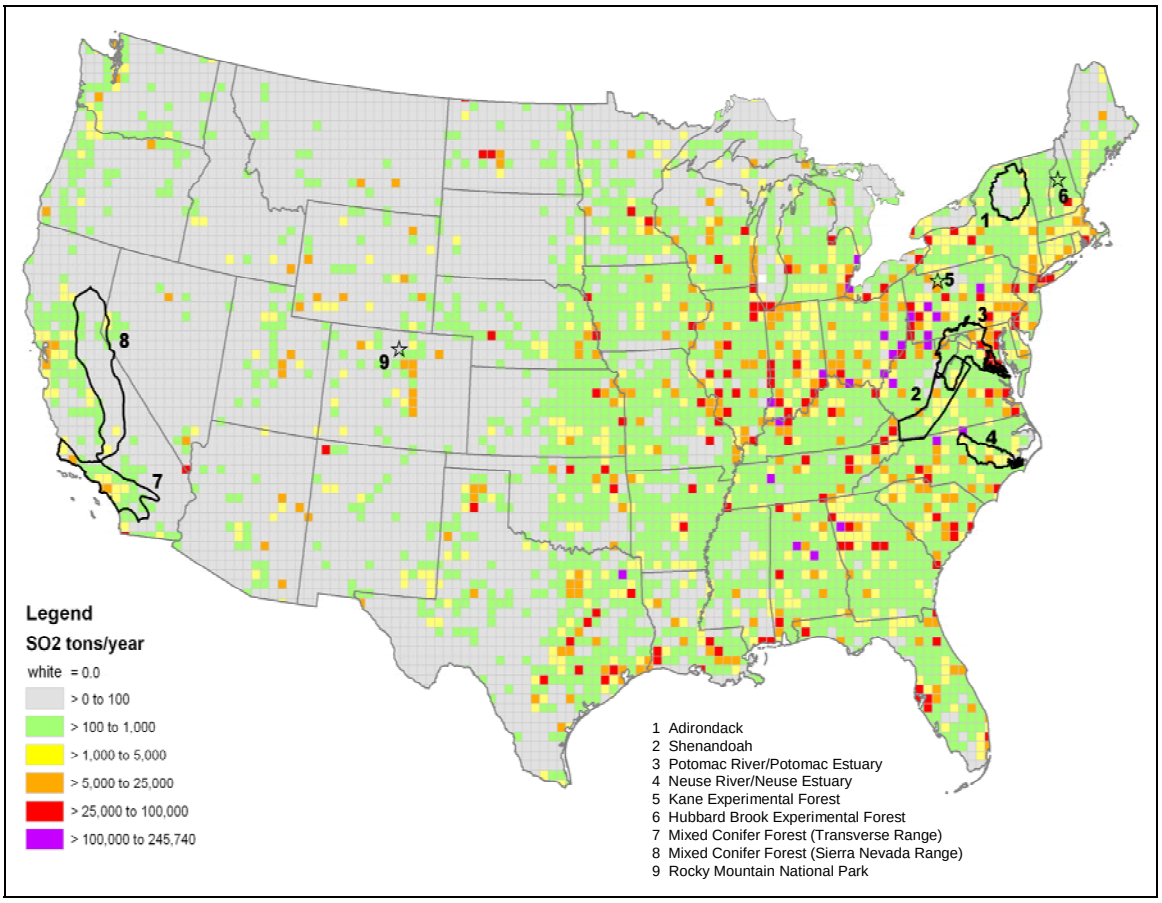

Figure 3.2-3. Spatial distribution of annual total SO_2 emissions (tons/yr) for 2002.

3.2.2 Nationwide Atmospheric Concentrations of NO_x and SO_x

This section provides a nationwide view of the magnitude and spatial patterns in atmospheric concentrations of NO_x and SO_x. Measurements of these pollutants are made at numerous sampling sites comprising several routine and special study monitoring networks in the United States (see Section 2.9 of the ISA [U.S. EPA, 2008b] for a comprehensive review of these networks and measurement techniques). Monitoring data generally provide the most direct approach to characterizing concentrations in a particular location. However, for NO_x, and to some extent SO_2, the lack of geographic coverage and limitations in spatial representativeness of most existing sites affect the extent to which these monitoring data can be used to infer NO_x and SO_2 concentrations in unmonitored areas, particularly rural locations. As noted in the ISA (U.S. EPA, 2008b), ambient NO_2 is normally measured at only a few locations in a given area. In view of the limitations of existing monitoring networks, and the large spatial gradients in NO_2, as suggested by the gradients in NO_y described below, the ISA states that air quality model predictions might be helpful for capturing the large-scale features of NO_2 concentrations and

could be used in conjunction with measurements to provide a more complete picture of the variability of NO_2 across the United States. Monitoring data are not as spatially limited for SO_2 as for NO_2 because SO_2 measurements are also available from the Clean Air Status and Trends Network (CASTNET; http://www.epa.gov/CASTNET), which covers rural and remote locations, particularly in the eastern United States.

This analysis used measured data, along with air quality model predictions of NO_x and SO_2, to characterize NO_2 and SO_2 concentrations in the United States. The air quality model predictions were taken from applications of the Community Multiscale Air Quality modeling system (Byun and Schere, 2006; U.S. EPA, 1999). CMAQ is a chemistry transport model that treats the chemical interactions among NO_x; SO_x; other pollutants and their precursors; the formation of secondary aerosols containing nitrogen, sulfur, and other species; the multi-day transport of these pollutants from local to national scales; and the removal of pollutants by deposition. CMAQ was used to simulate concentrations and deposition for 2002 using meteorology and emissions for that year. In this application, CMAQ was run with a horizontal resolution of approximately 12 × 12 km. Hourly predictions of NO_x and SO_2 were aggregated to provide annual average concentration fields of these pollutants across the United States. Additional information on this CMAQ application is provided in Appendix 1 of this report.

3.2.2.1 NO_x Concentrations

For the period 2003 through 2005, mean annual average NO_2 concentrations were ~15 parts per billion (ppb) with an interquartile range of 10 to 25 ppb and a 90th percentile value of ~30 ppb, based on measurements at all monitoring sites within metropolitan statistical areas (MSAs) in the United States (U.S. EPA, 2008b). Nationwide, NO_2 concentrations have been trending downward, with an overall 30% decrease in concentrations from 1990 to 2006 (U.S. EPA, 2008b) as a result of various federal and state NO_x emissions-control programs.

As stated in Chapter 1, the terms “oxides of nitrogen” and “nitrogen oxides” in this document refer to all forms of oxidized nitrogen compounds, including NO, NO_2, and all other oxidized nitrogen-containing compounds transformed from NO and NO_2. In the scientific community and in terms of the predictions from CMAQ, this definition of oxides of nitrogen is referred to as NO_y. Thus, we are using CMAQ predictions of NO_y in our analysis to characterize concentrations of oxides of nitrogen from a national perspective. The spatial field of model-predicted 2002 annual average NO_y concentrations is shown in **Figure 3.2-4**.

The patterns in NO_y concentrations show some similarity to the general patterns of NO_x emissions shown in **Figure 3.2-1**. For the most part, highest concentrations are predicted in the core portions of urban areas with a relatively large drop in concentrations with distance from the location of peak values. The spatial gradients from urban and rural areas appear to be greater in the West compared to those in the East. In the West, NO_y concentrations outside source areas drop off rapidly to below 3 ppb. Annual average concentrations of NO_y are predicted to exceed 3 ppb in rural areas within broad portions of the East. The highest rural concentrations in the East extend across portions of the Midwest, Pennsylvania, and along the Northeast Corridor. Annual average NO_y concentrations exceeding 10 ppb are predicted in portions of the Potomac River/Potomac Estuary, Neuse River/Neuse River Estuary, and Mixed Conifer Forest (Transverse Range portion) case study areas. The Kane Experimental Forest Case Study Area is within the area of regionally high NO_y that extends across Pennsylvania. The other case study areas (Adirondack, Hubbard Brook Experimental Forest, and Mixed Conifer Forest [Sierra Nevada Range portion]) as well as the Rocky Mountains are predicted to have annual average NO_y concentrations of ~3 ppb or less.

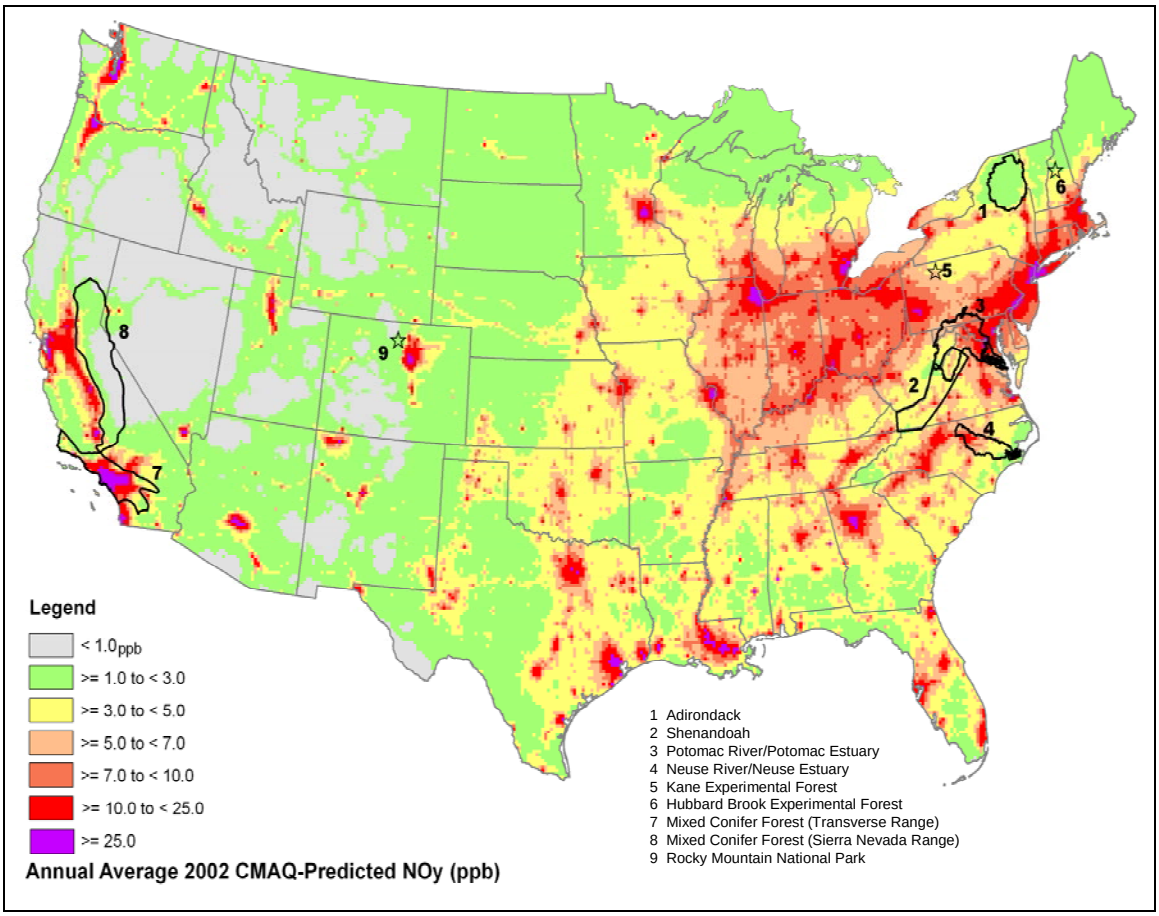

Figure 3.2-4. Model-predicted annual average NO_y concentrations (ppb) for 2002.

3.2.2.2 SO_2 Concentrations

Measured annual average SO_2 concentrations for the period 2003 through 2005 are presented in Table 2-23 of the ISA (U.S. EPA, 2008b). SO_2 concentrations aggregated across urban sites and nonurban sites were generally very low at ~4 ppb. Interquartile concentrations were in the range of 1 to 6 ppb for urban sites and 1 to 5 ppb for nonurban sites. Urban and non-urban concentrations at the 90th percentile were 8 ppb. In an analysis of 11 cities, sites with the highest annual mean SO_2 concentrations were in Steubenville, OH (8.6 to 14 ppb), and Pittsburgh, PA (6.8 to 12 ppb) (U.S. EPA, 2008b). Both of these cities are in areas with very high SO_2 emissions from electric generating units. At suburban and rural CASTNET sites, annual average SO_2 concentrations in 2007 were much higher by far at sites in the East compared to the West (U.S. EPA, 2008a). In the East, the highest concentrations were measured across the Midwest, Southeast, and mid-Atlantic states. Relatively low concentrations were measured across New England.

The 2002 annual average model-predicted SO_2 concentration fields are shown in **Figure 3.2-5.** The model predictions are generally consistent with the magnitude and spatial patterns of concentrations from measured data. Peak predicted concentrations, exceeding 10.0 ppb, coincide with the location of highest emissions (see **Figure 3.2-3**), with large decreases in concentrations with distance from sources. In the East, the localized peak concentrations are within a broad area of concentrations exceeding 1.0 ppb. SO_2 predictions exceed 3.0 ppb in portions of the Midwest, across Pennsylvania, and into the mid-Atlantic states and decline to <0.5 ppb in northern Maine. In the West, SO_2 predictions are much lower than in the East and are generally <0.5 ppb, except in the vicinity of sources of SO_2.

The Potomac River/Potomac Estuary Case Study Area has the highest SO_2 predictions among the six case study areas in the East. The portion of the Potomac River/Potomac Estuary Case Study Area in western Virginia is predicted to have concentrations in the range of 1 to 3 ppb, which increases to 3 to 5 ppb in Maryland. SO_2 concentrations in the Kane Experimental Forest, Shenandoah, and Neuse River/Neuse River Estuary case study areas are in the range of 1.0 to 3.0 ppb, with some locations having up to 3.0 to 5.0 ppb. The Adirondack, Hubbard Brook Experimental Forest, Mixed Conifer Forest (Sierra Nevada Range portion) case study areas, as well as the Rocky Mountains, all have predicted SO_2 concentrations of <1.0 ppb. The portion of Mixed Conifer Forest (Transverse Range portion) Case Study Area near the city of Los Angeles has predictions exceeding 10.0 ppb.

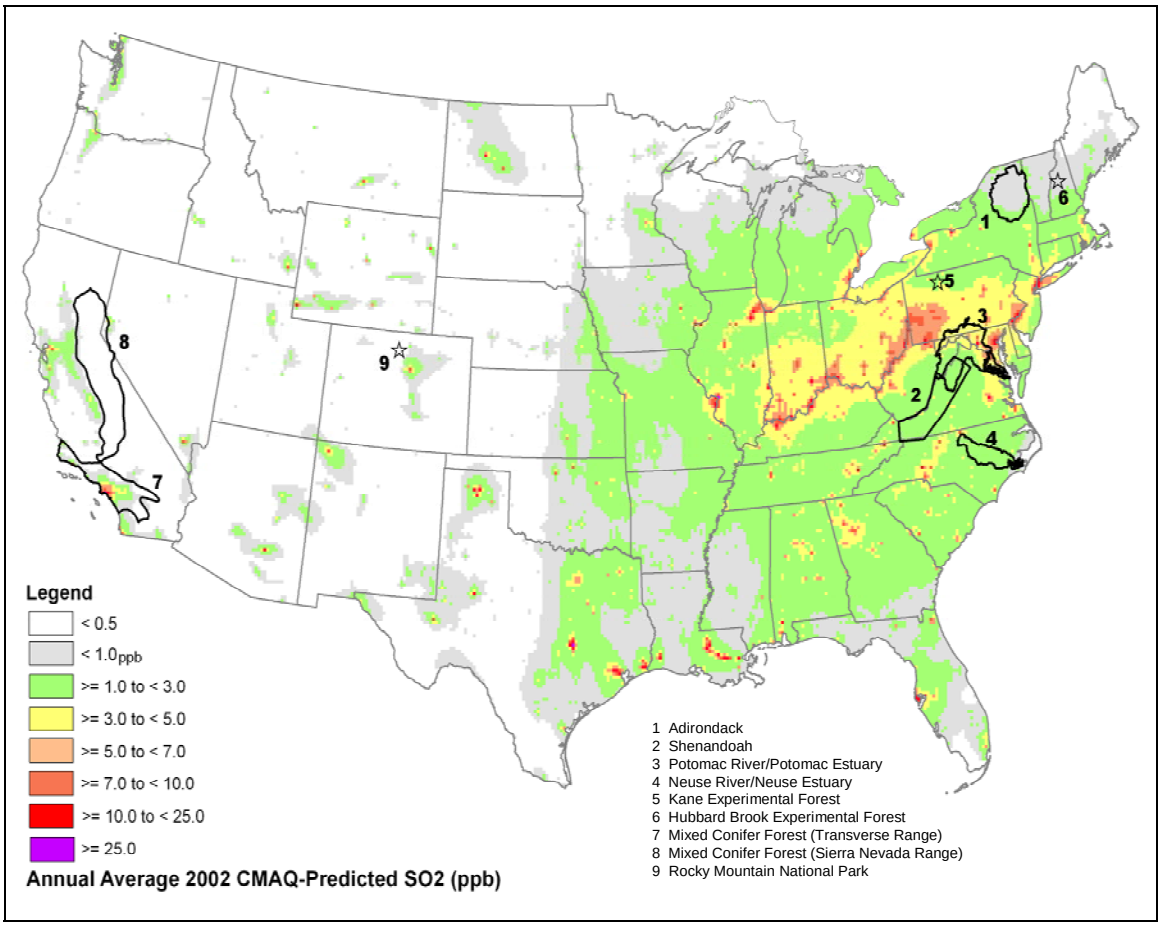

Figure 3.2-5. Model-predicted annual average SO_2 concentrations (ppb) for 2002.

3.2.3 Nationwide Deposition of Nitrogen and Sulfur

As noted in Section 3.1 of this report, gaseous and particulate deposition of nitrogen and sulfur species to land and water surfaces occurs through both dry deposition and wet deposition processes. Additionally, nitrogen deposition is composed of both oxidized and reduced forms of total reactive nitrogen. The nationwide analysis of deposition examined the magnitude and spatial patterns of total sulfur deposition, total nitrogen deposition, and the oxidized and reduced forms of total reactive nitrogen. The analysis of current levels and trends in nitrogen and sulfur deposition is based in part on measured data as described in Section 2.10 of the ISA (U.S. EPA, 2008b). A combination of measured data and model predictions to glean additional information on the magnitude and spatial patterns in deposition across the United States were also used.

3.2.3.1 Approach for Assimilating Measured Data and Model Predictions

To create spatial fields of deposition, wet deposition measurements from the National Atmospheric Deposition Program (NADP) National Trends Network

(http://nadp.sws.uiuc.edu/nadpoverview.asp) were used. Estimates of dry deposition are available from the CASTNET network (http://www.epa.gov/castnet/) (Clarke et al., 1997), but these data are calculated based on an "inferential model" involving measured air concentrations coupled with species- and location- dependent deposition velocities that reflect local land use and meteorological conditions at each monitoring site (U.S. EPA, 2008b). These dry deposition estimates may not be representative of dry deposition fluxes in unmonitored areas where land use or meteorological conditions are different from those at monitoring sites. Therefore, for the nationwide assessment of deposition, dry deposition predictions from the 2002 CMAQ model simulation were used because the model has information about meteorology and land use in each grid cell of the domain; therefore, it is not restricted to the cleared area nearest to the monitors, as is the case for the measurements. Thus annual total 2002 wet deposition from NADP measurements, coupled with the 2002 model-predicted dry deposition from CMAQ, were used.

NADP data are collected at more than 250 locations across the contiguous United States. From these points, analysts at the NADP generated continuous surfaces at a 2.5-km grid cell resolution by using an inverse distance weighted (IDW) algorithm available at http://www.epa.gov/monitor/programs/nadpntn.html. Wet deposition of sulfur was calculated from deposition measurements of sulfate (SO_4^{2-}). Oxidized nitrogen wet deposition was calculated from measured nitrate (NO_3^-) deposition, and reduced nitrogen wet deposition was calculated from measurements of wet ammonium (NH_4^+) deposition.

The CMAQ data were generated at a 12-km grid cell size and consisted of many estimated deposition values, including total dry sulfur, total dry nitrogen, total dry oxidized nitrogen, and total dry reduced nitrogen. The oxidized nitrogen species extracted from CMAQ are NO_3^-, HNO_3, NO, NO_2, dinitrogen pentoxide (N_2O_5), PAN, HONO, and organic nitrates (NTR), while the reduced nitrogen species are NH_3 and NH_4^+. Both the measured and modeled datasets provided deposition values in kg/ha/yr. The NADP data were at a finer spatial resolution, and in order to add the two gridded datasets together, the finer NADP dataset was resampled up to the 12-km scale of the CMAQ data. Once both datasets were at the same spatial resolution, the wet and dry deposition values for each component (e.g., oxidized nitrogen) were added together on a grid-cell by grid-cell basis to provide spatial fields of estimated annual total (i.e., wet plus dry) deposition across the United States. The combined measured plus modeled deposition fields were also used as input for the individual case study ecological modeling described in Chapters 4 and 5 and Appendices 4 through 7 of this report.

3.2.3.2 Nitrogen Deposition

As noted in the ISA, increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly ten-fold increase in atmospherically deposited nitrogen (U.S. EPA, 2008b). Increased deposition of reduced nitrogen in the United States, measured as NH_4^+ deposition, correlates well with the local and regional increases in agricultural intensity. Although total reactive nitrogen deposition trends based on a sample of 34 NADP sites in the East show an overall decline from deposition levels in 1990, more recent trends beginning in the late 1990s have been less consistent (U.S. EPA, 2008b; Sickles and Shadwick, 2007a).

From 2004 to 2006, estimated dry combined with measured wet nitrogen deposition was greatest in the Ohio River Valley, specifically in Indiana and Ohio, where there were values as high as 9.2 and 9.6 kg N/ha/yr, respectively. Nitrogen deposition was lower at sites in other parts of the East, including Florida and in northern New England, where nitrogen deposition was 4.0 kg N/ha/yr or less. The greatest deposition in the central United States occurred in Kansas and Oklahoma, with estimates of 7.0 and 6.5 kg N/ha/yr, respectively. Nitrogen deposition levels were much lower in the West where values ranged from ~1.0 to 3.0 kg N/ha/yr. The highest deposition in the West (~4.0 to 5.0 kg N/ha/yr) was found at sites near Los Angeles, CA. In most areas of the country, measured wet deposition dominates estimated dry deposition in terms of the contribution to total deposition. The extent of wet versus dry deposition varies regionally to some extent because some western sites have more similar or higher rates of dry versus wet deposition than the more humid sites in the East.

The spatial fields of oxidized nitrogen deposition, reduced nitrogen deposition, and total reactive nitrogen deposition across the United States for 2002 are shown in **Figures 3.2-6, 3.2-7, and 3.2-8**, respectively. In general, on a regional basis, both forms of nitrogen deposition are much higher in the East compared to the West. Within the eastern United States, there is a broad area with oxidized nitrogen deposition of 5.5 kg N/ha/yr or greater that extends from Louisiana northeastward across portions of the Southeast and Midwest to the mid-Atlantic region and most of New England. This area of elevated oxidized nitrogen deposition roughly corresponds to the areas with model-predicted NO_x concentrations of 3.0 ppb or greater and, in general, where NO_x emissions are regionally highest. Oxidized nitrogen deposition levels of 7.5 kg N/ha/yr or greater are evident in and near NO_x source areas and within much of a multistate area from Tennessee

northeastward to central New England. In the West, oxidized nitrogen deposition is 1.5 kg N/ha/yr or less across most of the region, except in urban areas, where NO_x emissions are highest.

As shown in **Figure 3.2-7**, the geographic patterns in reduced nitrogen deposition, indicate that the areas of high reduced nitrogen deposition in both the East and West generally correspond to areas of high NH_3 emissions in each region (see **Figure 3.2-2**). In the East, deposition of reduced nitrogen of 3.5 kg N/ha/yr or greater is seen from central Texas, across the eastern Great Plains and the Midwest, to western Pennsylvania and western New York. Elsewhere in the East, high levels of reduced nitrogen deposition are found in and near areas of livestock/swine/poultry operations. Between these areas of elevated deposition, reduced nitrogen deposition levels are generally in the range of 1.5 to 3.5 kg N/ha/yr. In the West, reduced nitrogen deposition is <1.5 kg N/ha/yr, except near NH_3 emissions source areas, especially the Central Valley of California.

The spatial patterns of total reactive nitrogen deposition in **Figure 3.2-8** reflect the combination of the deposition from the reduced and oxidized nitrogen components. Much of the East has total nitrogen deposition of 9 to 14 kg N/ha/yr. Higher amounts of 14 kg N/ha/yr or greater cover portions of the Midwest and Northeast, as well as in or near sources of NO_x and/or NH_3 emissions in other parts of the East. In the West, total nitrogen deposition is highest in and near NO_x and NH_3 source areas, particularly those in California, where deposition exceeds 20 kg N/ha/yr. In most rural or remote portions of the West, total nitrogen deposition is generally <3 kg N/ha/yr.

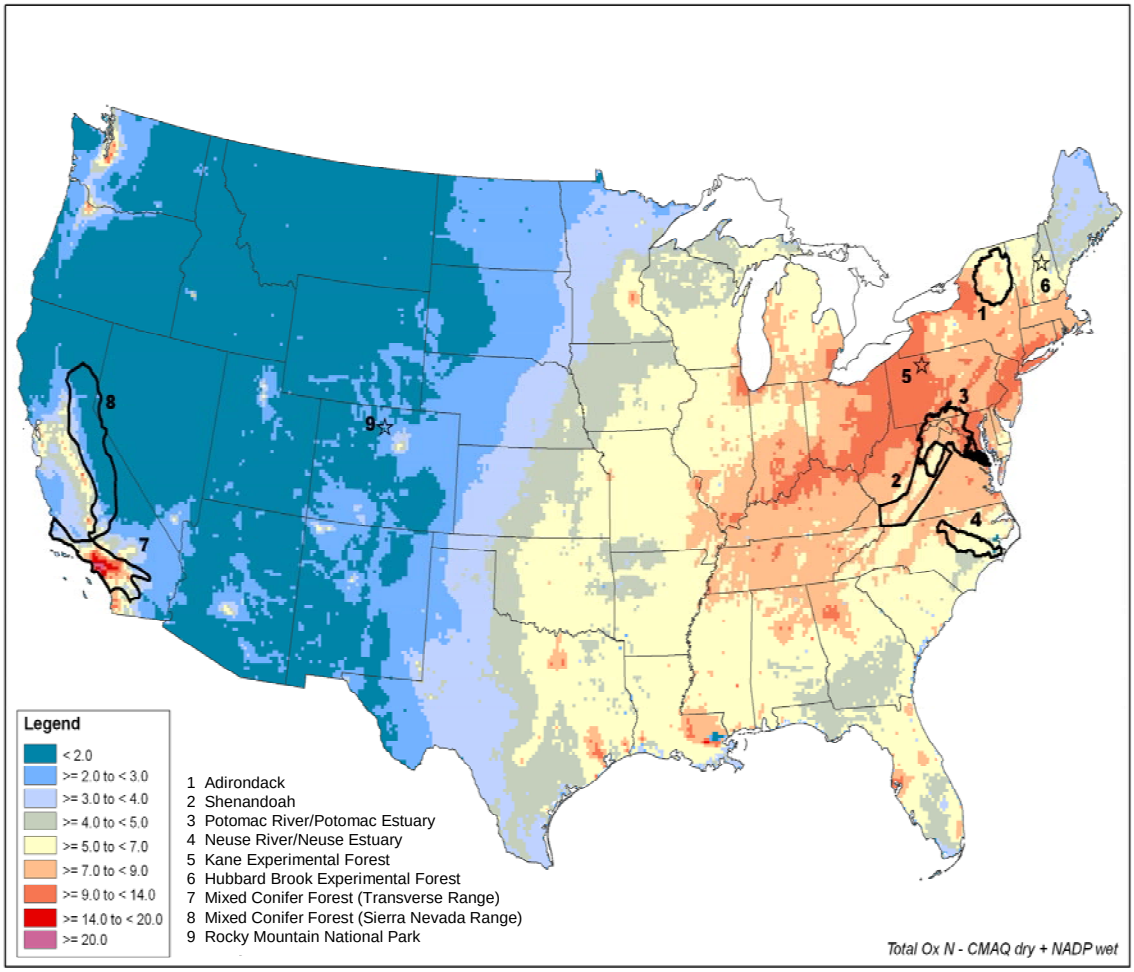

Figure 3.2-6. Total wet plus dry oxidized nitrogen deposition (kg N/ha/yr) in 2002.

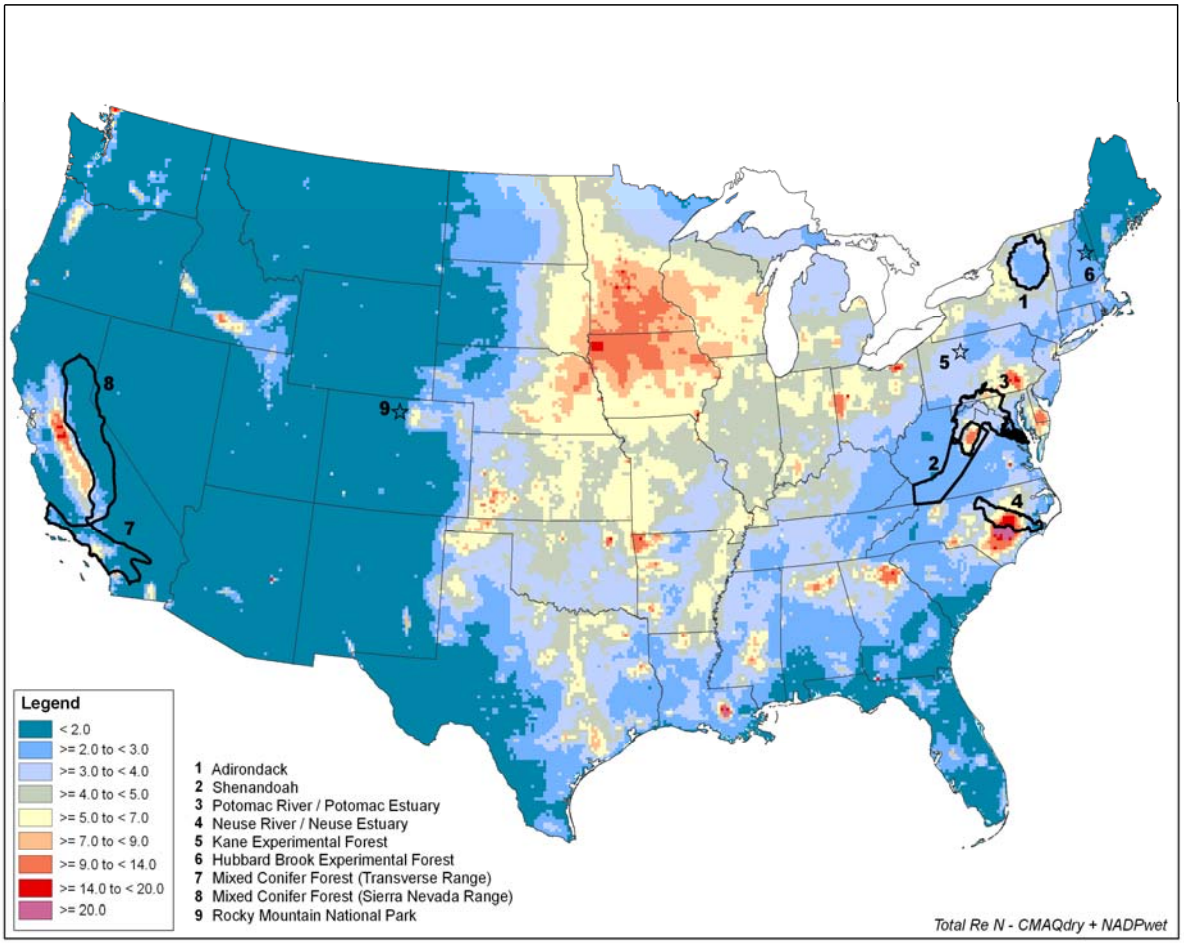

Figure 3.2-7. Total wet plus dry reduced nitrogen deposition (kg N/ha/yr) in 2002.

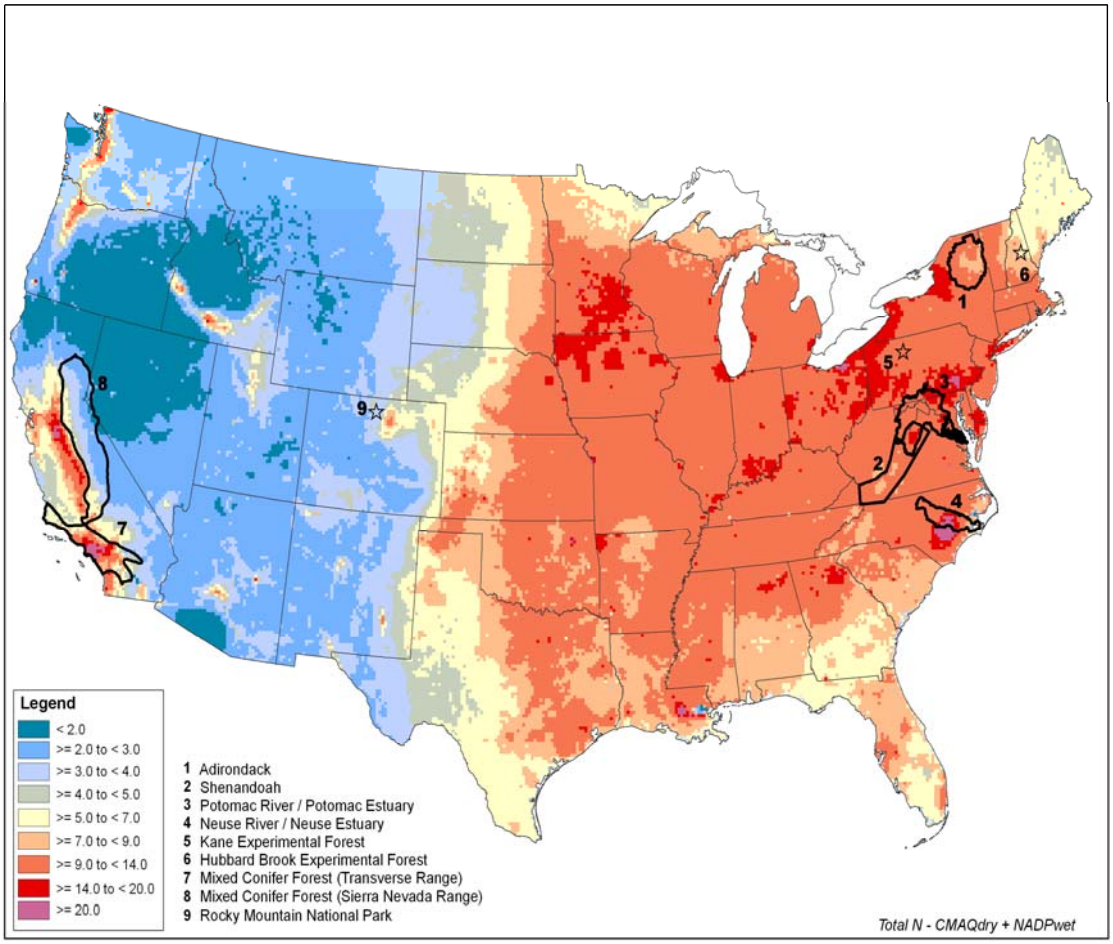

Figure 3.2-8 Total reactive nitrogen deposition (kg N/ha/yr) in 2002.

3.2.3.3 Sulfur Deposition

Annual average measured sulfur deposition during 2004 to 2006 was highest in the Ohio River Valley. In this region, measured sulfur deposition was 21.3 kg S/ha/yr at one monitoring site, and most sites reported 3-year averages >10.0 kg S/ha/yr (U.S. EPA, 2008b). Total sulfur deposition measured in the West was relatively low, and generally <2.0 kg S/ha/yr, with many sites measuring <1.0 kg S/ha/yr. The primary form of sulfur deposited is wet SO_4^{2-}. Smaller contributions to deposition are made by dry SO_2 and dry SO_4^{2-}.

The spatial fields of sulfur across the United States for 2002 are shown in **Figure 3.2-9**. As with the deposition of nitrogen species, sulfur deposition is much higher in the East than the West. Sulfur deposition across most of the West is <3.0 kg S/ha/yr. In the East, high levels of deposition exceeding 18 kg S/ha/yr are seen in the immediate vicinity of isolated major sources, as well as in and near areas having a high concentration of SO_2 sources. This is particularly

notable along the Ohio River Valley, extending across Pennsylvania. The areas of highest deposition are within a broad area of sulfur deposition in the range of 6 to 12 kg S/ha/yr, which covers much of the East.

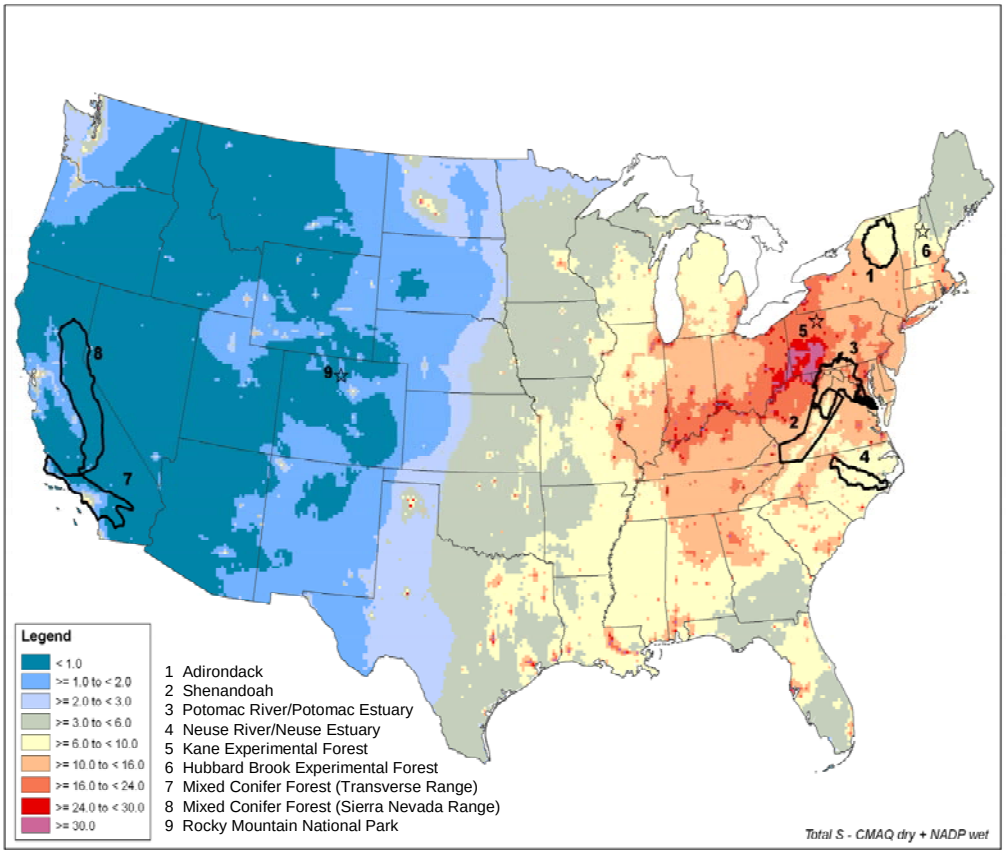

Figure 3.2-9. Total wet and dry sulfur deposition (kg S/ha/yr) in 2002.

3.2.4 Policy-Relevant Background Concentrations

Policy-relevant background concentrations are those concentrations that would occur in the United States in the absence of anthropogenic emissions in the continental North America (i.e., United States, Canada, Mexico). These analyses for the current ambient indicators, NO_2 and SO_2, as well as NO_y and SO_x, are summarized below (U.S. EPA 2008). Note that the analyses for the Risk and Exposure Assessment examined the contribution of total reactive nitrogen and sulfur above the policy-relevant background concentrations.

For NO_2, policy-relevant background concentrations are <300 parts per trillion (ppt) over most of the continental United States and <100 ppt in the eastern United States on an annual average basis (U.S. EPA, 2008b). In contrast to the levels associated with policy relevant background concentrations, 24-hour ambient NO_2 concentrations in urban areas near monitoring

locations averaged <20 ppb and have a 99 percentile value of <50 ppb. Annual average NO_2 concentrations over the continental United States are <5 ppb for nearly all urban, rural, and remote sites. According to the ISA (U.S. EPA, 2008b), background SO_2 concentrations are <10 ppt throughout most of the continental United States, except in areas of the Pacific Northwest, where natural SO_2 sources are particularly strong because of volcanic activity. Maximum policy-relevant background SO_2 concentrations are 30 ppt. In general, policy-relevant background concentrations of SO_2 contribute <1% of current concentrations, except in the Pacific Northwest, where policy-relevant background concentrations can contribute up to 80% (U.S. EPA, 2008b).

The spatial pattern of policy-relevant background NO_Y (defined in the model as HNO_3 + NH_4NO_3 + NO_x + HO_2NO_2 +$RONO_2$) in wet and dry deposition shows that the highest values are found in the eastern United States in and downwind of the Ohio River Valley. The pattern of nitrogen deposition in the PRB simulation shows maximum deposition centered over Texas and in the Gulf Coast region, reflecting a combination of nitrogen emissions from lightning in the Gulf Coast region, biomass burning in the southeast, and microbial activity in soils with maxima in central Texas and Oklahoma. The policy-relevant background contribution to nitrogen deposition is <20% over the eastern United States, and typically <50% in the western United States, where NO_Y deposition is already lower.

Present-day deposition of SO_x (SO_2 and pSO_4) is largest in the Ohio River Valley due to coal-burning power plants in that region, while background deposition is typically at least an order of magnitude smaller. Over the eastern United States, the predicted background contribution to SO_x deposition was <10%, and even smaller, <1%, where present-day SO_x deposition was highest. The predicted contribution of policy-relevant background to sulfur deposition was highest in the western United States at >20% because of the geothermal sources of SO2 and oxidation of dimethyl sulfide at the water surface of the eastern Pacific. In summary, the PRB contribution to NO_x and SO_x concentrations and deposition over the continental United States. is very small, except for SO_2 in areas with volcanic activity.

3.2.5 Non-atmospheric Loadings of Nitrogen and Sulfur

Not all loadings of nitrogen and sulfur compounds to ecosystems are due to atmospheric deposition. Other inputs, such as runoff from agricultural soils to waterbodies and point-source discharges, also contribute to acidification and nutrient enrichment. This assessment examines the atmospheric contribution due to total reactive nitrogen and sulfur, recognizing that some

systems may be solely impacted by atmospheric deposition, while effects in other systems might be largely due to non-atmospheric sources. This source distinction will play an important role in the standard-setting process.

3.3 SPATIAL AND TEMPORAL CHARACTERIZATION OF DEPOSITION FOR CASE STUDY AREAS

3.3.1 Purpose and Intent

The purpose of this section is to describe the spatial and temporal patterns of total reactive nitrogen and sulfur deposition for the eight case study areas and the Rocky Mountain National Park supplemental study area. These areas are shown on the map in **Figure 2.1-1**. This analysis focused on the magnitude, spatial gradients, and the intra-annual (i.e., seasonal) and inter-annual (i.e., between 2002–2005) variation in nitrogen and sulfur deposition for each of these case study areas. In addition to improving the overall understanding of the spatial and temporal behavior of nitrogen and sulfur deposition, the results and findings of this analysis are intended to provide information on the case study areas about (1) the relative portion of total nitrogen deposition that is in the form of oxidized versus reduced nitrogen, and (2) the relative amounts of wet versus dry deposition of nitrogen and sulfur.

These analyses are intended to aid in understanding the characteristic patterns of deposition in the case study areas and their current contribution to negative ecological effects. It is beyond the scope of this analysis to fully explain the characteristics revealed by the modeled and measured deposition and concentrations. Further exploration of these relationships and interactions should be the subject of future research efforts.

3.3.2 Data and Analytical Techniques

As previously discussed, both measured data and model predictions for the analyses were used in this assessment. The measured data include wet deposition of nitrogen and sulfur, as calculated from NO_3^-, NH_4^+, and SO_4^{2-} wet deposition samples collected at NADP sites during the period 2002 through 2005. These wet deposition data are available as annual totals for each of the years 2002 through 2005 as spatial fields of gridded data at 12 × 12 km resolution for the continental United States. The CMAQ[8] model predictions include wet and dry deposition of

[8] The CMAQ applications are described in detail in Appendix 1 of this report.

nitrogen and sulfur from applications of CMAQ over this same time period. The hourly model predictions were aggregated to seasonal and annual time periods, as needed, for this assessment.

For 2002, CMAQ predictions were at a resolution of 12 km for the continental United States[9]. These 2002 model predictions are based on model runs with CMAQ v4.6. The dry deposition predictions for 2002 from CMAQ v4.6 were coupled with the 2002 NADP wet deposition data to provide annual total reactive nitrogen and annual total sulfur deposition for input to the aquatic and terrestrial ecosystem modeling analyses described in Chapters 4 and 5 of this report. In October 2008, the EPA Office of Research and Development (ORD) released an updated version of CMAQ (CMAQ v4.7) and an updated version of CMAQ's meteorological preprocessor (MCIPv3.4)[10]. Recently, the EPA ORD used the updated versions of CMAQ and Meteorology-Chemistry Interface Processor (MCIP) to remodel 2002 deposition and to model 2003, 2004, and 2005 deposition. These 2002 through 2005 CMAQ runs were performed at 12-km resolution for the East[11] and at 36-km resolution for the West. This Risk and Exposure Assessment uses both sets of CMAQ runs. The CMAQ v4.6 2002 predictions are used in the analyses to characterize the magnitude, relative amounts, and spatial gradients in deposition within each case study area, as well as to examine the seasonal variability in deposition for 2002. The predictions for 2002 through 2005 from CMAQv4.7 were used as a consistent set of estimates to assess inter-annual variability in deposition and to determine whether the magnitude and relative amounts of deposition in 2002 are representative of conditions over the longer-term, 4-year time period. A comparison of the two sets of 2002 CMAQ predictions is presented as part of the discussion on uncertainties in Section 3.5 of this report.

In general, the case study analyses rely upon a combination of NADP-measured wet deposition and CMAQ (v4.6 or v4.7) dry deposition, with one exception. CMAQ predictions of both wet and dry deposition were used in the analysis of seasonal variations because gridded wet deposition data from NADP are not available at a subannual temporal resolution.

[9] The CMAQ modeling domains are shown in Figure 1 of Appendix 1 of this report.

[10] The scientific updates in CMAQ v4.7 and MCIP v3.4 can be found at the following web links:
http://www.cmascenter.org/help/model_docs/cmaq/4.7/RELEASE_NOTES.txt
http://www.cmascenter.org/help/model_docs/mcip/3.4/ReleaseNotes

[11] The 99° west meridian to separate the eastern and western United States was used in this assessment.

3.3.2.1 Spatial Allocation of Gridded Data to Case Study Areas

The gridded measured and modeled data were linked to the case study areas using several geographic information systems (GIS)–based techniques that differ depending on the geographic definition of each area, as follows[12]. The Potomac River/Potomac Estuary Case Study Area and Neuse River/Neuse River Estuary Case Study Area include contiguous watersheds that are defined in terms of 8-digit Hydrologic Unit Codes[13] (HUCs). For these two areas, GIS was used to calculate the spatially weighted average deposition for each of these areas as a whole. The Adirondack Case Study Area includes individual noncontiguous watersheds[14] that contain the lakes/ponds selected for ecological modeling as part of the aquatic acidification analysis (see Chapter 4 of this report). Similarly, the Shenandoah Case Study Area includes those watersheds[15] containing the streams selected for ecological modeling. For the Adirondack and Shenandoah case study areas, individual grid cells were linked to each watershed if any part of the grid cell touched a portion of a watershed in the area. The Hubbard Brook Experimental Forest, Kane Experimental Forest, and Mixed Conifer Forest (Transverse Range and Sierra Nevada Range) case study areas, as well as the Rocky Mountain National Park, do not contain finer geographic elements. For these areas, GIS was used to calculate the spatially weighted average deposition for each area as a whole.

3.3.3 Characterization of Deposition in Case Study Areas

The characterizations of nitrogen and sulfur deposition for each case study area are discussed in this section as follows:

- Overall area-wide magnitude of deposition in 2002
- Variation in annual total deposition between 2002 through 2005
- Relative amount of wet and dry, oxidized, and reduced nitrogen to total reactive nitrogen deposition and wet and dry to total sulfur deposition in 2002
- Geographic variations in annual deposition for 2002 within and near the case study areas

[12] The number of 12 km grid cells assigned to each case study area as a result of this process is as follows: Adirondacks – 141; Shenandoah – 78; Potomac River/Potomac Estuary – 325; Neuse River/Neuse River Estuary – 136; Kane Experimental Forest – 2; Hubbard Brook Experimental Forest – 2; Rocky Mountain National Park – 1; Transverse Range – 297; Sierra Nevada Range – 554.

[13] These codes are used to identify the drainage basins within the United States. See http://imnh.isu.edu/digitalatlas/hydr/huc/huctxt.htm for additional information on HUCs.

[14] The Adirondack watersheds are defined by 10-digit HUCs.

[15] The Shenandoah watersheds are defined by 12-digit HUCs.

- Seasonal variations in each component of deposition for 2002.

The table and figures that provide and display the data used for this analysis are identified below. For ease of reference, the table and figures are provided at the end of each subsection.

The modeled plus measured annual total reactive nitrogen and sulfur depositions for 2002 for each case study area, as a whole, are presented in **Table 3.3-1**. The inter-annual variations in total reactive nitrogen deposition from 2002 through 2005 are shown in **Figures 3.3-1a and 3.3-1b** for each case study area in the East and West. The relative amounts of oxidized versus reduced nitrogen deposition for each case study area in 2002 are shown in **Figure 3.3-2**. The relative amounts of wet and dry, oxidized, and reduced nitrogen deposition for 2002 are shown in **Figures 3.3-3(a–i)**. The spatial patterns in annual nitrogen depositions for 2002 are shown in **Figures 3.3-4(a–e)** for the East and in **Figures 3.3-5(a–c)** for the West. The seasonal variations in total reactive nitrogen deposition for each case study area are shown in **Figures 3.3-6(a–i)**. The seasonal data are presented in terms of the percentage of annual deposition that occurs in each season[16]. For wet and dry, oxidized and reduced nitrogen deposition seasonal variations are shown in **Figures 3.3-7(a–i),** along with the seasonal variation in precipitation. Seasonal patterns of NH_3 emissions are shown in **Figure 3.3-8**.

The annual total sulfur deposition from 2002 through 2005 is shown in **Figures 3.3-9 (a and b)** for each case study area in the East and West. The relative amounts of wet and dry sulfur deposition in 2002 and, on average, for the period 2002 through 2005 are shown in **Figures 3.3-10 and 3.3-11**. The spatial patterns in annual sulfur deposition for 2002 are shown in **Figures 3.3-12(a–c)** for the East and in **Figure 3.3-13** for the West. The seasonal variation in total sulfur deposition for each case study area is shown in **Figures 3.3-14(a–i)**. Wet and dry sulfur deposition seasonal variations are shown in **Figures 3.3-15(a–i)**.

[16] For the purposes of this analysis, data for December, January, and February 2002 were included in "winter;"; data for March, April, and May 2002 were included in "spring;" data for June, July, and August 2002 were included in "summer;" and data for September, October, and November 2002 were included in "fall." Thus, data for December 2002 were included with data for January and February of this same year.

3.3.3.1 Magnitude of Total Reactive Nitrogen Deposition in 2002 and Analysis of Inter-annual Variability[17]

The amount of total reactive nitrogen deposition in 2002 varies among the case study areas (see **Table 3.3-1**). In the East, total reactive nitrogen deposition ranges from 8 kg N/ha/yr for the Hubbard Brook Experimental Forest Case Study Area up to 14 kg N/ha/yr for the Neuse River/Neuse River Estuary Case Study Area. Total reactive nitrogen deposition in 2002 is also high in the Transverse Range portion of the Mixed Conifer Forest Case Study Area (10 kg N/ha/yr), which reflects the high levels of NO_x emissions in and around the Los Angeles urban area. The Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, as well as the Rocky Mountain National Park, have very low amounts of nitrogen deposition (4 kg N/ha/yr for each location), which is consistent with the low amounts of NO_x emissions near these areas.

Annual total reactive nitrogen depositions varied by 1 to 3 kg N/ha/yr or less in individual case study areas from 2002 through 2005 (see **Figures 3.3-1a and 3.3-1b**). There is some evidence of a decline in deposition during this 4-year time period for the six case study areas in the East. No definitive trend[18] is evident for the case study areas in the West. Since the negative effects of nitrogen deposition on sensitive ecosystems may be the result of long-term exposures, recent trends in measured deposition were examined to determine how the amounts of deposition in the 2002 analysis year relate to current conditions over a longer time period. As described in Section 3-2, analyses by CASTNET for an aggregate of 34 sites in the East indicates that dry nitrogen deposition has shown a general decline overall since 2002, but the annual concentration of nitrogen in precipitation has remained fairly steady over this time period (U.S. EPA, 2009). In general, inter-annual variations in meteorology and emissions lead to inter-annual variations in concentrations and deposition.

In this section, information available from the NADP National Trends Network[19] on nitrogen deposition for those sites located in and/or near each case study area is examined. To be included in this analysis, the site had to have valid measurements in 2002, as determined by

[17] Slight differences between the deposition reported in Table 3.3-1 versus what is shown in Figure 3.3-1a and b are due to the use of different versions of CMAQ, as described above in Section 3.3.2.

[18] In this analysis, we use the term "trend" to refer to the overall temporal signal (i.e., increase or decrease) in deposition for a particular time period. It is not the intent of this analysis to ascribe any statistical significance to the characterization of long-term trends in deposition at any individual location.

[19] See http://nadp.sws.uiuc.edu/sites/ntnmap.asp?

NADP completeness criteria[20]. The charts showing annual deposition for sites selected for this analysis are provided in Appendix 2 of this report. The level of measured annual total wet deposition in 2002 at each site was compared to the amount of deposition in other years over the most recent 10 years (i.e., 1998 through 2007)[21]. The trend information indicates that overall, for each case study area, the amount of nitrogen deposition in 2002 is generally representative of current conditions.

However, deposition trends can vary from site to site, even within a case study area[22]. This is most notable for the two sites in the Adirondack Case Study Area and the three sites in the Potomac River/Potomac Estuary Case Study Area. In the Adirondack Case Study Area, the data from the Huntington Wildlife Forest site indicates that wet nitrogen deposition in 2002 is within the range of values measured during other years over the most recent 10-year period. Data from the Whiteface site shows that wet nitrogen deposition in 2002 was high compared to that in other years. The data at both sites show a downward pattern to 2006, with nitrogen deposition increasing again in 2007. For the Potomac River/Potomac Estuary Case Study Area, the trends in wet nitrogen deposition at the Arendtsville, PA, and Parsons, WV, sites indicate that the amount of deposition in 2002 is similar to that from 1998 through 2007. The Wye, MD, site on the Eastern Shore of Maryland shows large inter-annual variations compared to the other sites in the Potomac River/Potomac Estuary Case Study Area and that wet nitrogen deposition in 2002 was on the low end of the range over this time period. In 2002, wet nitrogen deposition for both Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, as well as the Rocky Mountain National Park, were within the range of values measured from 1998 through 2007. For the Transverse Range portion of the Mixed Conifer Forest Case Study Area, wet nitrogen deposition was near the low end of the range of values for this period. It is beyond the scope of this analysis to determine the reasons for these differences other than to note that local terrain-induced meteorological conditions and differential source-receptor relationships across a case study area may contribute to the differences noted in deposition trends.

[20] See http://nadp.sws.uiuc.edu/documentation/completeness.asp

[21] Some sites do not have historical data back to 1998. For these sites, the amounts of deposition for the available data record were examined.

[22] See http://nadp.sws.uiuc.edu/sites/ntnmap.asp? for the location of NADP sites across.

Table 3.3-1. Annual Total Reactive Nitrogen Deposition (kg N/ha/yr) and Sulfur Deposition (kg S/ha/yr) in 2002 for Each Case Study Area, as Well as the Rocky Mountain National Park.

Case Study Areas[a]	2002 Annual Total Deposition	
	Total Reactive Nitrogen (kg N/ha/yr)	Total Sulfur (kg S/ha/yr)
Adirondack	10	9
Hubbard Brook Experimental Forest	8	7
Kane Experimental Forest	13	20
Potomac River/Potomac Estuary	12	14
Shenandoah	11	11
Neuse River/Neuse River Estuary	14	8
Mixed Conifer Forest (Sierra Nevada Range portion)	4	1
Mixed Conifer Forest (Transverse Range portion)	10	2
Rocky Mountain National Park (a supplemental area)	4	1

[a] Excludes the Coastal Sage Scrub Case Study Area.

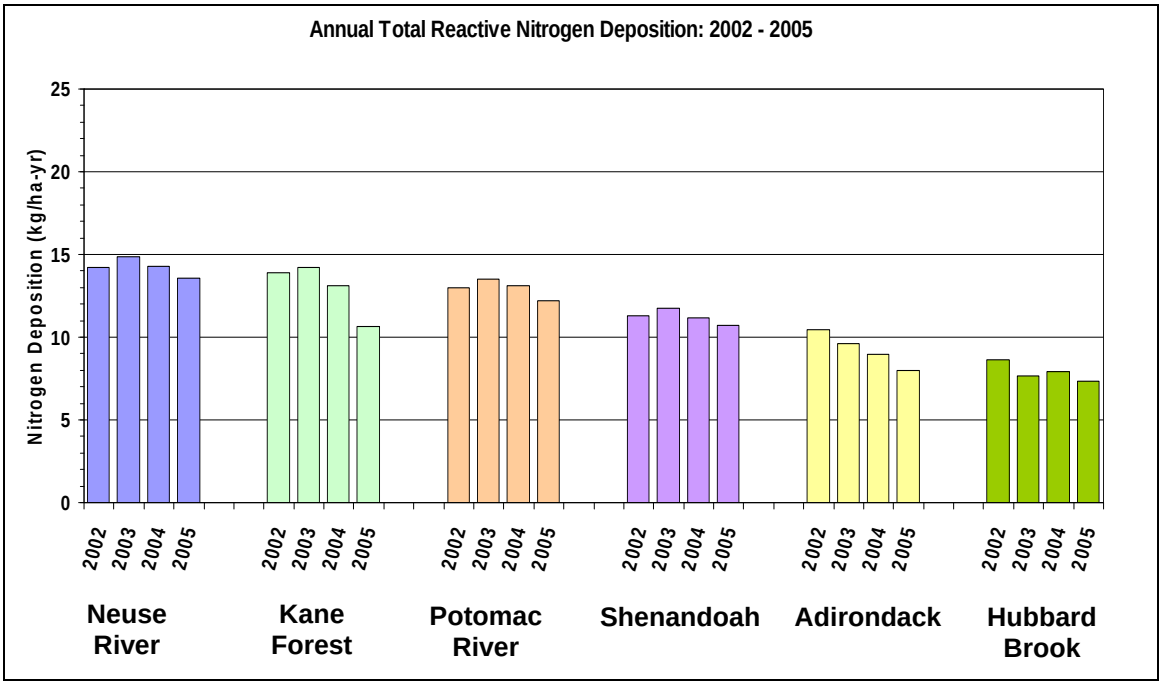

Figure 3.3-1a. Annual total reactive nitrogen deposition (kg N/ha/yr) from 2002 through 2005 for each case study area in the East.

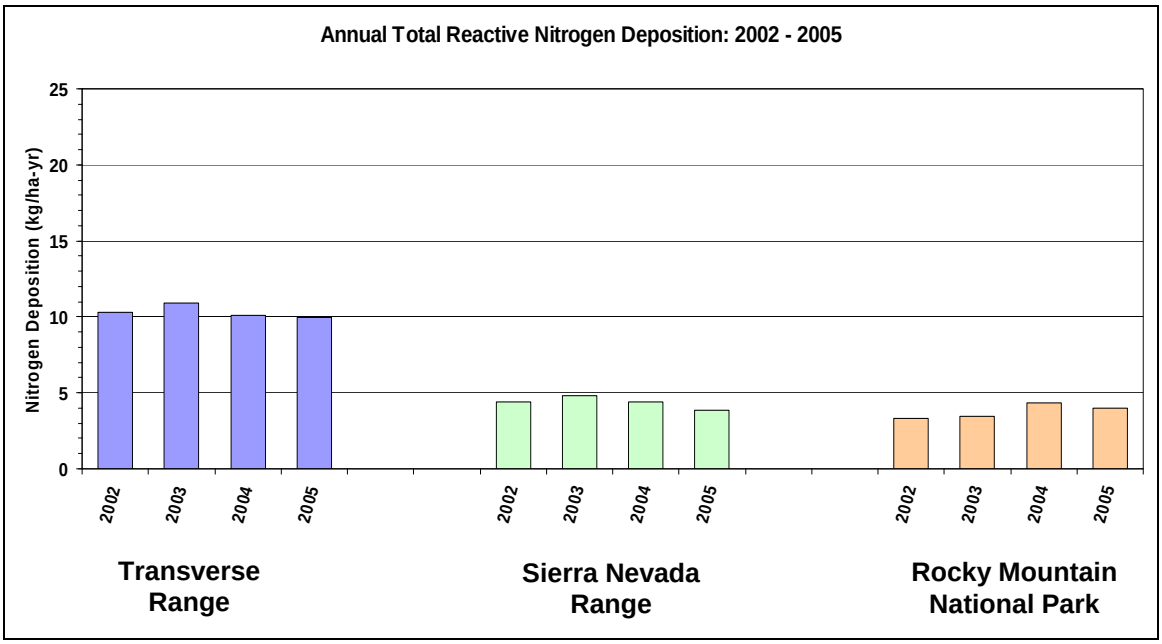

Figure 3.3-1b. Annual total reactive nitrogen deposition (kg N/ha/yr) from 2002 through 2005 for case study areas in the West, and the Rocky Mountain National Park.

3.3.3.2 Relative Amount of Oxidized and Reduced, Wet, and Dry Nitrogen Deposition

The relative amounts of oxidized and reduced nitrogen deposition in 2002 for each case study area, as well as the Rocky Mountain National Park, are shown in **Figure 3.3-2**. Oxidized nitrogen deposition is the dominant contributor to total reactive nitrogen deposition in nearly all of the case study areas. This is consistent with the relative amount of emissions of NO_x and NH_3. As indicated by comparing **Figures 3.2-2 and 3.2-3**, NO_x emissions are much greater and more widespread compared to emissions of NH_3, which are more local in nature.

In the Mixed Conifer Forest (Transverse Range portion), Hubbard Brook Experimental Forest, Kane Experimental Forest, and Adirondack case study areas, oxidized nitrogen comprises 70% or more of the total reactive nitrogen. Oxidized nitrogen is 66% to 67% of total reactive nitrogen deposition in the Shenandoah, Potomac River/Potomac Estuary case study areas as well as the Rocky Mountain National Park. In the Neuse River/Neuse River Estuary Case Study Area, reduced nitrogen deposition is >50% of total reactive nitrogen. These findings are consistent with the relative magnitude and geographic distribution of NO_x emissions compared with NH_3 emissions, as described above in Section 3.2.1. The relative amount of oxidized versus reduced nitrogen deposition in an area depends on the proximity of the area to local sources of NH_3. For example, certain portions of the Neuse River/Neuse River Estuary Case Study Area contain high

NH_3 emissions from hog farm operations, and this area, as a whole, has the largest relative amount of reduced nitrogen deposition. In contrast, the Hubbard Brook Experimental Forest, Kane Experimental Forest, and Adirondack case study areas are distant from sources of high NH_3 emissions, and they each have a low relative amount of reduced nitrogen deposition.

The relative amounts of wet and dry, oxidized, and reduced nitrogen for 2002 are shown for each case study area in **Figures 3.3-3(a–i)**. The relative amounts of total reactive nitrogen deposition based on average deposition for the period 2002 through 2005 are shown in Appendix 3 of this report. The relative amounts of total reactive nitrogen deposition in 2002 are indicative of conditions over the 4-year period. Looking at the relative amounts of total reactive nitrogen deposition for individual case study areas in the East indicates similar distributions of deposition for several areas. In the Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas, the relative amount of oxidized nitrogen is about evenly split between wet and dry deposition, whereas the vast majority of reduced nitrogen occurs through wet deposition. In contrast, in the Potomac River/Potomac Estuary and Shenandoah case study areas, dry deposition dominates wet deposition for oxidized nitrogen (~65% of oxidized nitrogen is dry deposited versus 35% wet deposited). However, in these two areas, wet deposition of reduced nitrogen is only slightly greater than dry reduced nitrogen deposition. The Neuse River/Neuse River Estuary Case Study Area is somewhat unique among the case study areas because of the high levels of local NH_3 emissions, which result in a relatively large amount of dry reduced nitrogen deposition compared to the other case study areas in the East. For the two case study areas in the West and the Rocky Mountain National Park, a common feature in the relative amount of nitrogen deposition is that dry oxidized nitrogen is the largest of the four components of total reactive nitrogen deposition at all three of these areas.

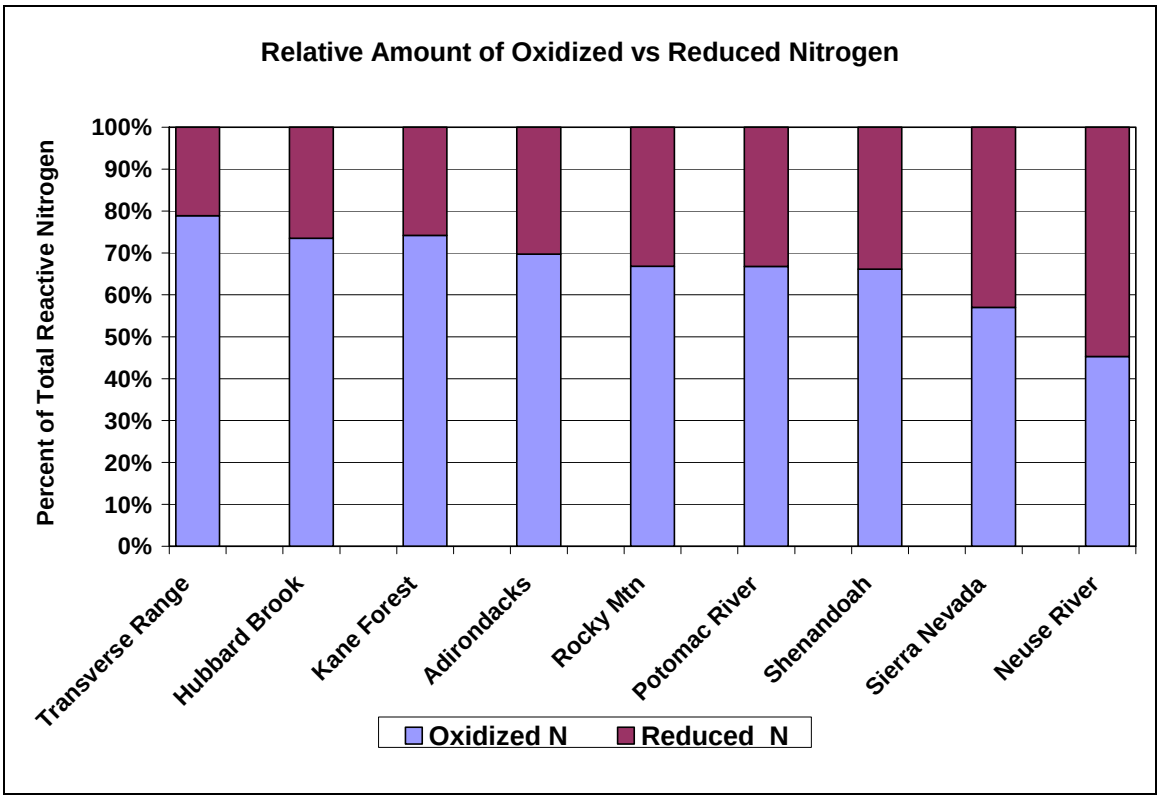

Figure 3.3-2. Relative amounts of oxidized and reduced nitrogen deposition in 2002 for case study areas and the Rocky Mountain National Park.

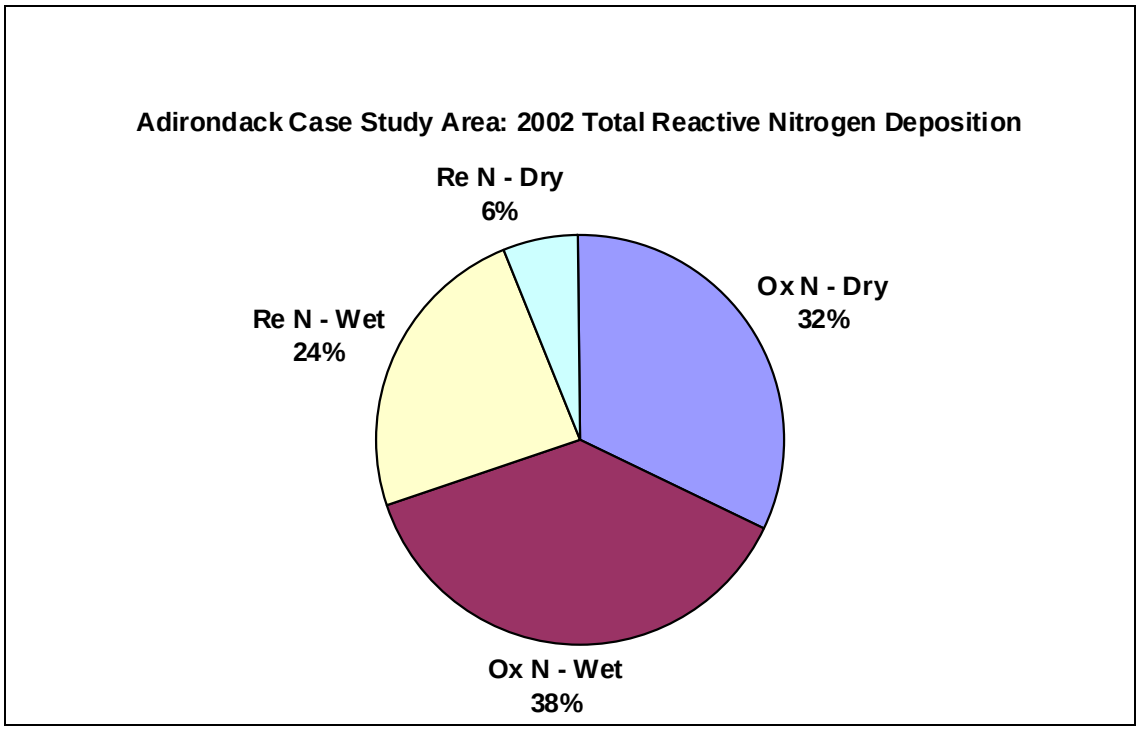

Figure 3.3-3a. Components of total reactive nitrogen deposition for 2002 in the Adirondack Case Study Area.

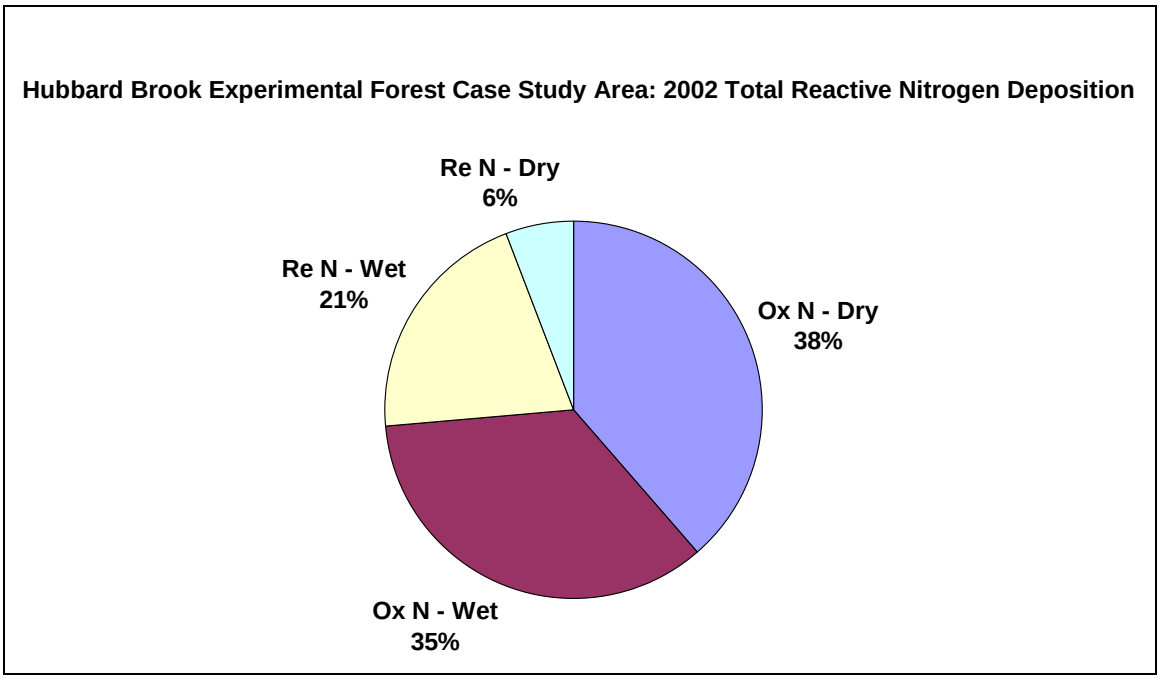

Figure 3.3-3b. Components of total reactive nitrogen deposition for 2002 in the Hubbard Brook Experimental Forest Case Study Area.

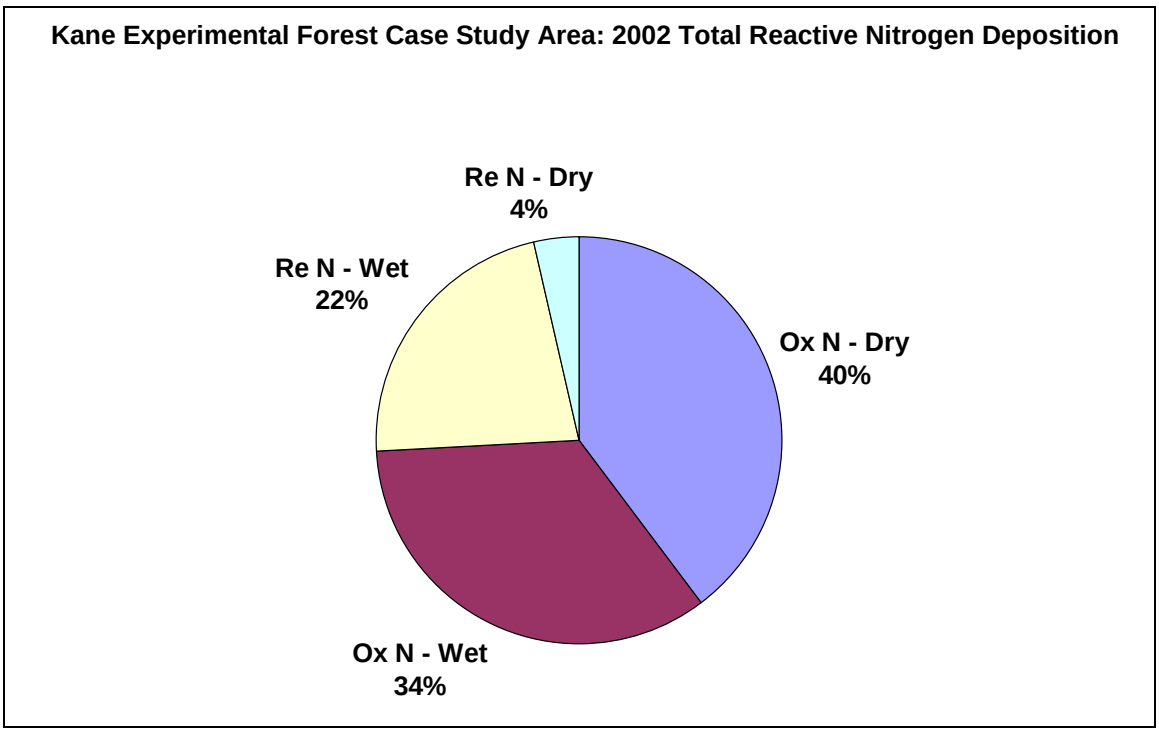

Figure 3.3-3c. Components of total reactive nitrogen deposition for 2002 in the Kane Experimental Forest Case Study Area.

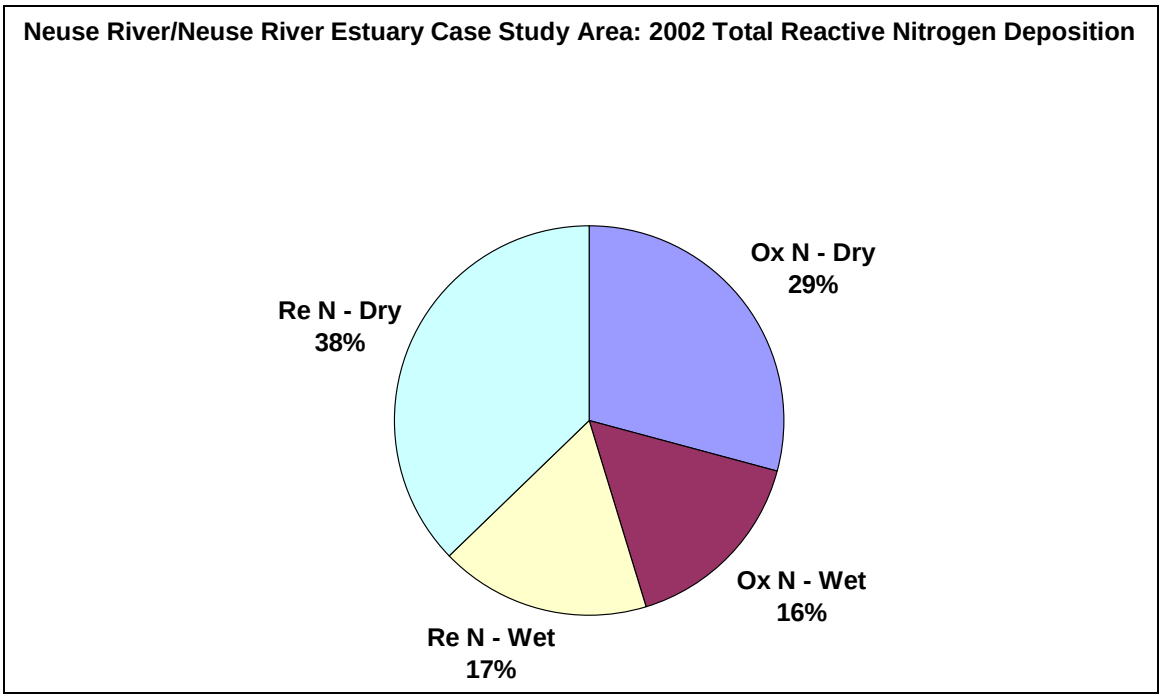

Figure 3.3-3d. Components of total reactive nitrogen deposition for 2002 in the Neuse River/Neuse River Estuary Case Study Area.

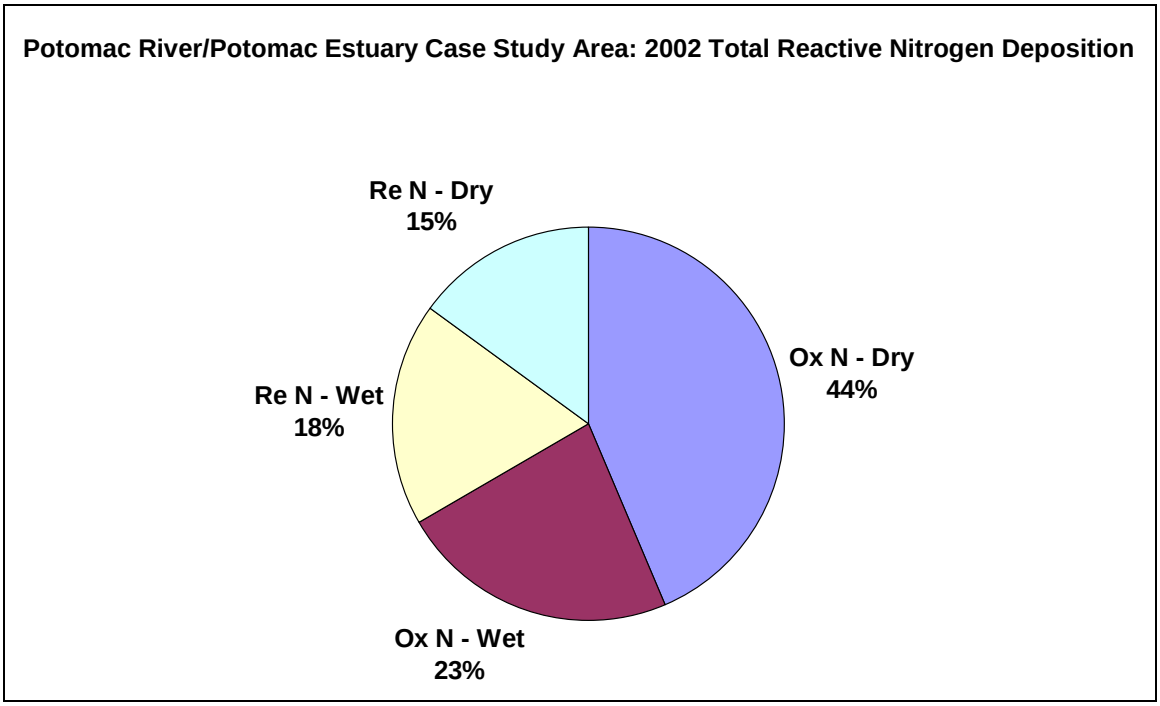

Figure 3.3-3e. Components of total reactive nitrogen deposition for 2002 in the Potomac River/Potomac Estuary Case Study Area.

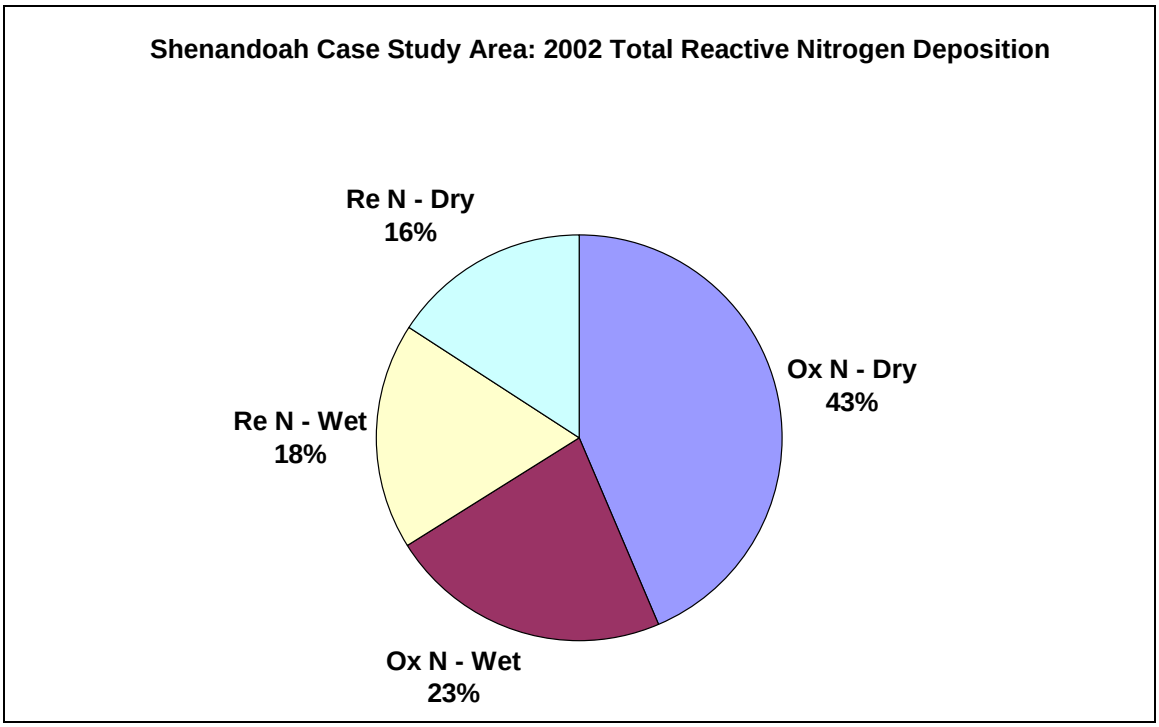

Figure 3.3-3f. Components of total reactive nitrogen deposition for 2002 in the Shenandoah Case Study Area.

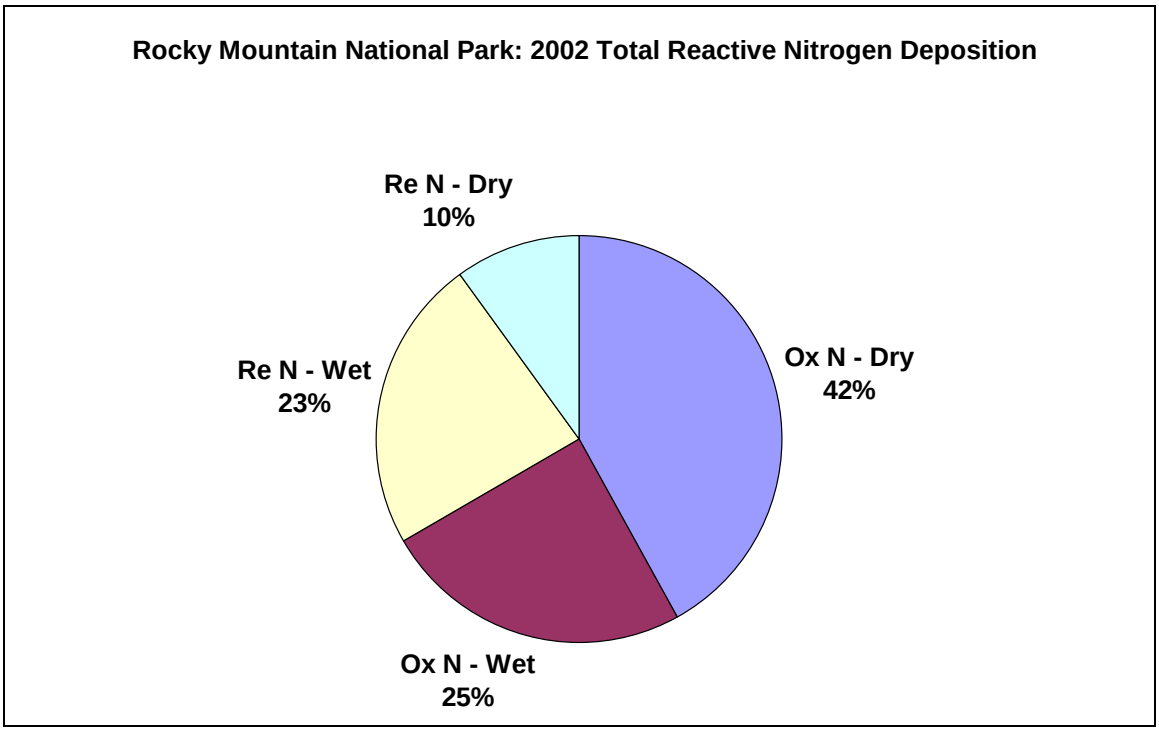

Figure 3.3-3g. Components of total reactive nitrogen deposition for 2002 in the Rocky Mountain National Park.

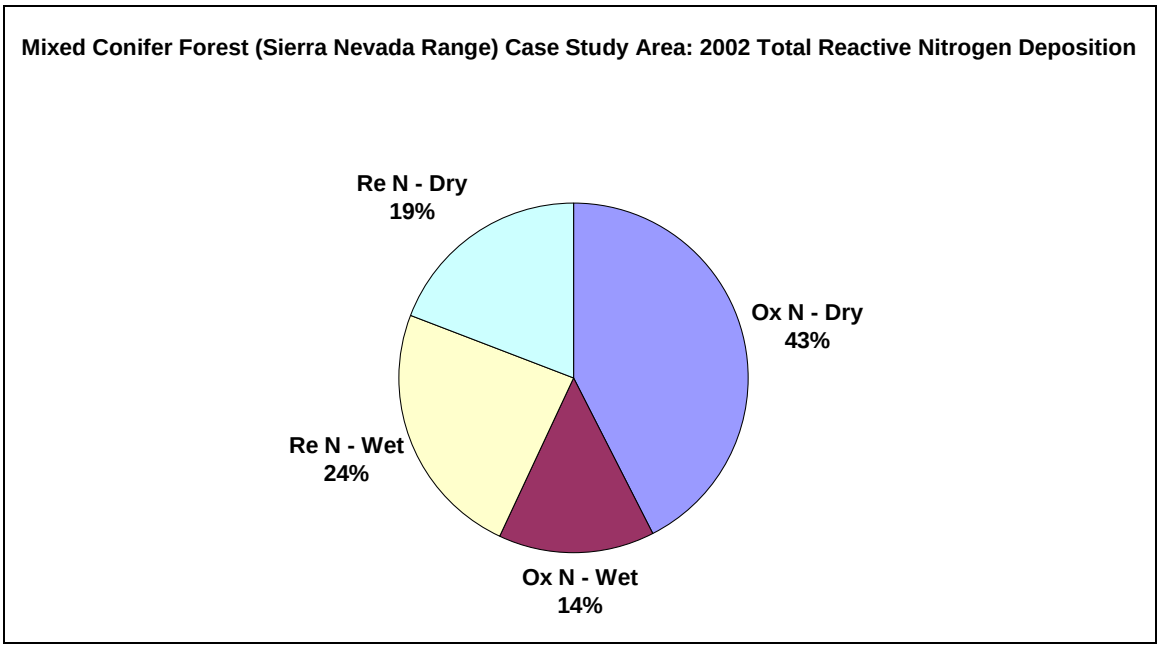

Figure 3.3-3h. Components of total reactive nitrogen deposition for 2002 in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area.

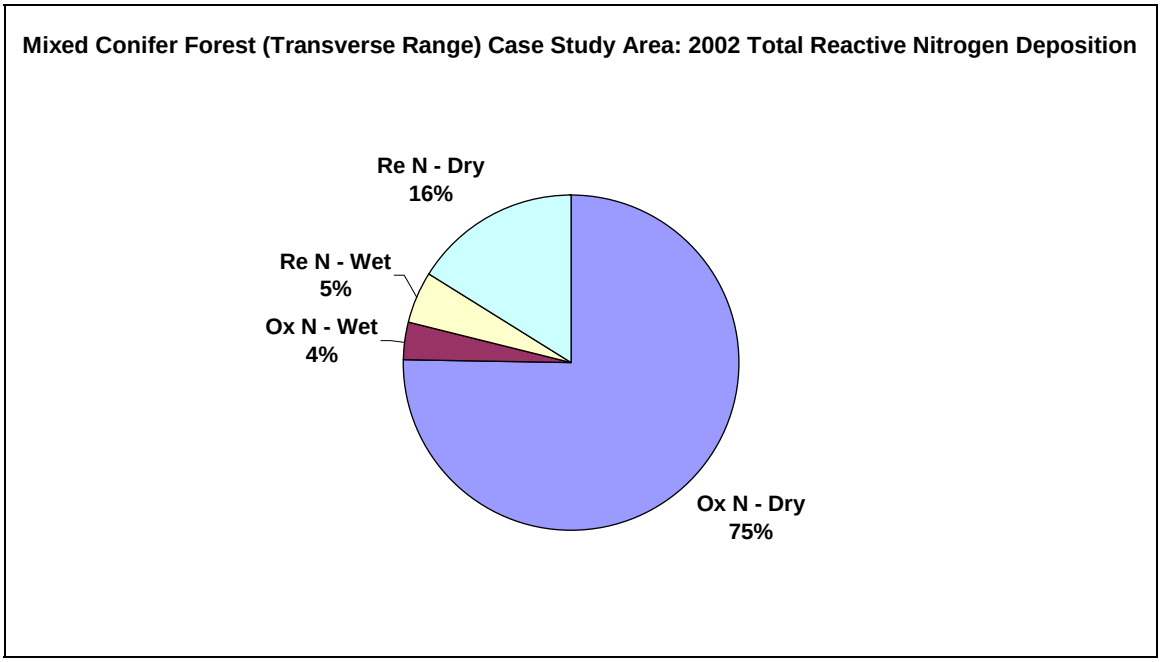

Figure 3.3-3i. Components of total reactive nitrogen deposition for 2002 in the Transverse Range portion of the Mixed Conifer Forest Case Study Area.

3.3.3.3 Geographic Variations in Annual Total Reactive Nitrogen Deposition for 2002[23]

The geographic variations in total reactive, oxidized, reduced, wet, and dry nitrogen deposition in 2002 are shown in **Figures 3.3-4(a–e)** for the case study areas in the East[24]. **Figures 3.3-5(a–c)** shows the geographic variations in total reactive nitrogen deposition and oxidized and reduced nitrogen deposition for the West[25].

Adirondack Case Study Area

As shown in **Figure 3.3-4a**, total reactive nitrogen deposition in 2002 decreases from southwest to northeast across the Adirondack Case Study Area. For example, total reactive nitrogen deposition is >12 kg N/ha/yr in the southwestern portion of the Adirondack Case Study Area compared to <8 kg N/ha/yr in some parts of the eastern portion of this area. By comparing the oxidized nitrogen deposition map in **Figure 3.3-4b** to the reduced nitrogen deposition map in **Figure 3.3-4c,** it is evident that oxidized nitrogen deposition is much greater than reduced nitrogen across the entire case study area. Oxidized nitrogen values are generally in the range of 5 to 7 kg N/ha/yr, with values of 7 to 9 kg N/ha/yr in the southwestern part of the area. In contrast, reduced nitrogen deposition is generally 2 to 3 kg N/ha/yr. From **Figure 3.3-4a,** it is evident that the relatively high total reactive nitrogen deposition in the far southwestern portion of this case study area is part of a broad area of high nitrogen deposition that stretches westward from the Adirondack Case Study Area along the southern shore of Lake Ontario toward western Pennsylvania and Ohio.

The spatial patterns in wet and dry nitrogen are shown in **Figure 3.3-4d** and **Figure 3.3-4e**, respectively. Wet deposition is in the range of 5 to 7 kg N/ha/yr across the region, with higher amounts in the southwestern section. Dry deposition is lower than wet deposition overall and declines fairly rapidly from values of 4 to 5 kg N/ha/yr in the western portion to 2 to 3 kg N/ha/yr in the eastern portion.

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[23] Note that an analysis of the spatial gradients in reactive nitrogen and sulfur deposition for the Kane Experimental Forest and Hubbard Brook Experimental Forest case study areas, as well as the Rocky Mountain National Park is not included because the size of each of these areas is small relative to the 12 x 12-km resolution-measured data and model predictions used in this analysis.

[24] Deposition in all of the figures is displayed at a resolution of 12 x 12 km to be consistent with the aggregated wet and dry deposition data sets described above.

[25] Because of the highly rugged terrain in the case study areas of the West, there is less confidence that the 12-km data represents the true geographic variations in deposition. This is particularly true for wet deposition, which is based on spatial interpolation from a relatively sparse monitoring network. Thus, a discussion of the geographic variations in wet and dry deposition for the case study areas in the West is not included.

Shenandoah Case Study Area

As shown in **Figure 3.3-4a**, total reactive nitrogen deposition in the southern portion of the Shenandoah Case Study Area is in the range of 8 to 10 kg N/ha/yr, increasing to ≥14 kg N/ha/yr for the northern portions. Oxidized nitrogen ranges from 5 to 9 kg N/ha/yr, which is greater than the reduced nitrogen deposition in most of this area. However, the highest levels of nitrogen deposition found in the northern portion are mostly due to reduced nitrogen deposition, which can be seen by comparing **Figure 3.3-4b** with **Figure 3.3-4c**. The higher reduced nitrogen deposition (>9 kg N/ha/yr) is largely the result of high NH_3 emissions in this northern portion of this case study area, as shown in **Figure 3.2-3**. These NH_3 emissions are associated with poultry farm operations in this general location. Elsewhere across the Shenandoah Case Study Area, reduced nitrogen deposition is in the range of 2 to 3 kg N/ha/yr.

Over most of the Shenandoah Case Study Area, wet nitrogen deposition in 2002 is in the range of 4 to 5 kg N/ha/yr, with lower amounts of 3 to 4 kg N/ha/yr in parts of the southern portion of this area. In contrast, dry nitrogen deposition exhibits a peak of relatively high NH_3 emissions in the northern portion of the area. There, the amount of dry nitrogen deposition is 14 kg N/ha/yr or greater.

Potomac River/Potomac Estuary Case Study Area

As shown in **Figure 3.3-4a**, there are large spatial variations in annual total reactive nitrogen deposition across the Potomac River/Potomac Estuary Case Study Area. The highest levels of total reactive nitrogen deposition in 2002 are seen in the portion of this area over northwestern Virginia and from southern Pennsylvania to the Baltimore-Washington, DC, metropolitan area. In these portions of this case study area, annual total reactive nitrogen deposition exceeds 14 kg N/ha/yr. Between these areas of high deposition, total reactive nitrogen deposition declines to the general range of 10 to 12 kg N/ha/yr.

The spatial patterns in oxidized and reduced nitrogen deposition are shown in **Figures 3.3-4b and 3.3-4c**. From these figures, it is clear that oxidized nitrogen deposition is greater that reduced nitrogen deposition across most of this case study area. Oxidized nitrogen deposition is in the range of 9 to 14 kg N/ha/yr in and near the Baltimore-Washington, DC, urban area. Oxidized nitrogen levels decline from east to west across the remainder of this case study area down to the range of 5 to 7 kg N/ha/yr over the western portions of this area. The localized high levels of reduced nitrogen deposition correspond to the locations of high NH_3 emissions, as

shown in **Figure 3.2-3**. Elsewhere in this case study area, reduced nitrogen deposition is fairly low, mostly in the range of 3 to 4 kg N/ha/yr.

The patterns of wet nitrogen deposition in the Potomac River/Potomac Estuary Case Study Area indicate that in 2002, the northern portion of this area had higher amounts of wet nitrogen deposition (5 to 7 kg N/ha/yr) compared with the southern portion (4 to 5 kg N/ha/yr). Dry deposition was highest in the vicinity of the high NH_3 emissions in the far southwestern portion of this area. Relatively large amounts of dry nitrogen deposition are also seen in the eastern half of this area. Considering the spatial distribution of NO_x and NH_3 emissions in and near the Potomac River, it appears that NH_3 emissions from livestock farms in south-central Pennsylvania may be contributing to the higher amounts of dry nitrogen deposition close to the Maryland-Pennsylvania border. In contrast, the high NO_x emissions near the Washington, DC, area may be contributing to the relatively high dry nitrogen deposition in this part of the Potomac River/Potomac Estuary Case Study Area.

Neuse River/Neuse River Estuary Case Study Area

The central portions of the Neuse River/Neuse River Estuary Case Study Area are impacted by high amounts of total reactive nitrogen deposition in amounts >20 kg N/ha/yr (see **Figure 3.3-4a**). These high levels of deposition are associated with high NH_3 emissions from swine and poultry production facilities in the southeastern part of North Carolina (see **Figure 3.2-3**). In contrast to the large spatial gradients seen in reduced nitrogen deposition, oxidized nitrogen deposition is fairly homogenous across this case study area. Most of the area has oxidized nitrogen deposition in the range of 5 to 7 kg N/ha/yr, which increases to 7 to 9 kg N/ha/yr near the Raleigh-Durham urban area.

Wet and dry nitrogen deposition in the Neuse River/Neuse River Estuary Case Study Area show similar patterns in that the highest amounts of deposition are in the vicinity of high NH_3 emissions near the central portion of this area. The lowest amounts of wet and dry nitrogen deposition are near the coast.

Sierra Nevada Range (a Portion of the Mixed Conifer Forest Case Study Area)

As seen from **Figure 3.3-5a**, there is a west to east gradient in total reactive nitrogen deposition across the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area. In the extreme western portion of this area, which is near the San Joaquin Valley, total reactive nitrogen depositions are in the range of 6 to 8 kg N/ha/yr. Total reactive nitrogen deposition

declines to the range of 2 to 3 kg N/ha/yr in the eastern half of this case study area. Both oxidized and reduced nitrogen deposition exhibit similar west to east gradient in deposition as seen in **Figures 3.3-5b and 3.3-5c**.

Transverse Range (a Portion of the Mixed Conifer Forest Case Study Area)

High amounts of total reactive nitrogen deposition are evident across much of the Transverse Range portion of the Mixed Conifer Forest Case Study Area as evident in **Figure 3.3-5a**. This figure shows total reactive nitrogen deposition levels of 12 kg N/ha/yr or greater over portions of the San Bernardino Mountains to the west and northwest of the Los Angeles urban area. As indicated above, oxidized nitrogen deposition is much greater than reduced nitrogen deposition throughout nearly all of this case study area. The large amounts of oxidized nitrogen deposition are associated with the high levels of NO_x emissions in this portion of southern California, as seen in **Figure 3.2-2**.

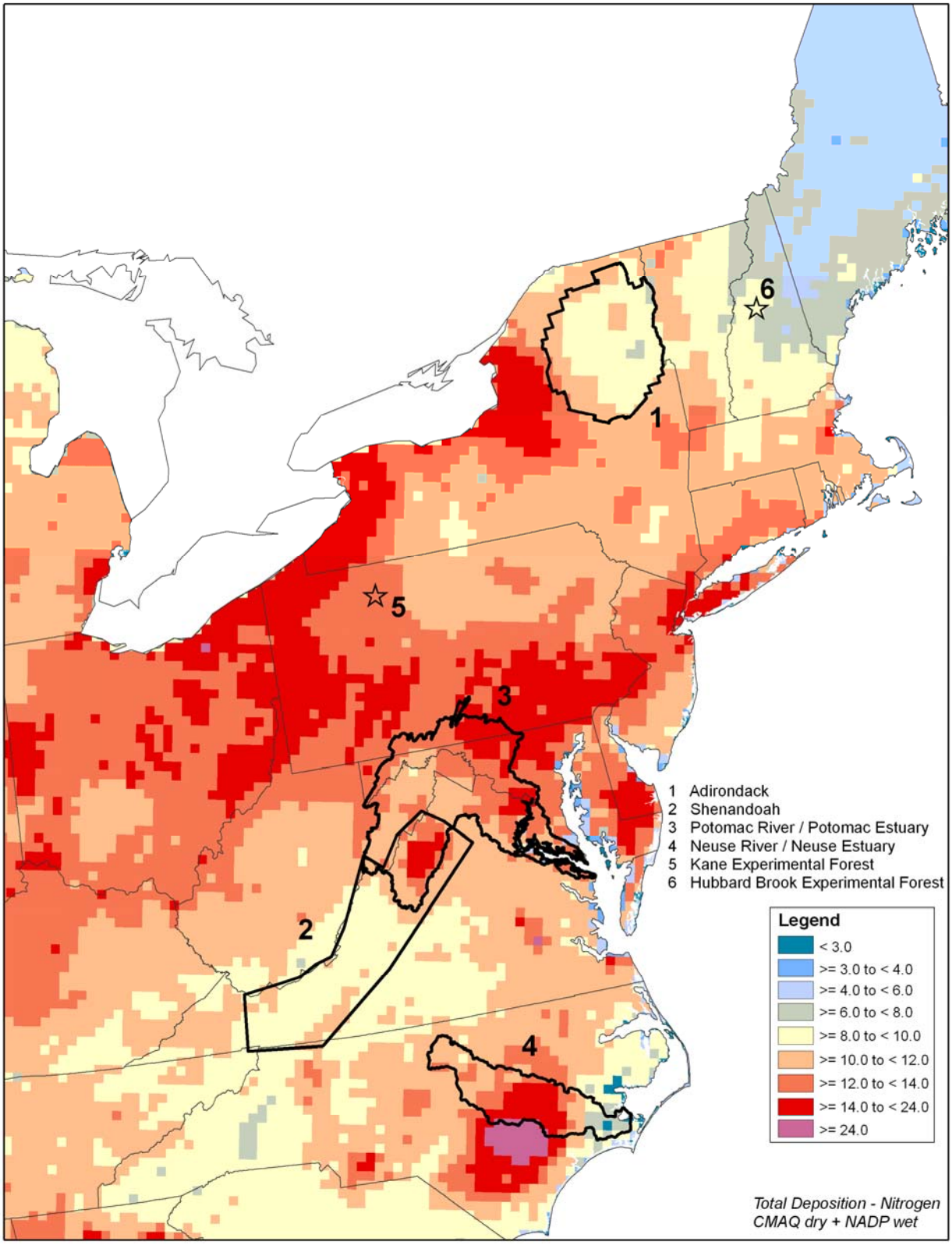

Figure 3.3-4a. Annual total dry plus wet reactive nitrogen deposition (kg N/ha/yr) in 2002 for the case study areas in the East.

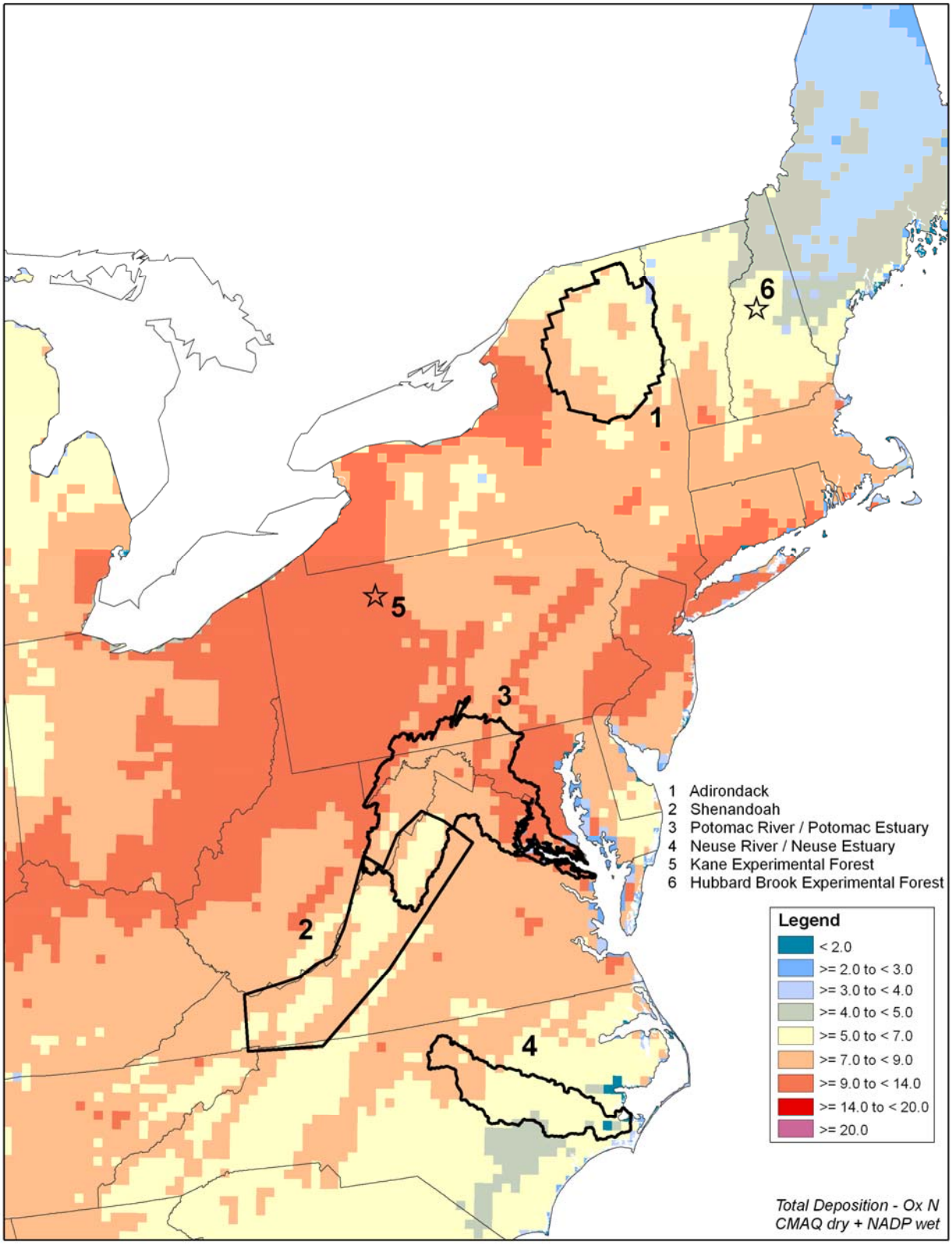

Figure 3.3-4b. Annual total dry plus wet oxidized nitrogen deposition (kg N/ha/yr) in 2002 for the case study areas in the East.

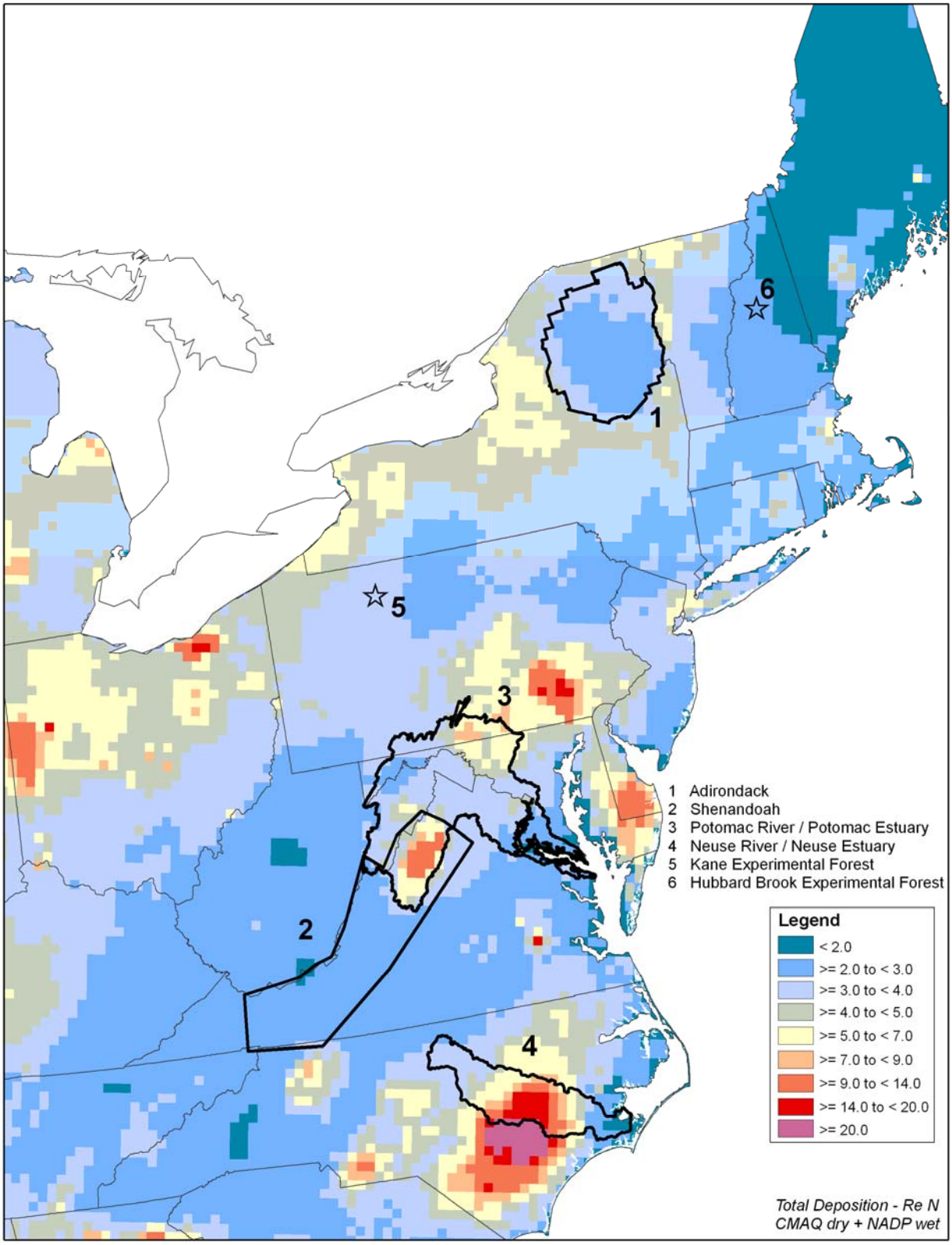

Figure 3.3-4c. Annual total dry plus wet reduced nitrogen deposition (kg N/ha/yr) in 2002 for the case study areas in the East.

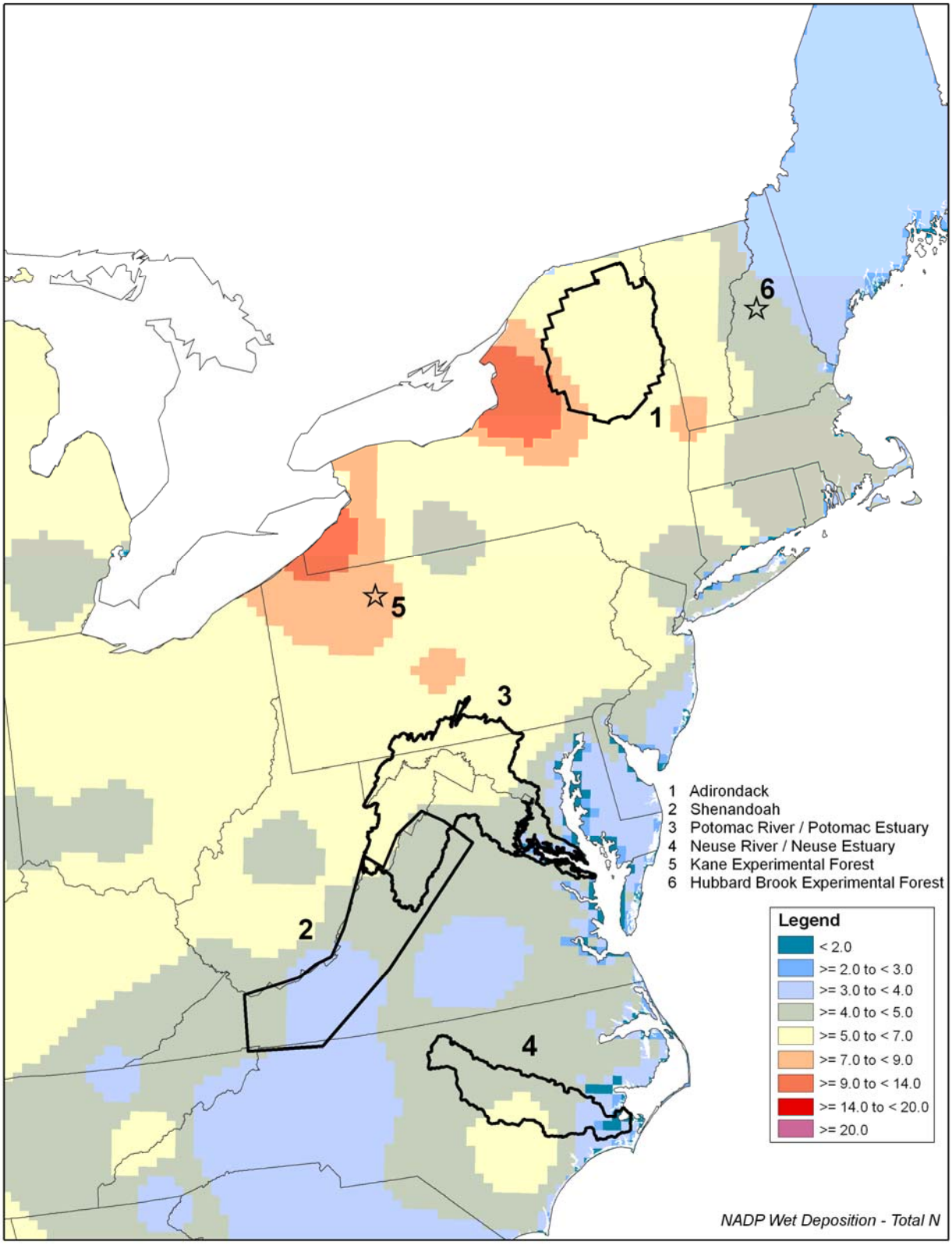

Figure 3.3-4d. Annual total wet reactive nitrogen deposition (kg N/ha/yr) in 2002 for the case study areas in the East.

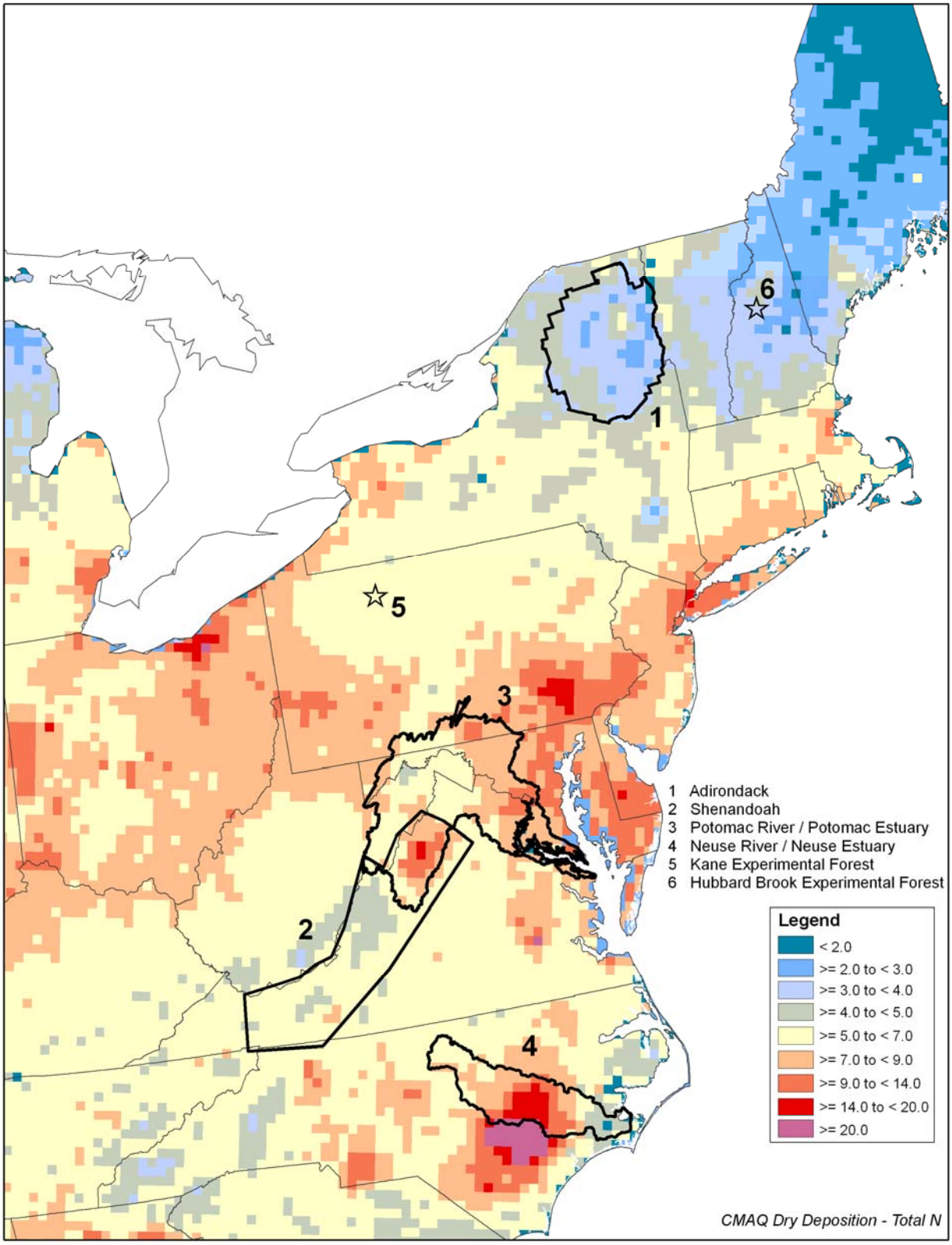

Figure 3.3-4e. Annual total dry reactive nitrogen deposition (kg N/ha/yr) in 2002 for the case study areas in the East.

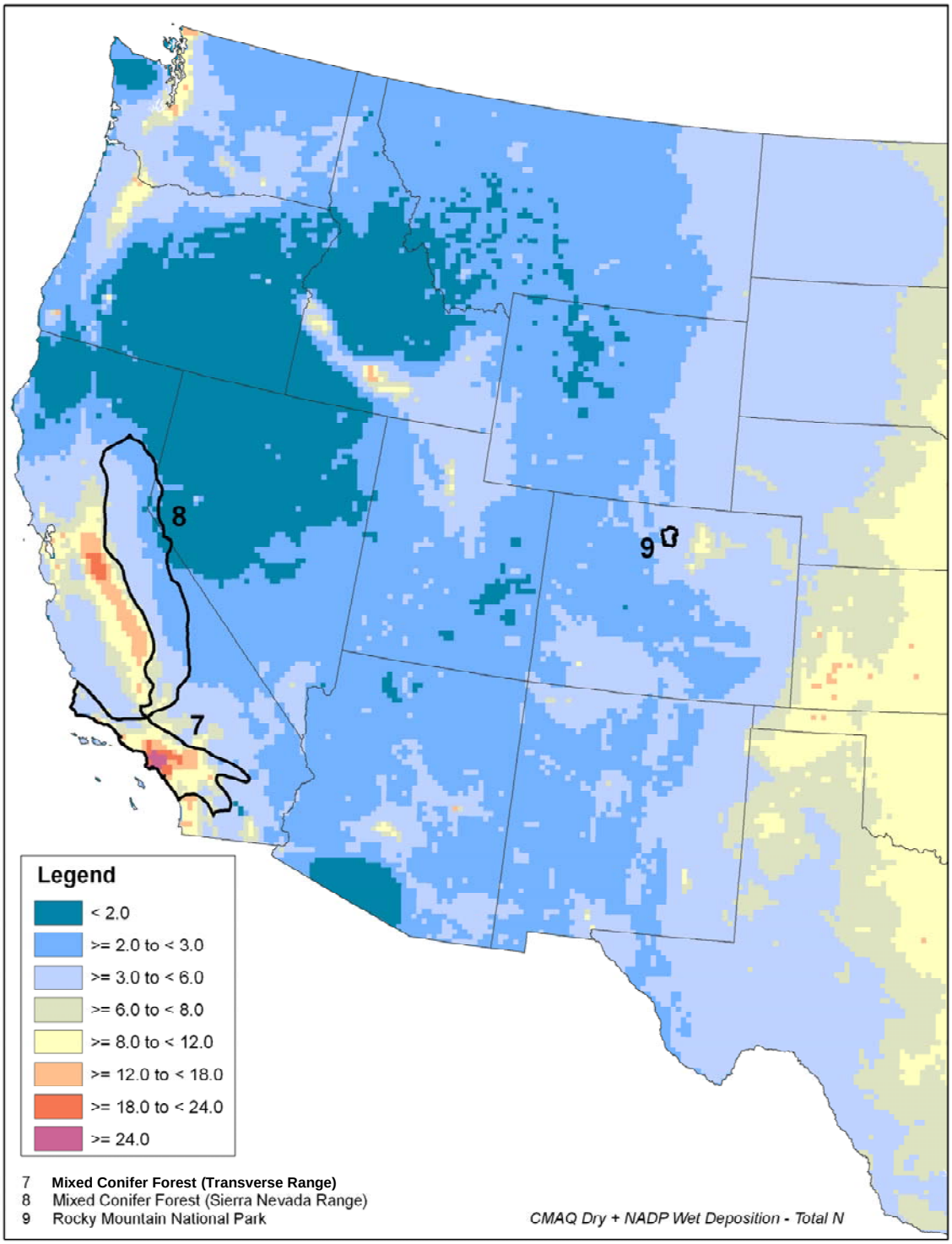

Figure 3.3-5a. Annual total dry plus wet reactive nitrogen deposition (kg N/ha/yr) in 2002 for case study areas and Rocky Mountain National Park in the West.

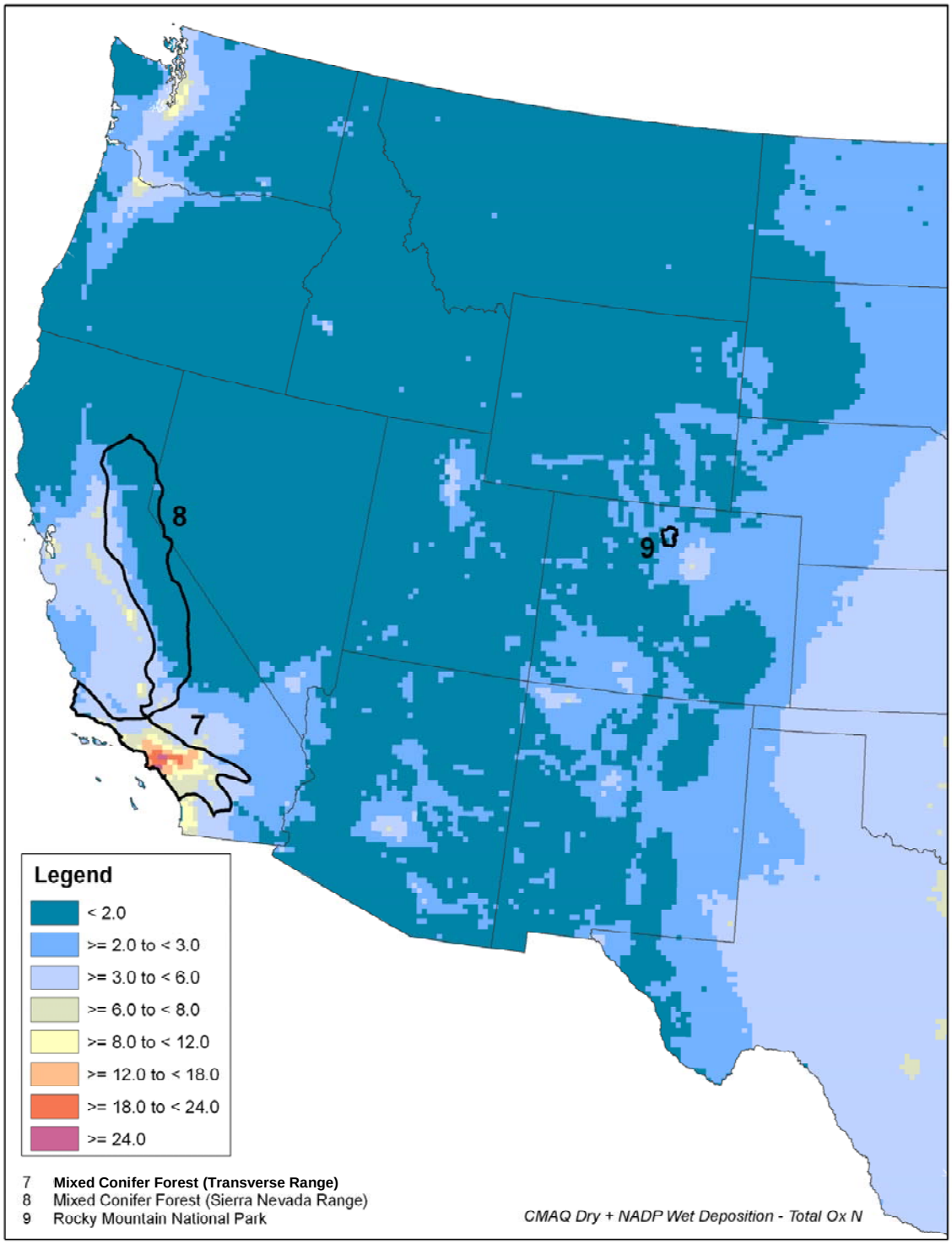

Figure 3.3-5b. Annual total dry plus wet oxidized nitrogen deposition (kg N/ha/yr) in 2002 for case study areas and Rocky Mountain National Park in the West.

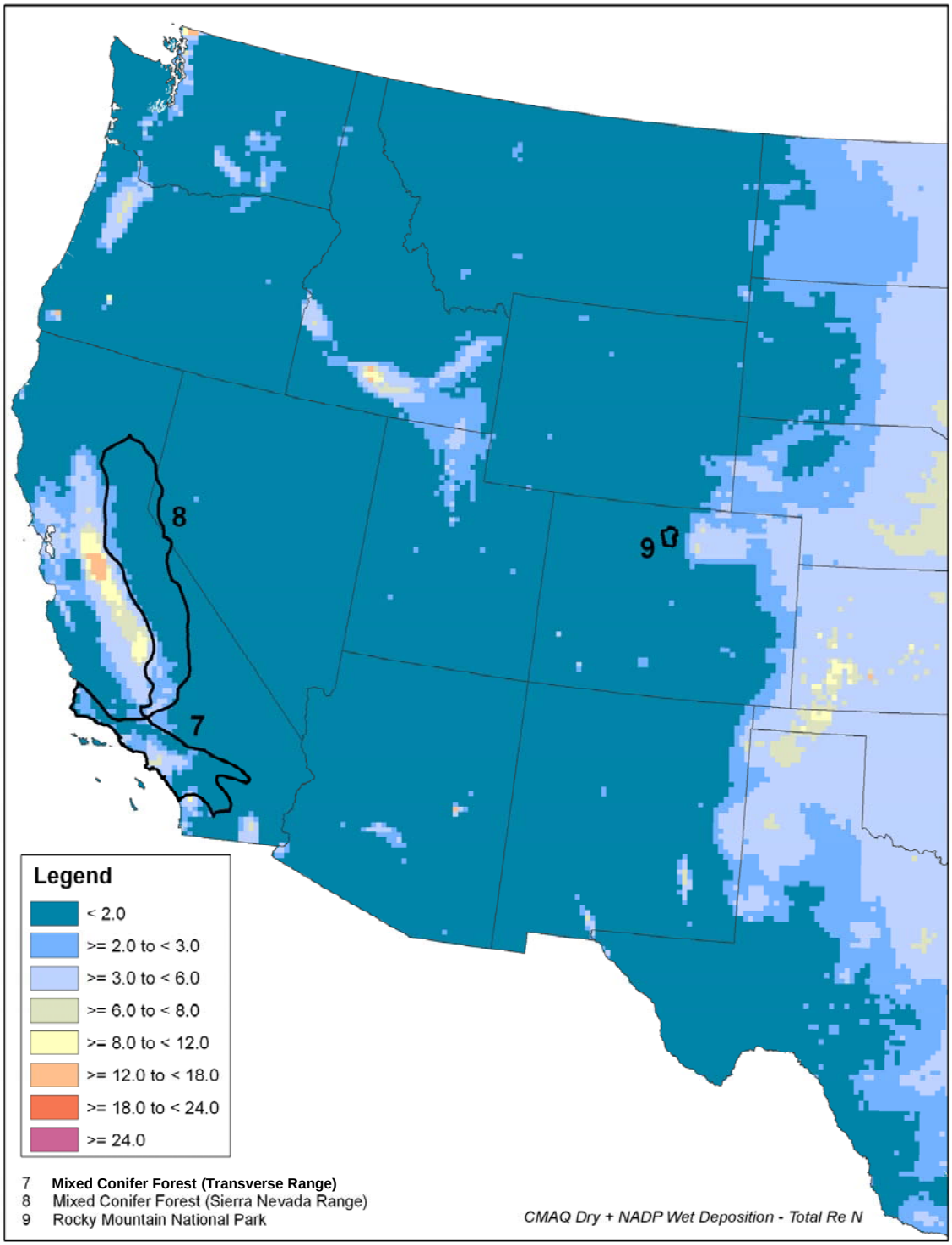

Figure 3.3-5c. Annual total dry plus wet reduced nitrogen deposition (kg N/ha/yr) in 2002 for case study areas and Rocky Mountain National Park in the West.

3.3.3.4 Seasonal Variations in Total Reactive Nitrogen Deposition for 2002

The seasonal variations in model-predicted 2002 total reactive nitrogen deposition for each case study area are shown in **Figures 3.3-6(a–i)**. In most of the case study areas, total reactive nitrogen is highest in spring or summer. Among the case study areas in the East, total reactive nitrogen is highest in spring for the Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas. In these areas, total reactive nitrogen deposition in spring is 30% or more of the annual total. The temporal variation in total reactive nitrogen deposition is fairly uniform in the other three seasons (20% to 25% of the annual total). The results on the seasonal patterns in nitrogen deposition for the case study areas in the East are generally consistent with the findings by Sickles and Shadwick (2007b). In the West, the seasonal variations in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area and the Rocky Mountain National Park are similar, with a peak in spring and relatively high amounts of deposition also seen in summer. Total reactive nitrogen deposition is highest in summer in the Transverse Range portion of the Mixed Conifer Forest Case Study Area.

The seasonal variations in total reactive nitrogen deposition reflect the aggregate of the variations in dry and wet, oxidized, and reduced nitrogen deposition, which are shown in **Figures 3.3-7(a–i)**[26]. Seasonal patterns in precipitation[27] for each case study area are also shown in **Figures 3.3-7(a–i)**. Dry oxidized nitrogen deposition peaks in spring or summer and tends to have the least seasonal variation among the four components of total reactive nitrogen deposition. In contrast, reduced nitrogen deposition peaks in summer and exhibits a fairly large seasonal variation in each of the case study areas. The amount of reduced nitrogen dry deposition in summer accounts for >40% of the annual total reduced nitrogen dry deposition in each area, except for the Kane Experimental Forest Case Study Area and the Transverse Range portion of the Mixed Conifer Forest Case Study Area, where in summer, dry reduced nitrogen is 30% to 35% of the annual total. The intra-annual variations in dry reduced nitrogen deposition are generally consistent with the temporal patterns in NH_3 emissions, which exhibit a primary peak in summer and a secondary peak in spring for the states in which the case study areas are located, as shown in **Figure 3.3-8**. Wet reduced nitrogen deposition seasonal variations generally, but not always, align with the seasonal variations in precipitation. Seasonal variations in wet oxidized

[26] In these figures the percent of deposition by season for each category sums to 100 percent.

[27] The precipitation data used in this analysis are based on the MM-5 meteorological model predictions, which are used as inputs to the CMAQ model simulations.

nitrogen deposition also appear to reflect precipitation patterns, but not as closely as do wet reduced nitrogen deposition.

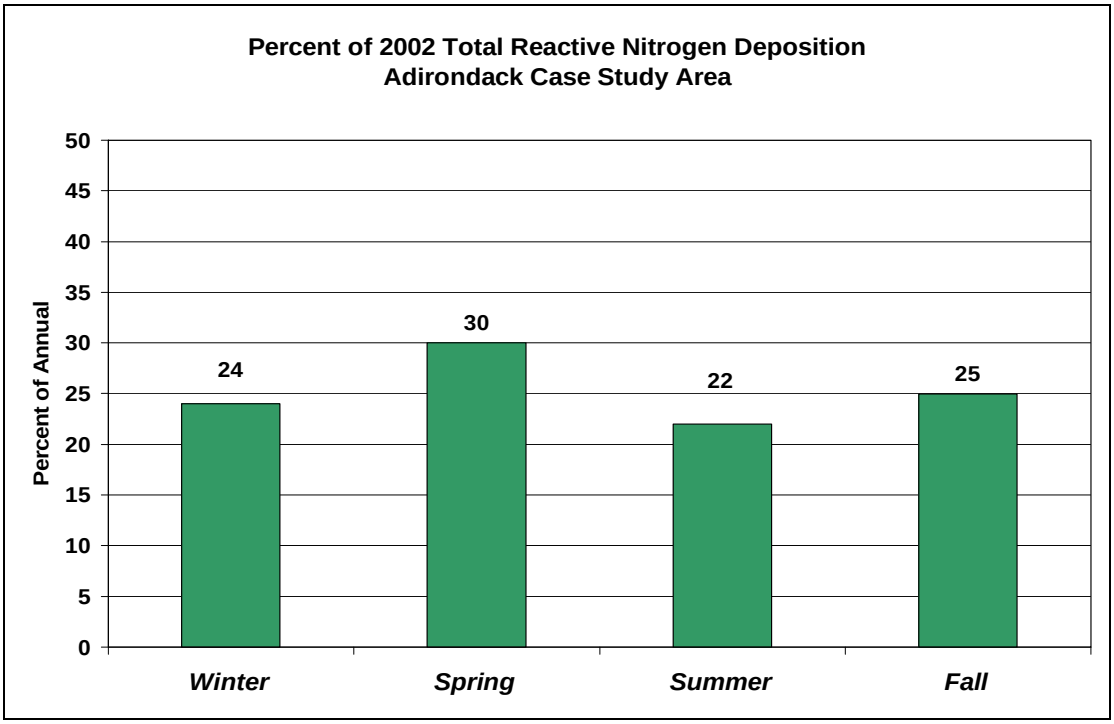

Figure 3.3-6a. Percentage of 2002 total reactive nitrogen deposition in the Adirondack Case Study Area.

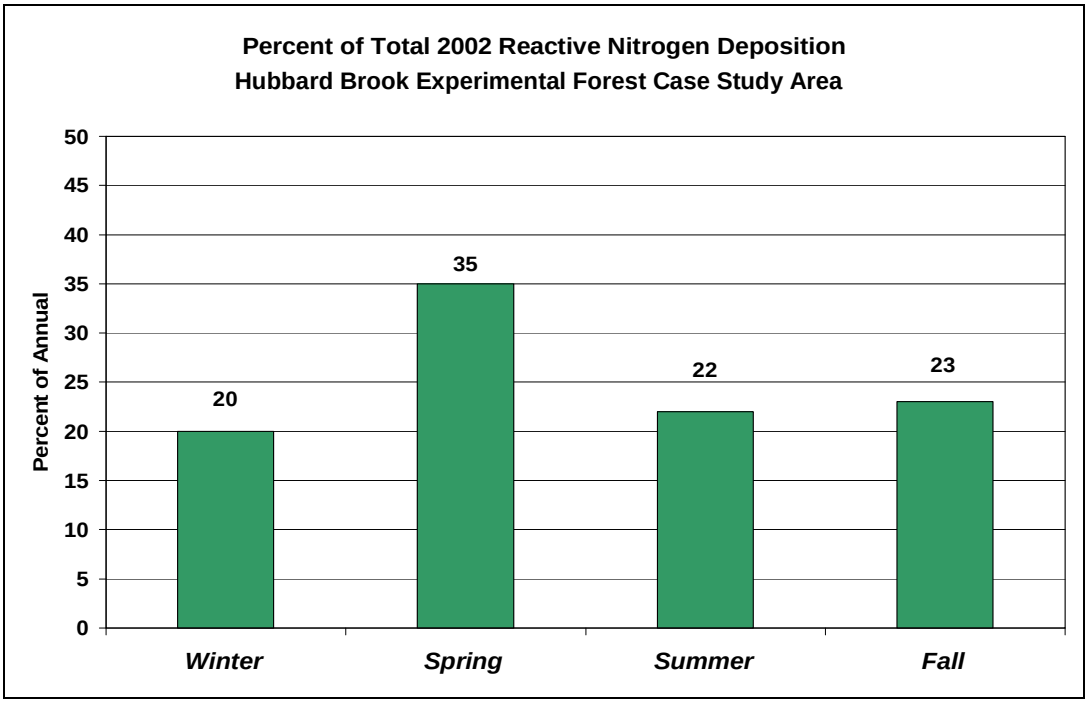

Figure 3.3-6b. Percentage of 2002 total reactive nitrogen deposition in the Hubbard Brook Experimental Forest Case Study Area.

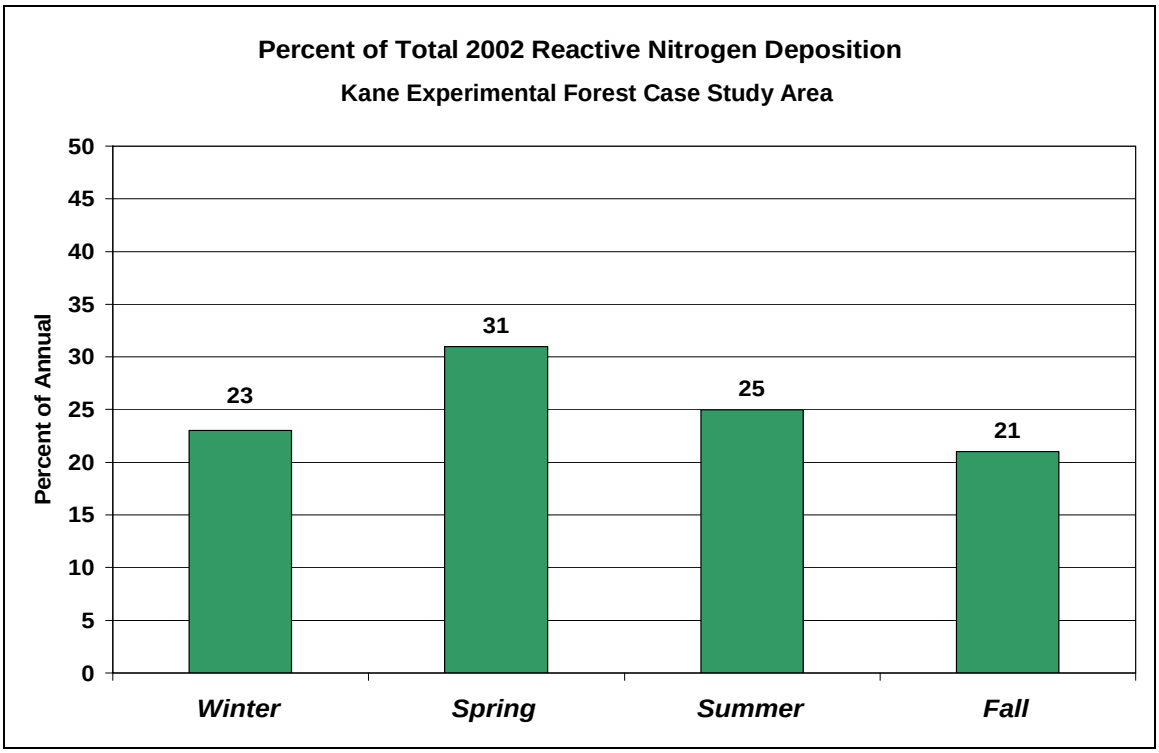

Figure 3.3-6c. Percentage of 2002 total reactive nitrogen deposition in the Kane Experimental Forest Case Study Area.

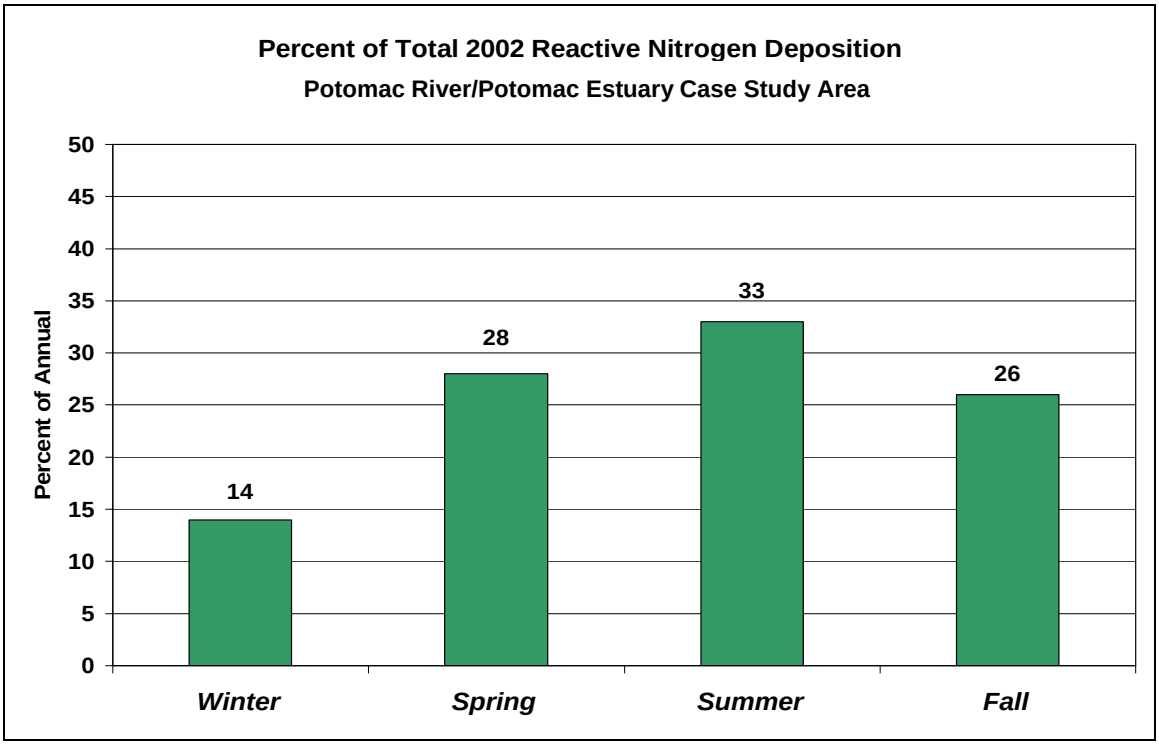

Figure 3.3-6d. Percentage of 2002 total reactive nitrogen deposition in the Potomac River/Potomac Estuary Case Study Area.

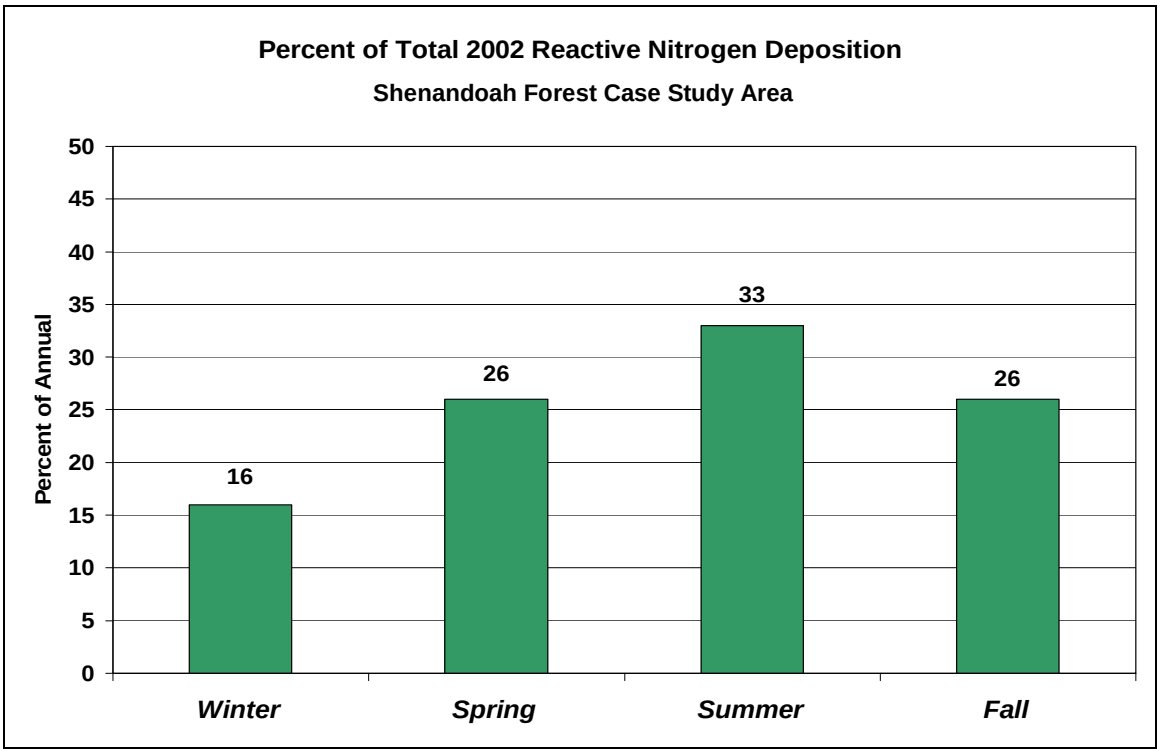

Figure 3.3-6e. Percentage of 2002 total reactive nitrogen deposition in the Shenandoah Case Study Area.

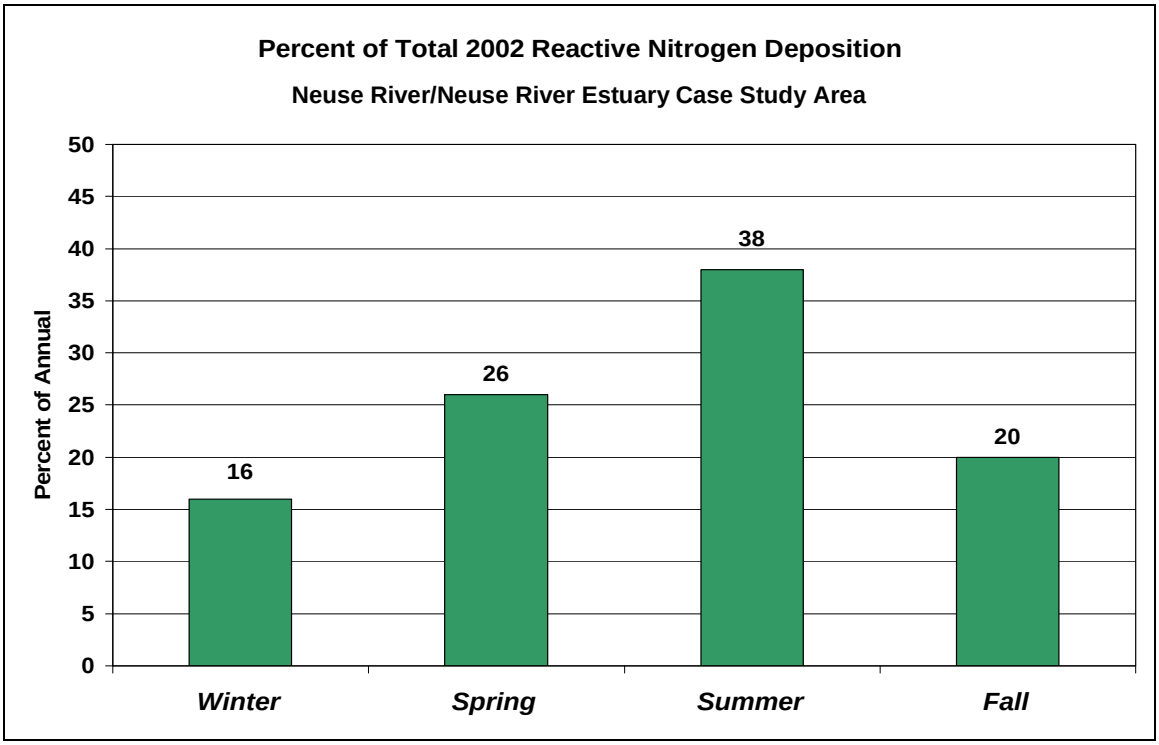

Figure 3.3-6f. Percentage of 2002 total reactive nitrogen deposition in the Neuse River/Neuse River Estuary Case Study Area.

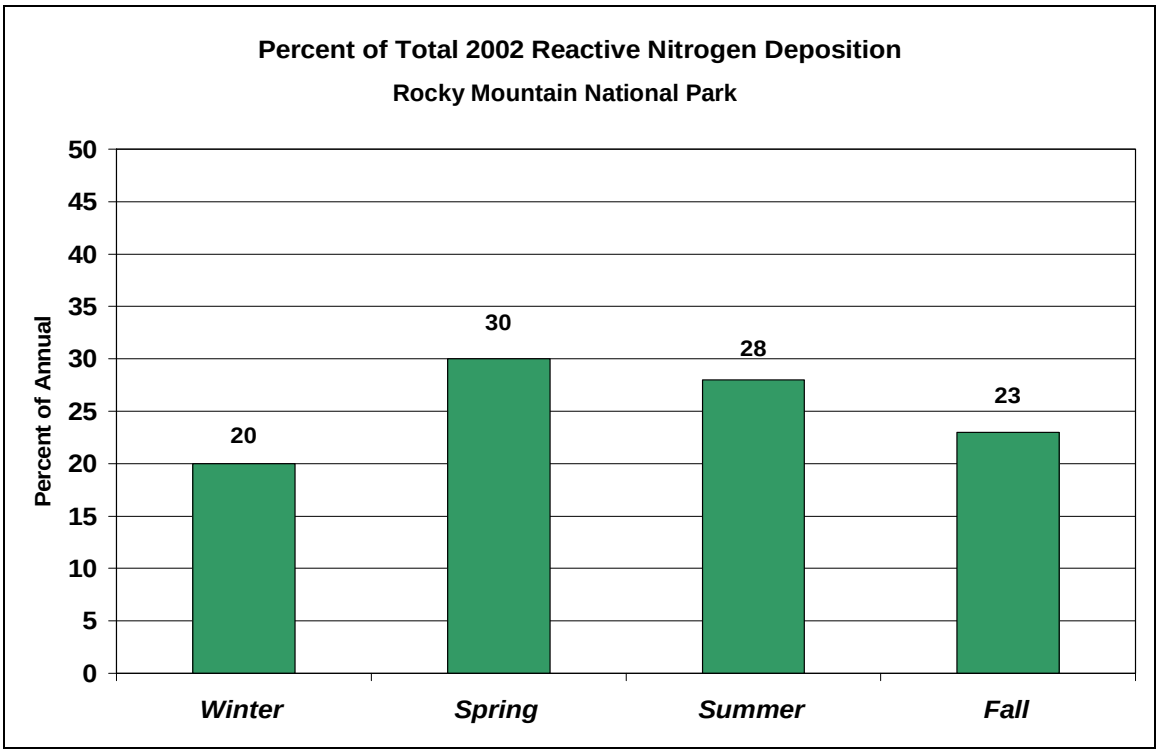

Figure 3.3-6g. Percentage of 2002 total reactive nitrogen deposition in the Rocky Mountain National Park.

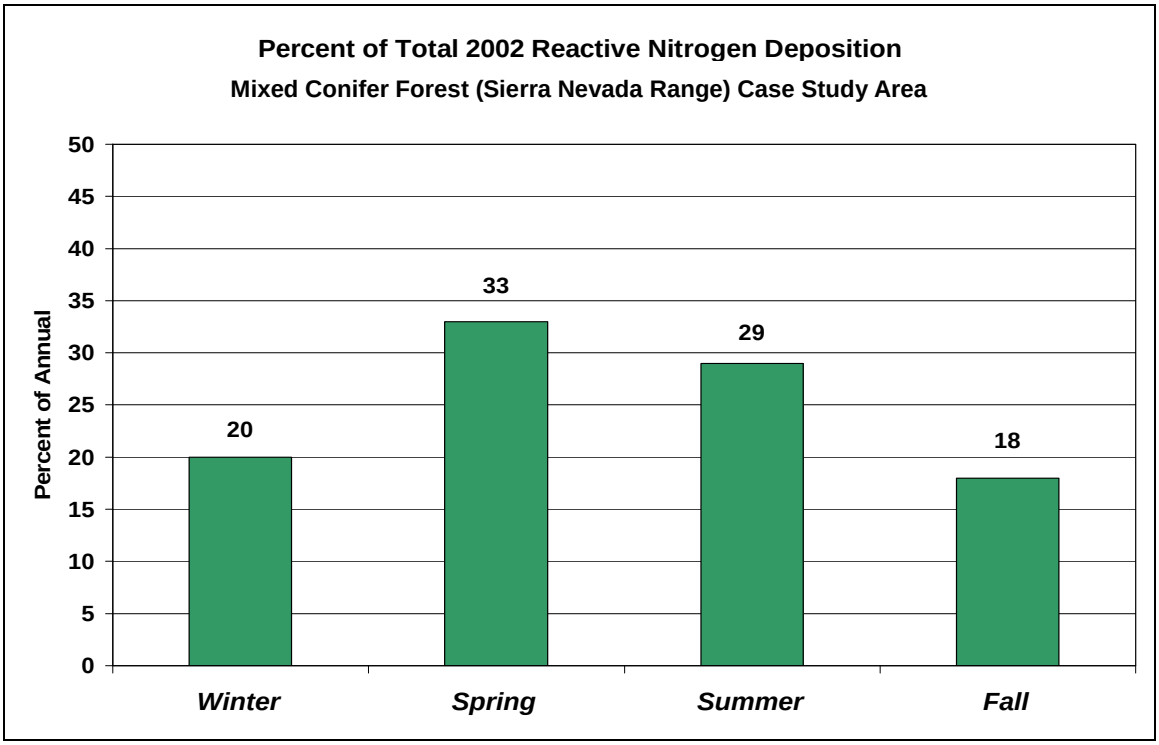

Figure 3.3-6h. Percentage of 2002 total reactive nitrogen deposition in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area.

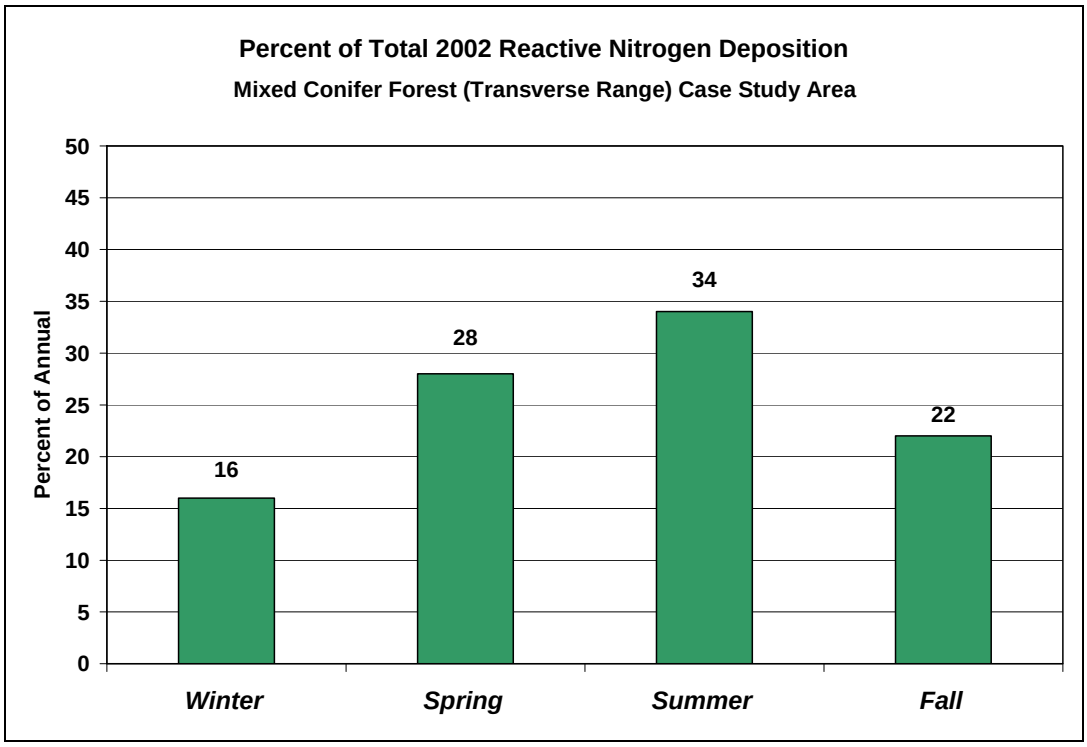

Figure 3.3-6i. Percentage of 2002 total reactive nitrogen deposition in the Transverse Range portion of the Mixed Conifer Forest Case Study Area.

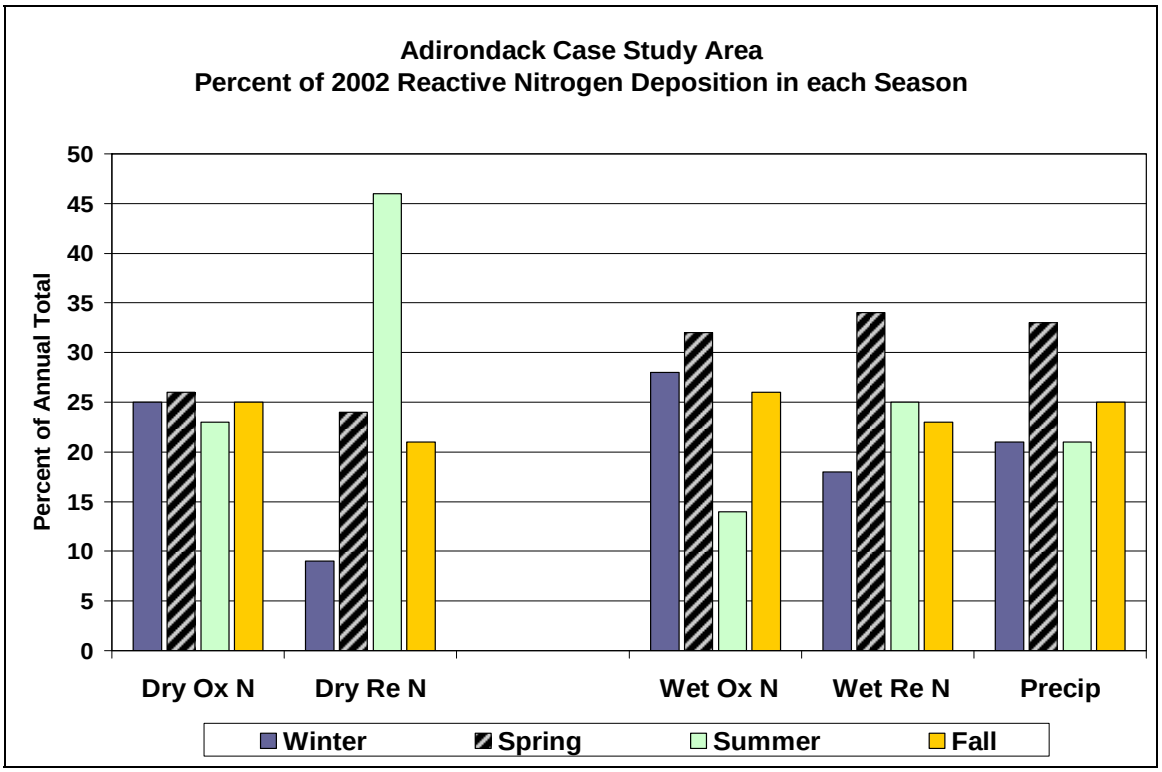

Figure 3.3-7a. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Adirondack Case Study Area.

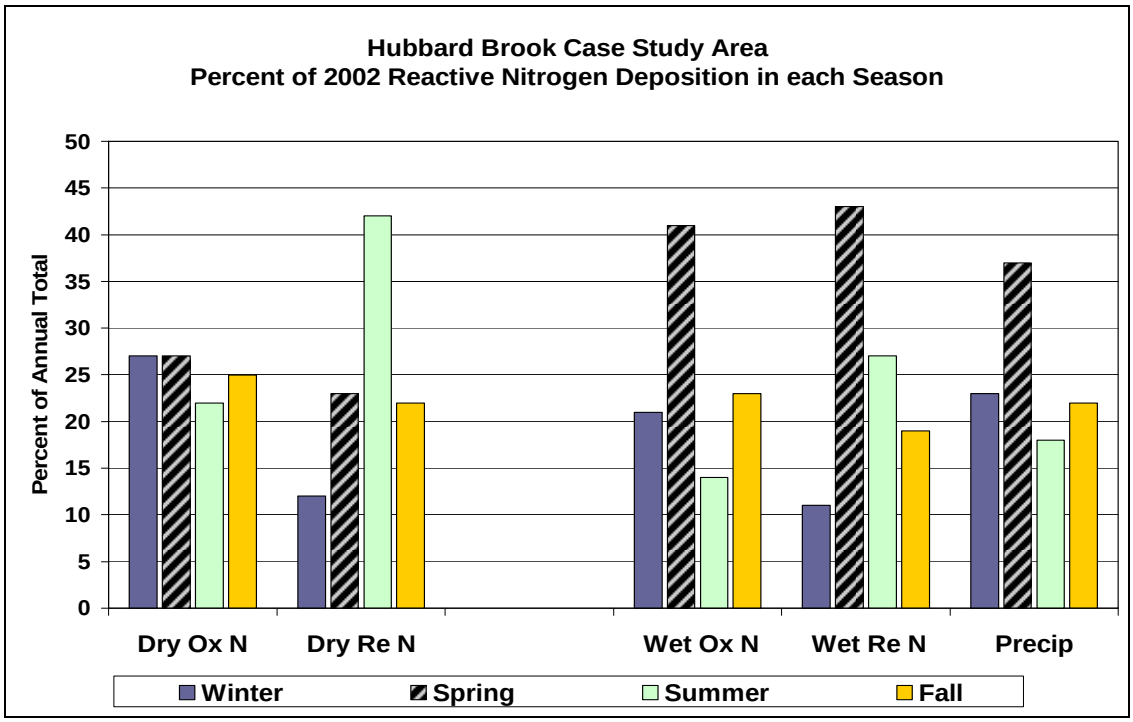

Figure 3.3-7b. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Hubbard Brook Experimental Forest Case Study Area.

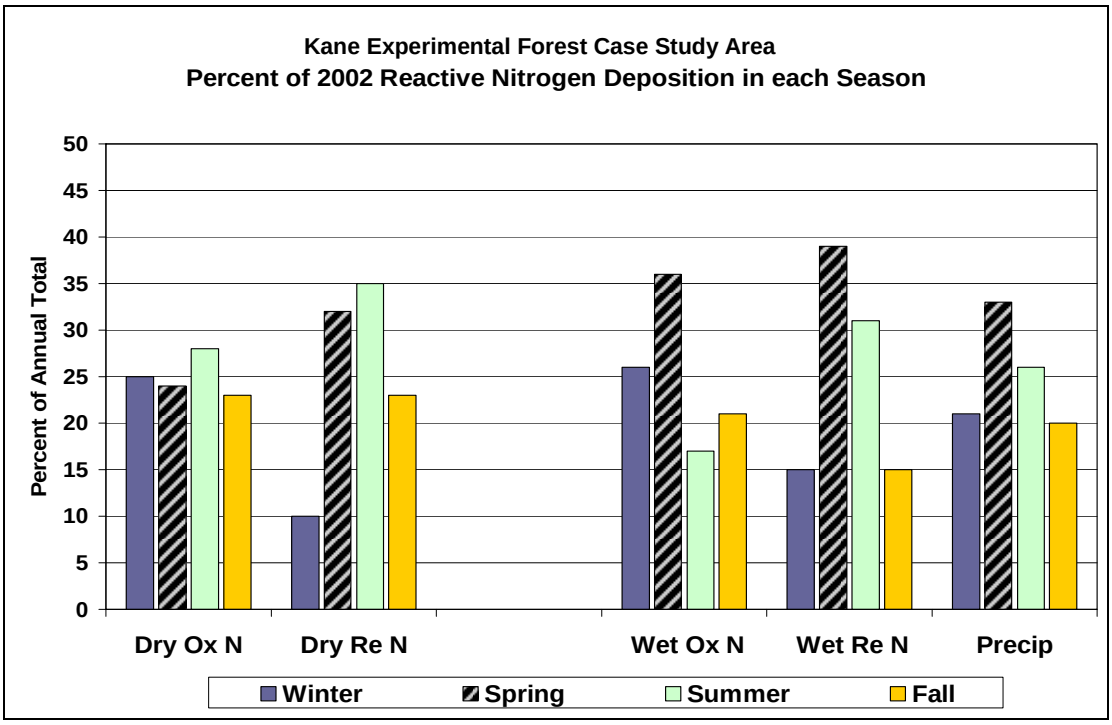

Figure 3.3-7c. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Kane Experimental Forest Case Study Area.

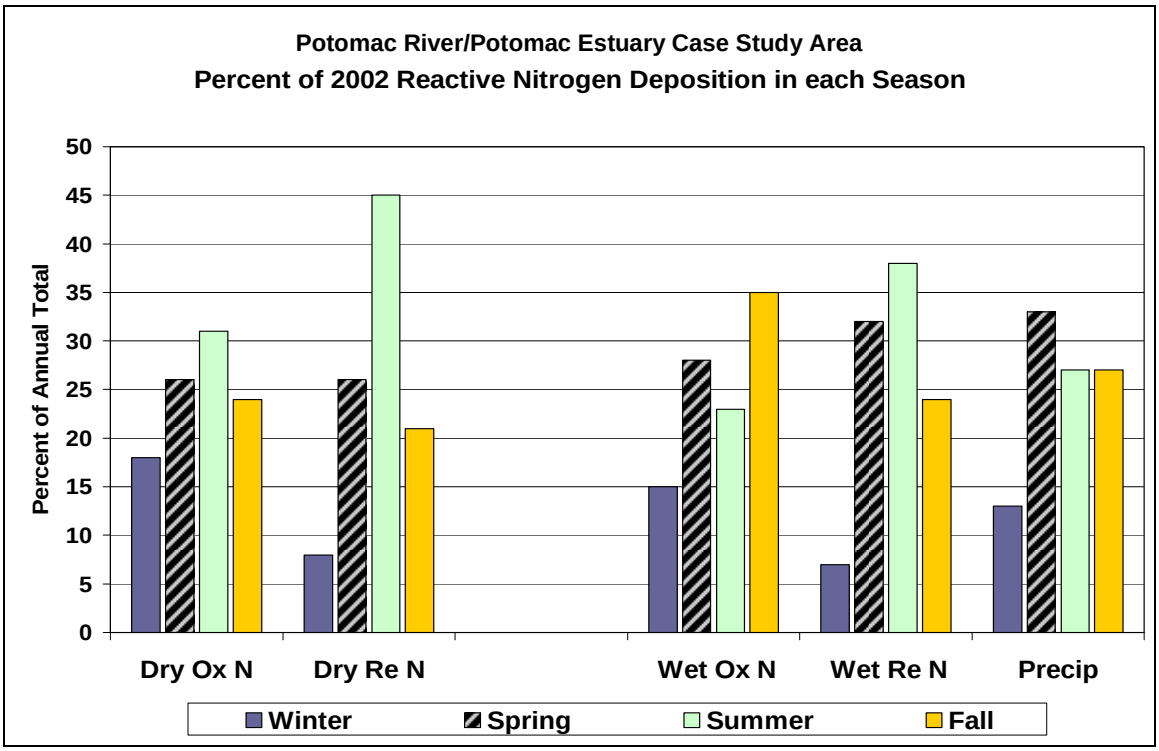

Figure 3.3-7d. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Potomac River/Potomac Estuary Case Study Area.

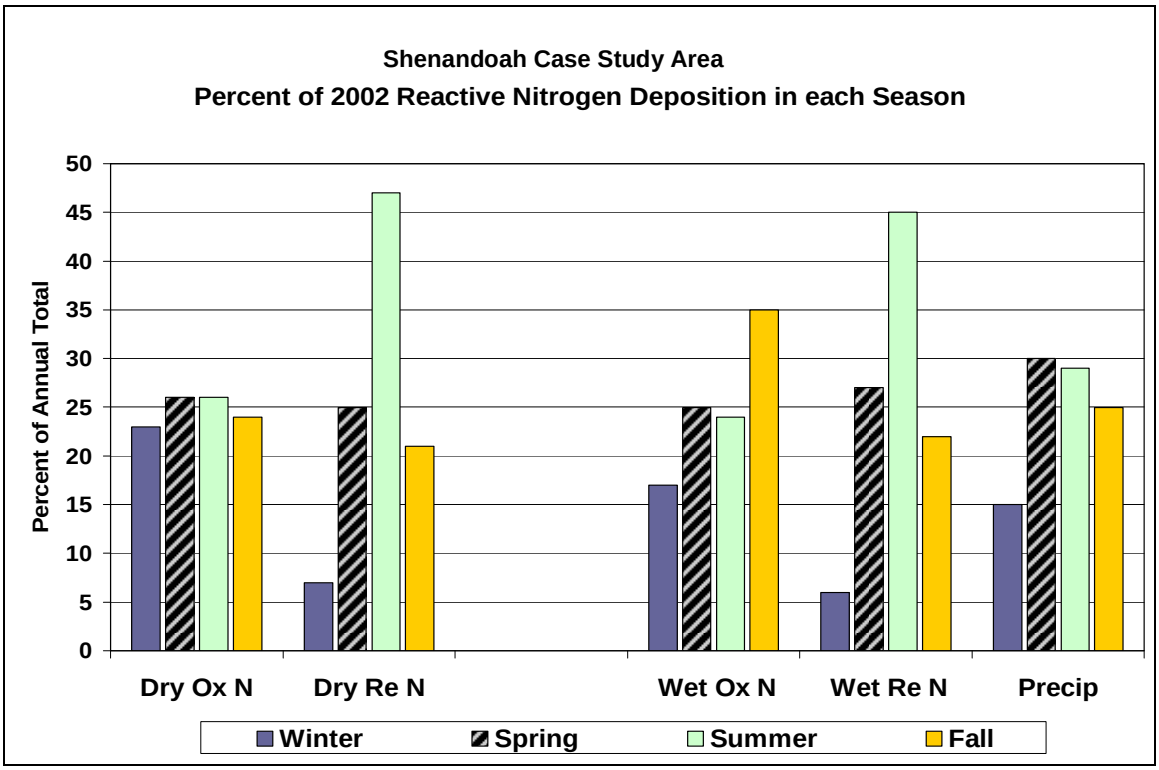

Figure 3.3-7e. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Shenandoah Case Study Area.

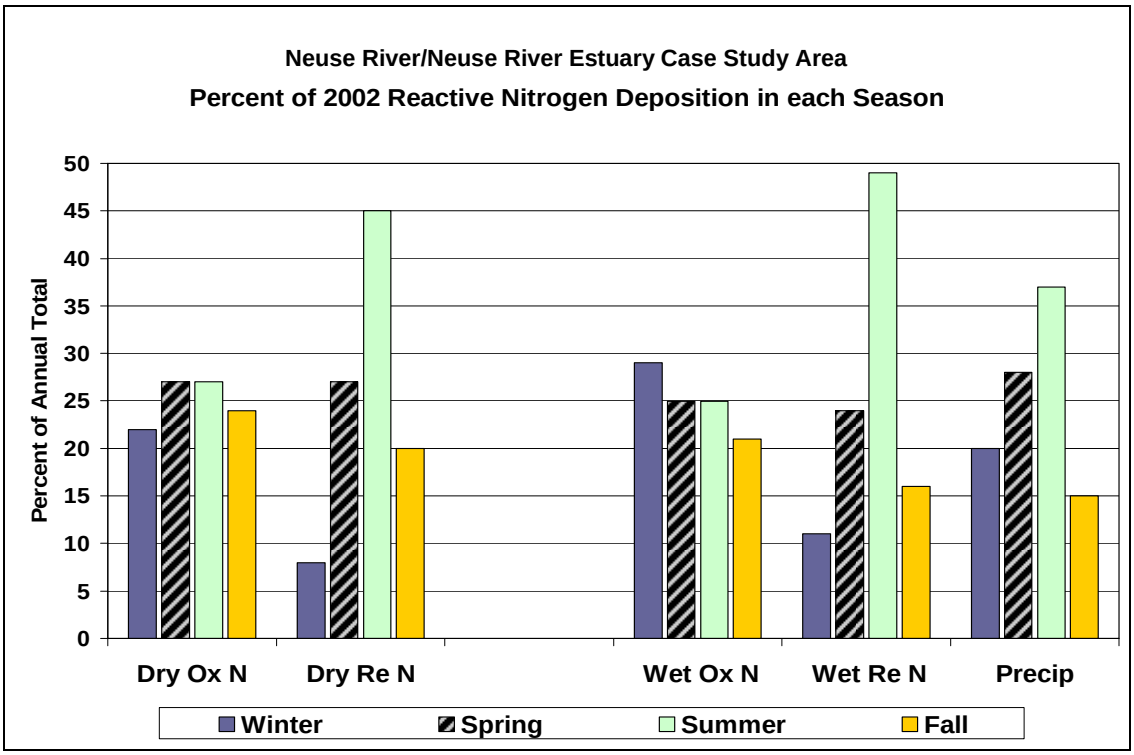

Figure 3.3-7f. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Neuse River/Neuse River Estuary Case Study Area.

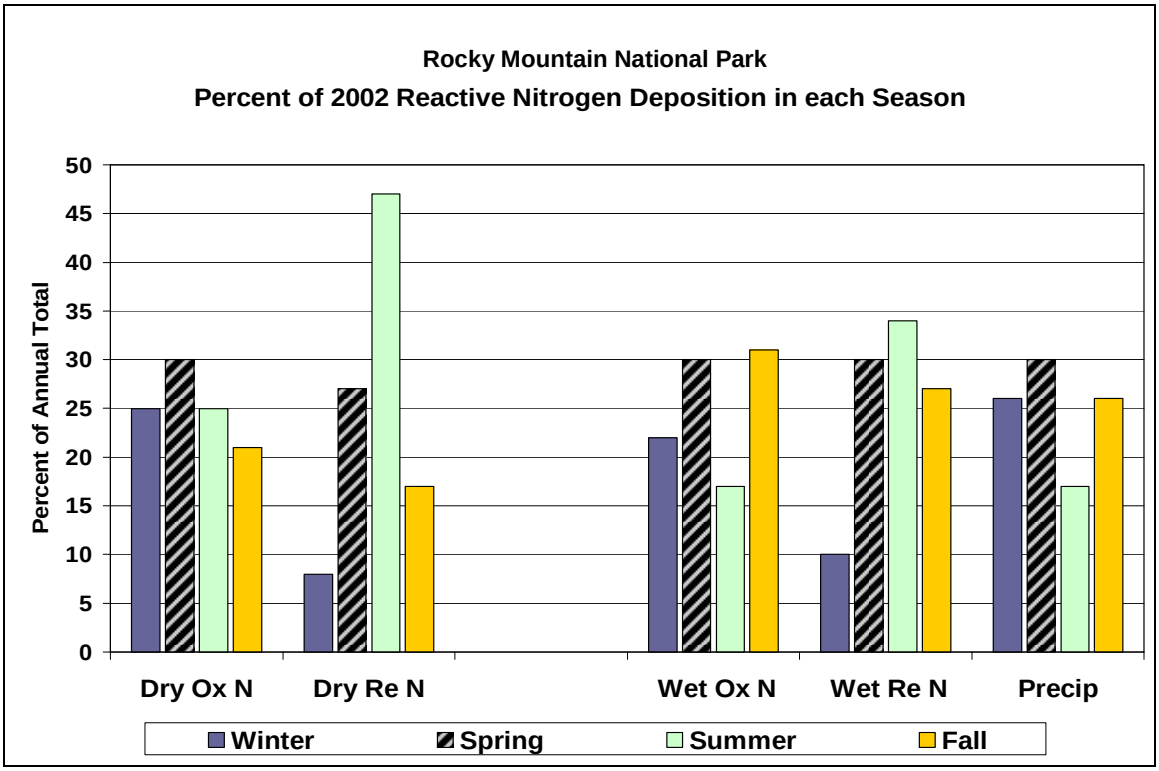

Figure 3.3-7g. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Rocky Mountain National Park.

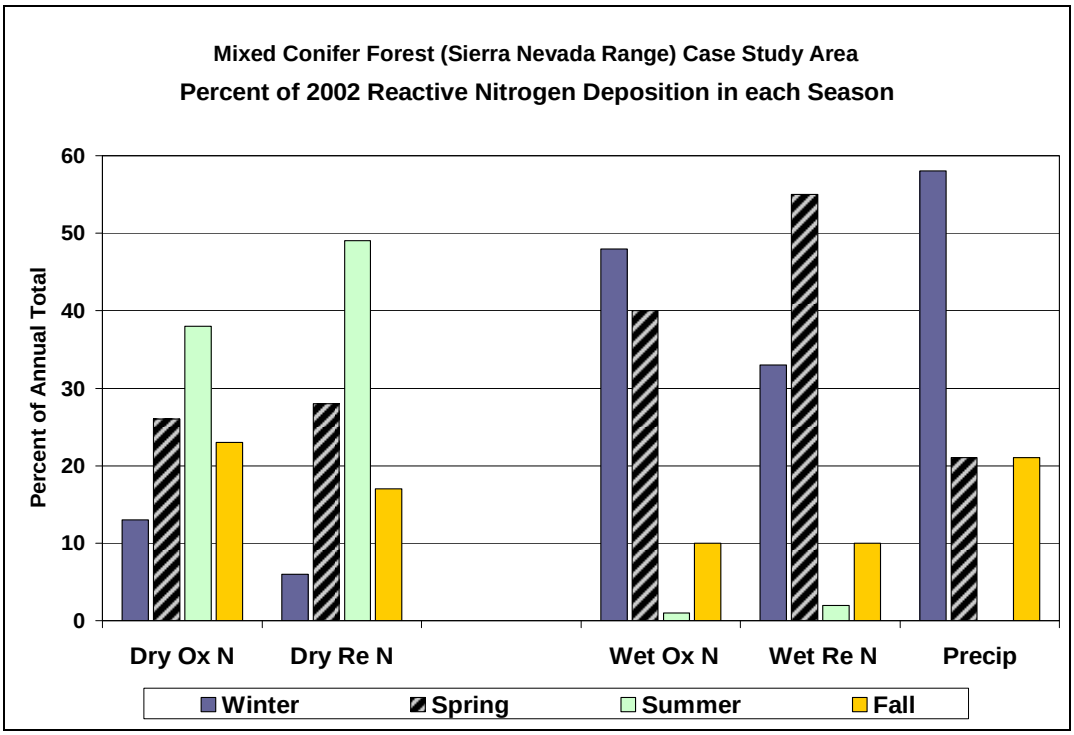

Figure 3.3-7h. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area.

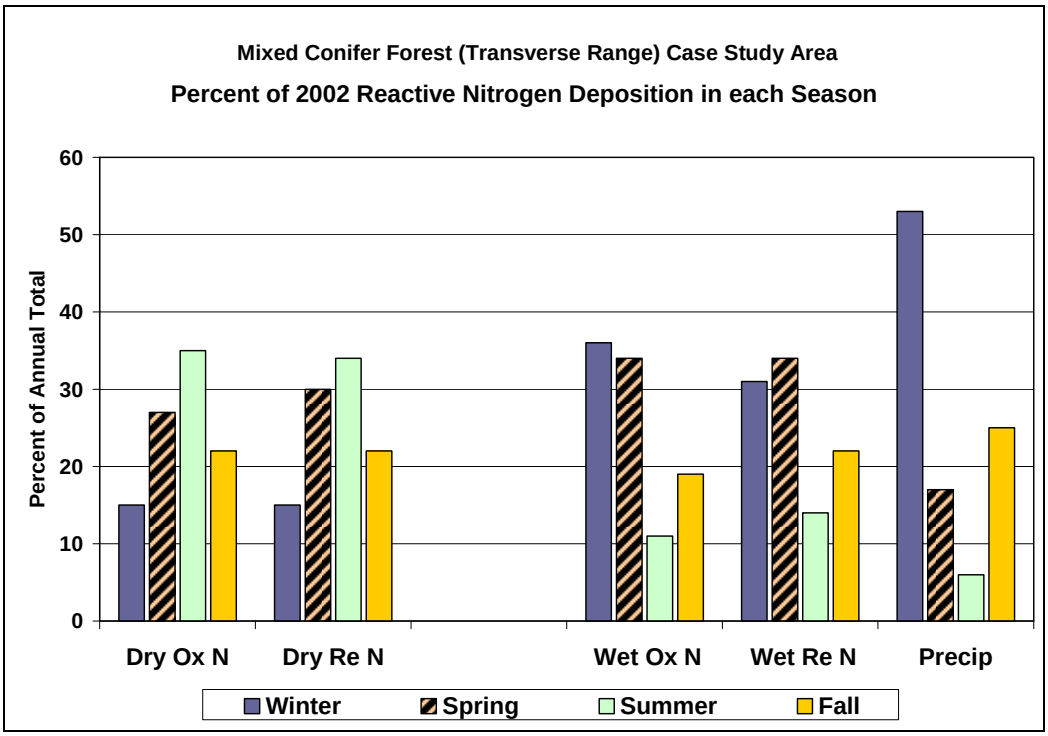

Figure 3.3-7i. Percentage of 2002 reactive nitrogen deposition for each component of nitrogen deposition in the Transverse Range portion of the Mixed Conifer Forest Case Study Area.

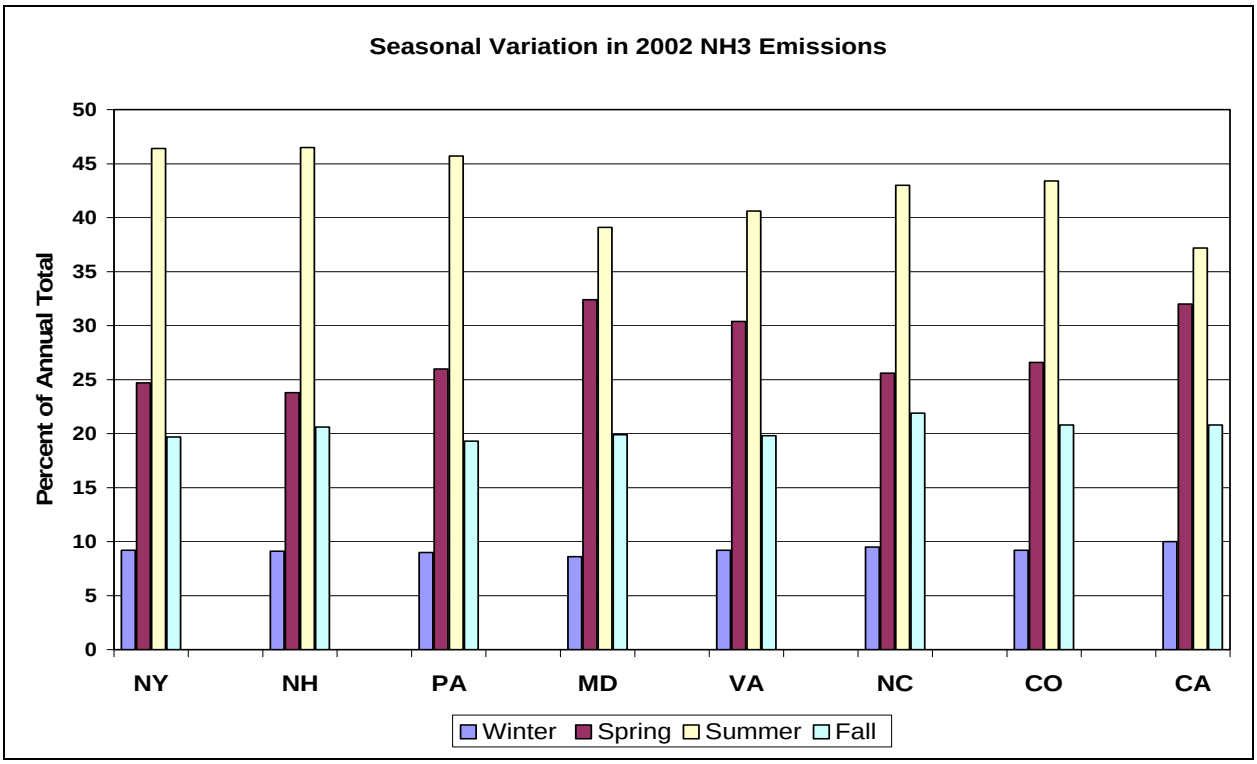

Figure 3.3-8. Percentage of 2002 NH_3 emissions by season for each state containing a case study area.

3.3.3.5 Magnitude of Sulfur Deposition in 2002 and Analysis of Inter-annual Variability

The amount of reactive sulfur deposition in 2002 varies among the case study areas (see **Table 3.3-1**). In the East, sulfur deposition ranges from 7 kg S/ha/yr at the Hubbard Brook Experimental Forest Case Study Area and up to 20 kg S/ha/yr at the Kane Experimental Forest Case Study Area (see **Figure 3.3-9a**). Sulfur deposition in the case study areas in the West is very low and ranged from 1 to 2 kg S/ha/yr (see **Figure 3.3-9b**).

Annual sulfur deposition from 2002 through 2005 varied by 1 to 3 kg S/ha/yr or less at individual case study areas, except for the Kane Experimental Forest Case Study Area, where the range during this period was 8 kg S/ha/yr. There is evidence of a downward trend during this 4-year time period for the Adirondack and Kane Experimental Forest case study areas. No trend is evident during this period for the other case study areas. Trends analyses by CASTNET for an aggregate of 34 sites in the East indicate that dry sulfur deposition levels were fairly steady from 2002 through 2005, followed by a decrease in deposition in 2006 and 2007 (U.S. EPA, 2009). Overall for these 34 sites, sulfur concentrations in wet deposition declined from 2002 to 2004, but then increased from 2005 to 2007 back to the levels monitored in 2002. As in the analysis for

nitrogen deposition, trends over the most recent 10-year period were reviewed for wet deposition of sulfur for NADP sites in or near each case study area (see Appendix 2). The site-specific trend information indicates that overall, for each case study area, the amount of sulfur deposition in 2002 is generally representative of current conditions. As was found in the analysis of nitrogen deposition, trends in sulfur deposition can vary from site to site, even within a case study area, with the same sites showing high/low amounts of sulfur deposition. In the Adirondack Case Study Area, the data from the Huntington Wildlife Forest site indicate that wet sulfur deposition in 2002 is within the range of values over the most recent 10-year period. However, data from the Whiteface site show that wet sulfur deposition in 2002 was high compared to that in other years. The data at both sites show a downward trend to 2005, with nitrogen deposition increasing again by 2007. For the Potomac River/Potomac Estuary Case Study Area, the trends in wet sulfur deposition at the Arendtsville, PA, and Parsons, WV, sites indicate that the amount of deposition in 2002 is similar to that from 1998 through 2007. However, the Wye, MD, site on the Eastern Shore of Maryland shows large inter-annual variations compared with the other sites in the Potomac River/Potomac Estuary Case Study Area, and that wet sulfur deposition in 2002 was on the low end of the range over this time period. During the most recent 10-year period, wet sulfur deposition in the two case study areas and Rocky Mountain National Park in the West was low, and generally in the range of 1 to 3 kg S/ha/yr. In 2002, wet sulfur deposition for both the Transverse Range portion of the Mixed Conifer Forest Case Study Area and the Rocky Mountain National Park was at the low end of this range. In the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, wet sulfur deposition in 2002 was in the range of the magnitude of deposition in other years during the period 1998 to 2007. Similar to the analysis of nitrogen deposition trends, it was beyond the scope of the current analysis to determine the reasons for the observed trends other than to note that local terrain-induced meteorological conditions and differential source-receptor relationships across a case study area may contribute to the differences noted in deposition trends.

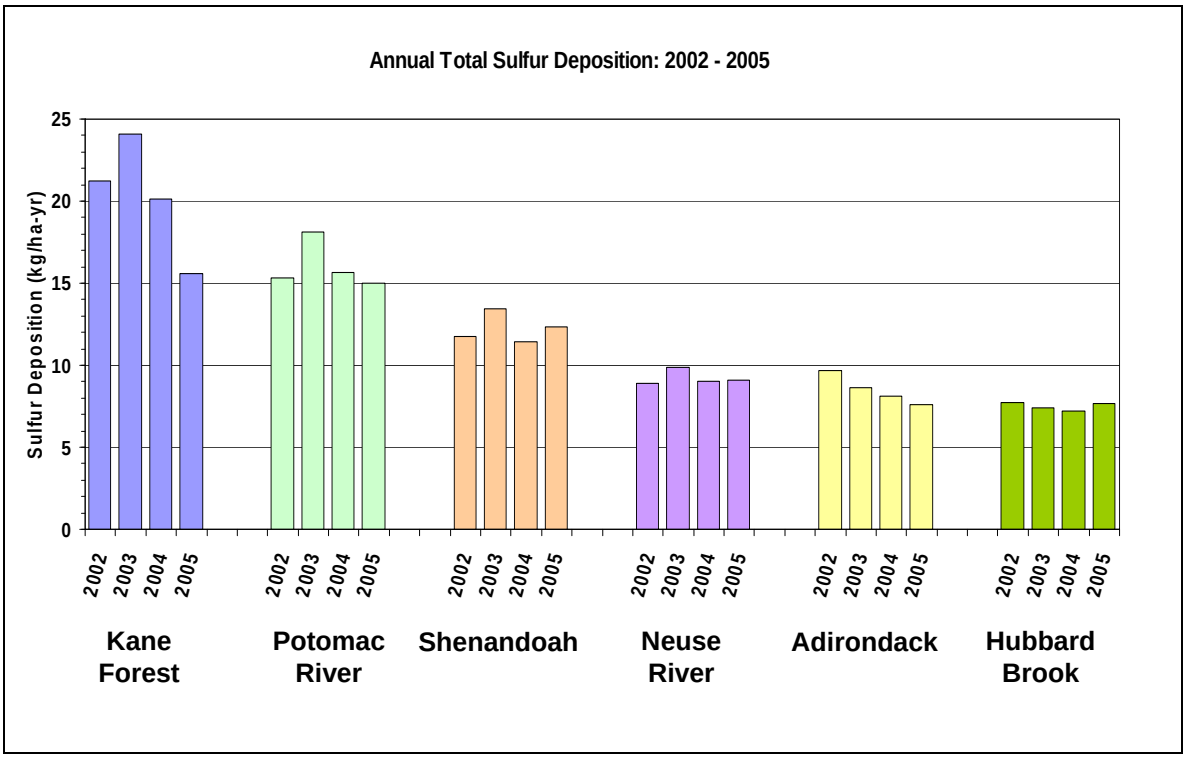

Figure 3.3-9a. Annual sulfur deposition (kg S/ha/yr) from 2002 through 2005 for each case study area in the East.

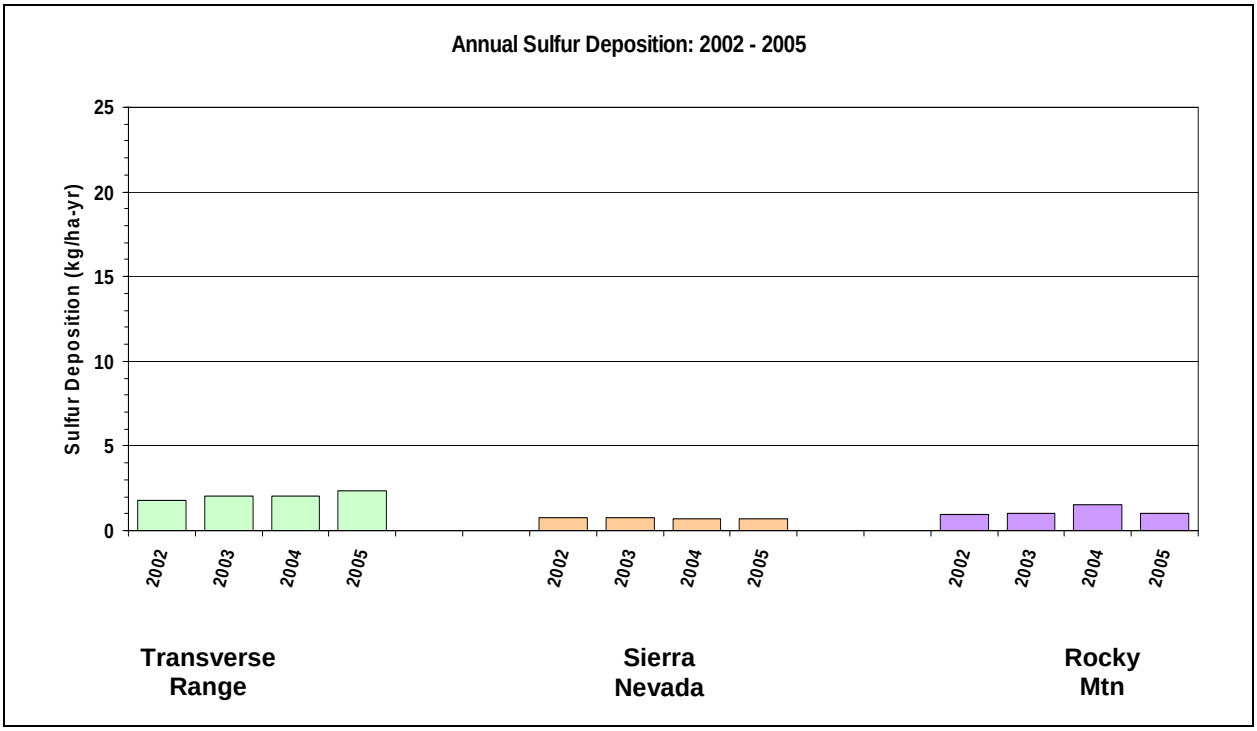

Figure 3.3-9b. Annual sulfur deposition (kg S/ha/yr) from 2002 through 2005 for case study areas in the West, as well as the Rocky Mountain National Park.

3.3.3.6 Relative Amount of Wet and Dry Sulfur Deposition

The relative amounts of wet and dry sulfur deposition for each case study area are shown in **Figure 3.3-10** for 2002 and in **Figure 3.3-11** for the average of 2002 through 2005. These figures indicate that the relative amounts of wet and dry sulfur deposition in 2002 are consistent with the average over the 4-year time period. The results for the case study areas of the East, as described below, are generally consistent with the findings of Sickles and Shadwick (2007b) on the relative amount of wet and dry sulfur deposition for an aggregation of 34 eastern CASTNET sites. Factors that can influence the relative amounts of wet and dry sulfur deposition in a given location include geographic variations and climatological conditions, which determine the amount of precipitation and transport patterns and the proximity to local sources of SO_2. In general, for the case study areas, those areas that are farthest from sources of high SO_2 emissions tend to have more sulfur deposition from wet deposition than from dry deposition. Approximately 60% of total sulfur deposition in 2002 occurred through wet deposition in the Hubbard Brook Experimental Forest, Adirondack and Mixed Conifer Forest (Sierra Nevada Range portion) case study areas, as well as the Rocky Mountain National Park. Each of these areas is fairly distant from sources of high SO_2 emissions. The relative amounts of wet and dry deposition are about the same in the Shenandoah and Neuse River/Neuse River Estuary case study areas. In the Kane Experimental Forest and Potomac River/Potomac Estuary case study areas, which contain or are close to sources of relatively high SO_2 emissions, dry deposition contributes nearly 60% of the total sulfur deposition. In the Transverse Range portion of the Mixed Conifer Forest Case Study Area, which has a more arid climatology compared with the other areas, >70% of the total sulfur deposition is dry deposited.

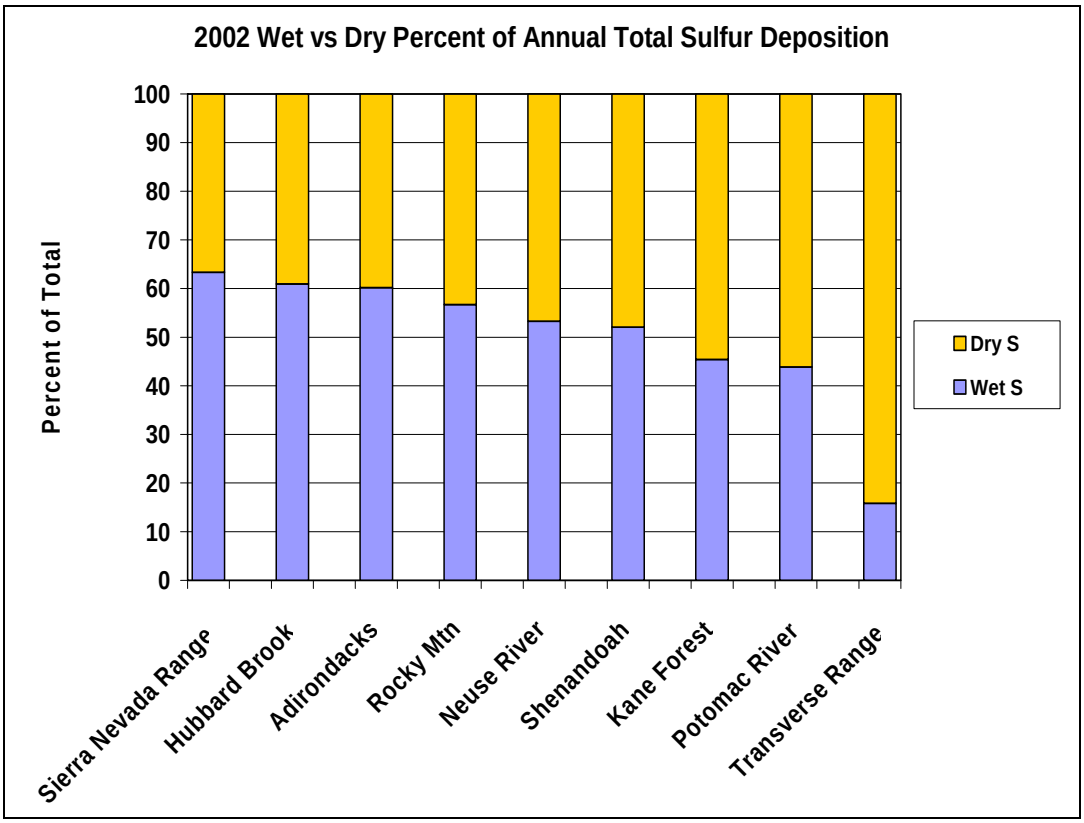

Figure 3.3-10. Relative amount of wet and dry annual sulfur deposition in 2002 for case study areas.

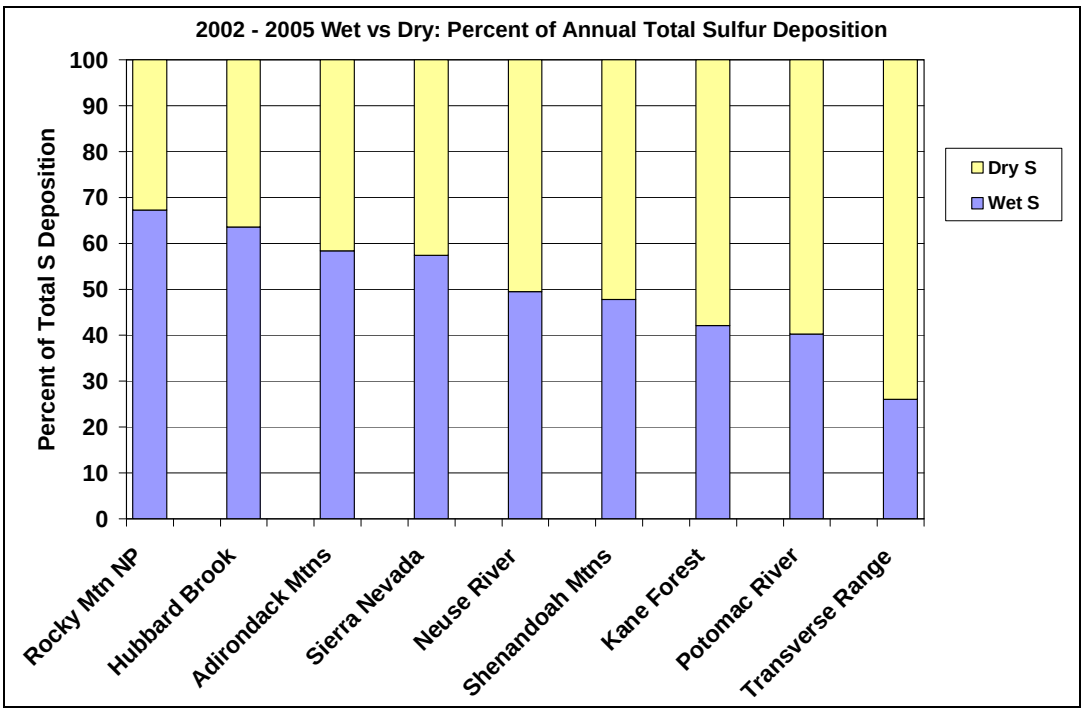

Figure 3.3-11. Relative amount of wet and dry annual sulfur deposition based on deposition for the period 2002 through 2005 for each case study area and the Rocky Mountain National Park.

3.3.3.7 Geographic Variations in Annual Sulfur Deposition for 2002[28]

The spatial patterns in total sulfur deposition and wet and dry sulfur deposition in the East are shown in **Figures 3.3-12(a–c)**. Spatial patterns in total sulfur deposition in the West are shown in **Figure 3.3-13**[29].

Adirondack Case Study Area

The highest amounts of sulfur deposition in the Adirondack Case Study Area are found in the southwestern portion of this area, where sulfur deposition is >10 kg S/ha/yr. In the central and eastern sections of this area, sulfur deposition is <8 kg S/ha/yr. Wet deposition of sulfur is greater than dry deposition across all of this area. The spatial gradients in wet sulfur deposition appear to be much stronger than the gradients in dry sulfur deposition. Like nitrogen deposition, the relatively high total sulfur deposition in the southwestern portion of the Adirondack Case Study Area is part of a broad area of high sulfur deposition that stretches along the southern shore of Lake Ontario into western Pennsylvania and beyond.

Shenandoah Case Study Area

The Shenandoah Case Study Area is on the eastern side of the region of high sulfur deposition that covers portions of the Ohio River Valley and West Virginia. Within the Shenandoah Case Study Area, there are several relatively isolated locations with sulfur deposition of >14 kg S/ha/yr. These locations appear to correspond to the location of local sources of high SO_2 emissions, as shown in **Figure 3.2-5**. There is a large range in dry sulfur deposition within the Shenandoah Case Study Area, with amounts ranging from 3 to 4 kg S/ha/yr up to 14 kg S/ha/yr. Wet sulfur deposition appears to be spatially more homogeneous than dry sulfur deposition. Amounts of wet sulfur deposition range from 5 to 6 kg S/ha/yr across most of the area, with higher amounts, up to the range of 6 to 7 kg S/ha/yr, found in the northwestern part of the area.

[28] Note that an analysis of the spatial gradients in reactive nitrogen and sulfur deposition for the Kane Experimental Forest and Hubbard Brook Experimental Forest case study areas, as well as the Rocky Mountain National Park, is not included because the size of each of these areas is small relative to the 12 × 12-km resolution-measured data and model predictions used in this analysis.

[29] See footnote 19 for caveats concerning the analysis of geographic variations in deposition for the case study areas in the West.

Potomac River/Potomac Estuary Case Study Area

There was considerable variation in sulfur deposition across the Potomac River/Potomac Estuary Case Study Area in 2002. The highest amounts of sulfur deposition in this area, of 24 kg S/ha/yr or more, are found in the far northwestern portion of this area, which is near sources of high SO_2 emissions in western Pennsylvania. Lower amounts of sulfur deposition of 14 kg S/ha/yr or more is found over the eastern half of the Potomac River/Potomac Estuary Case Study Area. The lowest amount of sulfur deposition, in the range of 8 to 10 kg S/ha/yr, is seen in the far southwest portion of this area. Wet and dry sulfur depositions are both relatively high in the northwestern portion of this area. In the eastern portion of this area, near the sources of SO_2 emissions in the vicinity of Washington, DC, dry sulfur deposition is greater than wet.

Neuse River/Neuse River Estuary Case Study Area

In the Neuse River/Neuse River Estuary Case Study Area, sulfur deposition is highest near the Raleigh-Durham urban area (14 kg S/ha/yr or more), and in particular, near a source of high SO_2 emissions located near the North Carolina/Virginia border. Sulfur deposition generally decreases from northwest to southeast down to 6 to 8 kg S/ha/yr in the eastern portion of this area. Most of the spatial variation in sulfur deposition appears to be associated with dry deposition. Dry sulfur deposition increases from 2 to 3 kg S/ha/yr near the mouth of the Neuse River up to 9 to 14 kg S/ha/yr in the northwest corner of this case study area. In contrast, the amount of wet sulfur deposition appears to be fairly homogeneous across most of the case study area, with amounts in the range of 4 to 5 kg S/ha/yr.

Sierra Nevada Range (a Portion of the Mixed Conifer Forest Case Study Area)

There appears to be very little spatial variation in sulfur deposition in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area. The amount of sulfur deposition is <1 kg S/ha/yr across most of this area. The highest amounts (1 to 2 kg S/ha/yr) are found in the extreme western portion of this area.

Transverse Range (a Portion of the Mixed Conifer Forest Case Study Area)

In the Transverse Range portion of the Mixed Conifer Forest Case Study Area, sulfur deposition decreases with distance from the Los Angeles urban area. Sulfur deposition in the San Bernardino Mountains north of Los Angeles is in the range of 0.5 to 2 kg S/ha/yr.

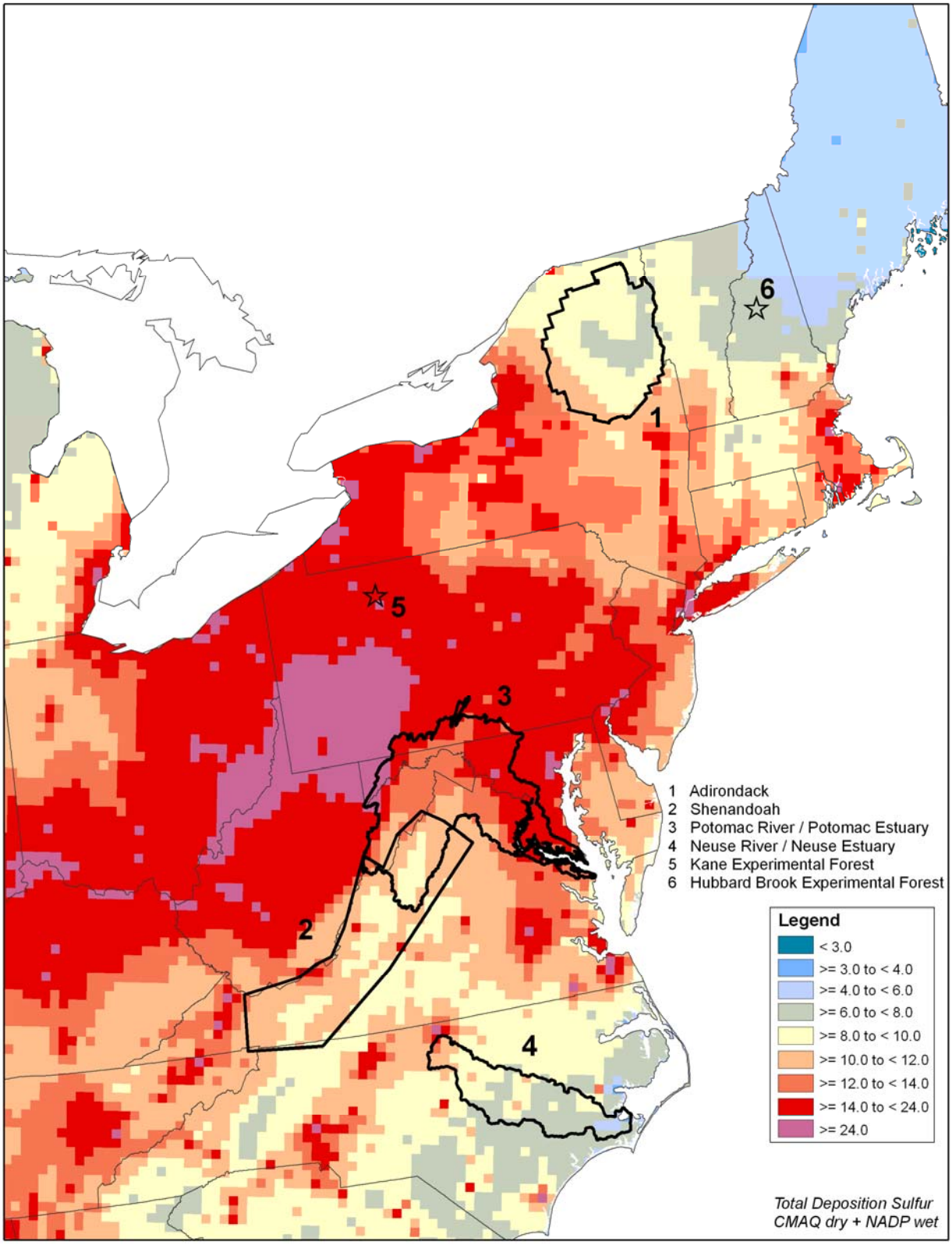

Figure 3.3-12a. Annual total dry plus wet sulfur deposition (kg S/ha/yr) in 2002 for the case study areas in the East.

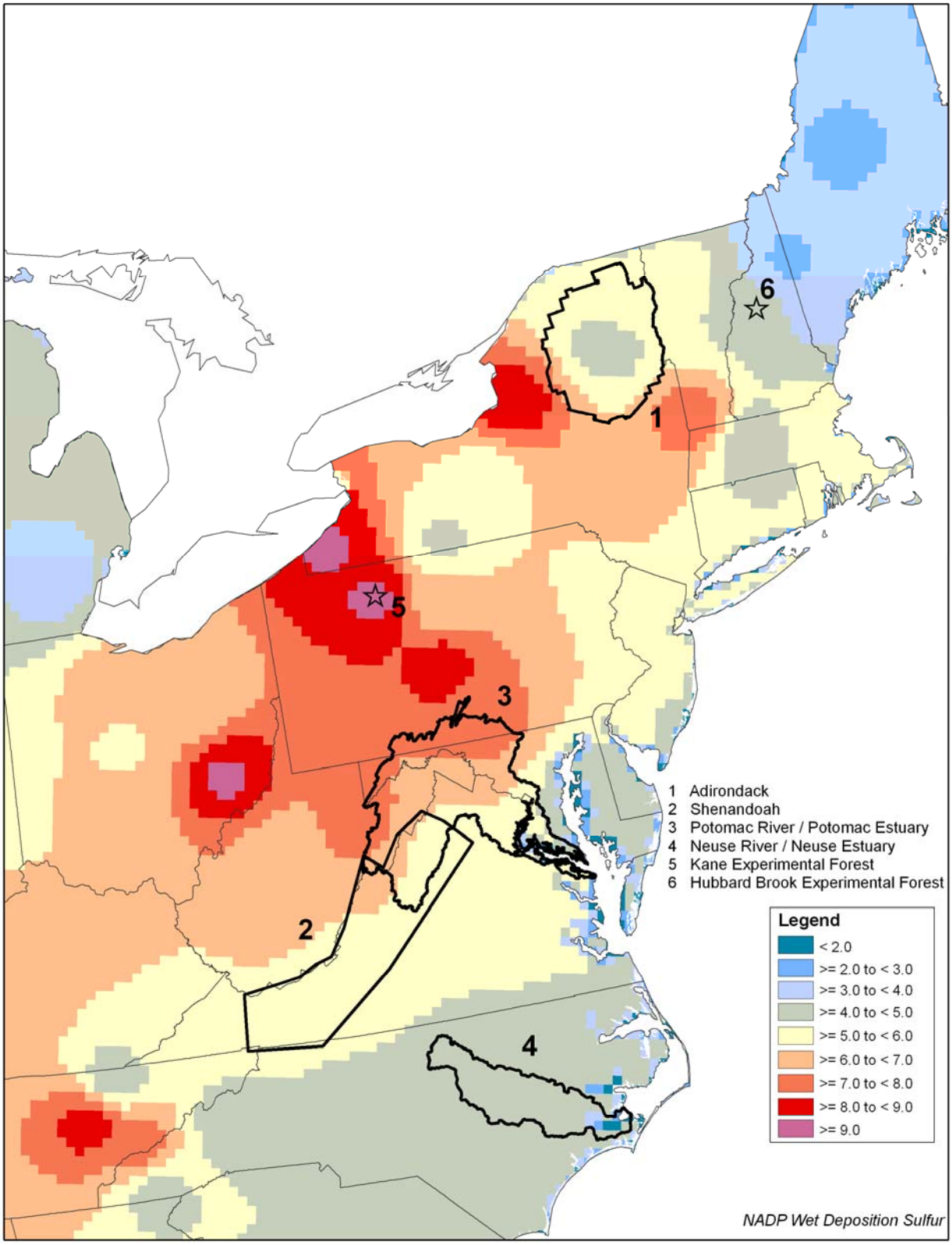

Figure 3.3-12b. Annual wet sulfur deposition (kg S/ha/yr) in 2002 for the case study areas in the East.

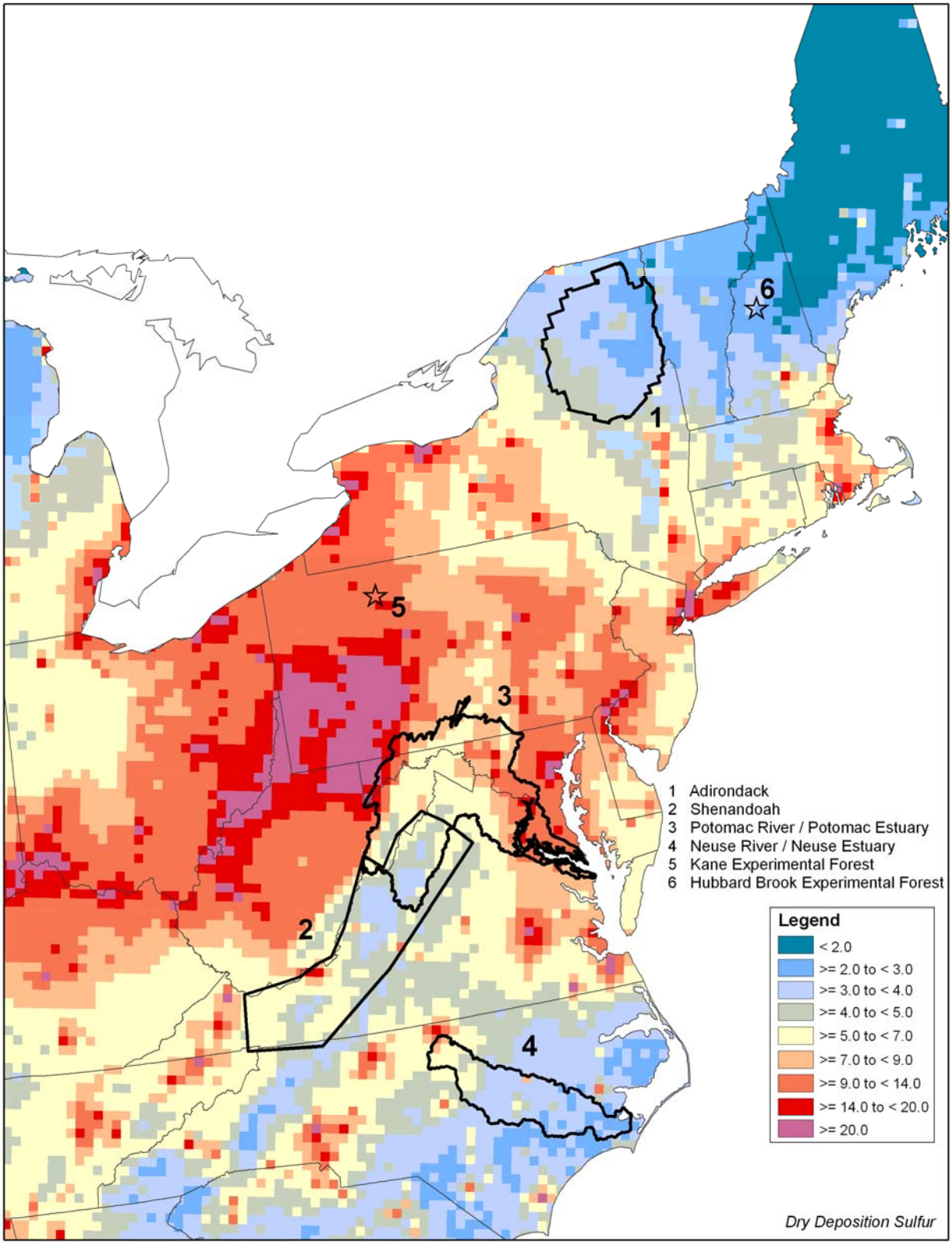

Figure 3.3-12c. Annual dry sulfur deposition (kg S/ha/yr) in 2002 for the case study areas in the East.

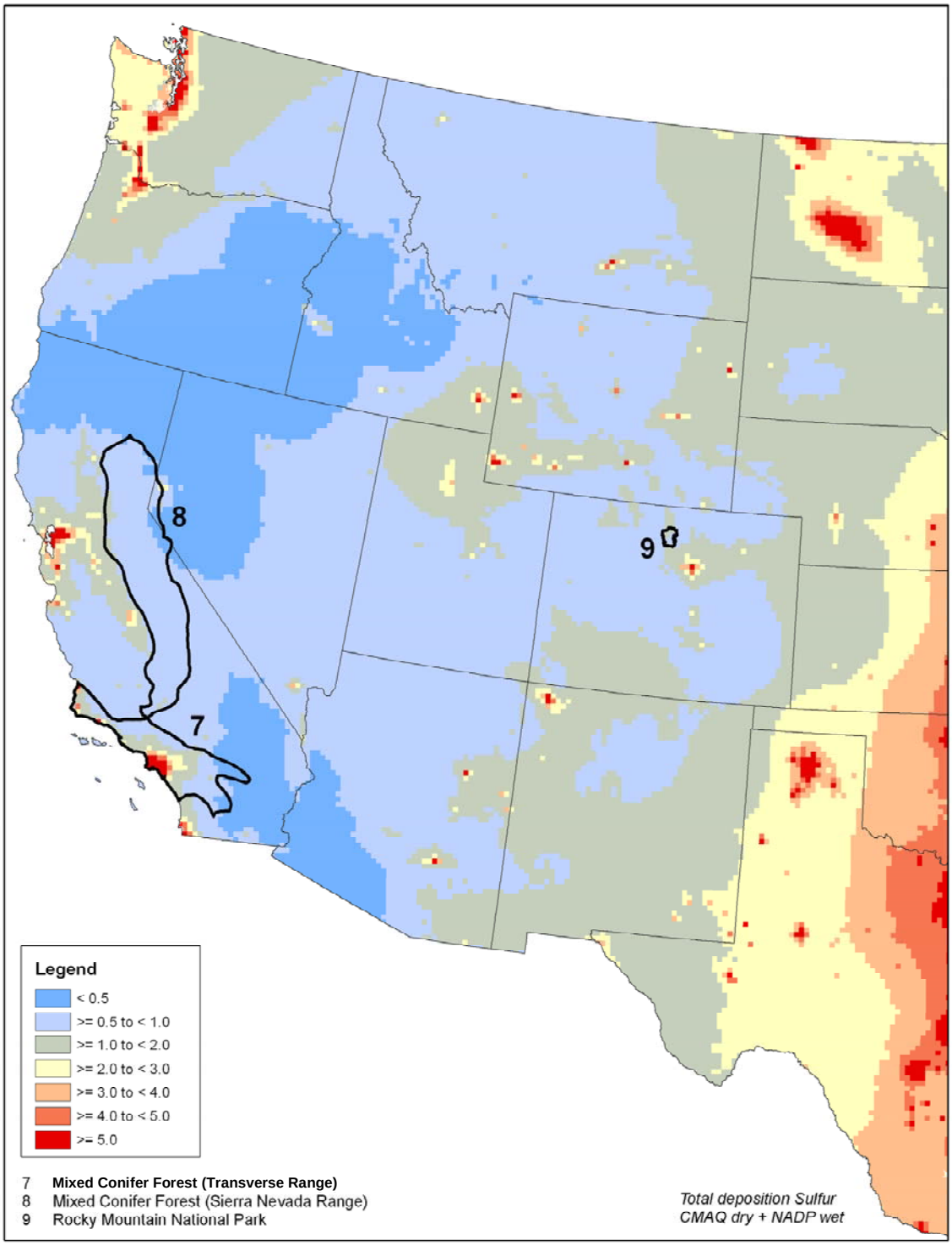

Figure 3.3-13. Annual total dry plus wet sulfur deposition (kg S/ha/yr) in 2002 for case study areas and Rocky Mountain National Park in the West.

3.3.3.8 Seasonal Variations in Sulfur Deposition for 2002

The seasonal patterns in total sulfur deposition for each case study area are shown in **Figures 3.3-14(a–i),** and the seasonal patterns for wet and dry sulfur deposition and precipitation are shown in **Figures 3.3-15(a–i)**. Sulfur deposition is greatest in spring or summer, except in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, as described below. For the case study areas of the East, the seasonal patterns in sulfur deposition are generally similar to those of total reactive nitrogen deposition. Thus, these areas are affected by the highest amount of sulfur deposition and total reactive nitrogen deposition during the same season. Examination of the seasonal variations in wet and dry sulfur deposition in the case study areas in the East indicates that dry sulfur deposition is highest in winter and lowest in summer, whereas wet sulfur deposition peaks in spring or summer and generally tracks the seasonal patterns in precipitation.

In the case study areas in the West, the seasonal patterns in wet sulfur deposition are very similar to the precipitation patterns that were found for the case study areas in the East. In the Sierra Nevada Range and Transverse Range (Mixed Conifer Forest Case Study Area), there are large seasonal variations in precipitation, which affect the seasonal variations in wet sulfur deposition. In these two areas, nearly all of the wet sulfur deposition occurs during winter and spring, which are the seasons with the most of the precipitation. The seasonal patterns in total sulfur deposition reflect the net effect of the seasonal variations in wet and dry sulfur deposition. In the Rocky Mountain National Park and the Transverse Range portion of the Mixed Conifer Forest Case Study Area, total sulfur deposition peaks in spring. In contrast, in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, both winter and spring have much higher sulfur deposition compared with summer and fall.

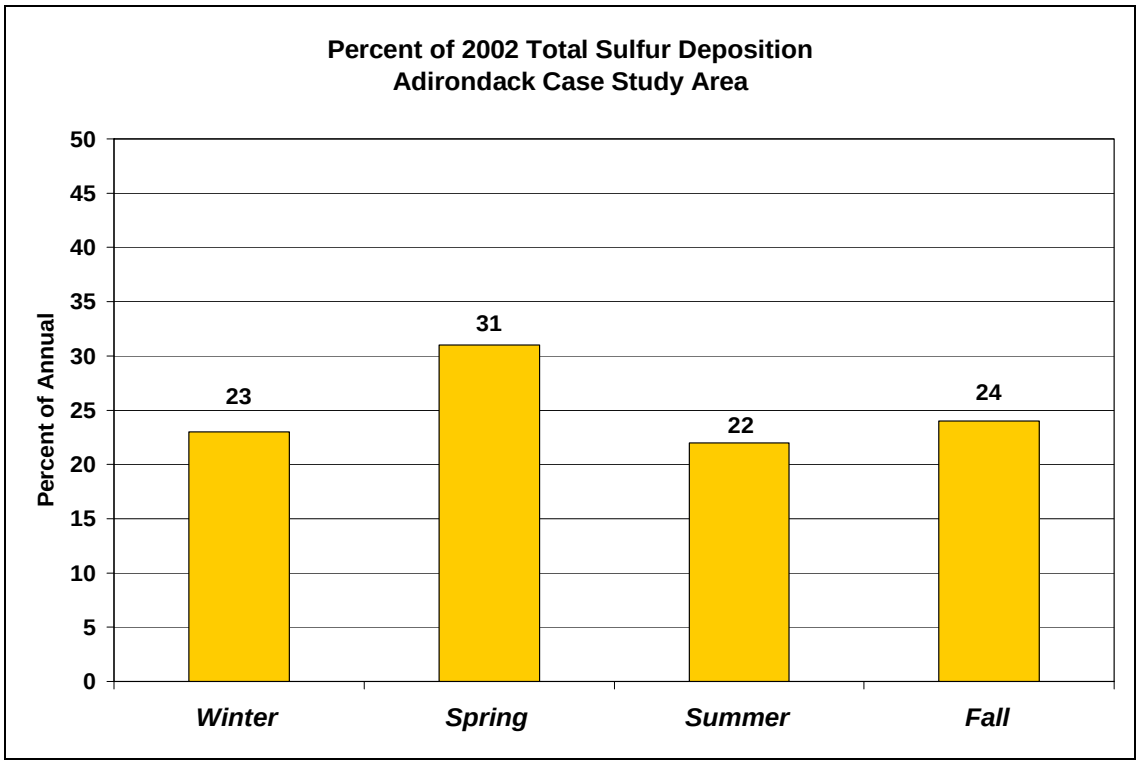

Figure 3.3-14a. Percentage of 2002 total sulfur deposition in the Adirondack Case Study Area.

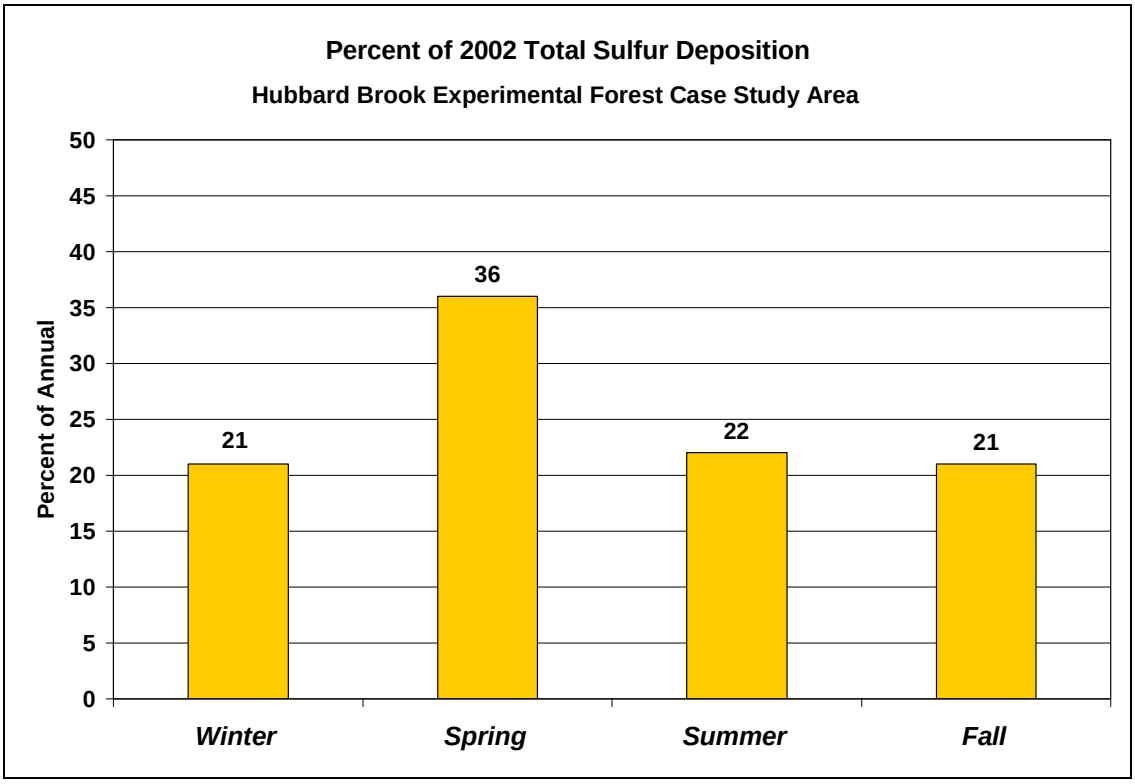

Figure 3.3-14b. Percentage of 2002 total sulfur deposition in the Hubbard Brook Experimental Forest Case Study Area.

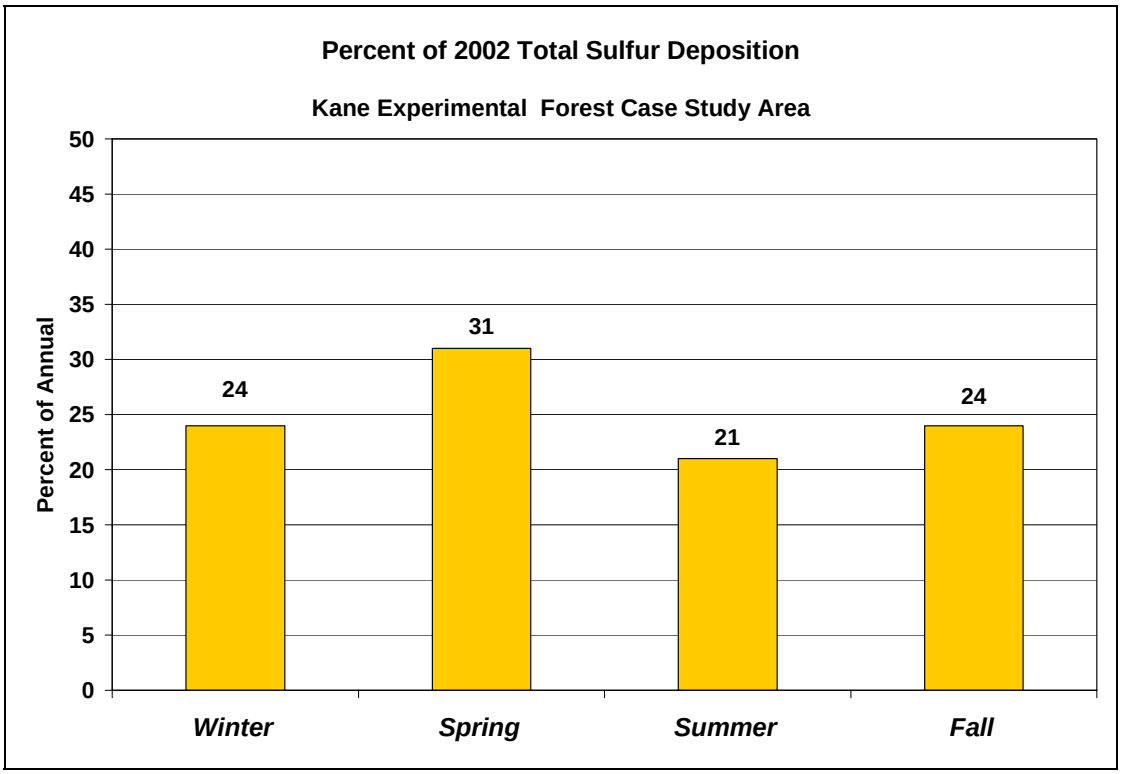

Figure 3.3-14c. Percentage of 2002 total sulfur deposition in the Kane Experimental Forest Case Study Area.

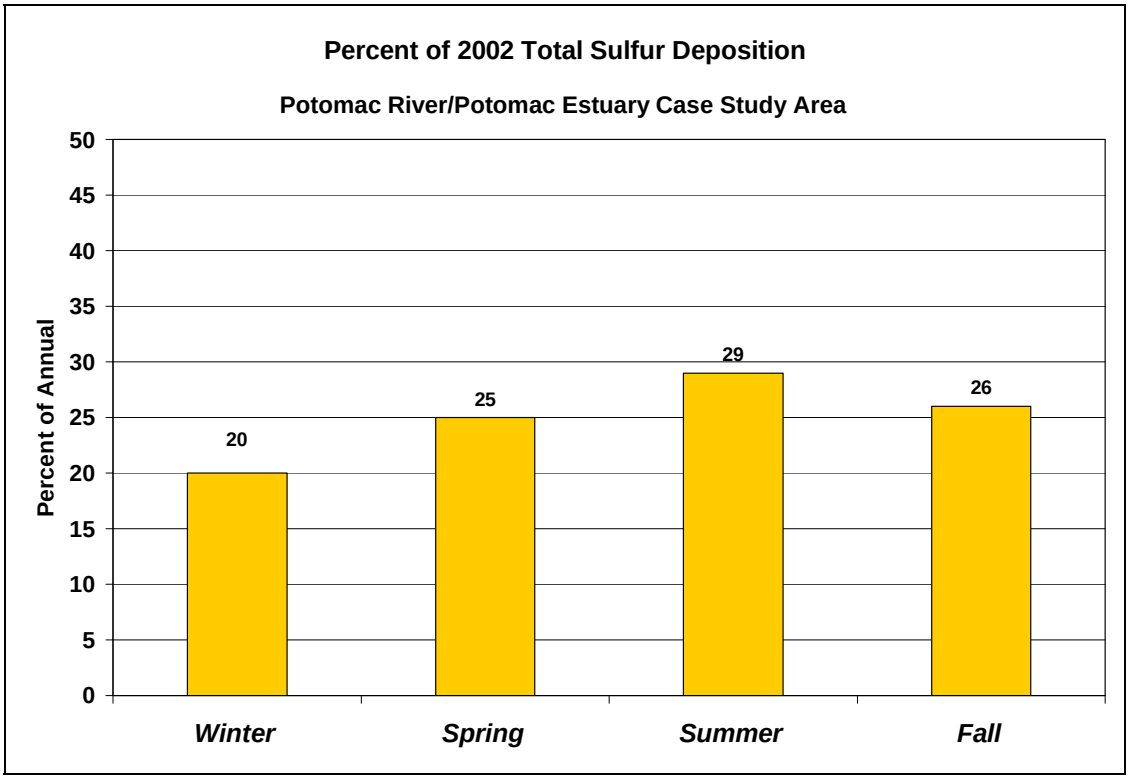

Figure 3.3-14d. Percentage of 2002 total sulfur deposition in the Potomac River/Potomac Estuary Case Study Area.

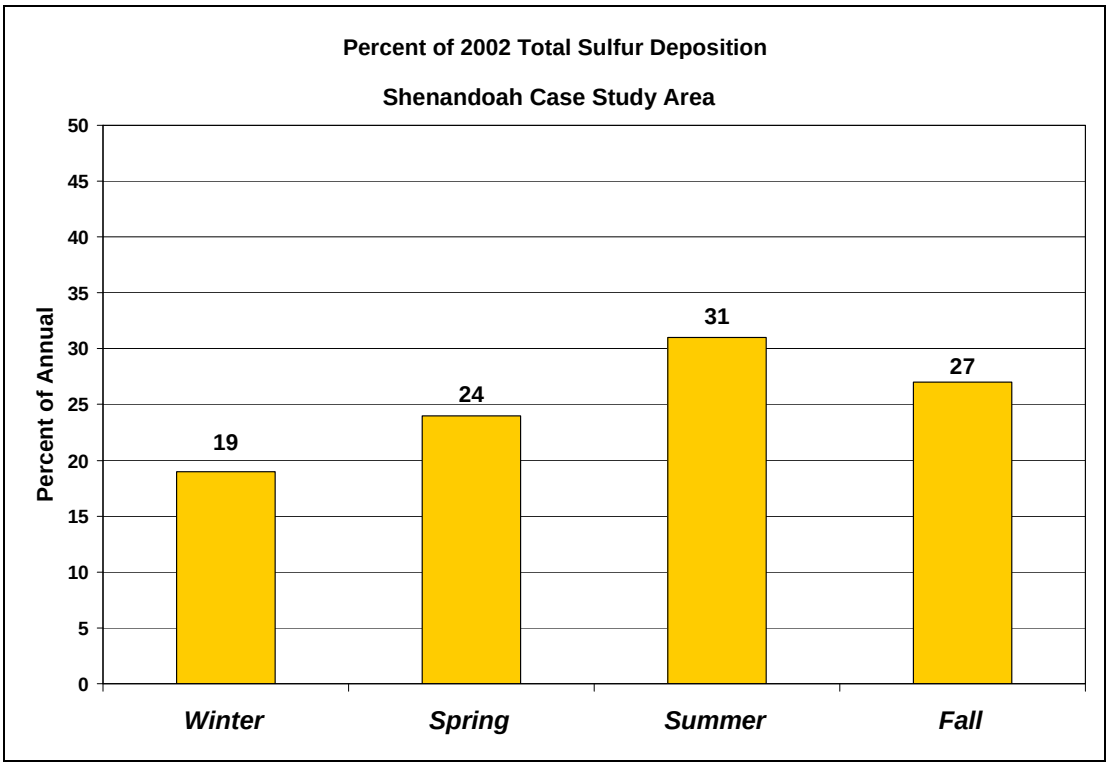

Figure 3.3-14e. Percentage of 2002 total sulfur deposition in the Shenandoah Case Study Area.

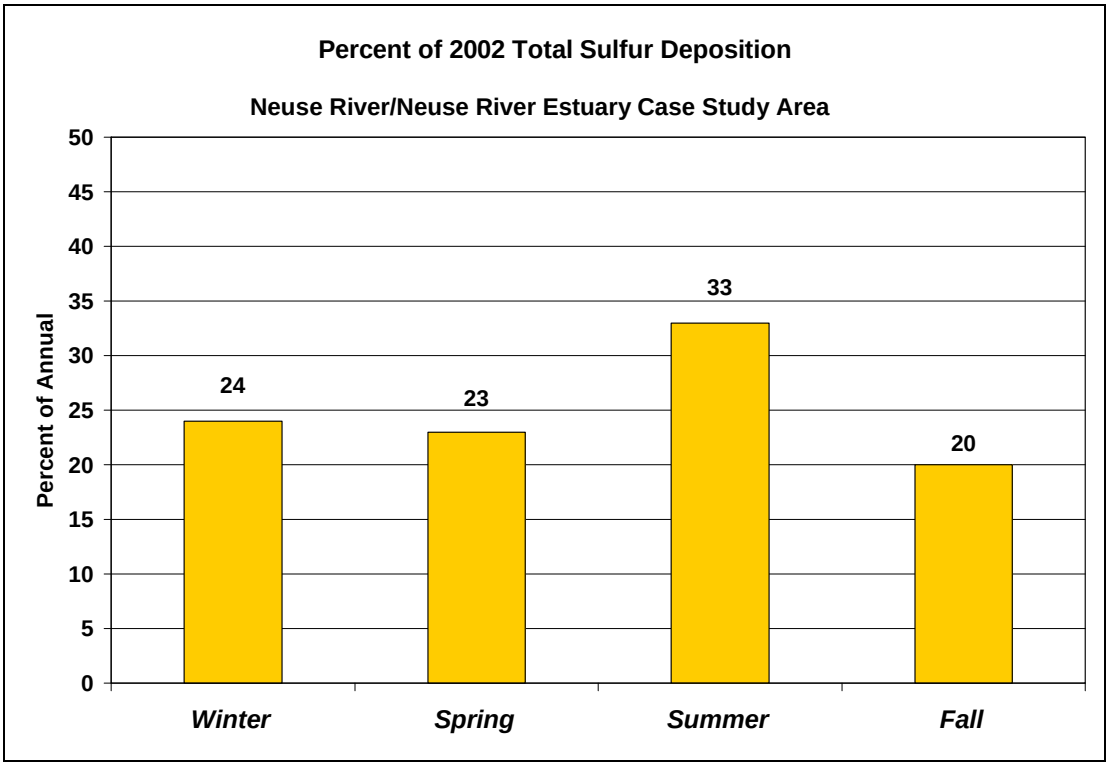

Figure 3.3-14f. Percentage of 2002 total sulfur deposition in the Neuse River/Neuse River Estuary Case Study Area.

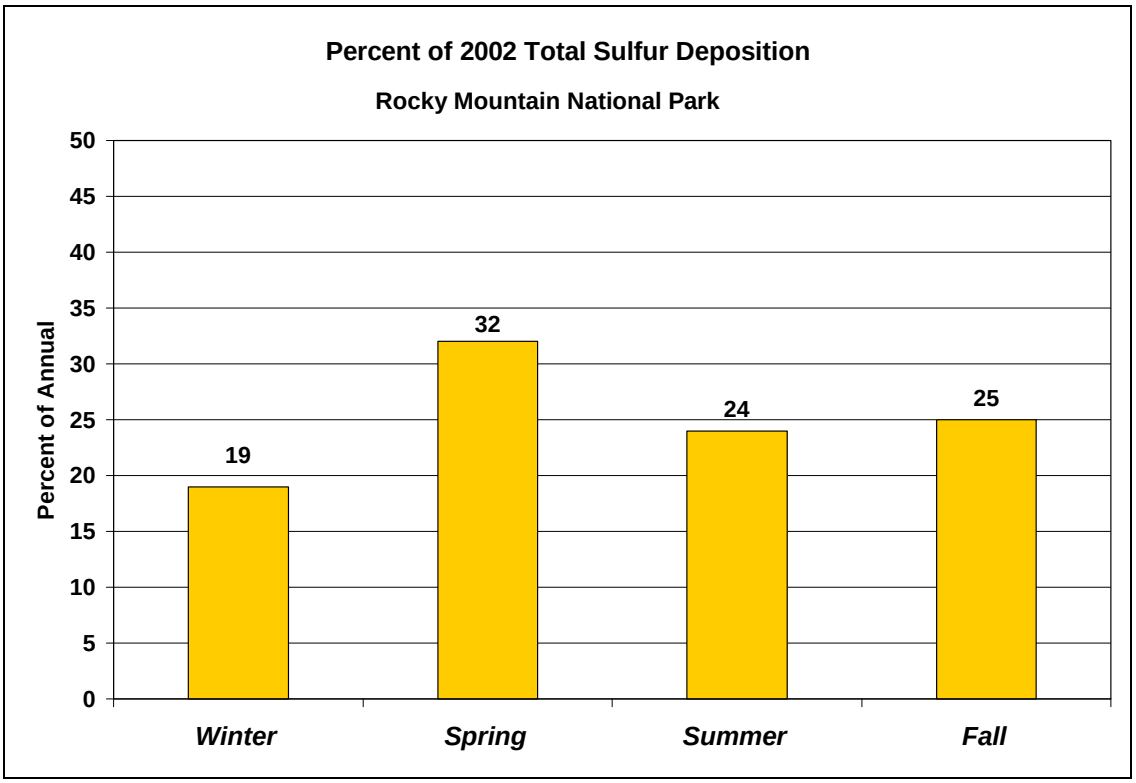

Figure 3.3-14g. Percentage of 2002 total sulfur deposition in the Rocky Mountain National Park.

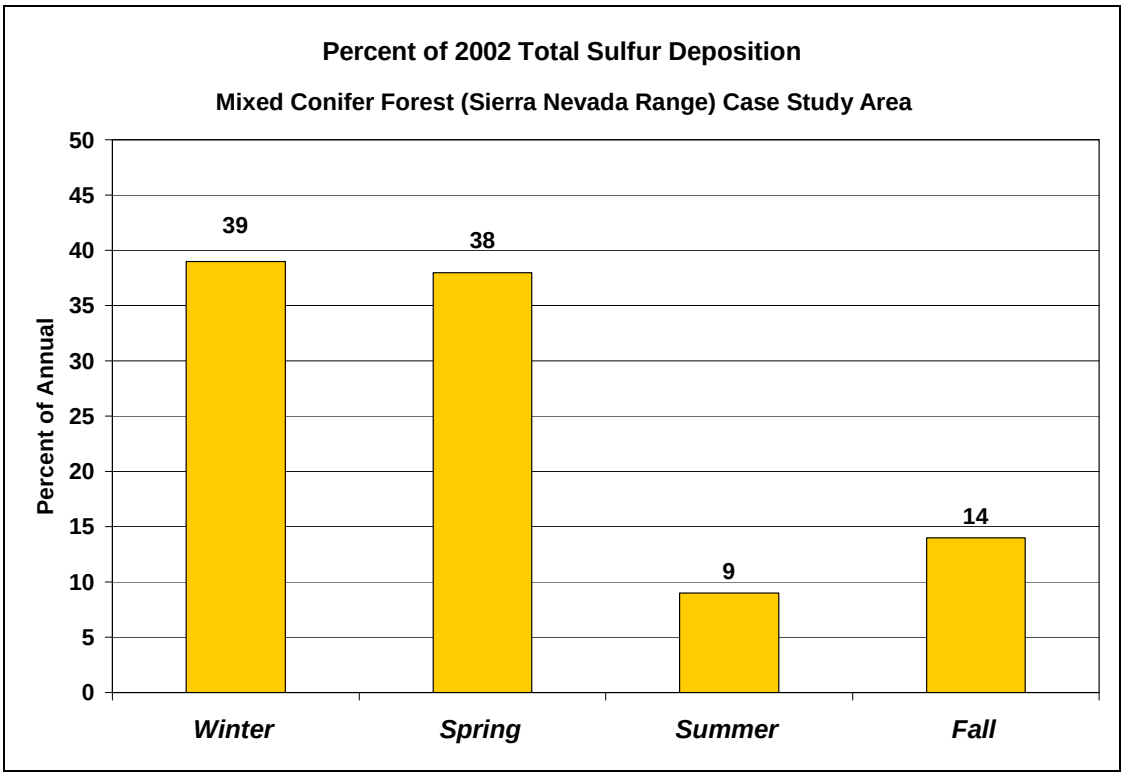

Figure 3.3-14h. Percentage of 2002 total sulfur deposition in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area.

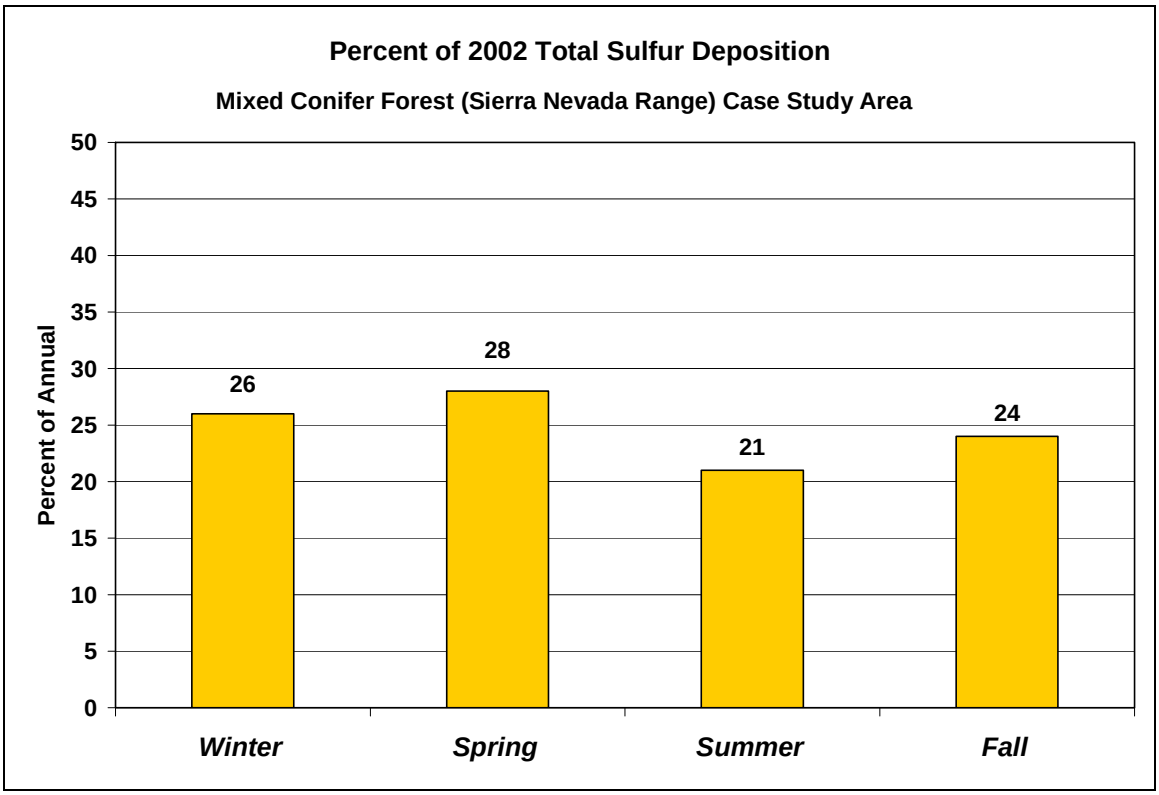

Figure 3.3-14i. Percentage of 2002 total sulfur deposition in the Transverse Range portion of the Case Study Area.

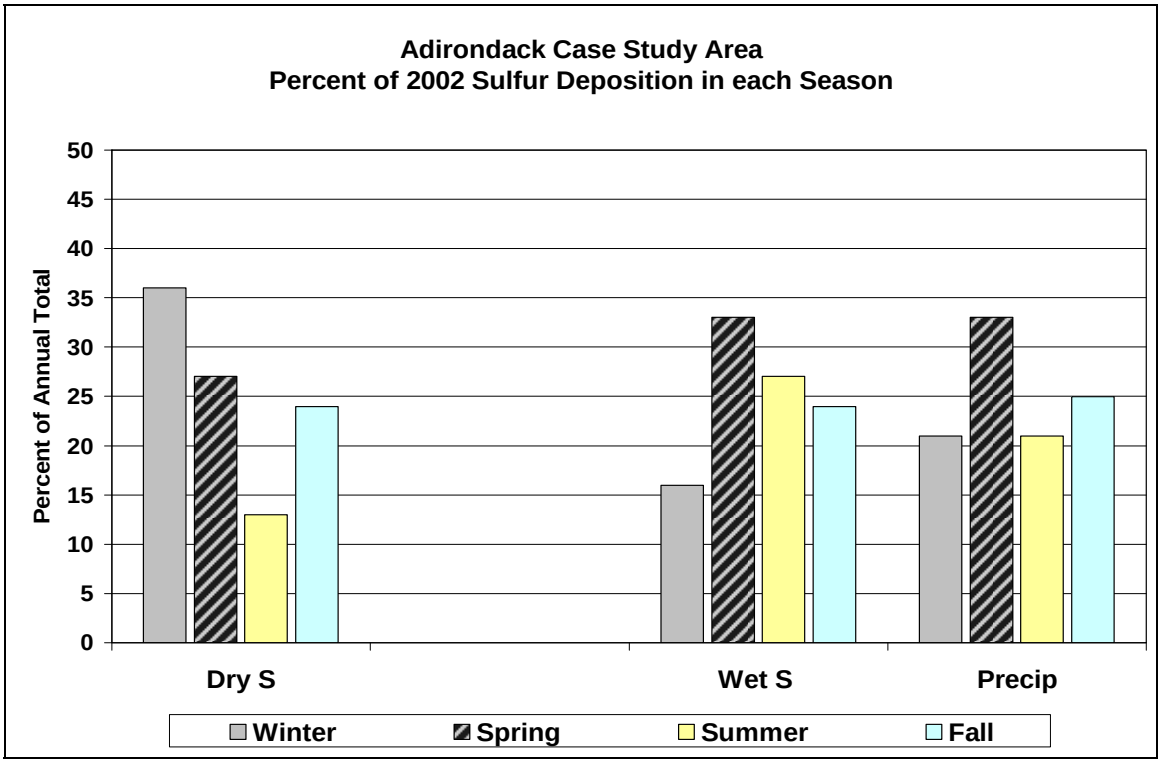

Figure 3.3-15a. Percentage of 2002 deposition for each component of sulfur deposition in the Adirondack Case Study Area.

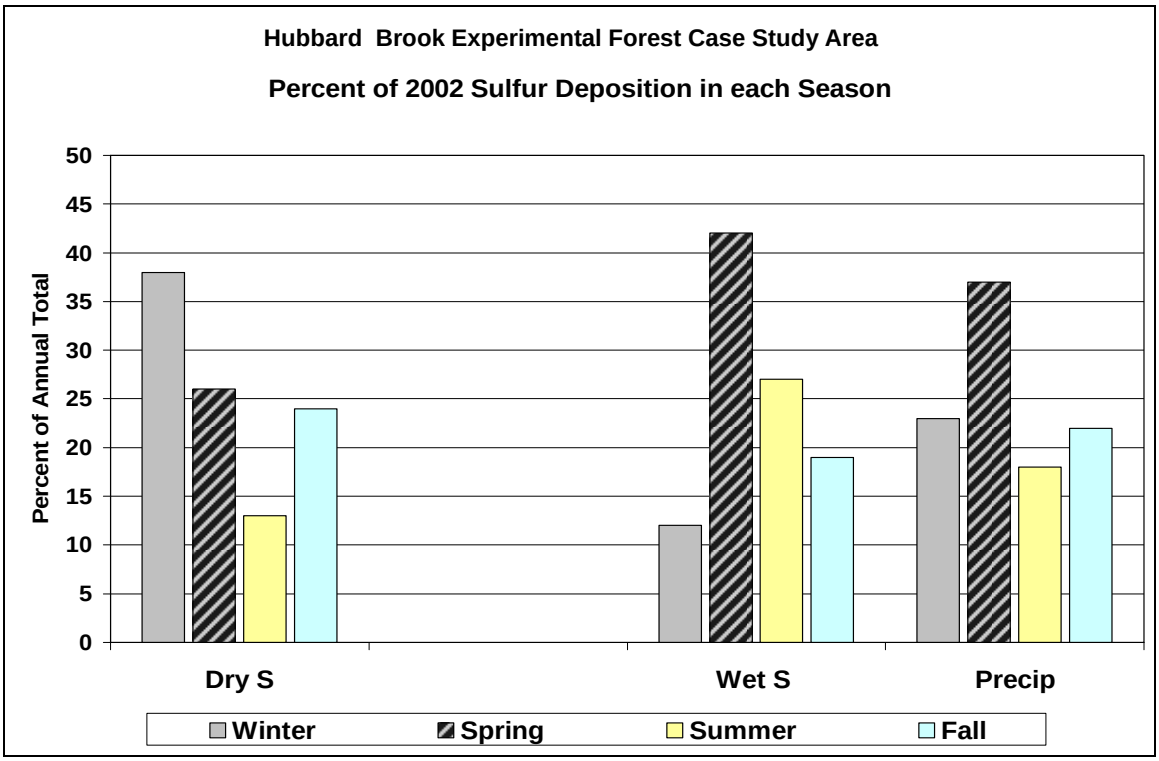

Figure 3.3-15b. Percentage of 2002 deposition for each component of sulfur deposition in the Hubbard Brook Experimental Forest Case Study Area.

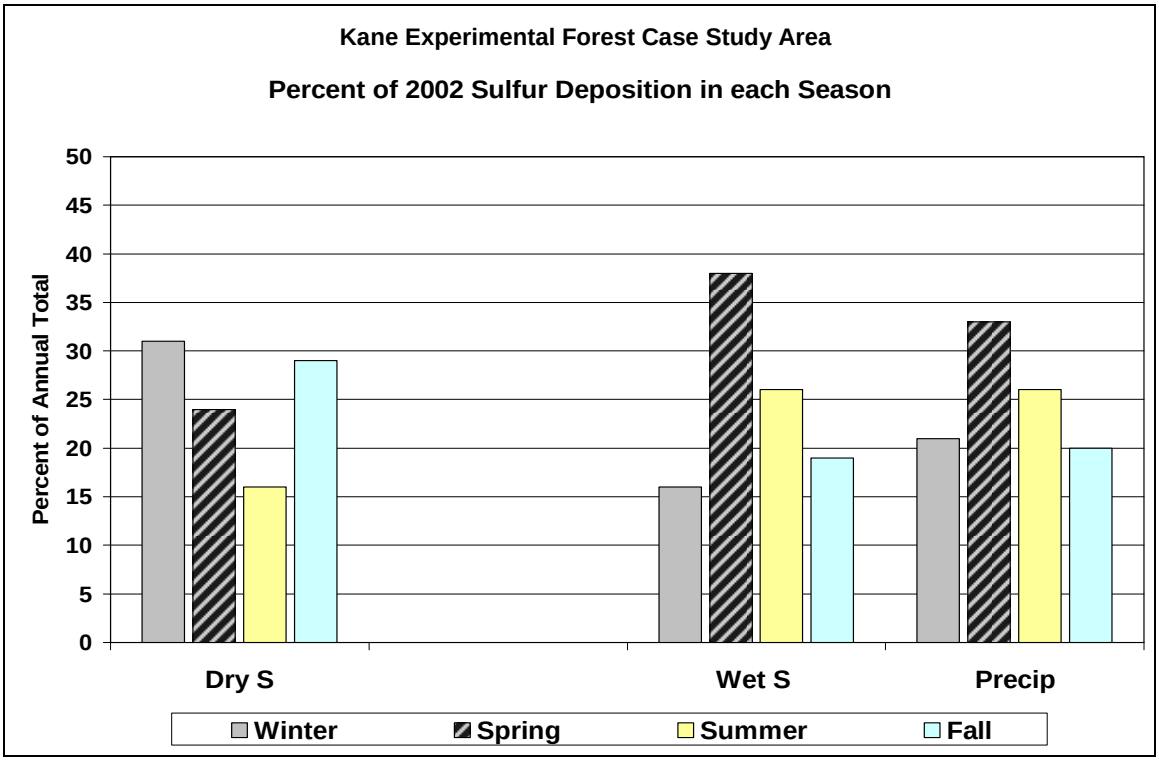

Figure 3.3-15c. Percentage of 2002 deposition for each component of sulfur deposition in the Kane Experimental Forest Case Study Area.

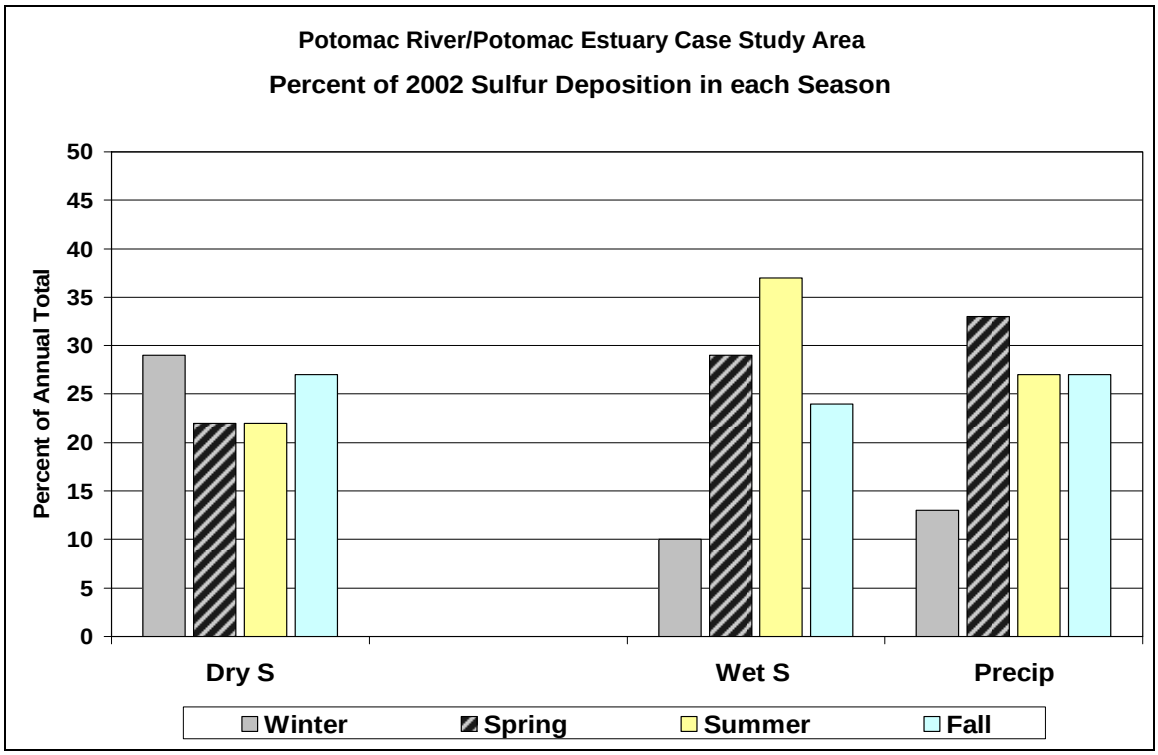

Figure 3.3-15d. Percentage of 2002 deposition for each component of sulfur deposition in the Potomac River/Potomac Estuary Case Study Area.

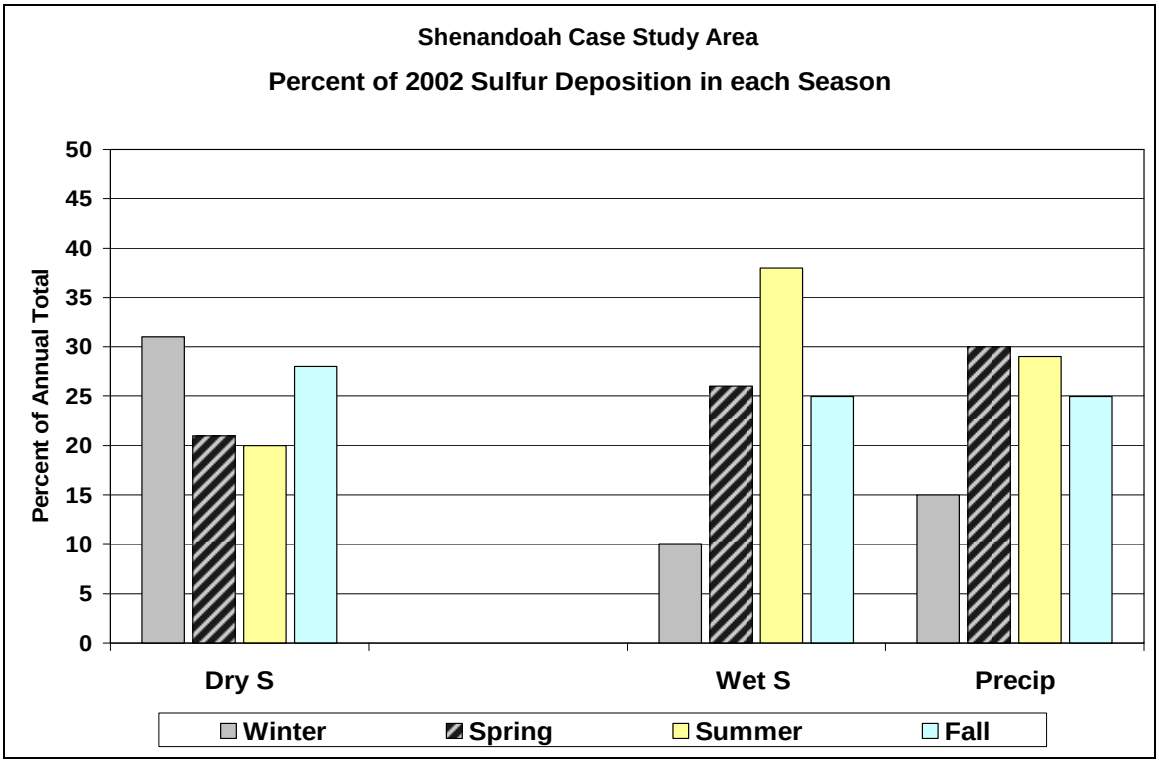

Figure 3.3-15e. Percentage of 2002 deposition for each component of sulfur deposition in the Shenandoah Case Study Area.

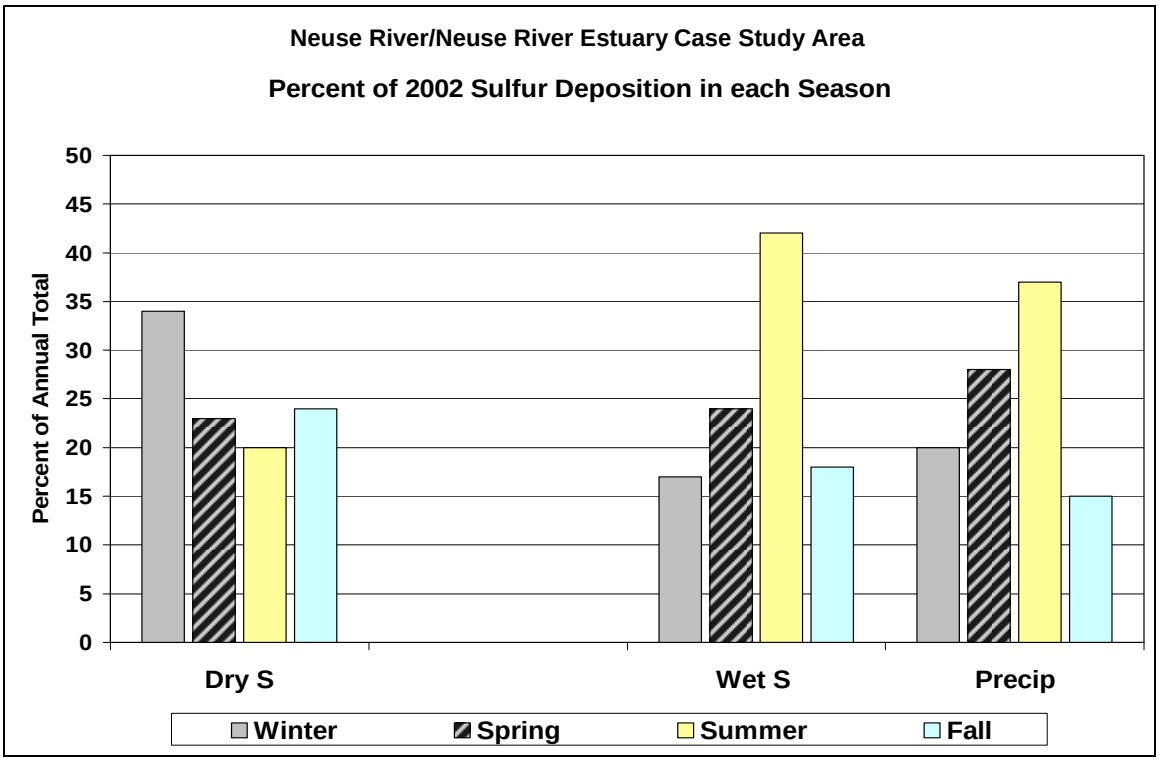

Figure 3.3-15f. Percentage of 2002 deposition for each component of sulfur deposition in the Neuse River/Neuse River Estuary Case Study Area.

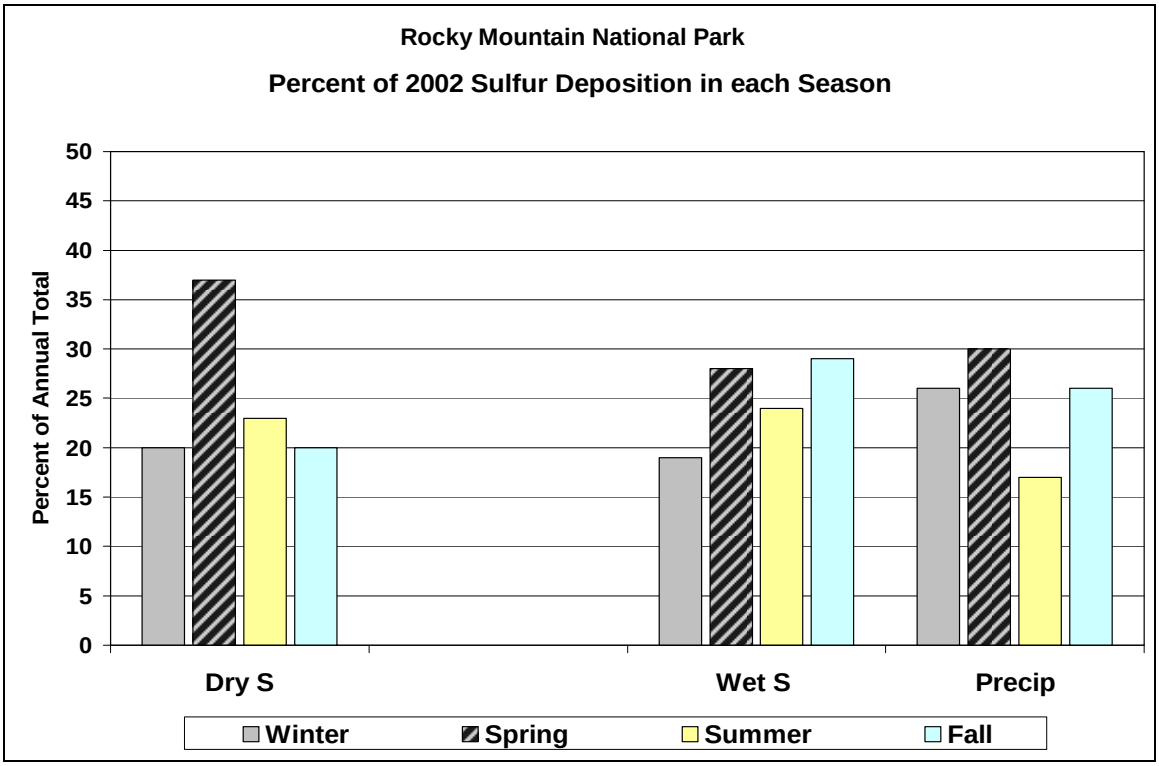

Figure 3.3-15g. Percentage of 2002 deposition for each component of sulfur deposition in the Rocky Mountain National Park.

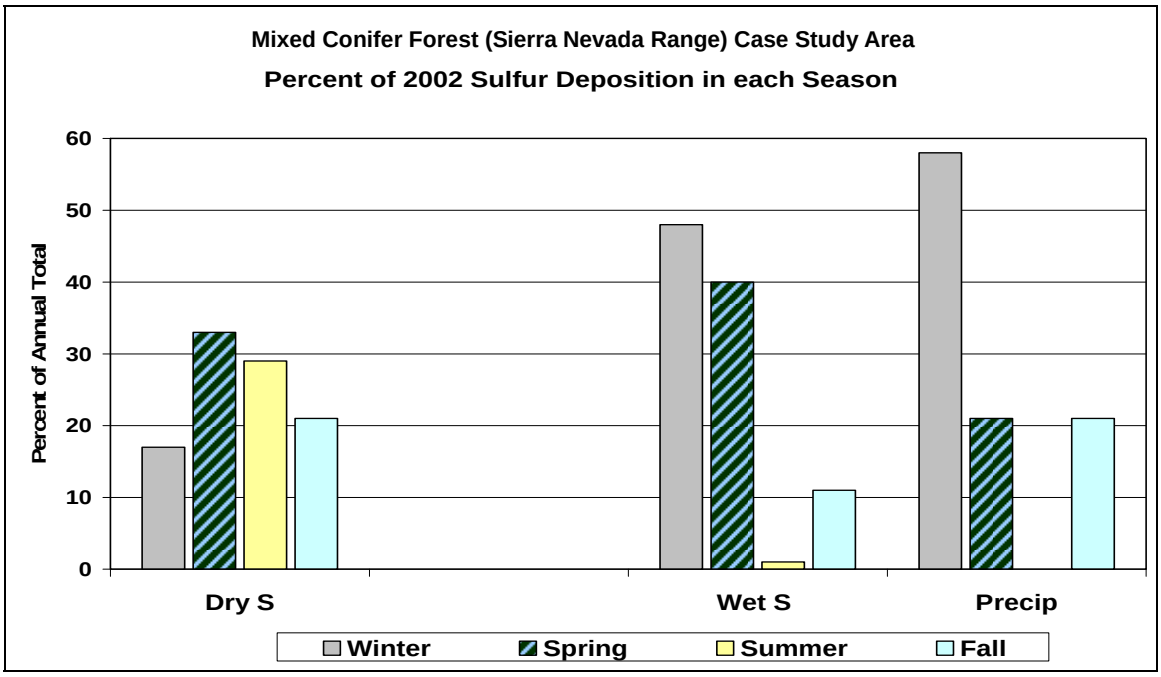

Figure 3.3-15h. Percentage of 2002 deposition for each component of sulfur deposition in the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area.

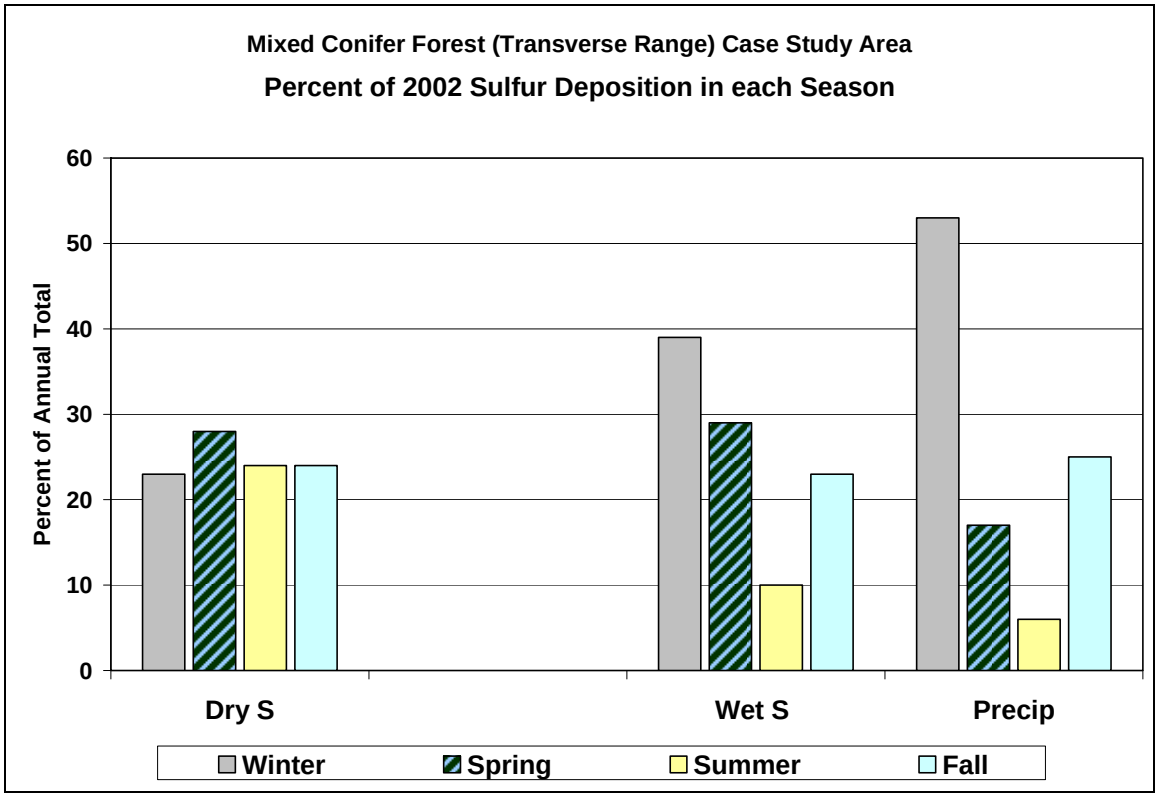

Figure 3.3-15i. Percentage of 2002 deposition for each component of sulfur deposition in the Transverse Range portion of the Mixed Conifer Forest Case Study Area.

3.3.3.9 Summary of Case Study Analysis Findings

The key findings from the case study analyses are summarized below.

(1) Total reactive nitrogen deposition and sulfur deposition are much greater in the East compared to most areas of the West.

(2) These regional differences in deposition correspond to the regional differences in NO_x and SO_2 concentrations and emissions, which are also higher in the East.

(3) NO_x emissions are much greater and generally more widespread than NH_3 emissions nationwide; high NH_3 emissions tend to be more local (e.g., eastern North Carolina) or sub-regional (e.g., the upper Midwest and Plains states).

(4) The relative amounts of oxidized versus reduced nitrogen deposition are consistent with the relative amounts of NO_x and NH_3 emissions.

(a) Oxidized nitrogen deposition exceeds reduced nitrogen deposition in most of the case study areas; the major exception being the Neuse River/Neuse River Estuary Case Study Area.

(b) Reduced nitrogen deposition exceeds oxidized nitrogen deposition in the vicinity of local sources of NH_3.

(5) There can be relatively large spatial variations in both total reactive nitrogen deposition and sulfur deposition within a case study area; this occurs particularly in those areas that contain or are near a high emissions source of NO_x, NH_3, and/or SO_2.

(6) The seasonal patterns in deposition differ between the case study areas.

(a) For the case study areas in the East, the season with the greatest amounts of total reactive nitrogen deposition correspond to the season with the greatest amounts of sulfur deposition. Deposition peaks in spring in the Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas, and it peaks in summer in the Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas.

(b) For the case study areas in the West, there is less consistency in the seasons with greatest total reactive nitrogen and sulfur deposition in a given area. In general, both nitrogen and/or sulfur deposition peaks in spring or summer. The exception to this is the Sierra Nevada Range portion of the Mixed Conifer Forest Case Study Area, in which sulfur deposition is greatest in winter.

3.4 CONTRIBUTIONS OF EMISSIONS OF NO_X AND NH_3 TO DEPOSITION OF NITROGEN

3.4.1 Purpose and Intent

The targeted ecological effect areas' public welfare effects of concern in this review associated with ambient NO_x and SO_x do not occur due to direct exposure to ambient concentrations of NO_x and SO_x, but rather due to deposition of these compounds in the environment. Ecosystem effects occur because of ecological exposures to loadings of all forms of nitrogen and sulfur, and this is due, in part, to atmospheric deposition of nitrogen and sulfur. Atmospheric deposition of nitrogen and sulfur is directly related to the concentrations of NO_x, NH_3, and SO_x in the atmosphere, and thus, decreasing atmospheric emissions of NO_x, NH_3, and SO_x will directly impact deposited nitrogen and sulfur and the associated ecosystem effects. In order to set ambient standards for NO_x and SO_x that are protective of public welfare, it is necessary to understand the contribution of ambient NO_x and SO_x to the ecosystem pollutants of concern: sulfur and total reactive nitrogen. Because the focus of this review is on oxides of nitrogen, rather than on total reactive nitrogen, it is important to understand the contribution of NO_x relative to reduced forms of nitrogen (NH_3 and NH_4^+) to deposition. This section describes the analysis of the contribution of NO_x relative to reduced forms of nitrogen. It also examines the contributions of SO_x emissions to sulfur deposition. These analyses use CMAQ sensitivity runs to estimate the relative percentage contribution of NO_x, NH_3, and SO_x emissions to total nitrogen deposition (the oxidized and reduced forms of nitrogen and total sulfur deposition).

3.4.2 Analytical Techniques

For a more informed understanding of the roles of NO_x, NH_3, and SO_x in deposition of nitrogen and sulfur, the CMAQ model for several sensitivity simulations were run. These simulations include three separate model runs in which anthropogenic emissions of NO_x, NH_3, or SO_x were reduced by 50% from base case emissions levels (i.e., one run for each of the three pollutants). The 2005 12-km CMAQ run for the eastern United States was used as the base case for this analysis. The NO_x, NH_3, and SO_x emissions reductions were applied to the 2005 emissions for all states within the eastern modeling domain[30]. The 50% NO_x reduction scenario

[30] The CMAQ model configuration and modeling domain for these applications are described in Appendix 1 of this report.

resulted in a NO_x emissions reduction of ~ 9 million tons. This amount is more than four times the amount of emissions reduced in the 50% NH_3 scenario (~ 2 million tons of NH_3). The 50% SO_x emissions reduction scenario removed ~ 7 million tons of SO_x from states in the eastern modeling domain.

Each sensitivity run was performed for January, April, July, and October 2005, to represent differences in emissions and meteorology in each season of that year. The wet and dry deposition predictions from the CMAQ base case and sensitivity runs were used to calculate the 4-month average deposition in each grid cell. The results are used to estimate (1) the relative contribution of emissions of NO_x and NH_3 to deposition of total, reduced, and oxidized nitrogen deposition, and (2) the relative contribution of SO_x emissions to sulfur deposition. The focus is on the percentage contribution in the six case study areas of the East.

3.4.3 Results and Findings

3.4.3.1 Contributions of NO_x Emissions to Total Reactive Nitrogen Deposition

Figure 3.4-1 shows the impacts of the 50% NO_x scenario on total reactive nitrogen deposition in the East. In general, a 50% reduction in NO_x had a 30% to 40% impact (i.e., reduction) on total reactive nitrogen deposition across much of the East, including all or most of the Kane Experimental Forest, Potomac River/Potomac Estuary, and Shenandoah case study areas. Portions of the East where NO_x emissions had the least impact on total reactive nitrogen deposition, including the Neuse River/Neuse River Estuary Case Study Area, generally correspond to areas of highest NH_3 emissions.

To further explore the relationships between NO_x emissions and total reactive nitrogen deposition, the impact on oxidized and reduced nitrogen deposition, as shown in **Figures 3.4-2 and 3.4-3,** was examined. These figures reveal that the 50% reduction in NO_x emissions resulted in a 40% to 50% reduction in oxidized nitrogen deposition, indicating that nearly all of the oxidized nitrogen deposition is due to NO_x emissions. The Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas each had reductions in oxidized nitrogen of 45% to 50%. The impacts were somewhat less in the Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas.

The 50% reduction in NO_x generally had a small impact on reduced nitrogen deposition across the East ($\pm$ 6%). Some case study areas had lower reduced nitrogen, whereas others had

slight increases. The Adirondack, Kane Experimental Forest, and Hubbard Brook Experimental Forest case study areas all had lower reduced nitrogen deposition. However, in the Neuse River/Neuse River Estuary Case Study Area and in portions of the Potomac River/Potomac Estuary and Shenandoah case study areas, the NO_x emissions impacts are slightly positive, suggesting that NO_x emissions contribute to greater deposition of reduced nitrogen. This relationship reflects the atmospheric reactions that lead to deposition of reduced nitrogen. One possible explanation for this is that reducing NO_x reduces HNO_3, which limits NH_4NO_3 formation, thereby increasing the lifetime of NH_3. This change may result in a net increase in NH_3/NH_4^+ deposition. Because the deposition velocity of NH_3 is much higher than the deposition velocity for NH_4^+ aerosol, dry deposition of NH_x increases closer to sources of NH_3.

3.4.3.2 Contributions of NH_3 Emissions to Total Reactive Nitrogen Deposition

Figure 3.4-4 shows the relative impact of the 50% NH_3 emissions scenario on deposition of total reactive nitrogen. The locations with the greatest contributions from NH_3 emissions are generally the same locations where the contribution from NO_x is the least. These locations include portions of the Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas. In the Adirondack, Kane Experimental Forest, and Hubbard Brook Experimental Forest case study areas, the contribution of total reactive nitrogen is generally 10% to 20% or less.

Figures 3.4-5 and 3.4-6 explore the relationship between NH_3 emissions and nitrogen deposition in more detail, examining separately the relative impacts of NH_3 on oxidized and reduced forms of nitrogen. In the Potomac River/Potomac Estuary, Shenandoah, Kane Experimental Forest, and Neuse River/Neuse River Estuary case study areas, the 50% NH_3 emissions scenario results in a 40% to 50% impact, indicating that nearly all of the reduced nitrogen in these areas is likely associated with NH_3 emissions. The contributions from NH_3 to reduced nitrogen deposition were somewhat less (generally 30% to 40%) for the Adirondack and Hubbard Brook Experimental Forest case study areas. Also, in the Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas, the NH_3 scenario resulted in a slight increase in oxidized nitrogen deposition. This relationship reflects the atmospheric reactions that lead to the deposition of reduced and oxidized nitrogen. Reducing NH_3 limits NH_4NO_3 aerosol formation, increasing the lifetime of HNO_3. The ratio of HNO_3 to nitrate (NO_3^-) increases, and because the deposition velocity of HNO_3 is much larger than that of

NO_3^- aerosol, dry deposition of total oxidized nitrogen increases. In the Adirondack, Kane Experimental Forest, and Hubbard Brook Experimental Forest case study areas, the 50% NH_3 scenario produced a small decrease (up to 2%) in oxidized nitrogen deposition.

3.4.3.3 Contributions of SO_2 Emissions to Sulfur Deposition

As shown in **Figure 3.4-7**, a 50% reduction in SO_x emissions resulted in nearly a 50% reduction in sulfur deposition in the Kane Experimental Forest, Potomac River/Potomac Estuary, Shenandoah, and Neuse River/Neuse River Estuary case study areas. The contribution is somewhat less in the Adirondack and Hubbard Brook Experimental Forest case study areas, which are more distant from sources of high SO_2 emissions compared with the other case study areas. In general, the contribution of SO_2 emissions to sulfur deposition is fairly linear for the 50% reduction scenario that was modeled.

3.4.4 Summary of Findings

From this study of the contribution of emissions to deposition in the East, it is found that NO_x emissions have significant impacts on total nitrogen deposition and account for almost all of the oxidized nitrogen deposition. The contributions of NO_x emissions compared with NH_3 emissions appear to be separable in that NO_x affects mainly oxidized nitrogen whereas NH_3 affects mainly reduced nitrogen. Because oxidized nitrogen deposition is a greater portion of total reactive nitrogen deposition in most areas, NO_x emissions contribute more to total reactive nitrogen than emissions of NH_3. However, local NH_3 emissions do make significant contributions to total reactive nitrogen deposition near the sources of these emissions.

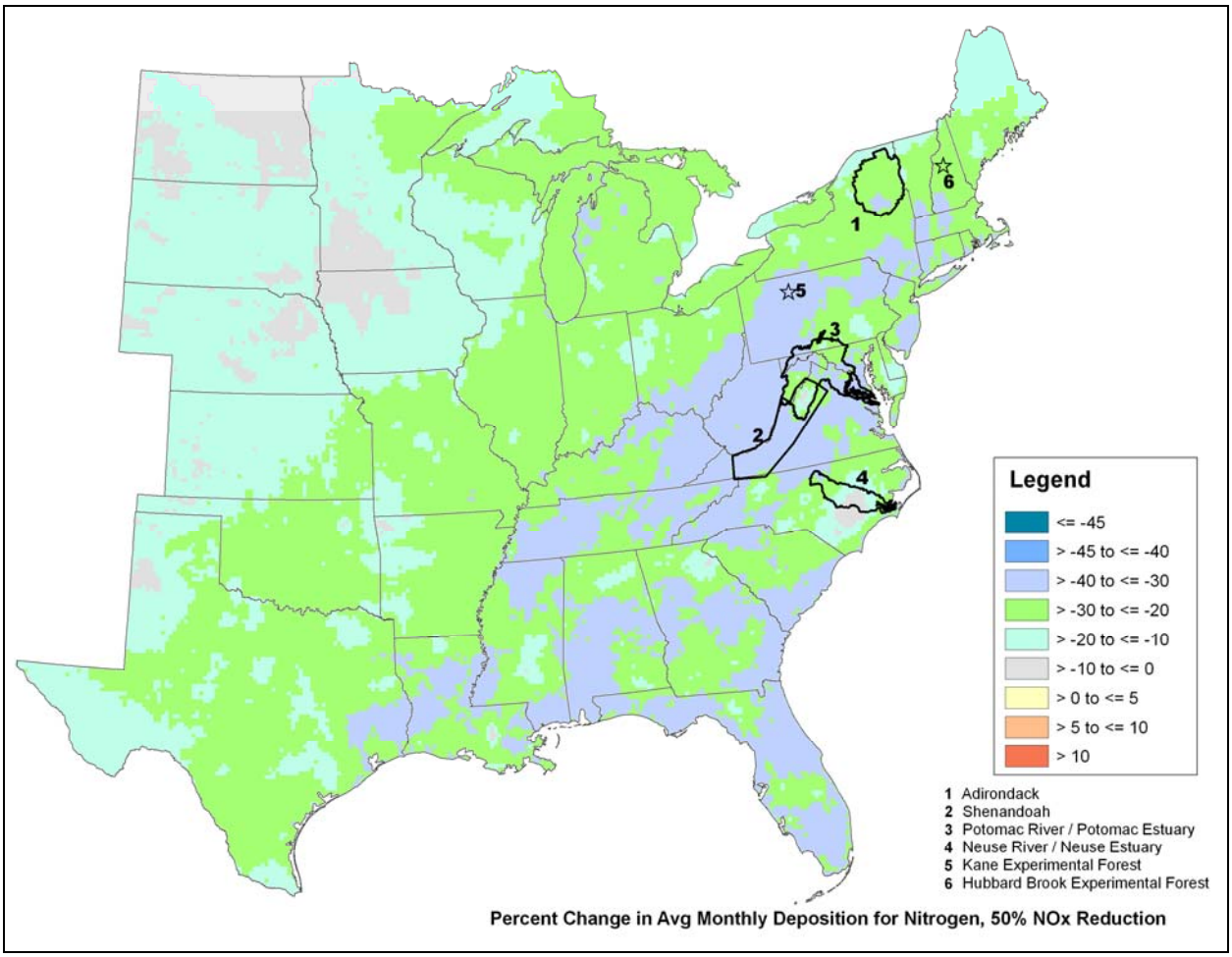

Figure 3.4-1. The percentage impacts of a 50% decrease in NO_x emissions on total reactive nitrogen deposition in the East.

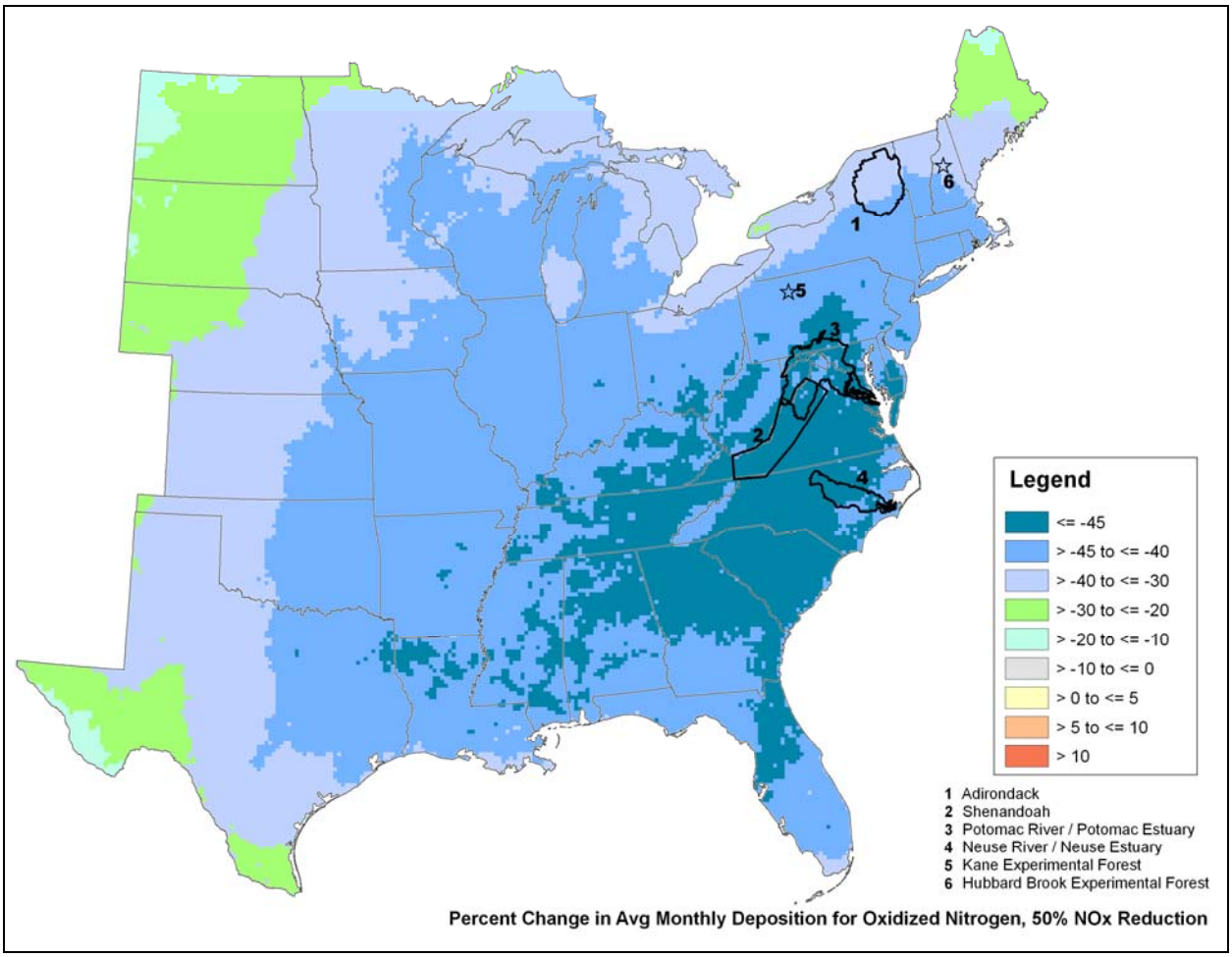

Figure 3.4-2. The percentage impacts of a 50% decrease in NO_x emissions on oxidized nitrogen deposition in the East.

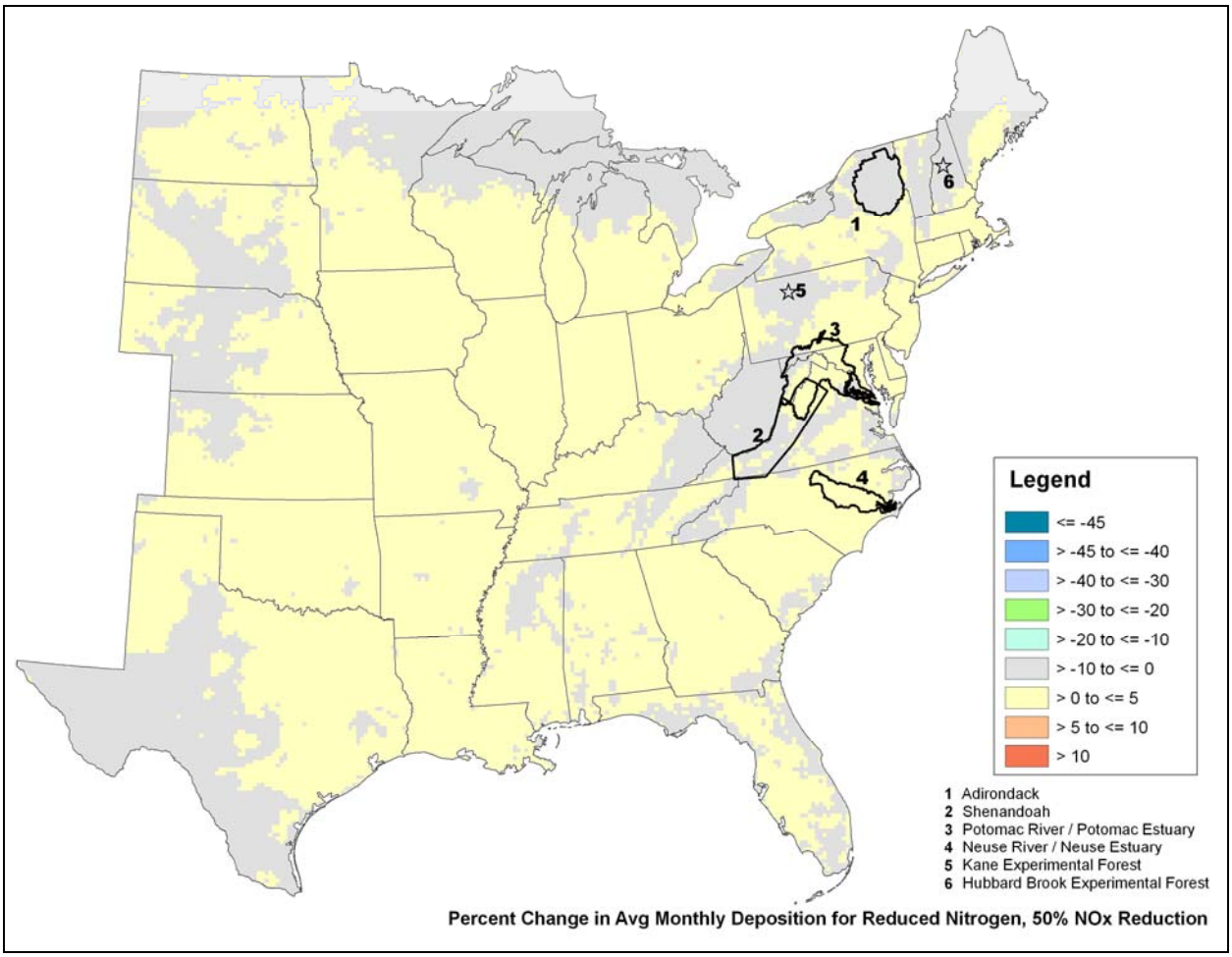

Figure 3.4-3. The percentage impacts of a 50% decrease in NO_x emissions on reduced nitrogen deposition in the East.

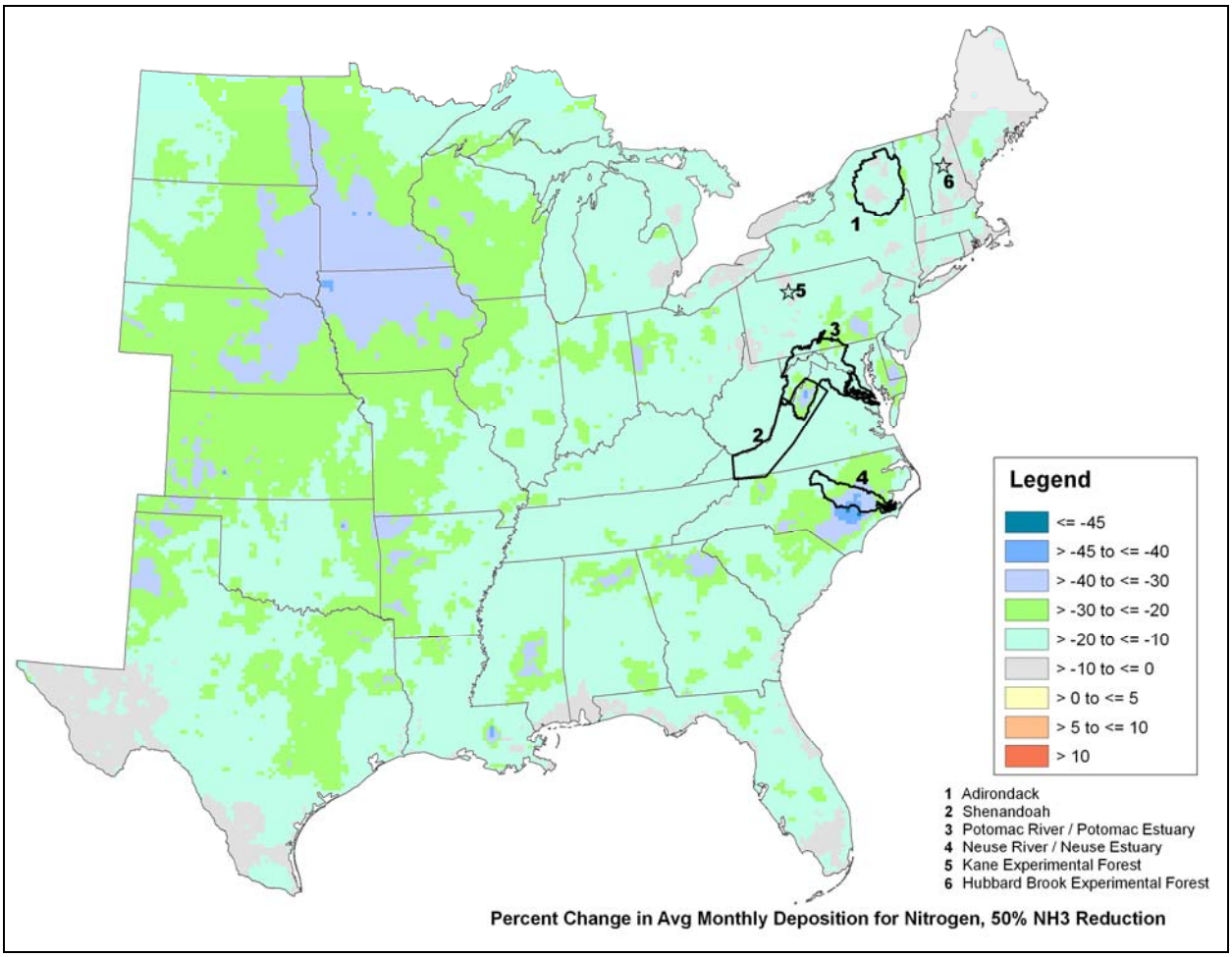

Figure 3.4-4. The percentage impacts of a 50% decrease in NH_3 emissions on total reactive nitrogen deposition in the East.

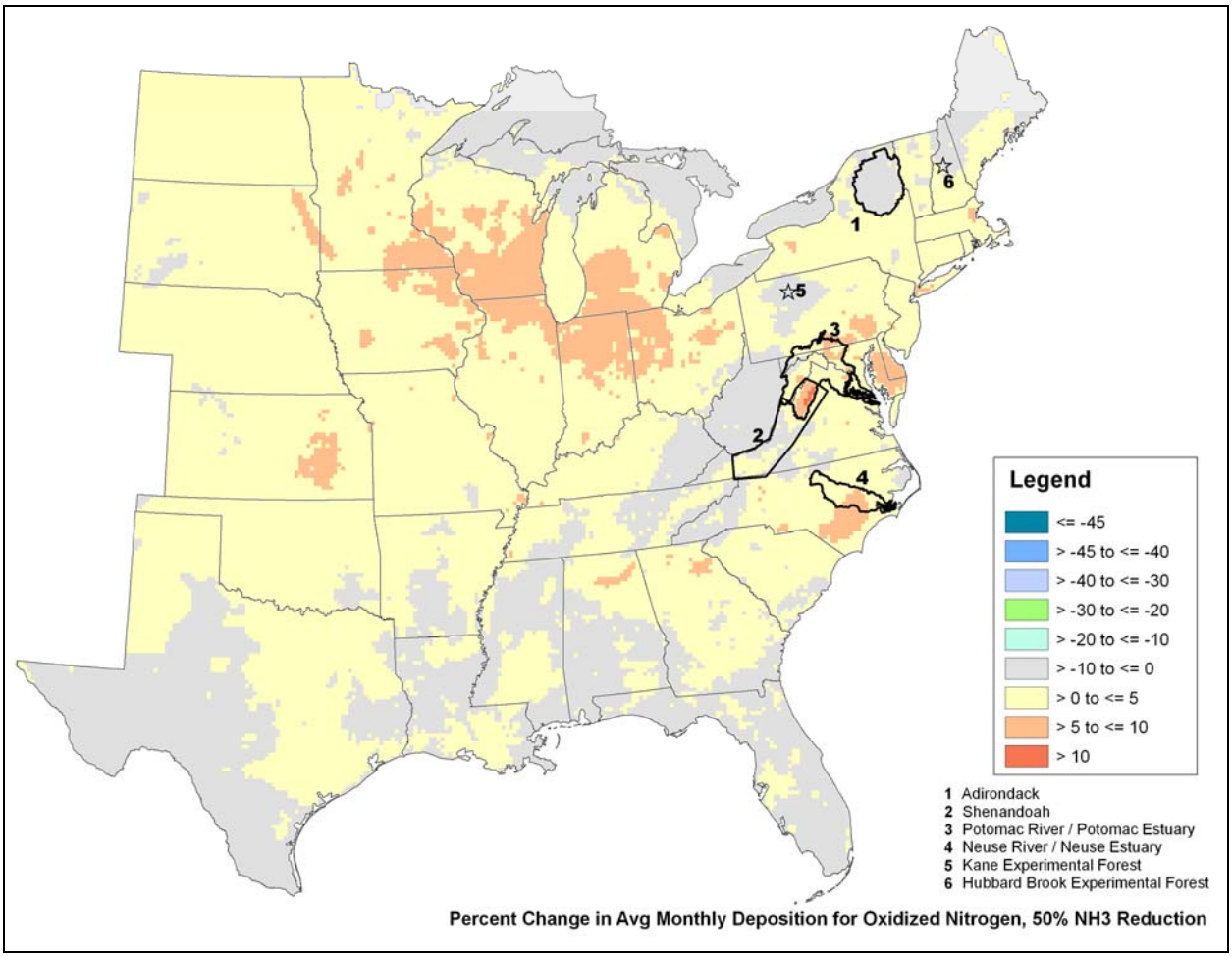

Figure 3.4-5. The percentage impacts of a 50% decrease in NH_3 emissions on oxidized nitrogen deposition in the East.

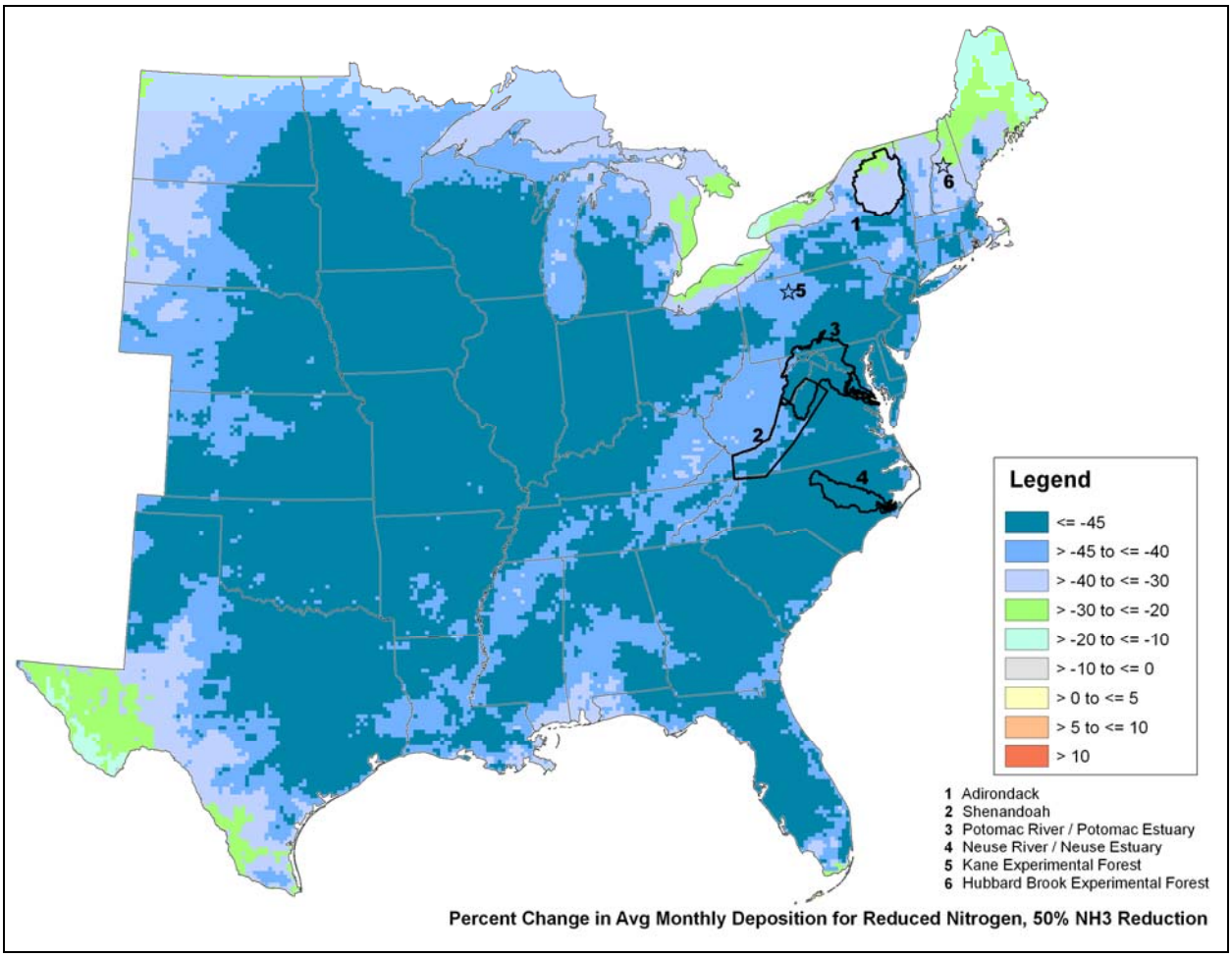

Figure 3.4-6. The percentage impacts of a 50% decrease in NH_3 emissions on reduced nitrogen deposition in the East.

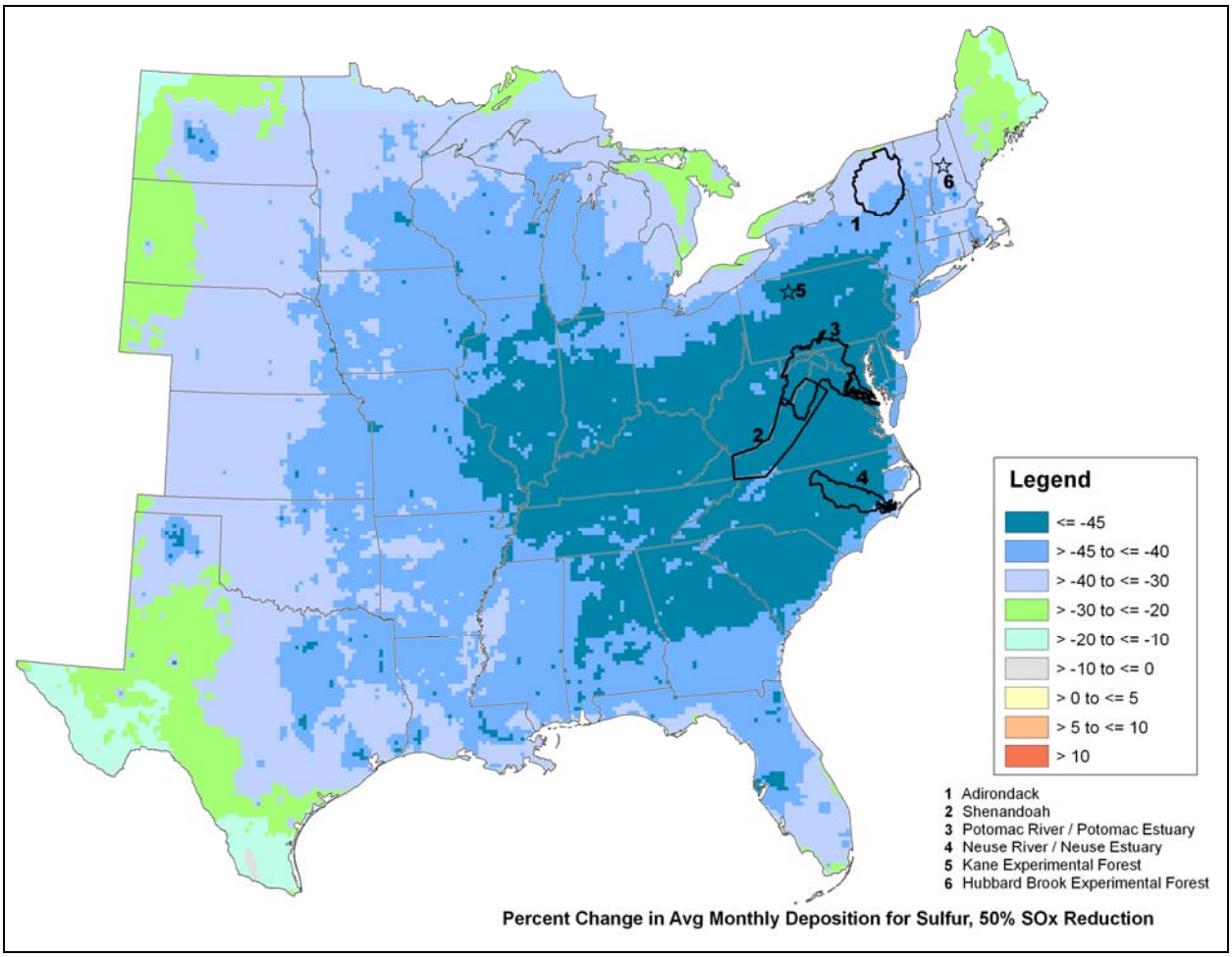

Figure 3.4-7. The percentage impacts of a 50% decrease in SO_x emissions on sulfur deposition in the East.

3.5 RELATIONSHIPS BETWEEN DEPOSITION AND CONCENTRATIONS

To address the framing questions that guide the scope of this review, this chapter has focused on characterizing the emissions, concentrations, and deposition of nitrogen and sulfur compounds. Characterizing the relationships between ambient air concentrations and deposition of both NO_x and SO_x is a key aspect of defining the Atmospheric Deposition Transformation function (box 3 of **Figure 1.4-1**) which is a central element of this analysis. In the policy assessment phase of this review, it will be important to use such relationships to estimate the amounts of nitrogen and sulfur deposition associated with ambient air concentrations. In this section we present one approach to quantifying the relationships between deposition and concentration for NO_x and SO_x. This approach expresses the relationships between deposition

and concentration using the ratio of nitrogen deposition to nitrogen concentration and sulfur deposition to sulfur concentrations. To calculate the deposition to concentration ratios we used CMAQ predicted 2002 annual total wet and dry deposition and annual average concentrations of sulfur and nitrogen from the individual species of NO_x (i.e., NO, NO_2, NO_3, HNO_3, NH_3, N_2O_5, HONO, PANs, and nitrate) and SO_x (i.e., SO_2 and sulfate). The CMAQ predictions were used to calculate annual total nitrogen and sulfur deposition and annual average nitrogen and sulfur concentrations. These calculations were performed for the predictions in each CMAQ grid cell, nationwide. The estimates of deposition and concentration were then used to calculate the ratio of nitrogen deposition to nitrogen concentration and sulfur deposition to sulfur concentration. The nitrogen ratios are expressed in units of kg N/ha/µg/m^3, and the sulfur ratios are expressed in units of kg S/ha/µg/m^3. The ratios provide a means of comparing the amount of deposition per unit amount of concentration for different geographic areas. The nitrogen and sulfur deposition to concentration ratios are displayed in **Figure 3.5-1** for nitrogen and **Figure 3.5-2** for sulfur. For most parts of the country, the deposition to concentration ratios for both nitrogen and sulfur are in the range of 0.5 to 7 kg/ha/µg/m^3. Locations with ratios near the lower end of this range receive less deposition per unit concentration than locations with ratios near the upper end of this range.

In the following analysis, we describe several observations about the spatial variation in the magnitude of nitrogen and sulfur deposition to concentration ratios. Characterizing the physical and chemical processes that lead to these spatial patterns will be the subject of future research. As indicated by the map in **Figure 3.5-1**, the largest nitrogen deposition to concentration ratios are estimated to occur in areas of relatively elevated terrain (e.g., the Adirondacks) which may potentially reflect the effects higher wet deposition in such areas associated with terrain induced precipitation. The lower ratios tend to align geographically with locations of highest NO_x emissions and NO_y concentrations, as shown in **Figure 3.2-1** and **Figure 3.2-4**, respectively. It is interesting to note that although there are large geographic differences in NO_x emissions and NO_y concentrations between the East and West, there is no clear East-West difference in the deposition to concentration ratios. In both the East and West, areas in and near sources of NO_x tend to have ratios less than 1 kg N/ha/µg/m^3. In most, but clearly not all, other lower terrain areas of the East and West nitrogen deposition to concentration ratios are in the range of 1 to 2 kg N/ha/µg/m^3. Many of the elevated terrain areas in the East and West are characterized by ratios of 3 kg N/ha/µg/m^3 or greater.

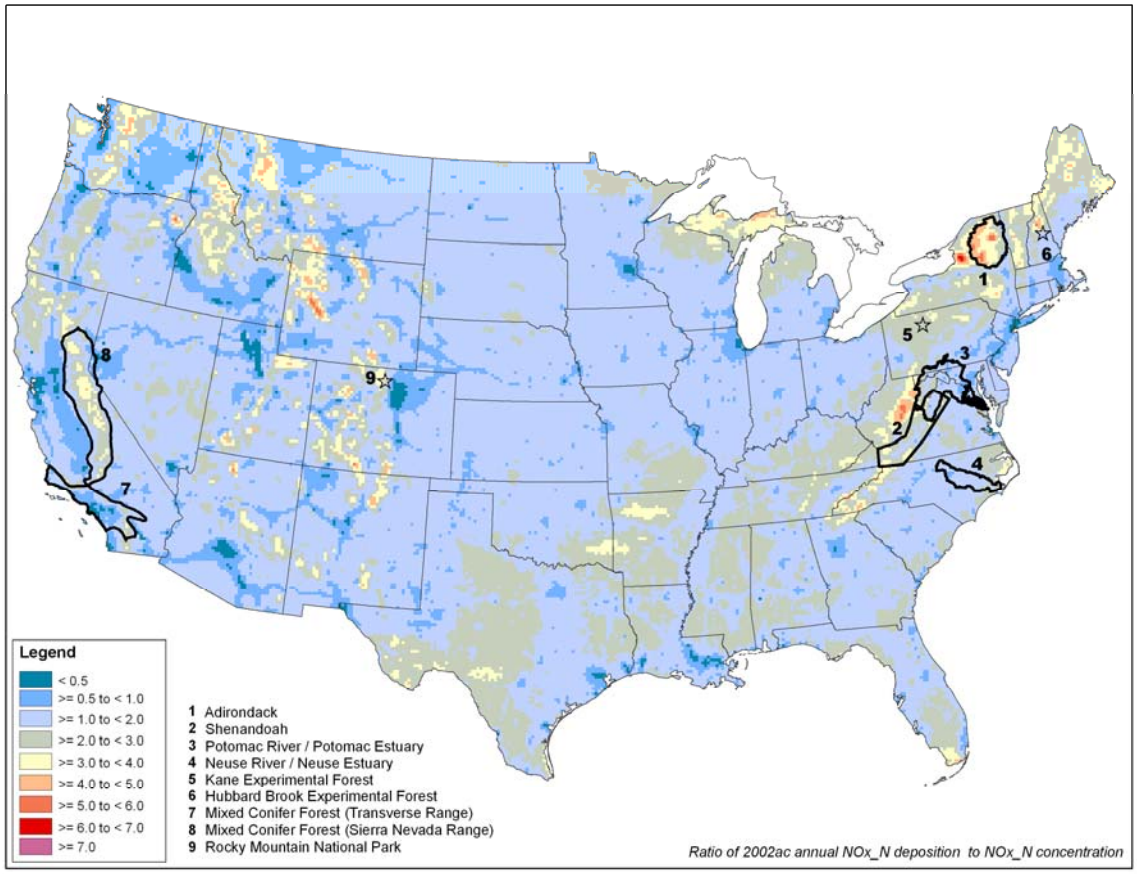

Figure 3.5-1. Ratio of nitrogen deposition to nitrogen concentration based on oxidized nitrogen deposition and concentration (kg N/ha/µg/m^3).

As indicated by the map in **Figure 3.5-2**, the deposition to concentration ratios for sulfur are largest in areas of elevated terrain. In locations outside of these elevated terrain areas, there are notable differences between the East and West with respect to the magnitude of sulfur deposition to concentration ratios. In the lower terrain areas of the East, the sulfur deposition to concentration ratios are generally greater than 2 kg S/ha/µg/m^3, whereas in the lower terrain areas of the West, ratios are generally less than 2 kg S/ha/µg/m^3. The general East-West difference in sulfur deposition to concentration ratios may be related to the East-West difference in SO_x emissions and SO_2 concentrations, as indicated by the maps in **Figure 3.2-3** and **Figure 3.2-5**, respectively. In elevated terrain areas of both the East and West, sulfur deposition to concentration ratios are 4 kg S/ha/µg/m^3 or more.

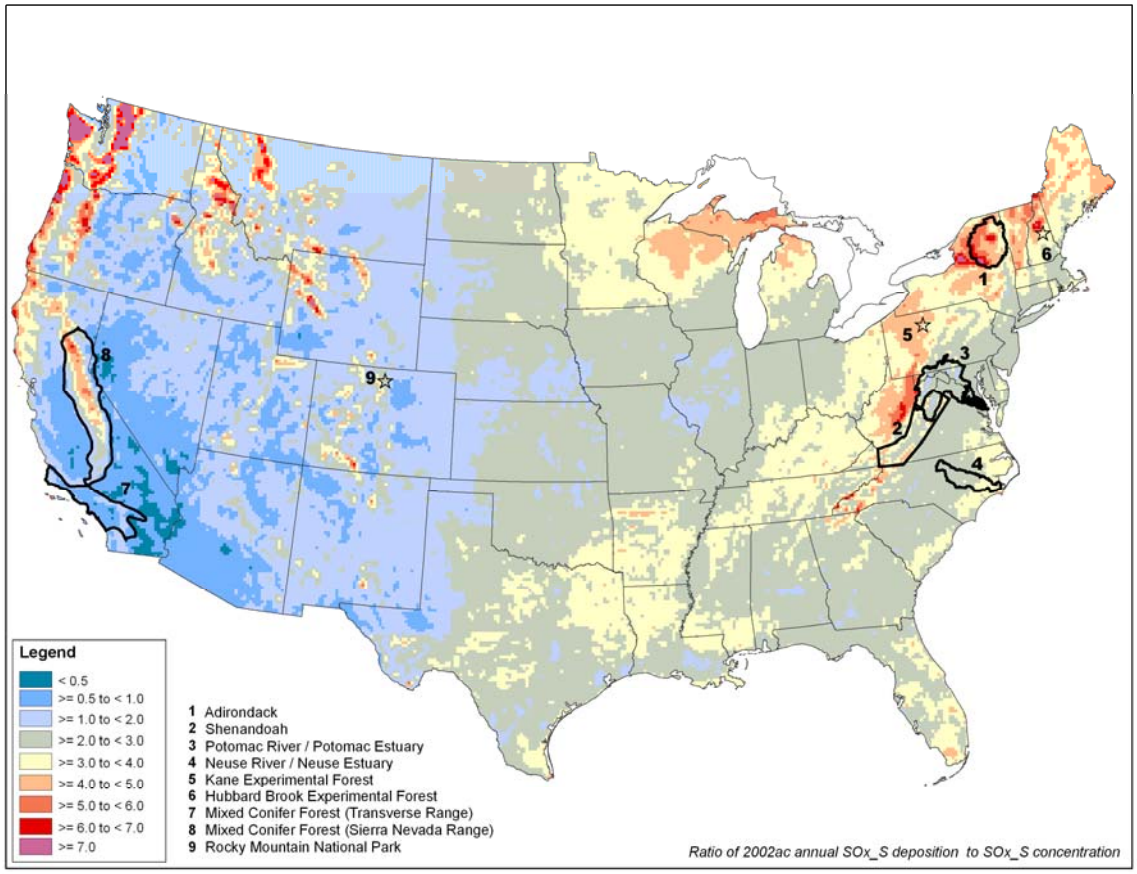

Figure 3.5-2. Ratio of sulfur deposition to sulfur concentration based on oxidized sulfur deposition and concentration (kg S/ha/µg/m^3).

There are other possible deposition to concentration ratios which may be informative for examining the relationships between deposition and concentration. In this regard, we have provided in Appendix 2national maps of the following ratios species based on the CMAQ predictions for 2002 (the corresponding Appendix 2 figure numbers are provided in parentheses):

- Ratio of annual total dry sulfur deposition to annual average SO_2 concentrations (**Figure 2-1**)
- Ratio of annual total wet sulfur deposition to annual average SO_2 concentrations (**Figure 2-2**)
- Ratio of annual total wet+dry sulfur deposition to annual average SO_2 concentrations (**Figure 2-3**)
- Ratio of annual total wet oxidized nitrogen deposition to annual average NO_2 concentrations (**Figure 2-7**)

- Ratio of annual total dry oxidized nitrogen deposition to annual average NO_2 concentrations (**Figure 2-8**)
- Ratio of annual total wet+dry oxidized nitrogen deposition to annual average NO_2 concentrations (**Figure 2-9**)
- Ratio of annual total dry nitrogen deposition to annual average NO_2 concentrations (**Figure 2-13**)
- Ratio of annual total wet nitrogen deposition to annual average NO_2 concentrations (**Figure 2-14**)
- Ratio of annual total wet+dry nitrogen deposition to annual average NO_2 concentrations (**Figure 2-15**).

In addition to the above maps, we have also included in Appendix 2 the following maps showing the ratio of CMAQ predicted 2002 deposition to 2002 emissions (the corresponding Appendix 2 figure numbers are provided in parentheses):

- Ratio of annual total dry sulfur deposition to annual total SO_2 emissions (**Figure 2-4**)
- Ratio of annual total wet sulfur deposition to annual total SO_2 emissions (**Figure 2-5**)
- Ratio of annual total wet+dry sulfur deposition to annual total SO_2 emissions (**Figure 2-6**)
- Ratio of annual total dry oxidized nitrogen deposition to annual total NO_2 emissions (**Figure 2-10**)
- Ratio of annual total wet oxidized nitrogen deposition to annual total NO_2 emissions (**Figure 2-11**)
- Ratio of annual total wet+dry oxidized nitrogen deposition to annual total NO_2 emissions (**Figure 2-12**)
- Ratio of annual total dry nitrogen deposition to annual total NO_2 emissions (**Figure 2-16**)
- Ratio of annual total wet nitrogen deposition to annual total NO_2 emissions (**Figure 2-17**)
- Ratio of annual total wet+dry nitrogen deposition to annual total NO_2 emissions **(Figure 2-18)**.

3.6 DISCUSSION OF UNCERTAINTIES

This section provides a nationwide overview of NO_x, SO_x, and NH_3 emissions; NO_x and SO_x concentrations; and nitrogen and sulfur deposition, as well as a more focused characterization of nitrogen and sulfur deposition for the aquatic and terrestrial case study areas.

When considering the uncertainties in this analysis, it is important to recognize that the characterization of deposition in the case study areas and the estimates of deposition used as input to our ecological modeling relied upon measurements of wet deposition from the NADP network and predictions of dry deposition from the CMAQ model. The NADP data and the CMAQ predictions each contain a number of areas of uncertainty. In general, we expect that there is greater uncertainty in the model predictions of dry deposition than there is in the measurements of wet deposition. This section identifies and describes uncertainties associated with the various aspects of this analysis, but does not attempt to quantify these uncertainties.

3.6.1 Uncertainties Associated with Use of Model Predictions

A key uncertainty for this assessment is the lack of true measurements of dry deposition for nitrogen and sulfur. As noted in Section 3.2, above, the dry-deposition estimates from CASTNet are calculated based on an "inferential model" involving measured air concentrations coupled with species- and location-dependent deposition velocities that reflect local land use and meteorological conditions at each monitoring site (U.S. EPA, 2008b). These dry-deposition estimates may not be representative of dry-deposition fluxes in unmonitored areas where land use or meteorological conditions are different from those at monitoring sites. Therefore, to characterize deposition nationwide and across each case study area, as well as to provide deposition estimates for ecological modeling, dry deposition predictions from the CMAQ model were used.

Although CMAQ is a "state-of-the-science" photochemical model, uncertainties in CMAQ, like those in other photochemical models, arise due to uncertainties in model formulation and in the inputs that drive the simulated chemistry and transport processes within the model. The model formulation uncertainties most relevant for this assessment include the aspects of the non-linear photochemical processes that determine the chemical form and transformations of NO_x and SO_x in the atmosphere over multiday time periods, and the processes that affect the removal of NO_x and SO_x through deposition.

The uncertainties associated with NO_x, SO_x, and NH_3 emissions and other emissions input to CMAQ vary based on the method and underlying measurements used to determine or estimate the particular set of emissions. The least uncertain of the various source categories is likely to be emissions from electric generating units, because emissions from these sources are determined by Continuous Emissions Monitors. For many other source categories, emissions are

based on the application of emissions factors to the sector's activity data. Uncertainties in emissions may increase for a particular source category if the types and extent of source measurements and analytical procedures used to derive emissions factors are not fully representative of the source category for which they are applied. For some source categories, the calculations of emissions involve complex models that may not fully represent actual levels of emissions in a particular location at a particular time. In addition, activity data used in "top-down" inventories that allocate national emissions to individual counties may not properly reflect local emissions for all areas. Of the three key pollutants for this assessment (SO_2, NO_x, and NH_3) SO_2 emission may be expected to have the least uncertainty. Emissions of SO_2 are dominated by electric generation units[31] and, as noted above, most of these sources have Continuous Emissions Monitors that measure SO_2 on an hourly basis. Emissions of NO_x are less certain than emissions of SO_2. Although 22% of nationwide NO_x emissions are based on Continuous Emissions Monitor data from electric generation units, 55% of the NO_x emissions are estimated using on-road and nonroad mobile models that may not fully reflect emissions rates across all vehicle types and operating conditions.

Not included in our CMAQ modeling are emissions of NO_x from lightning which may be a significant contributor to regional NO_x concentrations in the middle and upper free troposphere. Estimates of lighting NO_x emissions are highly uncertain (U.S. EPA, 2008b, Section 2.2.2.4), and more research is needed to adequately characterize the contributions of lightning to NO_x concentrations in the lower troposphere and to nitrogen deposition. The uncertainties in current estimates of lightning NO_x stem from several factors, including (1) the magnitude of NO production rates per meter of flash length, (2) differential NO production rates due to cloud-to-ground compared to in-cloud flashes, and (3) flash rates for cloud-to-ground and in-cloud flashes.

Emissions of NH_3 are likely to be more uncertain than emissions of NO_x and SO_2 because of significant gaps and uncertainties in measurements needed to characterize emissions factors, activity levels, and the temporal patterns of emissions at animal feeding operations and from fertilized soils. In addition, estimates of NH_3 emissions input to air quality models do not account for the extent of re-emissions of NH_3 (i.e., "bi-directional flux") that affects NH_3 concentrations

[31] Nationwide, 70% of annual emissions of SO_2 are from electric generation units.

and NH_4 deposition and the neutralization of sulfuric acid and nitric acid in the formation of sulfate and nitrate particles, respectively.

Uncertainties in meteorological inputs, including the presence of clouds and fog, the occurrence and amount of precipitation, and the extent of vertical mixing, affect the uncertainty in model predictions of pollutant concentrations and deposition. The degree of uncertainty in these inputs may be greater in complex terrain, in part because the 12 x 12 km resolution used for the model simulations may not be able to fully resolve finer-scale meteorological events, especially terrain-induced precipitation. In addition, the model simulations do not account for occult deposition. It is likely that the deposition in high-terrain areas and coastal locations has been underestimated where occult deposition may be most important.

The results of a model performance evaluation of 2002 CMAQ predictions compared to corresponding measurements in 2002 are provided in Appendix 1. The purpose of this evaluation is to determine the degree of comparability between predictions and observations. The model performance statistics do not necessarily represent a quantitative estimate of model uncertainty since, aside from uncertainties in the modeling system, uncertainties exist in the measurements and uncertainty is introduced by the incommensurability between the grid-cell average model predictions and the point measurements at monitoring sites.

In the analysis to characterize deposition in each of the case study areas, predictions of dry deposition for 2002 from both CMAQv4.6 and CMAQv4.7 were used. The rationale for using two versions of CMAQ for this purpose is presented in Section 3.3.2. Annual total wet plus dry deposition for 2002 in each case study area is presented in **Table 3.6-1, Table 3.6-2,** and **Table 3.6-3** for oxidized nitrogen, reduced nitrogen, and sulfur, respectively. The estimates of annual total deposition from CMAQv4.6 are generally comparable to those from CMAQv4.7 for each case study area for the two forms of nitrogen deposition and for sulfur deposition. On average, across all case study areas, CMAQv4.7 is higher than v4.6 by 0.45 kg N/ha/yr for oxidized nitrogen, 0.09 kg N/ha/yr for reduced nitrogen, and 0.69 kg S/ha/yr for sulfur deposition.

Table 3.6-1. Annual Total Wet Plus Dry Oxidized Nitrogen Deposition (kg N/ha/yr) Predicted by CMAQv4.6 and CMAQ v4.7 for 2002

Case Study Area	Oxidized Nitrogen Deposition		
	CMAQ v4.7	**CMAQ v4.6**	**(v4.7 - v4.6)**
Adirondack	7.52	6.87	0.65
Hubbard Brook Experimental Forest	6.48	6.16	0.31
Kane Experimental Forest	10.06	9.41	0.65
Neuse River	6.51	5.90	0.61
Potomac River	8.64	8.09	0.55
Shenandoah	7.53	7.07	0.46
Rocky Mountain National Park	1.79	1.90	-0.11
Sierra Nevada Range	2.59	2.14	0.44
Transverse Range	8.17	7.70	0.46
		Average Difference =	0.45

Table 3.6-2. Annual Total Wet Plus Dry Reduced Nitrogen Deposition (kg N/ha/yr) Predicted by CMAQv4.6 and CMAQ v4.7 for 2002

Case Study Area	Reduced Nitrogen Deposition		
	CMAQ v4.7	**CMAQ v4.6**	**(v4.7 - v4.6)**
Adirondack	3.33	3.07	0.26
Hubbard Brook Experimental Forest	2.42	2.39	0.03
Kane Experimental Forest	3.21	2.97	0.23
Neuse River	8.06	8.07	-0.01
Potomac River	4.14	4.15	-0.01
Shenandoah	3.96	3.98	-0.02
Rocky Mountain National Park	0.93	0.74	0.18
Sierra Nevada Range	1.35	1.19	0.16
Transverse Range	1.81	1.84	-0.04
		Average Difference =	0.09

Table 3.6-3. Annual Total Wet Plus Dry Sulfur Deposition (kg S/ha/yr) Predicted by CMAQv4.6 and CMAQ v4.7 for 2002

Case Study Area	Sulfur Deposition		
	CMAQ v4.7	**CMAQ v4.6**	**(v4.7 - v4.6)**
Adirondack	11.5	10.2	1.25
Hubbard Brook Experimental Forest	9.0	8.3	0.71
Kane Experimental Forest	23.0	21.6	1.43
Neuse River	10.1	9.4	0.73
Potomac River	16.2	15.3	0.91
Shenandoah	12.9	12.0	0.90
Rocky Mountain National Park	1.2	1.0	0.17
Sierra Nevada Range	0.9	0.9	0.04
Transverse Range	1.8	1.7	0.12
		Average Difference =	0.69

3.6.2 Uncertainties Associated with Use of Measured Data

Areas of uncertainty in characterizing NO_x and SO_x concentrations and nitrogen and sulfur deposition levels include uncertainties in monitoring instrumentation and measurement protocols, as well as limitations in the spatial extent of existing monitoring networks for these pollutant species. Another aspect of uncertainty applicable to this analysis is associated with the combination of wet deposition from NADP measurements with dry deposition from CMAQ. For example, uncertainties in the modeling system may result in times when the transport patterns and precipitation events simulated in the model do not fully align in space and time with actual atmospheric conditions in a particular location. This may result physical and chemical inconsistencies between the measured wet deposition and the modeled dry deposition. For example, because the NADP sites are in non-urban areas, the spatial allocation of NADP wet deposition is unlikely to capture the influence of urban emissions sources, whereas the CMAQ predictions of dry deposition will more closely reflect urban sources. This may skew the relationship between wet and dry deposition in and near urban/suburban areas, as well as in the vicinity of large point sources.

3.6.3 Uncertainties of Wet Deposition in Complex Terrain

In addition to the uncertainties identified above, there are uncertainties associated with the spatial resolutions of the measured and modeled data used in this analysis. This includes uncertainties associated with (1) gridding the NADP measurements to a 12-km resolution and (2) the representativeness of 12-km data for characterizing deposition in the case study areas, especially for those areas with complex terrain. To examine this issue, the 2002 12-km gridded NADP deposition fields were compared to outputs from a high-resolution wet deposition model32 (Grimm-Lynch), which provides fine-scale estimates of deposition for 2002 based on an integration of measured precipitation and wet deposition and topography. The CMAQ 12-km gridded wet deposition predictions were also included in this comparison since these data were used in Section 3.3.3.4 to characterize seasonal trends in deposition. For the purposes of this analysis, the Grimm-Lynch data was used as the benchmark even though there are also uncertainties in this data set.

The analysis of spatial resolution was conducted for the Adirondack Case Study Area because this area has the highest elevations and the most complex terrain of all the case study areas in the eastern United States. The comparison of gridded data includes annual wet deposition of oxidized and reduced nitrogen and sulfur for 2002 for (a) 12-km CMAQ data, (b) 12-km NADP data, (c) fine-scale Grimm-Lynch data, and (d) an aggregation of the fine-scale data to 12 km. The 12-km aggregation of the fine-scale data was included to isolate the effects of grid resolution from the confounding effects introduced by other properties and uncertainties of the CMAQ and NADP data sets. Maps showing the magnitude and spatial patterns of wet deposition for the four data sets are provided in **Figures 3.6-1, 3.6-2, and 3.6-3** for oxidized and reduced nitrogen deposition and for sulfur deposition, respectively. The figures reveal both similarities and differences in wet deposition. Comparing the native fine-scale Grimm-Lynch data to the 12-km aggregate of these data indicates only slight, very local differences between the fine-scale and 12-km deposition for each of the three deposition species. Thus, it does not appear that the use of the 12-km resolution data masks any significant terrain-induced features of deposition, at least for this case study area. There are both similarities and notable differences between the CMAQ, NADP, and Grimm-Lynch deposition fields at 12 km. Again, using the Grimm-Lynch predictions as the benchmark, the NADP fields are perhaps too smooth while the

[32] Grimm, J.W. and J.A. Lynch. Enhanced Wet Deposition Estimates Using Modeled Precipitation Inputs. Environmental Monitoring and Assessment 90: 243-268, 2004.

CMAQ predictions tend to show enhanced spatial gradients. All three data sets show an area of relatively high wet deposition which extends westward from Lake Ontario across the southwest portion of the Adirondack Case Study Area. The Grimm-Lynch data also suggest that a secondary maximum of wet deposition extends from the northern border of the Adirondack Case Study Area southward into the central portion of the area. The CMAQ shows this feature as a small area of high deposition near the central part of the Adirondack Case Study Area. The secondary maximum does not appear to be captured by the NADP 12-km gridded data. Overall, the spatial patterns in nitrogen and sulfur deposition across the Adirondacks seen from the three data sets examined here are similar to the patterns in NO_3^- and SO_4^{2-} wet deposition, respectively, found by Ito, Mitchell, and Driscoll (2002) based on an analysis of measured precipitation, temperature, precipitation chemistry, elevation and other factors.

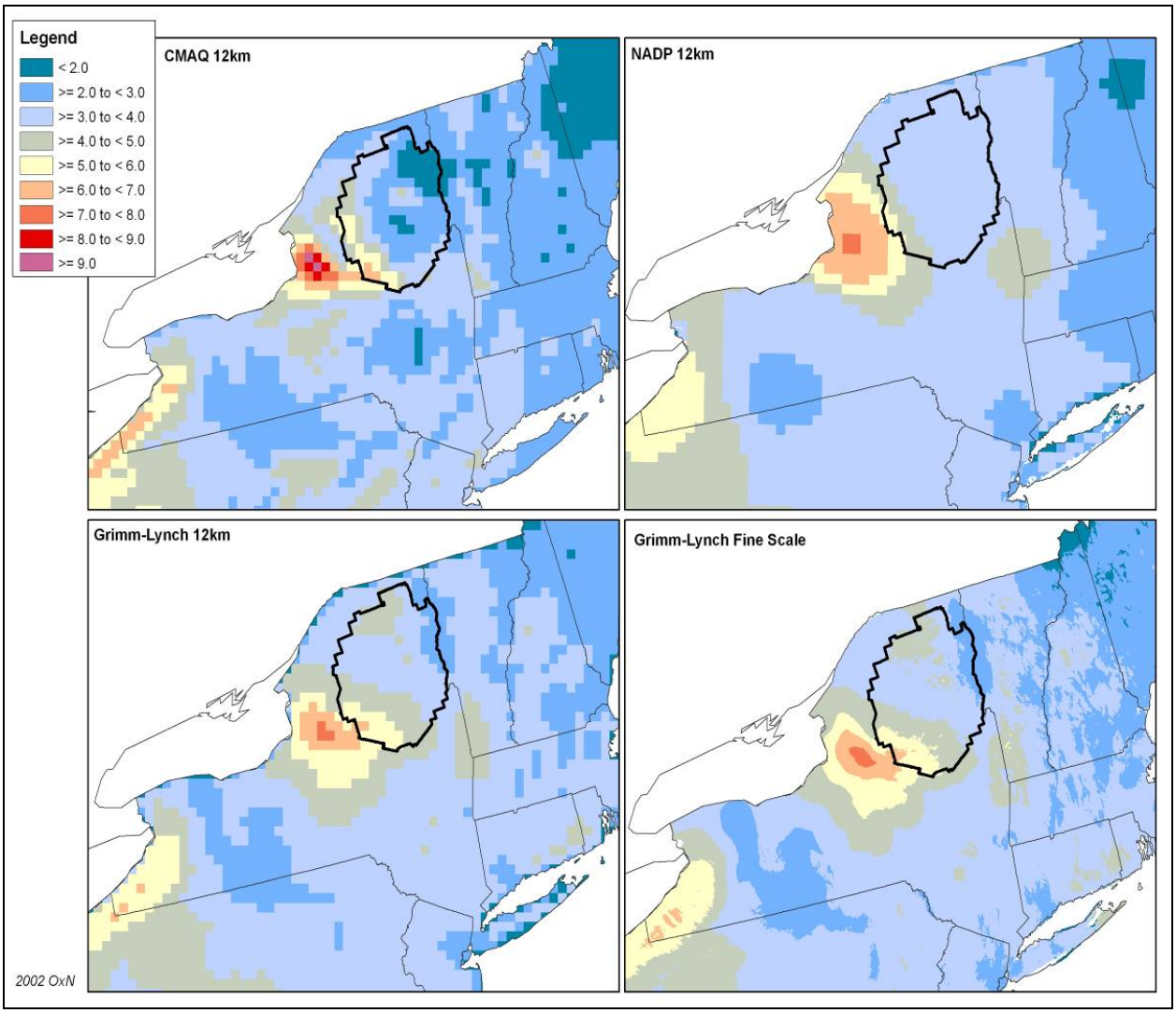

Figure 3.6-1. Fine-scale and 12-km annual total wet oxidized nitrogen deposition for the Adirondack Case Study Area and the surrounding region.

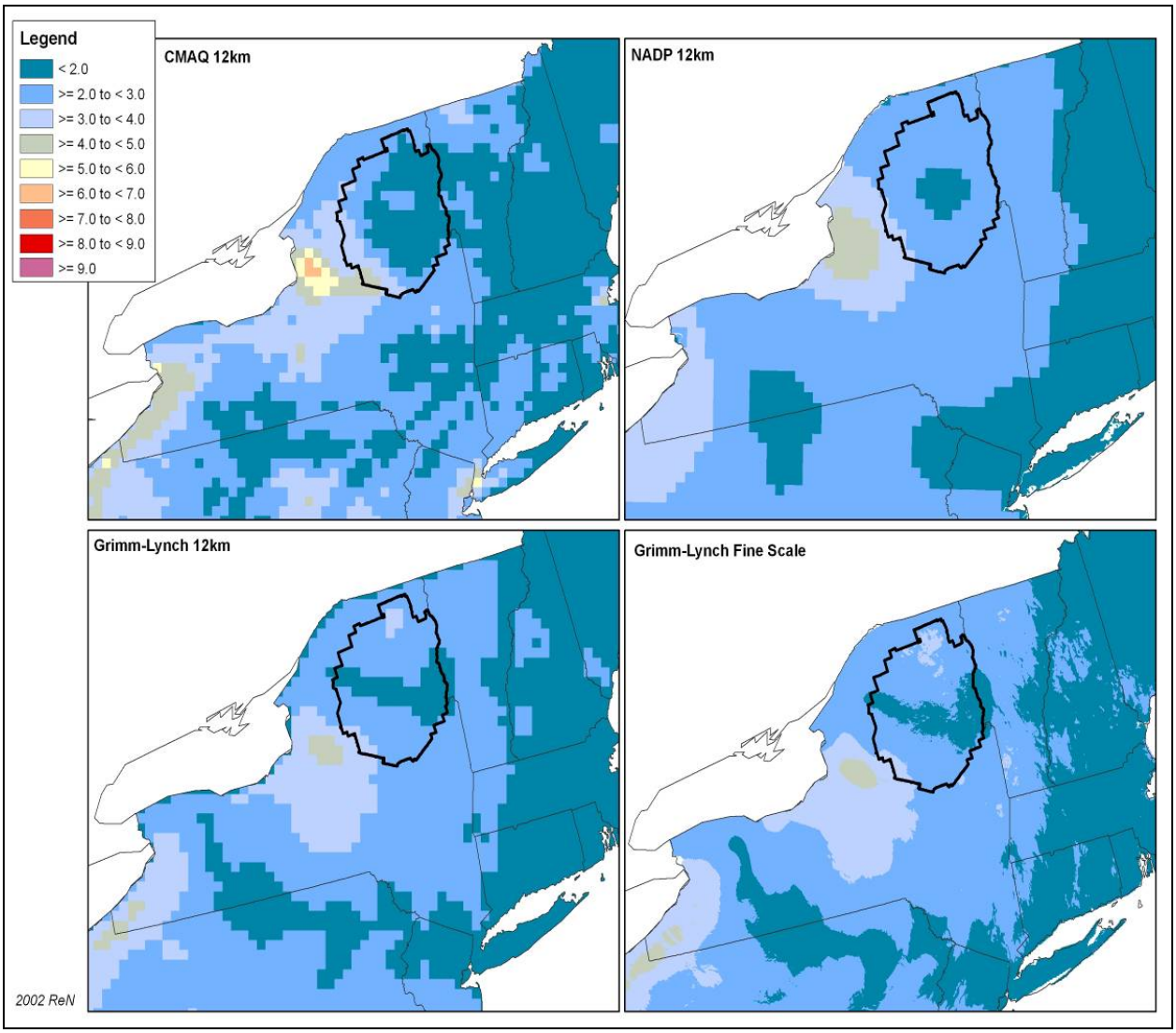

Figure 3.6-2. Fine-scale and 12-km annual total wet reduced nitrogen deposition for the Adirondack Case Study Area and the surrounding region.

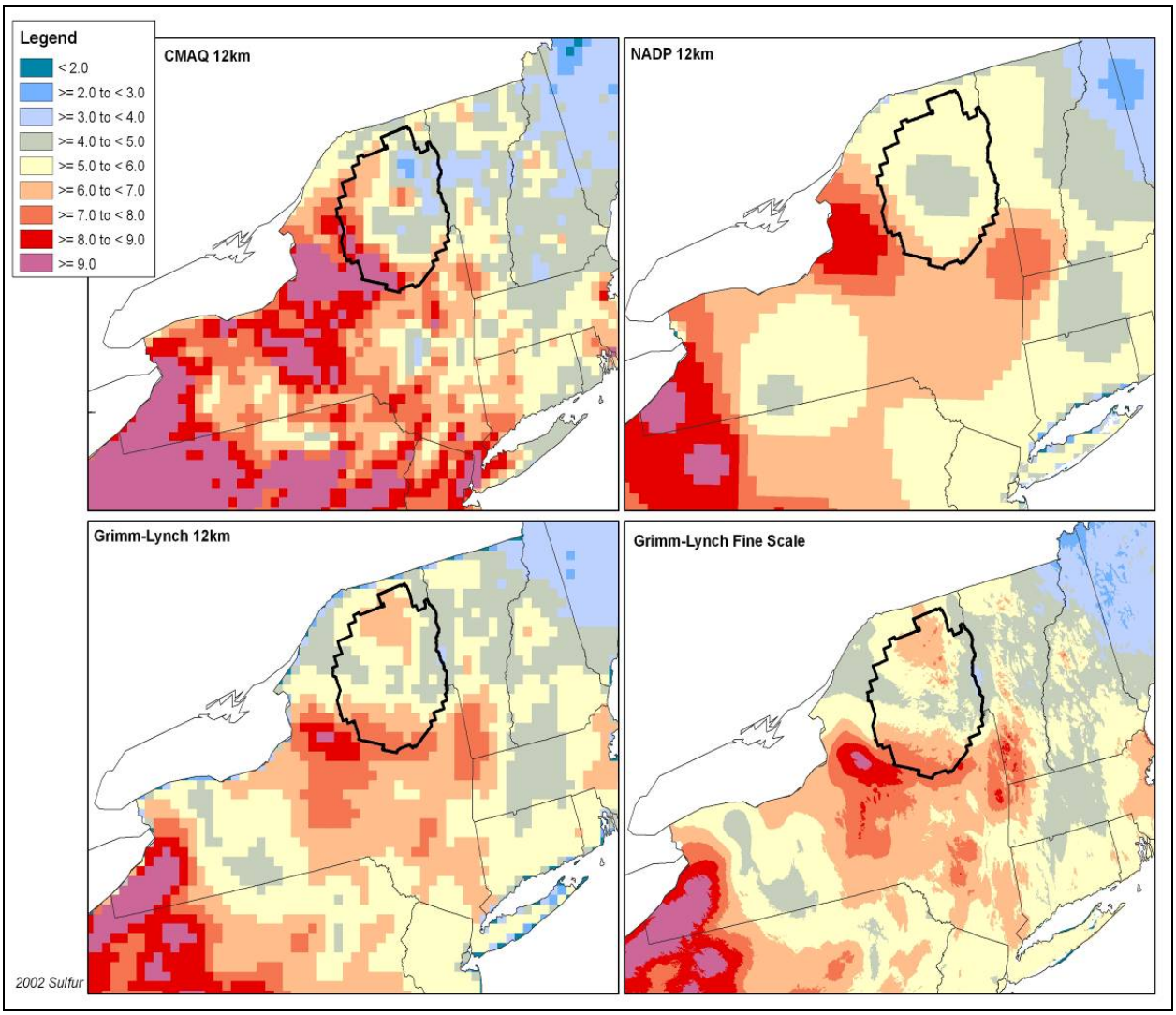

Figure 3.6-3. Fine-scale and 12-km annual total wet sulfur deposition for the Adirondack Case Study Area and the surrounding region.

While there are uncertainties in the data, models, and techniques used for this assessment, this analysis relies upon the most applicable measurements and state-of-the-science models. In addition, we have attempted to use these data and models in a manner that considers their relative strengths and limitations. Although we are not able to quantify the uncertainties associated with the tools, data, and predictions used in this assessment, we recognize that measurement, modeling and other analytical research efforts by EPA, academia, and other organizations will, over time, increase the certainty of our ability to characterize nitrogen and sulfur deposition and concentrations for sensitive ecosystems in future risk and exposure assessments for a secondary NO_x/SO_x NAAQS review.

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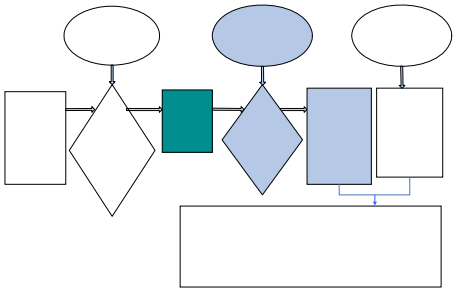


4.0 ACIDIFICATION

4.1 SCIENCE OVERVIEW

> Acidification is the decrease of **acid neutralizing capacity** in water or **base saturation** in soil caused by natural or anthropogenic processes.

Air emissions of sulfur oxides (SO_x), nitrogen oxides (NO_x), and reduced forms of nitrogen (NH_x) react in the atmosphere through a complex mix of reactions and thermodynamic processes in gaseous, liquid, and solid phases to form various acidifying compounds. These compounds are removed from the atmosphere through wet (e.g., rain, snow), cloud and fog, or dry (e.g., gases, particles) deposition. Deposition of SO_x, NO_x, and NH_x leads to ecosystem exposure to acidification. The *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008) reports that acidifying deposition has altered major biogeochemical processes in the United States by increasing the sulfur and nitrogen content of soils, accelerating sulfate (SO_4^{2-}) and nitrate (NO_3^-) leaching from soil to drainage water, depleting soil exchangeable base cations (especially calcium [Ca^{2+}] and magnesium [Mg^{2+}]) from soils, and increasing the mobility of aluminum (Al) (U.S. EPA, 2008, Section 3.2.1)

The extent of soil acidification is a critical factor that regulates virtually all acidification-related ecosystem effects from sulfur and nitrogen deposition. Soil acidification occurs in response to both natural factors and acidifying deposition (U.S. EPA, 2008, Section 3.2.1). Under conditions of low atmospheric deposition of nitrogen and sulfur, the naturally produced bicarbonate anion is often the dominant mobile anion, with SO_4^{2-} and NO_3^- playing a limited role with respect to cation leaching. Increased atmospheric deposition of sulfur and nitrogen can result in marked increases in SO_4^{2-} and NO_3^- soil fluxes resulting in the concomitant leaching of nutrient (Ca^{2+}, Mg^{2+}) and toxic (Al^{n+} and H^+ cations).

Acidification can impact the health of terrestrial and aquatic ecosystems. One of the effects of soil acidification is the increased mobility of dissolved inorganic Al, which is toxic to tree roots, fish, algae, and aquatic invertebrates (U.S. EPA, 2008, Sections 3.2.1.5, 3.2.2.1, and 3.2.3).

Both the aquatic and terrestrial effects of acidification have been studied and are highlighted in this chapter. For each effect, information is presented on the following:

- Ecological indicators, ecological responses, and ecosystem services
- Characteristics of areas sensitive to acidification
- Criteria for case study selection
- Current conditions in case study areas
- The ability to extrapolate case study findings to larger areas
- Current conditions for these other areas
- Ecological effect functions
- Uncertainty and variability identified for the case studies.

The case studies on aquatic acidification and terrestrial acidification were performed as part of this Risk and Exposure Assessment (Appendices 4 and 5, respectively) to aid in determining whether a link can be established between NO_x and SO_x deposition and ecosystem response. These case studies are also intended to test whether area-based risk and exposure assessments are a suitable method for predicting acidification effects on other ecosystems and geographic regions. The studies facilitate extrapolation of impacts from smaller-scale (yet representative) areas to other sensitive areas in the country.

4.1.1 Aquatic Acidification

The changes in major biogeochemical processes and soil conditions caused by acidifying deposition have significant ramifications for the water chemistry and biological functioning of associated surface waters. Surface water chemistry indicates the negative effects of acidification on the biotic integrity of freshwater ecosystems. Because surface water chemistry integrates the sum of terrestrial and aquatic processes that occur upstream within a watershed. Important terrestrial processes include nitrogen saturation, forest decline, and soil acidification (Stoddard et al., 2003). Thus, water chemistry integrates and reflects changes in soil and vegetative properties and biogeochemical processes (U.S. EPA, 2008, Section 3.2.3.1).

The Aquatic Acidification Case Study, reported in Appendix 4 and summarized in this chapter, is intended to estimate the ecological exposure and risk posed to aquatic ecosystems from the acidification effects of the deposition of nitrogen and sulfur for two sensitive regions of the eastern United States: the Adirondack Mountains and Shenandoah National Park (Virginia) and the surrounding areas of Virginia (henceforth referred to as the Adirondack Case Study Area and the Shenandoah Case Study Area, respectively).

4.1.2 Terrestrial Acidification

Deposition of NO_x and SO_x can result in acidification of some terrestrial ecosystems. Terrestrial acidification occurs as a result of both natural biogeochemical processes and acidifying deposition where strong mineral acids (e.g., H_2SO_4 and HNO_3) are deposited or generated within the soil. If soil base saturation (i.e., the concentration of exchangeable base cations as a percentage of the total cation exchange capacity, or the sum total of exchangeable cations that a soil can absorb) is 20% to 25%, or lower, dissolved inorganic Al can be mobilized, leading to the leaching of Al from soils to surface waters (Reuss and Johnson, 1985). Because ecosystems and biological species may respond differently to acidic deposition, case studies have been used to illustrate the potential effects of acidification on different ecosystem and species. Section 4.3 of this chapter presents the quantitative approach used to analyze the acidification effects of total nitrogen, NO_x (as a component of total nitrogen), and SO_x deposition on red spruce and sugar maple.

4.2 AQUATIC ACIDIFICATION

> For the purpose of this case study, acid neutralizing capacity (ANC) of surface waters is simply measured as the total amount of strong base ions minus the total amount of strong acid anions:
> $ANC = (Ca^{2+} + Mg^{2+} + K^{+} + Na^{+} + NH_4) – (SO_4^{2-} + NO_3^{-} + Cl^{-})$
> The unit of ANC is usually microequivalents per liter (μeq/L). If the sum of the equivalent concentrations of the base cations exceeds those of the strong acid anions, then the ANC of a waterbody will be positive. To the extent that the base cation sum exceeds the strong acid anion sum, the ANC will be higher. Higher ANC is generally associated with high pH and Ca^{2+} concentrations; lower ANC is generally associated with low pH and Al^{3+} concentrations and a greater likelihood of toxicity to biota.

When sulfur or nitrogen leaches from soils to surface waters in the form of SO_4^{2-} or NO_3^{-} an equivalent amount of positive cations, or countercharge, is also transported. This maintains electroneutrality. If the countercharge is provided by base cations, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), or potassium (K^{+}), rather than hydrogen (H^{+}) and aluminum (Al^{3+}), the acidity of the soil

water is neutralized, but the base saturation of the soil is reduced. Continued SO_4^{2-} or NO_3^- leaching can deplete available base cation pools in the soil. As the base cations are removed, continued deposition and leaching of SO_4^{2-} and/or NO_3^- (with H^+ and Al^{3+}) leads to acidification of soil water, and by connection, surface water. Loss of soil base saturation is a cumulative effect that increases the sensitivity of the watershed to further acidifying deposition.

It is important to note that these chemical changes can occur over both long- and short-term timescales. Short-term (i.e., hours or days) episodic changes in water chemistry have can also have significant biological effects. Episodic chemistry refers to conditions during precipitation or snowmelt events when proportionately more drainage water is routed through upper soil horizons that tends to provide less acid neutralizing than was passing through deeper soil horizons. Surface water chemistry has lower pH and acid neutralizing capacity (ANC) during events than during baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed "episodic acidification." Some streams may have chronic or base flow chemistry that is suitable for aquatic biota, but may be subject to occasional acidic episodes with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the eastern United States and are caused partly by acidifying deposition and partly by natural processes.

The ISA concludes the following:

- The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems. The strongest evidence comes from studies of changes in surface water chemistry, including concentrations of SO_4^{2-}, NO_3^-, dissolved inorganic Al and Ca, surface water pH, sum of base cations, ANC, and base cation surplus.
- The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota. The

Documented Evidence of Changes in Aquatic Biota Due to Acidifying Deposition

Species
- Mayflies, crustaceans, and mollusks from some streams
- Salmonid fish, smallmouth bass (*Micropterus dolomieu*)
- young-of-the year brook trout.

Community
- Species richness of plankton, invertebrates, and fish
- Invertebrate taxa, including mayflies, amphipods, snails, and clams
- Loss of species diversity and absence of several sensitive fish species
- Early life stages more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults.

(U.S. EPA, 2008, Section 3.2.3.4)

strongest evidence comes from studies of aquatic systems exposed to elevated levels of acidifying deposition that support fewer species of fish, macroinvertebrates, and diatoms. Decreases in ANC and pH and increases in dissolved inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish.

4.2.1 Ecological Indicators, Ecological Responses, and Ecosystem Services

4.2.1.1 Ecological Indicators

Surface water chemistry is a primary indicator of acidification and the resulting negative effects on the biotic integrity of freshwater ecosystems. Chemical parameters can be used to assess effects of acidifying deposition on lake or stream acid-base chemistry. These receptors include surface water pH and concentrations of SO_4^{2-}, NO_3^-, Al, and Ca^{2+}; the sum of base cations; and the recently developed base cation surplus. Another widely used water chemistry indicator for both atmospheric deposition sensitivity and effects is ANC. The utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al. ANC is also used because it integrates overall acid status and because surface water acidification models do a better job projecting ANC than they do for projecting pH and dissolved inorganic Al concentrations. The Aquatic Acidification Case Study, therefore, used ANC as the indicator of aquatic acidification.

Process-based models, such as the Model of Acidification of Groundwater in Catchment (MAGIC) and PnET-BGC (an integrated biogeochemical model), use the ANC calculated from charge balance.

4.2.1.2 Ecological Responses

Low ANC coincides with effects on aquatic systems (e.g., individual species fitness loss or death, reduced species richness, altered community structure). At the community level, species richness is positively correlated with pH and ANC (Kretser et al., 1989; Rago and Wiener, 1986) because energy cost in maintaining physiological homeostasis, growth, and reproduction is high at low ANC levels (Schreck, 1981, 1982; Wedemeyer et al., 1990). For example, Sullivan et al. (2006) found a logistic relationship between fish species richness and ANC class for Adirondack Case Study Area lakes (**Figure 4.2.-1, a**) that indicates the probability

of occurrence of an organism for a given value of ANC. In the Shenandoah Case Study Area, a statistically robust relationship between acid-base status of streams and fish species richness was also documented (**Figure 4.2-1, b**). In fact, ANC has been found in various studies to be the best single indicator of the biological response and health of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006).

Biota are generally not harmed when ANC values are >100 microequivalents per liter (μeq/L). The number of fish species also peaks at ANC values >100 μeq/L (Bulger et al., 1999; Driscoll et al., 2001; Kretser et al., 1989; Sullivan et al., 2006). Below 100 μeq/L, ANC fish fitness and community diversity begin to decline (**Figure 4.2-1).** At ANC levels between 100 and 50 μeq/L, the fitness of sensitive species (e.g., brook trout, zooplankton) also begins to decline. When ANC concentrations are <50 μeq/L, they are generally associated with death or loss of fitness of biota that are sensitive to acidification (Kretser et al., 1989; Dennis and Bulger, 1995).

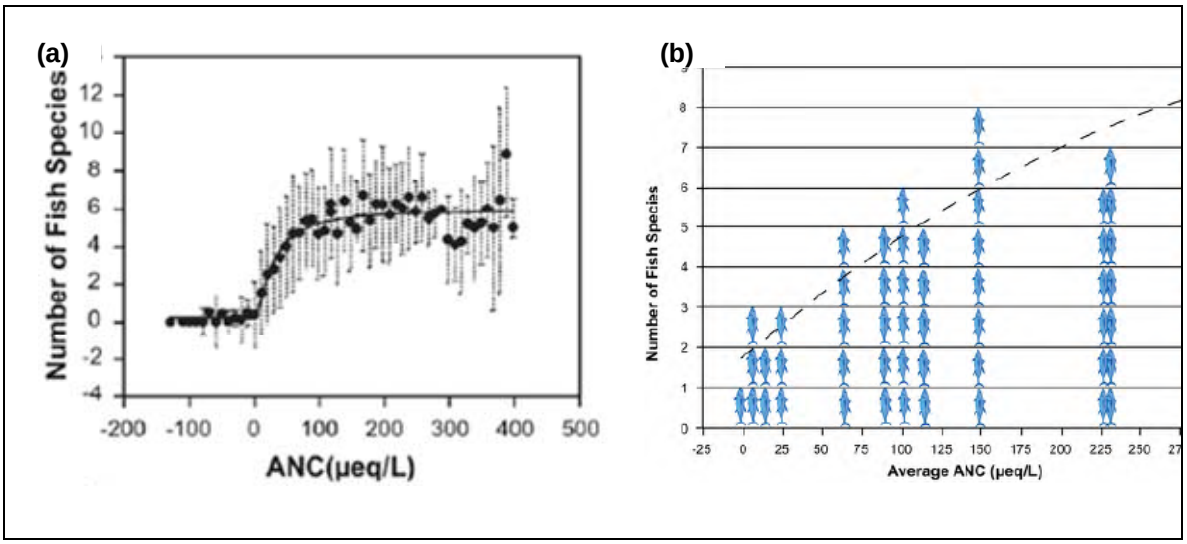


Figure 4.2-1. (a) Number of fish species per lake or stream versus acidity, expressed as acid neutralizing capacity for Adirondack Case Study Area lakes (Sullivan et al., 2006). **(b)** Number of fish species among 13 streams in Shenandoah National Park. Values of acid neutralizing capacity are means based on quarterly measurements from 1987 to 1994. The regression analysis shows a highly significant relationship ($p < .0001$) between mean stream acid neutralizing capacity and the number of fish species.

When ANC levels drop to <20 μeq/L, all biota exhibit some level of negative effects. Fish and plankton diversity and the structure of the communities continue to decline sharply to levels where acid-tolerant species begin to outnumber all other species (Matuszek and Beggs,

1988; Driscoll et al., 2001). Stoddard et al. (2003) showed that to protect biota from episodic acidification in the springtime, base flow ANC levels need to have an ANC of at least 30–40 μeq/L (Figure 4.1-1 of Appendix 4).

Complete loss of fish populations and extremely low diversity of planktonic communities occur when ANC levels stay <0 μeq/L. Only acidophilic species are present, but their population numbers are sharply reduced (Sullivan et al., 2006).

4.2.1.3 Ecosystem Services

Because acidification primarily affects the diversity and abundance of aquatic biota, it also affects the ecosystem services that are derived from the fish and other aquatic life found in these surface waters.

Provisioning Services

Food and fresh water are generally the most important provisioning services provided by inland surface waters (MEA, 2005). Whereas acidification is unlikely to have serious negative effects on, for example, water supplies for municipal, industrial, or agricultural uses, it can limit the productivity of surface waters as a source of food (i.e., fish). In the northeastern United States, the surface waters affected by acidification are not a major source of commercially raised or caught fish; however, they are a source of food for some recreational and subsistence fishermen and for other consumers. Although data and models are available for examining the effects on recreational fishing, relatively little data are available for measuring the effects on subsistence and other consumers. For example, although there is evidence that certain population subgroups in the northeastern United States, such as the Hmong and Chippewa ethnic groups, have particularly high rates of self-caught fish consumption (Hutchison and Kraft, 1994; Peterson et al., 1994), it is not known if and how their consumption patterns are affected by the reductions in available fish populations caused by surface water acidification.

Cultural Services

Inland surface waters support several cultural services, such as aesthetic and educational services; however, the type of service that is likely to be most widely and significantly affected by aquatic acidification is recreational fishing. Recreational fishing in lakes and streams is among the most popular outdoor recreational activities in the northeastern United States. Data from the 2006 National Survey of Fishing, Hunting, and Wildlife Associated Recreation

(FHWAR) indicate that >9% of adults in this part of the country participate annually in freshwater (excluding Great Lakes) fishing. The total number of freshwater fishing days occurring in those states (by both residents and nonresidents) in 2006 was 140.8 million days. Roughly two-thirds of these fishing days were at ponds, lakes, or reservoirs, and the remaining one-third were at rivers or streams. Based on studies conducted in the northeastern United States, Kaval and Loomis (2003) estimated average consumer surplus values per day of $35.91 for recreational fishing (in 2007 dollars); therefore, the implied total annual value of freshwater fishing in the northeastern United States was $5.06 billion in 2006. Consumer surplus value is a commonly used and accepted measure of economic benefit (see, for example, U.S. EPA, 2000). It is the difference between (1) the maximum amount individuals are, on average, willing and able to pay for a good, service, or activity (in this case, a day of recreational fishing) and (2) the amount they actually pay (in out-of-pocket and time costs). For recreation days, it is most commonly measured using recreation demand, travel cost models.

Regulating Services

In general, inland surface waters, such as lakes, rivers, and streams provide a number of regulating services associated with hydrological and climate regulation. There is little evidence that acidification of freshwaters in the northeastern United States has significantly degraded these services; however, freshwater ecosystems also provide biological control services by providing environments that sustain aquatic food webs. These services are certainly disrupted by the toxic effects of acidification on fish and other aquatic life. Although it is difficult to quantify these services and how they are affected by acidification, it some of these services may be captured through measures of provisioning and cultural services.

4.2.2 Characteristics of Sensitive Areas

The ISA reports that the principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition is geology (particularly surficial geology). Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Other factors that contribute to the sensitivity of soils and surface waters to acidifying deposition include topography, soil chemistry, land use, and hydrologic flowpath. Surface waters in the same setting can have different sensitivities to acidification, depending on the relative contributions of near-surface drainage water and deeper groundwater (Chen et al., 1984; Driscoll et al., 1991; Eilers et al., 1983). Lakes and streams in

the United States that are sensitive to episodic and chronic acidification in response to SO_x, and to a lesser extent NO_x, deposition tend to occur at relatively high elevation in areas that have base-poor bedrock, high relief, and shallow soils (U.S. EPA, 2008, Section 3.2.4.1).

The regions of the United States with low surface water ANC values are sensitive to acidifying deposition. The majority of lakes and streams in the United States have ANC levels >200 μeq/L and are not sensitive to the deposition of NO_x and SO_x air pollution. **Figure 4.2-2** shows the acid-sensitive regions of the eastern United States with the potential of low surface water ANC, as determined by geology and surface water chemistry.

Freshwater surveys and monitoring in the eastern United States have been conducted by many programs since the mid-1980s, including EPA's Environmental Monitoring and Assessment Program (EMAP), National Surface Water Survey (NSWS), Temporally Integrated Monitoring of Ecosystems (TIME) (Stoddard, 1990), and Long-term Monitoring (LTM) (Ford et al., 1993; Stoddard et al., 1998) programs. Based on analyses of surface water data from these programs, New England, the Adirondack Mountains, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), northern Florida, and the Upper Midwest contain the most sensitive lakes and streams (i.e., ANC less than about 50 μeq/L) since the 1980s.

New England, the Adirondack Mountains, the northern Appalachian Plateau, the Ridge/Blue Ridge region, and the Upper Midwest contain 95% of the lakes and 84% of the streams in the United States that have been anthropogenically acidified through deposition. Stoddard et al. (2003) suggested that although improvement in ANC had occurred, ~8% of lakes in the Adirondack Mountains and from 6% to 8% of streams in the northern Appalachian Plateau and Ridge/Blue Ridge region were acidic at base-flow conditions. Because they are still receiving substantial NO_x/SO_x deposition inputs and still contain a large number of waterbodies that are acidic, areas in New England, the Adirondack Mountains, the Northern Appalachian Plateau, and the Ridge/Blue Ridge region provide ideal case study areas to assess the risk to aquatic ecosystems from NO_x/SO_x acidifying deposition.

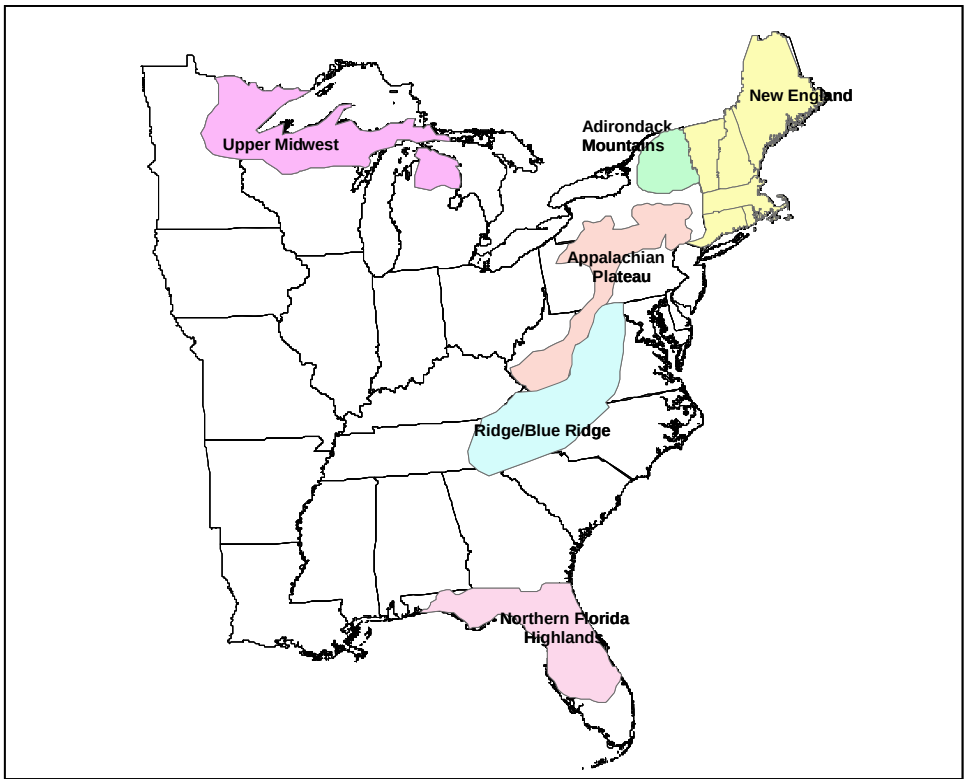


Figure 4.2-2. Ecosystems sensitive to acidifying deposition in the eastern United States (U.S. EPA, modified from NAPAP, 2005).

4.2.3 Case Study Area Selection

Selection of case study areas was based on **Figure 4.2-2** (showing areas of the potential sensitivity to aquatic acidification), potential case study areas identified in the ISA (U.S. EPA, 2008, Table 4-4), and sites recommended for consideration by the Ecological Effects Subcommittee (EES) of the Advisory Council for Clean Air Compliance Analysis (U.S. EPA, 2005). Using the rationale described in the following subsections, the Adirondack Mountains and Shenandoah Mountains were selected for case study areas.

4.2.3.1 Adirondack Case Study Area

The Adirondack Case Study Area is situated in northeastern New York and is characterized by dense forest cover and abundant surface waters, with 46 peaks that extend up to 1600 meters (m) in elevation. This area includes the headlands of five major drainage basins: Lake Champlain and the Hudson, Black, St. Lawrence, and Mohawk rivers. There are more than 2,800 lakes and ponds, and more than 1,500 miles of rivers that are fed by an estimated 30,000 miles of brooks and streams.

The Adirondack Case Study Area, particularly its southwestern section, is sensitive to acidifying deposition because it receives high precipitation amounts with high concentrations of pollutants, has shallow base-poor soils, and is underlain by igneous bedrock with low weathering rates and buffering ability (Driscoll et al., 1991; Sullivan et al., 2006). The Adirondack Case Study Area is among the most severely acid-impacted regions in North America (Driscoll et al., 2003; Landers et al., 1988; Stoddard et al., 2003). It has long been used as an indicator of the response of forest and aquatic ecosystems to changes in emissions of sulfur dioxide (SO_2) and NO_x resulting, in part, from the Clean Air Act Amendments of 1990 (NAPAP, 1998; U.S. EPA, 1995).

Wet deposition in the Adirondack Case Study Area has been monitored by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) since 1978 at two sites (i.e., Huntington Forest and Whiteface Mountain) and since the 1980s at seven other sites. Since 1990, wet SO_4^- and NO_3^- deposition at these NADP/NTN sites in the Adirondack Case Study Area has declined by about 45% and 40%, respectively (**Figure 4.2-3**). However, annual total wet deposition is still more than 15 and 10 kilograms/hectare/year (kg/ha/yr) of SO_4^{2-} and NO_3^-, respectively.

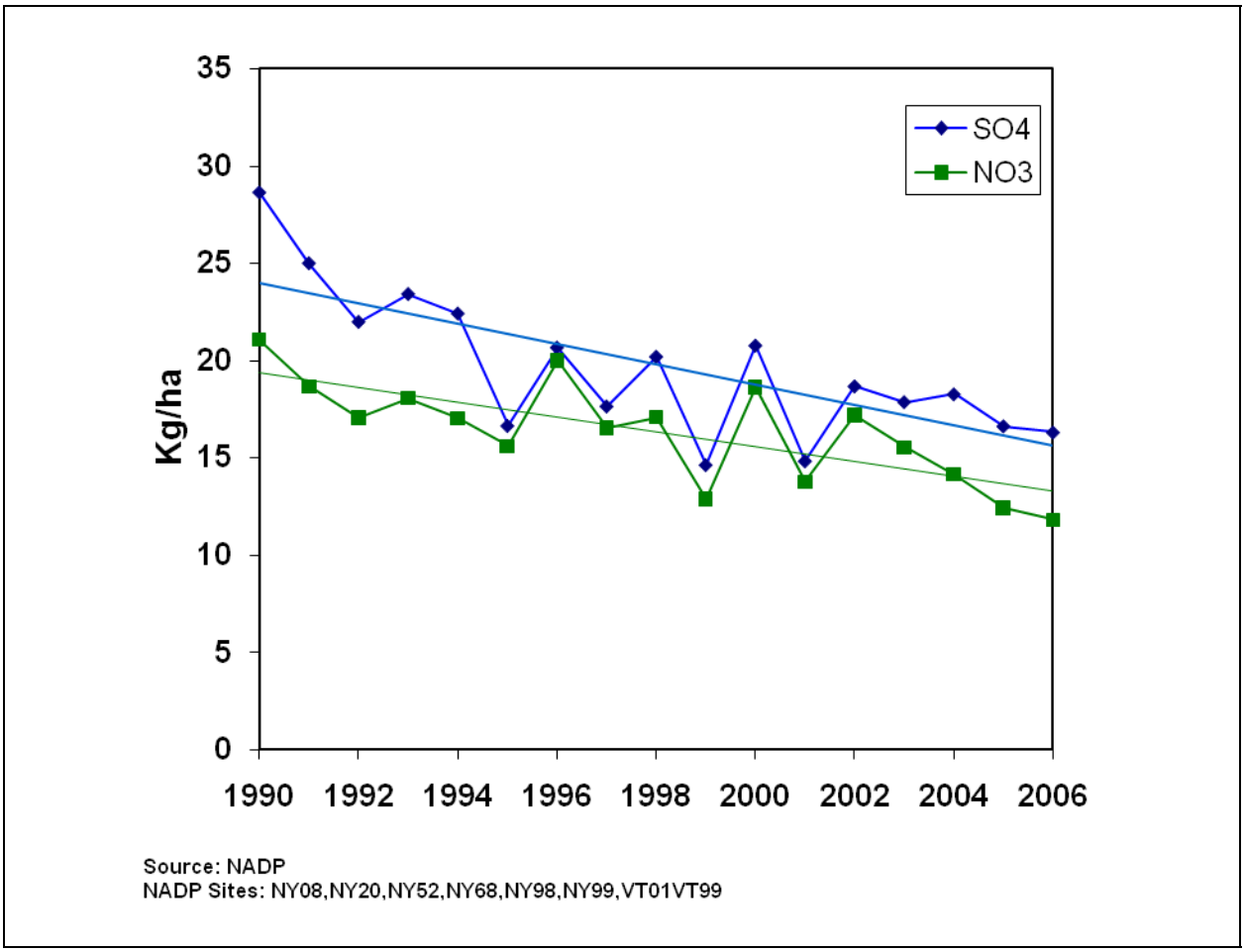


Figure 4.2-3. Annual average total wet deposition (kg/ha/yr) for the period 1990 to 2006 in SO_4^{2-} (green) and NO_3^- (blue) from eight NADP/NTN sites in the Adirondack Case Study Area.

4.2.3.2 Shenandoah Case Study Area

The Shenandoah Case Study Area straddles the crest of the Blue Ridge Mountains in western Virginia, on the eastern edge of the central Appalachian Mountain region. Several areas in Shenandoah National Park have been designated Class 1 Wilderness areas. Shenandoah National Park is known for its scenic beauty, outstanding natural features, and biota. Air pollution within the Shenandoah Case Study Area, including concentrations of sulfur, nitrogen, and ozone (O_3),

> "Bulger et al. (2000) predicted that future losses of native brook trout (*Salvelinus fontinalis*) populations in the streams of western Virginia will be substantial unless acidic deposition reductions are much greater than the 1990 Clean Air Act Amendments will provide…Despite recent declines in acidic deposition and some encouraging evidence for initial recovery in other parts of the country, recovery in the central Appalachian region in general, and the Shenandoah National Park in particular, has been limited and impairment of surface waters due to acidic deposition continues (Stoddard et al. 2003; Webb et al. 2004)." (Webb, 2004)

is higher than in most other national parks in the United States.

This area is sensitive to acidifying deposition because it receives high precipitation, has shallow base-poor soils, and is underlain by igneous and silicon (Si)-based bedrock with low weathering rates and poor ANC. The Shenandoah Case Study Area is also among the most severely acid-impacted regions in North America (Stoddard et al., 2003; Webb et al., 2004).

Wet deposition in the Shenandoah National Park monitored at 7 sites by the NADP/NTN since the 1980s shows wet SO_4^{2-} and NO_3^- deposition declining by about 28% and 20%, respectively (**Figure 4.2-4, a and b**). However, annual total deposition is still over 15 and 10 kg/ha/yr of SO_4^{2-} and NO_3^-, respectively.

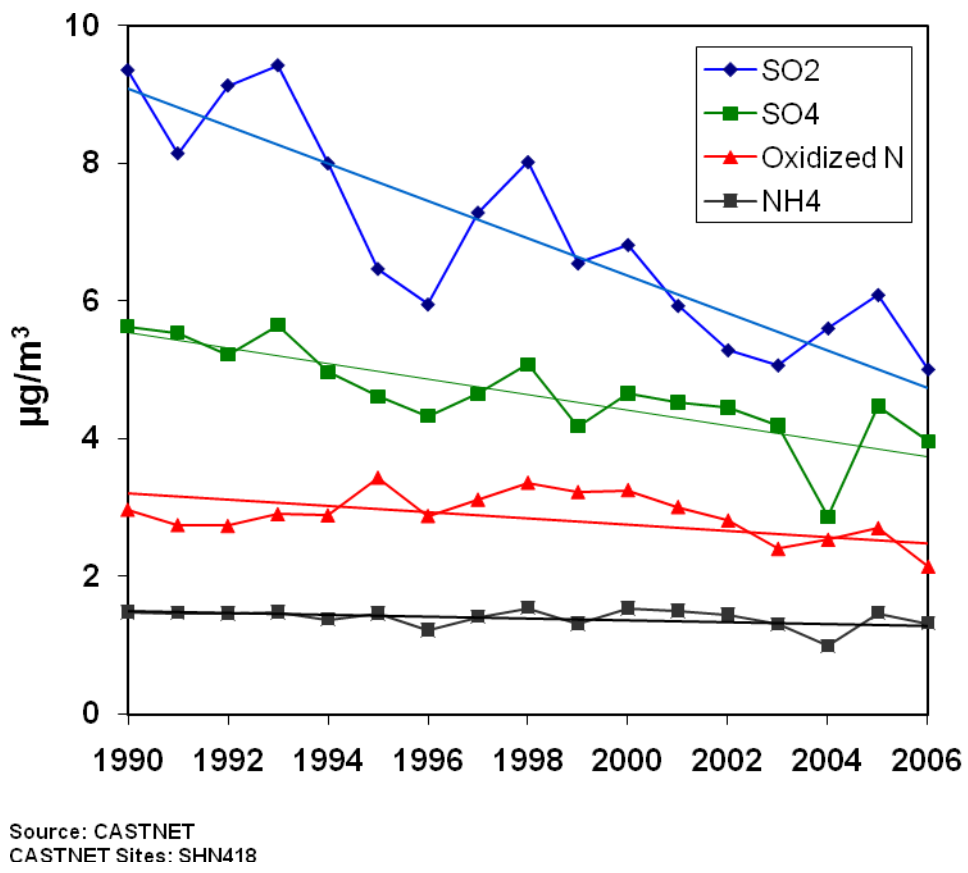


Figure 4.2-4. Air pollution concentrations and deposition for the period 1990 to 2006 using one CASTNET and seven NADP/NTN sites in the Shenandoah Case Study Area. **(a)** Annual average air concentrations of SO_2 (blue), oxidized nitrogen (red), SO_4^{2-} (green), and reduced nitrogen (black). **(b)** Annual average total wet deposition (kg/ha/yr) of SO_4^{2-} (green) and NO_3^- (blue).

4.2.4 Current Conditions in Case Study Areas

4.2.4.1 Surface Water Trends and Input Data

Status of current conditions and trends in SO_4^{2-} and NO_3^- concentrations and ANC measured in surface water were used to characterize links to the effects of acidifying deposition on the acid-base chemistry of a waterbody. Trends in these sensitive chemical receptors show whether the conditions of a waterbody are improving and heading toward recovery or are continuing to degrade.

MAGIC Modeling and Input Data

To assess surface water trends in SO_4^{2-} and NO_3^- concentrations and ANC surface water monitoring data from the EPA-administered LTM program were used (see Appendix 4's Attachment 4.B for more details on TIME/LTM network). Trends in SO_4^{2-} and NO_3^- concentrations and ANC were assessed using average yearly values for the period from 1990 to 2006.

The preacidification condition of a waterbody is rarely known because historical measurements are not available. Likewise, it is also difficult to empirically determine whether a waterbody has recovered or will recover from acidification as acidifying deposition inputs decline, because recovery may take many years to occur. For these reasons, biogeochemical models, such as MAGIC, enable estimates of past, present, and future water chemistry that can be used to evaluate (1) the associated risk and uncertainty of the current levels of acidification as compared with preacidification conditions, and (2) low concern **(Table 4.2-1).**

MAGIC was used to determine the past (preacidification), present (2002 and 2008), and future (2020 and 2050) acidic conditions of 44 lakes in the Adirondack Case Study Area and 60 streams in the Shenandoah Case Study Area (**Figure 4.2-5**). Furthermore, MAGIC was used to evaluate the associated risk and uncertainty of the current levels of acidification given the pre-acidification water quality and the levels of uncertainty in the input parameters. The MAGIC model output for each waterbody was summarized into five ANC levels that correspond to the aquatic status categories *Acute Concern, Severe Concern, Elevated Concern, Moderate Concern,* and *Low Concern.* This grouping offers an assessment of the current risk to the biota of current condition compared to preacidification and future conditions. Surface water chemistry data were used from two EPA-administered surface water monitoring and survey programs: the TIME and

the LTM programs. Average yearly ANC concentrations were calculated from annual measurements.

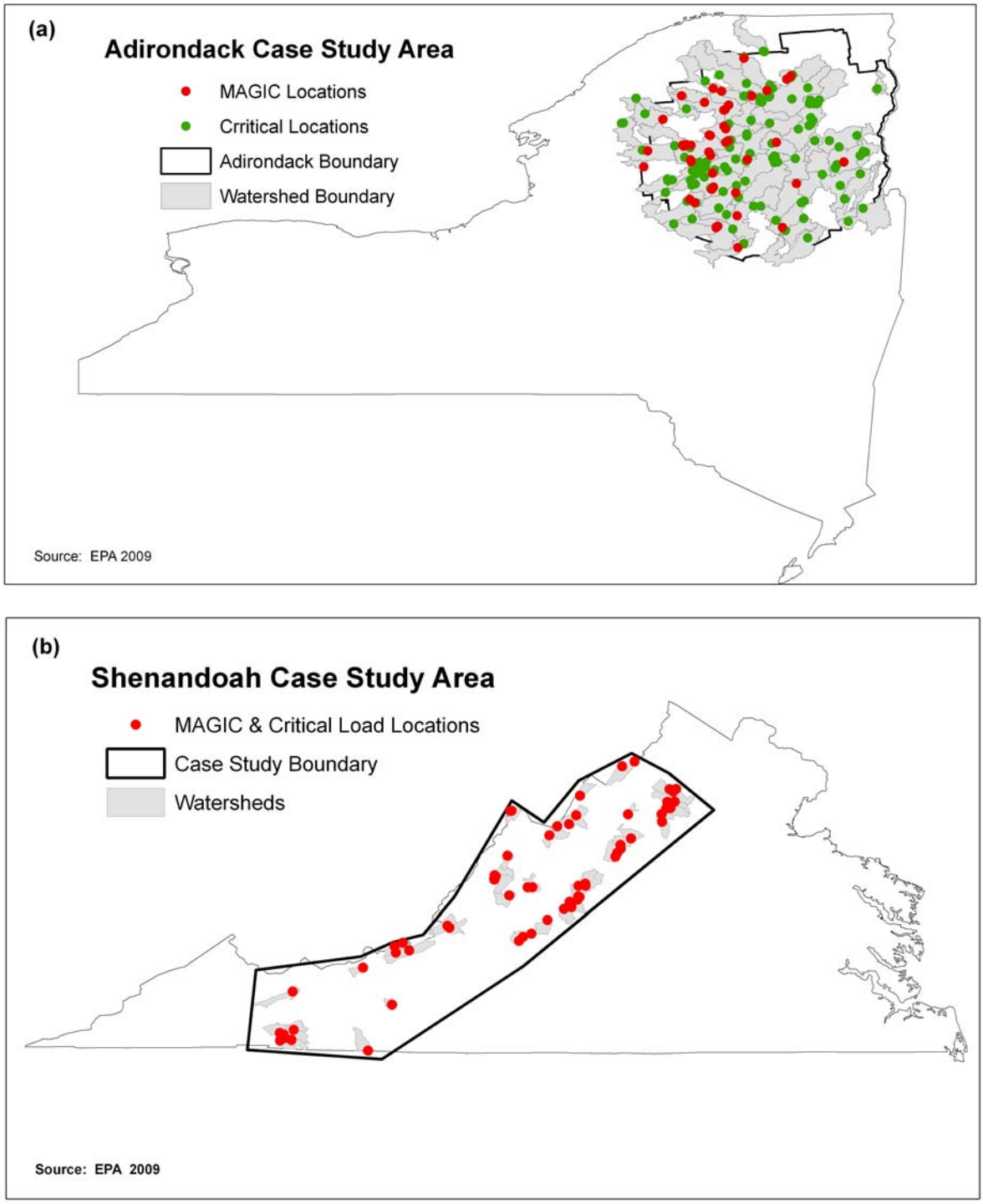


Figure 4.2-5. (Top) The location of lakes in the Adirondack Case Study Area used for **MAGIC** (red dots) and critical load (green dots) modeling sites. (Bottom) The location of streams used for both MAGIC and critical load modeling for the Shenandoah Case Study Area.

Critical Load and Input Data

Connecting current total nitrogen and sulfur deposition to acid-base conditions of lakes and streams: The critical load approach. The critical load approach was used to connect current deposition of nitrogen and sulfur to the acid-base condition and biological risk to biota of lakes and streams in the study. Calculating critical load exceedances (i.e., the amount of deposition above the critical load) allows the determination of whether current deposition poses a risk of acidification to a given group of waterbodies. This approach also allows for the comparison of different levels of ANC thresholds (e.g., 0, 20, 50, 100 μeq/L) and their associated risk to the biological community. **Table 4.2-1** provides a summary of the biological effects experienced at each of these limits.

Critical loads and their exceedances at four levels of biological protection were calculated for 169 lakes in the Adirondack Case Study Area and 60 streams in the Shenandoah Case Study Area. Four ANC limits (i.e., ANC_{limit}) of biological protection were used: 0 μeq/L (acidic), 20 μeq/L (minimal protection), 50 μeq/L (moderate protection), and 100 μeq/L (full protection). A full and complete description of the biological effects at a given ANC limit appears in Appendix 4, Section 4.1.

From the 169 modeled lakes and 60 streams in the Adirondack and Shenandoah case study areas, respectively, the number and percentage of waterbodies that receive acidifying deposition above their critical loads for a given ANC limit of 0, 20, 50, and 100 μeq/L were determined.

The **critical load approach** provides a means of gauging whether a group of lakes or streams in a given area receives deposition that results in a level of biological harm that is defined by an ANC concentration, known as the critical limit, which corresponds to harmful biological effects (e.g., ANC of 50 μeq/L). A critical load estimate is analogous to determining the "susceptibility" of a waterbody to become acidified from the deposition of nitrogen and sulfur. Low critical load values (i.e., less than 50 $meq/m^2 \cdot yr$) mean that the watershed has a limited ability to neutralize the addition of acidic anions, and hence, it is susceptible to acidification. The greater the critical load value, the greater the ability of the watershed to neutralize the additional acidic anions and protect aquatic life.

Table 4.2-1. Aquatic Status Categories

Category Label	ANC Levels*	Expected Ecological Effects
Acute Concern	<0 micro equivalent per Liter (µeq/L)	Near complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acidophilic forms. The number of individuals in plankton species that are present is greatly reduced.
Severe Concern	0–20 µeq/L	Highly sensitive to episodic acidification. During episodes of high acidifying deposition, brook trout populations may experience lethal effects. Diversity and distribution of zooplankton communities decline sharply.
Elevated Concern	20–50 µeq/L	Fish species richness is greatly reduced (i.e., more than half of expected species can be missing). On average, brook trout populations experience sublethal effects, including loss of health, reproduction capacity, and fitness. Diversity and distribution of zooplankton communities decline.
Moderate Concern	50–100 µeq/L	Fish species richness begins to decline (i.e., sensitive species are lost from lakes). Brook trout populations are sensitive and variable, with possible sublethal effects. Diversity and distribution of zooplankton communities also begin to decline as species that are sensitive to acidifying deposition are affected.
Low Concern	>100 µeq/L	Fish species richness may be unaffected. Reproducing brook trout populations are expected where habitat is suitable. Zooplankton communities are unaffected and exhibit expected diversity and distribution.

4.2.4.2 Current Conditions in Adirondack Case Study Area Surface Waters

Current and Preacidification Conditions of Surface Waters

Since the mid-1990s, lakes in the Adirondack Case Study Area have shown signs of improvement in NO_3^- and SO_4^{2-} concentrations in surface waters. Wet deposition rates for SO_2 and NO_x, and their atmospheric reaction products, have decreased (see **Figure 4.2-3**), and, as a result, NO_3^- and SO_4^{2-} concentrations have decreased in surface

Table 4.2-2. Estimated Average Concentrations (and associated uncertainties) of Surface Water Chemistry at 44 Lakes in the Adirondack Case Study Area Modeled Using MAGIC for Preacidification (1860) and Current (2006) Conditions

	Preacidification		Current	
µeq/L	Avg.	(±)	Avg.	(±)
ANC	120.3	13.6	62.1	15.7
SO_4^{2-}	12.4	2.1	66.1	1.24
NO_3^-	0.2	1.7	3.4	14.8
NH_4^+	0.0	0.0	0.1	0.1

waters by approximately 26% and 13%, respectively (**Figure 4.2-6**).

The decline in SO_4^{2-} concentrations in surface waters in the Adirondack Case Study Area is −2.1 µeq/L/year, while the decline in NO_3^- is −0.23 µeq/L/year. However, current concentrations of NO_3^- and SO_4^{2-} are still well above preacidification conditions based on MAGIC model simulations. **Figure 4.2-7** and **Figure 4.2-8** show the modeled condition of the lakes in 1860 "preacidification" and in 2006 "current" conditions. On average, NO_3^- and SO_4^{2-} concentrations are 17- and 5-fold higher today, respectively (**Table 4.2-2**).

Current NO_3^- and SO_4^{2-} concentrations are 17- and 5-fold higher in Adirondack Case Study Area lakes today than they were in 1860.

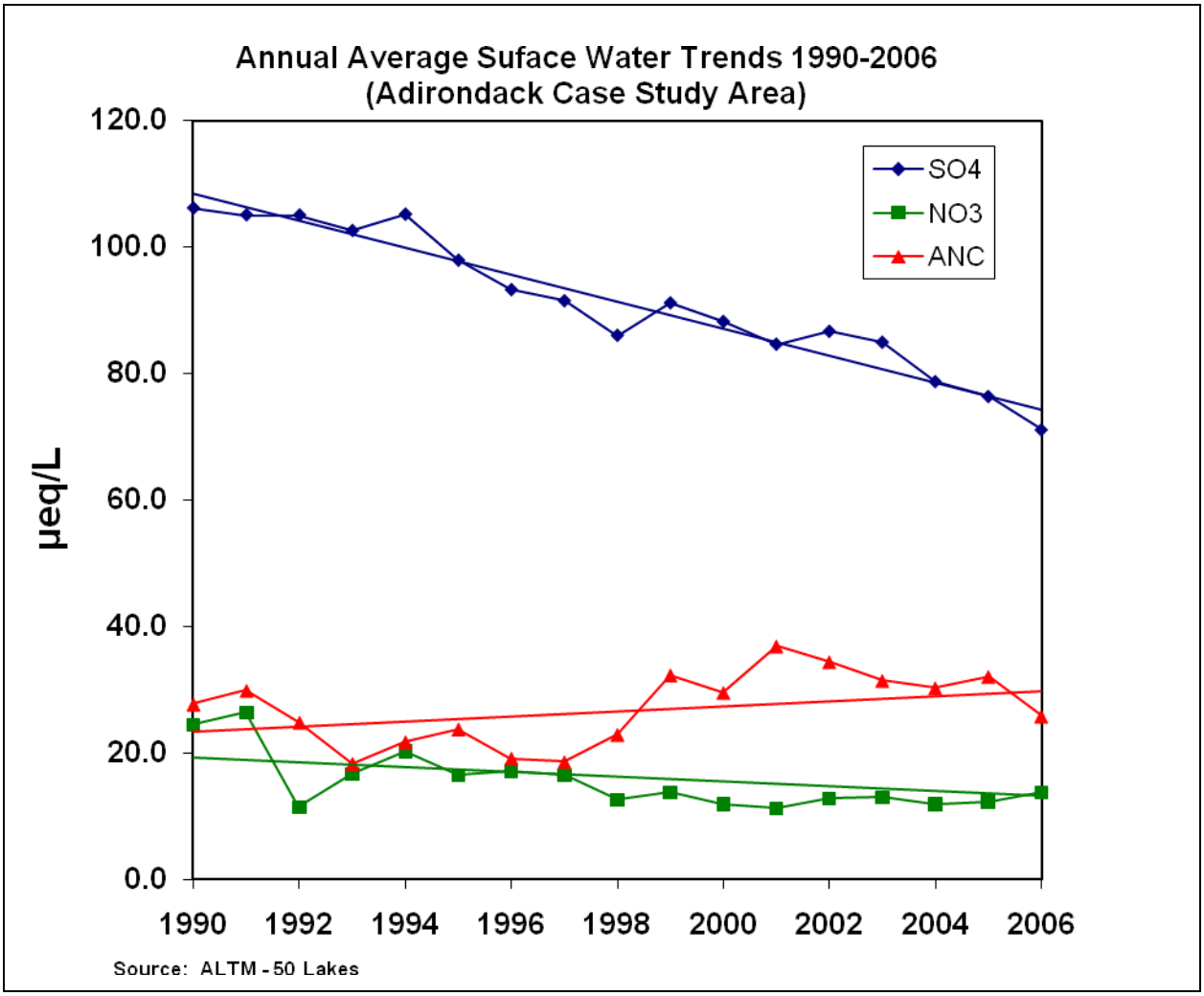


Figure 4.2-6. Trends over time for SO_4^{2-}, NO_3^-, and acid neutralizing capacity in 50 LTM lakes. SO_4^{2-} and NO_3^- concentrations have decreased in surface waters by approximately 26% and 13%, respectively.

Although NO_3^- deposition can be an important factor in acid precipitation, these current results demonstrate that acidification in the Adirondack Case Study Area is currently being driven by SO_4^{2-} deposition because the current average SO_4^{2-} concentration in the 44 modeled lakes is some 19-fold greater than NO_3^- concentrations in surface waters (**Table 4.2-2**).

An increase in ANC of +1 μeq/L/year has corresponded to the declines in NO_3^- and SO_4^{2-}, despite reductions in base cations of Ca^{2+} and Mg^{2+} during the same period of time. This decline in base cation concentration is important because base cation supply neutralizes the inputs of NO_3^- and SO_4^{2-}, which will likely limit future recovery of ANC. In the Adirondack Case Study Area, levels of dissolved inorganic Al also declined slightly (data not shown).

Based on the observed annual average concentration of ANC, there is still a substantial number of lakes in the Adirondack Case Study Area that have *Elevated* (i.e., ANC <50 μeq/L) to *Severe* (i.e., ANC <20 μeq/L) condition of acidity (**Figure 4.2-9**).

Based on monitoring data, only 22% of monitored lakes are "not acidic," which include the *Moderate* to *Low Concern* classes, and thus have water quality that poses little risk to aquatic biota. On the other hand, 78% of all monitored lakes have a current risk of *Elevated, Severe*, or *Acute*. Of that 78%, 31% experience episodic acidification (i.e., severe concern) and 18% are chronically acidic today (i.e., acute concern).

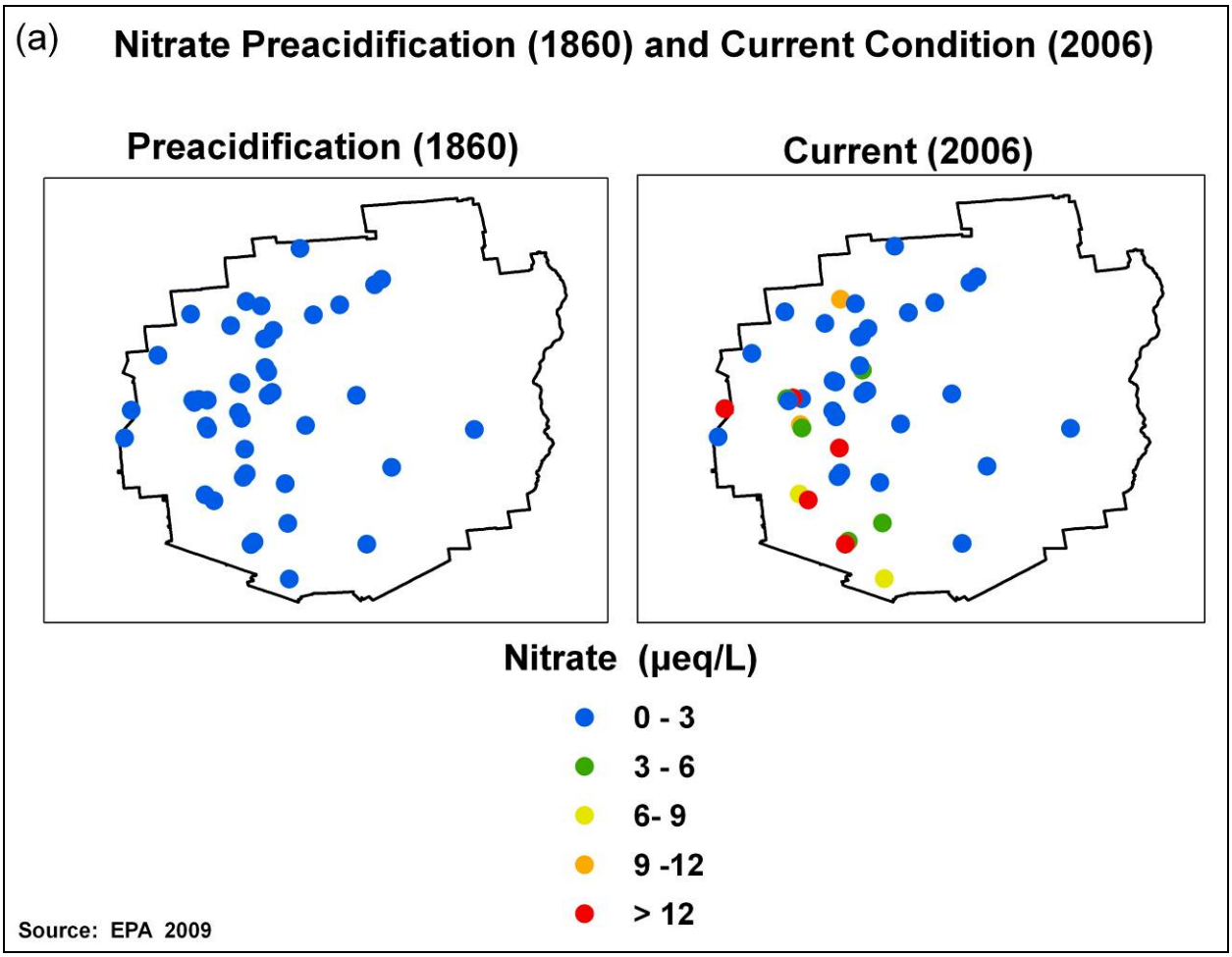


Figure 4.2-7. NO_3^- concentrations of years 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC.

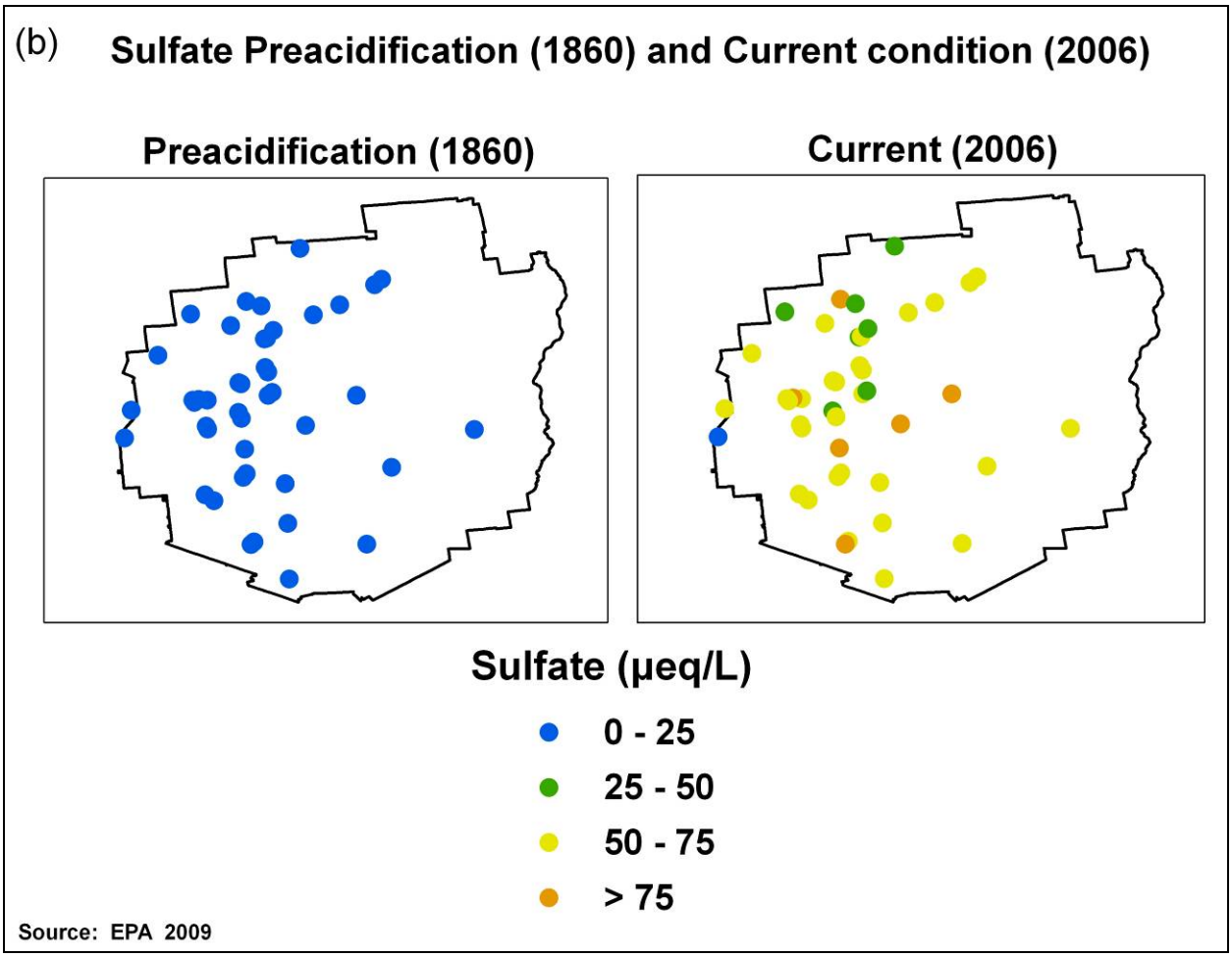


Figure 4.2-8. SO_4^{2-} concentrations of years 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC.

An estimate of the level of current condition at these lakes that can be attributed to the effects of industrially generated acidifying deposition can be made by examining the hindcast conditions of the lakes derived from the MAGIC model output. Based on these simulations, preacidification average ANC concentration of 44 modeled lakes was 120.3±13.6 ueq/L, as compared with 62.1±15.7 µeq/L for today (see **Table 4.2-2**). Furthermore, 89% of the modeled lakes were likely "not acidic" prior to the onset of acidifying deposition (**Figure 4.2-10** and **Figure 4.2-11**). The other 11% of lakes have ANC of >20 µeq/L. The hindcast simulations produced no lakes with *Acute* or *Severe Concern* preacidification condition, suggesting that current ambient concentrations of NO_x and SO_x and their associated levels of NO_3^- and SO_4^{2-} deposition pose a risk of acidification to approximately 32% of modeled lakes.

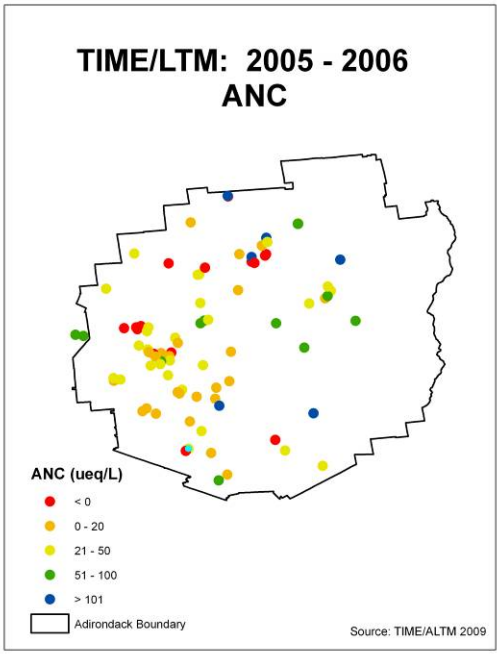


Figure 4.2-9. Acid neutralizing capacity concentrations from 88 lakes in the Adirondack Case Study Area. Monitoring data from the TIME/LTM programs.

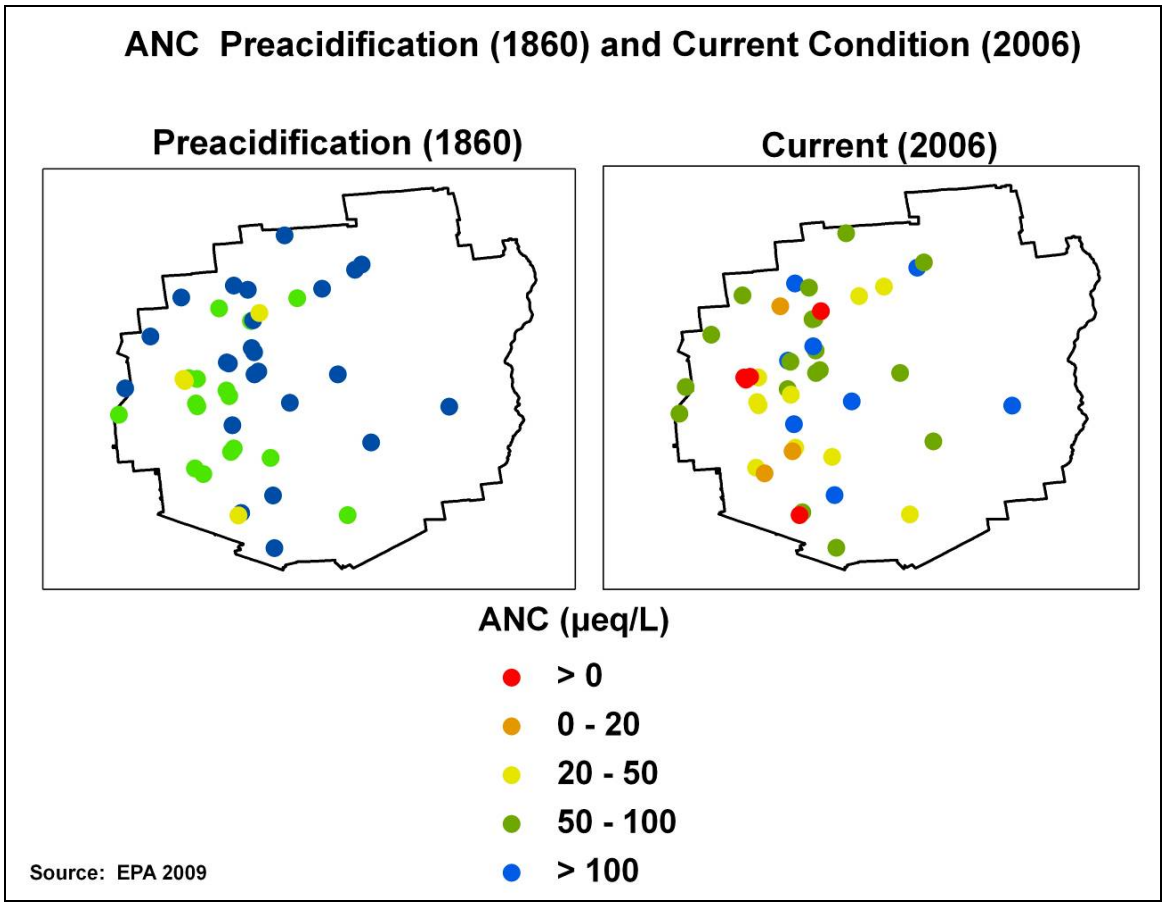


Figure 4.2-10. Acid neutralizing capacity levels of preacidification (1860) and current (2006) conditions based on hindcasts of 44 modeled lakes in the Adirondack Case Study Area.

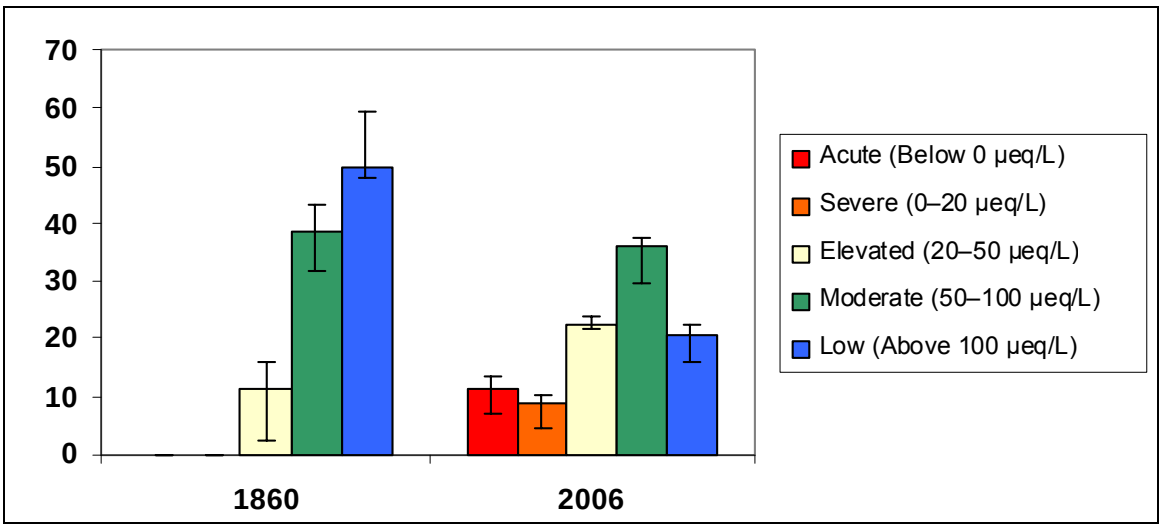


Figure 4.2-11. Percentage of Adirondack Case Study Area lakes in the five classes of acidification (i.e., Acute, Severe, Elevated, Moderate, Low) for years 1860 (preacidification) and 2006 (current condition) for 44 lakes modeled using MAGIC. Error bar indicates the 95% confidence interval.

The biological risk from current total nitrogen and sulfur deposition: Critical load assessment. In **Figure 4.2-12**, a critical load indicates the amount of acidic input of total sulfur and nitrogen deposition that a lake can neutralize and still maintain an ANC of 50 μeq/L. Sites labeled by red or orange circles have less neutralizing ability than sites labeled with yellow and green circles, and hence, indicate those lakes that are most sensitive to acidifying deposition, due to a host of environmental factors. Approximately 50% of the 169 lakes modeled in the Adirondack Case Study Area are sensitive or at risk to acidifying deposition.

In **Figure 4.2-13**, a critical load exceedance "value" indicates combined total sulfur and nitrogen deposition in year 2002 that is greater than the amount of deposition the lake could neutralize and still maintain the ANC level above each of the four different ANC limits of 0, 20, 50, and 100 μeq/L. For the year 2002, 18%, 28%, 44%, and 58% of the 169 lakes modeled received levels of combined total sulfur and nitrogen deposition that exceeded their critical load with critical limits of 0, 20, 50, and 100 μeq/L, respectively (**Table 4.2-3**).

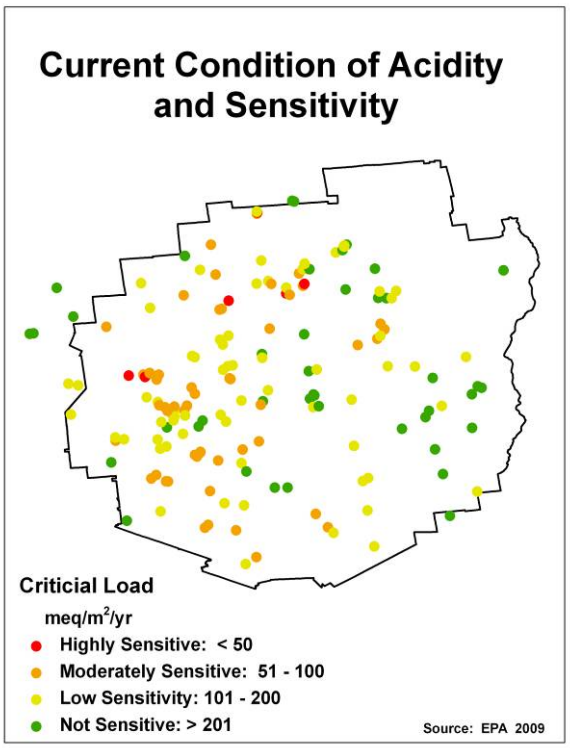


Figure 4.2-12. Critical loads of acidifying deposition that each surface waterbody in the Adirondack Case Study Area can receive while maintaining or exceeding an acid neutralizing capacity concentration of 50 μeq/L based on 2002 data. Watersheds with critical load values <100 meq/m^2/yr (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values >100 meq/m^2·yr (yellow and green circles) are the least sensitive sites.

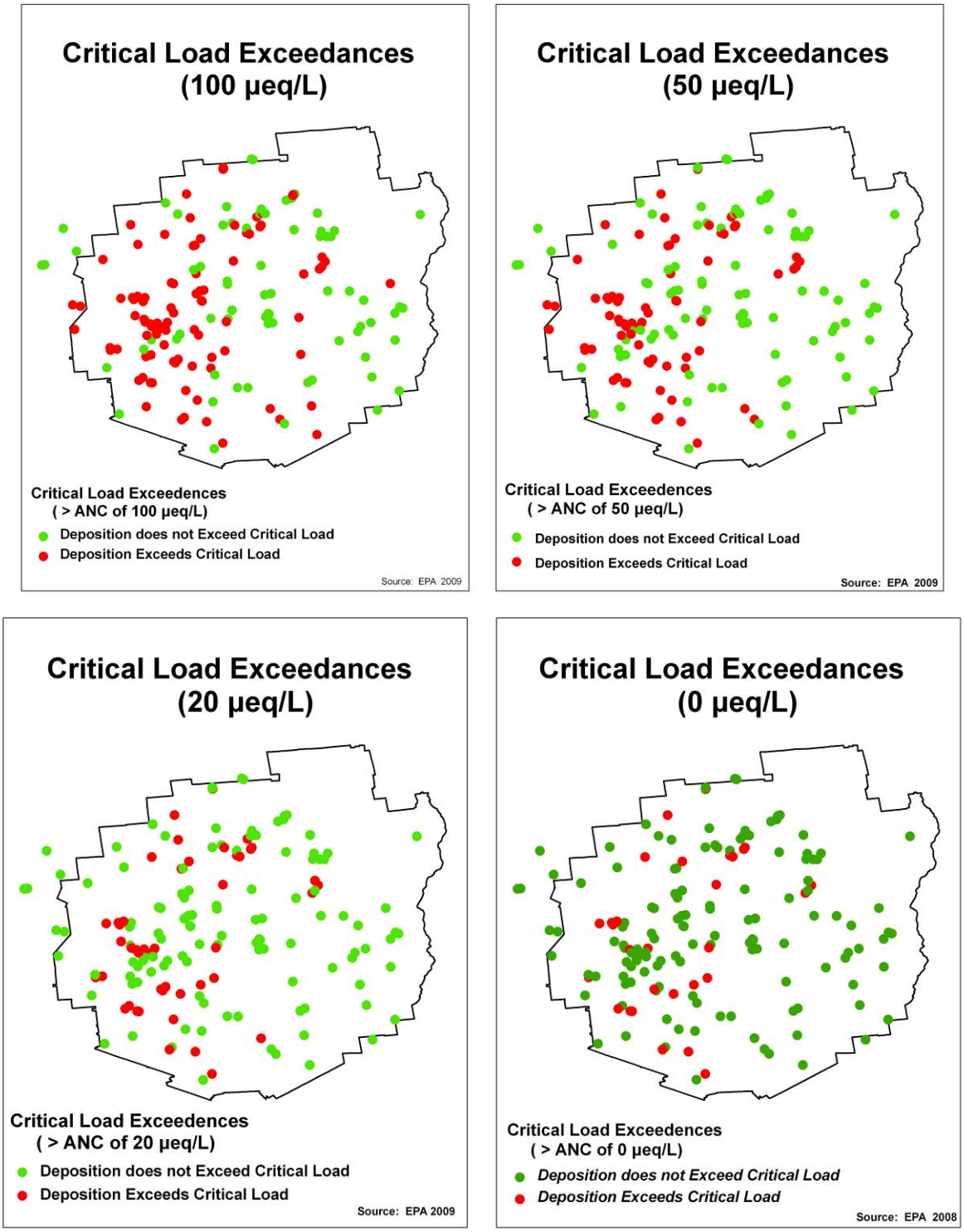


Figure 4.2-13. Critical load exceedances (red circles) based on 2002 deposition magnitudes for Adirondack Case Study Area waterbodies where the critical limit acid neutralizing capacity is 0, 20, 50, and 100 µeq/L, respectively. Green circles represent lakes where current total nitrogen and sulfur deposition is below the critical load (see **Table 4.2-3**).

Recovery from Acidification Given Current Emission Reductions.

In considering the future responses of lakes, the question becomes whether lakes can recover to healthy systems (i.e., ANC > 50 μeq/L) under current levels of deposition. The forecast model runs using MAGIC were used to determine whether current deposition could lead to recovery of the acidified lakes.

Based on a deposition scenario that maintains current emission levels up to years 2020 and 2050, the simulation forecast indicates no improvement in water quality over either of the periods. The percentage of lakes within the *Elevated* to *Acute Concern* classes remains the same in 2020 and 2050. Moreover, the percentage of modeled lakes classified as "not acidic" remains the same, suggesting that current emission will not likely improve the recovery from acidification.

Table 4.2-3. Critical Load Exceedances (Nitrogen + Sulfur Deposition > Critical Load) for 169 Modeled Lakes Within the TIME/LTM and EMAP Survey Programs. "No. Lakes" Indicates the Number of Lakes at the Given Acid Neutralizing Capacity Limit; "% Lakes" Indicates the Total Percentage of Lakes at the Given Acid Neutralizing Capacity Limit

ANC Limit 100 μeq/L		ANC Limit 50 μeq/L		ANC Limit 20 μeq/L		ANC Limit 0 μeq/L	
No. Lakes	**% Lakes**	**No. Lakes**	**% Lakes**	**No. Lakes**	**% Lakes**	**No. Lakes**	**% Lakes**
98	58	74	44	47	28	30	18
Lake No. = 169							

4.2.4.3 Current Conditions in Shenandoah Case Study Area Surface Waters

Current and Preacidification Conditions of Surface Waters

Since the mid-1990s, streams in the Shenandoah Case Study Area have shown slight signs of improvement in NO_3^- and SO_4^{2-} concentrations in surface waters. Deposition of SO_x and NO_x has decreased, but has not resulted in much improvement in NO_3^- and SO_4^{2-} stream concentrations (**Figure 4.2-14**). However, ANC concentrations increased from the about 50 μeq/L in the early 1990 to >75 μeq/L until 2002, when ANC levels declined back to 1991 to 1992 levels (**Figure 4.2-14**). It is not known what has caused this temporal pattern of ANC in this case study.

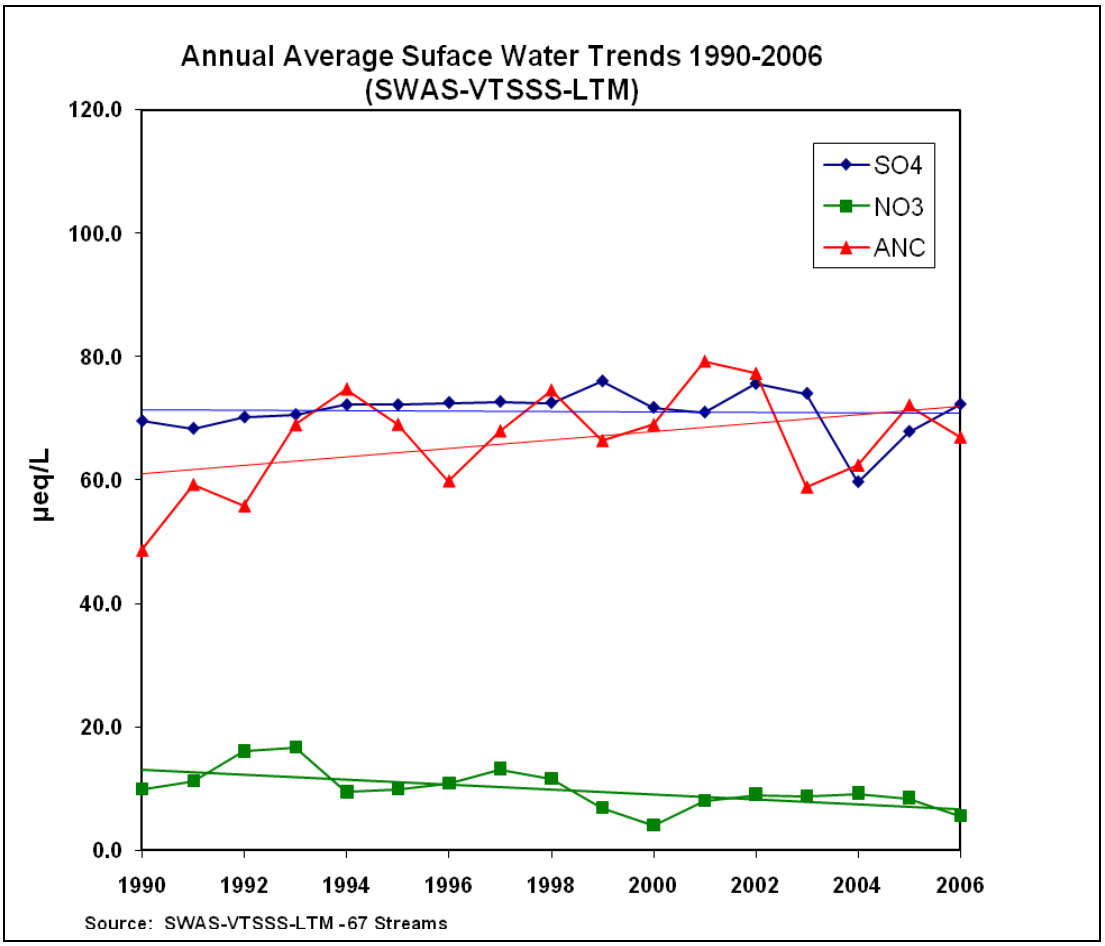


Figure 4.2-14. Trends over time for SO_4^{2-} (blue), NO_3^- (green) and acid neutralizing capacity (red) concentrations in VTSSS LTM-monitored streams in the Shenandoah Case Study Area.

The slight decline in SO_4^{2-} concentrations in surface waters of the Shenandoah Case Study Area is −0.09 µeq/L/year, while the decline in NO_3^- is −0.1 µeq/L/year. Current concentrations of NO_3^- and SO_4^{2-} are still well above preacidification conditions based on MAGIC model simulations. **Figure 4.2-15** and **Figure 4.2-16** show the condition of the streams in 1860 (preacidification) and in 2006 (current) conditions. On average, NO_3^- and SO_4^{2-} concentrations are 10- and 32-fold higher today, respectively (**Table 4.2-4**).

Table 4.2-4. Model Simulated Average Concentrations (and associated uncertainties) for Stream Chemistry at 60 Modeled Streams in the Shenandoah Case Study Area for Preacidification and Current Conditions

	Pre-Acidification		**Current**	
µeq/L	**Avg.**	**(±)**	**Avg.**	**(±)**
ANC	101.4	9.5	57.9	4.5
SO_4^{2-}	2.1	0.1	68.0	8.4
NO_3^-	0.6	0.01	6.2	0.1
NH_4^+	N/A	N/A	N/A	N/A

N/A = Not available.

Current NO_3^- and SO_4^{2-} concentrations are 10- and 32-fold higher in Shenandoah Case Study Area streams today than in 1860.

Although NO_3^- deposition can be an important factor in acid precipitation, these results demonstrated that acidification in the Shenandoah Case Study Area is currently being driven by SO_4^{2-} deposition since current average SO_4^{2-} concentration is 11-fold greater than NO_3^- concentrations in surface waters (**Table 4.2-4**).

An increase in ANC concentrations of +0.08 μeq/L/year has occurred since 1990, but for the majority of the 68 monitoring sites of the Shenandoah Case Study Area, ANC levels did not significantly differ from 1990 to 2006.

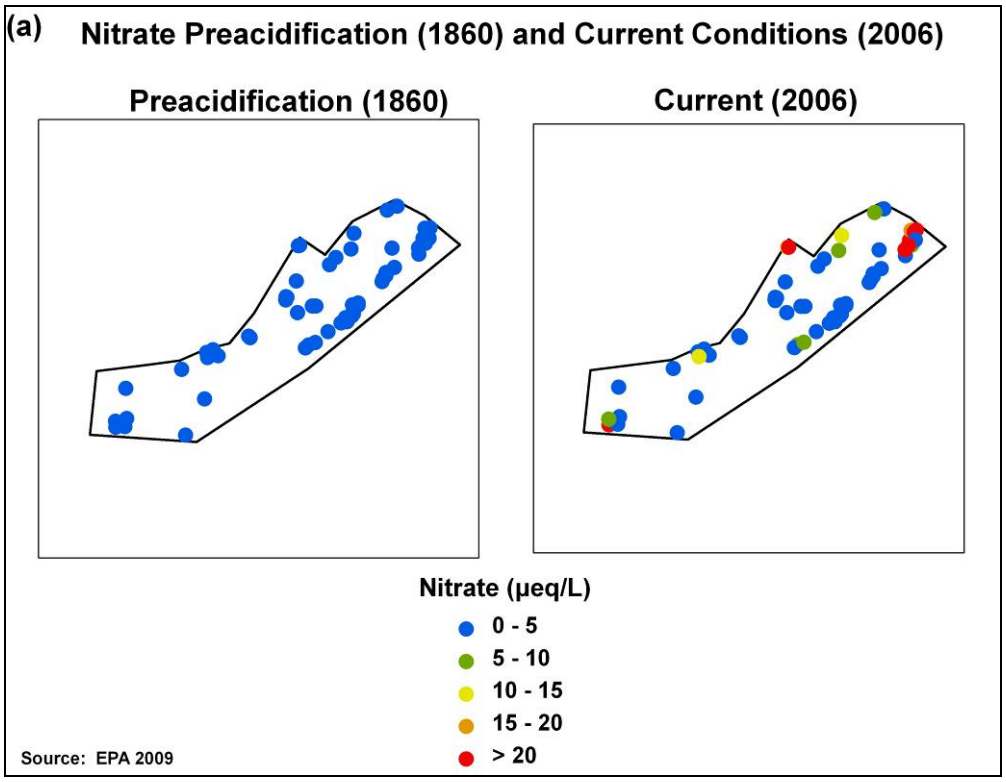


Figure 4.2-15. NO_3^- concentrations of preacidification (1860) and current (2006) conditions based on hindcasts of 60 streams modeled using MAGIC in the Shenandoah Case Study Area.

Based on the monitored annual average for ANC, there are a significant number of streams in the Shenandoah Case Study Area that currently have *Elevated* (ANC <50 μeq/L) to *Severe* (ANC <20 μeq/L) classes of acidity (**Figure 4.2-17**). Only 45% of monitored streams are considered "not acidic" (i.e., of *Moderate* to *Low Concern*) and thus have water quality that poses less risk to aquatic biota. Approximately 55% of all monitored streams have a current risk of *Elevated, Severe*, or *Acute Concern*. Of that 55%, 18% experience episodic acidification

(*Severe Concern*) and 12% are chronically acidic (i.e., *Acute Concern*) at current level of acidifying deposition and ambient concentration of NO_x and SO_2.

An estimate of how much of this current condition is attributed to the effects of acidifying deposition can be made by examining the hindcast conditions of the streams. Based on the MAGIC model simulations, preacidification average ANC concentration of the 60 modeled streams was 101.4±9.5 μeq/L, as compared with 57.9 ±4.5 μeq/L for today (**Table 4.2-4**).

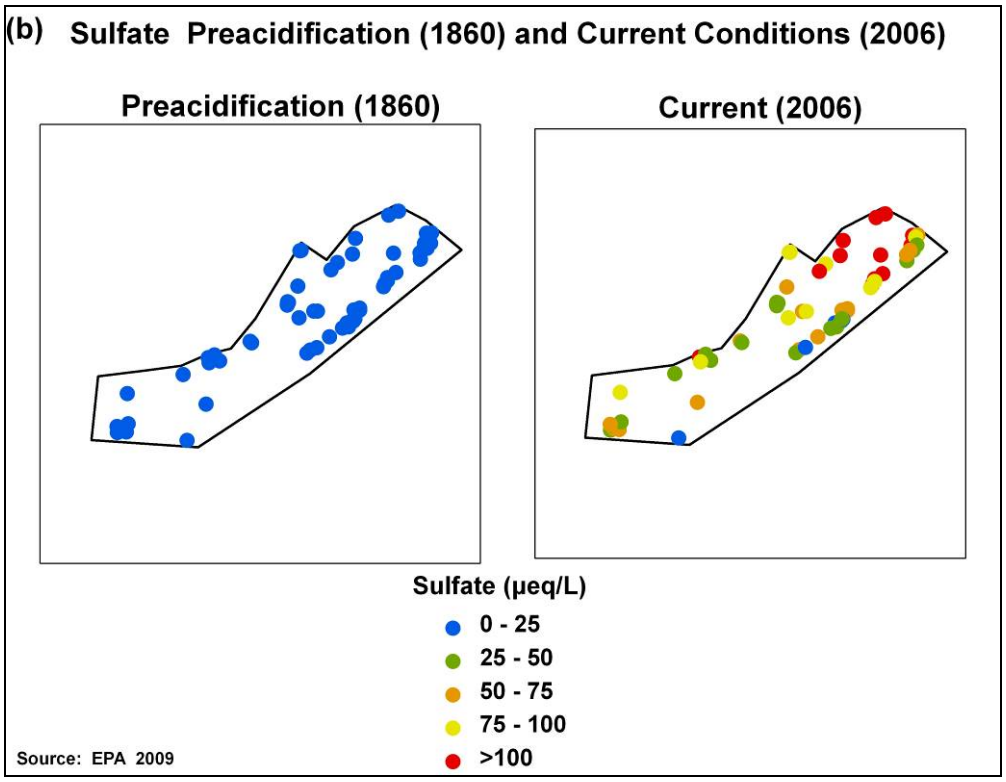


Figure 4.2-16. SO_4^{2-} concentrations of preacidification (1860) and current (2006) conditions based on hindcasts of 60 streams modeled using MAGIC in the Shenandoah Case Study Area.

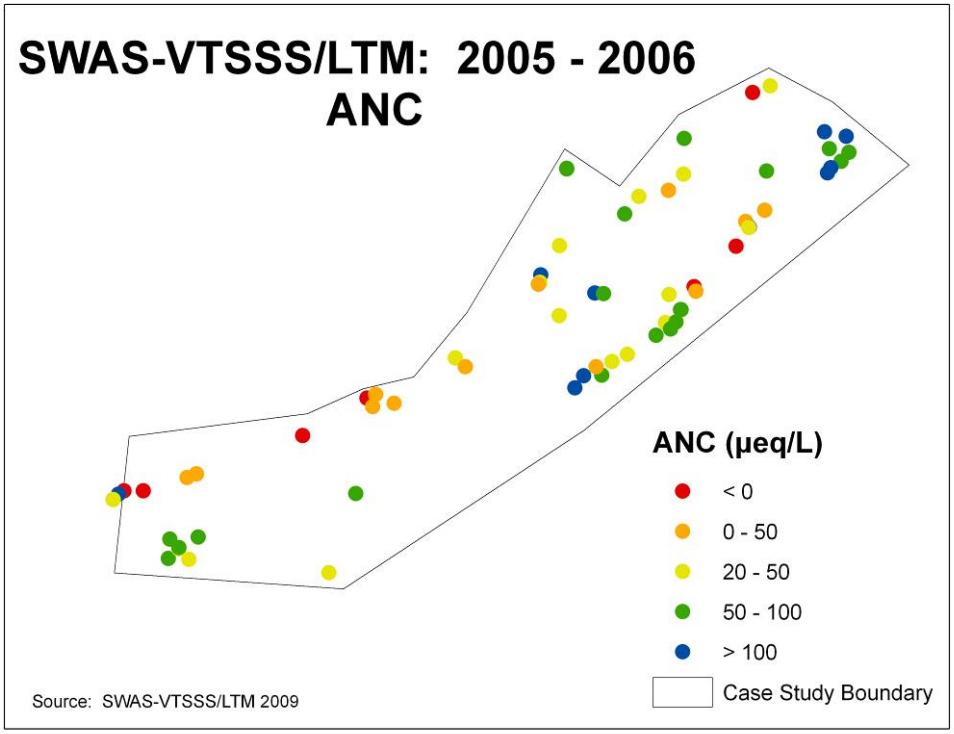


Figure 4.2-17. Acid neutralizing capacity concentrations from 67 streams in the VTSSS-SWAS/LTM monitoring network in the Shenandoah Case Study Area (2005–2006 data).

Furthermore, 92% of the modeled streams likely were "not acidic" prior to the onset of acidifying deposition (**Figure 4.2-18** and **Figure 4.2-19**). The other 8% of streams had ANC of >27 µeq/L. The hindcast simulations produced no streams with *Acute* or *Severe Concern*. These results based on model reconstructions suggest that current and recent ambient concentrations of NO_3^- and SO_4^{2-} and their associated anthropogenic acidifying deposition are likely responsible for acidifying (ANC below 50 µeq/L) approximately 45% of streams modeled in the Shenandoah Case Study Area.

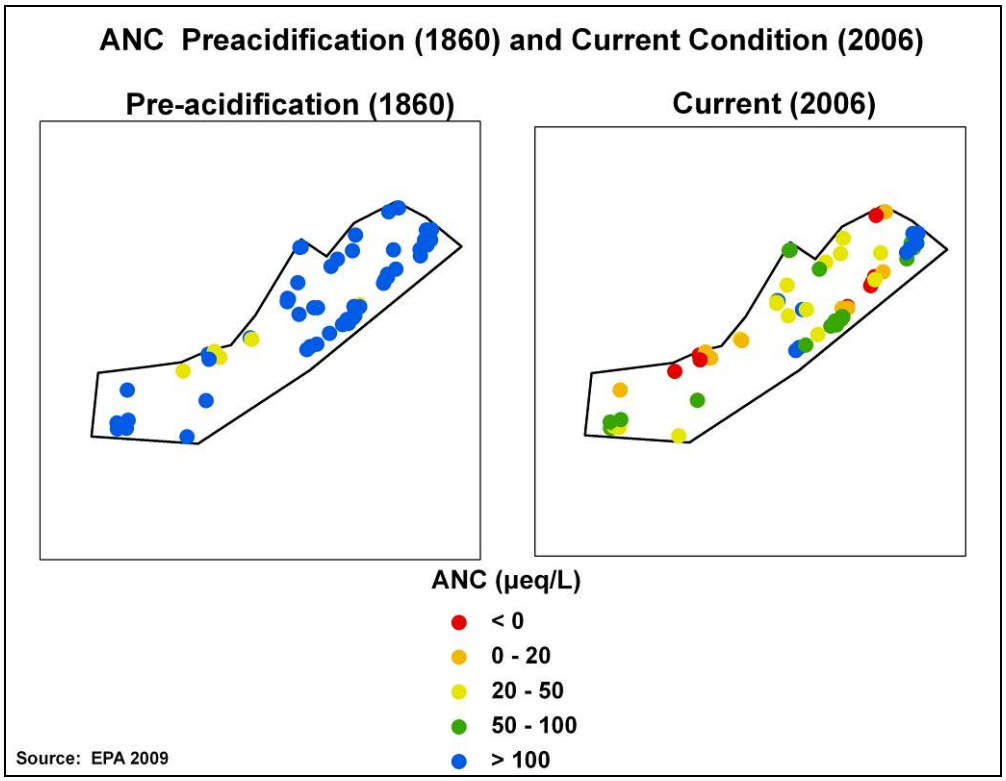


Figure 4.2-18. Acid neutralizing capacity concentrations of preacidification (1860) and current (2006) conditions based on hindcasts of 60 streams modeled using MAGIC in the Shenandoah Case Study Area.

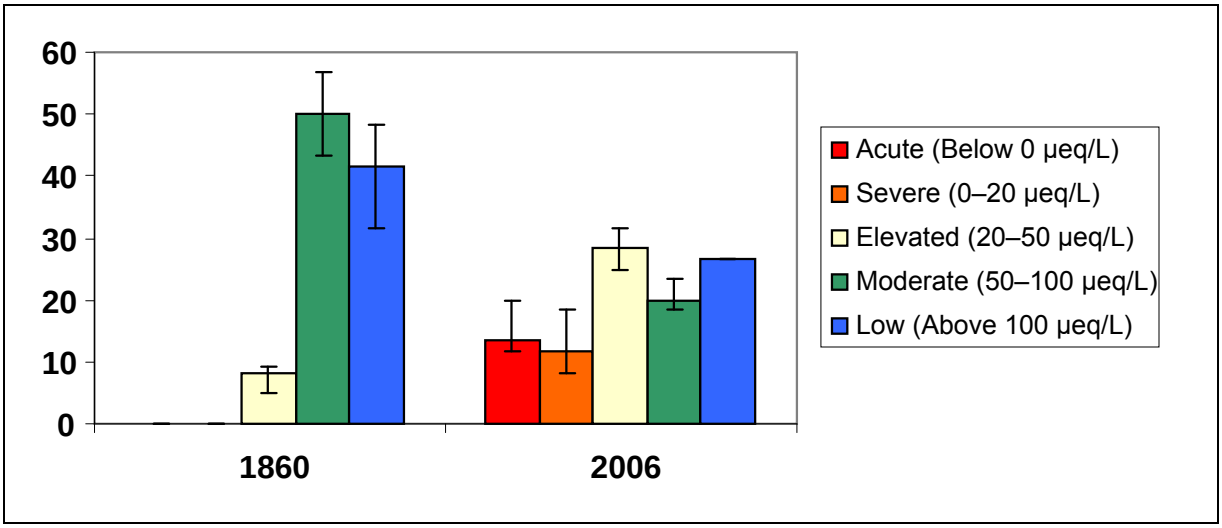


Figure 4.2-19. Percentage of streams in the five classes of acidification (i.e., Acute, Severe, Elevated, Moderate, Low Concern) for years 2006 and 1860 (pre-acidification) for 60 streams modeled using MAGIC in the Shenandoah Case Study Area. The number of streams in each class is above the bar. Error bars indicate the 95% confidence interval.

The biological risk from current total nitrogen and sulfur deposition: Critical load assessment. In **Figure 4.2-20**, sites labeled by red or orange circles have less ability to neutralize acid inputs than sites labeled with yellow and green circles, and hence, indicate those streams that are most sensitive to acidifying deposition, due to a host of environmental factors. Approximately 75% of the 60 streams modeled in the Shenandoah Case Study Area are sensitive or at risk to acidifying deposition.

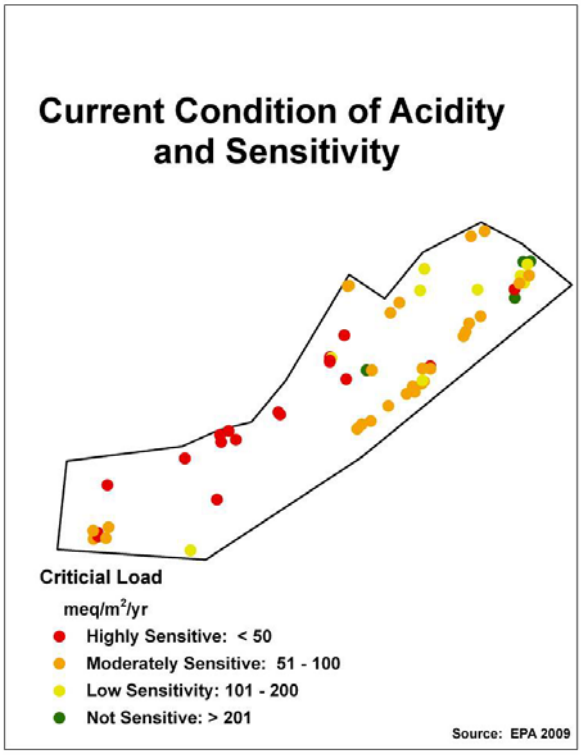


Figure 4.2-20. Critical loads of surface water acidity for an acid neutralizing capacity concentration of 50 µeq/L for streams in the Shenandoah Case Study Area. Each circle represents an estimated amount of acidifying deposition (i.e., critical load) that each stream's watershed can receive and still maintain a surface water acid neutralizing capacity concentration >50 µeq/L. Watersheds with critical load values <100 meq/m^2/yr (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values >100 meq/m^2/yr (yellow and green circles) are the least sensitive sites.

In **Figure 4.2-21**, a critical load exceedance "value" indicates combined total sulfur and nitrogen deposition in year 2002 that is greater than the amount of deposition the stream could buffer and still maintain the ANC level of above each of the four different ANC limits of 0, 20, 50, and 100 µeq/L. For the year of 2002, 52%, 72%, 85%, and 92% of the 60 streams modeled receive levels of combined total sulfur and nitrogen deposition that exceeded their critical load with critical limits of 0, 20, 50, and 100 µeq/L, respectively (**Table 4.2-5**).

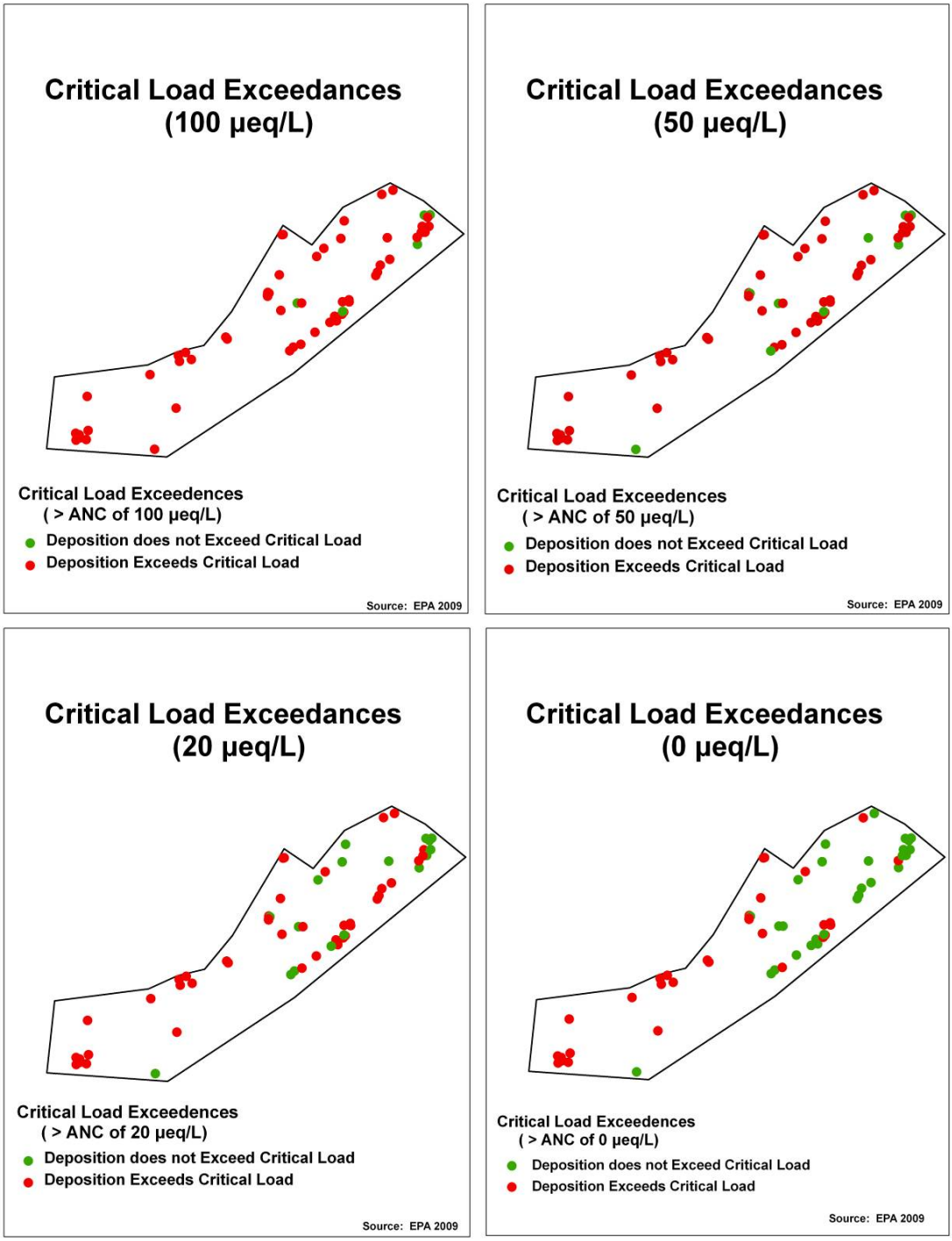


Figure 4.2-21. Critical load exceedances for acid neutralizing capacity concentrations of 0, 20, 50, and 100 µeq/L for streams in the Shenandoah Case Study Area. Green circles represent lakes where current total nitrogen and sulfur deposition is below the critical load and that maintain an acid neutralizing capacity concentration of 0, 20, 50, and 100 µeq/L, respectively. Red circles represent streams where current total nitrogen and sulfur deposition exceeds the critical load, indicating they are currently impacted by acidifying deposition. See **Table 4.2-5**.

Table 4.2-5. Critical Load Exceedances (Nitrogen + Sulfur Deposition > Critical Load) for 60 Modeled Streams Within the VTSSS-LTM Monitoring Program in the Shenandoah Case Study Area. "No. Streams" Indicates the Number of Streams at the Given Acid Neutralizing Capacity Limit; "% Streams" Indicates the Total Percentage of Streams at the Given Acid Neutralizing Capacity Limit.

ANC Limit 100 µeq/L		ANC Limit 50 µeq/L		ANC Limit 20 µeq/L		ANC Limit 0 µeq/L	
No. Streams	**% Streams**	**No. Streams**	**% Streams**	**No. Streams**	**% Streams**	**No. Streams**	**% Streams**
55	92	51	85	43	72	31	52
Stream No. = 60							

Recovery from Acidification Given Current Emission Reductions

Based on a deposition scenario that maintains current emission levels up to years 2020 and 2050, a large number of streams in the Shenandoah Case Study Area will still have *Elevated* to *Acute* problems with acidity. In the short term (i.e., by the year 2020) and in the long term (i.e., by the year 2050), the response of the 60 modeled streams shows no improvement in the number of streams that are "not acidic." In fact, the modeling suggests conditions may degrade by 2050 under current emission levels. From 2006 to 2050, the percentage of streams in *Acute Concern* increases by 5%, while the percentage of streams in *Moderate Concern* decreases by 5%.

4.2.5 Degree of Extrapolation to Larger Assessment Areas

The EPA EMAP and Regional-EMAP (REMAP) surveys have been conducted on lakes and streams throughout the United States with the objective of characterizing the ecological condition of various populations of surface waters. EMAP surveys are probability surveys where sites are selected using a spatially balanced systematic randomized sample, so that the results can be used to make regional estimates of surface water conditions (e.g., number of lakes, length of stream). Sampling typically consists of measures of aquatic biota, water chemistry, and physical habitat. With respect to acidifying deposition effects, two EMAP surveys were conducted in the 1990s: the Northeastern Lake Survey and the Mid-Atlantic Highlands Assessment (MAHA) of streams. To make more precise estimates of the effects of acidifying deposition, the sampling grid was intensified to increase the sample-site density in the Adirondack Case Study Area and New England Upland areas known to be especially susceptible to acidifying deposition. The

MAHA study was conducted on 503 stream sites from 1993 to 1995 in the states of West Virginia, Virginia, Pennsylvania, Maryland, and Delaware and the Catskill Mountain region of New York (Herlihy et al., 2000). Results from both of these surveys were used to develop and select the sampling sites for the TIME program.

The TIME program and the LTM program are two surface water chemistry monitoring programs, administered by EPA, that inform the assessment of aquatic ecosystem responses to changes in atmospheric deposition. These efforts focus on portions of the United States most affected by the acidifying influence of total sulfur and nitrogen deposition, including lakes in the Adirondack Case Study Area and in New England, and streams in the Shenandoah Case Study Area.

At the core of the TIME project is the concept of probability sampling, whereby each sampling site is chosen statistically from a predefined target population. The target populations in these regions include lakes and streams likely to be responsive to changes in acidifying deposition, defined in terms of ANC. Measurement of Gran ANC uses the Gran technique to find the inflection point in an acid-base titration of a water sample (Gran, 1952). In the Northeast, the TIME target population consists of lakes with a Gran ANC <100 μeq/L. In the mid-Atlantic, the target population is upland streams with Gran ANC <100 μeq/L. In both regions, the sample sites selected for future monitoring were selected from the EMAP survey sites in the region that met the TIME target population definition. Each lake or stream is sampled annually (in summer for lakes; in spring for streams), and results are extrapolated with known confidence to the target population(s) as a whole using the EMAP site population expansion factors or weights (Larsen et al., 1994; Larsen and Urquhart, 1993; Stoddard et al., 1996; Urquhart et al., 1998).

Data from 43 Adirondack Case Study Area lakes can be extrapolated to the target population of low ANC lakes in that region. There are about 1,000 low-ANC Adirondack Case Study Area lakes, out of a total population of 1,842 lakes with surface areas greater than 1 hectare (ha). Data from 30 lakes (representing about 1,500 low-ANC lakes, out of a total population of 6,800) form the basis for TIME monitoring in New England. Probability monitoring of mid-Atlantic streams began in 1993. Stoddard et al. (2003) analyzed data from 30 low-ANC streams in the Northern Appalachian Plateau (representing about 24,000 kilometer (km) of low-ANC stream length out of a total stream length of 42,000 km). After pooling TIME target sites taken from both MAHA and another denser random sample in 1998, there are now 21

TIME sites in the Blue Ridge and Ridge and Valley that can be used for trend detection in this aggregate region in the mid-Atlantic in addition to the Northern Appalachian Plateau ecoregion.

As a complement to the statistical lake and stream sampling in TIME, the LTM program samples a subset of generally acid-sensitive lakes and streams that have long-term data, many dating back to the early 1980s. These sites are sampled 3 to 15 times per year. Monitored water chemistry variables include pH, ANC, major anions and cations, monomeric Al, Si, specific conductance, dissolved organic carbon, and dissolved inorganic carbon. Details of LTM data from each region include the following:

- **New England lakes.** Data from 24 New England lakes were available for the trend analysis reported by Stoddard et al. (2003) for the time period 1990 to 2000. The majority of New England LTM lakes have mean Gran ANC values ranging from 20 to 100 μeq/L; two higher ANC lakes (Gran ANC between 100 and 200 μeq/L) are also monitored.
- **Adirondack lakes.** The trend analysis of Stoddard et al. (2003) included data from 48 Adirondack lakes. Sixteen of the lakes have been monitored since the early 1980s; the others were added to the program in the 1990s. The Adirondack LTM dataset includes both seepage and drainage lakes, most with Gran ANC values in the range –50 to 100 μeq/L; three lakes with Gran ANC between 100 μeq/L and 200 μeq/L are also monitored.
- **Appalachian Plateau streams.** Data from four streams in the Catskill Mountains (collected by the USGS; Murdoch and Stoddard, 1993) and five streams in Pennsylvania (collected by Pennsylvania State University; DeWalle and Swistock, 1994) were analyzed by Stoddard et al. (2003). All of the Northern Appalachian LTM streams have mean Gran ANC values in the range 25 to 50 μeq/L.
- **Upper Midwest lakes.** Forty lakes in the Upper Midwest were originally included in the LTM project, and due to funding constraints, sampling has continued at only a subset of Wisconsin lakes, as well as an independent subset of seepage lakes in the state. The data reported by Stoddard et al. (2003) included 16 lakes (both drainage and seepage) sampled quarterly (Webster et al., 1993) and 22 seepage lakes sampled annually in the 1990s. All of the Upper Midwest LTM lakes exhibit mean Gran ANC values from 30 to 80 μeq/L.
- **Ridge/Blue Ridge streams.** Data from the Ridge and Blue Ridge provinces consist of a large number of streams sampled quarterly throughout the 1990s as part of the Virginia Trout Stream Sensitivity Study (Webb et al., 1989) and a small number of streams sampled more intensively (as in the Northern Appalachian Plateau). A total of 69 streams

had sufficient data for the trend analyses by Stoddard et al. (2003). All of these streams were located in the Ridge section of the Ridge and Valley province or within the Blue Ridge province, and all were within the state of Virginia. Mean Gran ANC values for the Ridge and Blue Ridge data range from 15 to 200 μeq/L, with 7 of the 69 sites exhibiting mean Gran ANC >100 μeq/L.

Appendix 4's Attachment 4.B of the Aquatic Acidification case study report provides a more complete discussion of the EMAP/TIME/LTM programs.

4.2.6 Current Conditions for the Adirondack Case Study Area and the Shenandoah Case Study Area

4.2.6.1 Regional Assessment of All Lakes in the Adirondack Case Study Area

Estimating regional risks due to ambient NO_x and SO_x concentrations and deposition associated with acidification in lakes involved scaling up from the 169 modeled lakes to the entire population of lakes in the Adirondack Case Study Area. Of the 169 lakes modeled for critical loads, 117 of these lakes were within the 1,842 in the entire Adirondack Case Study Area. Using weighting factors derived from the EMAP probability survey and critical load calculations from the 117 lakes, estimates of exceedances were derived for the entire 1,842 lakes in the Adirondack Case Study Area. Based on this approach, 945, 666, 242, and 135 lakes exceed their critical load for ANC limits of 100, 50, 20, and 0 μeq/L, respectively (**Table 4.2-6**).

Given a low level of protection from acidification (i.e., an ANC limit of 20 μeq/L), the current risk of acidification is 242 lakes, or 13% of the total population. Because some lakes in the Adirondack Case Study Area have natural sources of acidity, some lakes would have never had ANC concentrations of above 50 and 100 μeq/L. For this reason, the actual number of lakes at risk of acidification at an ANC level of 50 and 100 μeq/L is lower than the estimate based solely using the critical load criterion. Using the hindcast simulation from the MAGIC model, 11% of modeled lakes have preacidification (1860) ANC levels of less than 50 μeq/L. Excluding these naturally acidic lakes, the current risk of acidification is 666 lakes or 36% for a moderate protective ANC concentration of 50 μeq/L. For an ANC level of 100 μeq/L, 51% of lakes have natural ANC concentrations below 100 μeq/L. Excluding these naturally acidic lakes, the current risk is 945 lakes or 51% for a protective ANC concentration of 100 μeq/L. Even with corrections

for natural acidity, 8 to 41% of lakes in the Adirondack Case Study Area are at risk of acidification given current ambient concentration of NO_x and SO_2.

Because some lakes in the Adirondack Case Study Area have natural sources of acidity, some lakes would never have ANC concentrations above 50 or 100 µeq/L, even in the absence of all anthropogenically derived acidifying deposition. Based on the hindcast simulations of 44 lakes using the MAGIC model, no modeled lakes have ANC levels below 20 µeq/L. However, 5 modeled lakes or 11% have ANC concentrations between 22 and 47 µeq/L. This equates to approximately 300 lakes or 16% of the representative population of lakes in the Adirondack Case Study Area that likely had preacidification ANC concentrations below 50 µeq/L. On the other hand, potentially more than 52% of lakes likely had preacidification ANC concentrations below 100 µeq/L. The higher percentage of lakes in the regional population compared to the modeled population is because the lake classes or sizes likely to have a preacidification ANC concentration below 50 or 100 µeq/L are more abundant in the Adirondack Case Study Area than lakes with a preacidification ANC concentration above 50 or 100 µeq/L.

Table 4.2-6. Critical Load Exceedances (Nitrogen + Sulfur Deposition > Critical Load) for the Regional Population of 1,842 Lakes in the Adirondack Case Study Area That Are from 0.5 to 2000 ha in Size and at Least 1 m in Depth. Estimates Are Based on the EMAP Lake Probability Survey of 1991 to 1994.

ANC Limit 100 µeq/L		ANC Limit 50 µeq/L		ANC Limit 20 µeq/L		ANC Limit 0 µeq/L	
No. Lakes	**% Lakes**	**No. Lakes**	**% Lakes**	**No. Lakes**	**% Lakes**	**No. Lakes**	**% Lakes**
945	51	666	36	242	13	135	7
Lake No. = 1842							

4.2.6.2 Regional Assessment of All Streams in the Shenandoah Case Study Area

The 60 trout streams modeled are characteristic of first- and second-order streams on nonlimestone bedrock in the Shenandoah Case Study Area. Because of the strong relationship between bedrock geology and ANC in this region, it is possible to consider the results in the context of similar trout streams in the Southern Appalachian Mountains that have similar bedrock geology and size. The total number of brook trout streams in the Shenandoah Case Study Area represented is 440, of which 308 lie on limestone and/or have not been significantly affected by human activity within their watersheds. In addition, the 60 modeled streams are a

subset of 344 streams sampled by the Virginia Trout Stream Sensitivity Study, of which 304 represent the different sizes and bedrock types found to be sensitive to acidification. Using the 304 streams to which the analysis applies directly as the total, 279, 258, 218, and 157 streams exceed their critical load for 2002 deposition with critical limits of 100, 50, 20, and 0 μeq/L, respectively. However, it is likely that many more of the ~12,000 trout streams in the Shenandoah Case Study Area would exceed their critical load given the extent of similar bedrock geology outside the study area in the Southern Appalachian Mountains.

4.2.7 Ecological Effect Function for Aquatic Acidification

Atmospheric deposition of NO_x and SO_x contributes to acidification in aquatic ecosystems through the input of acid anions, such as NO_3^- and SO_4^{2-}. The acid balance of headwater lakes and streams is controlled by the level of this acidifying deposition of NO_3^- and SO_4^{2-} and a series of biogeochemical processes that produce and consume acidity in watersheds. In basic soils, inputs of NO_3^- and SO_4^{2-} will have little or no effect on the acid balance of headwater waterbodies. The biotic integrity of freshwater ecosystems is then a function of the acid-base balance and the resulting acidity-related stress on the biota that occupy the water.

The calculated ANC of the surface waters is a measure of the acid-base balance:

$$ANC = [BC]^* - [AN]^* \quad (1)$$

where [BC]* and [AN]* are the sum of base cations and acid anions (NO_3^- and SO_4^-), respectively. Although ANC has not generally been used as a parameter for predicting the health of the biotic communities, it provides useful information of the potential acidity related biotic stress and, hence, is a useful ecological indicator.

The ANC concentration then provides a link between the surface water acidification and the ecological integrity of the aquatic community where a given level of ANC corresponds to an ecological effect (see **Table 4.2-1**). It also provides a link between the deposition of NO_x and SO_x and the acidification through the input of acid anions of NO_3^- and SO_4^-.

Equation (1) forms the basis of the linkage between deposition and surface water acidic condition and the modeling approach used. Given some "target" ANC concentration [ANC_{limit}]), which protects biological integrity, the amount of deposition of acid anions (AN) or depositional load (DL(N) + DL(S)) is simply the input flux of acid anions from atmospheric deposition that result in a surface water ANC concentration equal to the [ANC_{limit}] when balanced by the

sustainable flux of base cations input and the sinks of nitrogen and sulfur in the lake and watershed catchment. The sustainable flux of base cations input and sinks of nitrogen and sulfur is equal to the uptake (N_{upt}), immobilization (N_{imm}), and denitrification (N_{den}) of nitrogen in the catchment, the in-lake retention of nitrogen (N_{ret}) and sulfur (S_{ret}), and the preindustrial flux of base cations ($[BC]_0^*$) to the watershed. Thus, the amount of deposition that will maintain an ANC level above an ANC_{limit} is described as

$$DL(N) + DL(S) = \{fN_{upt} + (1 - r)(N_{imm} + N_{den}) + (N_{ret} + S_{ret})\} + ([BC]_0^* - [ANC_{limit}])Q \quad (2)$$

where f and r are dimensionless parameters that define the fraction of forest cover in the catchment and the lake/catchment ratio, respectively, and Q is runoff. Surface water concentrations are converted to fluxes by multiplying concentration by runoff Q (mm/yr). Several major assumptions are made: (1) steady-state conditions exist, (2) the effect of nutrient cycling between plants and soil is negligible, (3) there are no significant nitrogen inputs from sources other than atmospheric deposition, (4) ammonium leaching is negligible because any inputs are either taken up by biota or adsorbed onto soils or nitrate compounds, and (5) long-term sinks of sulfate in the catchment soils are negligible.

It is not possible to define a maximal loading for a single total of acidity (i.e., both nitrogen and sulfur deposition) because the acid anions sulfate and nitrate behave differently in the way they are transported with hydrogen ions; one unit of deposition of sulfur will not have the same net effect on surface water ANC as an equivalent unit of nitrogen deposition. However, the individual maximum and minimum depositional loads for nitrogen and sulfur are defined when nitrogen or sulfur do not contribute to the acidity in the water. The maximum depositional load for sulfur ($DL_{max}(S)$) is equal to the amount of sulfur the catchment can remove and still maintain an ANC concentration above the ANC_{limit}:

$$DL_{max}(S) = [([BC]_0^* - [ANC_{level}])Q]/ (1- p_s) \quad (3)$$

when nitrogen deposition does not contribute to the acidity balance and where p_s defines the fraction of in-lake retention of $S_{ret.}$ Given the assumption that the long-term sinks of sulfate in the catchment soils are negligible, the amount of sulfur entering the catchment is equal to the amount loaded to the surface water. For this reason, the minimal amount of sulfur is equal to zero:

$$DL_{min}(S) = 0 \quad (4)$$

In the case of nitrogen, $DL_{min}(N)$ is the minimum amount of deposition of total nitrogen (NH_x + NO_x) that catchment processes can effectively remove (e.g., $N_{upt} + N_{imm} + N_{den} + N_{ret}$) without contributing to the acidic balance:

$$DL_{min}(N) = fN_{upt} + (1\text{-}r)(N_{imm} + N_{den}) \quad (5)$$

The $DL_{max}(N)$ is the load for total nitrogen deposition when sulfur deposition is equal to zero:

$$DL_{max}(N) = fN_{upt} + (1\text{-}r)(N_{imm} + N_{den}) + [([BC]_0^* - [ANC_{level}])Q]/ (1\text{-}p_n) \quad (6)$$

where p_n defines the fraction of in-lake retention of N_{ret}.

In reality, neither nitrogen nor sulfur deposition will ever be zero, so the depositional load for the deposition of one is fixed by the deposition of the other, according to the line defining in **Figure 4.2-22**.

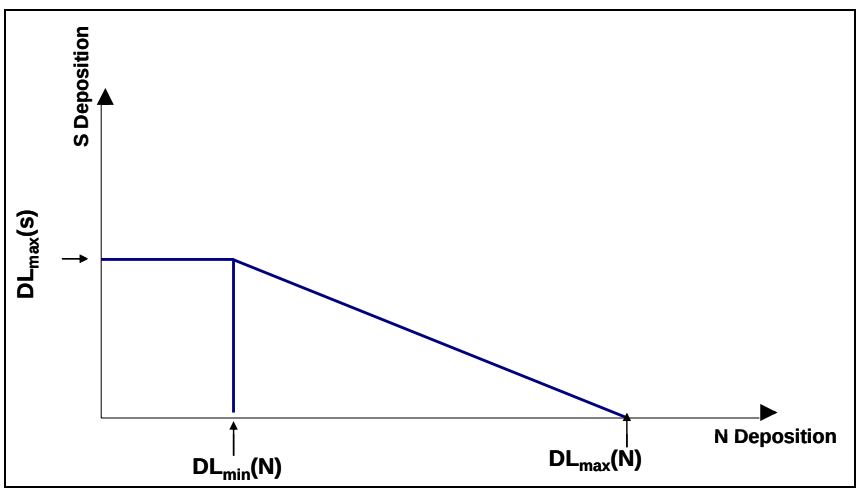
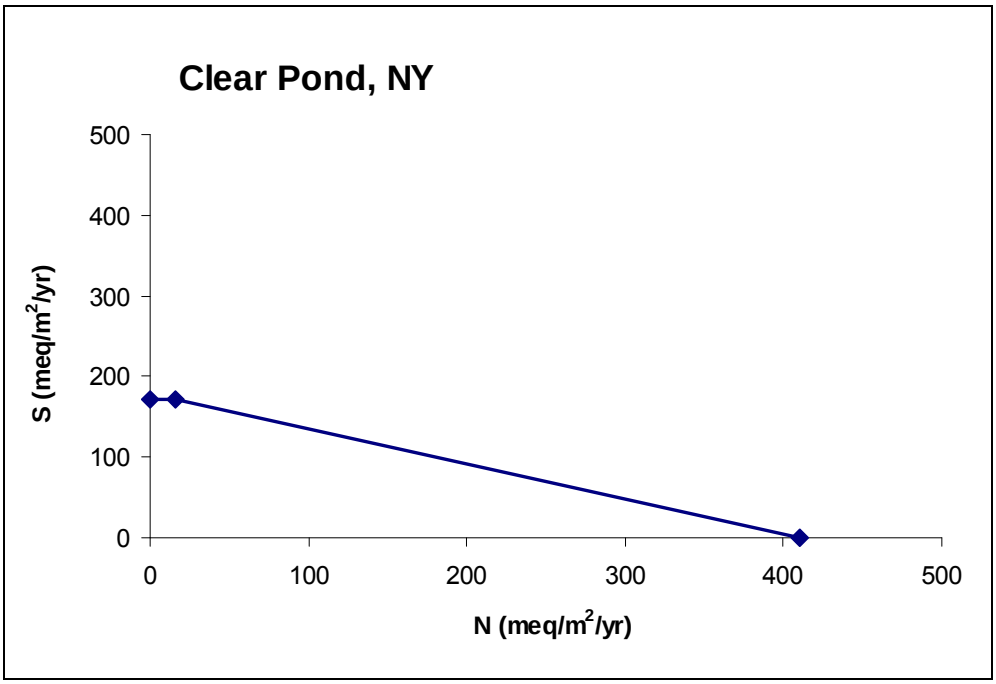


Figure 4.2-22. The depositional load function defined by the model.

The thick lines indicate all possible combinations of depositional loads of nitrogen and sulfur acidity that a catchment can receive and still maintain an ANC concentration equal to its ANClimit. Note that in the above formulation, individual depositional loads of nitrogen and sulfur are not specified; each combination of depositions (S_{dep} and N_{dep}) fulfilling Equations 2 through 6. (**Figure 4.2-23**) shows the depositional load function for two lakes in New York



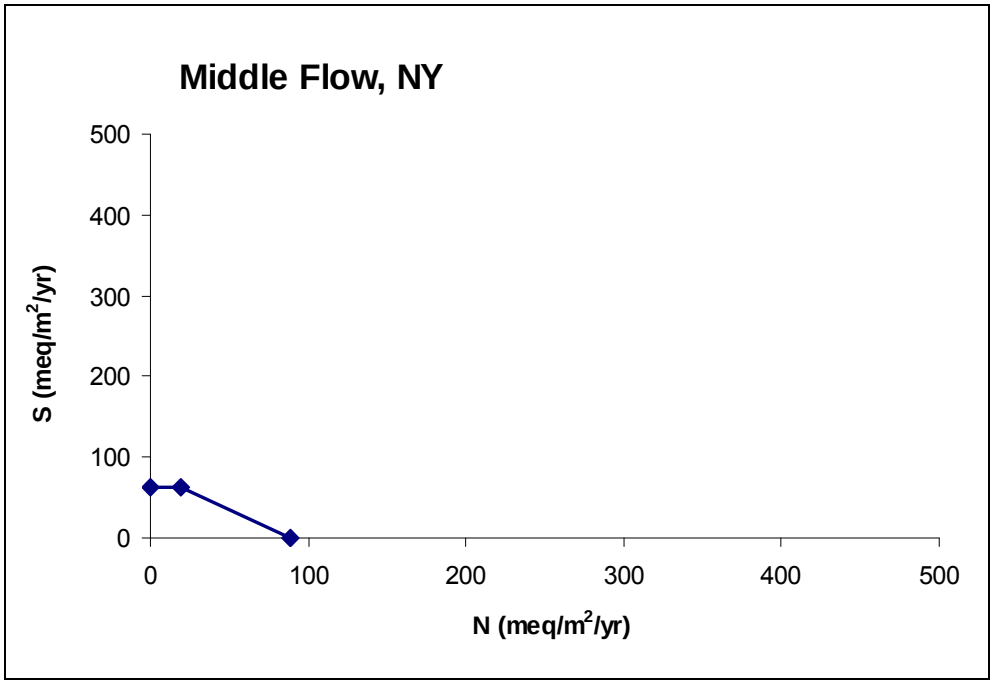


Figure 4.2-23. Deposition load graphs for Clear Pond and Middle Flow Lake, New York.

4.2.8 Uncertainty and Variability

4.2.8.1 Steady-State Critical Load Modeling

There is uncertainty associated with the parameters in the steady-state critical load model used to estimate aquatic critical loads. The strength of the critical load estimate and the exceedance calculation relies on the ability to estimate the catchment-average base-cation supply

(i.e., input of base cations from weathering of bedrock and soils and air), runoff, and surface water chemistry. The uncertainty associated with runoff and surface water measurements is fairly well known. However, the ability to accurately estimate the catchment supply of base cations to a water body is still poorly known. This is important because the catchment supply of base cations from the weathering of bedrock and soils is the factor that has the most influence on the critical load calculation and also has the largest uncertainty (Li and McNulty, 2007). Although the approach to estimate base-cation supply in the case study areas (e.g., F-factor approach) has been widely published and analyzed in Canada and Europe, and has been applied in the United States (e.g., Dupont et al., 2005), the uncertainty in this estimate is unclear and is likely large. For this reason, an uncertainty analysis of the state-steady critical load model was completed to evaluate the uncertainty in the critical load and exceedances estimations.

A probabilistic analysis using a range of parameter uncertainties was used to assess (1) the degree of confidence in the exceedance values and (2) coefficient of variation (CV) of the critical load and exceedance values. The probabilistic framework is Monte Carlo, whereby each steady-state input parameter varies according to specified probability distributions and their range of uncertainty (**Table 4.2-7**). The purpose of the Monte Carlo methods was to propagate the uncertainty in the model parameters in the steady-state critical load model.

Table 4.2-7. Parameters used and their uncertainty range. The range of surface water parameters (e.g. CA, MG, CL, NA, NO_3, SO_4) were determined from surface water chemistry data for the period from 1992 to 2006 from the TIME-LTM monitoring network. Runoff(Q) and Acidic Deposition were set at 50% and 25%.

Parameter	Units	Uncertainty range	Distribution
Q	µeq/L	50%	Normal
CA	µeq/L	65%	Normal
MG	µeq/L	64%	Normal
CL	µeq/L	52%	Normal
NA	µeq/L	58%	Normal
NO_3	µeq/L	30%	Normal
SO_4	µeq/L	57%	Normal
Acidic Deposition (NO_x & SO_4)	meq/L	25%	Lognormal

Within the Monte Carlo analysis, model calculations were run a sufficient number of times (i.e. 1,000 times) to capture the range of behaviors represented by all variables. The analysis tabulated the number of lakes where the confidence interval is entirely below the critical load, the confidence interval is entirely above the critical load, and the confidence interval straddles zero. Similar results are given for the number of sites with all realizations above the critical load, all realizations below the critical load, and some realizations above and some below the critical load. An inverse cumulative distribution function for exceedances was constructed from the 1000 model runs for each site, which describes the probability of a site to exceed its critical load. For each site, the probability of exceeding its critical load (i.e. probability of exceedance) is determined at the percent of the cumulative frequency distribution that lies above zero. The probability of exceedance, where the percentage of the cumulative frequency distribution lies above zero, was calculated for all sites and assigned to one of the following five classes:

- • 0–5% probability: unlikely to be exceeded
- • 5–25% probability: relatively low risk of exceedance
- • 25–75% probability: potential risk of exceedance
- • 75–95% probability: relatively high risk of exceedance
- • >95% probability: highly likely to be exceeded.

This provides a measure of the degree of confidence in whether the site exceeds its critical load. The CDF for Little Hope Pond is shown in **Figure 4.2-24**.

The CV was also calculated on each site for both the critical load and exceedance calculations. The CV represents the ratio of the standard deviation to the mean and is a useful statistic for comparing the degree of variation in the data. The CV allows a determination of how much uncertainty (risk) comparison to its mean.

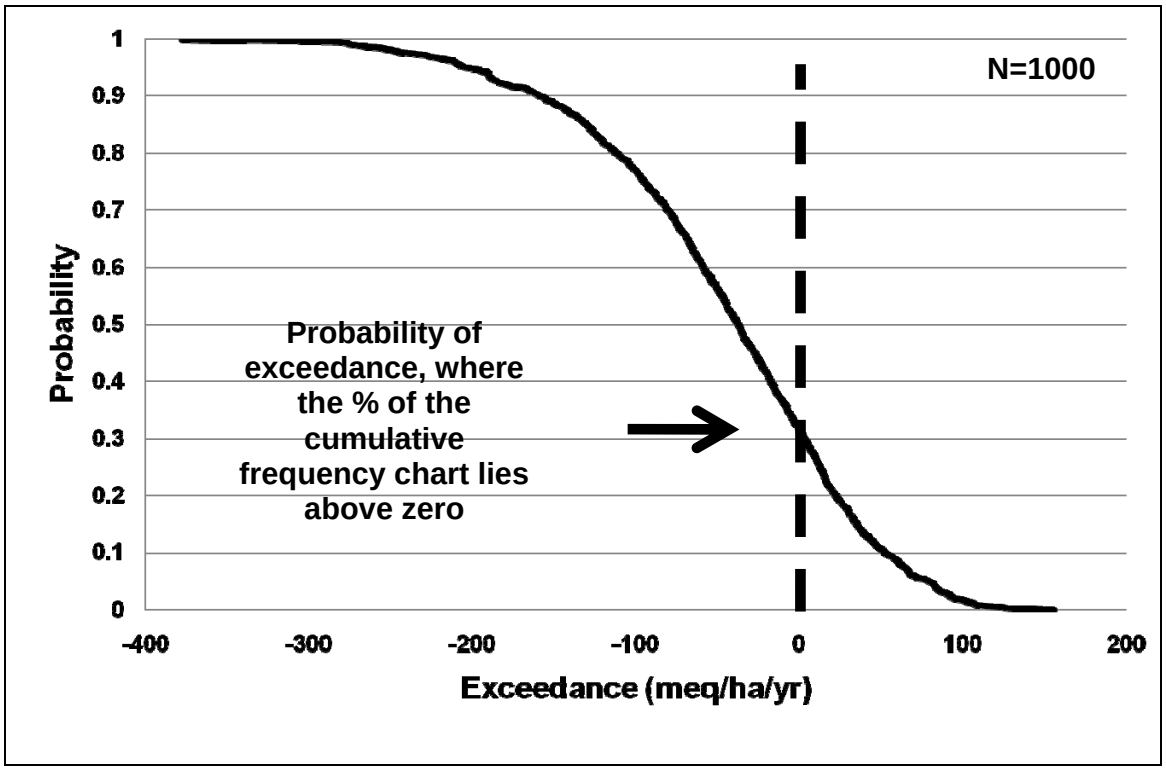


Figure 4.2-24. The inverse cumulative frequency distribution for Little Hope Pond. The x-axis shows critical load exceedance in meq/ha/yr and y-axis is the probability. The dashed lines represent zero exceedance. In the case of Little Hope Pond, the dash line divides mostly the probability distribution on the left hand side, indicating Little Hope Pond has a relative low probability of being exceeded (0.3). Critical load and exceedances values were based on a critical level of protection of ANC = 50 μeq/L.

Results of the Uncertainty Analysis

The means and CVs for critical load (CL(A)) and exceedances (EX(A)) values are shown for all sites in **Table 4.2-8** for four ANC limits (0, 20, 50, 100 μeq/L. The average CV for the various critical load values for all sites are remarkably low except for those calculated using a critical limit of 100 μeq/L. It is noticeable that although all the relevant input parameters have spreads of 25% to 65%, the CVs for CL(A) are only 4%, 5%, 9%, and 100% for critical load limits of 0%, 20%, 50%, and 100% μeq/L, respectively. In the case of the absolute value of the exceedances (EX(A)), the average CVs for all sites are higher, but still relatively low at 18%, 17%, 25%, and 33%. The individual CV for each site and an ANC limit of 50 μeq/L are shown in **Figure 4.2-25**. Although the average CV is relatively small for the population of sites modeled, an individual site CV can varies from 1% to 45% for CL(A) and to 5% to over 100% for EX(A). This difference is due to the high degree of uncertainty in site-specific parameters for

particular sites and a low degree of confidence in the exceedance value itself for these sites. In addition, when the mean value is near zero, as is the case for exceedance values, the CV is sensitive to small changes in the mean, which likely explains why some sites have high CV compare to others.

Table 4.2-8. Means and coefficients of variation of critical loads and exceedances for surface water.

Parameter	Critical load Limit (µeq/L)	Mean (meq/L)	Coefficient of variation (%)
CL(A)	0	247.8	4
	20	227.0	5
	50	196.7	9
	100	140.3	100
EX(A)	0	-178.3	18
	20	-157.6	17
	50	-127.2	25
	100	-75.0	33

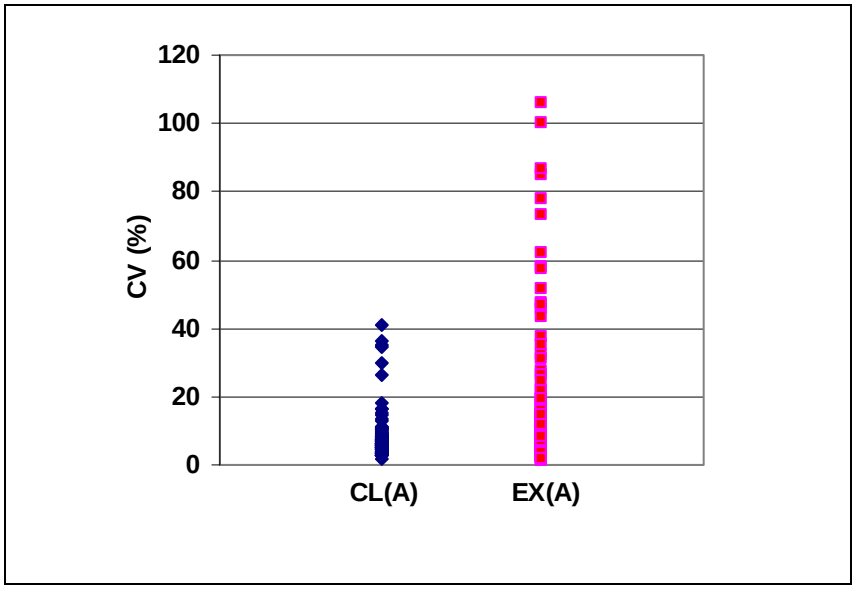


Figure 4.2-25. Coefficients of variation of surface water critical load for acidity CL(A) and exceedances (EX(A)). Critical load and exceedances values were based on a critical level of protection of ANC = 50 µeq/L.

The probability of exceedance results, where the percentage of the cumulative frequency distribution lies above zero, are shown in **Figure 4.2-26**. Those areas that have less than 5%

probability of exceedance are those with a high degree of confidence that the critical loads are not exceeded; conversely, areas with more than a 95% probability of exceedance are the most certain to be exceeded.

For the sites in the aquatic case study areas, the probability of exceeding the critical load at an ANC limit of 0, 20, 50, and 100 μeq/L were relatively high. The waterbodies that exceeded their critical loads had a greater than 80% probability of doing so. The range of probability of exceedance was from 80% to 98%, indicating a relatively high confidence that these sites exceeded their critical load. The results suggest a relatively robust estimate of critical loads and exceedance rates for the case study areas. It is important to note that this analysis may understate the actual uncertainty because some of the range and distribution types of parameters are not well known for the United States at this time.

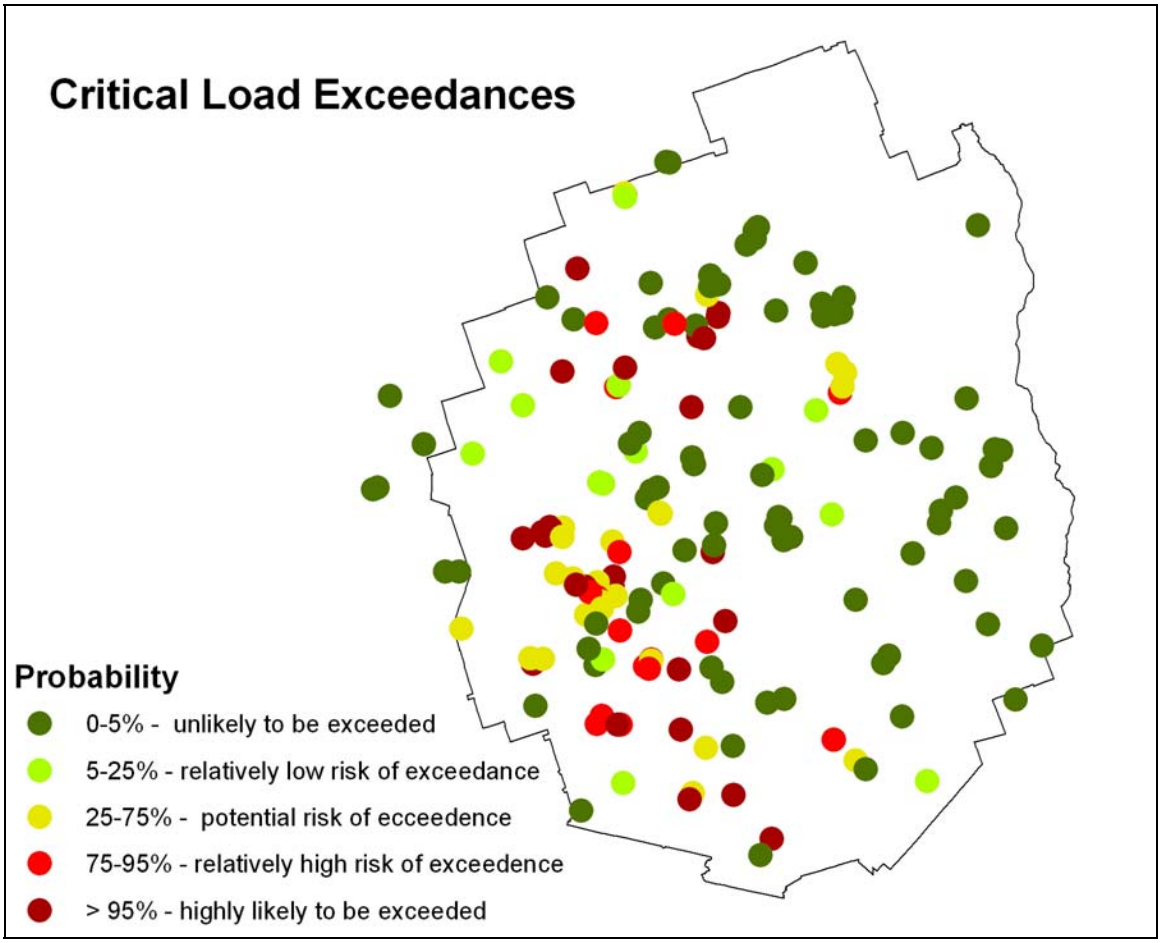


Figure 4.2-26. Probability of exceedance of critical load for acidity for 2002.

4.2.8.2 MAGIC Modeling

The sensitivity analyses described above were designed to address specific assumptions or decisions that had to be made in order to assemble the data for the 44 or 60 modeled sites in a form that could be used for calibration of the model. In all cases, the above analyses address the questions of what the effect would have been if alternate available choices had been taken. These analyses were undertaken for a subset of sites for which the alternate choices were available at the same sites. As such, the analyses above are informative, but they provide no direct information about the uncertainty in calibration or simulation arising from the choices that were incorporated into the final modeling protocol for all sites. That is, having made the choices about soils assignments, high elevation deposition, and stream samples for calibration (and provided an estimate of their inherent uncertainties), the need arises for a procedure for estimating uncertainty at each and all of the individual sites using the final selected calibration and simulation protocol.

These simulation uncertainty estimates were derived from the multiple calibrations at each site provided by the "fuzzy optimization" procedure employed in this project. For each of the modeled sites, 10 distinct calibrations were performed with the target values, parameter values, and deposition inputs for each calibration, reflecting the uncertainty inherent in the observed data for the individual site. The effects of the uncertainty in the assumptions made in calibrating the model (and the inherent uncertainties in the data available) can be assessed by using all successful calibrations for a site when simulating the response to different scenarios of future deposition. The model then produces an ensemble of simulated values for each site. The median of all simulated values in a year is considered the most likely response of the site. The simulated values in the ensemble can also be used to estimate the magnitude of the uncertainty in the projection. Specifically, the difference in any year between the maximum and minimum simulated values from the ensemble of calibrated parameter sets can be used to define an "uncertainty" (or a "confidence") width for the simulation at any point in time. All 10 of the successful model calibrations will lie within this range of values. These uncertainty widths can be produced for any variable and any year to monitor model performance.

Direct comparison of simulated versus observed water chemistry values were compared to determine the uncertainty and variability in the MAGIC model output. Average water chemistry (SO_4^{2-}, NO_3^-, and ANC) simulated versus observed values during the calibration

period (i.e., reference year) were compared for all modeled sites. In addition, simulated versus observed average yearly values for ANC for the period of 1980 to 2007 for 4 sites were completed. The observed water chemistry data were from the Adirondack Long-Term Monitoring Virginia Trout Stream Sensitivity Survey (VTSSS) Long-Term Monitoring, and Temporally Integrated Monitoring of Ecosystems (TIME) water quality measurement programs and represent annual average concentrations. The statistic of Root Mean Squared Error (RMSE) was also calculated for predicted versus observed values for both the calibration period and the period of 1980 to 2007. RMSE is a frequently used measure of the differences between values predicted by a model or an estimator and the values actually observed from the thing being modeled or estimated. The RMSE was based on an annual average ANC over a 5-year period.

Results of the Uncertainty Analysis

Based on the MAGIC model simulations, the 95% confidence interval for the pre-acidification and current average ANC concentrations of the 44 modeled lakes was 106.8 to 134.0 and 50.5 to 81.8 μeq/L, respectively, which is on average a 15 μeq/L difference in ANC concentrations, or 10%. The 95% confidence interval for pre-acidification and current average ANC concentrations of the 60 modeled streams was 91.9 to 110.9 and 53.4 to 62.4 μeq/L, respectively, which is on average 8 μeq/L difference in ANC concentration, or 5%.

These direct comparisons show good agreement between simulated and observed water quality values. Results of predicted versus observed average water chemistry during the calibration period (i.e., reference year) are in **Figures 4.2-27and 4.2-28** for MAGIC modeling. The model showed close agreement with measured values at all sites for the one-year comparison of modeled values. For all sites' SO_4^{2-}, NO_3^-, and ANC simulations, the RMSE for predicted versus observed values were 0.1 μeq/L, 0.05 μeq/L, and 3.5 μeq/L for lakes in the Adirondack Case Study Area and 1.0 μeq/L, 0.06 μeq/L, and 1.0 μeq/L for streams in the Shenandoah Case Study Area. Plots of simulated and observed ANC values for the period of 1980 to 2007 are graphed in **Figures 4.2-29 and 4.2-30** for two lakes in the Adirondack Case Study Area and for two streams in the Shenandoah Case Study Area. The RMSE of ANC was 7.8 μeq/L and 5.1 μeq/L for the two lakes in the Adirondack Case Study Area and was 11.8 μeq/L and 4.0 μeq/L for the two streams in Shenandoah Case Study Area.

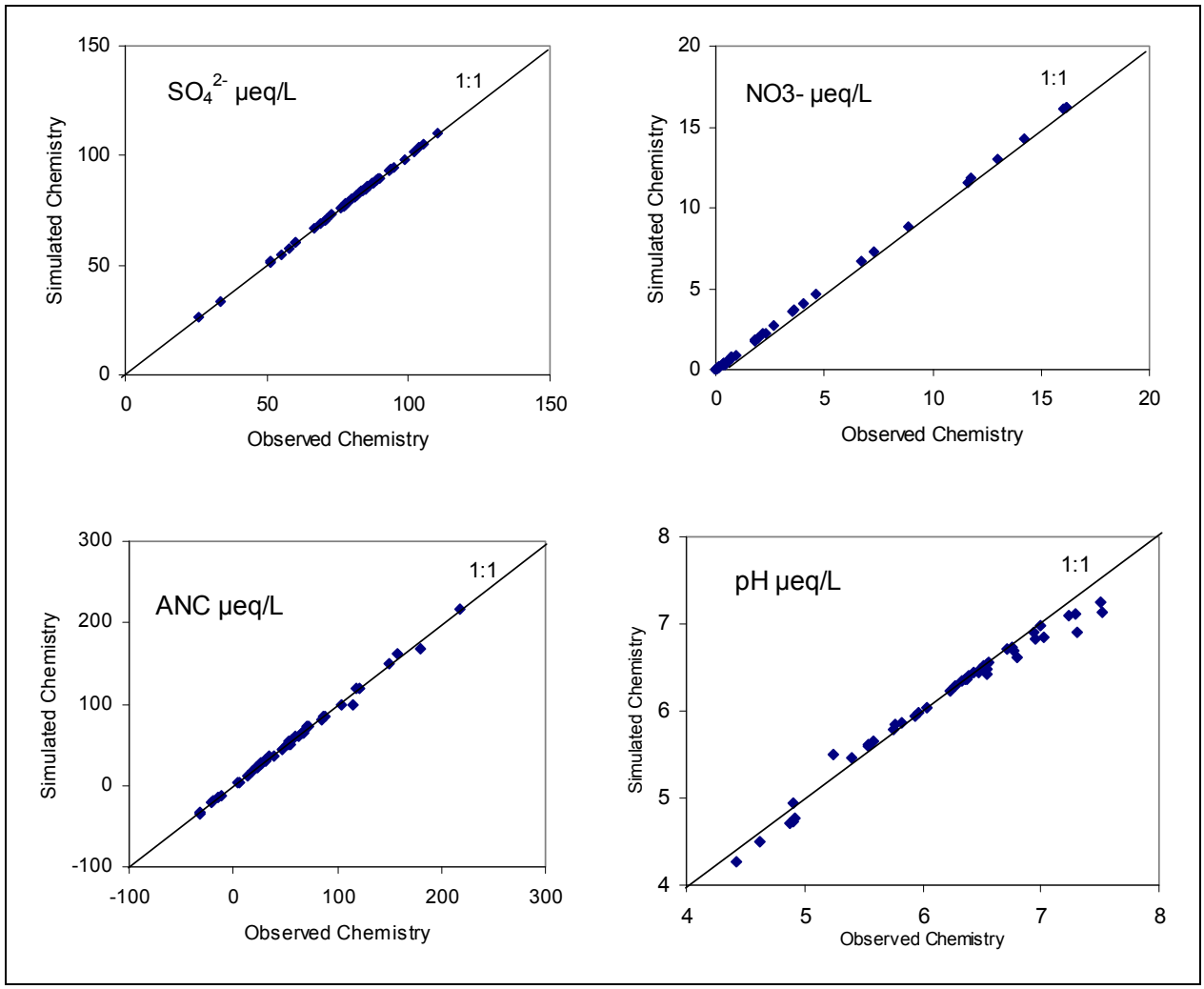


Figure 4.2-27. Simulated versus observed annual average surface water SO_4^{2-}, NO_3^-. ANC, and pH during the model calibration period for each of the 44 lakes in the Adirondack Case Study Area. The black line is the 1:1 line.

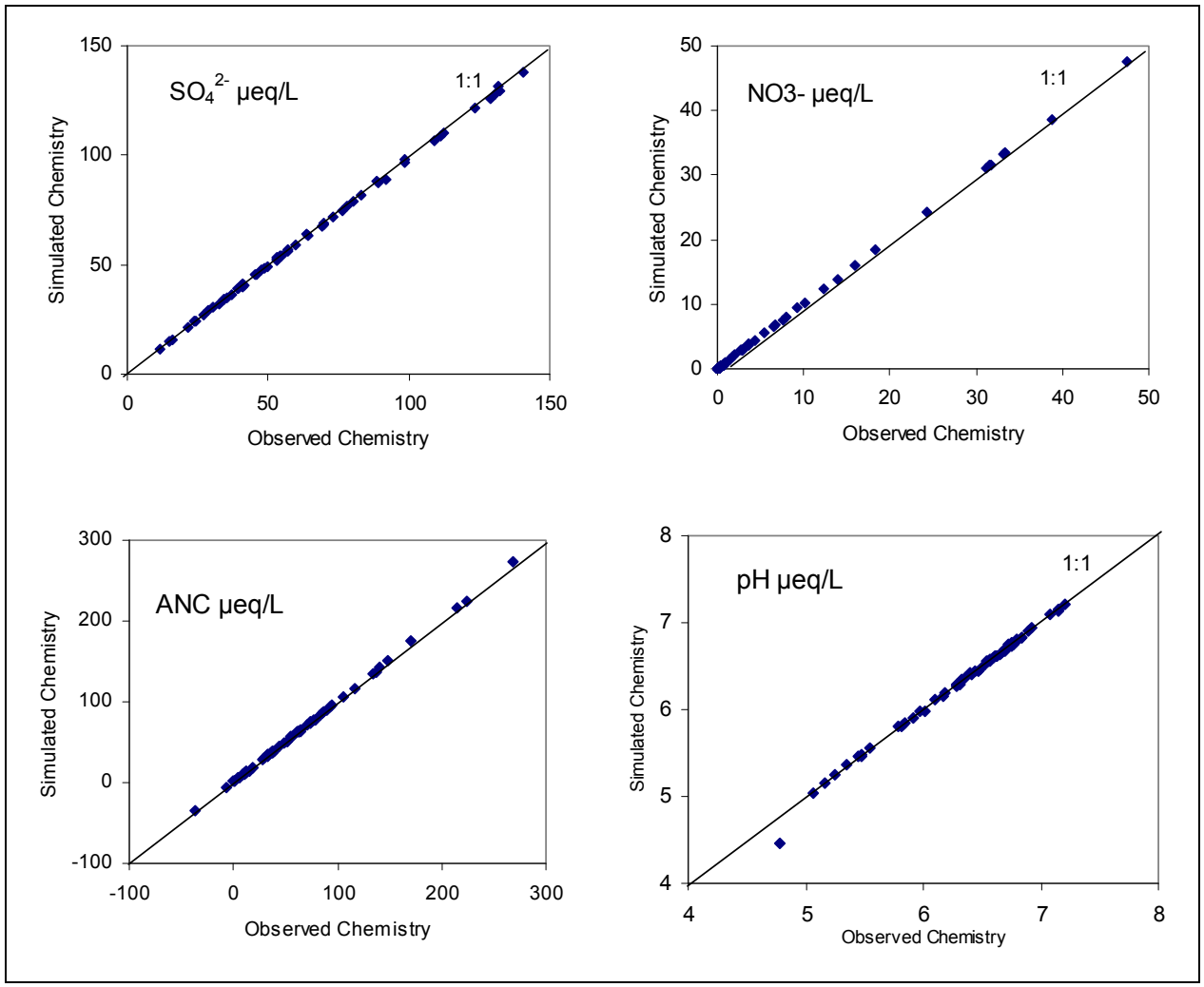


Figure 4.2-28. Simulated versus observed annual average surface water SO_4^{2-}, NO_3^-. ANC, and pH during the model calibration period for each of the 60 streams in the Shenandoah Case Study Area. The black line is the 1:1 line.

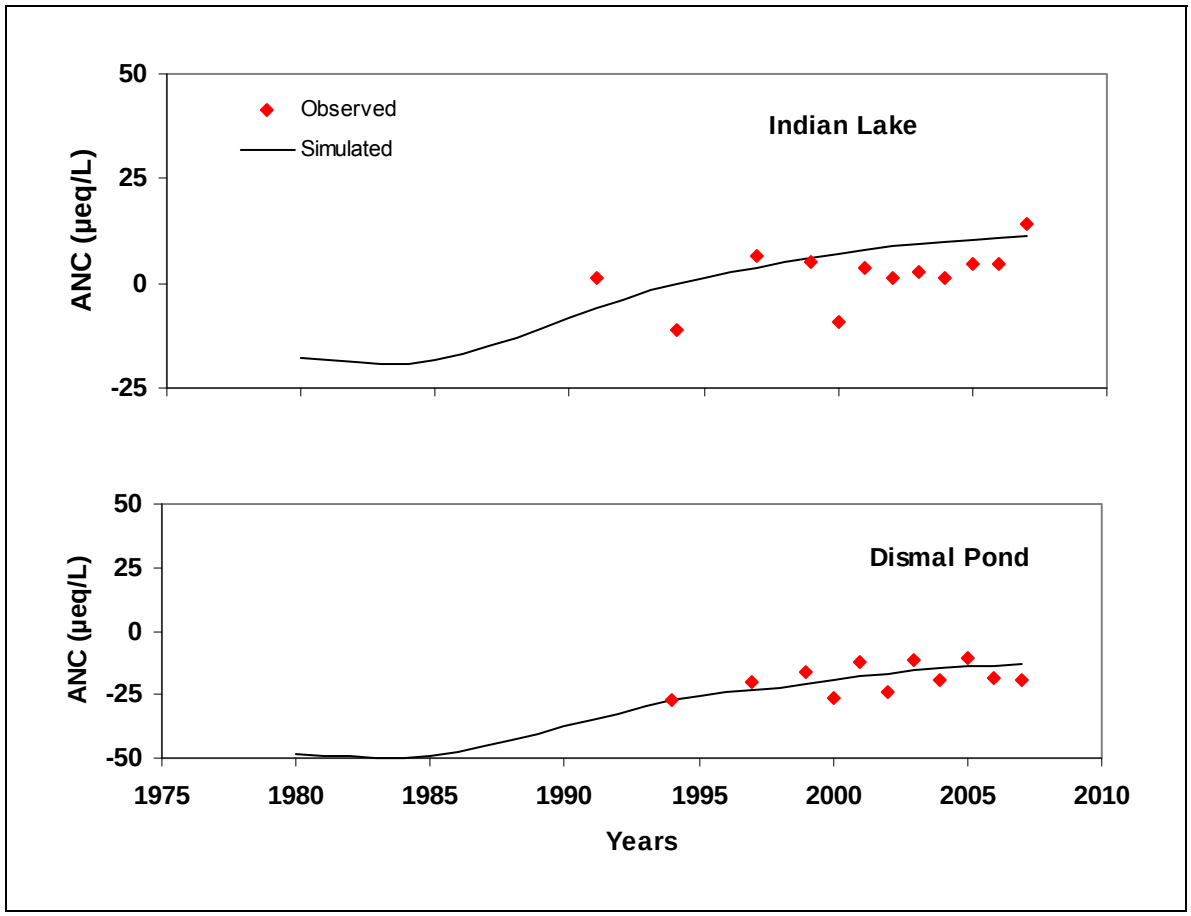


Figure 4.2-29. MAGIC simulated and observed values of ANC for two lakes in the Shenandoah Case Study Area. Red points are observed data and the simulated values are the line. The Root Mean Squared Error (RMSE) for ANC was 7.81 µeq/L for Indiana Lake and 5.1 µeq/L for Dismal Pond.

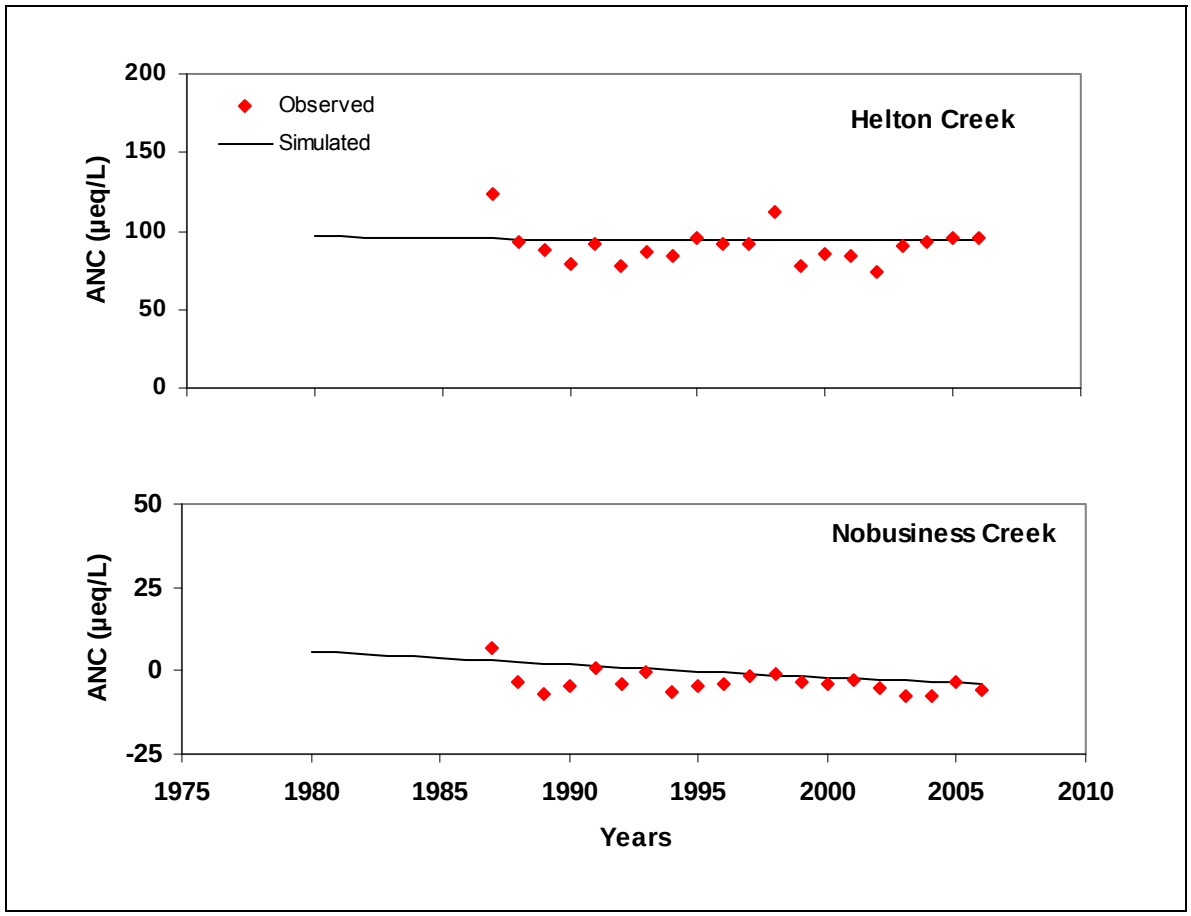


Figure 4.2-30. MAGIC simulated and observed values of ANC for two lakes in the Shenandoah Case Study Area. Red points are observed data and the simulated values are the line. The Root Mean Squared Error (RMSE) for ANC was 11.8 µeq/L for Helton Creek and 4.0 µeq/L for Nobusiness Creek.

4.3 TERRESTRIAL ACIDIFICATION

4.3.1 Ecological Indicators, Ecological Responses, and Ecosystem Services

4.3.1.1 Ecological Indicators

Indicator: The Bc/Al molar ratio in the soils solution was selected as the indicator to estimate critical deposition loads of acidity for the Terrestrial Acidification Case Study.

The ISA (U.S. EPA, 2008) identified a variety of indicators supported by the literature that can be used to measure the effects of acidification in soils. Much of the literature discussing terrestrial acidification focuses on Ca^{2+} and Al as the primary indicators of detrimental effects for trees and other terrestrial vegetation. Both of these indicators are strongly influenced by soil acidification, and both have been shown to have quantitative links to tree health (see Appendix 5 for more information).

Therefore, the Ca/Al ratio in soil solution was selected as the basis for the indicator in the Terrestrial Acidification Case Study (Appendix 5) to evaluate the critical load of acidity in terrestrial systems. Within the calculations of critical loads, the base cation (Bc) to Al ratio (Bc/Al), consisting of molar equivalents of Ca^{2+}, Mg^{2+} and K^{+}, was used to represent the Ca/Al indicator. This Bc/Al ratio was selected because it is the most commonly used indicator or critical ratio ($Bc/Al_{(crit)}$) in the Simple Mass Balance (SMB) model used to estimate critical acid loads in the European Union, Canada, and the United States (McNulty et al., 2007; Ouimet et al., 2006; UNECE, 2004), and the SMB model was applied to this case study (see Section 4.3.4 for description of model). In addition, tree species show similar sensitivities to Ca/Al and Bc/Al soil solution ratios. Therefore, the Bc/Al ratio represents a good indicator of the negative impacts of soil acidification on terrestrial vegetation. Sverdrup and Warfvinge (1993), in a meta-data analysis of laboratory and field studies, reported that the critical Bc/Al ratios for a large variety of tree species ranged from 0.2 to 0.8. This range is similar to that described by Cronan and Grigal (1995) for Ca/Al. In their meta-data assessment of studies examining sensitivities to the Ca/Al ratio, plant toxicity or nutrient antagonism was reported to occur at Ca/Al ratios ranging from 0.2 to 2.5.

4.3.1.2 Ecological Responses

In a meta-analysis of studies that explored the relationship between Bc/Al ratio in soil solution and tree growth, Sverdrup and Warfvinge (1993) reported the Bc/Al ratios at which growth was reduced by 20% relative to control trees. **Figure 4.3-1** presents the findings of Sverdrup and Warfvinge (1993) based on 46 of the tree species (native and introduced) that grow in North America. This summary indicates that there is a 50% chance of negative tree response (i.e., >20% reduced growth) at a soil solution Bc/Al ratio of 1.2 and a 75% chance at a Bc/Al ratio of 0.6. These findings clearly demonstrate a relationship between Bc/Al ratio and tree health; as the Bc/Al is reduced, there is a greater likelihood of a negative impact on tree health.

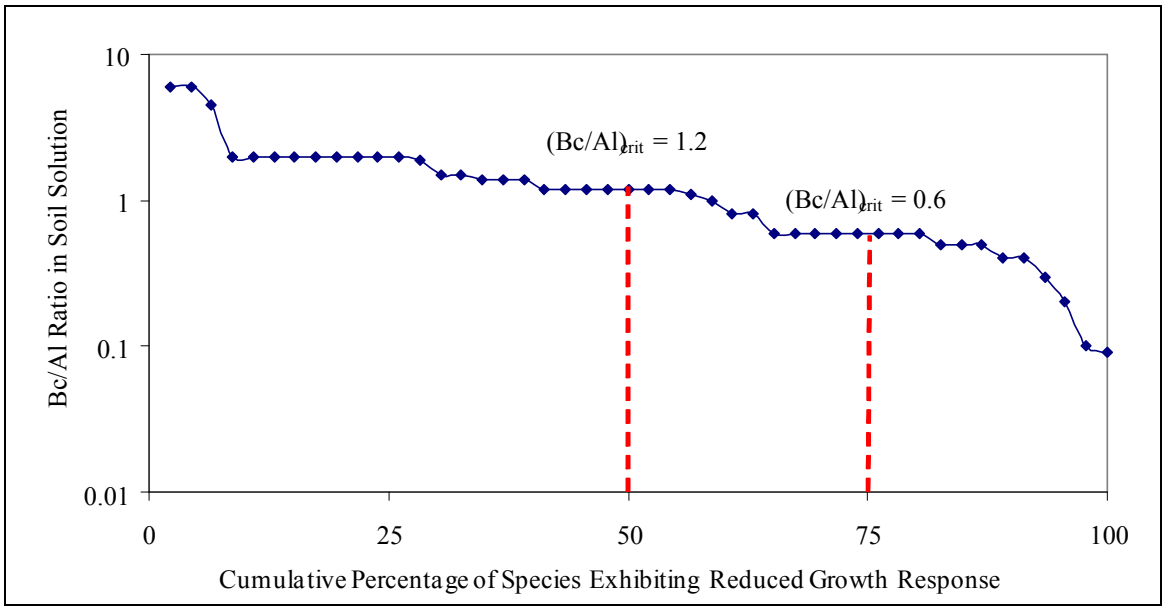


Figure 4.3-1. The relationship between the Bc/Al ratio in soil solution and the percentage of tree species (found growing in North America – native and introduced species) exhibiting a 20% reduction in growth relative to controls (after Sverdrup and Warfvinge, 1993).

The tree species most commonly studied in North America to assess the impacts of acidification due to total nitrogen and sulfur deposition are red spruce (i.e., *Picea Rubens*) and sugar maple (i.e., *Acer saccharum*). Based on the results from a compilation of laboratory studies, red spruce growth can be reduced by 20% at a Bc/Al soil solution ratio of approximately 1.2, and a similar reduction in growth may be experienced by sugar maple at a Bc/Al ratio of 0.6 (Sverdrup and Warfvinge 1993). Both species are found in the eastern United States, and soil acidification is widespread throughout this area (Warby et al., 2009).

Red spruce is found scattered throughout high-elevation sites in the Appalachian Mountains, including the southern peaks. Noticeable fractions of the canopy red spruce died within the Adirondack, Green, and White mountains in the 1970s and 1980s. Although a variety of conditions, such as changes in climate and exposure to ozone, may impact the growth of red spruce (Fincher et al., 1989; Johnson et al., 1988), acidifying deposition has been implicated as one of the main factors causing this decline. Based on the research conducted to date, acidic deposition can cause a depletion of base cations in upper soil horizons, Al toxicity to tree roots, and accelerated leaching of base cations from foliage (U.S. EPA, 2008, Section 3.2.2.3). Such nutrient imbalances and deficiencies can reduce the ability of trees to respond to stresses, such as insect defoliation, drought, and cold weather damage (DeHayes et al., 1999; Driscoll et al.,

2001), thereby decreasing tree health and increasing mortality. Additional linkages between acidifying deposition and red spruce physiological responses are indicated in **Table 4.3-1**. Within the southeastern United States, periods of red spruce decline slowed after the 1980s, when a corresponding decrease in SO_2 emissions, and therefore acidic deposition, was recorded (Webster et al., 2004).

Sugar maple is found throughout the northeastern United States and the central Appalachian Mountain region. This species has been declining in the eastern United States since the 1950s. Studies on sugar maple have found that one source of this decline in growth is related to both acidifying deposition and base-poor soils on geologies dominated by sandstone or other base-poor substrates (Bailey et al., 2004; Horsley et al., 2000). These site conditions are representative of the conditions expected to be most susceptible to impacts of acidifying deposition because of probable low initial base cation pools and high base cation leaching losses (U.S. EPA, 2008, Section 3.2.2.3). The probability of a decrease in crown vigor or an increase in tree mortality has been noted to increase at sites with low Ca^{2+} and Mg^{2+} as a result of leaching caused by acidifying deposition (Drohan and Sharpe, 1997). Low levels of Ca^{2+} in leaves and soils have been shown to be related to lower rates of photosynthesis and higher antioxidant enzyme activity in sugar maple stands in Pennsylvania (St. Clair et al., 2005). Additionally, plots of sugar maples in decline were found to have Ca^{2+}/Al ratios less than 1, as well as lower base cation concentrations and pH values compared with plots of healthy sugar maples (Drohan et al., 2002). Sugar maple regeneration has also been noted to be restricted under conditions of low soil Ca^{2+} levels (Juice et al., 2006). These indicators have all been shown to be related to the deposition of atmospheric nitrogen and sulfur. Additional linkages between acidifying deposition and sugar maple physiological responses are indicated in **Table 4.3-1**.

Table 4.3-1. Summary of Linkages Between Acidifying Deposition, Biogeochemical Processes That Affect Ca^{2+}, Physiological Processes That Are Influenced by Ca^{2+}, and Effect on Forest Function

Biogeochemical Response to Acidifying deposition	Physiological Response	Effect on Forest Function
Leach Ca^{2+} from leaf membrane	Decrease the cold tolerance of needles in red spruce	Loss of current-year needles in red spruce
Reduce the ratio of Ca^{2+}/Al in soil and soil solutions	Dysfunction in fine roots of red spruce blocks uptake of Ca^{2+}	Decreased growth and increased susceptibility to stress in red spruce

Biogeochemical Response to Acidifying deposition	Physiological Response	Effect on Forest Function
Reduce the ratio of Ca^{2+}/Al in soil and soil solutions	More energy is used to acquire Ca^{2+} in soils with low Ca^{2+}/Al ratios	Decreased growth and increased photosynthetic allocation to red spruce roots
Reduce the availability of nutrient cations in marginal soils	Sugar maples on drought-prone or nutrient-poor soils are less able to withstand stresses	Episodic dieback and growth impairment in sugar maple

Source: Fenn et al., 2006.

Although the main focus of the Terrestrial Acidification Case Study is an evaluation of the negative impacts of nitrogen and sulfur deposition on soil acidification and tree health, it should be recognized that under certain conditions, nitrogen and sulfur deposition can have a positive impact on tree health. Nitrogen limits the growth of many forests (Chapin et al., 1993; Killam, 1994; Miller, 1988), and therefore, in such forests, nitrogen deposition may act as a fertilizer and stimulate growth. Forests where critical acid loads are not exceeded by nitrogen and sulfur deposition could potentially be included within this group of forests that respond positively to deposition. These potential positive growth impacts of nitrogen and sulfur deposition are discussed further, and the results of analyses are presented, in Attachment A of Appendix 5.

End Point: The health of sugar maple and red spruce was selected as the endpoints to estimate critical deposition loads of acidity in this case study.

In summary, among potential influencing factors, including elevated ozone levels and changes in climate, the acidification of soils is one of the factors that can negatively impacts the health of red spruce and sugar maple. Mortality and susceptibility to disease and injury can be increased and growth decreased with acidifying deposition. Therefore, the health of sugar maple and red spruce was used as the endpoints (ecological responses) to evaluate acidification in terrestrial systems. “Health” in the context of this case study is defined as the physiological condition of a tree that impacts growth and/or mortality,

4.3.1.3 Ecosystem Services

A number of impacts on the ecological endpoints of forest health, water quality, and habitat exist, including the following:

- Decline in habitat for threatened and endangered species—cultural

- Decline in forest aesthetics—cultural
- Decline in forest productivity—provisioning
- Increases in forest soil erosion and reductions in water retention—cultural and regulating.

These impacts are described below. (Existing ecosystem services that are primarily impacted by the terrestrial acidification resulting from total nitrogen and sulfur deposition are being quantified for the Risk and Exposure Assessment.)

Provisioning Services

Forests in the northeastern United States provide several important and valuable provisioning services, which are reflected in measures of production and sales of tree products.

Sugar maples (also referred to as hard maples) are a particularly important commercial hardwood tree species in the United States. The two main types of products derived from sugar maples are wood products and maple syrup. The wood from sugar maple trees is particularly hard, and its primary uses include construction, furniture, and flooring (Luzadis and Gossett, 1996). According to data from the U.S. Forest Service's National Forest Inventory and Analysis (FIA) database, the total removal of sugar maple saw timber from timberland in the United States was almost 900 million board feet in 2006 (USFS, 2006). During winter and early spring (depending, in part, on location and diurnal temperature differences), sugar maple trees also generate sap that is used to produce maple syrup. From 2005 to 2007, annual production of maple syrup in the United States varied between 1.2 million and 1.4 million gallons, which accounted for roughly 19% of worldwide production. The total annual value of U.S. production in these years varied between $157 million and $168 million (NASS, 2008).

Red spruce is a common commercial softwood species whose wood is used in a variety of products including lumber, pulpwood, poles, plywood, and musical instruments. According to FIA data, the total removal of red spruce saw timber from timberland in the United States was 328 million board feet in 2006 (USFS, 2006).

Figure 4.3-2 shows and compares the value of annual production of sugar maple and red spruce wood products and of maple syrup in 2006. Across states in the northeastern United States, wood from sugar maple harvests consistently generated the highest total sales value of the three products. Although total sales of red spruce saw timber and maple syrup were of roughly the same magnitude in the United States as a whole, the red spruce harvest was concentrated in Maine, whereas maple syrup production was largest in Vermont and New York.

Cultural Services

Forests in the northeastern United States are also an important source of cultural ecosystem services—nonuse (i.e., existence value for threatened and endangered species), recreational, and aesthetic services. Red spruce forests are home to two federally listed species and one delisted species:

- Spruce-fir moss spider (*Microhexura montivaga*)—endangered
- Rock gnome lichen (*Gymnoderma lineare*)—endangered
- Virginia northern flying squirrel (*Glaucomys sabrinus fuscus*)—delisted, but important.

Forest lands support a wide variety of outdoor recreational activities, including fishing, hiking, camping, off-road driving, hunting, and wildlife viewing. Regional statistics on recreational activities that are specifically forest based are not available; however, more general data on outdoor recreation provide some insights into the overall level of recreational services provided by forests. For example, most recent data from the National Survey on Recreation and the Environment (NSRE) indicate that, from 2004 to 2007, 31% of the U.S. adult (16 and older) population visited a wilderness or primitive area during the previous year, and 32% engaged in day hiking (Cordell et al., 2008). From 1999 to 2004, 16% of adults in the northeastern United States[1] participated in off-road vehicle recreation, for an average of 27 days per year (Cordell et al., 2005). Using the meta-analysis results reported by Kaval and Loomis (2003), which found that the average consumer surplus value per day of off-road driving in the United States was $25.25 (in 2007 dollars), the implied total annual value of off-road driving recreation in the northeastern United States was more than $9.25 billion.

State-level data on other outdoor recreational activities associated with forests are also available from the *2006 National Survey of Fishing, Hunting, and Wildlife-Associated Recreation* (U.S. FWS and U.S. Census Bureau, 2007). Five and one-half percent of adults in the northeastern United States participated in hunting, and the total number of hunting days occurring in those states was 83.8 million. Data from the survey also indicated that 10% of adults in northeastern states participated in wildlife viewing away from home. The total number of away-from-home wildlife viewing days occurring in those states was 122.2 million in 2006. For these recreational activities in the northeastern United States, Kaval and Loomis (2003)

[1] This area includes Connecticut, Delaware, District of Columbia, Illinois, Indiana, Maine, Maryland, Massachusetts, Michigan, New Hampshire, New Jersey, New York, Ohio, Pennsylvania, Rhode Island, Vermont, West Virginia, and Wisconsin.

estimated average consumer surplus values per day of $52.36 for hunting and $34.46 for wildlife viewing (in 2007 dollars). The implied total annual value of hunting and wildlife viewing in the northeastern United States was, therefore, $4.38 billion and $4.21 billion, respectively, in 2006.

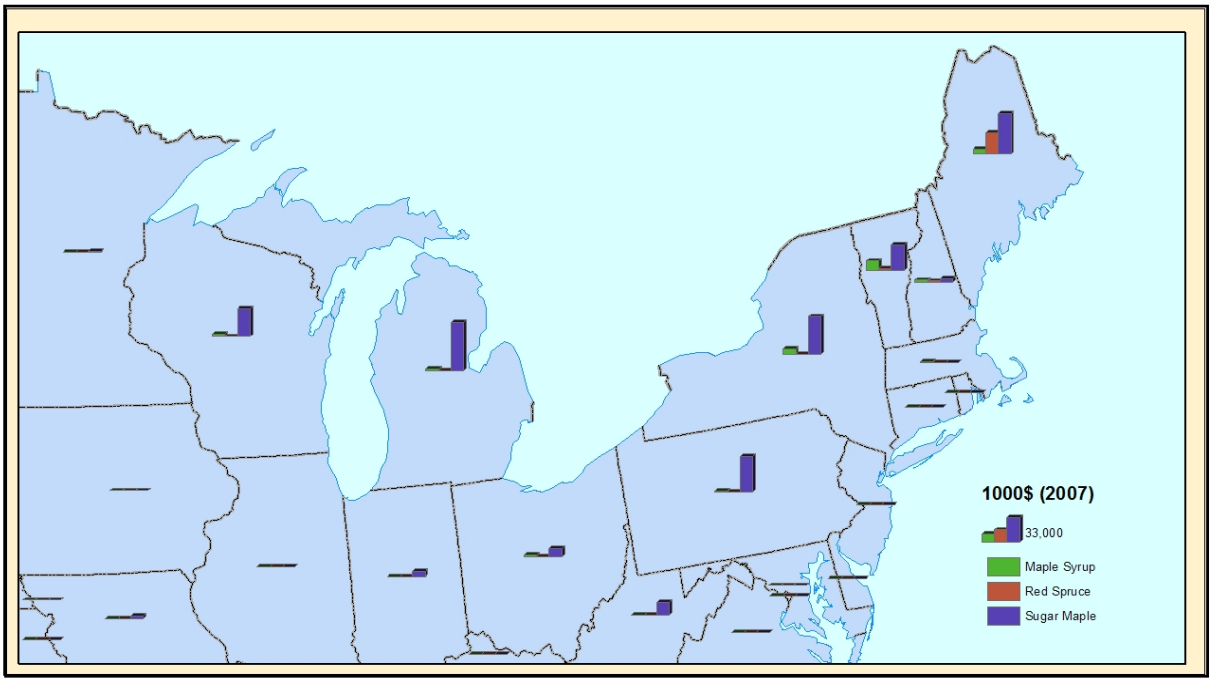


Figure 4.3-2. 2006 annual value of sugar maple and red spruce harvests and maple syrup production, by state.

As previously mentioned, it is difficult to estimate the portion of these recreational services that are specifically attributable to forests and to the health of specific tree species. However, one recreational activity that is directly dependent on forest conditions is fall color viewing. Sugar maple trees, in particular, are known for their bright colors and are, therefore, an essential aesthetic component of most fall color landscapes. Statistics on fall color viewing are much less available than for the other recreational and tourism activities; however, a few studies have documented the extent and significance of this activity. For example, based on a 1996 to 1998 telephone survey of residents in the Great Lakes area, Spencer and Holecek (2007) found that roughly 30% of residents reported at least one trip in the previous year involving fall color viewing. In a separate study conducted in Vermont, Brown (2002) reported that more than 22% of households visiting Vermont in 2001 made the trip primarily for the purpose of viewing fall colors. Unfortunately, data on the total number or value of these trips are not available, although

the high rates of participation suggest that numbers might be similar to the wildlife viewing estimates reported above.

Although these statistics provide useful indicators of the total recreational and aesthetic services derived from forests in the northeastern United States, they do not provide estimates of how these services are affected by terrestrial acidification. Very few empirical studies have directly addressed this issue; however, there are two studies that have estimated values for protecting high-elevation spruce forests in the southern Appalachian Mountains. Kramer et al., (2003) conducted a contingent valuation study estimating households' willingness to pay (WTP) for programs to protect remaining high-elevation spruce forests from damages associated with air pollution and insect infestation (Haefele et al., 1991; Holmes and Kramer, 1995). The study collected data from 486 households using a mail survey of residents living within 500 miles of Asheville, NC. The survey presented respondents with photographs representing three stages of forest decline and explained that, without forest protection programs, high-elevation spruce forests would all decline to worst conditions (with severe tree mortality). The survey then presented two potential forest protection programs, one of which would prevent further decline in forests along roads and trail corridors (one-third of the at-risk ecosystem) and the other would prevent decline in all at-risk forests. Both programs would be funded by tax payments going to a conservation fund. Median household WTP was estimated to be roughly $29 (in 2007 dollars) for the first program, and $44 for the more extensive program.

Jenkins et al. (2002) conducted a very similar study in 1995, using a mail survey of households in seven Southern Appalachian states. In this study, respondents were presented with one potential program, which would maintain forest conditions at initial (status quo) levels. It was explained that, without the program, forest conditions would decline to worst conditions (with 75% dead trees). In contrast to the previously described study, in this survey the *initial* level of forest condition was varied across respondent. In one version of the survey, the initial condition was described and shown as 5% dead trees, while the other version described and showed 30% dead trees. Household WTP was elicited from 232 respondents using a dichotomous choice and tax payment format. The overall mean annual WTP for the forest protection programs was $208 (in 2007 dollars), which is considerably larger than the WTP estimates reported by Kramer et al. (2003). One possible reason for this difference is that respondents to the Jenkins et al. (2002) survey, on average, lived much closer to the affected ecosystem. Multiplying the average WTP estimate from this study by the total number of

households in the seven-state Appalachian region results in an aggregate annual value of $3.4 billion for avoiding a significant decline in the health of high-elevation spruce forests in the Southern Appalachian region.

Regulating Services

Forests in the northeastern United States also support and provide a wide variety of valuable regulating services, including soil stabilization and erosion control, water regulation, and climate regulation (Krieger, 2001). Forest vegetation plays an important role in maintaining soils in order to reduce erosion, runoff, and sedimentation that can negatively impact surface waters. In addition to protecting the *quality* of water in this way, forests also help store and regulate the *quantity* and flows of water in watersheds. Finally, forests help regulate climate locally by trapping moisture and globally by sequestering carbon. The total value of these ecosystem services is very difficult to quantify in a meaningful way, as is the reduction in the value of these services associated with total nitrogen and sulfur deposition. As terrestrial acidification contributes to root damages, reduced biomass growth, and tree mortality, all of these services are likely to be affected; however, the magnitude of these impacts is currently very uncertain.

4.3.2 Characteristics of Sensitive Areas

In general, forest ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachian Mountains are considered to be the regions most sensitive to terrestrial acidification effects from acidifying deposition (U.S. EPA, 2008). Such areas tend to be dominated by relatively nonreactive bedrock in which base cation production via weathering is limited (Elwood et al., 1991). The soils also usually have thick organic horizons, high organic matter content in the mineral horizons, and low pH (Joslin et al., 1992). Because of the largely nonreactive bedrock, base-poor litter and organic acid anions produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these high elevation forests tends to be below 10%, and the soil cation exchange complex is generally dominated by Al (Eagar et al., 1996; Johnson and Fernandez, 1992). These soil systems have a lower capacity to neutralize acidic deposition and are not able to recover from the input of acidifying anions as easily as other systems. The areas where sugar maples appear to be at greatest risk are along ridges and where this species occurs on nutrient-poor soils (U.S. EPA,

2008, Section 3.2.4). In addition, these forests support the growth of sugar maple and red spruce, two species that are particularly sensitive to acidification.

Several characteristics were used to identify areas potentially sensitive to terrestrial acidification. These characteristics included the following:

- Soil depth
- Bedrock composition
- Soil pH
- Presence of sugar maple or red spruce.

Geology is one of the most important factors in determining the potential sensitivity of an area to terrestrial acidification (U.S. EPA, 2008, Section 3.2.4). In particular, the characteristics of the soils and the upper portion of the bedrock can impact the acid-neutralizing ability of the soils in a particular area. Acid-sensitive soils are those which contain low levels of exchangeable base cations and low base saturation (U.S. EPA, 2008, Section 3.2.4).

It is important that soils be of sufficient depth for the rooting zone. Fine roots, which are responsible for the vast majority of nutrient uptake, are typically concentrated in the upper 10 to 20 centimeters (cm) of soil (van der Salm and de Vries, 2001). These roots are most susceptible to the impacts of acidification.

Bedrock composition and soil pH are two characteristics that are directly related to the ability of a system to neutralize acid. Soils overlying bedrock, such as calcium carbonate (e.g., limestone), which is reactive with acid, are more likely to successfully neutralize acidifying deposition than soils overlying nonreactive bedrock. In addition, soils with higher pH (i.e., more alkaline) have a greater capacity to neutralize acidifying deposition.

Areas with acid-sensitive geology were cross-referenced with the geographical ranges of the ecological endpoints for this case study. As a result, locations with sugar maple or red spruce, soil pH less than or equal to 5.0, soils less than or equal to 51 cm in depth, and bedrock with a low ability to neutralize acid inputs (not dominated by carbonate rocks) were selected to represent areas with potential sensitivity to acidification. A geographic information systems (GIS) analysis was performed on datasets and data layers of physical, chemical, and biological properties to map areas of potential sensitivity to acidification in the United States (**Figure 4.3-3**).

4.3.3 Case Study Selection

Following the identification of regions of potential sensitivity to acidification, risk and exposure assessment sites recommended in the ISA (U.S. EPA, 2008, Appendix A) by the Science Advisory Board – Ecological Effects Sub-committee (SAB-EES) (U.S. EPA, 2005) and the body of published and unpublished literature were reviewed to determine the most suitable areas for the red spruce and sugar maple case study areas.

Selection of an area for the sugar maple case study focused on the Allegheny Plateau region in Pennsylvania, where a large proportion of published and unpublished research has been focused. A significant amount of the research work in the Plateau region has been sponsored by the United States Forest Service (USFS) and has produced extensive datasets of soil and tree characteristics (Bailey et al., 2004; Hallett et al., 2006; Horsley et al., 2000). The USFS-designated Kane Experimental Forest (KEF) was selected as the area for the sugar maple terrestrial acidification case study. The KEF has been the focus of several long-term studies since the 1930s. Seven plots (plot 1-plot 7) in the forest were assessed for this case study of the effects of terrestrial acidification on sugar maples. Sugar maple accounted for 23% to 44% of the basal area in these plots.

Selection of a case study area for red spruce involved the consideration of a variety of regions. Four studies that examined the relationship between the Ca^{2+}/Al soil solution ratio and tree health were identified, and relevant soil and tree information for each of the study regions was compiled**.** A review of this information led to the selection of the Hubbard Brook Experimental Forest (HBEF) in New Hampshire's White Mountains as the area for the red spruce terrestrial acidification case study. The HBEF was also recommended in the ISA (U.S. EPA, 2008, Appendix A) as a good area for risk and exposure assessment. This forest has experienced high total nitrogen and sulfur deposition levels and low Ca^{2+}/Al soil solution ratios, and has been the subject of extensive nutrient investigations and provided a large data set from which to work on the case study. The case study of the effects of terrestrial acidification on red spruce focused on a study area consisting of nine grid cells (total of 0.56 ha) within Watershed 6 in the HBEF. Red spruce accounted for 19% of the total basal area (131.3 m^2/ha) in this 0.56 ha study area.

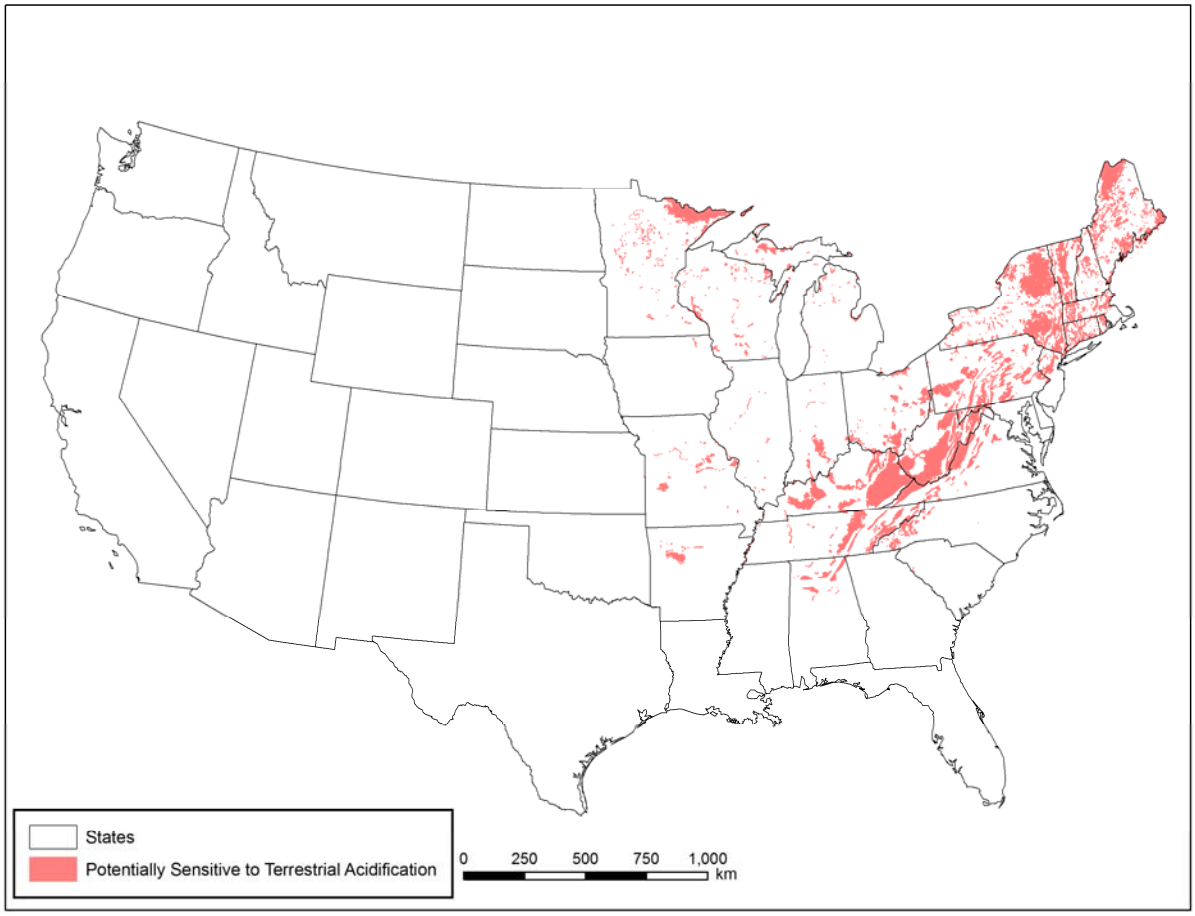


Figure 4.3-3. Map of areas of potential sensitivity of red spruce and sugar maple to acidification in the United States (see Table 1.2-1 of Appendix 5 for a listing of data sources to produce this map).

4.3.4 Current Conditions Assessment

The Simple Mass Balance (SMB) model, outlined in the International Cooperative Programme (ICP) Mapping and Modeling Manual[2] (UNECE, 2004), was used to evaluate critical loads of acidifying nitrogen and sulfur deposition in the KEF and HBEF case study areas, according to Equation 7

$$CL(S+N) = BC_{dep} - Cl_{dep} + BC_{w} - Bc_{u} + N_{i} + N_{u} + N_{de} - ANC_{le,crit} \quad (7)$$

where

CL(S+N) = forest soil critical load for combined nitrogen and sulfur acidifying deposition ($N+S_{comb}$)

[2] The ICP Mapping and Modeling Manual (UNECE, 2004) recommends that wet deposition be corrected for sea salt on sites within 70 km of the coast. Neither the HBEF nor KEF case study areas are located less than 70 km for the coast, so this correction was not used.

BC_{dep} = base cation ($Ca^{2+} + K^{+} + Mg^{2+} + Na^{+}$) deposition
Cl_{dep} = chloride deposition
BC_{w} = base cation ($Ca^{2+} + K^{+} + Mg^{2+} + Na^{+}$) weathering
Bc_{u} = uptake of base cations ($Ca^{2+} + K^{+} + Mg^{2+}$) by trees
N_{i} = nitrogen immobilization
N_{u} = uptake of nitrogen by trees
N_{de} = denitrification
$ANC_{le,crit}$ = forest soil acid neutralizing capacity of critical load leaching

This model is currently one of the most commonly used approaches to estimate critical loads and has been widely applied in Europe (Sverdrup and de Vries, 1994), the United States (McNulty et al., 2007; Pardo and Duarte, 2007), and Canada (Arp et al., 2001; Ouimet et al., 2006; Watmough et al., 2006). It examines a long-term, steady-state balance of base cation, chloride, and nutrient inputs, "sinks," and outputs within an ecosystem, and base cation equilibrium is assumed to equal the system's critical load for ecological effects. A limitation of the SMB model is that it is a steady-state model and does not capture the cumulative changes in ecosystem conditions. However, as stated by the UNECE (2004), "Since critical loads are steady-state quantities, the use of dynamic models for the sole purpose of deriving critical loads is somewhat inadequate." In addition, if a dynamic model is "used to simulate the transition to a steady state for the comparison with critical loads, care has to be taken that the steady-state version of the dynamic model is compatible with the critical load model." Therefore, the selection of the SMB model was seen as the most suitable approach for this case study examining critical loads for sugar maple and red spruce.

A component of critical load determinations is the establishment of the critical load function (CLF). The CLF expresses the relationship between the critical load and all combinations of total nitrogen and sulfur deposition ($N+S_{comb}$) of an ecosystem. To define the CLF, minimum and maximum amounts of total nitrogen and sulfur deposition that combine to create the critical load must be determined (UNECE, 2004). The maximum amount of sulfur in the critical load ($CL_{max}(S)$) occurs when total nitrogen deposition does not exceed the nitrogen sinks (i.e., nitrogen immobilization, nitrogen uptake and removal by tree harvest, and denitrification) within the ecosystem. These nitrogen sinks are accounted for by the minimum amount of nitrogen in the critical load ($CL_{min}(N)$. Above this $CL_{min}(N)$ level, total nitrogen deposition can no longer be absorbed by the system, and acidification effects can occur. The maximum amount of nitrogen in the critical load ($CL_{max}(N)$) occurs when there is no sulfur deposition, and all of the acidity is due to the deposition of nitrogen.

An example of a CLF is depicted in **Figure 4.3-4.** All combinations of total nitrogen and sulfur deposition that fall on the black line representing the CLF are at the critical load. Any deposition combination that falls below the line or within the grey area is below the critical load. All combinations of nitrogen and sulfur deposition that are located above the line or within the white area are greater than the critical load.

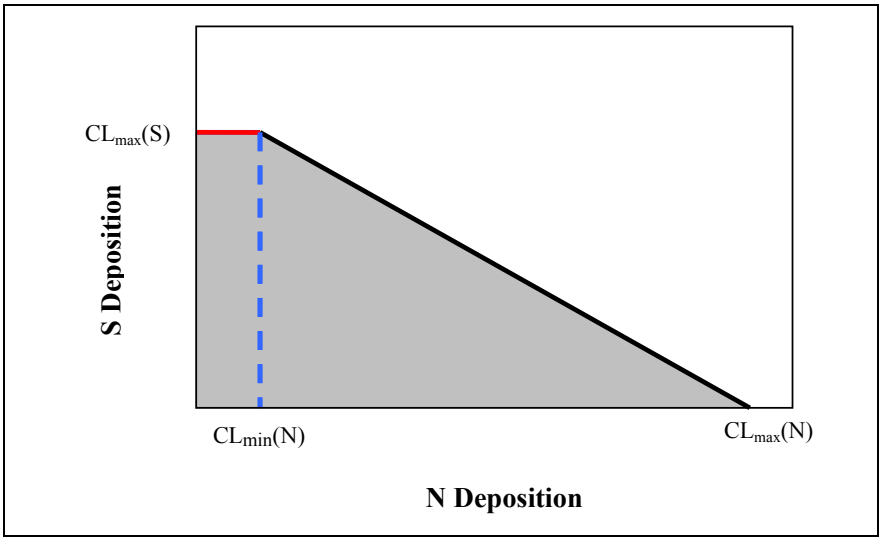


Figure 4.3-4. The critical load function created from the calculated maximum and minimum levels of total nitrogen and sulfur deposition (eq/ha/yr). The grey areas show deposition levels less than the established critical loads. The red line is the maximum amount of total sulfur deposition (valid only when nitrogen deposition is less than the minimum critical level of nitrogen deposition [blue dotted line]) in the critical load. The flat line portion of the curves indicates nitrogen deposition corresponding to the $CL_{min}(N)$ (nitrogen absorbed by nitrogen sinks within the system).

4.3.4.1 Input Data

This section summarizes the input data used in the calculations, the results for each case study area, and a comparison of these results with 2002 wet and dry nitrogen and sulfur deposition (combination of Community Multiscale Air Quality [CMAQ]-modeled 2002 deposition results and 2002 National Atmospheric Deposition Program [NADP] deposition data). Additional detail, including an examination of the influence of different parameter values and methods, on the assessment of current conditions in the KEF and HBEF case study areas can be found in Appendix 5. Only the parameter values that were chosen to represent the current condition of the KEF and HBEF case study areas are presented here.

The majority of the data used to calculate critical loads for sugar maple and red spruce in the KEF and HBEF case study areas was specific to the case study areas and was compiled from published research studies and models, site-specific databases, or spatially-explicit GIS data

layers. However, several of the parameters (e.g., denitrification, nitrogen immobilization, the gibbsite equilibrium constant, rooting zone soil depth) required the use of default values or values used in published critical load assessments. Denitrification loss of nitrogen was assumed to be 0 eq/ha/yr because both the KEF and HBEF study plots are upland forests, and denitrification is considered negligible in such forests (McNulty et al. 2007; Ouimet et al., 2006; Watmough et al., 2006). The nitrogen mobilization value was set to 42.86 eq/ha/yr for both forests in this case study (McNulty et al., 2007). A 300 m^6/eq^2 value for the gibbsite equilibrium constant (K_{gibb}) (used in the calculation of ANC) was selected because it is the most commonly used default value (UNECE, 2004). Fifty centimeters (0.5 m) was selected as the rooting zone soil depth for the forest soils of the two case study areas (Sverdrup and de Vries, 1994; Hodson and Langan 1999). Base cation weathering (BC_w) rates were calculated using the clay-substrate method (McNulty et al., 2007; Watmough et al., 2006). This is one of the most commonly used methods to estimate base cation weathering for critical load analyses in North America. Base cation (Bc_u) and nitrogen (N_u) uptake values were calculated in two different ways for the two case study areas. In the SMB model, if a stand is not actively harvested, nutrient (i.e., nitrogen and base cation) uptake is estimated to be 0 eq/ha/yr because the nutrients are assumed to be recycled within the forest and not removed from the site. Watershed 6, in the HBEF Case Study Area, is a reference watershed. Although this watershed was harvested in 1906 and 1917 (Aber et al., 2002), it has not been actively managed since that time and will not be harvested in the future. Therefore,, Bc_u and N_u were assumed to be 0 eq/ha/yr in the critical load calculations. In contrast, in the KEF Case Study Area, the case study plots were assumed to be recently managed and harvested on a regular basis. Values of Bc_u and N_u for this scenario were therefore calculated using species-specific tree data and uptake estimates and were >0 eq/ha/yr. Three values of the indicator of critical load, $(Bc/Al)_{crit}$ soil solution ratio, were selected to represent different levels of tree protection associated with total nitrogen and sulfur deposition: 0.6, 1.2, and 10 (**Table 4.3.2**). The $(Bc/Al)_{crit}$ ratio of 0.6 represents the highest level of impact (lowest level of protection) to tree health and growth and was selected because 75% of species found growing in North America experience reduced growth at this Bc/Al ratio (see **Figure 4.3.1**). In addition, a soil solution Bc/Al ratio of 0.6 has been linked to a 20% and 35% reduction in sugar maple and red spruce growth, respectively. The $(Bc/Al)_{crit}$ ratio of 1.2 is considered to represent a moderate level of impact, as the growth of 50% of tree species (found growing in North America) was negatively impacted at this soil solution ratio. The $(Bc/Al)_{crit}$ ratio of 10.0 represents the lowest

level of impact (greatest level of protection) to tree growth; it is the most conservative value used in studies that have calculated critical loads in the United States and Canada (Canada (McNulty et al. 2007; NEG/ECP, 2001; Watmough et al., 2004).

Table 4.3-2. The Three Indicator $(Bc/Al)_{crit}$ Soil Solution Ratios and Corresponding Levels of Protection to Tree Health and Critical Loads

Indicator $(Bc/Al)_{crit}$ Soil Solution Ratio	Level of Protection to Tree Health	Critical Load
0.6	Low	High
1.2	Intermediate	Intermediate
10.0	High	Low

4.3.5 Results for the Case Study Areas

Based on the input data described above, the three critical loads for the KEF case study area, in order of lowest to highest protection level, were 2,009, 1,481 and 910 eq/ha/yr (for $Bc/Al_{(crit)}$ = 0.6, 1.2, and 10.0, respectively). In the HBEF Case Study Area, these values, in the same order of protection, were 1,237, 892, and 487 eq/ha/yr (for $Bc/Al_{(crit)}$ = 0.6, 1.2, and 10.0, respectively).

The $(Bc/Al)_{crit}$ ratio of 0.6 represents the highest level of impact (lowest level of protection) to tree health and growth; as much as 75% of 46 tree species found in North America experience reduced growth at this ratio (Sverdrup and Warfvinge, 1993). Both red spruce and sugar maple show at least a 20% reduction in growth at the 0.6 $(Bc/Al)_{crit}$ ratio.

4.3.5.1 Comparison with 2002 Deposition Data

This section discusses the impact of 2002 CMAQ/NADP total nitrogen and sulfur deposition relative to the estimated critical loads at the KEF and HBEF case study areas. According to 2002 CMAQ/NADP total nitrogen and sulfur deposition, the KEF Case Study Area received 13.6 kg N/ha (967.5 eq/ha) and 20.7 kg S/ha (646.4 eq/ ha), and the HBEF Case Study Area experienced 8.4 kg N/ha (601.1 eq/ha) and 7.5 kg S/ha (233.1 eq/ha).

As outlined above, 2,009, 1,481, and 910 eq/ha/yr were the critical loads selected to represent the three levels of protection for the KEF Case Study Area and 1,237, 892, and 487 eq/ha/yr were the critical loads selected for the HBEF Case Study Area. These estimates are based on the critical load parameters suggested and most frequently used by scientists and

previous research. When compared to the 2002 CMAQ/NADP total nitrogen and sulfur deposition levels, it was evident that the deposition levels were greater than the most protective critical load ($Bc/Al_{(crit)}$ = 10.0) for both case study areas and also greater than the intermediate protection critical load ($Bc/Al_{(crit)}$ = 1.2) for the KEF Case Study Area (**Figure 4.3-5** and **Figure 4.3-6**). In these comparisons, total nitrogen and sulfur deposition exceeded the KEF Case Study Area critical load by 132 – 704 eq/ha/yr and exceeded the HBEF Case Study Area's critical load by 347 eq/ha/yr. Similar results have been reported in other studies that have assessed the two case study areas. McNulty et al. (2007) and Pardo and Driscoll (1996) found that deposition levels were greater than the estimated critical loads in the HBEF Case Study Area. McNulty et al. (2007) also reported that total nitrogen and sulfur deposition in the KEF exceeded the calculated critical loads for the case study area in KEF. These results suggest that the health of red spruce at HBEF and sugar maple at KEF may have been compromised by the acidifying nitrogen and sulfur deposition received in 2002.

Acidifying total nitrogen deposition consists of both reduced (NH_x) and oxidized (NO_x) forms of nitrogen. However, only NO_x is currently regulated as a criteria pollutant. Therefore, to gain an understanding of the relationship between the two states (reduced and oxidized) of total nitrogen deposition and the critical loads for the KEF and HBEF case study areas, total nitrogen deposition must be separated into NH_x-N and NO_x-N. **Figure 4.3-7** and **Figure 4.3-8** present the CLF response curves for the most protective critical load condition ($Bc/Al_{(crit)}$ = 10.0) for the KEF and HBEF case study areas, respectively. In these relationships, the CLF function has been modified by maintaining NH_x-N deposition at the 2002 deposition level; only sulfur and NO_x-N deposition levels vary to indicate the combined critical load. Based on 2002 CMAQ/NADP total nitrogen and sulfur deposition, NH_x-N accounted for 25.7 % (249 eq/ha) and 26.4 % (159 eq/ha) of total nitrogen deposition in the KEF and HBEF case study areas, respectively. These fixed amounts of NH_x-N influenced the highest protection CLF response curves for both areas. For both case studies, the maximum sulfur critical load ($CL_{max}(S)$) and the maximum nitrogen critical load ($CL_{max}(N)$), as NO_x, were lowered. In the calculations for the KEF Case Study Area, the $CL_{max}(S)$ was reduced by 5 % to 661 eq/ha/yr, and in the HBEF Case Study Area calculations, the $CL_{max}(S)$ was reduced by 26 % to 328 eq/ha/yr. Similarly, the $CL_{max}(N)$ (as NO_x) for the KEF Case Study Area was reduced by 27% to 661 eq/ha/yr, and the $CL_{max}(N)$ (as NO_x) for the HBEF Case Study Area was reduced by 33% to 328 eq/ha/yr when NH_x-N deposition was held constant.

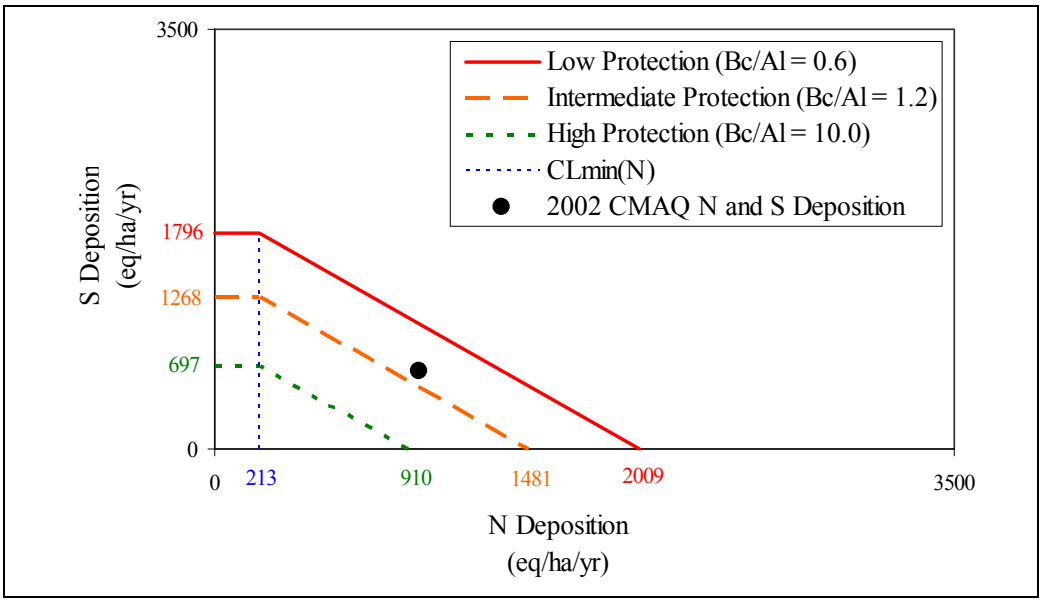


Figure 4.3-5. Critical load function response curves for the three selected critical loads conditions (corresponding to the three levels of protection) for the Kane Experimental Forest Case Study Area. The 2002 CMAQ/NADP total nitrogen and sulfur ($N+S_{comb}$) deposition was greater than the highest and intermediate level of protection critical loads. The flat line portion of the curves indicates total nitrogen deposition corresponding to the $CL_{min}(N)$ (nitrogen absorbed by nitrogen sinks within the system).

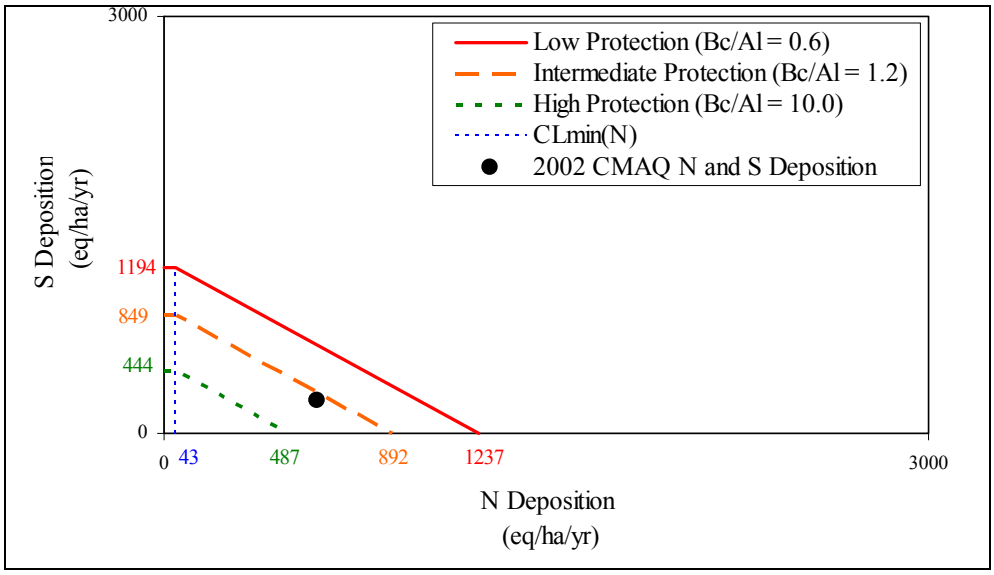


Figure 4.3-6. Critical load function response curves for the three selected critical loads conditions (corresponding to the three levels of protection) for the Hubbard Brook Experimental Forest Case Study Area. The 2002 CMAQ/NADP total nitrogen and sulfur ($N+S_{comb}$) deposition was greater than the highest level of protection critical load. The flat line portion of the curves indicates total nitrogen deposition corresponding to the $CL_{min}(N)$ (nitrogen absorbed by nitrogen sinks within the system).

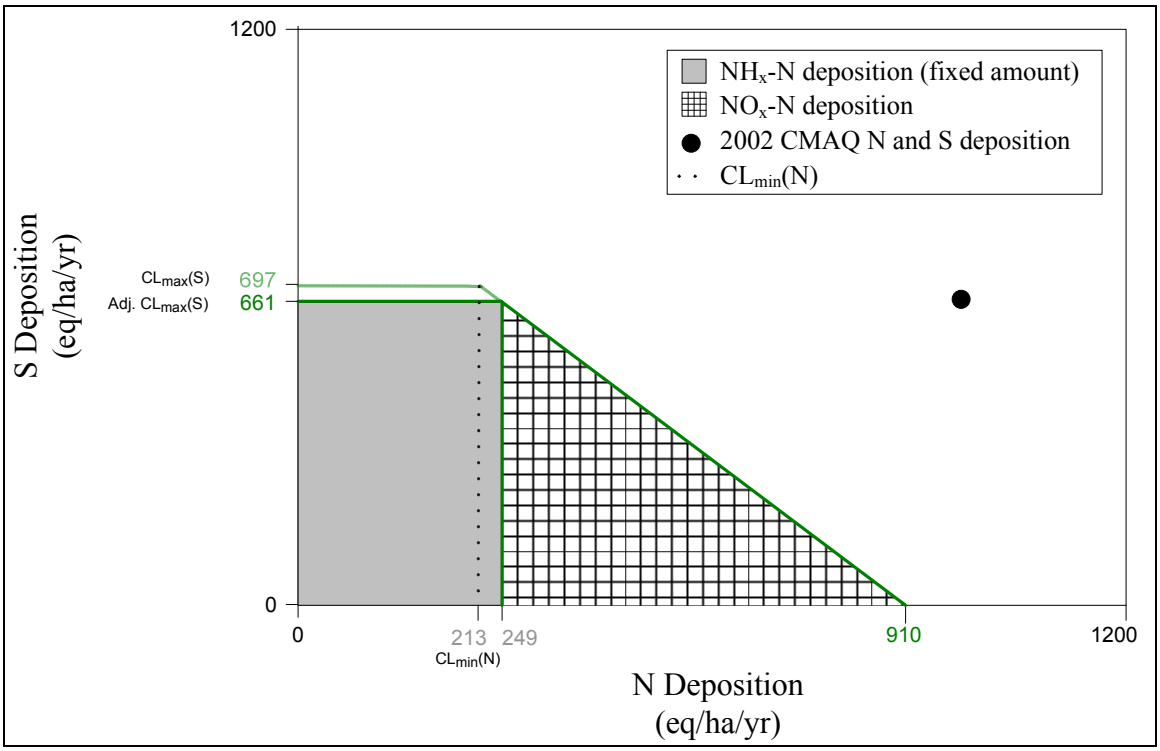


Figure 4.3-7. The influence of the 2002 CMAQ/NADP total reduced nitrogen (NH_x-N) deposition on the critical function response curve, and in turn, the maximum amounts of sulfur ($CL_{max}(S)$) and oxidized nitrogen (NO_x-N) in the critical load for the Kane Experimental Forest Case Study Area. The critical load of oxidized nitrogen (NO_x-N) is 661 eq/ha/yr (910−249). The $CL_{min}(N)$ (nitrogen absorbed by nitrogen sinks within the system) corresponds to the value depicted in **Figure 4.3-5**.

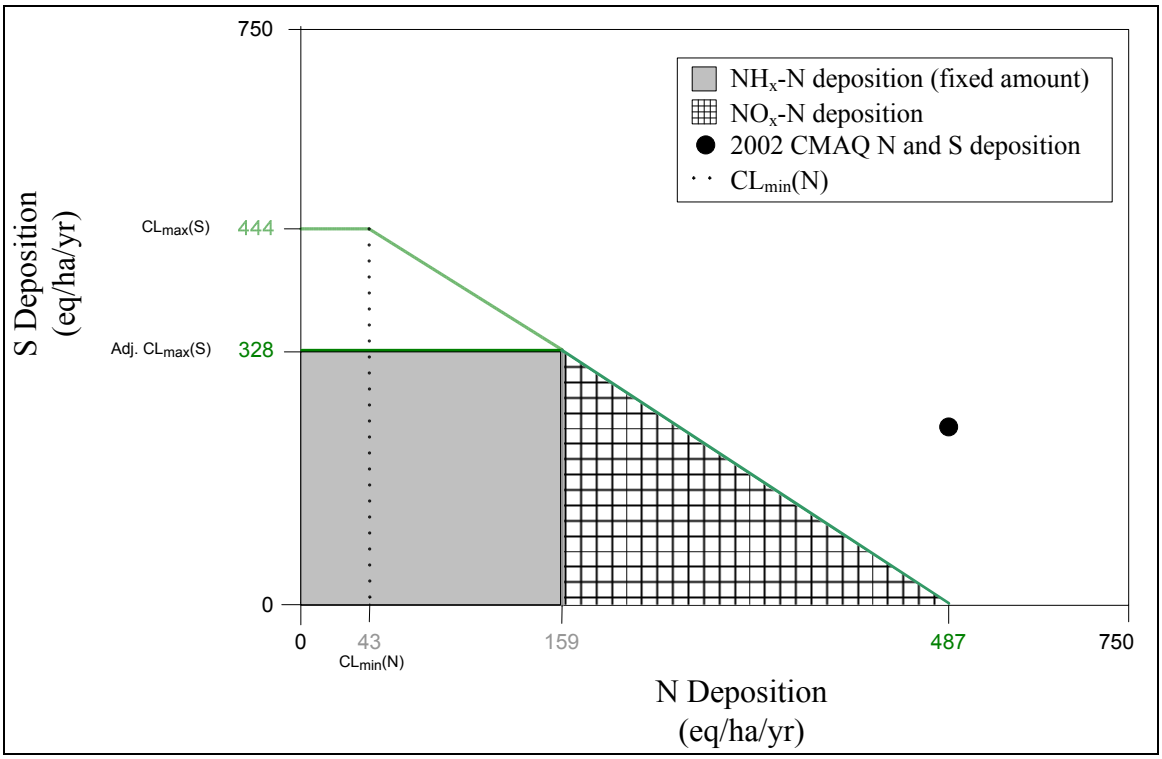


Figure 4.3-8. The influence of the 2002 CMAQ/NADP total reduced nitrogen (NH_x-N) deposition on the critical load function response curve and, in turn, the maximum amounts of sulfur ($CL_{max}(S)$) and oxidized nitrogen (NO_x-N) in the critical load for the Hubbard Brook Experimental Forest Case Study Area. The critical load of oxidized nitrogen (NO_x-N) is 328 eq/ha/yr (487−159). The $CL_{min}(N)$ (nitrogen absorbed by nitrogen sinks within the system) corresponds to the value depicted in **Figure 4.3-6**.

4.3.6 Evaluation of Representativeness of Case Study Areas

Although the case studies estimated critical load assessments for red spruce and sugar maple in two areas and established that 2002 CMAQ/NADP total nitrogen and sulfur deposition was greater than the calculated loads, these results cannot be directly extrapolated to the full ranges of the two species. Critical loads are largely determined by soil characteristics, and these characteristics vary by location. Therefore, to characterize the critical loads of sugar maple and red spruce and determine the extent to which total nitrogen and sulfur deposition is greater than or less than these loads, it is necessary to calculate critical loads in multiple locations throughout the ranges of the two species to determine the critical loads for these species.

Critical load calculations were applied to multiple areas within 24 states for sugar maple and in 8 states for red spruce. Individual site locations within each state were determined by the U.S. Forest Service Forest Inventory and Analysis (FIA) database permanent sampling plots'

locations on forestland[3] (timberland[4] for New York, Arkansas, Kentucky, and North Carolina), each covering 0.07 ha. Only database information for nonunique[5], permanent sampling plots that supported the growth of sugar maple or red spruce and had the necessary soil, parent material, atmospheric deposition, and runoff data were included in the analyses. With these restrictions, 7,992 of the 14,669 sugar maple plots and 763 of the 2,875 red spruce plots were included in the calculations of the plot-specific critical loads (**Table 4.3-3**). Although only a subset of the total sugar maple and red spruce plots were included in the analyses, the results are thought to accurately capture the range and trends of critical loads of the two species. Because of the randomness of the plot restrictions, it is unlikely that a bias was incorporated into the analyses.

The calculated critical loads for the three levels of protection ($Bc/Al_{(crit)}$ = 0.6, 1.2, and 10.0) for all plots were compared to 2002 CMAQ/NADP total nitrogen and sulfur deposition to determine which plots with sugar maple and/or red spruce experienced deposition levels greater than the critical load values.

Table 4.3-3. Number and Location of USFS FIA Permanent Sampling Plots (each plot is 0.07 ha) Used in the Analysis of Critical Loads for Full Geographic Ranges of Sugar Maple and Red Spruce

State	Sugar Maple	Red Spruce
Alabama	13	–
Arkansas	10	–
Connecticut	35	–
Illinois	29	–
Indiana	306	–
Iowa	13	–
Kansas	NA	–
Kentucky	14	–
Maine	271	560

[3] Forestland is defined as, "land at least 10 percent stocked by forest trees of any size, or formerly having such tree cover, and not currently developed for non-forest uses, with a minimum area classification of 1 acre." (USFS, 2002a).

[4] Timberland is defined as, "forest land capable of producing in excess of 20 cubic feet per acre per year and not legally withdrawn from timber production, with a minimum area classification of 1 acre." (USFS, 2002b).

[5] Nonunique permanent sampling plot locations are those that have critical load attribute values (e.g., soils, runoff, atmospheric deposition) that are not distinct and are repeated within a 250-acre area of the plot location. This "confidentiality" filter is a requirement of the USFS to prevent the disclosure of data that can be directly linked to a location on private land. To comply with the necessary "confidentiality," full coverages of the data required for the critical load deposition calculations were given to the USFS, and the USFS matched and provided the data to each nonunique, permanent sampling plot.

State	Sugar Maple	Red Spruce
Maryland	4	–
Massachusetts	33	3
Michigan	633	–
Minnesota	289	–
Missouri	147	–
New Hampshire	82	55
New Jersey	6	–
New York	485	52
North Carolina	17	1
Ohio	374	–
Pennsylvania	285	NA
Rhode Island	NA	–
South Carolina	NA	–
Tennessee	319	1
Vermont	114	11
Virginia	175	NA
West Virginia	378	7
Wisconsin	960	–
TOTAL	**4,992**	**763**

NA = data not available for state
"–" = tree species not present on forestland in state

4.3.7 Current Conditions for Sugar Maple and Red Spruce

The critical loads of acidifying deposition for sugar maple in 24 states for the three levels of protection were found to range from 107 to 6,008 eq/ha/yr (**Table 4.3-4**). Critical loads for red spruce in the 8 states ranged from 180 to 4,278 eq/ha/yr. In a comparison of the 2002 CMAQ/NADP total nitrogen and sulfur deposition levels and calculated critical loads, 3% to 75% of all sugar maple plots and 3% to 36% of all red spruce plots were found to have total nitrogen and sulfur deposition greater than the critical loads; the highest protection critical loads ($Bc/Al_{(crit)}$ = 10.0) had the highest frequency of exceedance (**Table 4.3-5**). Aggregated by state, a large proportion of the sugar maple and red spruce plots showed high levels of critical load exceedance for the highest protection level ($Bc/Al_{(crit)}$ = 10.0), and comparatively lower exceedance frequency at the lowest protection level (($Bc/Al_{(crit)}$ = 0.6)) (**Table 4.3-5**). In general, New Hampshire displayed the greatest degree of critical load exceedance at all protection levels for both species.

Collectively, given the limitations and uncertainties associated with the SMB model to estimate critical acid loads (see Section 4.3.9 in Chapter 4 and Section 5 in Appendix 5 for further description), these results suggest that the health of at least a portion of the sugar maple and red spruce growing in the United States may have been compromised with the acidifying total nitrogen and sulfur deposition in 2002; even with the lowest level of protection, half the states contained sugar maple and red spruce stands that were negatively impacted by acidifying deposition. At the highest level of protection ($Bc/Al_{(crit)}$ = 10.0), the apparent impact of the 2002 CMAQ/NADP total nitrogen and sulfur deposition was much greater. A large portion of sugar maple (i.e., >80% of plots in 13 of 24 states) and the majority of red spruce (i.e., 100% of plots in 5 of 8 states) experienced deposition levels that exceeded the critical loads. If this high protection critical load accurately represents the conditions of the two species, a large proportion of both sugar maple and red spruce, throughout their ranges, were most likely negatively impacted by total nitrogen and sulfur deposition in 2002.

Table 4.3-4. Ranges of Critical Load Values, by Level of Protection ($Bc/Al_{(crit)}$ = 0.6, 1.2, and 10.0) and by State, for the Full Geographical Distribution Ranges of Sugar Maple and Red Spruce

State	Ranges of Critical Load Values (eq/ha/yr)					
	Sugar Maple			Red Spruce		
	Bc/Al = 0.6	Bc/Al = 1.2	Bc/Al = 10.0	Bc/Al = 0.6	Bc/Al = 1.2	Bc/Al = 10.0
Alabama	1,592 to 5,337	1,114 to 3,638	617 to 2,015	–	–	–
Arkansas	2,239 to 4,290	1,536 to 2,913	857 to 1,623	–	–	–
Connecticut	1,519 to 2,468	1,058 to 1,702	581 to 941	–	–	–
Illinois	2,543 to 3,671	1,730 to 2,485	965 to 1,390	–	–	–
Indiana	1,478 to 5,859	1,020 to 3,971	573 to 2,214	–	–	–
Iowa	2,260 to 3,791	1,533 to 2,560	854 to 1,424	–	–	–
Kansas	NA	NA	NA	–	–	–
Kentucky	2,044 to 3,994	1,390 to 2,707	749 to 1,497	–	–	–
Maine	746 to 4,284	535 to 2,983	295 to 1,620	599 to 4,278	439 to 2,979	249 to 1,623
Maryland	2,066 to 3,090	1,417 to 2,122	929 to 1,178	–	–	–
Massachusetts	791 to 2,414	566 to 1,661	319 to 919	1,706 to 1,736	1,191 to 1,213	656 to 669
Michigan	400 to 6,008	294 to 4,070	169 to 2,269	–	–	–
Minnesota	220 to 4,916	166 to 3,318	107 to 1,861	–	–	–
Missouri	978 to 4,891	681 to 3,304	377 to 1,843	–	–	–
New Hampshire	580 to 1,994	419 to 1,439	236 to 780	418 to 1,994	324 to 1,439	180 to 780

State	Ranges of Critical Load Values (eq/ha/yr)					
	Sugar Maple			Red Spruce		
	Bc/Al = 0.6	**Bc/Al = 1.2**	**Bc/Al = 10.0**	**Bc/Al = 0.6**	**Bc/Al = 1.2**	**Bc/Al = 10.0**
New Jersey	1,452 to 2,651	1,029 to 1,824	566 to 1,012	–	–	–
New York	503 to 4,467	370 to 3,039	209 to 1,686	526 to 3,146	386 to 2,156	217 to 1,195
North Carolina	1,415 to 3,444	1,010 to 2,426	558 to 1,319	1256	926	501
Ohio	1,226 to 4,986	855 to 3,366	469 to 1,877	–	–	–
Pennsylvania	1,026 to 4,047	723 to 2,752	402 to 1,530	NA	NA	NA
Rhode Island	NA	NA	NA	–	–	–
South Carolina	NA	NA	NA	–	–	–
Tennessee	921 to 5,755	653 to 3,901	351 to 2,175	2,065	1,433	788
Vermont	479 to 5,660	351 to 3,846	201 to 2,142	846 to 2,305	601 to 1,648	336 to 888
Virginia	1,036 to 5,852	726 to 3,968	410 to 2,208	NA	NA	NA
West Virginia	369 to 4,134	270 to 2,819	152 to 1,560	2,300 to 3,634	1,610 to 2,533	884 to 1,382
Wisconsin	400 to 5,031	290 to 3,393	166 to 1,898	–	–	–
Combined (all plots)	**220** to **6,008**	**166** to **4,070**	**107** to **2,269**	**418** to **4,278**	**324** to **2,979**	**180** to **1,623**

NA = data not available for state
"–" = tree species not present on forestland in state

Table 4.3-5. Percentages of Plots, by Protection Level ($Bc/Al_{(crit)}$ = 0.6, 1.2, and 10.0) and by State, Where 2002 CMAQ/NADP Total Nitrogen and Sulfur Deposition Was Greater Than the Critical Loads for Sugar Maple and Red Spruce

State	Percentage of Plots Where Critical Load is Exceeded (%)					
	Sugar Maple			Red Spruce		
	Bc/Al = 0.6	**Bc/Al = 1.2**	**Bc/Al = 10.0**	**Bc/Al = 0.6**	**Bc/Al = 1.2**	**Bc/Al = 10.0**
Alabama	0	23	31	–	–	–
Arkansas	0	0	10	–	–	–
Connecticut	0	23	100	–	–	–
Illinois	0	0	66	–	–	–
Indiana	0.3	12	87	–	–	–
Iowa	0	0	23	–	–	–
Kansas	NA	NA	NA	–	–	–
Kentucky	0	0	86	–	–	–
Maine	0	0.7	20	0.2	0.5	16
Maryland	0	25	100	–	–	–
Massachusetts	6	33	100	0	100	100
Michigan	6	14	70	–	–	–
Minnesota	2	7	30	–	–	–
Missouri	0.7	2	46	–	–	v

State	Percentage of Plots Where Critical Load is Exceeded (%)					
	Sugar Maple			Red Spruce		
	Bc/Al = 0.6	Bc/Al = 1.2	Bc/Al = 10.0	Bc/Al = 0.6	Bc/Al = 1.2	Bc/Al = 10.0
New Hampshire	29	38	84	27	38	78
New Jersey	0	67	100	–	–	–
New York	6	20	95	14	15	79
North Carolina	0	6	71	0	0	100
Ohio	1	16	95	–	–	–
Pennsylvania	7	22	98	NA	NA	NA
Rhode Island	NA	NA	NA	–	–	–
South Carolina	NA	NA	NA	–	–	–
Tennessee	0.3	3	50	0	0	100
Vermont	2	7	99	2	6	100
Virginia	2	9	59	NA	NA	NA
West Virginia	2	8	95	0	0	100
Wisconsin	2	10	82	–	–	–
Combined (all plots)	**3**	**12**	**75**	**3**	**5**	**36**

NA = data not available for state
"–" = tree species not present on forestland in state

4.3.8 Ecological Effect Function for Terrestrial Acidification

As described earlier and explained in greater detail in Appendix 5, there is an established relationship between atmospheric deposition of nitrogen and sulfur and the Bc/Al ratio in the soil solution. In areas with high amounts of acidifying nitrogen and sulfur deposition, protons can replace exchangeable base cations, which are then leached from the soil, and the resulting lower soil pH increases the mobilization of soil Al. The Bc/Al ratio in the soil solution is thereby decreased, and this can negatively impact trees through direct Al toxicity to roots and reduced uptake of base cation nutrients. As indicated in **Figure 4.3.1**, as the Bc/Al ratio in the soil solution decreases, the incidence of reduced tree growth increases.

The Bc/Al ratio in the soil solution is the indicator selected to estimate critical loads of acidity for terrestrial acidification and is an influential parameter in the ANC term of the SMB model critical load equation (Equation 7 in Section 4.3.4). The equation to estimate ANC is presented below, in Equation 8.

$$\mathrm{ANC}_{(\mathrm{le,crit})} = -Q^{2/3} \times \left(1.5 \times \frac{\mathrm{Bc}_{\mathrm{dep}} + \mathrm{Bc}_{\mathrm{w}} - \mathrm{Bc}_{\mathrm{u}}}{K_{\mathrm{gibb}} \times \left(\frac{\mathrm{Bc}}{\mathrm{Al}}\right)_{\mathrm{crit}}} \right)^{1/3} - 1.5 \times \frac{\mathrm{Bc}_{\mathrm{dep}} + \mathrm{Bc}_{\mathrm{w}} - \mathrm{Bc}_{\mathrm{u}}}{\left(\frac{\mathrm{Bc}}{\mathrm{Al}}\right)_{\mathrm{crit}}} \qquad (8)$$

where

Q	=	annual runoff in m^3/ha/yr
Bc_{dep}	=	base cation (Ca^{2+}+ K^+ + Mg^{2+}) deposition[6]
Bc_w	=	soil base cation (Ca^{2+}+ K + Mg^{2+}) weathering[7]
Bc_u	=	base cation (Ca^{2+}+ K + Mg^{2+}) uptake by trees
K_{gibb}	=	the gibbsite equilibrium constant (a function of forest soil organic matter content that affects Al solubility) (UNECE, 2004)
$(Bc/Al)_{crit}$	=	the base cation to aluminum ratio (indicator)

The three $(Bc/Al)_{crit}$ ratios (0.6, 1.2, and 10.0) used in this case study were selected to represent the range of protection levels to the health of red spruce and sugar maple. The Bc/Al(crit) ratio of 10.0 corresponds to the highest level of protection, and, when included in the calculation of the ANC term, results in the lowest critical load. A terrestrial system with such a condition would only be able to tolerate comparatively low levels of total nitrogen and sulfur deposition. A $(Bc/Al)_{crit}$ ratio of 1.2 represents an intermediate level of protection and moderate critical load. The $(Bc/Al)_{crit}$ ratio of 0.6 ratio provides the lowest level of protection to tree health and results in the estimation of a high critical load.

In the expansion of the critical load assessments to the full geographic ranges of sugar maple and red spruce, as discussed in Section 4.3.6, critical loads were estimated in multiple locations for each of the three levels of protection $(Bc/Al)_{crit}$ = 0.6, 1.2, and 10.0) for each species. Because of the differences in soil conditions, runoff, base cation, and chloride deposition patterns, this analysis produced a wide range of critical load estimates. Depicting the extremes (lowest and highest) and the average critical load values in CLF curves provides an indication of the combinations of total nitrogen and sulfur deposition that could occur without exceeding the critical loads associated with the upper and lower limits and averages of the three protection levels (**Figure 4.3.9** and **Figure 4.3.10**). As is depicted in the figures, the lowest critical loads corresponding to the three protection levels $(Bc/Al)_{crit}$ ratio = 0.6, 1.2, and 10.0) were 387, 284,

[6] Bc_{dep} is **not** the same as BC_{dep} used in Equation 1. BC_{dep} includes Ca^{2+}, K^+, Mg^{2+}, and Na^+, whereas Bc_{dep} includes base cations that are taken up by vegetation (i.e., only includes Ca^{2+}, K^+, and Mg^{2+}).

[7] Bc_w is **not** the same as BC_w used in Equation 1. BC_w includes Ca^{2+}, K^+, Mg^{2+}, and Na^+, whereas Bc_w includes base cations that are taken up by vegetation (i.e., only includes Ca^{2+}, K^+, and Mg^{2+}).

and 163 eq/ha/yr for sugar maple and 526, 386, and 217 eq/ha/yr for red spruce. In contrast, the highest critical loads for the three protection levels for sugar maple were 5,660, 3,846, and 2,142 eq/ha/yr and for red spruce were 4,265, 2,976, and 1621 eq/ha/yr. The 1,979 to 5,273 eq/ha/yr differences between the extreme estimates for sugar maple and 1,404 to 3,739 eq/ha/yr differences for the red spruce estimates indicate the amount of total nitrogen and sulfur deposition that separates the lower and upper limits of the lowest and highest protection levels.

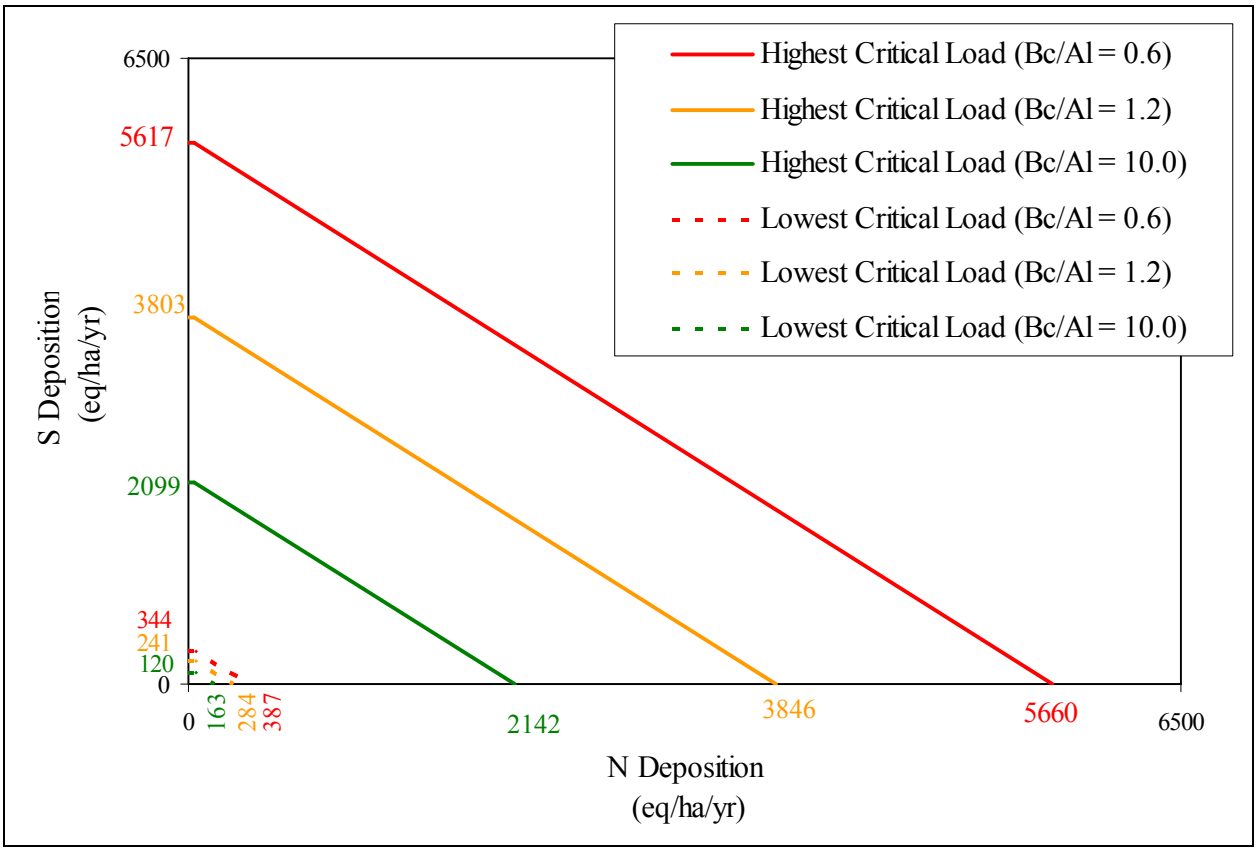


Figure 4.3.9. The lowest and highest critical load function response curves for the three levels of protection ($(Bc/Al)_{crit}$ = 0.6, 1.2, and 10.0) for the critical load assessments for the full geographical range of sugar maple. The $CL_{min}(N)$ value for all curves is 42.86 eq/ha/yr, but this value is not indicated in the figure.

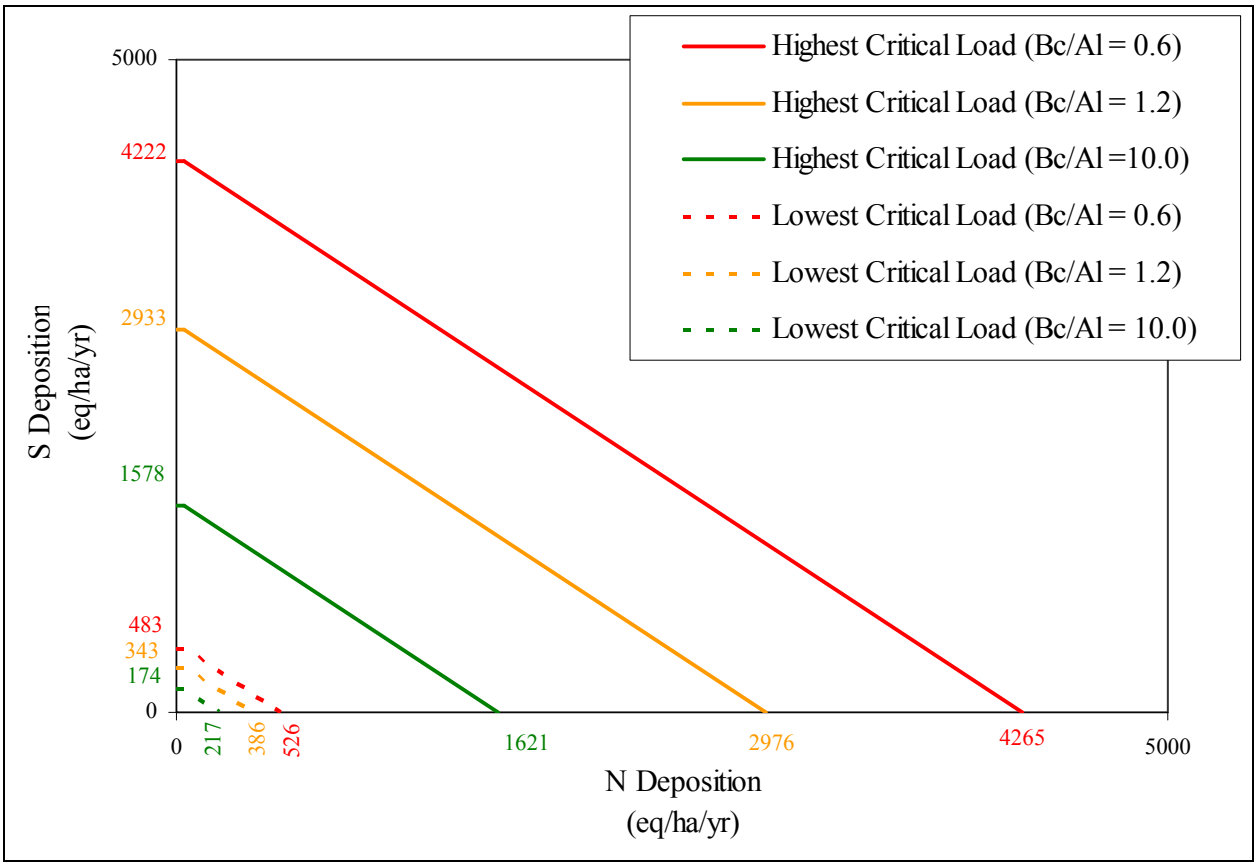


Figure 4.3.10. The lowest and highest critical load function response curves for the three levels of protection ($(Bc/Al)_{crit}$ = 0.6, 1.2, and 10.0) for the critical load assessments for the full geographical range of red spruce. The $CL_{min}(N)$ value for all curves is 42.86 eq/ha/yr, but this value is not indicated in the figure.

4.3.9 Uncertainty and Variability

4.3.9.1 Kane Experimental Forest and Hubbard Brook Experimental Forest Case Study Areas

Despite the extensive use of the SMB model to estimate critical loads, there is uncertainty regarding the output from the model and calculations. To a large degree, this uncertainty comes from the dependence of the SMB calculations on assumptions made by the researcher and the use of default values. Parameters including base cation weathering, forest soil ANC of critical load leaching, Kgibb, base cation and nitrogen uptake, nitrogen immobilization, and denitrification are rarely measured at each location and must be selected based on the literature or on other calculations and models. In an analysis conducted by Li and McNulty (2007), it was determined that the base cation weathering and forest soil ANC of critical load leaching

parameters were the main sources of uncertainty, with each respectively contributing 49% and 46% to the total variability in critical load estimates. It has, therefore, been suggested that the calculation of critical loads using a relevant range of parameter values can provide the foundation for an uncertainty analysis (Hall et al., 2001; Hodson and Langan 1999; Li and McNulty, 2007;); it is likely that the correct critical load of a system will be contained within the range of load estimates from such an approach. If all or a large majority of estimates indicate that the critical load of a system is exceeded with current total nitrogen and sulfur deposition rates, it is likely that deposition is greater than the critical load and that the trees and vegetation in that system are being negatively impacted by acidification. Conversely, if deposition is not greater than the majority of critical load estimates, there can be greater confidence that the system is not being impacted by acidifying deposition. Under a scenario of a near equal number of estimates indicating exceedance and nonexceedance, however, it is not possible to confidently determine the actual acidification status of a system. Nonetheless, such results do suggest that the system is near the critical load level and should be monitored or assessed more thoroughly.

> "Uncertainty is a measure of the knowledge of the magnitude of a parameter. Uncertainty can be reduced by research, i.e., the parameter value can be refined. Uncertainty is quantified as a distribution. For example, the volume of a lake may be estimated from its surface area and an average depth. This estimate can be refined by measurement. Variance is a measure of the heterogeneity of a landscape parameter or the inherent variability in a chemical property. Variance can not be reduced by further research. It is quantified as a distribution. For example, the organic carbon content of the soil in a region may vary, even over short distances. The soil is not homogenous and thus the organic carbon content can be described with a distribution of values" (Webster and MacKay, 2003).

In this case study, multiple values were used for several parameters in the SMB calculations and are detailed in Appendix 5. Therefore, it was possible to use the range of output values from the calculations to access the certainty of the acidification status of the HBEF and KEF case study areas. The patterning of the results suggest that the 2002 total nitrogen and sulfur deposition levels were very close to, if not greater than, the critical loads of the two case study areas, and both ecosystems are likely to be sensitive to any future changes in the levels of nitrogen and sulfur acidifying deposition.

4.3.9.2 Expansion of Critical Load Assessments to Determine Current Conditions for Sugar Maple and Red Spruce

Critical load estimates for individual plots within the distribution ranges of sugar maple and red spruce were calculated using the clay-substrate method to estimate BC_w. As discussed

earlier, the BC_w term within the SMB model is one of the most influential terms in the calculation of a critical load, and the determination of this BC_w value is strongly influenced by the classified acidity of the soil parent material. In large-scale analyses, descriptions of the mineralogy of parent material underlying the soil may be missing, nondescriptive, only suggestive of mineralogy, or these may only represent the dominant mineralogy in a large area (and therefore not accurately capture the smaller-scale variation in mineralogy). Therefore, it is possible to misclassify the parent material acidity in the BC_w term.

In the analyses of critical loads for the full distribution ranges of sugar maple and red spruce in this Risk and Exposure Assessment, two fine-scale databases, the Soil Survey Geographic Database (SSURGO) of soils [USDA-NRCS, 2008] and USGS state-level geology [USGS, 2009] databases, were used as the sources for parent material mineralogy to allow for location-specific mineralogy descriptions. In addition, a systematic protocol based on known and probable silica and ferromagnesium content, spatial patterns of local and geologic settings, and implied depositional mechanisms and environments was used to determine the parent material acidity classifications. Therefore, steps were taken to determine accurate, location-specific acidity classifications. Nonetheless, parent material in some of the plots may have been misclassified.

To evaluate the degree to which critical load estimates could change with a misclassification of parent material acidity, a simple analysis of absolute (eq/ha/yr) and percentage change associated with misclassifications of parent materials was conducted, using the critical loads associated with the three levels of protection ($(Bc/Al)_{crit}$ = 0.6, 1.2, and 10.0) for sugar maple and red spruce. The differences between all combinations of critical loads calculated with basic, intermediate, and acidic parent materials were determined, and these differences in values were expressed as a percentage of the original critical load estimates (described further in Appendix 5).

The comparisons of critical loads revealed that changes in critical load values could range from 0 to 3,631 eq/ha/yr for sugar maple and 0 to 1,584 eq/ha/yr for red spruce with the misclassification of parent material acidity. These ranges corresponded to percentage differences ranging from 0% to 492% and 0% to 453% for sugar maple and red spruce, respectively. The results also indicated that the biggest impacts of a misclassification on critical load estimates would occur with an acidic parent material being misclassified as basic; the average percentage changes in the estimated critical loads, in such a scenario, were 67% to 70% for sugar maple and

74% to 78% for red spruce, and the median percentage changes were 60% to 61% and 71% to 74% for the two species, respectively. In contrast, the smallest impacts on critical load estimates would occur when a basic parent material was incorrectly classified as intermediate and vice versa. In this scenario, the average and median percentage changes in critical load estimates were only 7% to 8% and 6% to 7% for sugar maple and 5% to 6% and 4% to 5% for red spruce. Given the potential significant impacts of a misclassification of parent material acidity on critical load estimates, this potential source of error should be considered in the accuracy and application of the critical load estimates.

4.4 SUMMARY AND KEY FINDINGS

Sulfur and nitrogen deposition have been linked to changes in biogeochemistry related to aquatic ecosystems. Deposition of SO_x, NO_x, and NH_x leads to ecosystems' exposure to acidification due to the reactions in the atmosphere that form various acidifying compounds. Acidifying deposition can lower the pH and ANC of aquatic systems. As ANC values decline below 100 μeq/L, an increase in the direct effects are exhibited on individual aquatic species, including fitness loss or death, reduced species richness, and altered community structure. Further, acidifying deposition can significantly increase the concentration of anions in soil, leading to an accelerated base cation leaching of Ca^{2+} and Mg^{2+} and, subsequently, an increase in the mobility of inorganic Al, which is toxic to fish, algae, and aquatic invertebrates.

The role of aquatic acidification in two eastern United States areas—northeastern New York's Adirondack area and the Shenandoah area in western Virginia—was analyzed to assess surface water trends in SO_4^{2-} and NO_3^- concentrations and ANC levels and to affirm the understanding that reductions in deposition could influence the risk of acidification. Monitoring data from the EPA-administered TIME/LTM and EMAP programs were assessed for the years 1990 to 2006, and past, present, and future water quality levels were estimated both steady-state and dynamic biogeochemical models. A summary of findings follows:

- Although wet deposition rates for SO_2 and NO_x in the Adirondack Case Study Area have been reduced since the mid-1990s, current concentrations in are still well above preacidification (1860) conditions. MAGIC modeling predicts NO_3^- and SO_4^{2-} are 17- and 5-fold higher today, respectively. The estimated average ANC for 44 lakes in the Adirondack Case Study Area is 62.1 μeq/L (± 15.7 μeq/L); 78 % of all monitored lakes in

the Adirondack Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 78%, 31% experience episodic acidification, and 18% are chronically acidic today.

- Based on the steady-state critical load model for the year 2002, 18%, 28%, 44%, and 58% of 169 modeled lakes received combined total sulfur and nitrogen deposition that exceeded their critical load, with critical ANC limits of 0, 20, 50, and 100 μeq/L, respectively.
- Based on a deposition scenario that maintains current emission levels to 2020 and 2050, the simulation forecast indicates no improvement in water quality in the Adirondack Case Study Area. The percentage of lakes within the *Elevated* to *Acute Concern* classes remains the same in 2020 and 2050.
- Since the mid-1990s, streams in the Shenandoah Case Study Area have shown slight declines in NO_3^- and SO_4^{2-} concentrations in surface waters. ANC levels increased from about 50 μeq/L in the early 1990 to >75 μeq/L until 2002 when ANC levels declined back to 1991–1992 levels. Current concentrations are still above preacidification (1860) conditions. MAGIC modeling predicts surface water concentrations of NO_3^- and SO_4^{2-} are 10- and 32-fold higher today, respectively. The estimated average ANC for 60 streams in the Shenandoah Case Study Area is 57.9 μeq/L (± 4.5 μeq/L). 55% of all monitored streams in the Shenandoah Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 55%, 18% experience episodic acidification, and 18% are chronically acidic today.
- Based on the steady-state critical load model for the year 2002, 52%, 72%, 85%, and 93% of 60 modeled streams received combined total sulfur and nitrogen deposition that exceeded their critical load, with critical ANC limits of 0, 20, 50, and 100 μeq/L, respectively.
- Based on a deposition scenario that maintains current emission levels to 2020 and 2050, the simulation forecast indicates that a large number of streams still have *Elevated* to *Acute* problems with acidity. In fact, from 2006 to 2050, the percentage of streams with *Acute Concern* increases by 5%, while the percentage of streams in *Moderate Concern* decreases by 5%.

Tree health has been linked to base cations (Bc) in soil (such as Ca^{2+}, Mg^{2+} and potassium), as well as soil Al content. Acidifying nitrogen and sulfur deposition can deplete soils of base cations and subsequently mobilize Al, making the toxic Al available to sensitive trees and other terrestrial vegetation. A critical load analysis was performed for sugar maple and red

spruce forests in the eastern United States by using the ratio of Bc to Al in acidified forest soils as an indicator to assess the impact of nitrogen and sulfur deposition on tree health. These are the two most commonly studied species in North America for impacts of acidification. At a Bc/Al ratio of 1.2, red spruce growth can be reduced by 20%. Sugar maple growth can be reduced by 20% at a Bc/Al ratio of 0.6. Key findings of the case study are summarized below.

- Case study results suggest that the health of at least a portion of the sugar maple and red spruce growing in the United States may have been compromised with acidifying total nitrogen and sulfur deposition in 2002:
  - 2002 CMAQ/NADP total nitrogen and sulfur deposition levels exceeded three selected critical loads in 3% to 75% of all sugar maple plots across 24 states. The three critical loads ranged from 107 to 6,008 eq/ha/yr for the Bc/Al ratios of 0.6, 1.2, and 10.0 (increasing levels of tree protection).
  - 2002 CMAQ/NADP total nitrogen and sulfur deposition levels exceeded three selected critical loads in 3% to 36% of all red spruce plots across eight states. The three critical loads ranged from 180 to 4,278 eq/ha/yr for the Bc/Al ratios of 0.6, 1.2, and 10.0 (increasing levels of tree protection).
- The Simple Mass Balance model assumptions made for base cation weathering (Bcw) and forest soil ANC input parameters are the main sources of uncertainty since these parameters are rarely measured and require researchers to use default values. Bcw contributed 49% to the total variability in the critical load estimates, and forest soil ANC contributed 46% to the total variability.
- The pattern of case study results suggests that nitrogen and sulfur acidifying deposition in the sugar maple and red spruce forest areas studied were very close to, if not greater than, the critical loads for those areas, and both ecosystems are likely to be sensitive to any future changes in the levels of deposition.

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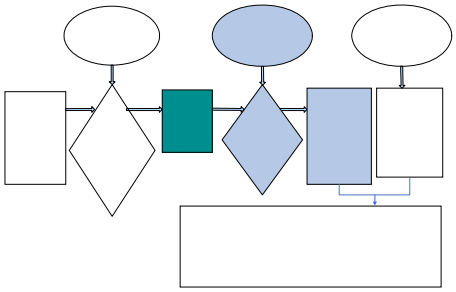


5.0 NUTRIENT ENRICHMENT

5.1 SCIENCE OVERVIEW

> Nutrient enrichment is an increase in a nutrient, such as nitrogen, that may result in an imbalance in ecological stoichiometry, causing effects on processes, structure, and function. Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability (Sterner and Elser, 2002).

Nitrogen and sulfur enrichment represents a continuum of effects that can be characterized as positive or negative, depending on the selected ecological endpoint, location, and baseline conditions of an ecosystem. Nutrient enrichment describes a condition where an increase in a nutrient, such as nitrogen, may result in an imbalance in ecological stoichiometry, causing effects on ecological processes, structure, and function. Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability (Sterner and Elser, 2002). Some organisms may at first respond positively to an initial increase in nutrients, exhibiting a fertilized increase in growth. However, as the nutrient load continues to rise, the imbalance can have negative effects in the organism's response or the invasion of new organisms that benefit from increased nutrients. In general, ecosystems that are most responsive to nutrient enrichment from atmospheric nitrogen deposition are those that receive high levels of deposition relative to nonanthropogenic nitrogen loading, those that are nitrogen-limited, or those that contain species that have evolved in nutrient-poor environments (U.S. EPA, 2008, Section 3.3). Nutrient enrichment in ecosystems may alter the native terrestrial species composition (e.g., species shift from wildflower meadows to shrubs) and can result in eutrophication in aquatic systems (see Section 3.3 of the *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008).

Both aquatic and terrestrial effects of nutrient enrichment have been studied, and nitrogen enrichment is highlighted in this chapter. (Sulfur enrichment is discussed in Chapter 6.) For each effect, information is presented on the following:

- Ecological indicators, ecological responses, and ecosystem services
- Characteristics of areas sensitive to nutrient enrichment
- Selection of case study area(s)
- Current conditions in case study areas
- The ability to extrapolate case study findings to larger regions
- Current conditions for larger regions (based on extrapolation)
- Ecological effect functions
- Uncertainty and variability associated with the case study analyses.

Case studies on aquatic nutrient enrichment and terrestrial nutrient enrichment were performed as part of this Risk and Exposure Assessment (Appendices 6 and 7, respectively) to aid in determining whether a link can be established between deposition of nitrogen oxides (NO_x) (and/or total reactive nitrogen) and ecosystem response, as well as the impact of total reactive nitrogen deposition relative to NO_x deposition. These case studies are also intended to test whether area-based risk and exposure assessments are a suitable method for predicting nutrient enrichment effects on other ecosystems and geographic regions. The studies facilitate extrapolation of impacts from smaller-scale that are representative of sensitive areas to similar ecosystems across the country.

It should be noted that while the case studies were designed to provide the best representation of an ecosystem and its response to nutrient enrichment as the state of science allows, not all nutrient-cycling processes could be detailed. Specifically, while the volatilization of nitrogen from both aquatic and terrestrial ecosystems is recognized as an important piece of the nitrogen cycle (as highlighted in Annex C of the ISA [U.S. EPA, 2008] and discussed in Appendix 6 of this Risk and Exposure Assessment), the complexity of the environmental controls on the nutrient cycling processes involved precluded quantifying or considering volatilization.

5.1.1 Aquatic Nutrient Enrichment

Nutrient enrichment can result in eutrophication of aquatic systems (U.S. EPA, 2008, Section 3.3). Eutrophication is the process whereby a body of water becomes overenriched in nutrients, resulting in increased productivity. As productivity increases with concomitant increases in organic matter production, dissolved oxygen levels in the waterbody may decrease and lead to hypoxia (i.e., low dissolved oxygen levels). Total reactive nitrogen (Nr) can promote eutrophication in inland freshwater, estuarine, and coastal marine ecosystems. Eutrophication ultimately reduces biodiversity because of the lack of available oxygen needed for the survival of many aquatic plants and animals. The ISA concluded that there is sufficient evidence to infer a causal relationship between nitrogen deposition and the biogeochemical cycling of nitrogen in estuaries and coastal marine waters. Atmospheric nitrogen deposition is not the sole source of nitrogen loading to estuaries, and it is unknown if atmospheric deposition alone is sufficient to cause eutrophication. However, the contribution of atmospheric nitrogen deposition to total nitrogen load is calculated for some estuaries and can be >40%. In general, estuaries tend to be nitrogen-limited, and many currently receive high levels of nitrogen input from human activities to cause eutrophication. Because ecosystems may respond differently to enrichment, it is necessary to first perform risk and exposure assessments unique to the effect and ecosystem type. Appendix 6 presents a case study on two river basins and their estuaries: the Potomac River/Potomac Estuary and the Neuse River/Neuse River Estuary, and Section 5.2 summarizes the science, methodologies, and findings of the Aquatic Nutrient Enrichment Case Study.

5.1.2 Terrestrial Nutrient Enrichment

The ISA (U.S. EPA, 2008, Section 3.3) documented the current understanding of nutrient enrichment effects on terrestrial ecosystems and concluded that there is sufficient information to infer a causal relationship between atmospheric nitrogen deposition and biogeochemical cycling and fluxes of nitrogen in terrestrial systems. The ISA also concluded that there is a causal relationship between atmospheric nitrogen deposition and changes in species richness, species composition, and biodiversity in terrestrial systems. These conclusions are based on an extensive literature review, which is summarized in Table 4-4 of the ISA. The research involves both observational and experimental (nitrogen-addition) projects and includes alpine ecosystems, grasslands (including arid and semiarid ecosystems), forests, and deserts. It should be noted that

ecosystems and their component parts demonstrate different sensitivities to atmospheric nitrogen deposition. For example, shifts in lichen communities may occur at low levels of nitrogen deposition, 3 kg/ha/yr (Fenn et al., 2008), while shifts in serpentine grassland species were seen to occur at 10 to 15 kg N/ha/yr (Fenn et al., 2003).

The extensive documentation in the ISA was used to assist in the selection of the case study areas for this Risk and Exposure Assessment and to identify and compare ecological benchmarks of different ecosystems. Appendix 7 presents the case study report for two ecosystems: California coastal sage scrub (CSS) and San Bernardino Mountains mixed conifer forest (MCF). Section 5.3 summarizes the Terrestrial Nutrient Enrichment Case Study.

5.2 AQUATIC NUTRIENT ENRICHMENT

Aquatic nutrient enrichment is described in the ISA (U.S. EPA, 2008, Section 3.3) for both freshwater and coastal marine and estuarine systems. In nitrogen-limited freshwater aquatic systems, atmospheric inputs of nitrogen increase productivity and alter biological communities, especially phytoplankton. A freshwater lake or stream must be nitrogen-limited to be sensitive to nitrogen-mediated eutrophication. There are many examples of fresh waters that are nitrogen-limited or nitrogen and phosphorus co-limited (e.g., Baron, 2006; Bergström and Jansson, 2006; Bergström et al., 2005; Elser et al., 1990; Fenn et al., 2003; Tank and Dodds, 2003). In a meta-analysis that included 653 datasets, Elser et al. (2007) found that nitrogen limitation occurred as frequently as phosphorus limitation in freshwater ecosystems. Recently, a comprehensive study (Bergström and Jansson, 2006) of available data from the northern hemisphere survey of lakes along gradients of nitrogen deposition showed increased inorganic nitrogen concentrations and productivity to be correlated with atmospheric nitrogen deposition, leading to the conclusion that the results are evidence of nitrogen limitation in lakes with low ambient inputs of nitrogen and increased nitrogen concentration in lakes receiving nitrogen solely from atmospheric nitrogen deposition (Bergström and Jansson, 2006).

In coastal marine ecosystems, the nutrients most commonly associated with phytoplankton growth are nitrogen, phosphorus, and silicon. Interactions among the supplies of these nutrients can affect phytoplankton species composition in ways that might affect ecosystem function (Paerl et al., 2001a; Riegman, 1992). The relative proportions of these nutrients are important determinants of primary production, food web structure, and energy flow through the

ecosystem (Dortch and Whitledge, 1992; Justic et al., 1995a; Justic et al., 1995b; Turner et al., 1998).

There is strong scientific consensus that nitrogen is the principal cause of coastal eutrophication in the United States (NRC, 2000). On average, human activity has likely contributed to a six-fold increase in the nitrogen flux to U.S. coastal waters, and nitrogen now represents the most significant coastal pollution problem (Howarth et al., 2002b; Howarth and Marino, 2006). Atmospheric deposition is responsible for a portion of this nitrogen input (Howarth et al., 2002a).

Estuaries and coastal waters tend to be nitrogen-limited and are, therefore, inherently sensitive to increased nitrogen loading (D'Elia et al., 1986; Howarth and Marino, 2006). There is a scientific consensus that nitrogen-driven eutrophication in shallow estuaries has increased over the past several decades and that the environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl et al., 2001a). For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer et al., 1984) and Pamlico estuaries in North Carolina (Paerl et al., 1998) and along the continental shelf adjacent to the Mississippi and Atchafalaya rivers' discharges to the Gulf of Mexico (Eadie et al., 1994). It is partly because many estuaries and near-coastal marine waters are degraded by nutrient enrichment that they are highly sensitive to potential negative impacts from nitrogen addition from atmospheric deposition.

The Aquatic Nutrient Enrichment Case Study for this Risk and Exposure Assessment (Appendix 6) focuses on two estuarine systems—the Potomac Estuary and the Neuse River Estuary. The ecological indicator selected, risk and exposure assessment methodology, and findings for each system are described in this section.

5.2.1 Ecological Indicators, Ecological Responses, and Ecosystem Services

5.2.1.1 Indicators

Overview

Nitrogen is an essential nutrient for estuarine and marine ecosystem fertility; a key nutrient in the primary production of aquatic vegetation; and is often the algal growth-limiting nutrient (U.S. EPA, 2008, Section 3.3.5.3). Excessive nitrogen contributions increase primary productivity excessively and, in turn, cause habitat degradation, algal blooms, toxicity, hypoxia,

anoxia, fish kills, and decreases in biodiversity (Paerl, 2002). To evaluate these impacts, five biological indicators were used in the recent national assessment of estuary trophic condition: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and submerged aquatic vegetation (SAV) (Bricker et al., 2007). **Figure 5.2-1**, excerpted from the National Oceanic and Atmospheric Administration's (NOAA's) National Estuarine Eutrophication Assessment (NEEA) Update, provides a brief description of each of the indicators. For greater detail on each of the indicators, refer to the ISA (U.S. EPA, 2008, Section 3.3) and the NEEA Update (Bricker et al., 2007).

Primary symptoms	Description
Chlorophyll *a* (Phytoplankton)	A measure used to indicate the amount of microscopic algae (phytoplankton) growing in a water body. High concentrations can lead to low dissolved oxygen levels as a result of decomposition.
Macroalgal blooms	Large algae commonly referred to as "seaweed." Blooms can cause losses of submerged aquatic vegetation by blocking sunlight. Additionally, blooms may smother immobile shellfish, corals, or other habitat. The unsightly nature of some blooms may impact tourism due to the declining value of swimming, fishing, and boating.
Secondary symptoms	**Description**
Dissolved oxygen	Low dissolved oxygen is a eutrophic symptom because it occurs as a result of decomposing organic matter (from dense algal blooms), which sinks to the bottom and uses oxygen during decay. Low dissolved oxygen can cause fish kills, habitat loss, and degraded aesthetic values, resulting in the loss of tourism and recreational water use.
Submerged aquatic vegetation	Loss of submerged aquatic vegetation (SAV) occurs when dense algal blooms caused by excess nutrient additions (and absence of grazers) decrease water clarity and light penetration. Turbidity caused by other factors (e.g., wave energy, color) similarly affects SAV. The loss of SAV can have negative effects on an estuary's functionality and may impact some fisheries due to loss of a critical nursery habitat.
Nuisance/toxic blooms	Thought to be caused by a change in the natural mixture of nutrients that occurs when nutrient inputs increase over a long period of time. These blooms may release toxins that kill fish and shellfish. Human health problems may also occur due to the consumption of contaminated shellfish or from inhalation of airborne toxins. Many nuisance/toxic blooms occur naturally, some are advected into estuaries from the ocean; the role of nutrient enrichment is unclear.

Figure 5.2-1. Descriptions of the five eutrophication indicators used in the NEEA (Bricker et al., 2007).

Selection of an Ecological Indicator

After examining several estuarine assessment options, the most comprehensive evaluation technique that could be applied on a wide scale was determined to be an assessment of eutrophication as conducted in NOAA's NEEA. The NEEA Program defined and developed a Pressure-State-Response framework to assess the potential for eutrophication. This assessment framework has been titled the Assessment of Estuarine Trophic Status Eutrophication Index and is commonly referred to as ASSETS EI (Bricker et al., 2007). The "pressure" is the nitrogen, the

"state" is the current eutrophic condition, and the "response" would be the change in the state of the system. ASSETS EI is an estimation of the likelihood that the estuary is experiencing eutrophication or will experience eutrophication in the future based on the five indicators described above. The ASSETS EI served as the ecological indicator for the Aquatic Nutrient Enrichment Case Study.

The ASSETS EI incorporates indirect deposition over the watershed (i.e., deposition to terrestrial systems which, in turn, may be transported to aquatic systems) through the evaluation of nitrogen loading to the estuary. This was achieved by inputting 2002 Community Multiscale Air Quality (CMAQ)–modeled and National Atmospheric Deposition Program (NADP)–monitored data (see Chapter 3) to the U.S. Geological Survey's (USGS's) SPAtially Referenced Regressions on Watershed attributes (SPARROW) model. The combination of SPARROW modeling and the ASSETS EI (Appendix 6, Figure 2.2-1) provides a sound basis for conducting an eutrophication assessment.

ASSETS EI

The ASSETS EI (a Pressure-State-Response framework) is categorical, where each of three indices produces a score. The three scores are combined, and the overall score (the ASSETS EI) represents the estuary's health. The indices are as follows:

- **Influencing Factors/Overall Human Influence (OHI).** The physical, hydrologic, and anthropogenic factors that characterize the susceptibility of the estuary to the influences of nutrient inputs (also quantified as part of the index) and eutrophication.
- **Overall Eutrophic Condition (OEC).** An estimate of current eutrophic conditions derived from data for five symptoms known to be linked to eutrophication.
- **Determined Future Outlook (DFO).** A qualitative measure of expected changes in the system.

(See Figures 2.2-6 and 2.2-8 in Appendix 6 for the ASSETS EI approach to assessing OEC and DFO.)

The ASSETS EI scores fall into one of six categories: High, Good, Moderate, Poor, Bad, or Unknown. These ratings can be summarized as follows (Bricker et al., 2007):

- **High**: Low pressure, low eutrophic condition, and any expected improvement or no future change in eutrophic condition

- **Good**: Low to moderate pressure, low to moderate-low eutrophic condition, and any expected future change in condition
- **Moderate**: Any pressure, moderate-low to moderate-high eutrophic condition, and any expected future change in eutrophic condition
- **Poor**: Moderate-low to high pressure, moderate to moderate-high eutrophic condition, and any expected future change in condition
- **Bad**: Moderate to high pressure, moderate-high to high eutrophic condition, and any expected future change in eutrophic condition
- **Unknown**: Insufficient data for analysis.

NOAA's ASSETS EI method was first reported in 1999. Since that time, it has been used in several assessments across the country and internationally, and it has undergone revision and validation (Bricker et al., 1999, 2003, 2007; Ferreira et al., 2007; Whitall et al., 2007).

SPARROW

SPARROW is a watershed modeling technique designed and supported by the USGS. The model relies on a nonlinear regression formulation to relate water quality measurements throughout the watershed of interest to attributes of the watershed. (Note that with a nonlinear model, errors of the model are assumed to be independent across observations and have zero mean; the variance of each observation may be observation-specific.) Both point and diffuse sources within the watershed are considered, along with nonconservative transport processes (i.e., loss and storage of contaminants within the watershed). SPARROW follows the rules of mass balance while using a hybrid statistical and process-based approach. Utilization of the SPARROW model results in estimates of long-term, steady-state water quality in a stream (typically mean annual stream loadings of a contaminant).

A key component of SPARROW is its reliance on the spatial distribution of watershed characteristics and sources. The stream reach network is spatially referenced against all monitoring stations, geographic information systems (GIS) data for watershed properties, and source information. This structure allows for the simulation of fate and transport of contaminants from sources to streams and their downstream ecological endpoints. **Figure 5.2-2** shows how each watershed and stream reach within the stream network defined for the SPARROW application (represented by different colors in the figure) is processed separately and linked to derive a final loading at a downstream location (i.e., the star labeled X). The SPARROW model

is calibrated at each monitoring station (represented by stars in **Figure 5.2-2**) by comparing the modeled loads (i.e., a total of loads from each watershed segment and any upstream loads from previous calibrations) against monitored data at the station. In this case, the modeled load at downstream monitoring station X would include loads from upstream monitoring station Y and the five watershed segments between the two monitoring stations.

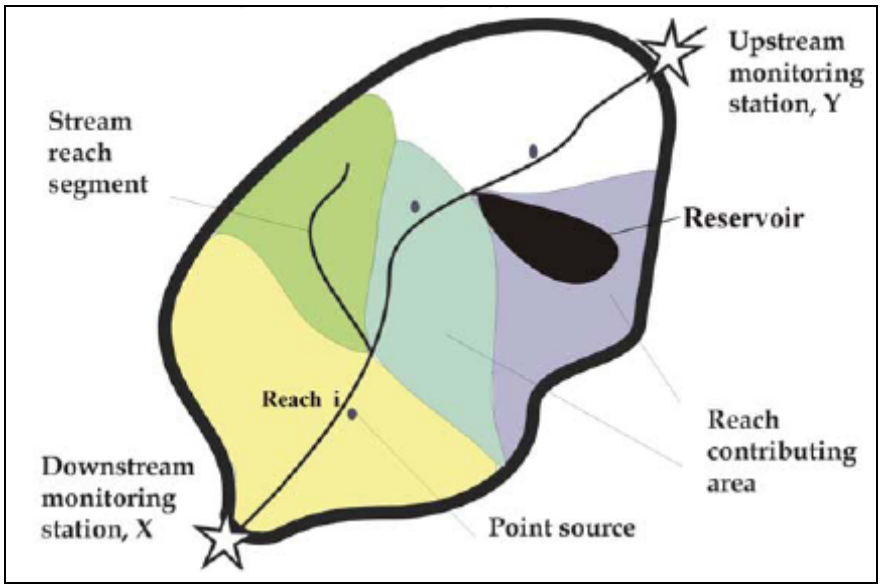


Figure 5.2-2. Conceptual illustration of a reach network.

The mathematical formulation of SPARROW used to determine nitrogen loadings for this case study is presented in Appendix 6. The equations used in SPARROW represent the mass loading, which includes sources, losses due to transport to the stream reaches (i.e., landscape characteristics that influence the delivery of diffuse sources of contamination to the stream), and instream or reservoir losses (i.e., stream attenuation processes that act on contaminant flux as it travels along stream reaches).

Within SPARROW, instream losses depend on a first-order loss rate and the length of the stream, while losses within a lake or reservoir depend on a first-order loss rate and the areal hydraulic load of the lake or reservoir (i.e., ratio of water-surface area to outflow discharge).

Results of the SPARROW model may be presented in three different accounting measures. These measures allow for the examination of how much nitrogen originates within a specific subbasin, how much of that nitrogen reaches the estuary, and finally, the total amount of nitrogen that reaches the estuary. Specifically, these measures are defined by the following:

- **Delivered Yield (load per area).** This is the amount of nutrients generated locally for each stream reach and weighted by the amount of instream loss that would occur with transport from the reach to the receiving water. The cumulative loss of nutrients from generation to delivery to the receiving water is dependent on the travel time and instream loss rate of each individual reach (Preston and Brakebill, 1999).
- **Incremental Yield (load per area).** This yield represents the local generation of nutrients. It is the amount of nutrients generated locally (independent of upstream load) and contributed to the downstream end of each stream reach. Each stream reach and associated watershed is treated as an independent unit, quantifying the amount of nutrient generated (Preston and Brakebill, 1999).
- **Total Yield (load per area).** This is the amount of nutrients, including upstream load, contributed to each stream reach. These estimates are calculated by stream reach and account for all potential sources cumulatively and individually (Preston and Brakebill, 1999).

The statistical basis of SPARROW means that the model is empirical, even though it attempts to represent fate and transport processes such as instream loss due to denitrification. As such, any model created by SPARROW is a function of the data used in the calibration. The steady-state, mean annual average predictions remain valid as long as there is no great change in the conditions (in this case, the nitrogen loadings within each subbasin) underlying the model. By using the same model for both the current conditions and the alternative effects levels, it is necessary to assume that the steady-state predictions remain valid over both assessments. Given the large decreases in atmospheric deposition loading being considered, this assumption may not be correct and is a limitation of the analysis. However, given the time and data availability for the analysis, the assumption was required to carry out both assessments. Further confounding factors of the SPARROW model are discussed with the assessment results.

5.2.1.2 Assessments of Ecological Responses Using SPARROW and ASSETS EI

To assess ecological response, the SPARROW output serves as the nitrogen load for the calculation of the OHI index in the ASSETS EI. In this case study, a complete analysis from atmospheric deposition load to the ASSETS EI ecological endpoint requires the following:

- An assessment of the relative changes in the deposition load

- The resulting instream nitrogen load to the estuary
- The change in the ASSETS EI.

Because an iterative assessment of changing nitrogen loads to predict ASSETS EIs has not been undertaken previously, a process to link the SPARROW model to the ASSETS EI was developed and used (See Appendix 6, Section 2.2.3).

A series of response curves was created to relate nitrogen inputs to ecosystem responses in the watershed and estuary. First, the SPARROW model was used to predict the total nitrogen loads at the outlet of the watershed that result from changes in the total nitrogen atmospheric deposition loads (i.e., changes in the ambient air NO_x concentrations and subsequent deposition that result from any new standard-setting scenarios). Second, a response curve was plotted for the ASSETS EI based on the OHI and OEC index scores (Appendix 6, Section 2.2.2), which are functions of total nitrogen load to the estuary. Bricker et al. (2007) noted that the shape of the response curve would vary depending on the susceptibility of the system.

It is possible to combine all the OEC, OHI, and DFO index scores with the ASSETS EI into a single response curve when the susceptibility rating and DFO index score are held constant. The DFO index score may be held constant when alternative effects levels are being evaluated based on a current condition scenario. The susceptibility rating is based on physical and hydrological conditions, which are unlikely to change. For example, **Figure 5.2-3** highlights this combination of scores where the susceptibility rating is "High" and the DFO index score is set at "Improve." Additionally, by holding the susceptibility constant, the OHI index score becomes a function of the instream nitrogen concentration. This is evident in the double x-axis. The state response is the OEC index score along the y-axis. Underlying these combinations of OHI and OEC index scores is the ASSETS EI.

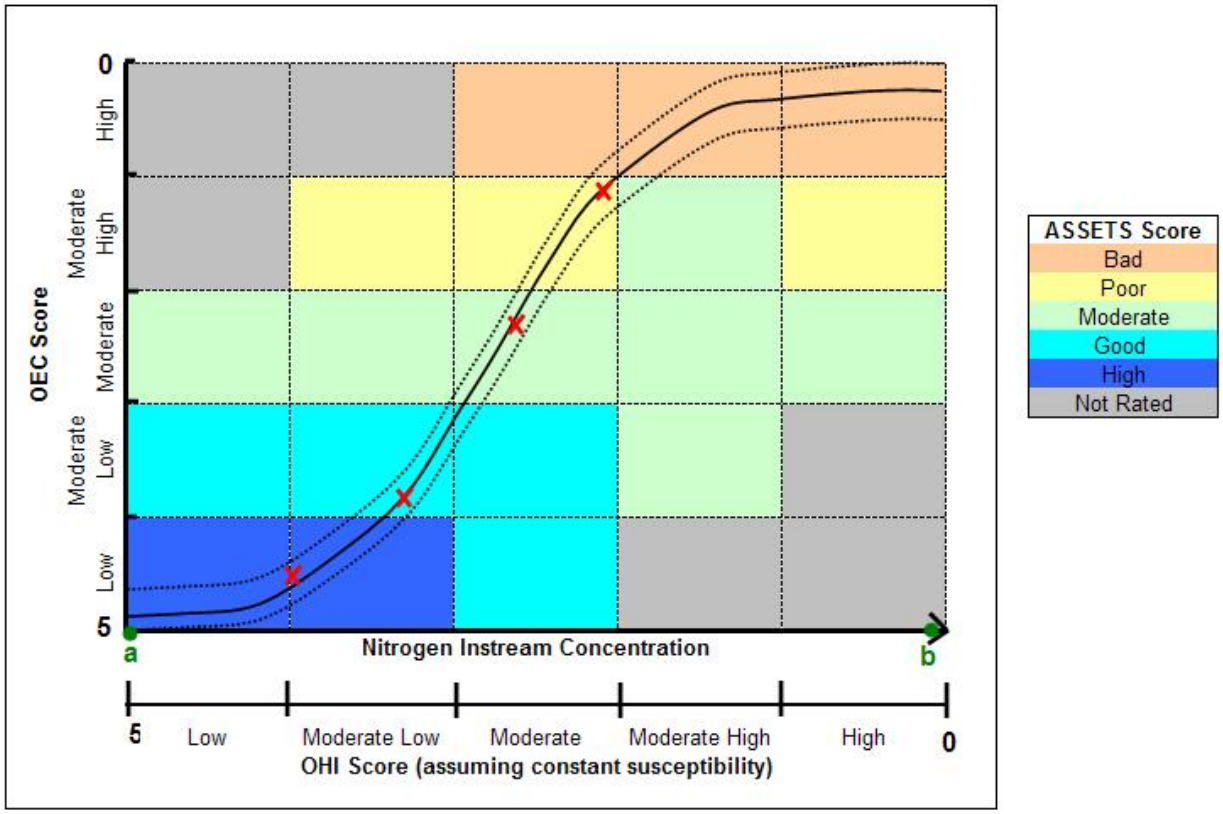


Figure 5.2-3. ASSETS EI response curve.

Within the analysis space created by both the OHI and OEC index scores, the axes are limited to the scores of zero (actually categorized as one in the NEEA Update) to five, but the corresponding instream nitrogen concentrations must be determined separately. Point "a" represents the background nitrogen concentration that would occur in the system with no anthropogenic inputs (assuming the system is not naturally eutrophic) or with the system at a pristine state. In almost all cases, this value will be unknown because of the extent to which anthropogenic inputs have influenced the nation's ecosystems. A lower bound and upper bound on this value were specified between which the algorithm randomly selects a different realization for each iteration. The upper bound of the instream total nitrogen concentration (TN_s), Point "b," is the maximum nitrogen concentration at which the stream is nitrogen-limited; above this point, the nitrogen inputs to the system no longer affect the eutrophication condition. Again, because of natural variations, a constant value is unknown, and upper and lower bounds of the value must be specified for uncertainty analyses.

The creation of the two response curves enables working backward from the ecological endpoint to the source of the impairment; in this case, from the ASSETS EI to the atmospheric

deposition loading of oxidized nitrogen. Specifically, the analysis in this case study sought to determine the change in oxidized nitrogen load required to improve the ASSETS EI by one, two, and three categories from its current level set in the 2002 current condition analysis.

5.2.1.3 Ecosystem Services

Provisioning Services

Estuaries in the eastern United States are an important source of food production, in particular fish and shellfish production. The estuaries are capable of supporting large stocks of resident commercial species, and they serve as the breeding grounds and interim habitat for several migratory species.

To provide an indication of the magnitude of provisioning services associated with coastal fisheries, from 2005 to 2007, the average value of total catch was $1.5 billion per year in 15 East Coast states. It is not known, however, what percentage of this value is directly attributable to or dependent upon the estuaries in these states. **Table 5.2-1** focuses specifically on commercial landings in Maryland and Virginia in 2007 and reports values for the main commercial species in these states. Although these values also include seafood caught outside of the Chesapeake Bay, the values for two key species—blue crab and striped bass—are predominantly from the estuary itself. These data indicate that blue crab landings in 2007 totaled nearly $44 million in the Chesapeake Bay. The value of striped bass and menhaden totaled about $9 million and $25 million, respectively.

To most accurately assess how eutrophication in East Coast estuaries is related to the long-term provisioning services from their seafood resources requires bioeconomic models (i.e., models that combine biological models of fish population dynamics with economic models describing fish harvesting and consumption decisions). In most cases, these models address the dynamic feedback effects between fish stocks and harvesting behavior, and they characterize conditions for a “steady-state” equilibrium, where stocks and harvest levels are stabilized and sustainable over time.

Section 5.2 describes one bioeconomic model linking blue crab harvests to nutrient loads in the Neuse River Estuary, and it applies the model to estimate how decreases in nitrogen loads to the estuary would affect the societal value of future blue crab harvests. In practice, however, very few other studies have developed empirical bioeconomic models to estimate how changes

in environmental quality affect seafood harvests and the value of these services (Knowler, 2002). One exception is Kahn and Kemp (1985), which estimated a bioeconomic model of commercial and recreational striped bass fishing using annual data from 1965 to 1979, measuring the effects of SAV levels on fish stocks, harvests, and social welfare. They estimated, for example, that a 50% decrease in SAV from levels existing in the late 1970s (similar to current levels [CBP, 2009]) would decrease the net social benefits from striped bass by roughly $16 million (in 2007 dollars).

In a separate analysis, Anderson (1989) developed an empirical dynamic simulation model of the effects of SAV changes on commercial blue crab harvests in the Virginia portion of the Chesapeake Bay. Applying the empirical model results, long-run (15-year) dynamic equilibria were estimated under baseline conditions (assuming SAV area constant at 1987 levels) and under conditions with "full restoration" of SAV (i.e., 284% increase). In equilibrium, the increase in annual producer surplus and consumer surplus with full restoration of SAV was estimated to be $3.5 million and $4.4 million (in 2007 dollars), respectively.

Table 5.2-1. Value of Commercial Landings for Selected Species in 2007 (Chesapeake Bay Region)

State	Species	Value
Maryland		
	Blue crab	$30,433,777
	Striped bass	$5,306,728
	Clams or bivalves	$5,007,952
	Sea scallop	$2,808,984
	Oyster, Eastern	$2,524,045
	Other	$6,190,474
	Total	$52,271,960
Virginia		
	Sea scallop	$62,891,848
	Menhaden	$25,350,740
	Blue crab	$13,222,135
	Croaker, Atlantic	$4,615,924
	Striped bass	$3,834,906
	Clam, Northern Quahog	$3,691,319
	Summer flounder	$3,186,229
	Other	$16,954,893
	Total	$130,561,765

Source: NOAA (2007, August). "Annual Commercial Landing Statistics." (http://www.st.nmfs.noaa.gov/st1/commercial/landings/annual_landings.html)

One study examining the short-term effects of dissolved oxygen (DO) levels on crab harvests is by Mistiaen et al. (2003). Focusing on three Chesapeake Bay tributaries—the Patuxent, Chester, and Choptank rivers—this study estimated a "stress-availability" model measuring the effects of DO levels on the availability of blue crabs for commercial harvest, given the stock levels and number of fishing vessels. The model results indicated that, below a threshold of 5 milligrams per liter (mg/L), decreases in DO cause a statistically significant decrease in commercial harvest and revenues. For the Patuxent River alone, a simulated decrease of DO from 5.6 to 4.0 mg/L was estimated to reduce crab harvests by 49% and decreased total annual earnings in the fishery by $275,000 (in 2007 dollars). However, this is an upper-bound estimate because it does not account for changes in fishing effort that would likely occur, and if the measured changes are due to migration of crab populations to other areas rather than to crab mortality, then the broader net effects on crab harvests may also be considerably smaller.[1]

In addition to affecting provisioning services through commercial seafood harvests, eutrophication in estuaries may also affect these services through its effects on the demand for seafood. For example, a well-publicized toxic pfiesteria bloom in the Maryland Eastern Shore in 1997, which involved thousands of dead and lesioned fish, led to an estimated $56 million (in 2007 dollars) in lost seafood sales for 360 seafood firms in Maryland in the months following the outbreak (Lipton, 1999). Additional evidence regarding potential losses in provisioning services due to eutrophication-related fish kills is provided by Whitehead et al. (2003) and Parsons et al. (2006). The survey used in both studies was conducted with more than 5,000 respondents in states bordering the Chesapeake Bay area and in North Carolina. The survey asked respondents to consider how their consumption patterns would change in response to news about a large fish kill caused by a toxic pfiesteria bloom. To address the fact that not all fish kills are the same, the size and type of the described fish kill—either "major," involving more than 300,000 dead fish and 75% with pfiesteria lesions, or "minor," involving 10,000 dead fish and 50% with lesions—were randomized across respondents. Based on respondents' stated behaviors, the

[1] The estimated relationship between harvest and DO is discontinuous at 5 mg/L. The size of the measured effect on harvests is relatively small below 5 mg/L and is zero above the 5 mg/L threshold; therefore, any sizable benefits would require DO to cross the 5 mg/L threshold. Moreover, the 5 mg/L threshold was an assumption of the model rather than a tested hypothesis, which raises additional questions about the accuracy of benefit estimates for changes across the threshold.

studies estimated decreases in consumer surplus per seafood meal ranging from $2 to $5.[2] The survey also found that 42% of residents in the four-state area (i.e., Maryland, Virginia, Delaware, and North Carolina) were seafood consumers and that the average number of seafood meals per month among these consumers was between four and five. As a result, they estimated aggregate consumer surplus losses of $43 million to $84 million (in 2007 dollars) in the month after a fish kill.

Cultural Services

Estuaries in the eastern United States also provide an important and substantial variety of cultural ecosystem services, including water-based recreational and aesthetic services. One of the difficulties with quantifying recreational services from estuaries is that much of the national and regional statistics are jointly collected and reported for estuarine and other coastal areas. Nevertheless, even these combined statistics provide several useful indicators of recreational service flows. For example, data from the Fishing, Hunting, and Wildlife-Associated Recreation (FHWAR) indicate that, in 2006, 4.8% of the 16 and older population in coastal states from North Carolina to Massachusetts participated in saltwater fishing (U.S. DOI, 2007). The total number of days of saltwater fishing in these states was 26.1 million in 2006. Based on estimates from Kaval and Loomis (2003), the average consumer surplus value for a fishing day was $35.91 (in 2007 dollars) in the Northeast and $87.23 in the Southeast. Therefore, the total recreational consumer surplus value from these saltwater fishing days was approximately $1.28 billion (in 2007 dollars). Consumer surplus value is a commonly used and accepted measure of economic benefit (see, for example, U.S. EPA, 2000b). It is the difference between (1) the maximum amount individuals are, on average, willing and able to pay for a good, service, or activity (in this case, a day of recreational fishing) and (2) the amount they actually pay (in out-of-pocket and time costs). For recreation days, it is most commonly measured using recreation demand, travel cost models.

Recreational participation estimates for several other coastal recreational activities were also available for 1999 to 2000 from the National Survey on Recreation and the Environment. Almost 6 million individuals age 16 and older participated in motorboating in coastal states from North Carolina to Massachusetts, for a total of nearly 63 million days annually during 1999 to

[2] Surprisingly, these estimates were not sensitive to whether the fish kill was described as major or minor or to the different types of information included in the survey.

2000. Using a national daily value estimate of $32.69 (in 2007 dollars) for motorboating from Kaval and Loomis (2003), the aggregate value of these coastal motorboating outings was $2.08 billion per year. Almost 7 million individuals participated in bird watching, for a total of nearly 175 million participant days per year, and more than 3 million individuals participated in visits to non-beach coastal waterside areas, for a total of more than 35 million participant days per year. In contrast, less than 1 million individuals per year participated in canoeing, kayaking, or waterfowl hunting.

Regulating Services

Estuaries and marshes have the potential to support a wide range of regulating services, including those that are important for the quality and quantity of water and those that have effects on climate, including impacts from storms (MEA, 2005c). It is more difficult, however, to identify the specific regulating services that are significantly impacted by changes in nutrient loadings. One potentially affected service is provided by SAV, which can help decrease wave energy levels and thus protect shorelines against excessive erosion. Declines in SAV may, therefore, also increase the risks of episodic flooding and associated damages to near-shore properties or public infrastructure. In the extreme, these declines may even contribute to shoreline retreat, such that land and structures are lost to the advancing waterline.

5.2.2 Characteristics of Sensitive Areas

> It is the general consensus that nitrogen is the limiting element to primary production in coastal marine ecosystems in the temperate zone.

Howarth and Marino (2006) provide a comprehensive summary of the literature and scientific findings on eutrophication over the past 3 decades. That summary has led to the general consensus (1) that freshwater lakes and estuaries differ in terms of nutrient limitation as the cause of eutrophication, and (2) that nitrogen is the limiting element to primary production in coastal marine ecosystems in the temperate zone. The factors that make estuarine systems sensitive to nutrient enrichment are still weakly understood, but it is suggested that factors that influence the residence time of the estuarine waters and the complex interactions affecting nutrient and light limitation all play a role in determining sensitivity (Howarth and Marino, 2006). In general, ecosystems that are most vulnerable to nutrient enrichment from atmospheric nitrogen deposition are those that receive high levels of deposition relative to

nonanthropogenic nitrogen loading, those that are nitrogen limited, or those that contain species that have evolved in nutrient-poor environments (U.S. EPA, 2008, Section 3.3)

The selection of case study areas specific to eutrophication began with national GIS mapping to identify sensitive areas. Spatial datasets were reviewed that included physical, chemical, and biological properties indicative of eutrophication potential in order to identify sensitive areas of the United States. Datasets included in the USGS National Water Quality Assessment (NAWQA) Program files, U.S. EPA STORage and RETrieval (STORET) database, NOAA Estuarine Drainage Areas data, and EPA's water quality standards nutrient criteria for rivers and lakes (see Appendix 6, Table 1.2-1). To define areas of national aquatic nutrient enrichment sensitivity, eutrophic estuaries from NOAA's Coastal Assessment Framework (CAF) and areas that exceed the nutrient criteria for lakes/reservoirs (U.S. EPA, 2002) were combined. Exceedance levels were determined by first converting nitrogen concentration nutrient criteria amounts (mg/l) to wet nitrogen deposition amounts (kg/ha/yr) using a formula published by Bergström and Jansson (2006). These nitrogen deposition amounts were then compared to wet NADP nitrogen deposition (2002) amounts to determine areas of the United States that are either above or below the nutrient criteria levels for lakes/reservoirs.

The resulting map revealed areas of highest potential sensitivity to nitrogen deposition as shown in **Figure 5.2-4**. These areas are identified in blue as nutrient-sensitive estuaries contained in NOAA's CAF, and in red in areas where deposition exceeds the nutrient criteria. Yellow areas indicate those areas that are below the nutrient criteria, but are within 5 kilograms (kg) N/ha/yr of exceeding it. White areas do not have EPA nutrient criteria for lake/reservoirs. While this map delineates those regions that are sensitive to deposition by virtue of bedrock and topography, it may not represent regions with perched waterbodies that receive nitrogen deposition.

The exceedance information was averaged spatially by nutrient criteria region using GIS. The nutrient criteria limit for total nitrogen for lakes/reservoirs, its equivalent in wet nitrogen deposition (using Bergström and Jansson's equation), the mean wet nitrogen deposition from NADP, and the difference are shown in **Table 5.2-2**. While none of the regions exceed the nutrient criteria level using this aggregated data, it should be noted that this comparison used only wet nitrogen deposition.

Table 5.2-2. Wet Nitrogen Deposition Level vs. EPA Total Nitrogen (TN) Criteria for Lakes and Reservoirs

	Agg Ecor II	**Agg Ecor III**	**Agg Ecor IV**	**Agg Ecor V**	**Agg Ecor VI**	**Agg Ecor VII**	**Agg Ecor VIII**	**Agg Ecor IX**	**Agg Ecor XI**	**Agg Ecor XII**	**Agg Ecor XIII**	**Agg Ecor XIV**
TN EPA criteria (µg/L)	100	400	440	560	780	660	240	360	460	520	1270	320
N wet dep (kg N/ha/yr)	4.46	12.55	13.47	16.13	20.65	18.23	8.57	11.60	13.93	15.26	29.72	10.62
NADP mean wet N dep (kg N/ha/yr)	1.19	1.16	2.36	3.02	5.01	6.36	5.21	4.44	4.93	3.28	3.35	4.22

Source: Prepared by Lingli Liu, U.S. EPA Office of Research and Development and transmitted in communication from Tara Greaver, U.S. EPA Office of Research and Development, May 2008. (Comparable information was not available for rivers and streams.)

Note: kg N/ha/yr = kilograms of nitrogen per hectare per year; µg/L = micrograms per liter.

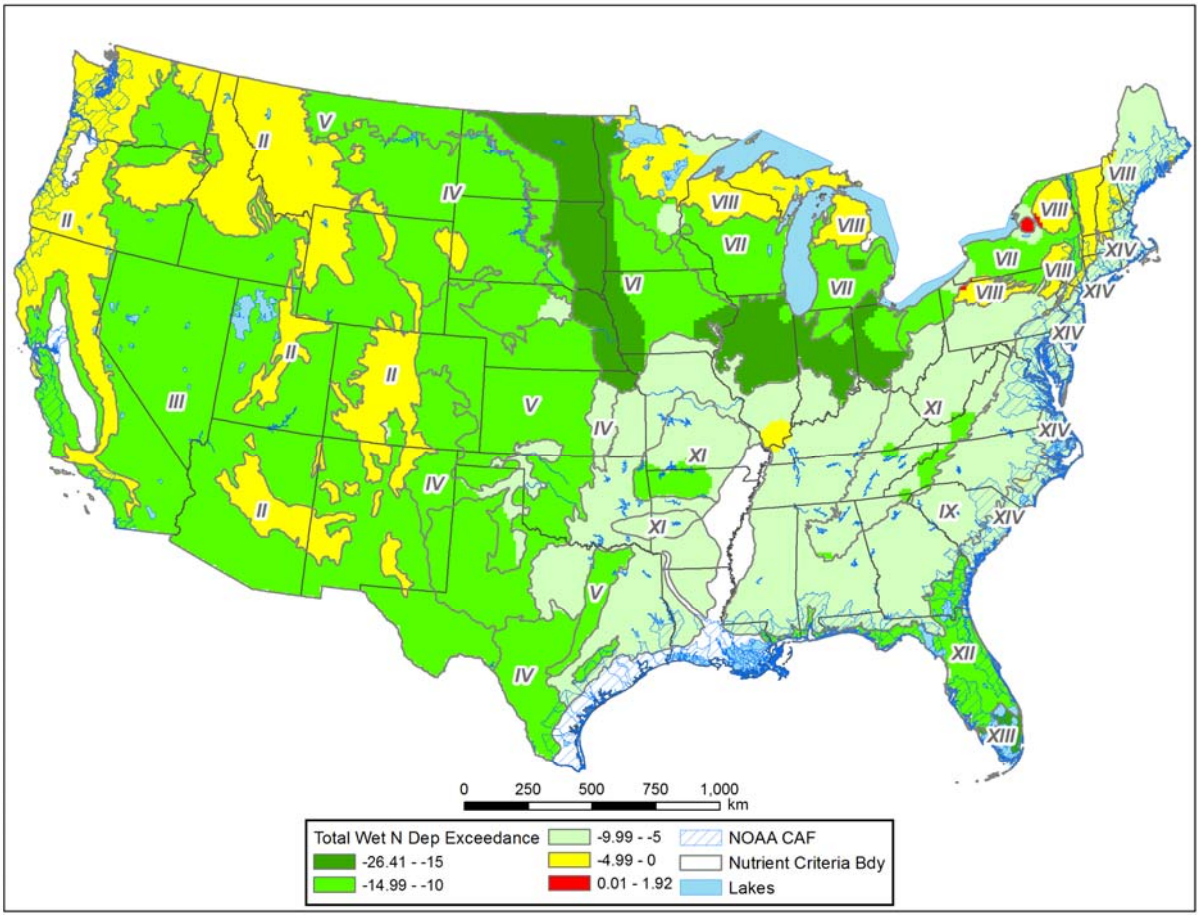


Figure 5.2-4. Areas potentially sensitive to aquatic nutrient enrichment. Areas in red are most sensitive, and areas in dark green are least sensitive to wet nitrogen deposition.

5.2.3 Case Study Selection

Recommended case study areas are presented in the ISA (U.S. EPA, 2008, Sections 3.2, 3.3, 3.4, 4.2, 4.3, 4.4, Annex B, and Annex C) as candidates for risk and exposure assessments. The Ecological Effects Subcommittee of the Advisory Council on Clean Air Compliance Analysis also made recommendations (see Appendix 6, Table 1.2-3). These recommendations, in tandem with the areas identified in the national characterization previously described, were used to select case study areas for this Risk and Exposure Assessment.

Two regions were selected for case study analysis to which a common methodology could be applied—the Chesapeake Bay and the Pamlico Sound. Both estuaries were selected primarily based on the availability of research data. For aquatic nutrient enrichment, special emphasis was given to the Chesapeake Bay region because it has been the focus of many previous studies and modeling efforts, and it is currently one of the few systems within the

United States in which economic-related ecosystem services studies have been conducted. The Pamlico Sound, an economically important estuary due to its fisheries, has been studied and modeled greatly by the local universities and has also been known to exhibit symptoms of extreme eutrophication. Factors including availability of atmospheric deposition data, existing water quality modeling, and generalization opportunities for risk analysis from results were considered in choosing these case study areas. Other candidate estuarine systems could be evaluated for potential future analyses, while freshwater ecosystems in the western United States would most likely require a separate analysis. Because the Chesapeake Bay and Pamlico Sound are fed by multiple river systems, the case study was scaled to one main stem river for each system: the Potomac River/Potomac Estuary and the Neuse River/Neuse River Estuary. Details on each basin are provided in Appendix 6, Sections 1.2.3 and 1.2.4, respectively.

The Potomac River contains diverse watersheds in terms of topography, elevation (e.g., extending into the Shenandoah Mountains), and nutrient point and nonpoint sources (e.g., forestland, farmland, and the Washington, DC, metropolitan area). The 14,670 mi^2 (38,000 kilometers $[km]^2$) basin lies in five geological provinces: the Appalachian Plateau, Ridge and Valley, Blue Ridge, Piedmont Plateau, and Coastal Plain. The watershed is approximately 12% urbanized, 36% agricultural use, and 52% forested. Atmospheric deposition has been reported to contribute from 5% to 15%–20% of the basin's total nitrogen load (U.S. EPA, 2000; Boyer et al., 2002).

The Neuse River is the longest river in North Carolina and is a mainstem river to the Pamlico Sound—one of the two largest estuaries on the Atlantic Coast. The drainage area for the basin is approximately 14,210 mi^2 (36,804 km^2) (NC DENR, 2002). The Neuse River watershed has a population of approximately 1,320,379, according to the 2000 census. Fifty-six percent of the land in the basin is forested, and approximately 23% is in cultivated cropland. There are 134,540 estuarine hectares (332,457 acres) classified for shellfish harvesting (Class SA [shellfishing]) in the Neuse River Estuary. Atmospheric deposition is believed to play a role in nutrient loading to the Neuse River and Pamlico Sound. According to Whitall and Paerl (2001), atmospheric deposition accounts for approximately 24% of the Neuse River watershed's total nitrogen loading. Of these atmospheric deposition measurements, it is expected that the contributions will be greater from reduced forms of nitrogen than from oxidized forms because of the large amounts of agriculture within the watershed. One of the reasons for selecting the

Neuse River/Neuse River Estuary Case Study Area is to evaluate the impact of a NO_x-based standard on an area dominated by reduced forms of nitrogen.

5.2.4 Current Conditions in the Case Study Areas

The Chesapeake Bay is the largest estuary in the United States and has a complex ecosystem of important habitats and food webs. The Potomac River is the second largest of five major rivers that feed the Chesapeake Bay. Most of the Chesapeake Bay's waters are degraded. Remediation goals over multiple categories were set forth in the Chesapeake 2000 Commitment, an agreement between the heads of several state and commission stakeholders (Chesapeake Bay Executive Council, 2000). Because there are numerous indices and categories in which remediation goals have been set, the reader is instructed to view the Chesapeake Bay Program's Remediation Web site for specific inquiries: http://www.chesapeakebay.net/bayrestoration.aspx?menuitem=13989. In 2007, it was 21% of the way toward meeting water quality goals (e.g., 40% decrease in nitrogen and phosphorus over 1987 levels). The Chesapeake Bay's current habitats and lower food web are at 44% of desired levels (e.g., increased number of oysters, restored area of wetlands). Many of the Chesapeake Bay's fish and shellfish populations are below historic levels. Currently, the Chesapeake Bay's fish and shellfish are at 52% of desired levels (e.g., counts of blue crabs, oysters, striped bass). Runoff from winter and spring rains delivers loads of sediment and nutrient pollutants that drive summer water quality conditions. Past observations reveal that summer weather conditions also contribute to summer water quality when intense storms increase erosion. Nutrients reach the Chesapeake Bay from point and nonpoint source discharges and atmospheric deposition from a 570,000-mi^2 airshed (CBP, 2009) The National Water Quality Assessment states that although nitrogen and phosphorus occur naturally, elevated concentrations of nutrients often result from human activities. Atmospheric deposition from combustion of fossil fuels alone accounts for 32% of nitrogen inputs (http://pubs.usgs.gov/circ/circ1166/circ1166.pdf). Although NAWQA states that the water quality concentration of nutrients in the Potomac River watershed does not pose a direct exposure threat to human health or wildlife, excessive nitrogen or phosphorus in streams can cause eutrophication. It is the condition of the Potomac Estuary (as a component of the Chesapeake Bay) and its eutrophication potential that are the focus of the Aquatic Nutrient Enrichment Case Study.

Eutrophication became a water quality concern in the lower Neuse River watershed in the late 1970s and early 1980s, and fish kills, algal blooms, and correspondingly high levels of chlorophyll *a* prompted the State of North Carolina to place the Neuse River Estuary on the 1994, 1996, 1998, and 2000 303(d) List of Impaired Waters.

To assess current conditions for the Potomac River/Potomac Estuary Case Study Area and Neuse River/Neuse River Estuary Case Study Area, it was necessary to have atmospheric deposition data available to input to SPARROW. The deposition data used for the Aquatic Nutrient Enrichment Case Study are based on the 2002 CMAQ model year and NADP monitoring data; therefore, current conditions for this case study evaluated ecosystem responses for the year 2002. In both the Potomac River/Potomac Estuary Case Study Area and the Neuse River/Neuse River Estuary Case Study Area, the best attempts were made to use monitoring and modeling data from that time period (2002). Annual averages for 2002 were used in this study.

5.2.4.1 Potomac River and Potomac Estuary Current Conditions

SPARROW Assessment

For the current condition 2002 analysis of the Potomac River/Potomac Estuary Case Study Area, an estimated 40,770,000 kg of total nitrogen was deposited in the Potomac River watershed for an average deposition of 12.9 kg N/ha/yr. **Figure 5.2-5** through **Figure 5.2-7** reveal highly different spatial patterns in oxidized, reduced, and total nitrogen atmospheric deposition across the watershed. Note that the scales across the three figures use the same increments and colors, so that they can be compared directly.

Application of a previously calibrated version of the SPARROW model for the Chesapeake Bay watershed provides estimates of the incremental yield derived within each catchment of the Potomac River watershed, as well as estimates of the delivered yield (i.e., the fraction of the incremental flux that ultimately reaches the estuary) (**Figure 5.2-8**). (Details on the use of the Version 3 Chesapeake Bay SPARROW model can be found in Appendix 6.) By looking at catchment-scale results, the spatial variability among the loading contributions across the watershed can be shown. Differences between the incremental and delivered yields reflect the instream losses that occur as the load from each catchment travels downstream to the target estuary.

For this application and analysis of the 2002 current condition case, SPARROW was used to model the loads from the Potomac River and its watershed to the upper portions of the Potomac Estuary. The most downstream modeled catchment in the analysis lies downstream of several major point sources between Washington, DC, and the mixing zone of the estuary. These point sources were major contributors of nutrients to the estuary, and by including them in the analysis, a more accurate load from the Potomac River watershed is defined rather than if the modeling stopped at the fall line of the river. Direct runoff from catchments surrounding the estuary and direct deposition to the estuary were not considered in this preliminary model application. The majority of the nitrogen loading to the estuary was expected to derive within the Potomac River watershed because of overall larger land area and applications of fertilizer and manure. Additionally, the major point sources to the Potomac Estuary were included in the most downstream watersheds at the mouth of the estuary modeled in this application.

Overall, the SPARROW model produced an estimate of total nitrogen loading to the Potomac Estuary of 36,660,000 kg N/yr. The atmospheric deposition load was estimated at 7,380,000 kg N/yr to the estuary, or 20% of the total loading. These modeling estimates are consistent with previous modeling estimates for the system (Preston and Brakebill, 1999). The instream total nitrogen concentration (TN_s) resulting from this loading was approximately 3.4 mg/L.

SPARROW modeling for 2002 predicts that atmospheric deposition was 20% of the total nitrogen loading to the Potomac River's estuary, producing an TN_s of 3.4 mg/L.

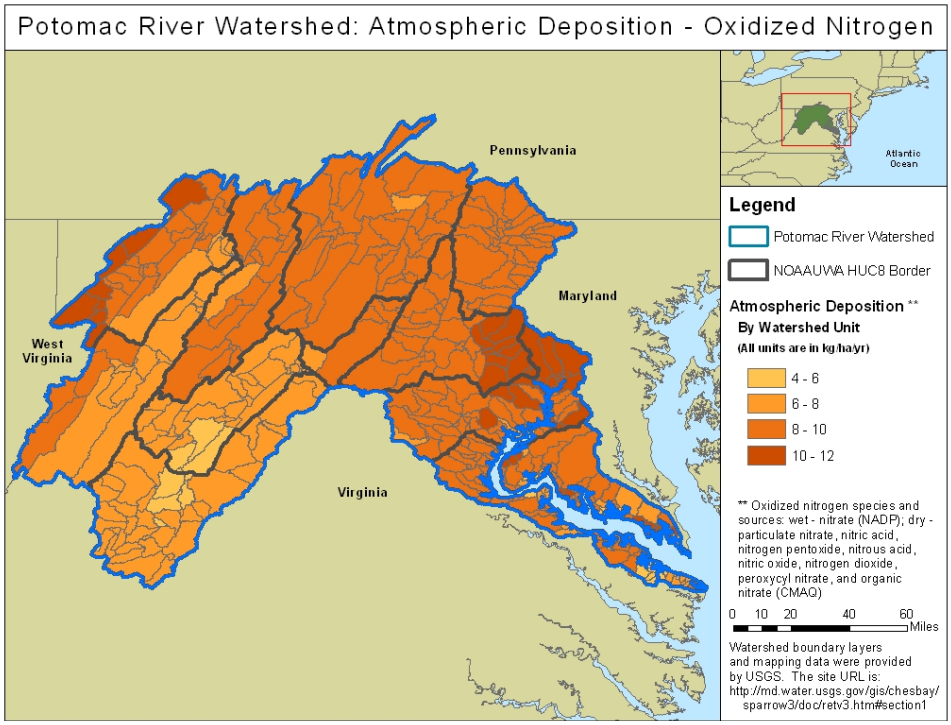


Figure 5.2-5. Atmospheric deposition yields of oxidized nitrogen over the Potomac River and Potomac Estuary watershed.

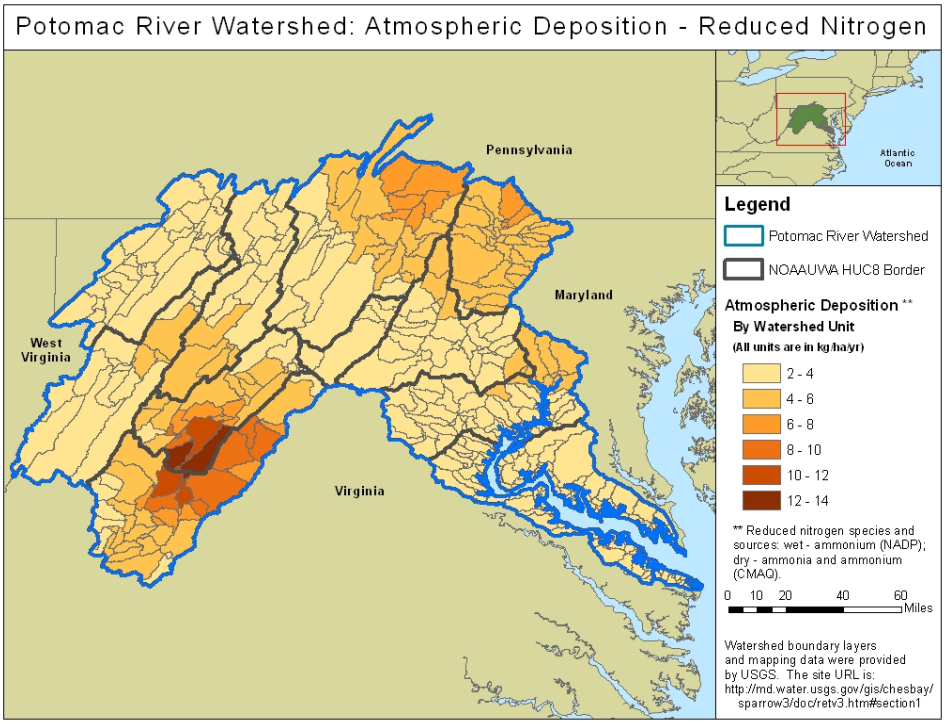


Figure 5.2-6. Atmospheric deposition yields of reduced nitrogen over the Potomac River and Potomac Estuary watershed.

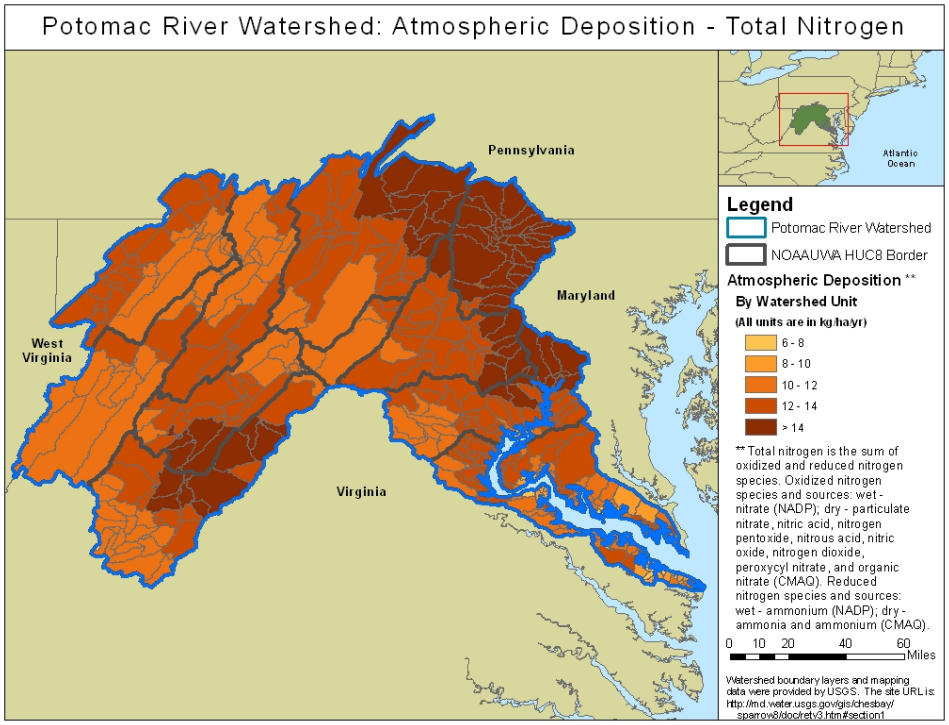


Figure 5.2-7. Atmospheric deposition yields of total nitrogen over the Potomac River and Potomac Estuary watershed.

ASSETS EI Assessment

An ASSETS EI was completed for the Potomac Estuary in a 2006 NOAA project on the Gulf of Maine (Bricker et al., 2006) using 2002 data to determine the scoring. That assessment showed that the system has a high susceptibility to pressures and a high score for nutrient inputs, resulting in a *High* OHI score. Individual scores for the primary and secondary indicators varied but resulted in an overall *High* OEC score. The score of *Improve Low* for the DFO is based on the expectations that future nutrient pressures will decrease and there will be significant population and development increases.

> The ASSETS EI for the 2002 Potomac River estuary current condition scenario is *Bad.*

For the Aquatic Nutrient Enrichment Case Study, the ratings for the nutrient inputs and OEC were re-created and verified using methods consistent with the 2007 NEEA Update, which included separate area-weighted consideration of the tidal fresh, mixing, and saltwater zones within the estuary (Bricker et al., 2007). Index scores for the updated analysis were compiled using the scoring methods and matrices as shown in Figures 2.2-6 and 2.2-7 of Appendix 6. Combination of the primary and secondary scores (both *High*) provided an overall OEC score of *High*, which agreed with the original analysis. The OHI score (confirmed with the

modeled nitrogen load from the 2002 SPARROW application) and the DFO scores remain the same as in the original analysis. Therefore, the ASSETS EI for the 2002 current condition scenario is *Bad*.

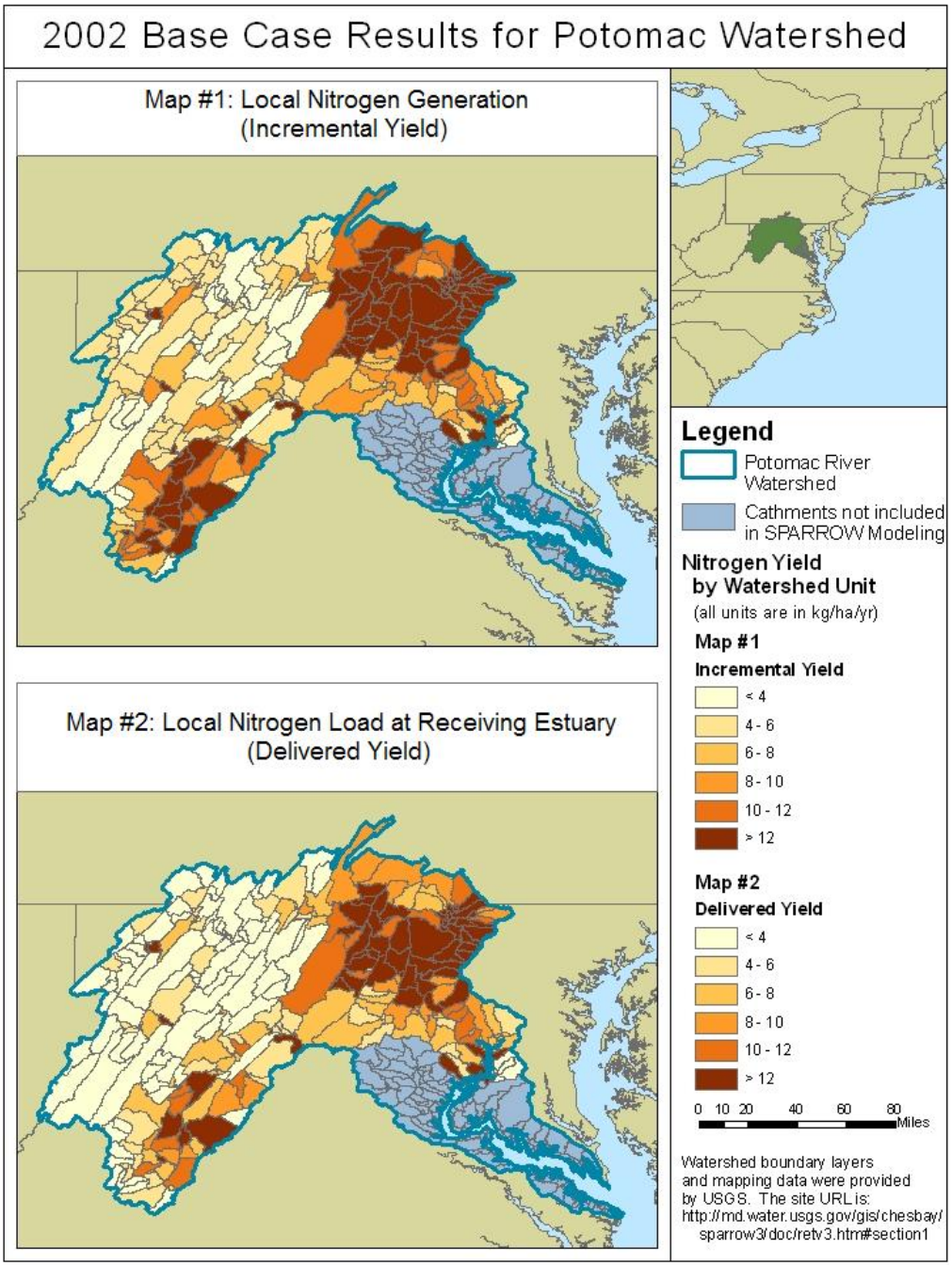


Figure 5.2-8. Total nitrogen yields from all sources as predicted using version 3 of the Chesapeake Bay SPARROW application with updated 2002 atmospheric deposition inputs.

5.2.4.2 Neuse River and Neuse River Estuary Current Conditions

The current condition 2002 analysis of the Neuse River and Neuse River Estuary used recently released data from the USGS to calibrate a new SPARROW application for 2002 to the Neuse watershed. (Because of a limited number of calibration points within the Neuse watershed itself, the SPARROW model assessment was expanded to include the Tar-Pamlico and Cape Fear River basins, providing a total of 41 calibration points on which to base the SPARROW model.) Developing the ASSETS EI for the Neuse River Estuary proved to be a greater challenge than for the Potomac Estuary due to data sources being less consolidated and more varied.

SPARROW Assessment

Figure 5.2-9 through **Figure 5.2-11** present the atmospheric deposition inputs used within the modeling effort. For 2002, an estimated 18,340,000 kg of total nitrogen was deposited in the Neuse River watershed for an average deposition of 14.0 kg N/ha/yr. The model was based on total nitrogen loads from deposition, but oxidized and total reactive nitrogen yields are also presented to highlight source information within the watershed. The Neuse River watershed is the location of major agricultural operations focusing on swine facilities. These operations are evident in the high levels of reduced nitrogen found within the south-central catchments of the watershed (**Figure 5.2-10**).

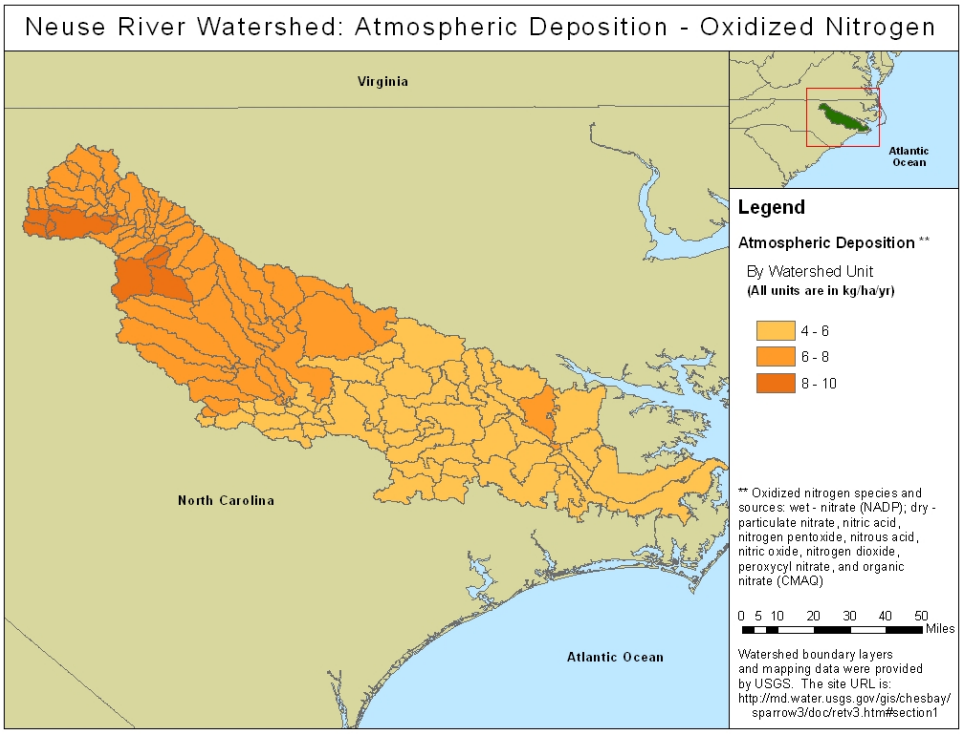


Figure 5.2-9. Atmospheric deposition yields of oxidized nitrogen over the Neuse River and Neuse River Estuary watershed.

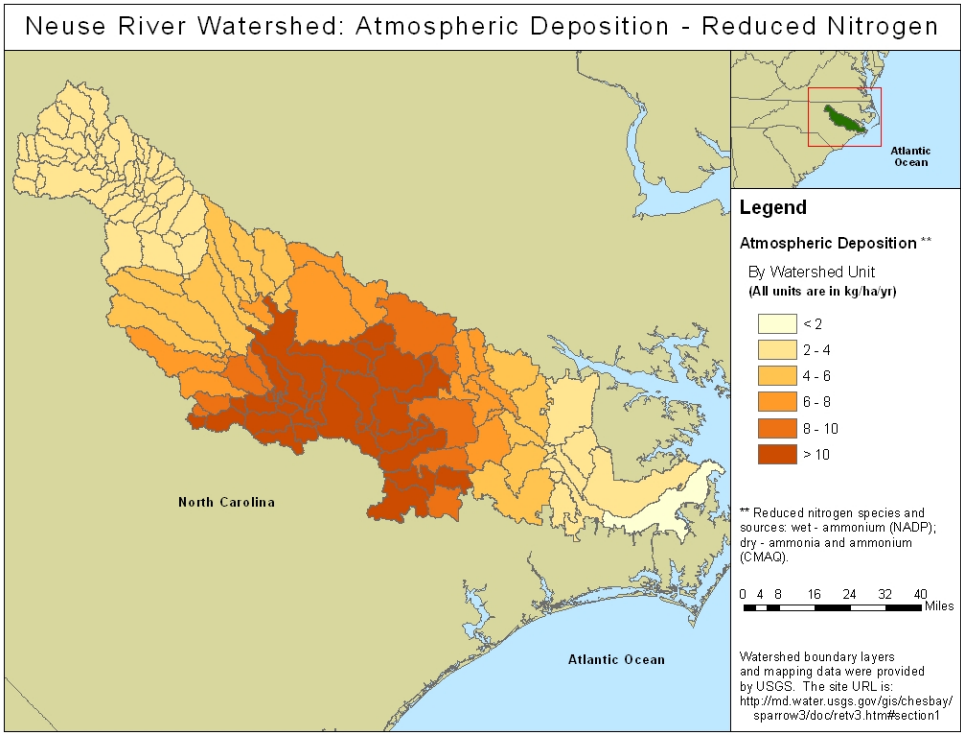


Figure 5.2-10. Atmospheric deposition yields of reduced nitrogen over the Neuse River and Neuse River Estuary watershed.

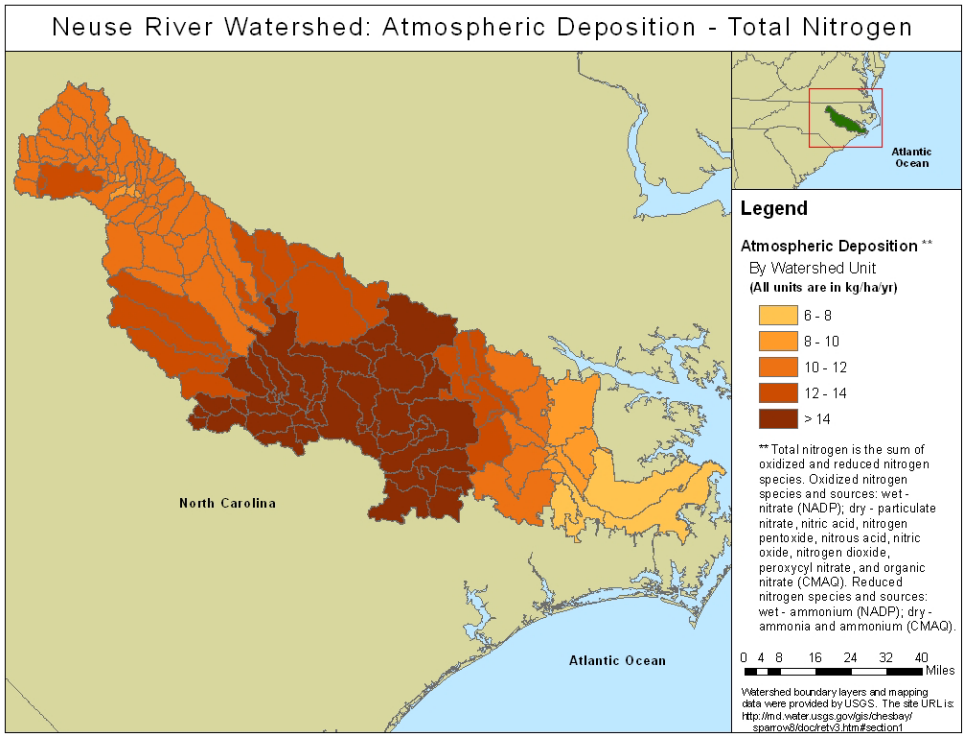


Figure 5.2-11. Atmospheric deposition yields of total nitrogen over the Neuse River and Neuse River Estuary watershed.

As with the Potomac River and Potomac Estuary watershed results, the Neuse River and Neuse River Estuary SPARROW application modeled watershed loads to the upper edges of the estuary. Both the incremental and delivered yields are presented in **Figure 5.2-12**. The total nitrogen load estimated to enter the estuary from the Neuse River is 4,380,000 kg N/yr, equating to a TN_s of 1.11 mg/L. Atmospheric deposition was estimated to contribute 1,150,000 kg N/yr, or 26% of the total load. These estimates fall in line with instream monitoring data and previous loadings from the Neuse River estimated at 9.61 million pounds or 4,359,000 kg N/yr (Spruill et al., 2004).

> SPARROW modeling for 2002 predicts that atmospheric deposition was 26% of the total nitrogen loading to the Neuse River's estuary, producing a TN_s of 1.1 mg/L.

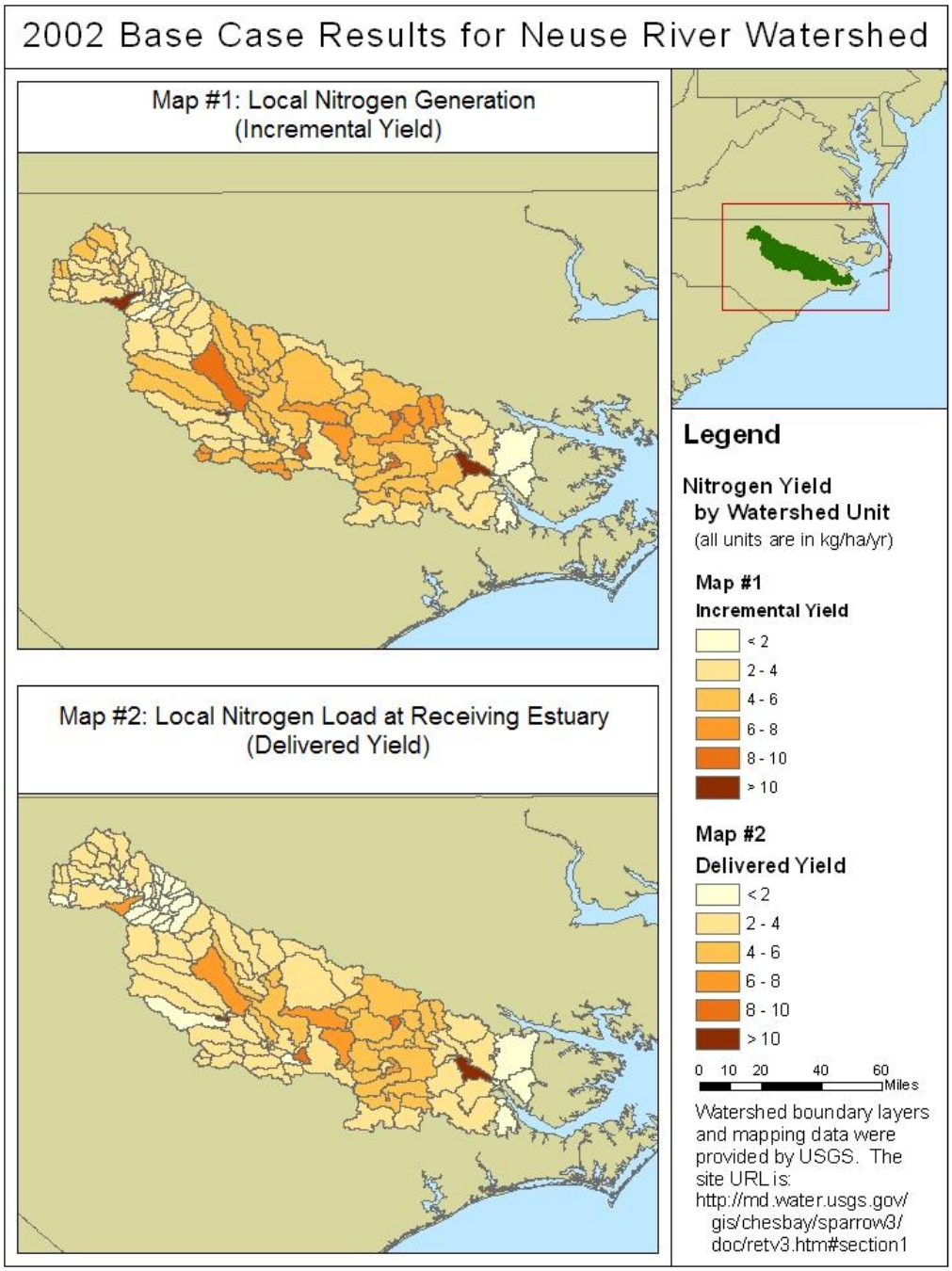


Figure 5.2-12. Total nitrogen yields from all sources predicted by a SPARROW application for the Neuse, Tar-Pamlico, and Cape Fear watersheds with 2002 data inputs.

ASSETS EI Assessment

Previous work was completed by NOAA using the ASSETS EI on the Neuse River Estuary as part of the NEEA Update (Bricker et al., 2007). The exact

Combining the OEC, OHI, and DFO indices results in an overall ASSETS EI for the Neuse River Estuary for 2002 of *Bad*.

source of the load estimate and the exact timeframe of the data used to calculate the ASSETS EI are still unknown at this time, although the data should fall between 2000 to 2002 (S. Bricker, personal communication, 2008). That analysis revealed a *Highly/Moderately Influenced* or *High* score for influencing factors where the nitrogen load was ranked as *Moderate to High,* resulting in a *Bad* overall ASSETS score for the estuary.

To develop an updated ASSETS EI specific to the 2002 baseline for this assessment, available data from multiple sources, including the Neuse River Estuary Modeling and Monitoring Project, were combined to form a 2002 OEC score. Because both the chlorophyll *a* and harmful algal bloom data were available and overwhelmingly pointed to a system with both *High* primary and secondary scores, a *High* OEC rating is given with confidence for 2002. The *High* susceptibility ranking, combined with the total nitrogen loads estimated by the SPARROW assessment, rank the OHI as *High* as well. The DFO set during the 2007 NEEA Update remains unchanged, with a ranking of *Worsen High* due to nutrient decreases from improved management practices in recent years being offset by increases in human populations and factors related to swine production (Burkholder et al., 2006). Combining the three indexes results in an overall ASSETS EI for the Neuse River/Neuse River Estuary Case Study Area for 2002 of *Bad*.

5.2.5 Degree of Extrapolation to Larger Assessment Areas

Selection of the analysis method for aquatic nutrient enrichment considered applications beyond a small number of case studies. The chosen method, consisting of a combination of SPARROW modeling for nitrogen loads and an assessment of estuary conditions under the NOAA ASSETS EI, provides a highly scalable and widely applicable analysis method. Both components have been applied on a national scale—the national nutrient assessment using SPARROW (Smith and Alexander, 2000) and the NEEA using the ASSETS EI (Bricker et al., 1999, 2007). Additionally, both have been used on a smaller scale. These previous analyses supply a large body of work—data, methods, and supporting experts—to draw from when conducting additional analyses or updating past applications.

Requirements for applying this method to other systems include mandatory data inputs, the ability to formulate a SPARROW application on a reliable stream network, and an estuary likely to be subject to eutrophication. Data requirements and model formulations have been described and detailed throughout this report.

The method is not currently designed to assess eutrophication impacts on inland waters; however, a separate analysis was conducted of the extent inland waters exceed national nutrient criteria for nitrogen. Results are presented in the GIS analysis for sensitive areas of the United States that are identified in Appendix 6. SPARROW modeling can be applied to determine nitrogen loadings to an inland waterway, but the ASSETS EI would not apply, and as such, the indicators and overall likelihood of eutrophication could not be assessed. For these inland waters, an alternate methodology would be necessary to examine the effects of changing nitrogen loads within the waterbody. A variety of methods could possibly be applied, including empirical relationships or dynamic modeling. An additional case study, the Aquatic Acidification Case Study, examines the effects of aquatic acidification on inland waters using dynamic modeling.

The scalability of the methods and approaches taken in these case studies will rely on the ability to group estuaries across the country into patterns of similar behavior either in terms of nitrogen sources or eutrophication effects. In 2003 and 2004, NOAA and the Kansas Geological Survey conducted a series of workshops to develop a type classification system for the 138 estuarine systems assessed in the original NEEA (Bricker et al., 1999). Participants considered 70 classification variables for grouping the estuarine systems. These variables included 51 physical characteristics (e.g., estuary depth and volume, tidal range, salinity, nitrogen and phosphorus concentrations, estimates of flushing time, evaporation), 10 perturbation characteristics (e.g., population in watershed, estimates of nutrient loading), and nine response characteristics (e.g., SAV loss, presence of nuisance, toxic blooms). Ultimately, the workgroup selected five variables (i.e., depth, openness of estuary mouth, tidal range, mean annual air temperature, the log of freshwater inflow/estuarine area) deemed to be the most critical physical and hydrological characteristics influencing nutrient processing and the expression of eutrophic symptoms in a waterbody. Based on these five variables, the 138 estuarine systems were classified into 10 groups (**Table 5.2-3; Figure 5.2-13**). The two estuary systems included in this case study, Potomac River Estuary and Neuse River Estuary systems, were in groups one and nine, respectively (Bricker et al., 2007).

Table 5.2-3. Typology Group Categorizations

Group	Number of Systems	Overriding Characteristics
Group 0	13	Low freshwater inflow:estuarine area ratio; low depth; low estuary mouth openness
Group 1	35	Medium depth; medium estuary mouth openness; high annual air temperature
Group 2	5	High depth; low annual air temperature
Group 3	8	High estuary mouth openness; high depth
Group 4	18	Low estuary mouth openness; high freshwater inflow:estuarine area ratio; low annual air temperature
Group 5	3	High estuary mouth openness; high depth
Group 6	2	High depth; high estuary mouth openness
Group 7	16	High tidal range; medium estuary mouth openness; low annual air temperature
Group 8	17	High freshwater inflow:estuarine area ratio; low depth
Group 9	21	Low depth; medium estuary mouth openness; high annual air temperature

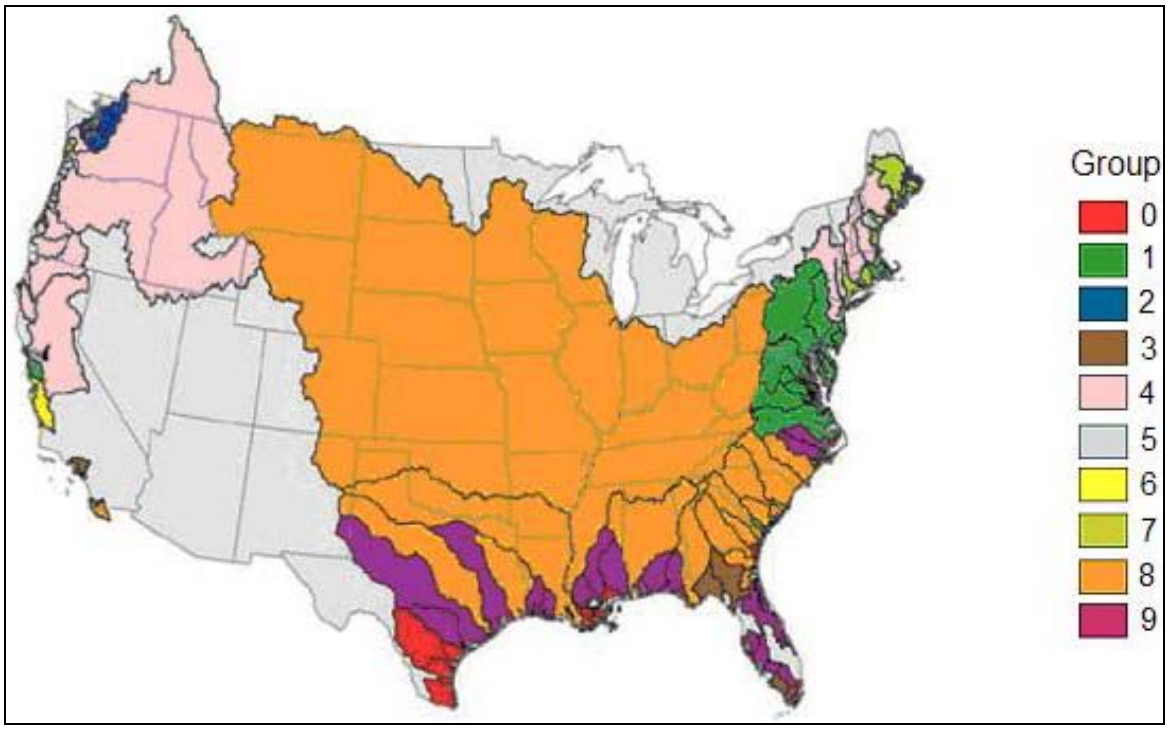


Figure 5.2-13. Preliminary classifications of estuary typology across the nation (modified from Bricker et al., 2007).

Given that the response curve of the OEC to total nitrogen (TN) is expected to change shapes with different values of susceptibility, the typology classes thus defined in **Table 5.2-3** provide an opportunity to assess the validity of this expectation. The first step in assessing this statement would be to examine the nutrient loadings in other estuaries that fall within groups 1 or 9, the groups corresponding to the two case studies. Once the shape and behavior of the response curve for the estuary grouping is confirmed, work can begin to scale the results between estuaries of that group. The ASSETS EI rating of an estuary may also be considered within this analysis.

Scaling of results will also need to account for the response of the watershed to atmospheric nitrogen deposition inputs. If SPARROW continues to be used, either through the in-development Web-enabled national SPARROW application or through regional or site-specific applications, the shape of the response curve will be determined by the model and its parameters. If a different approach is taken to developing total nitrogen loadings, then the systems will need to be grouped according to the shape and behavior of the response curve. Additional consideration should be given to the magnitude of the percentage contributions of the atmospheric deposition to the total nitrogen load to the watershed and the resulting total nitrogen load to the estuary.

5.2.6 Current Conditions for Other/Additional Estuaries

For 48 systems for which an ASSETS EI rating was developed in the 2007 NEEA Update, only one system was rated as *High* (i.e., Connecticut River), while five were rated as *Good* (i.e., Biscayne Bay, Pensacola Bay, Blue Hill Bay, Sabine Lake, Boston Harbor). Eighteen were rated as *Moderate,* and 24 systems were rated as *Poor* or *Bad* (**Figure 5.2-14**). Comparing the spatial distribution of these results to the preliminary typology groups described in the previous section, the majority of estuaries in Group one, the group to which the Potomac Estuary belongs, received scores of *Bad*. These conditions provide an opportunity to extrapolate between the analysis methods and results determined for the Potomac Estuary and the other estuaries matching in typology and current condition. For Group nine, to which the Neuse River Estuary belongs, a greater range in ASSETS EI scores is found. Extrapolation of results within this group must be examined in greater detail.

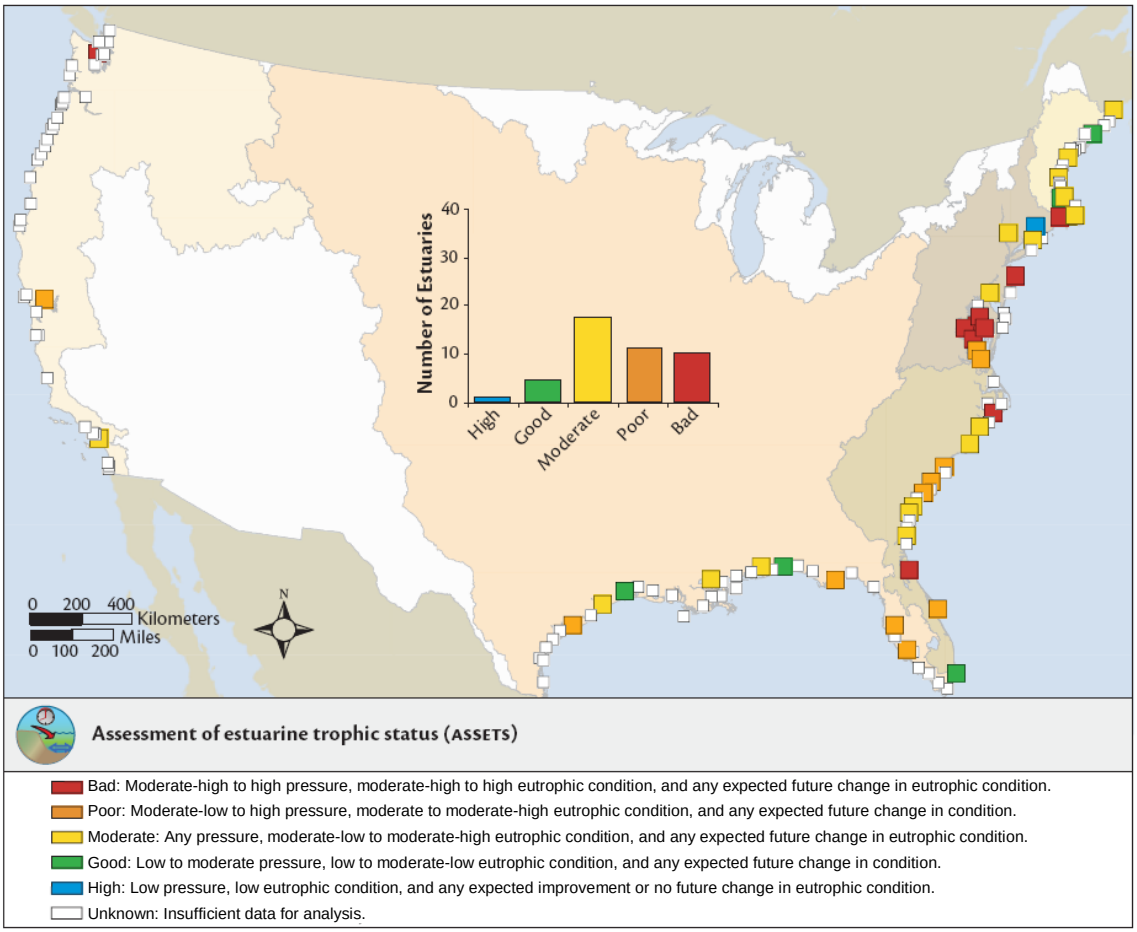


Figure 5.2-14. ASSETS EI scores for 48 systems examined in the 2007 NEEA Update (Bricker et al., 2007).

5.2.7 Ecological Effect Function for Aquatic Nutrient Enrichment

Alternative effects levels were assessed for both the Potomac River and Neuse River watersheds separately by applying percentage decreases to the oxidized nitrogen loads in the estimated atmospheric deposition. Model estimates then relied on the SPARROW models used (for the Potomac River) or developed (for the Neuse River) for the 2002 current condition analysis to determine how the changing atmospheric inputs (i.e., total nitrogen load evaluated with changes in oxidized nitrogen deposition, NO_x) affect the overall total nitrogen load to the estuary of interest. These results were used to create the response curve relating instream total nitrogen concentrations to atmospheric deposition loads as first described in Appendix 6, Section 2.2.3. The second response curve described in Section 2.2.3 was defined for the alternative effects level analysis using historical data compilations of OEC scores and instream total nitrogen concentrations while holding the susceptibility portion of the OHI (at its 2002 current

condition level— in both cases a ranking of *High*) and the DFO constant (at a ranking of *No Change* [3]).

Upon creation of the two response curves, the back calculation coded program described in Appendix 6, Section 2.2.3 (referred to as *BackCalculation* through the remainder of this document) was applied to the curves with the intent of defining the atmospheric loads that are needed to improve the ASSETS EI from a score of *Bad* (1) to *Poor* (2), *Moderate* (3), *Good* (4), or *High* (5). These improvements represent improvements by 1, 2, 3, and 4 categories.

5.2.7.1 Potomac River and Potomac Estuary

Beginning with the data and model used for the current condition analysis, the atmospheric deposition inputs derived from national coverage of CMAQ and NADP data were altered to create various alternative effects levels by decreasing the oxidized nitrogen loads by rates of 5%, 10%, 20%, 30%, and 40% from their original 2002 levels. A zero percentage decrease corresponds to the 2002 current condition analysis. The remaining inputs to the SPARROW model remained the same, and the model was rerun for each of these alternative effects level scenarios. The total nitrogen load to the estuary calculated from the model was then converted to TN_s using the annual average flow of the Potomac River. Plotting these concentrations against the new total nitrogen atmospheric deposition loading (TN_{atm}) incorporating the oxidized nitrogen decrease leads to the development of the first response curve and relationship (**Figure 5.2-15**) for the Potomac River and Potomac Estuary watershed.

For the second response curve, historical modeling data was used to determine total nitrogen loads to the Potomac Estuary, which are then combined with annual average flow values to calculate a final TN_s. These instream concentrations were then combined with the OEC index scores, which were also determined from historical data, to create the data points needed to create the 4-parameter logistic response curve in the *BackCalculation* program. **Figure 5.2-16** presents an example of the logistic curve fit to the Potomac River and Potomac Estuary data during an uncertainty analysis of a target ASSETS EI = 2.

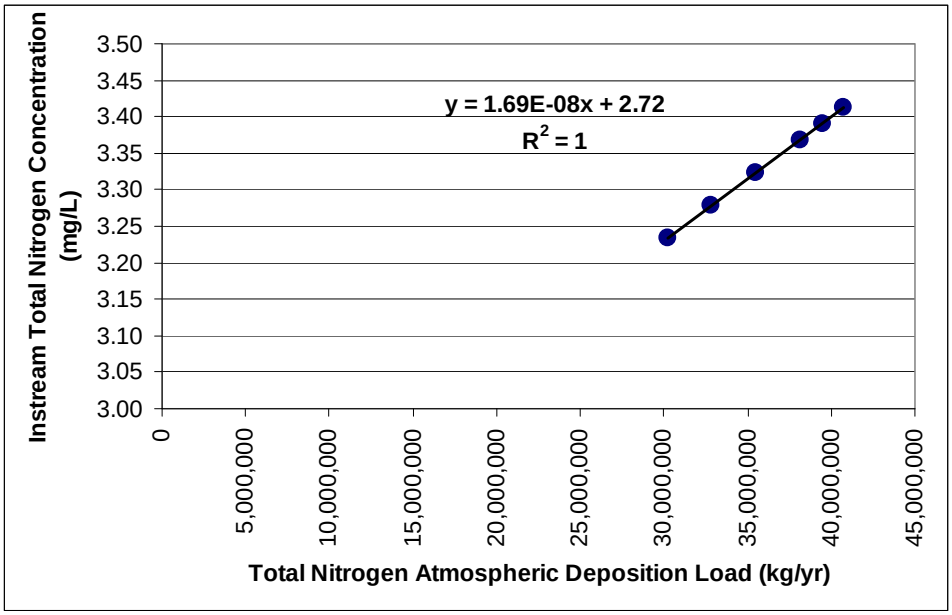


Figure 5.2-15. Response curve relating instream total nitrogen concentration (TN_s) to total nitrogen atmospheric deposition load (TN_{atm}) for the Potomac River watershed.

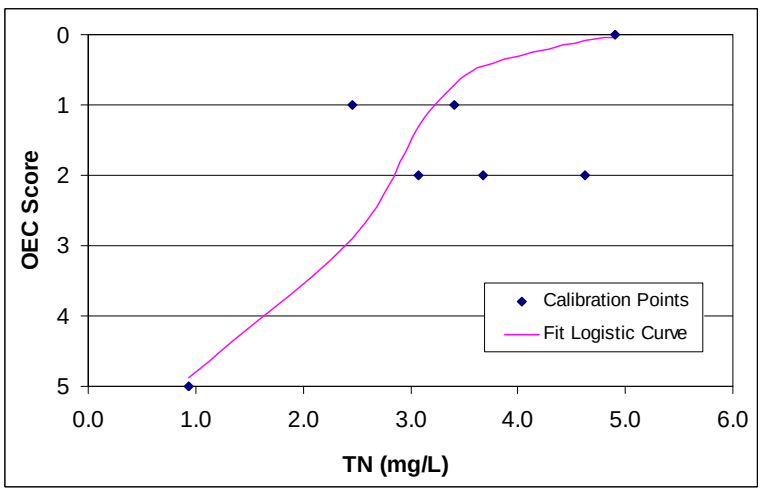


Figure 5.2-16. Example of fitted OEC curve for target ASSETS EI=2 for the Potomac Estuary.

Table 5.2-4 presents the summary statistics of 500 iterations for each target ASSETS EI scenario for the Potomac Estuary. In these Monte Carlo type simulations, the TN_{atm} to the watershed is evaluated as a function of the TN_s for each step in improvement of the ASSETS EI.

The target ASSETS EI scenario where EI = 2 (improving from an ASSETS EI score of *Bad* to *Poor*) is the most interesting scenario and illustrates the power of

There is a slim chance that the Potomac River Estuary can move from an EI score of *Bad* to a score of *Poor* by reducing deposition of total nitrogen by 78%.

the uncertainty analysis. The mean and median TN_{atm} values are negative, meaning again that not only must all total nitrogen atmospheric deposition load (including all NO_x) be removed, but additional nitrogen from other sources must be removed as well. However, there is a slim chance that scenario ASSETS EI = 2 can be attained only from TN_{atm} deposition load decrease, as indicated by the positive 95th percentile TN_{atm} value of 9.02×10^6 (representing a 78% decrease).

Table 5.2-4. Summary Statistics for Target Eutrophication Index Scenarios — Potomac Estuary

(Current condition Eutrophication Index score of *Bad)*

Statistic	TN_{atm} (kg N/yr)	% TN_{atm} Decrease
ASSETS EI = 2 (*Poor*)		
Mean	-1.78×10^6	104
Median	-1.46×10^6	104
5th Percentile	-3.67×10^6	109
95th Percentile	9.02×10^6	78
ASSETS EI = 3 (*Moderate*)		
No feasible solutions found		
ASSETS EI=4 (*Good*) and ASSETS EI = 5 (*High*)		
All $TN_{atm} = -1.61 \times 10^8$, i.e., $TN_s = 0$ mg/L		

Target scenario ASSETS EI = 3 (*Moderate*) is a unique case because all solutions were infeasible. With a TN_s value of 0 mg/L, the other (fixed) components of the ASSETS scoring methodology (i.e., DFO and Susceptibility Score) preclude satisfying any of the 95 combinations of DFO, OEC, and OHI that comprise the EI=3 combinations in the ASSETS lookup table.

Target scenario ASSETS EI = 4 and 5 had identical results. All 500 iterations returned a $TN_s^*{}_i = 0$, and a corresponding $TN_{atm}^*{}_i$ negative load equal to $TN_{atm}^*{}_i = (0 - 2.72)/1.69 \times 10^{-8} = -1.61 \times 10^{-8}$ kg/yr. Clearly, target EIs equaling 4 and 5 are very much unattainable when decreasing the total atmospheric nitrogen deposition load is the only policy option. To reach the target ASSETS EI scenario, total nitrogen atmospheric deposition (TN_{atm}) must be removed plus an additional amount (represented by the negative resultant load corresponding to $TN_s^*{}_i = 0$) that is approximately equal to one order of magnitude greater than the original atmospheric deposition load. These amounts could be compared to the other nitrogen sources in the watershed (e.g., fertilizer and manure application or point sources) that were used as inputs to the SPARROW model to determine the relative nature of the required removal with other sources in the watershed. However, consideration must be given that this load is a reflection of the characteristics of the source in the SPARROW model (e.g., spatial distribution, magnitude of loads, sources/sinks), and a decrease required in atmospheric load is not equal to a decrease in another source. Therefore, a decrease of an order of magnitude greater than the original

atmospheric deposition load may or may not be possible, depending on these different source contributors. Relative proportions can be examined by comparing the source characteristics and model parameters.

The SPARROW response curve can also be used to examine the role of atmospheric nitrogen deposition in achieving specified decreases in total nitrogen estuarine load. For example, the SPARROW modeling results predict that the 41×10^6 kg N/yr deposited (atmospheric deposition input) over the Potomac River watershed in 2002 results in a loading of 7,380,000 kg N/yr, or 20% of the annual total nitrogen load, to the Potomac Estuary. If a 30% decrease in annual total nitrogen load to the estuary (i.e., a decrease of 11×10^6 kg N/yr) were desired, a decrease of 61×10^6 kg N/yr in nitrogen inputs to the watershed would be required according to the SPARROW response curve based on atmospheric deposition. This represents a 100% decrease in the total nitrogen (including total reactive nitrogen) atmospheric deposition inputs (41×10^6 kg N/yr) plus an additional 20×10^6 kg N/yr removal of nitrogen from other sources in the Potomac River watershed (i.e., point and nonpoint sources). Note that this value of 20×10^6 kg N/yr is an approximate value when applied to the other sources because they differ in characteristics (e.g., spatial distribution and magnitude) from atmospheric deposition that was used to estimate the loading.

5.2.7.2 Neuse River and Neuse River Estuary

The same methods for creating alternative effects levels were applied to the data from the Neuse River/Neuse River Estuary Case Study Area as to data from the Potomac River/Potomac Estuary Case Study Area. The oxidized nitrogen atmospheric deposition loads were decreased by rates of 5%, 10%, 20%, 30%, and 40% from their original 2002 levels. A zero percent decrease corresponds to the 2002 current condition analysis. With the remaining inputs to the SPARROW model kept the same, the SAS-developed model was rerun for each of these alternative effects level scenarios. The total nitrogen load to the estuary calculated from the model was then converted to a TN_s using the annual average flow of the Neuse River. Plotting these concentrations against the new total nitrogen atmospheric deposition load and incorporating the oxidized nitrogen decreases leads to the development of the first response curve and relationship (**Figure 5.2-17**). Note that the instream concentration range is discussed at the end of this section.

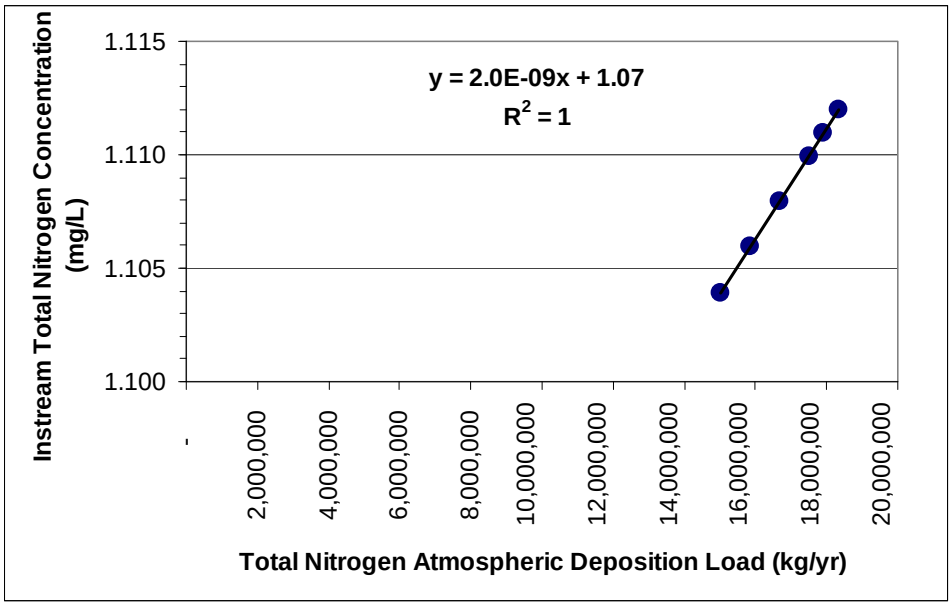


Figure 5.2-17. Response curve relating instream total nitrogen concentration to total nitrogen atmospheric deposition load for the Neuse River/Neuse River Estuary Case Study Area**.**

Historical monitoring data were used to determine instream total nitrogen concentrations at the downstream end of the Neuse River where the SPARROW model was used to determine current condition and alternative effects levels nitrogen loads. The monitoring data were derived from data downloaded from EPA's STORET Web site for monitoring location J8290000 from the North Carolina Division of Water Quality. These TN_s were then combined with the OEC index scores, which were also determined from historical data, to create the data points needed to create the logistic response curve in the *BackCalculation* program. Data from as many years as possible were gathered for both the TN_s and OEC index scores. However, due to the limited amount of complete data from the various sources identified under the current condition analysis, only three corresponding years of data were found. The theoretical ecological endpoints of the curve were also used to create the 4-parameter logistic curve representing the second response curve for the analysis (**Figure 5.2-18**).

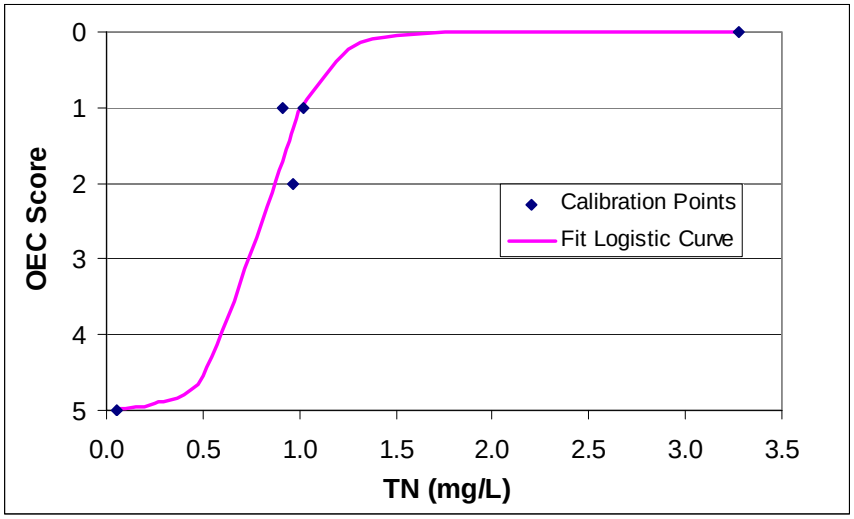


Figure 5.2-18. Example of fitted response curve for target ASSETS EI=2 for the Neuse River Estuary.

Each of the four ASSETS EI scores representing state improvements (*Poor*-2, *Moderate*-3, *Good*-4, *High*-5) was treated as a "target" ASSETS EI score, and 500 Monte Carlo simulations were run under each target ASSETS EI scenario to relate instream total nitrogen concentrations (TN_s) to total nitrogen atmospheric deposition (TN_{atm}).

The summary statistics of the 500 iterations for each target ASSETS EI scenario are presented in **Table 5.2-5**.

For target scenario ASSETS EI = 2 (improving from an ASSETS EI score of *Bad* to *Poor*), all decreases exceed 100%, meaning that not only must all TN_{atm} deposition load be removed to meet ASSETS EI = 2, but considerably more nitrogen from other sources as well. Given these results, the Neuse River Estuary is currently somewhere between these two ASSETS EI values (*Bad* and *Poor*) as was the Potomac Estuary. There is some evidence that it is slightly more eutrophic than the Potomac Estuary, because there was at least a slim

Table 5.2-5. Summary Statistics for Target Eutrophication Index Scenarios — Neuse River Estuary

(Current condition Eutrophication Index score of *Bad*)

Statistic	TN_{atm} (kg N/yr)	% TN_{atm} Decrease
ASSETS EI = 2 (*Poor*)		
Mean	-1.43×10^8	880
Median	-1.43×10^8	880
5th Percentile	-1.47×10^8	901
95th Percentile	-1.01×10^8	653
ASSETS EI = 3 (Moderate)		
No feasible solutions found		
ASSETS EI=4 (Good) and ASSETS EI = 5 (High)		
All $TN_{atm} = -5.35 \times 10^8$, i.e. $TN_s = 0$ mg/L		

chance for the Potomac Estuary (at the 95th percentile) that a decrease in TN_{atm} (of <100%) would achieve ASSETS EI = 2.

Target scenario ASSETS EI = 3 (*Moderate*) is again a unique case because all solutions were infeasible as described above for the Potomac River watershed and the Potomac Estuary. (See Appendix 6 for further explanation.)

Target scenarios ASSETS EI = 4 (*Good*) and 5 (*High*) had identical results. All 500 iterations returned a $TN_s = 0$, and a corresponding TN_{atm} negative load equal to $TN_{atm} = (0 - 1.07)/2.0 \times 10^{-9} = -5.35 \times 10^{8}$ kg/yr. Clearly, target scenarios of ASSETS EI equal 4 (*Good*) and 5 (*High*) are unattainable when decreasing the TN_{atm} (including all NO_x) is the only option. Again, the decrease required includes all of the total reactive nitrogen atmospheric deposition source plus a load an order of magnitude greater than the original atmospheric deposition load (10^8 kg/yr), which could be compared to the other nitrogen sources used as inputs to the SPARROW model giving consideration to the characteristics of each of these sources. Again, this additional magnitude of decrease may or may not be feasible based on the relative contributions from the other sources.

> To change the Neuse River Estuary's EI score from *Bad* to *Poor*, not only must 100% of the total atmospheric nitrogen deposition be eliminated, but considerably more nitrogen from other sources as well must be decreased.

The SPARROW response curve can be used to examine the role of atmospheric nitrogen deposition in achieving desired decreased loads to the Neuse River Estuary. In the Neuse River watershed, modeling results indicate that 18×10^6 kg N/yr was deposited in 2002. SPARROW modeling predicts that this deposition input results in a loading of 1.2×10^6 kg N/yr (26% of the annual total nitrogen load) to the Neuse River Estuary. Unlike the Potomac River and Potomac Estuary, little change is seen in the total nitrogen loading to the Neuse River Estuary, with large decreases in the nitrogen deposition. If all atmospheric nitrogen deposition inputs were eliminated (100% decrease), the total annual nitrogen load to the Neuse River Estuary would only decrease by 4%. This small effect is because the total nitrogen loadings to the Neuse River Estuary are so dependent on the other sources within the SPARROW model. That is, the SPARROW response curve cannot be used to predict the relative magnitudes of loads needed to produce decreases greater than this 4%. This lack of predictive power of the response curve based on atmospheric deposition is due to the differences in characteristics between the sources within the watershed, where fertilizer, in particular, has a strong signature (i.e., indicating the

large influence of agriculture within the watershed). This result shows that the SPARROW response curves of total nitrogen load to other sources would be quite different. **Figure 5.2-19** illustrates the theoretical response curves that may result when the SPARROW modeled loads are plotted against the other total nitrogen source inputs. The green curve, or least influential source, displays the behavior of the atmospheric deposition for the Neuse River Estuary. The red curve, or highly influential source, likely corresponds to how agricultural sources within the watershed behave. These response curves will depend on the source magnitudes, spatial distributions, and other characteristics.

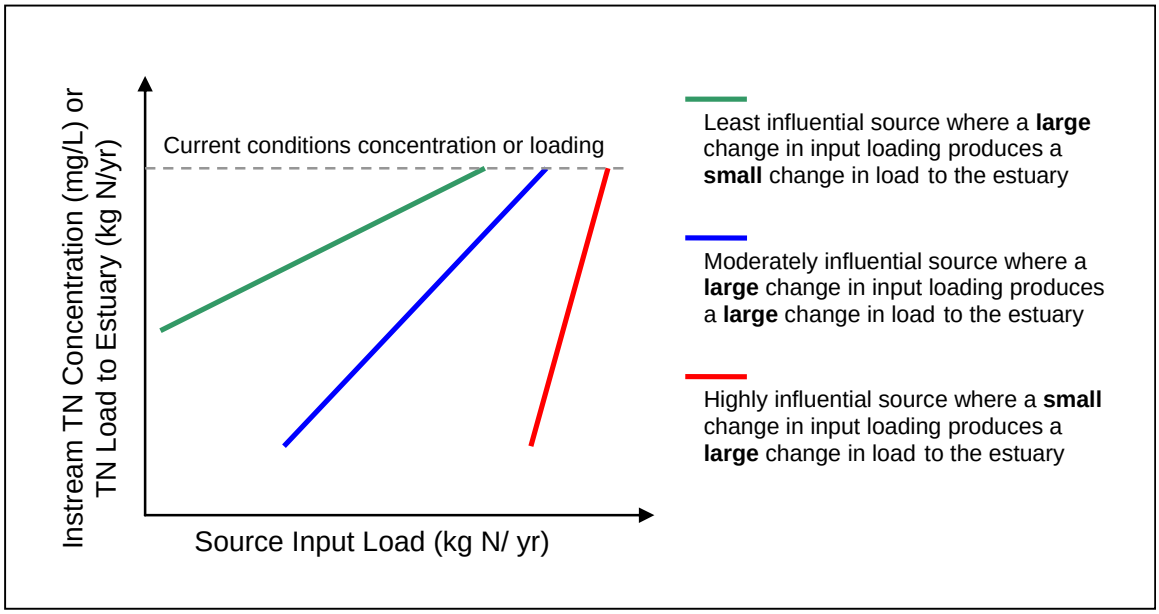


Figure 5.2-19. Theoretical SPARROW response curves demonstrating relative influence of sources on nitrogen loads to an estuary.

5.2.8 Uncertainty and Variability

The use of multiple datasets, predictive modeling, and a multi-indicator assessment tool, such as ASSETS, requires consideration of the impact of data variability and the uncertainties in case study results.

"Uncertainty is a measure of the knowledge of the magnitude of a parameter. Uncertainty can be reduced by research, i.e., the parameter value can be refined. Uncertainty is quantified as a distribution. For example, the volume of a lake may be estimated from its surface area and an average depth. This estimate can be refined by measurement. Variance is a measure of the heterogeneity of a landscape parameter or the inherent variability in a chemical property. Variance cannot be reduced by further research. It is quantified as a distribution. For example,

the organic carbon content of the soil in a region may vary, even over short distances. The soil is not homogenous and thus the organic carbon content can be described with a distribution of values." (Webster and MacKay, 2003)

Uncertainty with this method of assessment for aquatic nutrient enrichment may include the following:

- **Data inputs to SPARROW.** For this study, the data used were developed under separate studies and published by the USGS. Because the data were independently verified before publication by the USGS, only quality checks were performed on the data, rather than full validation exercises.
- **Modeling uncertainty in SPARROW estimates.** The Version 3 Chesapeake Bay SPARROW application met evaluation criteria based on degrees of freedom, model error, and R squared values. The calibration of the Neuse watershed SPARROW model using SAS examined the standard deviation, t-statistics, p-values, and Variance Inflation Factors (VIF) for each estimated parameter. The model derived for the Neuse River watershed did produce some model parameters (e.g., manure production, urban area, decay terms) that did not reach desired statistical significance levels.
- **Sensitivity of SPARROW formulation due to atmospheric inputs in the Aquatic Nutrient Enrichment Case Study.** While it is certain that the parameter estimated to apply to the atmospheric deposition source will change, what is uncertain at this point is the extent to which the other model parameters and the overall nitrogen load estimates will be affected by using the CMAQ/NADP estimates in the model calibrated against the wet nitrate deposition values.
- **Calibration data for SPARROW estimates.** Monitoring data were used to calibrate the SPARROW model. By relying on data from federally recognized data systems, the aim is to use data that has undergone quality assurance/quality control procedures. Additionally, collaboration has been completed with the researchers who have conducted the previous SPARROW applications in each case study area to provide a rigorous check on the data used.
- **Data inputs to the ASSETS EI.** Because of the numerous data requirements and sources required to conduct a full ASSETS EI analysis, there is a large range of uncertainty that can enter into the calculations. Best attempts were made to apply standardized evaluation

methods in order to minimize any uncertainties due to subjectivity or processing differences.

- **Heuristic estimates of future outlook.** The estimation of the future outlook score in the ASSETS EI currently relies on heuristic estimates from systems experts.
- **Steady-state estimates/mean annual estimates.** Both SPARROW and the ASSETS EI currently provide only longer-term estimates of the system conditions.
- **Use of a Screening Method.** The methods used in this study are only of the screening level. The screening method provides a response curve that can be used in the evaluation of ecosystem services. Additionally, many of the complex concepts linking the indicators of eutrophication to the effects of eutrophication are not highly developed or understood at this time (Howarth and Marino, 2006).
- **Use of a partially empirical framework.** Because SPARROW is, at its core, an empirical relationship, any model obtained using SPARROW is a function of the data used in the calibration. Therefore, the predictions remain valid as long as there is no great change in the conditions (in this case, the nitrogen loadings within each subbasin) underlying the model. This aspect of the model introduces uncertainty into the alternative effects results because they are calculated using a model calibrated under current conditions.

Uncertainties in the Back Calculation Methods include the following:

- **Missing ASSETS EI rankings per combinations of index scores.** The combinations of OHI, OEC, and DFO scores provided by Bricker et al. (2003) leave out 30 of the possible 125 combinations that represent overall ASSETS scores.
- **Better rationale for TN minimum and maximum uncertainty range.** The assigned uncertainty ranges were based on best professional judgment, but more research is needed. The results presented herein for the Potomac and Neuse River estuaries should be interpreted as illustrative of the methodology, not strictly valid.
- **Methodology to incorporate uncertainty in the SPARROW model.** Estimates of TN_s at the head of the estuary, predicted by SPARROW and driven by the TN_{atm} (i.e., total nitrogen deposition evaluated on decreases in NO_x) over the watershed and other nitrogen sources, are uncertain. That uncertainty was not considered in these two case studies;

therefore, the probability distributions of $TN_{atm}{}^{*}{}_{i}$ presented are artificially "tight" (i.e., the true distributions would exhibit more variability).

- **More convergence testing to determine appropriate numbers of samples.** Some modest convergence testing was completed to determine how many samples of the OEC(TN) function need to be used in order for the statistics of interest for the resulting NO_xi* distributions to be reasonably stable. More convergence testing is needed.
- **Crossing of a categorical ranking system with a continuous nitrogen concentration scale.** Several assumptions and considerations had to be made in order to create and evaluate the logistic response curve because the OEC index score is a categorical ranking of 1 through 5, whereas TN_s is a continuous variable. The functions evaluated in *BackCalculation* treat the OEC index score as a continuous function. Until higher-level models are developed to relate the nitrogen concentrations in the system to eutrophication effects, these assumptions are necessary. Future applications with additional data should be used to test and validate these assumptions and results.

5.3 TERRESTRIAL NUTRIENT ENRICHMENT

Terrestrial nutrient enrichment is described in the ISA (U.S. EPA, 2008, Section 3.3) for many different ecosystems. In particular, additional nitrogen may affect the plants in these sensitive ecosystems. Nitrogen, however, is known to limit the growth of trees in some forests, especially commercial forests, and growth may be enhanced initially in these systems in response to nitrogen additions (U.S. EPA, 2008, Section 4.3.1). In noncommercial ecosystems reviewed in this analysis, changes to the individual plants, as well as changes to populations and communities of plants, have been documented. Over the last half century, landscapes in the United States have been exposed to atmospherically deposited nitrogen from anthropogenic activities. Some of the highest nitrogen deposition has occurred in Southern California, where researchers have documented measurable ecological changes related to atmospheric deposition. Evidence from the two ecosystems discussed in this case study—CSS and MCF communities in the Sierra Nevada Range and San Bernardino Mountains of California—supports the finding that nitrogen alters these habitats. Changes in nitrogen loading may also affect the ecological services provided by the CSS and MCF ecosystems, including regulation (e.g., water, habitat), cultural and aesthetic value (e.g., recreation, natural landscape, sense of place), and provisioning (e.g., timber) (MEA,

2005). The Terrestrial Nutrient Enrichment Case Study also evaluated research conducted on these complex ecosystems to understand the relationships among the effects of nitrogen loads, fire frequency and intensity, and invasive plants.

Section 3.3 of the ISA (U.S. EPA, 2008) describes the ecosystems and species of concern, identifies trends in the ecosystems and the effects of these trends, and discusses research efforts that investigated the variables and driving forces that may affect the communities. The CMAQ 2002 modeling results and the NADP monitoring data for 2002 were used to gain an understanding of how atmospheric deposition of nitrogen is spatially distributed. GIS data on the spatial extent of the habitat and associated habitat changes, the location of fire threat, and the location of sensitive species were used to compare these patterns to the CMAQ/NADP data. In sum, spatial information and observed, experimental effects were used to help identify the trends in these ecosystems and to describe the past and current spatial extent of the ecosystems.

Current analysis of the effects of terrestrial nutrient enrichment from atmospheric nitrogen deposition in both CSS and MCF ecosystems seeks to improve scientific understanding of the interactions among nitrogen deposition, fire events, and community dynamics. The available scientific information is sufficient to identify ecological benchmarks that are affected by nitrogen deposition. Ecological benchmarks have been identified for CSS and MCF.

5.3.1 Ecological Indicators, Ecological Responses, and Ecosystem Services

5.3.1.1 Indicators

Ecosystems may respond to the addition of nitrogen in a number of ways. There may be gains in productivity and growth initially. Increasing levels of nitrogen; however, may lead to changes in community structure and function, with changes in species composition or changes in the abundance and distribution of organisms. If changes include loss of threatened, endangered or rare species, or rare communities or a diminished productivity or increased fire threat, then such changes would be cause for concern. Indicators of possible changes can be identified that would assist in determining an acceptable ambient air concentration of nitrogen oxides. Terrestrial nutrient enrichment research has measured ecosystems' exposure to deposition of various atmospheric nitrogen species, including nitrogen oxides, reduced nitrogen, and total nitrogen. The ISA (U.S. EPA, 2008, Section 3.3) documents current understanding of the effects

of nitrogen nutrient enrichment on terrestrial ecosystems. The ISA concludes that there is sufficient information to infer a causal relationship between atmospheric nitrogen deposition and biogeochemical cycling and fluxes of nitrogen in terrestrial systems. The ISA further concludes that there is a causal relationship between atmospheric nitrogen deposition and changes in species richness, species composition, and biodiversity in terrestrial systems. These conclusions are based on an extensive literature review that is summarized in Table 4-4 of the ISA. The science review includes both observational and experimental (nitrogen addition) research. Alpine ecosystems, grasslands (including arid and semiarid ecosystems), forests, and deserts were included. This extensive documentation was used to assist in selecting the case study sites to identify and compare ecological benchmarks from different ecosystems (see Section 5.3.3 for more detail on case study selection).

CSS is subject to several pressures, such as land conversion, grazing, fire, and pollution, all of which have been observed to induce declines in other ecosystems (Allen et al., 1998). Research has shown that both fire and increased nitrogen can enhance the growth of nonnative grasses in established CSS communities (Keeley et al., 2005; Wood et al., 2006). It is hypothesized that many CSS stands are no longer limited by nitrogen and have instead become nitrogen-saturated because of atmospheric nitrogen deposition (Allen et al., 1998; Westman, 1981). Nitrogen availability may favor the germination and growth of nonnative grasses, which can create a dense network of shallow roots that slow the diffusion of water through soil, decrease the percolation depth of precipitation, and decrease the water storage capability of the soil and underlying bedrock (Wood et al., 2006). CSS has been declining in land area and in shrub density for the past 60 years, and in many places it is being replaced by nonnative annual grasses (Allen et al., 1998; Padgett and Allen, 1999). Replacement by nonnative grasses results in less habitat for threatened and endangered species and also appears to increase fire vulnerability. Atmospheric nitrogen deposition has been suggested as a possible cause or factor in this ecosystem alteration (U.S. EPA, 2008, Section 3.3). Changes in community metrics may, therefore, be useful indicators of atmospheric nitrogen deposition for CSS.

The ISA discusses the extensive land areas in the western United States that receive low levels of atmospheric nitrogen deposition and that are interspaced with areas of relatively higher atmospheric deposition downwind of large metropolitan centers and agricultural areas. Fenn et al. (2008) determined that empirical critical loads (i.e., measured levels of nitrogen at a specific

location where biological impacts occur) for atmospheric nitrogen deposition in MCF based on changes in leached nitrate in receiving waters, decreased fine-root biomass in Ponderosa pine (*Pinus ponderosa*) and epiphytic lichen communities. Lichens are good early indicators of atmospheric nitrogen deposition effects on other MCF species because lichens rely entirely on atmospheric nitrogen and cannot regulate uptake (**Figure 5.3-1**).

From the lichen data, Fenn et al. (2008) predicted that a critical load of 3.1 kg N/ha/yr would be protective for all components of the forest ecosystem. The study further found that an atmospheric nitrogen deposition of 17 kg N/ha/yr was associated with NO_3^- leaching and an approximately 25% decrease in fine-root biomass.

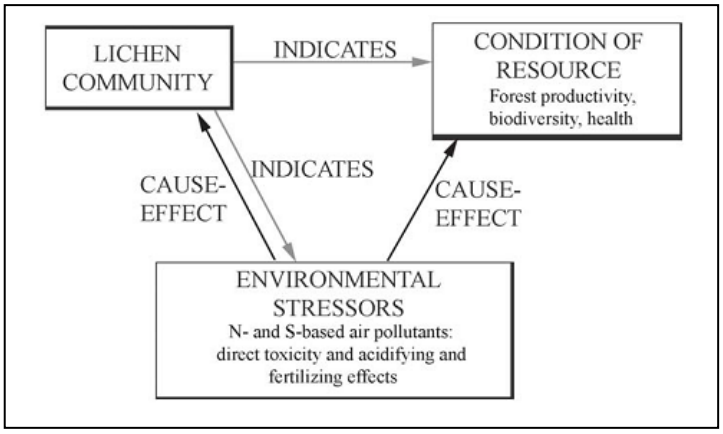


Figure 5.3-1. Importance of lichens as an indicator of ecosystem health (Jovan, 2008).

5.3.1.2 Ecological Responses: Benchmark Values Selected for This Case Study

The data limitations on atmospheric nitrogen deposition described above, along with current data to describe the full extent and distribution of nitrogen sensitive U.S. ecosystems, presented a barrier to designing a case study that uses quantitative monitoring and modeling tools. Instead, this case study used published research results to identify meaningful ecological benchmarks associated with different levels of atmospheric nitrogen deposition.

The ecological benchmarks that were identified for the CSS and the MCF are included in the suite of benchmarks identified in the ISA (U.S. EPA, 2008, Section 3.3). There are sufficient data to confidently relate the ecological effect to a loading of atmospheric nitrogen. For the CSS community, the following ecological benchmarks were identified:

- 3.3 kg N/ha/yr – the amount of nitrogen uptake by a vigorous stand of CSS; above this level, nitrogen may no longer be limiting
- 10 kg N/ha/yr – mycorrhizal community changes

For the MCF community, the following ecological benchmarks were identified:

- 3.1 kg N/ha/yr – shift from sensitive to tolerant lichen species

- 5.2 kg N/ha/yr – dominance of the tolerant lichen species
- 10.2 kg N/ha/yr – loss of sensitive lichen species
- 17 kg N/ha/yr – leaching of nitrate into streams.

These benchmarks, as well as those from other systems, are presented in **Figure 5.3-2.**

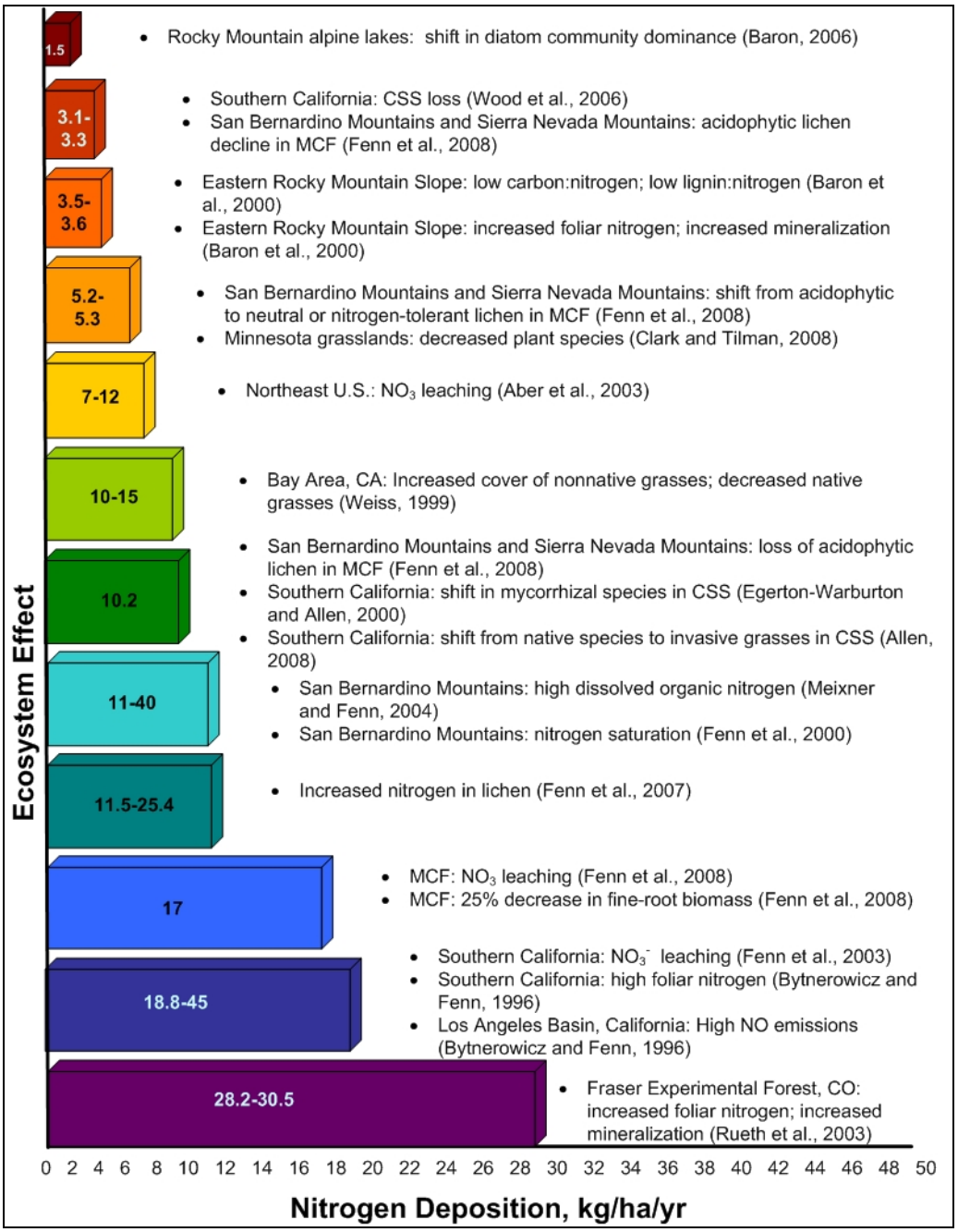


Figure 5.3-2. Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators with the inclusion of the diatom changes in the Rocky Mountain lakes.

5.3.1.3 Ecosystem Services

The ecosystem service impacts of terrestrial nutrient enrichment include primarily cultural and regulating services. This section provides a qualitative discussion of the services and benefits offered by these ecosystems. In CSS, concerns focus on a decline in CSS and an increase in nonnative grasses and other species, impacts on the viability of threatened and endangered species associated with CSS, and an increase in fire frequency. Changes in MCF include changes in habitat suitability and increased tree mortality, increased fire intensity, and a change in the forest's nutrient cycling that may affect surface water quality through nitrate leaching (U.S. EPA, 2008).

Both CSS and MCF are located in areas of California valuable for housing, recreation, and development. CSS runs along the coast through densely populated areas of California. MCF covers less densely populated areas that are valuable for recreation. (Appendix 8, Figure 5.1-1) The proximity of CSS and MCF to population centers and recreational areas and the potential value of these landscape types in providing regulating ecosystem services suggest that the value of preserving CSS and MCF to California could be quite high. The value that California residents and the U.S. population as a whole place on CSS and MCF habitats is reflected in the various federal, state, and local government measures that have been put in place to protect these habitats. Threatened and endangered species are protected by the Endangered Species Act. The State of California passed the Natural Communities Conservation Planning Program in 1991, and CSS was the first habitat identified for protection under the program (see http://www.dfg.ca.gov/habcon/nccp/). Private organizations, such as The Nature Conservancy, the Audubon Society, and local land trusts also protect and restore CSS and MCF habitats. According to the 2005 National Land Trust Census Report (Land Trust Alliance, 2006), California has the most land trusts of any state, with a total of 1,732,471 acres either owned, under conservation easement, or conserved by other means.

Cultural

The primary cultural ecosystem services associated with CSS and MCF are recreation, aesthetic, and nonuse values. The possible ecosystem service benefits from decreasing nitrogen enrichment in CSS and MCF and a general overview of the types and relative magnitude of the benefits are discussed below.

CSS, once the dominant landscape type in the area, is a unique ecosystem that provides cultural value to California and the nation as a whole. Culturally, the remaining patches of CSS contain a number of threatened and endangered species, and patches of CSS are present in a number of parks and recreational areas. More generally, the patches of CSS represent the iconic landscape of Southern California and serve as a reminder of what the area looked like pre-development. Changes that might impact cultural ecosystem services in CSS resulting from nutrient enrichment potentially include the following:

- Decline in CSS habitat, shrub abundance, and species of concern
- Increased abundance of nonnative grasses and other species
- Increase in wildfires.

For MCF, the changes from nutrient enrichment that might impact cultural ecosystem services include the following:

- Change in habitat suitability and increased tree mortality
- Decline in MCF aesthetics.

Recreation

CSS and MCF are found in numerous recreational areas in California. Three national parks and monuments in California contain CSS, including Cabrillo National Monument, Channel Islands National Park, and Santa Monica National Recreation Area. All three parks showcase CSS habitat with educational programs and information provided to visitors, guided hikes, and research projects focused on understanding and preserving CSS. A total of 1,456,879 visitors traveled through these three parks in 2008. MCF is highlighted in Sequoia and Kings Canyon National Park, Yosemite National Park, and Lassen Volcanic National Park, where a total of 5,313,754 people visited in 2008. In addition, numerous state and county parks encompass CSS and MCF habitat. For example, California's Torrey Pines State Natural Reserve protects CSS habitat (see http://www.torreypine.org/). Visitors to these parks engage in activities such as camping, hiking, attending educational programs, horseback riding, wildlife viewing, water-based recreation, and fishing.

The 2006 FHWAR for California (U.S. DOI, 2007) reports on the number of individuals involved in fishing, hunting, and wildlife viewing in California. Millions of people are involved in these three activities each year. The quality of these trips depends in part on the health of the ecosystems and their ability to support the diversity of plants and animals found in important

habitats. Based on estimates from Kaval and Loomis (2003), in the Pacific Coast region of the United States, a day of fishing has an *average* value of $48.86 (in 2007 dollars) based on 15 studies. For hunting and wildlife viewing in this region, average day values were estimated to be $50.10 and $79.81 from 18 and 23 studies, respectively. Multiplying these average values by the total participation days reported in Appendix 8, Table 5.1-1, the total benefits in 2006 from fishing, hunting, and wildlife viewing away from home in California were approximately $947 million, $169 million, and $3.59 billion, respectively.

In addition, data from California State Parks (2003) indicate that in 2002, 68.7% of adult residents participated in trail hiking, for an average of 24.1 days per year. Applying these same rates to Census estimates of the California adult population in 2007 suggests that there were roughly 453 million days of hiking by residents in California in 2007. According to Kaval and Loomis (2003), the average value of a hiking day in the Pacific Coast region is $25.59, based on a sample of 49 studies. Multiplying this average day value by the total participation estimate indicates that the aggregate annual benefit for California residents from trail hiking in 2007 was $11.59 billion.

Aesthetic

Beyond the recreational value, the CSS landscape and MCF provide aesthetic services to local residents and homeowners who live near CSS or MCF. Aesthetic services not related to recreation include the view of the landscape from houses, as individuals commute, and as individuals go about their daily routine in a nearby community. Studies find that scenic landscapes are capitalized into the price of housing. While there are no known studies that look at the value of housing as a function of the view in landscapes that include CSS or MCF, other studies document the existence of housing price premia associated with proximity to forest and open space (Acharya and Bennett, 2001; Geoghegan et al., 1997; Irwin, 2002; Mansfield, et al., 2005; Smith et al., 2002; Tyrvainen and Miettinen, 2000). The CSS landscape itself is closely associated with Southern California, which should increase the aesthetic value of the landscape in general. CSS areas border a number of areas along the coast near large cities with very high home values, as well as areas between the cities where home values are lower.

Nonuse Value

Nonuse value, also called existence value or preservation value, encompasses a variety of motivations that lead individuals to place value on environmental goods or services that they do

not use. The values individuals place on protecting rare species, rare habitats, or landscape types that they do not see or visit and that do not contribute to the pleasure they get from other activities are examples of nonuse values.

While measuring the public's willingness to pay to protect endangered species poses theoretical and technical challenges, it is clear that the public places a value on preserving endangered species and their habitats. Data on charitable donations, survey results, and the time and effort different individuals or organizations devote to protecting species and habitats suggest that endangered species have intrinsic value to people beyond the value derived from using the resource (e.g., recreational viewing or aesthetic value). CSS and MCF are home to a number of important and rare species and habitat types. CSS displays richness in biodiversity, with more than 550 herbaceous annual and perennial species. Of these herbs, nearly half are endangered, sensitive, or of special status (Burger et al., 2003). Additionally, avian, arthropod, herpetofauna, and mammalian species live in CSS habitat or use the habitat for breeding or foraging.

Communities of CSS are home to three important federally endangered species. MCF is home to one federally endangered species and a number of state-level sensitive species. The Audubon Society lists 28 important bird areas in CSS habitat and at least 5 in MCF in California (http://ca.audubon.org/iba/index.shtml).[3]

Only one known study has specifically estimated values for protecting CSS habitat in California. Stanley (2005) uses a contingent valuation (CV) survey to measure willingness to pay (WTP) to support recovery plans for endangered species in Southern California. The survey of Orange County, CA, residents asked respondents to value the recovery of a single species (i.e., the Riverdale fairy shrimp) and a larger bundle of 32 species found in the county. The acquisition of critical habitat and implementation of the recovery plan were the specific goods being valued in the WTP question, and the programs would be financed by an annual tax payment. The average WTP for Riverdale fairy shrimp recovery was roughly $29 (in 2007 dollars), and for all 32 species, it was $61 per household, depending on the model used. Aggregating benefits (i.e., multiplying average household WTP by the number of households in the county) results in total estimated WTP of more than $27 million annually for protecting Riverdale fairy shrimp and $57 million annually for protecting all 32 species.

[3] Important Bird Areas are sites that provide essential habitat for one or more species of bird.

In a more general study valuing endangered species protection, Loomis and White (1996) synthesize key results from 20 threatened and endangered species valuation studies using meta-analysis methods. They find that annual WTP estimates range from a low of $11 for the Striped Shiner fish to a high of $178 for the Northern Spotted Owl (in 2007 dollars). None of the studies summarized by Loomis and White are found in CSS or MCF, but the study provides another indication of the value that the public places on preserving endangered species in general.

Regulating

Excessive nitrogen deposition upsets the balance between CSS and nonnative plants, changing the ability of an area to support the biodiversity found in CSS. The composition of species in CSS changes fire frequency and intensity, as nonnative grasses fuel more frequent and more intense wildfires. More frequent and intense fires also decrease the ability of CSS to regenerate after a fire and increase the proportion of nonnative grasses (U.S. EPA, 2008). A healthy MCF ecosystem supports native species, promotes water quality, and helps regulate fire intensity. Excess nitrogen deposition leads to changes in the forest structure, such as increased density and loss of root biomass, which, in turn, can result in more intense fires and water quality problems related to nitrate leaching (U.S. EPA, 2008).

The importance of CSS and MCF as homes for sensitive species and their aesthetic services have been discussed in Appendix 8, Section 5.1.1. Here the contribution of CSS and MCF to fire regulation and water quality is discussed.

Fire Regulation

The terrestrial enrichment case study identified fire regulation as a service that could be affected by nutrient enrichment of the CSS and MCF ecosystems by encouraging growth of more flammable grasses. Wildfires represent a serious threat in California and cause billions of dollars in damage. Over the 5-year period from 2004 to 2008, Southern California experienced, on average, more than 4,000 fires per year burning, on average, more than 400,000 acres per year (NASF, 2009). Improved fire regulation leads to short-term and long-term benefits. The short-term benefits include the value of avoided residential property damages, avoided damages to timber, rangeland, and wildlife resources, avoided losses from fire-related air quality impairments, avoided deaths and injury due to fire, improved outdoor recreation opportunities, and savings in costs associated with fighting the fires and protecting lives and property. For example, the California Department of Forestry and Fire Protection (CAL FIRE) estimated that

average annual losses to homes due to wildfire from 1984 to 1994 were $163 million per year (CAL FIRE, 1996) and were more than $250 million in 2007 (CAL FIRE, 2008). In fiscal year 2008, CAL FIRE's costs for fire suppression activities were nearly $300 million (CAL FIRE, 2008). Therefore, even a 1% decrease in these damages and costs would imply benefits of more than $5 million per year.

CSS overlaps with areas of very high to extremely high fire threat. MCF is found in some areas closer to the coast with extremely high fire threat and in areas in the mountains also under very high fire threat.

In the long term, decreased frequency of fires could result in an increase in property values in fire-prone areas. Mueller et al. (2007) conducted a hedonic pricing study to determine whether increasing numbers of wildfires affect house prices in Southern California. They estimated that house prices would decrease 9.71% ($30,693 in 2007 dollars) after one fire and 22.7% ($71,722; $102,417 cumulative) after a second wildfire within 1.75 miles of a house in their study area. After the second fire, the housing prices took between 5 and 7 years to recover. The results come from a sample of 2,520 single-family homes located within 1.75 miles of one of five fires during the 1990s.

Long-term decreases in wildfire risks are also expected to provide outdoor recreation benefits. The empirical literature contains several articles measuring the relationship between wildfires and recreational values; however, very few address fires in California, particularly in CSS areas. One exception is Loomis et al. (2002), which estimates the changes in deer harvest and deer hunting benefits resulting from controlled burns or a prescribed fire in the San Bernardino National Forest in Southern California. Using a CV survey of deer hunters in California, they estimated that the net economic value of an additional deer harvested is on average $122 (in 2007 dollars). Based on predicted changes in deer harvest in response to a prescribed fire, they estimated annual economic benefits for an additional 1,000 acres of prescribed burning ranges from $3,328 to $3,893.

Water Quality

In the MCF Case Study, maintaining water quality emerged as a regulating service that can be upset by excessive nitrogen. When the soil becomes saturated, nitrates may leach into the surface water and cause acidification. Several large rivers and Lake Tahoe cut through MCF

areas (see Appendix 8, Figure 5.1-10). Additional nitrogen from MCF areas could further degrade waters that are already stressed by numerous other sources of nutrients and pollution.

Value of Coastal Sage Scrub and Mixed Conifer Forest Ecosystem Services

The CSS and MCF were selected as case studies for terrestrial nutrient enrichment because of the potential that these areas could be adversely affected by excessive nitrogen deposition. To date, the detailed studies needed to identify the magnitude of the adverse impacts due to nitrogen deposition have not been completed. Based on available data, this *Risk and Exposure Assessment* report provides a qualitative discussion of the services offered by CSS and MCF and a sense of the scale of benefits associated with these services. California is famous for its recreational opportunities and beautiful landscapes. CSS and MCF are an integral part of the California landscape, and together the ranges of these habitats include the densely populated and valuable coastline and the mountain areas. Through recreation and scenic value, these habitats affect the lives of millions of California residents and tourists. Numerous threatened and endangered species at both the state and federal levels reside in CSS and MCF. Both habitats may play an important role in wildfire frequency and intensity, an extremely important problem for California. The potentially high value of the ecosystem services provided by CSS and MCF justify careful attention to the long-term viability of these habitats.

5.3.2 Characteristics of Sensitive Areas

The ISA (U.S. EPA, 2008, Section 3.3) indicates that information is limited about the spatial extent and distribution of terrestrial ecosystems most sensitive to nutrient enrichment from atmospheric nitrogen deposition. Examples of sensitive ecosystems include the following:

> "Effects are most likely to occur where areas of relatively high atmospheric nitrogen deposition intersect with nitrogen limited plant communities. The factors that govern the sensitivity…include the degree of nitrogen limitation, rates and form of atmospheric nitrogen deposition, elevation, species composition, length of growing season, and soil nitrogen retention capacity." ISA, Section 3.3 (U.S. EPA 2008)

- Alpine tundra (low rates of primary production, short growing season, low temperature, wide moisture variation, low nutrient supply).
- Western United States ecosystems, such as the alpine ecosystems of the Colorado Front Range, chaparral watersheds of the Sierra Nevada Range, lichen communities in the San Bernardino Mountains and the Pacific Northwest, and CSS communities in Southern California.

- Eastern United States ecosystems, where sensitivities are typically assessed in terms of the degree of nitrate leaching from soils into ground and surface waters. These ecosystems are expected to include hardwood forests and grassland ecosystems, but effects on individual plant species have not been studied well.

In the Mediterranean systems of Southern California where rainfall is concentrated during some months of the year, dry deposition is particularly important. Individual studies measuring atmospheric nitrogen deposition to terrestrial ecosystems that involve throughfall estimates for forested ecosystems can provide better approximations for total atmospheric nitrogen deposition levels; however, such estimates and related bioassessment data are not available for the entire country. Further, dry deposition methodologies themselves need to be improved.

Finally, the exact relationship between atmospheric nitrogen loadings, fire frequency and intensity, and nonnative plants, particularly in the CSS ecosystem, have not been quantified. Various conceptual models linking these factors have been developed, but an understanding of cause and effect, seasonal influences, and thresholds remains undeveloped.

The selection of case study areas specific to terrestrial nutrient enrichment began with national GIS mapping to identify terrestrial areas potentially sensitive to atmospheric nitrogen deposition. GIS datasets of physical, chemical, and biological properties that were indicative of potential terrestrial nutrient enrichment were considered. Not all sensitive systems have adequate datasets. The case study areas considered included places where data on species sensitive or vulnerable to nitrogen deposition were available and excluded areas of the United States with anthropogenic influence (e.g., urban, farmland).

Acidophytic lichens are known to be sensitive to increased levels of nitrogen loading. In turn, other species are dependent upon lichens for both food and habitat. Locations where acidophytic lichen were identified were defined as being sensitive.

Urban and agricultural land covers were also mapped, so they could be used to exclude areas that are not sensitive to terrestrial nutrient enrichment, such as agricultural areas and urbanized areas. Analysis of the presence of lichen over time compared to atmospheric nitrogen deposition records and benchmarks can indicate the potential influence of nitrogen deposition.

Although there is no known nationwide species that has shown range loss because of additional nitrogen, it was possible to assemble a “patchwork quilt” of species and forest types

from across the United States that are identified in the published literature as sensitive. These species have evolved in settings across the United States to be able to assimilate specific levels of nitrogen exposure. Some settings may naturally have low background concentrations of nitrogen, so the species requires a relatively small amount to thrive. Other settings may have higher background concentrations, where native species have evolved to thrive at those levels. When exposed to nitrogen levels higher than natural background, the native species may be vulnerable to invasion from species that use nitrogen in the shallow root zone before the nutrient reaches deeper zones of the native ecosystem vegetation.

Soil nitrogen content data dating to pre-1980 were not available, and the quality of any available data was uncertain. The physiographic provinces of the United States were considered to provide leeward sides of mountains that tend to receive a greater amount of atmospheric nitrogen deposition. However, this dataset was not used because terrain is already taken into account by the CMAQ modeling.

The resulting map illustrates the areas of highest potential sensitivity (see **Figure 5.3-3**.), including CSS, grasslands, and desert, as well as certain forest species and lichens.
This information facilitated the review of candidate case study areas.

5.3.3 Case Study Selection

Figure 5.3-3, showing the areas of potential sensitivity to nutrient enrichment, was used in conjunction with potential areas identified in the ISA (U.S. EPA, 2008, Section 4.3.1.2, Table 4.4) to select ecosystems for the case study. After considering this information, California's CSS and MCF ecosystems were selected for this Terrestrial Nutrient Enrichment Case Study analysis based on the following selection factors, in addition to the factors listed in Section 5.3.1:

- Availability of atmospheric ambient and deposition data (monitored or modeled)
- Availability of digitized datasets of biotic communities; fire-prone areas; and sensitive, rare species
- Scientific results of research on nitrogen effects for the case study area
- Representation of western United States ecosystems potentially impacted by atmospheric nitrogen deposition
- Scalability and generalization opportunities for risk analysis results from the case studies.

California's CSS has been the subject of intensive research in the past 10 years, which has provided the data needed for a first phase of GIS analysis of the role of atmospheric nitrogen deposition in terrestrial ecosystems. California's MCF has an even longer record of study that includes investigations into the effects of atmospheric pollution, changes to forest structure, changes to the lichen communities, and measurements of nitrogen saturation. Another ecosystem that was considered, but not selected for this case study, was the alpine ecosystem in the Rocky Mountains (see Section 5.3.6). As noted in the ISA (U.S. EPA, 2008, Section 3.3), results from a number of studies indicate that nitrates may be leaching from alpine catchments, and there appear to be changes in plant communities related to the deposition of atmospheric nitrogen. The amount of data from these alpine ecosystems is more limited than that from the CSS and MCF. However, the ecological benchmarks suggested for alpine ecosystems were comparable to the lower-level benchmarks from CSS and MCF ecosystems (see **Figure 5.3-2**).

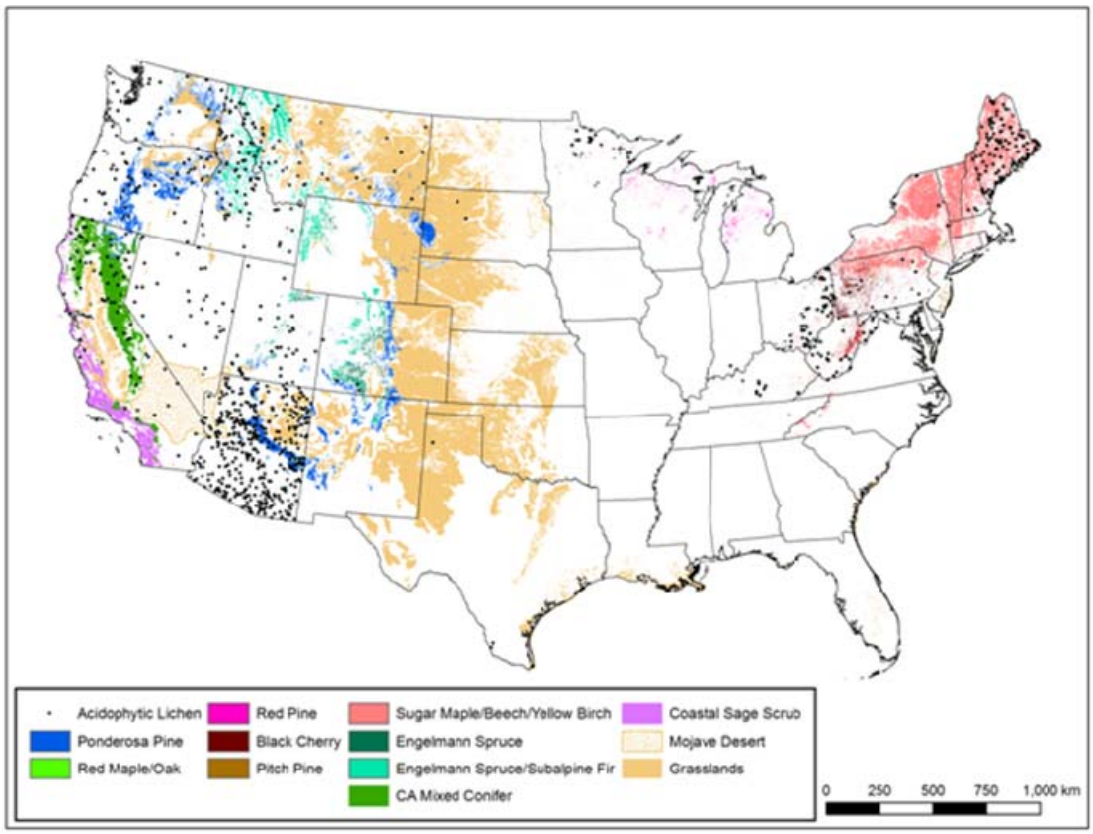


Figure 5.3-3. Areas of highest potential nutrient enrichment sensitivity. (Acidophytic lichens, tree species, and the extent of the Mojave Desert come from data obtained from the United States Forest Service. The extents of coastal sage scrub and California mixed conifer forest come from the California Fire and Resource Assessment Program. Grasslands were obtained from the National Land Cover Dataset [USGS]).

5.3.4 Current Conditions in Case Study Areas

To assess current conditions, the ISA (U.S. EPA, 2008) provided the basis for identifying the published scientific literature on CSS and MCF ecosystems. In addition, spatially distributed data are available and support a GIS analysis. Section 2.2 of Appendix 7 describes the data sources used in the GIS analysis.

One of the central analytical tasks was to quantify the amount of CSS (and MCF loss) and to see whether this corresponded spatially to areas of high total nitrogen deposition or fire threat, or both.

CSS and MCF were selected as case study areas for the following reasons:

- Significant geographic coverage and they are located where urban areas interface with wilderness areas.
- Nitrogen deposition gradients, ranging from low background levels to some of the highest deposition levels recorded in the United States.
- Researched for extended periods to understand the interactive effects of deposition, climate change, fire, and other stressors.
- Research investigations are well documented in the peer-reviewed literature.

5.3.4.1 Coastal Sage Scrub

CSS is subject to several pressures, such as land conversion, grazing, fire, and pollution, all of which have been observed to induce declines in other ecosystems (Allen et al., 1998). At one extreme, development pressure (i.e., the conversion of CSS to residential and commercial land uses) will simply eliminate acres of CSS. Other pressures will come into play in modifying the remaining ecosystem. Research suggests that both fire and increased atmospheric nitrogen deposition can enhance the growth of nonnative grasses in established CSS communities. Additionally, CSS declines have been observed when fire frequency is held constant and/or nitrogen is held constant, suggesting that both fire and nitrogen play a role in CSS decline when direct destructive factors are not an imminent threat. Table 3.1-1 of Appendix 7 contains a summary of selected experimental variables across multiple CSS study areas.

Increased atmospheric nitrogen deposition has been observed to alter vegetation types when nitrogen is a limiting nutrient to growth. This is observed in alpine plant communities in the Colorado Front Range, as well as in lichen communities in the western Sierra Nevada region (Fenn et al., 2003, 2008); however, in the case of CSS, it is hypothesized that many stands are no longer limited by nitrogen and have instead become nitrogen-saturated because of atmospheric nitrogen deposition (Allen et al., 1998; Westman, 1981). This is supported by the positive correlation between atmospheric nitrogen and soil nitrogen, increased long-term mortality of CSS shrubs, and increased nitrogen-cycling rates in soil and litter and soil fertility (Allen et al.,

1998; Padgett et al., 1999; Sirulnik et al., 2007; Vourlitis et al., 2007). **Figure 5.3-4** illustrates the levels of atmospheric nitrogen deposition in CSS communities using CMAQ/NADP data.

Table 5.3-1. Coastal Sage Scrub Ecosystem Area and Total Nitrogen Deposition

N Deposition (kg/ha/yr)	Area (hectares)	Percent of CSS Area, %
≥3.3	654048.4179	93.51
≥10	138019.8922	19.73

Wood et al. (2006) investigated the amount of nitrogen utilized by healthy and degraded CSS systems. In healthy stands, the authors estimated that 3.3 kg N/ha/yr was used for CSS plant growth (Wood et al., 2006). It is assumed that 3.3 kg N/ha/yr is near the point where nitrogen is no longer limiting in the CSS community. Therefore, this amount can be considered an ecological benchmark for the CSS community. **Figure 5.3-4** displays the spatial extent of CSS where total nitrogen deposition is above the ecological benchmark of 3.3 kg N/ha/yr. **Table 5.3-1** displays the areas (in hectares) of CSS experiencing different total nitrogen deposition levels.

In the rainy, winter season, deposited surface nitrogen is transported deeper into the soil and is rapidly mineralized by microbes, favoring the germination and growth of nonnative grasses (e.g., *Bromus madritensis*, *Avena fatua,* and *Hirschfeldia incana*). Flourishing of grasses can create a dense network of shallow roots, which slows the diffusion of water through soil, decreases the percolation depth of precipitation, and decreases the amount of water for soil and ground water recharge (Wood et al., 2006). Growth of CSS species, such as *Artemisia californica*, *Eriogonum fasciculatum*, and *Encelia farinose*, may be decreased because of decreased water and nitrogen availability at the deeper soil layers where more woody CSS tap roots are found (Keeler-Wolf, 1995; Wood et al., 2006).

Mutualistic fungal communities, such as arbuscular mycorrhizae (AM) (Egerton-Warburton and Allen, 2000; Siguenza et al., 2006), increase the surface area and capacity for nutrient uptake. CSS is predominantly colonized by a coarse AM species, and nonnative grasses are more likely mutualistic with finer AM species. In the presence of elevated nitrogen, coarse AM colonizations were depressed in number and volume. Egerton-Warburton and Allen (2000) documented shifts in AM species as well as declines in spore abundance and colonization at approximately 10 kg N/ha/yr. Therefore, it is suggested that these decreased mutualistic associations of coarse AM may contribute to a decline in the overall health of CSS via a loss in nutrient uptake capacity and represent an ecological benchmark for the CSS ecosystem. **Figure**

5.3-4 displays the levels of total nitrogen deposition on CSS communities above the ecological benchmark of 10 kg N/ha/yr using CMAQ/NADP data. The 12 km CMAQ/NADP data indicate that CSS communities within the Los Angeles and San Diego airsheds are likely to experience the noted effects at the 10 kg N/ha/yr ecological benchmark.

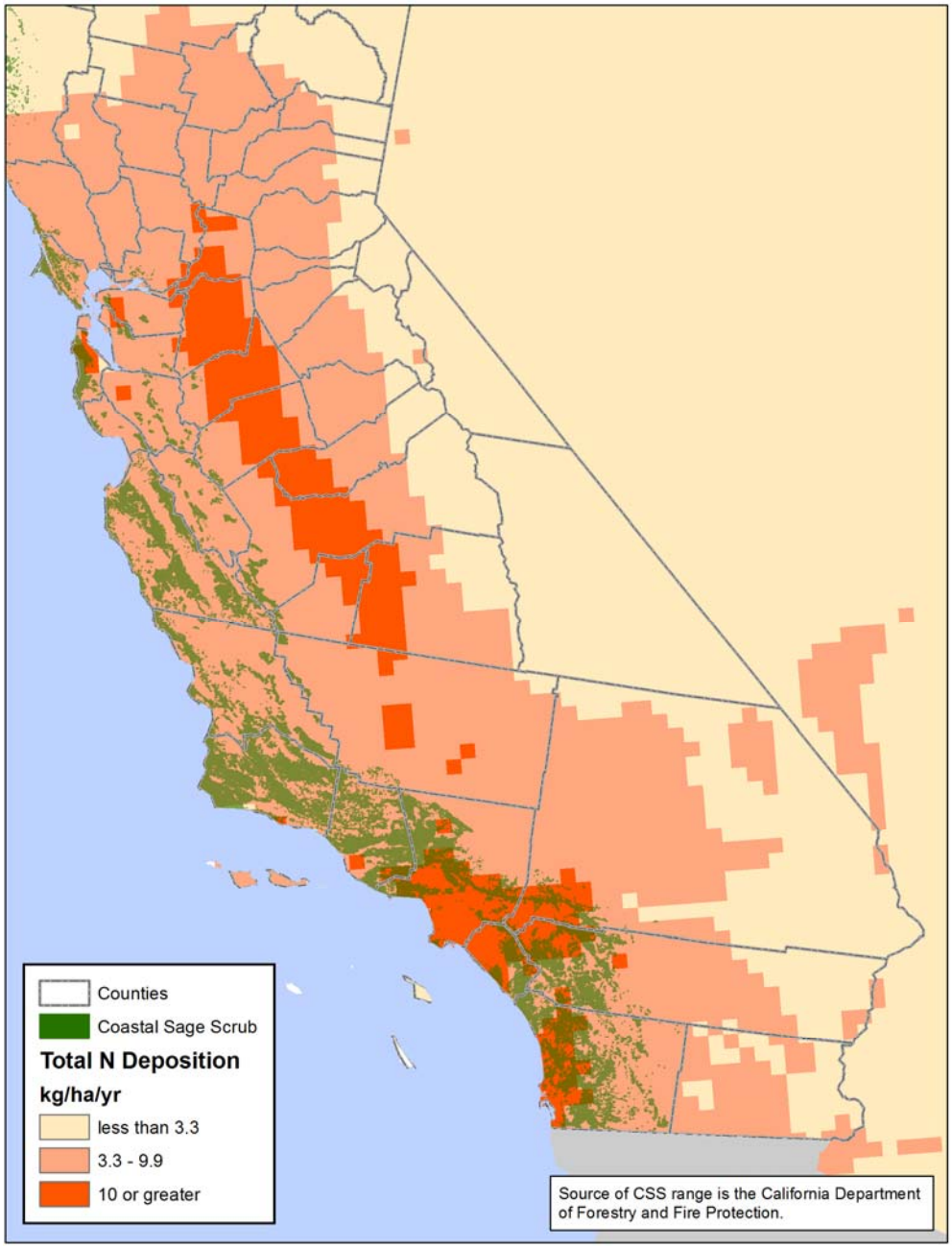


Figure 5.3-4. Coastal sage scrub range and total nitrogen deposition using CMAQ 2002 modeling results and NADP monitoring data.

Studies have suggested that plant-available nitrogen in soils may be increasing because of soil fertility in conjunction with atmospheric deposition, so that the soil itself becomes an intrinsic source of nitrogen (Padgett et al., 1999). In combination with decreased establishment and the capacity for nutrient uptake, these responses to elevated nitrogen levels may represent a detrimental and long-term pressure on CSS at varying levels of nitrogen additions. Table 3.1-3 of Appendix 7 summarizes the various ecosystem responses to nitrogen levels that affect CSS communities.

Fire is also an inextricable and significant component in CSS losses. Although CSS communities are fire resilient, nonnative grass seeds are quick to establish in burned lands, decreasing the water and nutrient amounts available to CSS for reestablishment (Keeler-Wolf, 1995). Additionally, when annual grasses have established dominance, these species alter and increase the fire frequency as they senesce earlier in the annual season, which increases dry, ignitable fuel availability (Keeley et al., 2005). With increased fire frequencies and faster nonnative colonizations, CSS seed banks are eventually eradicated from the soil, and the probability of reestablishment decreases significantly (Keeley et al., 2005). **Figure 5.3-5** represents the fire threats to CSS communities.

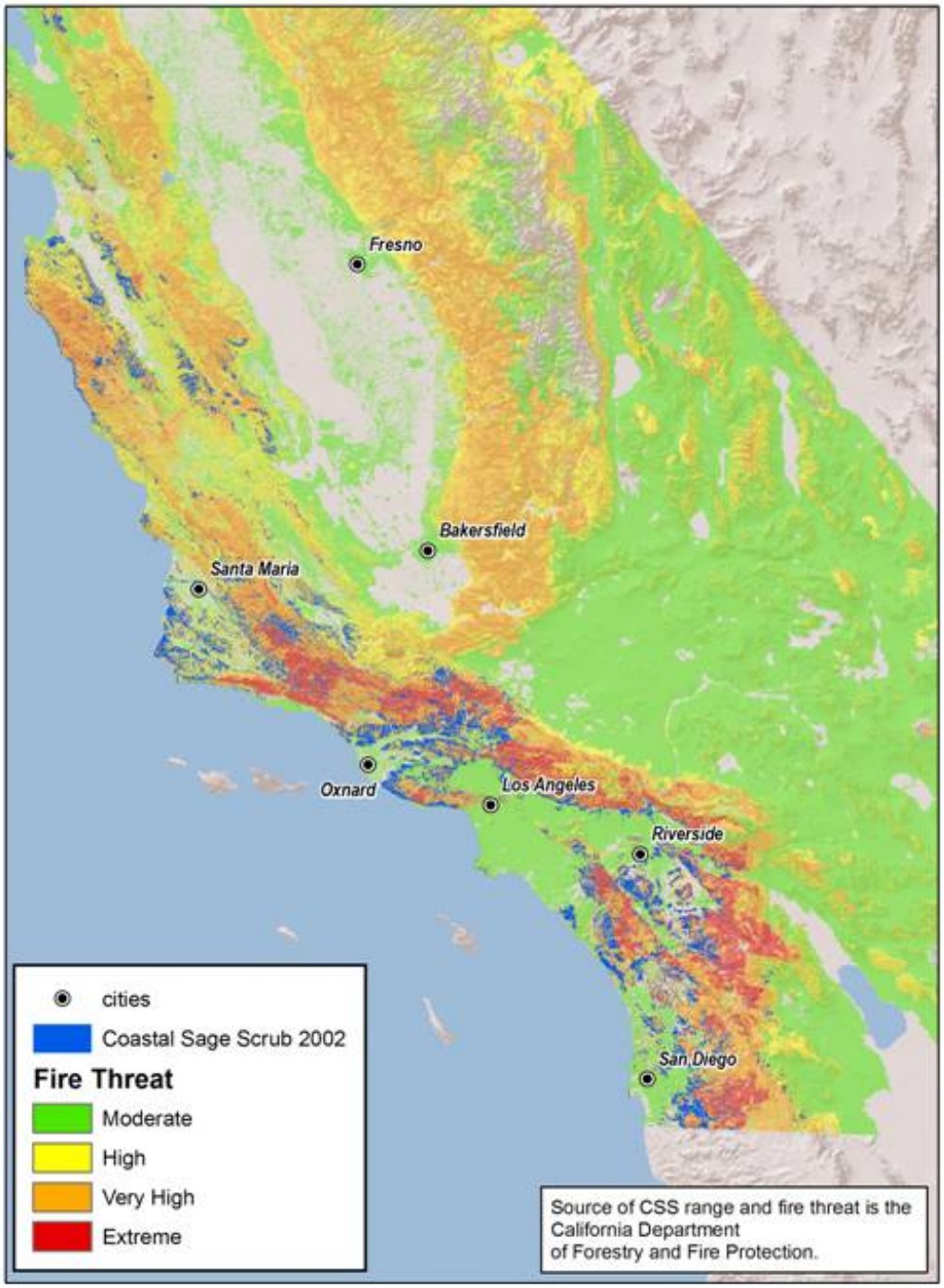


Figure 5.3-5. Current fire threats to coastal sage scrub communities.

5.3.4.2 Mixed Conifer Forest Ecosystems

The MCF ecosystem has been a subject of study for many years. There are a number of important stressors on the community, including fire, bark beetles, ozone, particulates, and atmospheric nitrogen. Although fire suppression in the 20th century is probably the most

significant change that has led to alterations in morphology and perhaps to shifts in forest composition (Minnich et al., 1995), stress from elevated levels of ambient atmospheric nitrogen concentrations is the subject of increasing research.

Measurements documenting increases in atmospheric nitrogen deposition have been recorded with some regularity since the 1980s (Bytnerowicz and Fenn, 1996); however, the Los Angeles area has seen elevated ambient atmospheric nitrogen concentrations for the last 50 years (Bytnerowicz and Fenn, 1996). Also, some data have been published for the primary nitrogen species of dry atmospheric nitrogen deposition in the San Bernardino Mountains (i.e., nitric acid [HNO_3] and ammonia gas [NH_3]) from passive samplers (Bytnerowicz et al., 2007). The pressures exerted on MCF ecosystems in California form a gradient across the Sierra Nevada Range and San Bernardino Mountains. Nitrogen throughfall levels in the northern Sierra Nevada Range are as low as 1.4 kg N/ha/yr, whereas forests in the western San Bernardino Mountains experience measured throughfall nitrogen levels up to 33 to71 kg N/ha/yr. (Note that the high levels of nitrogen seen in some measured throughfall values are not reflected in the CMAQ/NADP data, which is developed from 12 square km grids. Throughfall values reflect atmospheric deposition as well as canopy exchange.) The primary source of nitrogen in the western San Bernardino Mountains stems from fossil fuels combustion, such as vehicle exhaust. Other sources, such as agricultural processes, also play a prominent role in the western portions of the San Bernardino and Sierra Nevada Range (Grulke et al., 2008). **Figure 5.3-6** illustrates the current total atmospheric nitrogen deposition on MCF in California.

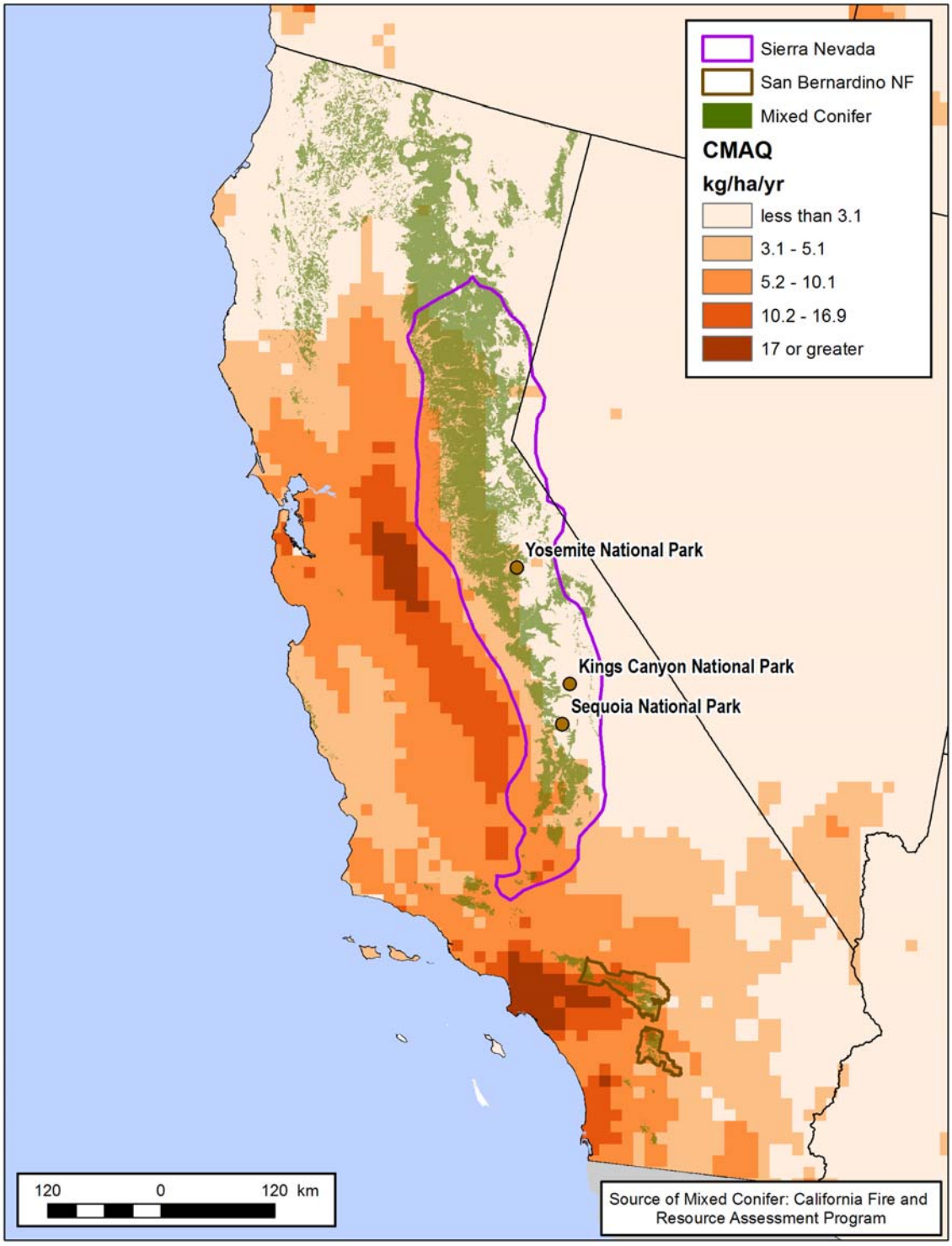


Figure 5.3-6. Mixed conifer forest range and total nitrogen deposition using CMAQ 2002 modeling results and NADP monitoring data.

At the individual tree level, elevated atmospheric nitrogen can shift the ratio of aboveground to belowground biomass. Elevated pollution levels allow increased uptake of

nutrients via the canopy, reduced nitrogen intake requirements on root structures, and increased demand for carbon dioxide (CO_2) uptake and photosynthetic structures to maintain the carbon balances. Therefore, the increased nutrient availability stimulates aboveground growth and increases foliar production while decreasing the demand for belowground nutrient uptake (Fenn et al., 2000) resulting in diminished fine-root biomass (Fenn and Bytnerowicz, 1997). Grulke et al. (1998) observed a 6- to 14-fold increase in fine-root mass in areas of low atmospheric nitrogen deposition as compared to areas of high deposition.

At the stand level, elevated atmospheric nitrogen has been associated with increased stand density, although other factors, such as fire suppression, also contribute to increased density and can increase mortality rates (U.S. EPA, 2008). As older trees die, they are replaced with younger, smaller trees. Smaller trees allow more sunlight through the canopy and, combined with an increased availability of nitrogen, may allow for more trees to be established. Increased stand densities with younger-age classes are observed in the San Bernardino Mountains, where air pollution levels are among the highest found in the California conifer ranges studied (Minnich et al., 1995; Fenn et al., 2008). These shifts in stand density and age distribution result in vegetation structure shifts which, in turn, may impact population and community dynamics of understory plants and animals, including threatened and endangered species.

It should be noted that the effects of ozone and atmospheric nitrogen are difficult to separate. The atmospheric transformation of nitrogen oxides can yield moderate concentrations of ozone as a byproduct (Grulke et al., 2008). Therefore, since elevated nitrogen levels are generally correlated with ozone concentrations, researchers often report changes in tree growth and vigor as being the result of both (Grulke and Balduman, 1999).

High concentrations of ozone and atmospheric nitrogen can generate increased needle and branch turnover. In areas subjected to low pollution, conifers may retain needles across 4 or 5 years; however, in areas of high pollution, such as Camp Paivika in the San Bernardino Mountains, needle retention was generally less than 1 year (Grulke and Balduman, 1999; Grulke et al, 2008). Needle turnover significantly increases litterfall. Litter biomass has been observed to increase in areas with elevated atmospheric nitrogen deposition up to 15 times more than in areas with low deposition, and the litter is seen to have higher concentrations of nitrogen (Fenn et al., 2000; Grulke et al., 2008). Elevated litter nitrogen levels may facilitate faster rates of microbial decomposition initially, but over the long term, high nitrogen levels slow litter decomposition

and litter accumulates on the forest floor (Grulke et al., 2008; U.S. EPA, 2008). The increased litter depth may then affect subcanopy growth and stand regeneration over long periods of time.

At the highest levels of atmospheric nitrogen deposition, native understory species were seen to decline (Allen et al., 2007). In addition to the decline in native understory diversity, changes in decreased fine-root mass, increased needle turnover, and the associated chemostructural alterations, MCF exposed to elevated pollutant levels have an increasing susceptibility to drought and beetle attack (Grulke et al., 1998, 2001; Takemoto et al., 2001). These stressors often result in the death of trees, producing an increased risk of wildfires.

Lichens emerged as an indicator of nutrient enrichment from the research on the effects of acid rain. Lichen species are sensitive to air pollution; in particular, atmospheric nitrogen. Since the 1980s, information about lichen communities has been gathered, and lichens have been used as indicators to detect changes in forest communities.

As atmospheric nitrogen deposition increases, the relative abundance of acidophytic lichens decreases, and the concentration of nitrogen in one of those species, *Letharia vulpine*, increases (Fenn et al., 2008). Fenn et al. (2008) were able to quantify the change in the lichen community, noting that for every 1 kg N/ha/yr increase, the abundance of acidophytic lichens declined by 5.6%. **Figure 5.3-7** illustrates the presence of acidophyte lichens and the total atmospheric nitrogen deposition in the California ranges.

In addition to abundance changes, species richness, cover, and health are affected in areas of high ozone and nitrogen concentrations. Fifty percent fewer lichen species were observed after 60 years of elevated air pollution in San Bernardino Mountains MCF, with the areas of highest pollution levels exhibiting low species richness, decreased abundance and cover, and morphological deterioration of existing lichens (Sigal and Nash, 1983).

Fenn et al. (2008) found that at 3.1 kg N/ha/yr, the community of lichens begins to change from acidophytic to tolerant species; at 5.2 kg N/ha/yr, the typical dominance by acidophytic species no longer occurs; and at 10.2 kg N/ha/yr, acidophytic lichens are totally lost from the community. Additional studies in the Colorado Front Range of the Rocky Mountain National Park support these findings and are summarized in Chapter 5.3.6.2 of this Risk and Exposure Assessment. These three values (3.1, 5.2, and 10.2 kilograms per hectare per year [kg/ha/yr]) are one set of ecologically meaningful benchmarks for the MCF. **Figure 5.3-7** shows the presence of acidophytic lichen species above the three ecological benchmarks. Nearly all of

the MCF communities receive total nitrogen deposition levels above the 3.1 N kg/ha/yr ecological benchmark according to the 12- km 2002 CMAQ/NADP data, with the exception of the easternmost Sierra Nevada Range. MCF in the southern portion of the Sierra Nevada forests and nearly all MCF communities in the San Bernardino forests receive total nitrogen deposition levels above the 5.2 N kg/ha/yr ecological benchmark. **Figure 5.3-7** also displays the potential areas where acidophytic lichens are extirpated because of nitrogen deposition levels above 10.2 kg N kg/ha/yr.

The established signs of nitrogen saturation have been shown within the MCF ecosystem. These symptoms include the following:

- Increased carbon and nitrogen cycling
- Decreased nitrogen uptake efficiency of plants
- Increased loss of forest nitrates to streamwater (NO_3^- leachate).

Fenn et al. (2008) established a critical loading benchmark of 17 kg throughfall N/ha/yr (which is the actual nitrogen deposited on the forest floor as opposed to modeled nitrogen deposition) in the San Bernardino and Sierra Nevada Range MCF ecosystems. This benchmark represents the level of atmospheric nitrogen deposition at which elevated concentrations of streamwater NO_3^- leachate or potential nitrogen saturation may occur. At this deposition level, a 26% decrease in fine-root biomass is anticipated (Fenn et al., 2008). Root:shoot ratios are, therefore, altered, and changes in nitrogen uptake efficiencies, litterfall biomass, and microbial decomposition are anticipated to be present at this atmospheric nitrogen deposition level. This benchmark is based on 30 to 60 years of exposure to elevated atmospheric concentrations. At longer exposure levels, the benchmark is lower because of decreased nitrogen efficiencies of the ecosystem. This benchmark is exceeded in areas of the western San Bernardino Mountains, such as Camp Paivika.

Nitrate leaching is a symptom that an ecosystem is saturated by nitrogen. Nitrate leaching is also known to cause acidification in adjacent surface waters. The ecological benchmark of 17 kg N/ha/yr is the last benchmark identified in this study. At this level of atmospheric nitrogen deposition, nitrate is observed in streams in the MCF (Fenn et al., 2008), denoting a change in ecosystem function.

Table 5.3-2 shows the area of MCF experiencing levels of nitrogen deposition corresponding to the identified benchmarks.

Table 5.3-2. Mixed Conifer Forest Ecosystem Area and Nitrogen Deposition

N Deposition (kg/ha/yr)	Area (hectares)	Percent of MCF Area, %
≥3.1	1099133.482	38.62
≥5.2	130538.2573	4.59
≥10.2	11963.08815	0.42
≥17	0	0.00

Note: According to the 12-km CMAQ data, there is too little area receiving >17 kg N/ha/yr to be measurable.

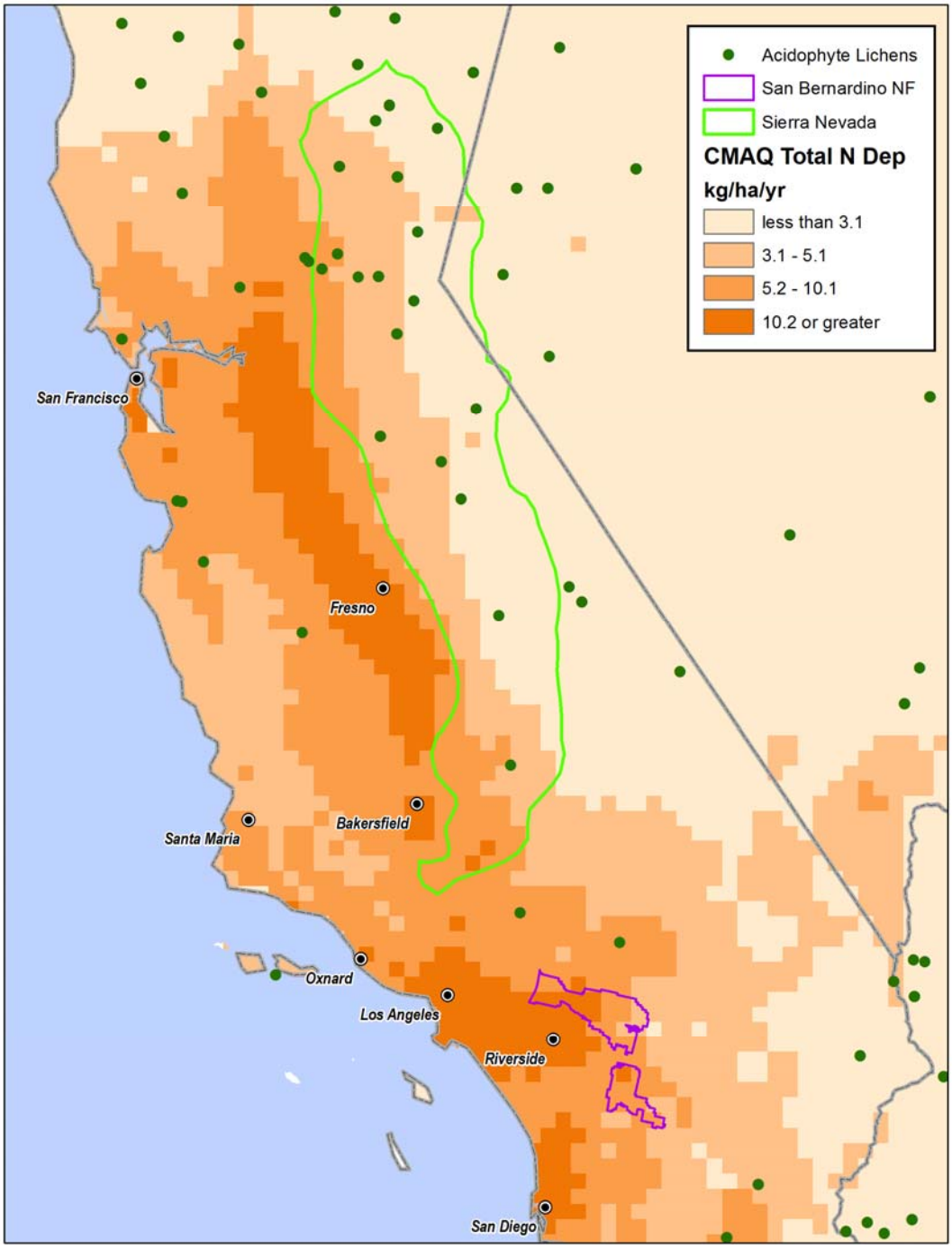


Figure 5.3-7. Presence of acidophyte lichens and total nitrogen deposition in the California mountain ranges using CMAQ 2002 modeling results and NADP monitoring data.

5.3.5 Degree of Extrapolation to Larger Assessment Areas

The Terrestrial Nutrient Enrichment Case Study examined the effects of atmospheric nitrogen on two ecosystem types in California, CSS and MCF. **Figure 5.3-8** presents CMAQ 2002–modeled and NADP-monitored deposition of total nitrogen in the western United States. In the western United States, other arid and forested ecosystems exposed to deposition at levels discussed in this case study may experience altered effects. As noted in the previous section, research on grasslands and chaparral ecosystems is underway. Nitrate leaching in forests with elevated deposition may result in nitrate leaching that subsequently enriches and affects aquatic ecosystems. Research on lichen species in the Pacific Northwest and in Central California that are also exposed to elevated levels of atmospheric nitrogen deposition is also being conducted. Extensive research on the eastern Front Range of the Rocky Mountain National Park has been conducted in alpine and subalpine terrestrial and aquatic systems at elevations about 3,300 meters (m), where communities are typically adapted to low nutrient availability but are now being exposed to >10 kg N/ha/yr in some study areas.

Locations were identified where data were available that might have implications for other ecosystems and ecosystem services, as well as where a compelling case may be found to show that the effects were due to atmospheric deposition of nitrogen. Other systems that are also sensitive might include the following:

- **Ecosystems with nitrogen-sensitive epiphytes, such as lichens or mycorrhizae.** Such systems may demonstrate shifts in community structure through changes in nutrient availability or modified provisioning services.
- **Ecosystems that may have been exposed to long periods of elevated atmospheric nitrogen deposition.** The established signs of nitrogen saturation are increased leaching of NO_3^- into streamwater, decreased nitrogen uptake efficiency of plants, and increased carbon and nitrogen cycling. At prolonged elevated nitrogen levels, ecosystems are generally less likely to use, retain, or recycle nitrogen species efficiently at both the species and community levels.
- **Critical habitats.** Ecosystems that are necessary for endemic species or special ecosystem services should be monitored for possible changes due to nitrogen.
- **Locations where there are seasonal releases of nitrogen.** In both the California CSS and MCF ecosystems discussed in the case study, a large portion of nitrogen is dry-

deposited and remains on the foliage and soil surface until the beginning of the winter rainy season when nitrogen will be flushed into the soil.

In addition to the documented signs of nitrogen saturation, it is interesting to note that both CSS and the MCF ecosystems had responses in epiphytic associations, as well as increased susceptibility to wildfire and invasion of exotic species. Water use was also modified in these systems. The implication and inferential magnitude of these results may warrant future investigations.

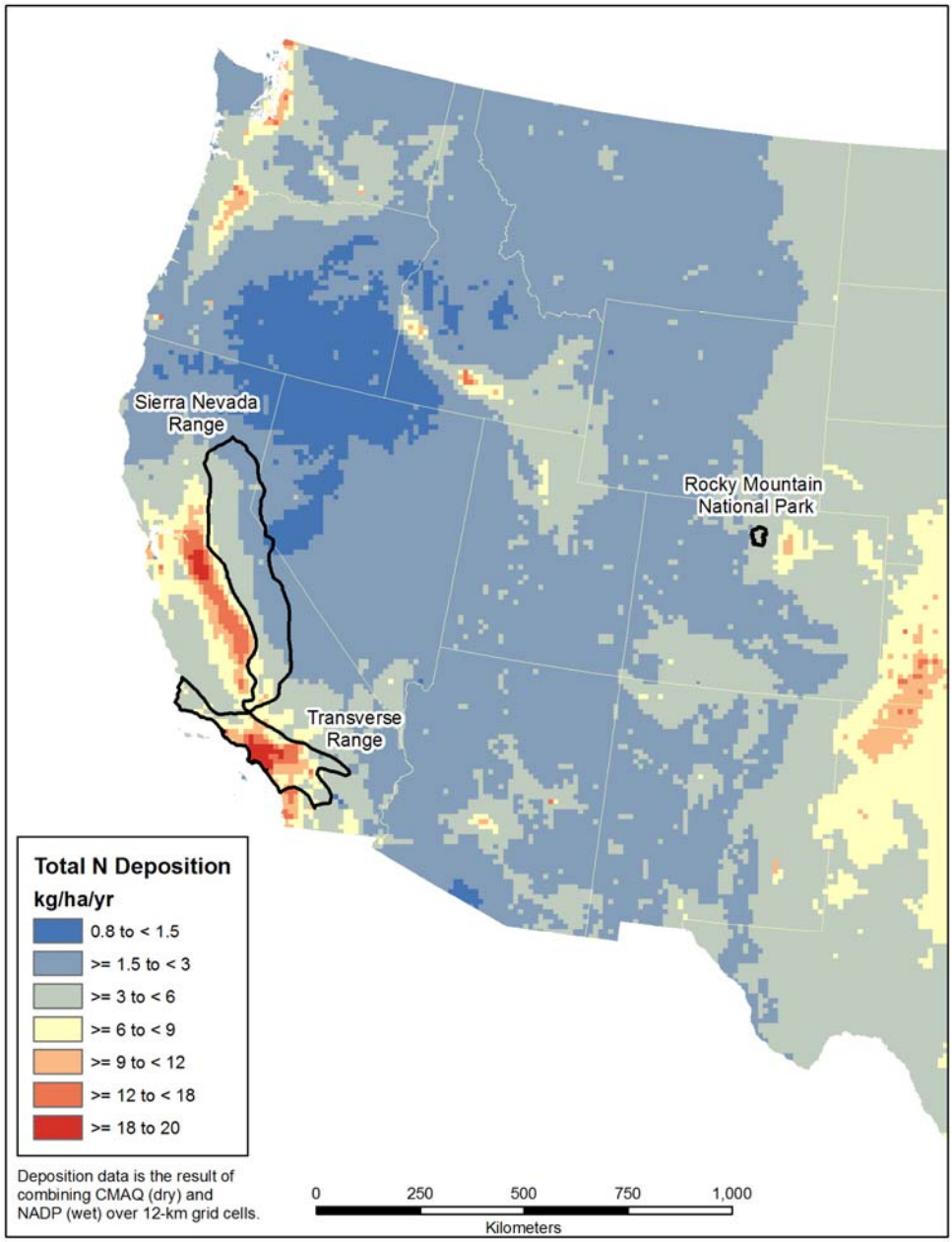


Figure 5.3-8. CMAQ 2002 modeling results and NADP monitoring data for deposition of total nitrogen in the western United States.

5.3.6 Current Conditions for Select Locations Nationwide

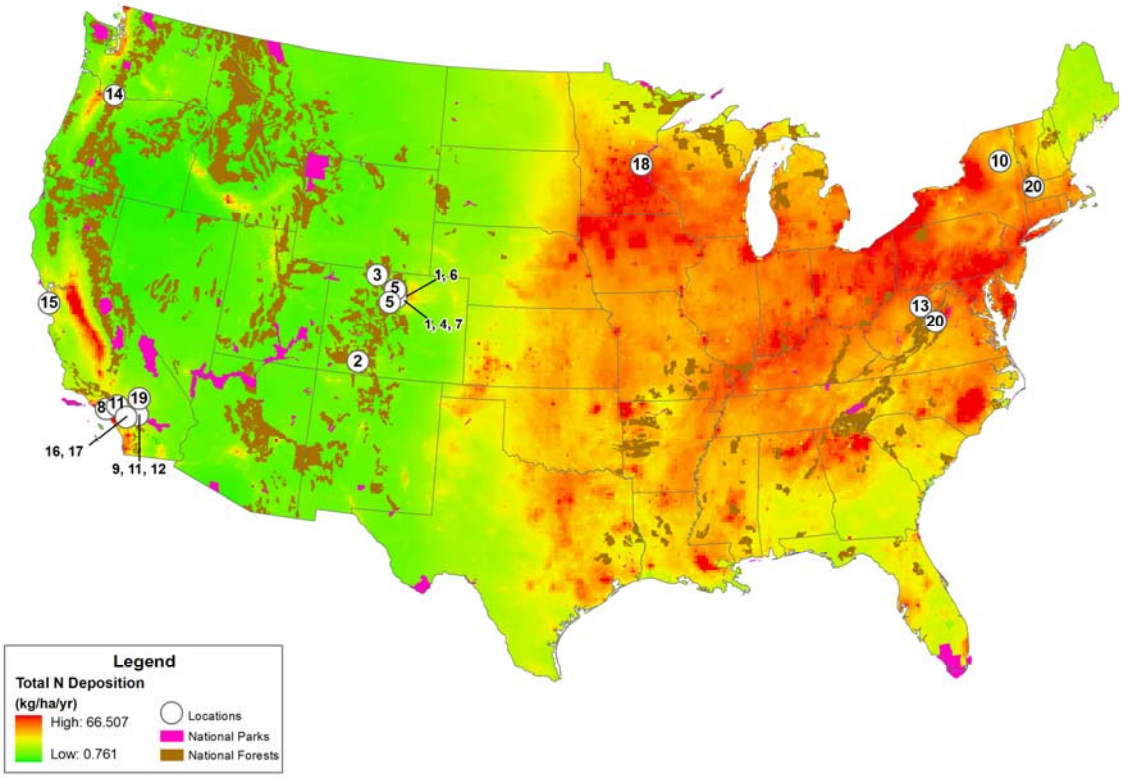
5.3.6.1 Overview

Figure 5.3-9 displays a map of observed effects from ambient and experimental atmospheric nitrogen deposition loads in relation to CMAQ 2002 modeling results and NADP monitoring data. The map depicts the sites where empirical effects of terrestrial nutrient

enrichment have been observed and site proximity to elevated levels of atmospheric nitrogen deposition. The ISA (U.S. EPA, 2008, Section 3.3) also identifies areas of the western United States where atmospheric nitrogen deposition effects have been reported.

A range of ecological benchmarks were developed in the results. All benchmarks are tied to a level of atmospheric nitrogen deposition but include a number of different ecological processes. All of the benchmarks are ecologically significant in that changes that are related to community structure and function are seen. The benchmarks span a range from 3.1 to 17 kg N/ha/yr (see **Figure 5.3-2**) and include the following:

- 3.1 kg N/ha/yr – shift from sensitive to tolerant lichen species in MCF
- 3.3 kg N/ha/yr – the amount of nitrogen uptake by a vigorous stand of CSS; above this level, nitrogen may no longer be limiting
- 5.2 kg N/ha/yr – dominance of tolerant lichen species in MCF
- 10 kg N/ha/yr – mycorrhizal community changes in CSS
- 10.2 kg N/ha/yr – loss of sensitive lichen species in MCF
- 17 kg N/ha/yr – nitrate leaching into streams in MCF.



1. Nitrogen enrichment or eutrophication of lakes (Loch Vale, CO: 0.5 to1.5 kg/ha/yr; Niwot Ridge, CO: 4.71 kg/ha/yr)
2. Alpine lakes increase shift in diatom species (Rocky Mountains, CO: 2 kg/ha/yr)
3. Alpine meadows' elevated NO_3^- levels in runoff (Colorado Front Range: 20, 40, 60 kg/ha/yr)
4. Alpine meadows' shift toward hairgrass (Niwot Ridge, CO: 25 kg/ha/yr)
5. Nitrogen enrichment or nitrogen saturation (e.g., soil and foliar nitrogen concentration) (eastern slope of Rocky Mountains: 1.2, 3.6 kg/ha/yr; Fraser Forest, CO: 3.2 to 5.5 kg/ha/yr)
6. Increased nitrogen mineralization rates and nitrification (Loch Vale, CO (spruce): 1.7 kg/ha/yr)
7. Alpine tundra with increased plant foliage and decreased species richness (Niwot Ridge, CO: 50 kg/ha/yr)
8. Nitrogen saturation, high NO_3^- in streamwater, soil, leaves; high nitric oxide (NO) emissions (Los Angeles, CA, air basin: saturation at 24 to 25 kg/ha/yr (dry) and at 0.8 to 45 kg/ha/yr (wet); northeastern U.S.: 3.3 to 12.7 kg/ha/yr)
9. Nitrogen saturation, high NO_3^- in streamwater (San Bernardino Mountains, CA (coniferous): 2.9 and 18.8 kg/ha/yr)
10. NO_3^- leaching (New England; Adirondack lakes: 8 to10 kg/ha/yr)
11. Nitrogen saturation, high dissolved inorganic nitrogen (San Bernardino Mountains, San Gabriel Mountains, CA, chaparral, hardwood, coniferous): 11 to 40 kg/ha/yr)
12. Increased tree mortality and beetle activity (San Bernardino Mountains, CA (Ponderosa): 8 and 82 kg/ha/yr)
13. Enhanced growth of black cherry and yellow poplar; possible decline in red maple vigor; increased foliar nitrogen (Fernow Forest, WV: 35.5 kg/ha/yr)
14. Impacts on lichen communities (California MCF: 3.1 kg/ha/yr; Columbia R. Gorge, OR/WA: 11/5 to 25.4)
15. Evidence that threatened and endangered species impacted San Francisco Bay, CA (checkerspot butterfly and serpentinitic grass invasion: 10 to15 kg/ha/yr; Jasper Ridge, CA: 70 kg/ha/yr)
16. Decreased diversity of mycorrhizal communities (Southern California: ~10 kg/ha/yr)
17. Decreased abundance of CSS (Southern California: 3.3 kg/ha/yr)
18. Loss of grasslands (Cedar Creek, MN: 5.3 [1.3 to 9.8] kg/ha/yr)
19. Decrease in abundance of desert creosote bush, increase in nonnative grasses (Mojave Desert and Chihuahuan Desert, CA: 1.7 kg/ha/yr and up)
20. Decrease in pitcher plant population growth rate (Hawley Bog, MA and Molly Bog, VA: 10 to14 kg/ha/yr)

Figure 5.3-9. Observed effects from ambient and experimental atmospheric nitrogen deposition loads in relation to using CMAQ 2002 modeling results and NADP monitoring data. Citations for effect results are from the ISA, Table 4.4 (U.S. EPA, 2008).

This range of ecological benchmarks may be used to develop a "green line/red line" schematic, similar to the forest screening model discussed in Lovett and Tear (2007) that illustrates the levels at which ecosystem effects may occur or are known to occur. In **Figure 5.3-10,** the green area/line denotes that point at which there do not appear to be any effects, and the red line denotes the point at which known negative effects occur.

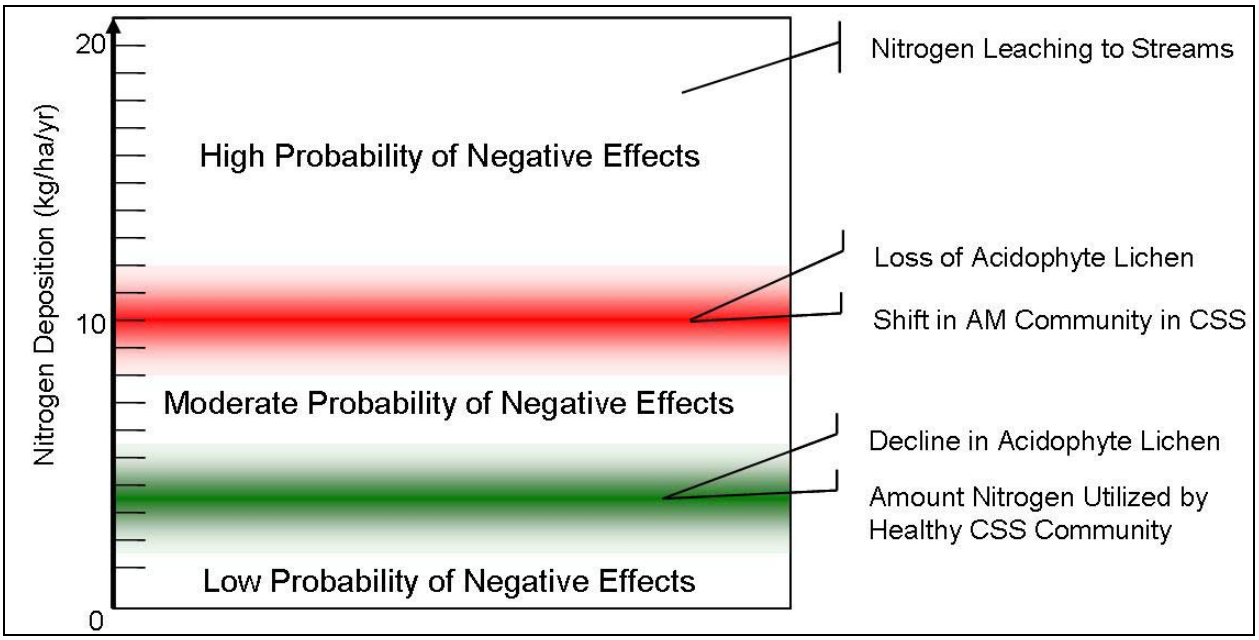


Figure 5.3-10. Illustration of the range of terrestrial ecosystem effects observed relative to atmospheric nitrogen deposition.

For the benchmarks identified, effects may occur at the level of atmospheric nitrogen deposition associated with the "green line" illustrated in **Figure 5.3-10**, so the "green line" may be somewhat lower. The higher levels of atmospheric nitrogen deposition (both at 10.2 and 17 kg/ha/yr) better resemble a "red line," where a known negative effect occurs.

The range of ecological benchmarks in CSS and MCF are not dissimilar from those identified in other ecosystems with related characteristics, such as arid systems, other forested systems, or grasslands (see **Figure 5.3-11**). Egerton-Warburton et al. (2001) report that at 10 kg N/ha/yr, nitrogen changes in mycorrhizal communities/grass biomass are observed in chaparral ecosystems. Nitrates are found to leach into streams of the northeastern United States at deposition levels between 9 and 13 kg N/ha/yr (Aber et al., 2003). Results from several studies suggest ecosystem changes that are related to atmospheric nitrogen deposition. The capacity of alpine catchments to sequester nitrogen is exceeded at input levels <10 kg N/ha/yr (Baron et al.,

1994). Changes in the *Carex* plant community were observed to occur at deposition levels near 10 kg N/ha/yr (Bowman et al., 2006). Clark and Tilman (2008) predict that at 5.3 kg N/ha/yr, there is a loss of species diversity in grasslands. In the Pacific Northwest and in Central California, a number of investigators have observed declines in sensitive lichen species as air pollution increases (Jovan and McCune, 2005; Geiser and Neitlich, 2007). In Europe, acidophyte decline has been identified in regions with 8 to 10 kg N/ha/yr (Bobbink, 1998; Bobbink et al., 1998).

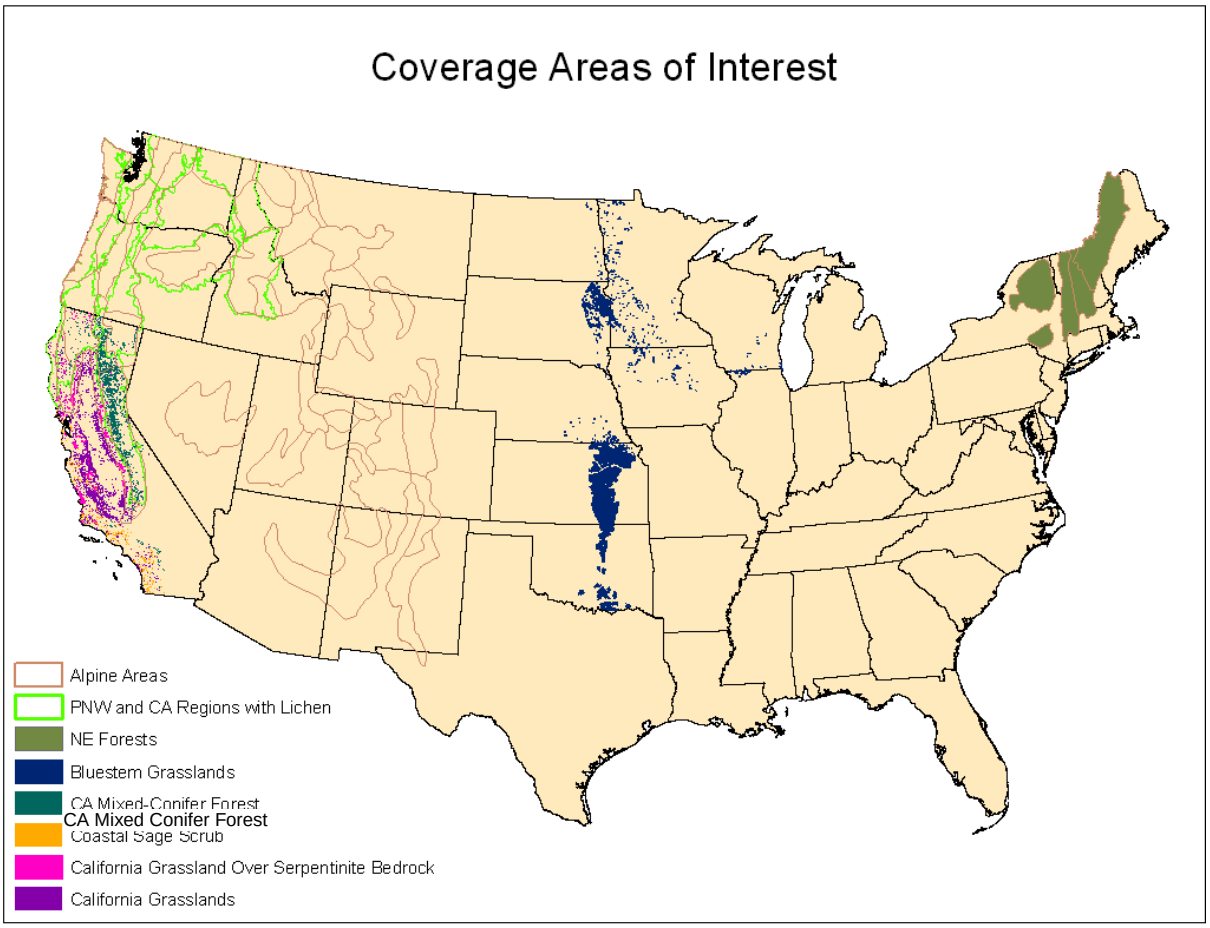


Figure 5.3-11. Habitats that may experience ecological benchmarks similar to coastal sage scrub and mixed conifer forest.

5.3.6.2 Atmospheric Nitrogen Deposition Influence on Eastern Slope of Rocky Mountains

Rocky Mountain National Park encompasses approximately 265,770 acres (1,076 km^2) of land in Colorado's northern Front Range. The park is split by the Continental Divide, which gives the eastern and western portions of the park a different character. The east side of the park

tends to be drier, with heavily glaciated peaks and cirques. The west side of the park is wetter and lusher, dominated by deep forests. The park contains 150 lakes and 450 miles (720 km) of streams. The park contains more than 60 named peaks higher than 12,000 feet (3,700 m), and over one-fourth of the park resides above tree line. The lowest elevations in the park are montane forests and grassland. The ponderosa pine, which prefers drier areas, dominates, though at higher elevations Douglas fir trees are found. Above 9,000 feet (2,700 m) the montane forests give way to the subalpine forest. Engelmann spruce and subalpine fir trees are common in this zone. These forests tend to have more moisture than the montane and tend to be denser. Above tree line, at approximately 11,500 feet (3,500 m), trees disappear, and it becomes alpine tundra.

Since Rocky Mountain National Park spans the Continental Divide, there are higher levels of atmospheric nitrogen deposition to the east (the Front Range) than for the western parts of the park due to transport of emissions from densely populated areas (e.g., the Denver metropolitan area). Most of the detailed scientific studies documenting acid rain effects have involved alpine or subalpine settings, usually at elevations of 3,100 m or more above mean sea level. Rocky Mountain National Park is surrounded by other federal public lands. The Niwot Ridge Long-Term Ecological Research (LTER) site is located in the Roosevelt National Forest to the immediate southwest of Rocky Mountain National Park, and Niwot Ridge research findings have applicability to patterns relevant to the Front Range (west of the Continental Divide) portions of Rocky Mountain National Park. **(Figure 5.3-12)**

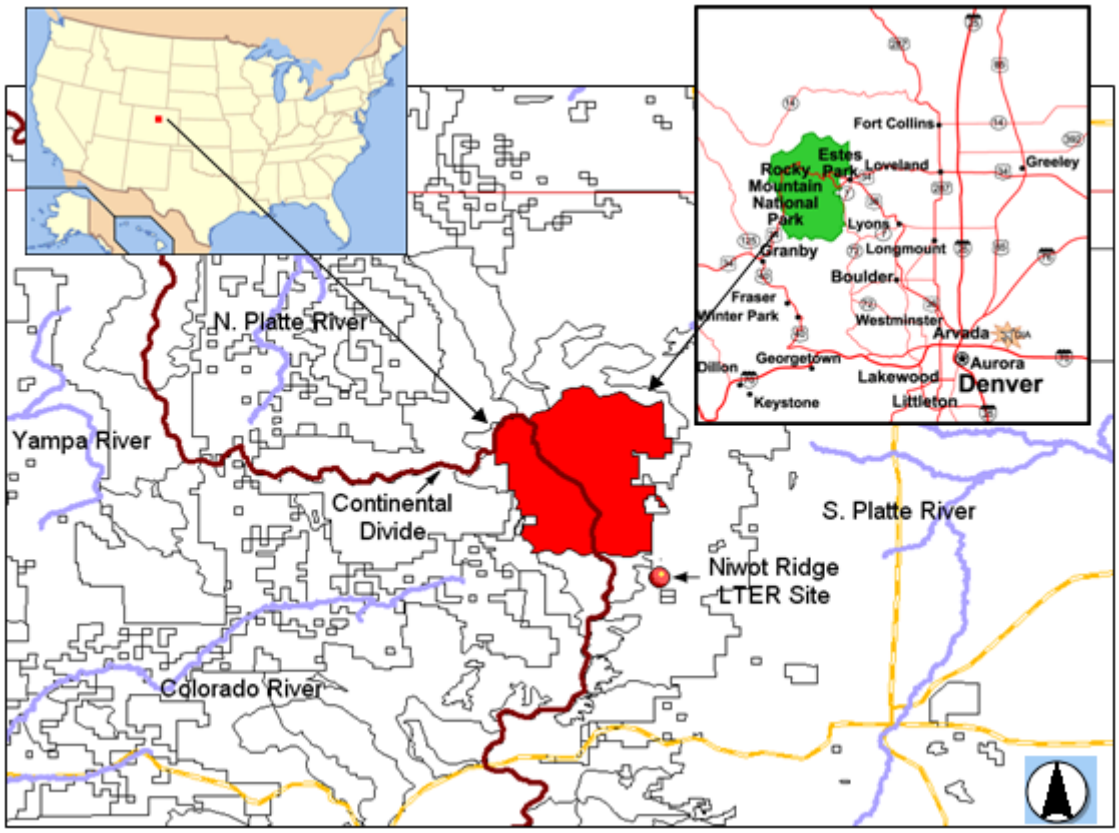


Figure 5.3-12. Rocky Mountain National Park location relative to the Niwot Ridge Long-Term Ecological Research site and Denver metropolitan area.

Aquatic Systems: Lakes and Streams

Some alpine lakes in the west (including the Rocky Mountains) show a seasonal pattern of episodic acidification for lakes (and also for streams) from melting of snowpack in the early spring, related to poor acid neutralizing capacity of the sparse soils and receiving waters and flushing of dissolved organic carbon (Denning et al., 1991;Williams and Tonnessen, 2000). The hydrologic cycle in higher elevation areas is dominated by the annual accumulation and melting of a dilute, mildly acidic snowpack. While these areas are not as sensitive as other parts of the West, the ISA (U.S. EPA, 2008) presents information showing that lakes in the Rocky Mountain area have been documented as acid-sensitive waters in the EPA Western Lakes Survey (Landers et al., 1987; Stoddard et al., 2003). Chronic acidification effects (e.g., as in the Adirondacks, are not prevalent for western lakes, but episodic acidification has been reported for lakes in the Colorado Front Range [Brooks et al., 1996; Williams et al., 1996]).

The ISA (U.S. EPA, 2008) presents scientific studies that show that increased atmospheric nitrogen deposition in lakes and streams can cause a shift in community

composition and decrease algal biodiversity. Elevated nitrogen deposition results in changes in algal species composition, especially in sensitive oligotrophic lakes. Field experiments show responses to nitrogen for two opportunistic diatom species, *Asterionella formosa* and *Fragilaria crotonensis* (McKnight et al., 1990; Lafrancois et al., 2004; Saros, 2005). These species now dominate the flora of at least several alpine and montane Rocky Mountain lakes, with similar filed data showing shifts in dominant algal species in other parts of the West. These shifts in the dominant algal species show up in Front Range lakes starting in the 1950s (Baron, 2006; Das et al., 2005; Enders et al., 2008; Wolfe et al., 2001, 2003). Ambient nitrogen levels associated with maximum species diversity for alpine lakes are estimated to be at or <3 micromoles (µmol) based on studies in the Yellowstone National Park (Interlandi and Kilham, 1998). A hindcasting exercise has concluded that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet nitrogen deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros et al., 2003).

Terrestrial Systems

Because alpine plant species are typically adapted to low nutrient availability, they often are sensitive to effects from nutrient enrichment. The ISA (U.S. EPA, 2008) presents results from several studies suggesting that the capacity of Rocky Mountain alpine catchments to sequester nitrogen is exceeded at input levels of about 4 kg N/ha/yr (Baron et al., 1994; Williams and Tonnessen, 2000). For the Front Range, atmospheric deposition levels are typically 3 to 5 kg N/ha/yr, with nitrogen deposition levels of 1 to 2 kg N/ha/yr typical in the areas to the west of the Continental Divide (Baron et al., 2000).

Research on nutrient enrichment effects on alpine and subalpine ecosystems in the western U.S. has been limited mainly to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge LTER site, both located east of the Continental Divide in Colorado (Burns, 2004). Research has been conducted in this area on both the terrestrial and aquatic effects of nutrient enrichment. At these locations, experiments have involved controlled fertilization to document the effects on species composition simulating the effects of nitrogen atmospheric deposition. Increased cover and total biomass of both grasses and sedges (*Carex* spp.) was a common response pattern.

High elevation alpine terrestrial communities exhibit a relatively low capacity to sequester atmospheric deposition of nitrogen because of steep slopes, shallow soils, sparse vegetation, short growing season, and other factors (Baron et al., 1994; Williams et al., 1996). Results from several studies suggest that the capacity of individual indicator species in Rocky Mountain alpine catchments to sequester nitrogen is exceeded at deposition levels of 3-4 kg N/ha/yr (Baron et al., 1994; Williams and Tonnessen, 2000). Effects of N_r deposition to alpine terrestrial ecosystems in this area could include community-level changes in plants, lichens, and mycorrhizae. A variety of species could serve as useful indicators. The changes in plant species that occur in response to atmospheric nitrogen deposition in the alpine zone can result in further increased leaching of NO_3^- from the soils, because the plant species favored by higher nitrogen supply are often associated with greater rates of nitrogen mineralization and nitrification than the preexisting species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al., 2006).

The ISA (U.S. EPA, 2008) presents results from several studies that suggest the capacity of Rocky Mountain alpine catchments to sequester nitrogen is exceeded at input levels <3-4 kg N/ha/yr (Baron et al., 1994; Williams et al., 1996). Changes in an individual species (*Carex rupestris* and *Trisetum spicatum*) were estimated to occur at deposition levels near 4 kg N/ha/yr (Bowman et al., 2006). Changes in the community, based on the first axis of a detrended correspondence analysis, were estimated to occur at deposition levels near 10 kg N/ha/yr. (Bowman et al., 2006). In comparison, critical loads for alpine plant communities in Europe are 5 to 15 kg N/ha/yr (Bobbink, 1998). It is also worth noting that some state agencies have pursued the use of critical loads independently to link science and policy in addressing the management of natural resources. For instance, in the State of Colorado, critical loads for atmospheric nitrogen deposition that were developed for Rocky Mountain National Park (Baron, 2006) are being used to develop goals for nitrogen emissions decreases by the State of Colorado, U.S. EPA, and NPS. (See "Nitrogen Deposition Reduction Plan" at http://www.cdphe.state.co.us/ap/rmnp.html)

Effects of N_r deposition to alpine terrestrial ecosystems in this area could include community-level changes in plants, lichens, and mycorrhizae. A variety of species could serve as useful indicators. The ISA (U.S. EPA, 2008) notes that there are difficulties, however, in correlating community or indicator species responses exclusively with atmospheric nitrogen

deposition. In many instances, the confounding influences of climatic change, particularly changes in precipitation, cannot be ruled out (Williams et al., 1996; Sherrod and Seastedt, 2001; Fenn et al., 2003).

5.3.7 Ecological Effect Function for Terrestrial Nutrient Enrichment

There are many factors that determine whether or not an ecological effect occurs in response to ambient concentrations of NO_x and SO_x. These may be ecological or atmospheric factors, both of which influence deposition or exposure and the subsequent ecological effects (i.e., acidification or nutrient enrichment). In the Terrestrial Nutrient Enrichment Case Study, establishing a quantitative linkage between a given ecological indicator and deposition, as influenced by the variable ecological factors, was not addressed because deposition was used, rather than a traditional environmental indicator, as the direct metric for this GIS analysis of ecological response.

5.3.8 Uncertainty and Variability

The analyses for the terrestrial nutrient enrichment case study were based on measured data and model predictions that each contain a number of areas of uncertainty. For example, characterizing NO_x and SO_x deposition includes uncertainties in monitoring instrumentation and measurement protocols, as well as limitations in the spatial extent of existing monitoring networks, especially in remote areas. Also, there are no "true" measurements of dry deposition. Geographic limitations in monitoring led to reliance on CMAQ model predictions. CMAQ has its own uncertainties in model formulation and in the inputs which drive the model's simulation chemistry and transport processes.

There are also uncertainties associated with the spatial resolutions of the measured and modeled data used in this case study, as well as spatial and temporal variability associated with measurement and modeling. Uncertainties are associated with gridding the NADP measurements to 12 km resolution and the representativeness of 12 km data for characterizing deposition in this case study area, particularly for the small sites of CSS as noted below. Specific areas of uncertainty associated with this case study of CSS include the following:

- CSS declines have been observed in the absence of fire when elevated nitrogen levels are present; declines have also been observed in the absence of elevated nitrogen, but due to fire. Therefore, there is still a need for quantifiable and predictive results to indicate the

- Many studies allude to a degradation of CSS by assessing species richness and abundance, but it is not clear that indicators of CSS ecosystem health have been adequately explored.
- Ongoing CSS experiments are beginning to show changes in CSS in response to elevated nitrogen over relatively long periods of time (Allen, personal communication, 2008). The incremental process may be occurring more slowly than previous field research experiments have lasted, making the reasons for the decline appear variable or imperceptible over the duration of a typical study.
- At this point, CSS is fragmented into many relatively small parcels. The CMAQ 2002 data is being modeled at 4-km resolution. When these 4-km data become available, there may be a better sense of the relationship between the current distribution of CSS and atmospheric nitrogen loads and fire threat.
- Very little research exists regarding the effects of ozone on CSS. Although there is some support that ozone is negatively correlated with CSS, the role has yet to be quantified or consistently studied (Westman, 1981).
- There is uncertainty in the relationship between current CSS distribution and the changing climate.

Areas of uncertainty for MCF include the following:

- The long-term consequences of increased nitrogen on conifers are unclear.
- The effects of ozone for both MCF and lichens confound the effects of nitrogen.
- The intermingling of fire and nitrogen cycling require additional research.
- Research suggests that critical load benchmarks can decrease over time if the nitrogen benchmark is exceeded for long periods of time because of decreasing nitrogen efficiencies within nitrogen-saturated ecosystems (Fenn et al., 2008).
- There remains considerable uncertainty in the potential response of soil carbon to increases in total reactive nitrogen additions.

- Although there are uncertainties in the data, models and techniques used for this case study, the most applicable measurements and state-of-the-science models were used with consideration for data and models' relative strengths and limitations.

5.4 CONCLUSIONS

This chapter has examined the sensitivity and effects of nutrient enrichment on aquatic and terrestrial ecosystems, and, although a diverse array of U.S. ecosystems exist, exposure levels at which negative effects are observed appear to be generally comparable to levels identified in other sensitive U.S. ecosystems (benchmarks range from 1.5 to 30.5 kg N/ha/yr). Enrichment benchmarks are also comparable to those found in the Aquatic Acidification and Terrestrial Acidification case studies (see Chapter 4). Further consideration of these comparable benchmarks can inform the decision-making process for mitigating terrestrial and aquatic acidification and enrichment.

5.5 SUMMARY AND KEY FINDINGS

Atmospheric nitrogen deposition has been linked quantitatively to negative ecological effects from overenrichment of nutrient-sensitive terrestrial and aquatic ecosystems. Although some organisms may at first respond positively to nutrient loads, their ability to use additional nitrogen may be limited. Overenrichment may lead to excess nitrogen leaching to water, or it may lead to shifts in communities to other organisms that are able to utilize higher levels of nitrogen.

5.5.1 Aquatic Nutrient Enrichment

The role of nitrogen deposition in two mainstem rivers feeding their respective estuaries was analyzed to determine if decreases in deposition could influence the risk of eutrophication as predicted using the ASSETS EI scoring system in tandem with SPARROW modeling. This modeling approach provides a transferrable, intermediate-level analysis of the linkages between atmospheric deposition and receiving waters, while providing results on which conclusions could be drawn. Future application of the methods to case study areas where atmospheric deposition plays a larger role in the nitrogen loading to an estuary will likely provide more tangible results. A summary of findings follows:

- 2002 CMAQ/NADP results showed that an estimated 40,770,000 kg of total nitrogen was deposited in the Potomac River watershed. SPARROW modeling predicted that 7,380,000 kg N/yr of the deposited nitrogen reached the estuary (20% of the total load to

the estuary). The overall ASSETS EI for the Potomac River and Potomac Estuary was *Bad*.

- A decrease of 78% or more in the 2002 atmospheric deposition load of total nitrogen to the watershed might possibly improve the Potomac River and Potomac Estuary ASSETS EI score from *Bad* to *Poor*.
- 2002 CMAQ/NADP results showed that an estimated 18,340,000 kg of total nitrogen was deposited in the Neuse River watershed. SPARROW modeling predicted that 1,150,000 kg N/yr of the deposited nitrogen reached the estuary (26% of the total load to the estuary). The overall ASSETS EI for the Neuse River/Neuse River Estuary was *Bad*.
- It was found that the Neuse River/Neuse River Estuary ASSETS EI score could not be improved from *Bad* to *Poor* with decreases only in the 2002 atmospheric deposition load to the watershed. Additional reductions would be required from other nitrogen sources within the watershed.

The small effect achieved from reducing atmospheric deposition in the Neuse River watershed is because the total nitrogen loadings to the Neuse River Estuary are dependent on the other nitrogen sources in the watershed as estimated with the SPARROW model. A waterbody's response to nutrient loading depends on the magnitude (e.g., agricultural sources have a high influence in the Neuse), spatial distribution, and other characteristics of the sources within the watershed.

5.5.2 Terrestrial Nutrient Enrichment

California CSS and MCF were the focus of the Terrestrial Nutrient Enrichment Case Study. GIS analysis supported a qualitative review of past field research to identify ecological benchmarks associated with CSS and mycorrhizal communities, as well as MCF's nutrient-sensitive acidophyte lichen communities, fine-root biomass in Ponderosa pine, and leached nitrate in receiving waters. These benchmarks, ranging from 3.1 to 17 kg N/ha/yr, were compared to 2002 CMAQ/NADP data to discern any associations between atmospheric deposition and changing communities. Evidence supports the finding that nitrogen alters CSS and MCF. Key findings include the following:

- 2002 CMAQ/NADP nitrogen deposition data show that the 3.3 kg N/ha/yr benchmark has been exceeded in more than 93% of CSS areas (654,048 ha). These deposition levels

are a driving force in the degradation of CSS communities. Although CSS decline has been observed in the absence of fire, the contributions of deposition and fire to the CSS decline require further research. CSS is fragmented into many small parcels, and the 2002 CMAQ/NADP 12-km grid data are not fine enough to fully validate the relationship between CSS distribution, nitrogen deposition, and fire.

- 2002 CMAQ/NADP nitrogen deposition data exceeds the 3.1 kg N/ha/yr benchmark in more than 38% (1,099,133 ha) of MCF areas, and nitrate leaching has been observed in surface waters. Ozone effects confound nitrogen effects on MCF acidophyte lichen, and the interrelationship between fire and nitrogen cycling requires additional research.

Ecological effects have also been documented across the United States where elevated nitrogen deposition has been observed (See Appendix 7, Figure 1.1-1.). On the eastern slope of the Rocky Mountains, shifts in dominant algal species in alpine lakes have occurred where wet nitrogen deposition was only about 1.5 kg N/ha/yr. High alpine terrestrial communities have a low capacity to sequester nitrogen deposition, and monitored deposition exceeding 3 to 4 kg N/ha/yr could lead to community-level changes in plant species, lichens, and mycorrhizae.

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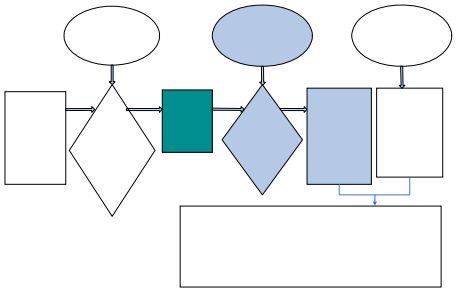

6.0 ADDITIONAL EFFECTS

The Clean Air Act (CAA) definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort and well-being. This Risk and Exposure Assessment focuses primarily on ecological effects resulting from current deposition of compounds containing nitrogen and sulfur as discussed in Chapter 1 and Chapter 2. Acidification (from both sulfur and nitrogen) and nutrient enrichment (from nitrogen) are the central ecological effects addressed in this Risk and Exposure Assessment (see Chapters 4 and 5). The additional welfare effects addressed in this chapter include the influence of sulfur oxides (SO_x) deposition effects on mercury methylation, nitrous oxide (N_2O) effects on climate, deposition effects of nitrogen oxides (NO_x) on biogenic greenhouse gas (GHG) fluxes, and phytotoxic effects on plants. While a quantitative assessment of these important effects is beyond the scope of this review, this chapter will evaluate them qualitatively.

6.1 VISIBILITY, CLIMATE, AND MATERIALS

It is well understood that impairment of visibility, effects on climate, and materials damage can result from atmospheric particulate matter (PM), which is composed in part of sulfate (SO_4^{2-})- and nitrate (NO_3^-)-based particulates (i.e., ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate [NH_4NO_3]). The relationship between PM and visibility impairment has been well established in previous National Ambient Air Quality Standards (NAAQS) reviews dating back as early as the 1982 *Air Quality Criteria for Particulate Matter and Sulfur Oxides* (PM/SO_x Air Quality Criteria Document [AQCD]) document (U.S. EPA, 1982b). Visibility impairment is caused by light scattering and absorption by suspended particles and gases. There is strong and consistent evidence that PM is the overwhelming source of visibility impairment in both urban

and remote areas. Furthermore, it has been acknowledged that decreases in visibility can adversely affect transportation safety, property values, aesthetics, and people's overall sense of well being. PM can also have effects on climate, including both direct effects on radiative forcing and indirect effects that involve cloud feedbacks that influence precipitation formation and cloud lifetimes. In addition to atmospheric effects, the deposition of PM has been shown to result in materials damage, such as accelerated corrosion of metal, erosion, soiling of paint, and soiling of buildings and other structures. Because these effects are largely considered to be PM effects, they are being addressed in detail in the PM NAAQS review currently underway (See http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_index.html for documents related to that review).

6.1.1 Nitrous Oxide

N_2O has not been considered in setting previous nitrogen dioxide (NO_2) NAAQS. In the first NO_x review, N_2O was not considered an air contaminant because there was "no evidence to suggest N_2O is involved in photochemical reactions in the lower atmosphere" (U.S. EPA, 1971). Nitrous oxide was addressed in both the 1982 and 1993 *Air Quality Criteria for Oxides of Nitrogen* (NO_x AQCD) documents (U.S. EPA, 1982a, 1993). In 1982, it was described as one of the eight nitrogen oxides that may be present in the ambient air, but "not generally considered a pollutant." The effect of N_2O on stratospheric ozone was described, and the 1982 NO_x AQCD noted that N_2O may cause a small decrease in stratospheric ozone (U.S. EPA, 1982a). Finally, the 1982 NO_x AQCD concluded that N_2O significantly contributes to the atmospheric greenhouse effect by trapping outgoing terrestrial radiation, and that although the issue was being investigated, many years of research were still needed to assess the issue reliably (U.S. EPA, 1982a). The 1993 NO_x AQCD also identified N_2O as an oxidized nitrogen compound that is not generally considered to be an air pollutant, but it does have an impact on stratospheric ozone and is considered to be among the more significant GHGs (U.S. EPA, 1993). Although not considered within the scope of the previous review, these documents clearly considered N_2O to be within the scope of the listed nitrogen oxides' criteria for pollutants.

The *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008, Section 2.2) acknowledges that N_2O is a potent GHG and discusses N_2O sources and emissions in the United States, as well as the

biogeochemistry of N_2O's microbial-mediated production via denitrification and nitrification in natural ecosystems. Based on the current U.S. GHG inventory (U.S. EPA, 2007b), N_2O contributes approximately 6.5% to total GHG emissions (in carbon dioxide [CO_2] equivalents) (**Figure 6.1-1**).

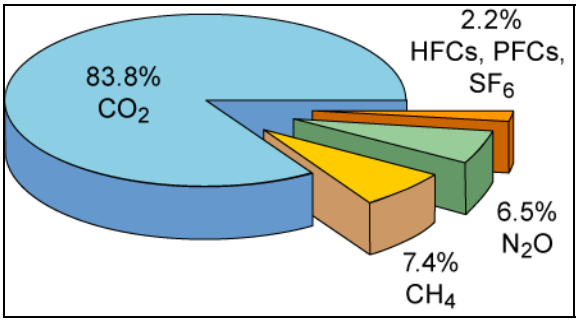

Figure 6.1-1. Percentage of total U.S. emissions of greenhouse gases in CO_2 equivalents (U.S. EPA, 2007b).

Since the definition of "welfare effects" includes effects on climate [CAA Section 302(h)], N_2O is included within the scope of this review. However, it is most appropriate to analyze the role of N_2O in anthropogenic climate change in the context of all of the GHGs. Because such an analysis is outside the scope of this review, it will not be a quantitative part of this assessment.

Although the atmospheric concentration of N_2O (319 parts per billion in 2005) is much lower than CO_2 (379 parts per million in 2005), its global warming potential per molecule is 296 times that of CO_2. Human activities have increased the atmospheric concentration of N_2O by 18% since preindustrial times (IPCC, 2007).

6.2 SULFUR AND MERCURY METHYLATION

Behavioral, reproductive, neurochemical, and hormonal effects due to mercury have been demonstrated in fish and in piscivorous mammals and birds (U.S. EPA, 1996; Scheuhammer et al., 2007). Methylmercury has been shown to be the mercury compound that accumulates in the tissues of affected fish and piscivorous species (Becker and Bigham, 1995; Bloom, 1992; Harris et al., 2003; Scheuhammer et al., 2007). The production of the large majority of methylmercury is mediated by sulfate-reducing bacteria (SRB), and changes in SO_4^{2-} deposition have resulted in changes in both mercury methylation and mercury concentrations in fish.

6.2.1 Science Background

> Current evidence indicates that in watersheds where mercury is present, increased SO_x deposition very likely results in methylmercury accumulation in fish (Munthe et al, 2007; Drevnick et al., 2007).

The ISA (U.S. EPA, 2008, Sections 3.4.1 and 4.5) states that mercury is a highly neurotoxic contaminant that enters the food web as a methylated compound, methylmercury. The contaminant is concentrated in higher trophic levels, including fish eaten by humans. Experimental evidence has established that only inconsequential amounts of methylmercury can be produced in the absence of SO_4^{2-}. Many variables influence how much mercury accumulates in fish, but elevated mercury levels in fish can only occur where substantial amounts of methylmercury are present. Current evidence indicates that in watersheds where mercury is present, increased SO_x deposition, specifically SO_4^{2-}, very likely results in methylmercury accumulation in fish (Drevnick et al., 2007; Munthe et al, 2007).

Establishing the quantitative relationship between SO_4^{2-} and mercury methylation in natural settings is difficult because of the presence of multiple interacting factors in aquatic and terrestrial environments, including wetlands, where SO_4^{2-}, SRBs, and mercury are present. The amount of methylmercury produced by bacteria varies with oxygen content, temperature, pH, and supply of labile organic carbon. When these interacting factors are outside of the ranges most favorable for methylation, increasing levels of SO_4^{2-} deposition will not increase the amount of methylmercury in the aquatic environment. For example, effects on mercury methylation in high-altitude lakes in the Western United States have been recorded with changes in SO_4^{2-} deposition, where some of those interacting factors were also outside of the ranges most favorable for methylation (U.S. EPA, 2008, Sections 3.4 and 4.5). Watersheds with conditions known to be conducive to mercury methylation have been identified in the northeastern United States and southeastern Canada (Chen et al., 2005; Evers et al., 2007; Scheuhammer and Blancher, 1994; Scheuhammer et al., 2007), but watersheds with elevated methylmercury levels observed in water or in fish are seen in most of the continental United States, where conditions have not been fully characterized.

Several interrelated factors seem to affect mercury uptake in fish, including low lake-water pH, dissolved organic carbon, and suspended PM concentrations in the water column (Driscoll et al., 1994; Grieb et al., 1990; Kamman et al., 2004; Mierle and Ingram, 1991; Suns

and Hitchin, 1990; U.S. EPA, 1996). For example, a lower pH can increase the ability of methylmercury to permeate fish membranes and speed the rate of uptake, thus increasing mercury residues in fish (Weiner et al., 2003). In addition, phosphorus and nitrogen can be important as these factors regulate aquatic productivity and, thus, mercury concentrations in aquatic organisms (Driscoll et al., 2007). The proportion of upland to wetland land area within a watershed, as well as wetland type and annual water yield, also appears to be important (St. Louis et al., 1996). **Figure 6.2-1** shows the process of mercury methylation in an aquatic environment.

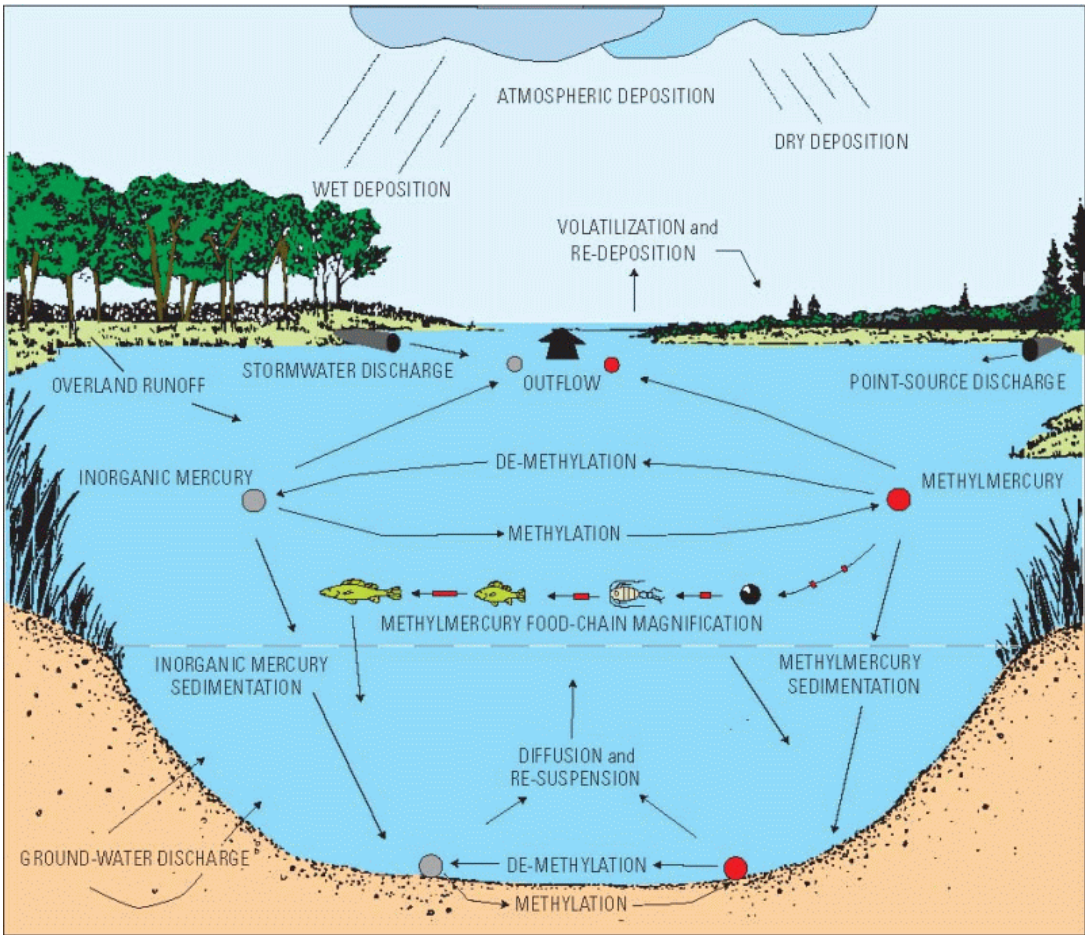

Figure 6.2-1. The mercury cycle in an ecosystem (USGS, 2006).

6.2.2 Qualitative Analysis

The role of atmospherically deposited sulfur species in mercury methylation varies greatly across ecosystems. Field studies have determined that the majority of mercury methylation occurs within anoxic waters and sediments (Gilmour et al., 1998; Hammerschmidt et

al., 2004; Watras et al., 1995); however, several studies have observed that quantitative prediction of mercury methylation is impeded by the presence of multiple known interacting factors whose influence on methylation has not been quantified. These include types of SRB, sulfur species, mercury species, pH, organic acids, and other factors (Benoit et al., 2003; Gilmour et al., 1992; Langer et al., 2001; Munthe et al., 2007; Watras and Morrison, 2008). Methylation via iron-reducing bacteria has also been observed in anoxic, iron-rich sediments; however, this process is not well understood and appears to be less extensive than the SRB-mediated mercury methylation (Fleming et al., 2006; Kerin et al., 2006).

Methyl mercury output by SRBs is a by-product of the conversion of SO_4^{2-} to sulfide (Benoit et al., 2003; Branfireun et al., 1999; Compeau and Bartha, 1985; Gilmour et al., 1992). In general, the rate of methylmercury generation depends on the factors that affect SRB propagation and activity, the availability of inorganic mercury, and the demethylation of mercury. The introduction of SO_4^{2-} to SRB in the presence of divalent mercury (Hg^{+2}), usually in low oxygen sediments, leads to the following biomediated transformation:

$$\begin{array}{l} Hg^{+2} \searrow \\ \qquad\qquad [SRB] \rightarrow MeHg^{+} \\ SO_4^{-2} \nearrow \end{array} \tag{1}$$

The presence of SO_4^{2-}, inorganic mercury, and SRB are, thus, the primary requirements for bacterially mediated sulfate-reducing mercury conversion. Additional factors affecting conversion include the presence of anoxic conditions, temperature, the presence and types of organic matter, the presence and types of mercury-binding species, and watershed effects (e.g., watershed type, land cover, waterbody limnology, runoff loading). Demethylation, which involves aerobic and anaerobic microbial processes, as well as sunlight-dependent processes (e.g., photodemethylation), can also have a substantial effect; therefore, increased methylation in natural environments should be understood as increased *net* mercury methylation (Benoit et al., 2003).

The role of SO_4^{2-} in mercury methylation has been confirmed through a series of independent and interdependent studies. As noted in the ISA, early studies on Little Rock Lake, WI, first observed the link between sulfur enrichment, acidification, and methylmercury concentrations (Hrabik and Watras, 2002). Other important studies include Branfireun et al.

(1999) and Jeremiason et al. (2006). The beneficial effect of decreased SO_4^{2-} deposition on fish tissue methylmercury concentrations has also recently been observed in an isolated Lake Superior ecosystem, where fish tissue concentrations fell below fish consumption advisory levels in the absence of any change in atmospheric mercury deposition (Drevnick et al., 2007). Other studies have focused on the biogeochemical process of mercury cycling to determine factors that are responsible for the link between methylmercury and acidification. Early research by Faust and Osman (1981) estimated that 90% to 99% of the total mercury concentration in surface waters was associated with sediment. With regard to methylmercury, the highest concentrations in the environment generally occur at or near the sedimentary surface, below the oxic–anoxic boundary. The formation of methylmercury has also been associated with macrophytic vegetation and periphyton (Mauro et al., 2002). Mercury methylation rate and organic carbon substrates (e.g., acetate, lactate) may fluctuate when associated with the presence of SRB and environmental conditions (Mitchell et al., 2008). **Figure 6.2-2** illustrates the general SRB methylation process. It should be noted that mercury can also be supplied from sediments.

Although mercury methylation can occur within the water column, there is generally a far greater contribution of mercury methylation from sediments because of anoxia and of greater concentrations of SRB, substrate, and SO_4^{2-}. The conditions within sediment pores and conditions affecting sediment porewater may, therefore, play a key role in mercury methylation. The relative contribution of methylmercury from porewater in the surficial sediment layer is dependent on the size of the hypolimnic anoxic zone, the location of the bacterioplankton activity, and several other factors, such as temperature, organic carbon content, and the presence of sulfides (Watras et al., 1995).

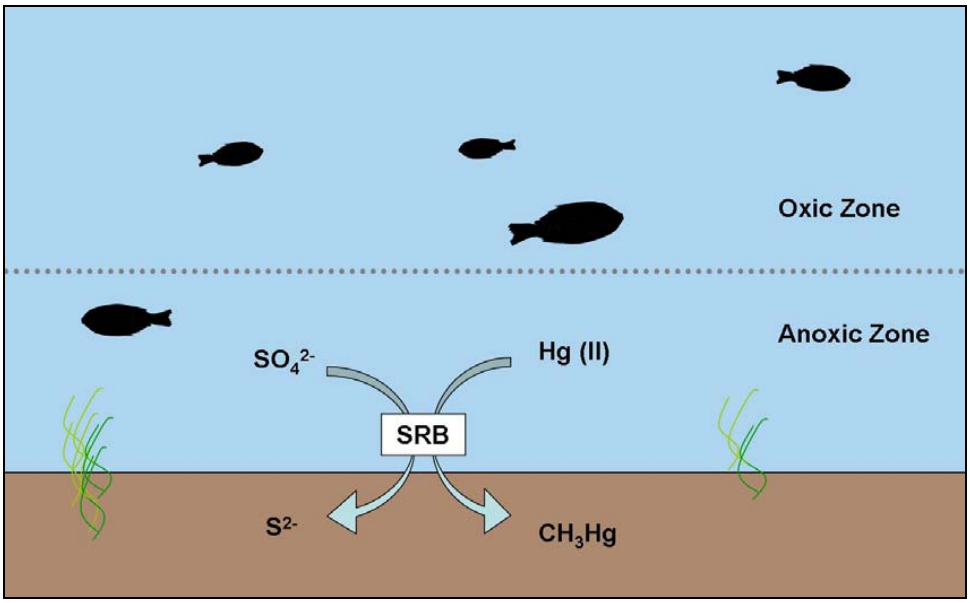

Figure 6.2-2. Biogeochemical process of mercury methylation.

6.2.2.1 Watershed Influences

The effect of watersheds on methylmercury production is dependent on many factors (e.g., dissolved organic carbon, temperature, anoxia, SO_4^{2-}); however, watershed influences also include physical, chemical, and ecological variables that, in turn, have an impact on those factors; they include land cover, precipitation response, hydrology, nutrient loading, and limnology. Watershed influences may also play a role in the uptake of methylmercury into fish and other aquatic species.

> Methylmercury production generally increases with increasing proportion of wetlands in the area contributing to surface water systems (Benoit et al., 2003; Watras and Morrison, 2008).

Land cover and land use affect the transport of chemical species, such as mercury, nutrients, and dissolved organic carbon. Methylmercury production generally increases with increasing proportion of wetlands in the contributing area to surface water systems (Benoit et al., 2003; Watras and Morrison, 2008). In general, wetland environments tend to promote mercury methylation because of increased anoxic environments, fresh organic matter, moderated temperature, and macrophytic environments for bacterial activity (Back et al., 2002). Additionally, increased forest cover and mixed agriculture have been correlated with increased mercury methylation in downstream surface waters, presumably due to organic matter (Driscoll et al., 2007; Krabbenhoft et al., 1999). Land disturbance may also contribute to increased mercury methylation downstream by increasing erosion and, therefore, the mobility of mercury and organic matter (Driscoll et al., 2007).

> There were 3,080 fish consumption advisories in the United States in 2006, with 48 states, one territory, and two tribes having mercury advisories.

State-level fish consumption advisories for mercury are based on state criteria, many of which are based on EPA's fish tissue criterion for methylmercury at 0.3 microgram per gram (µg/g) or on U.S. Food and Drug Administration action limits of 1.0 mg/kg, equal to 1ppm by weight. Fish tissue concentrations of methylmercury at this level or above are extremely unlikely to be observed without substantial methylating activity in the watershed affected. There were 2,436 fish consumption advisories across the United States in 2004; 2,682 in 2005; and 3,080 in 2006. Forty-eight states, one territory, and two tribes issued mercury advisories in 2006. Eighty percent of all fish consumption advisories have been issued, at least in part, because of mercury. In 2006, a total of 14,177,175 lake acres and 882,963 river miles were under advisory for mercury (U.S. EPA, 2007a). **Figure 6.2-3** summarizes the spatial distribution patterns by state for documented fish consumption advisory listings.

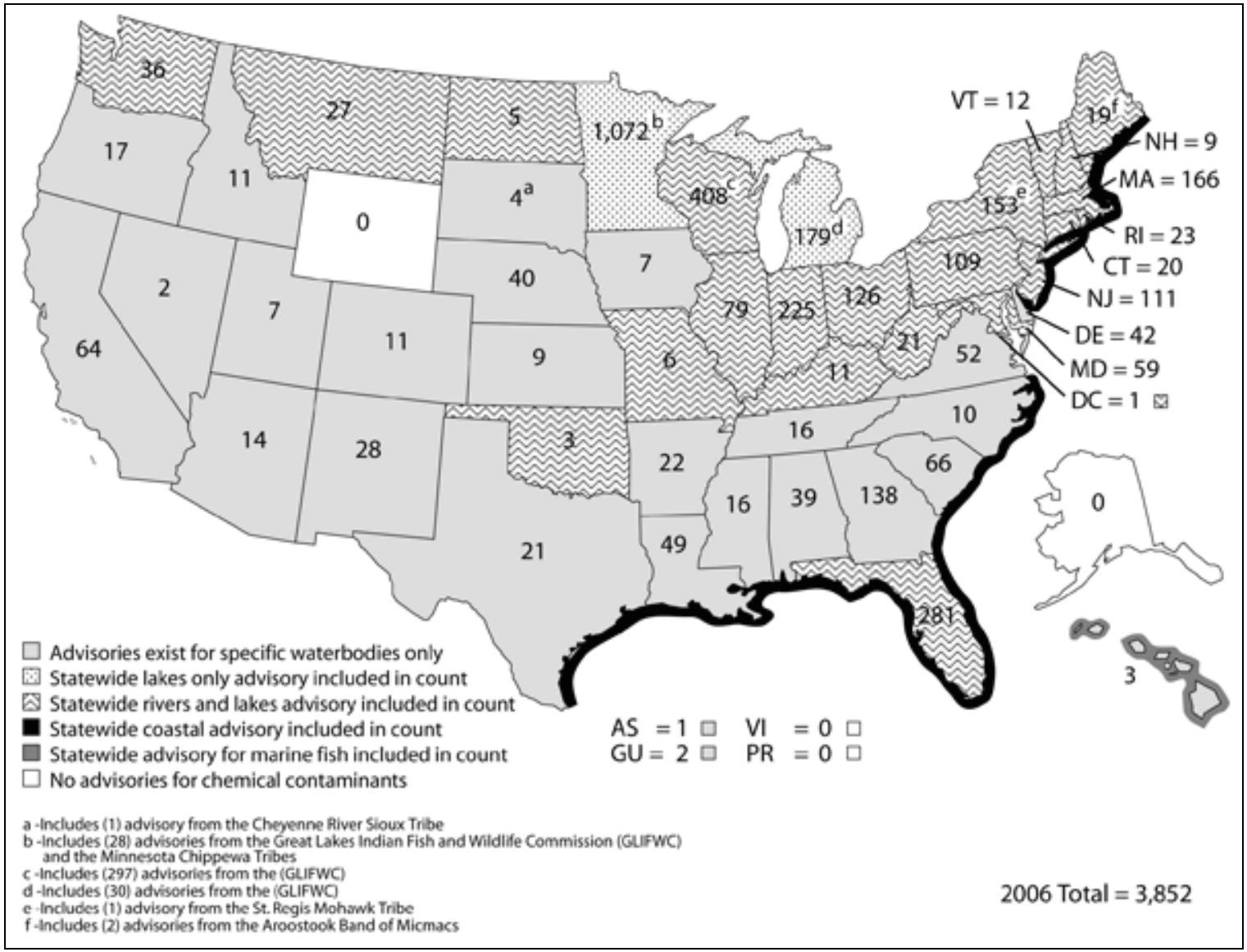

Figure 6.2-3. Distribution pattern in 2006 for state fish consumption advisory listings (U.S. EPA, 2007a).

6.2.2.2 Conclusions

The ISA concluded that evidence is sufficient to infer a casual relationship between sulfur deposition and increased mercury methylation in wetlands and aquatic environments. Specifically, there appears to be a relationship between SO_4^{2-} deposition and mercury methylation; however, the rate of mercury methylation varies according to several spatial and biogeochemical factors whose influence has not been fully quantified (see **Figure 6.2-4).** Therefore, the correlation between SO_4^{2-} deposition and methylmercury could not be quantified for the purpose of interpolating the association across waterbodies or regions. Nevertheless, because changes in methylmercury in ecosystems represent changes in significant human and ecological health risks, the association between sulfur and mercury cannot be neglected (U.S. EPA, 2008, Sections 3.4.1 and 4.5).

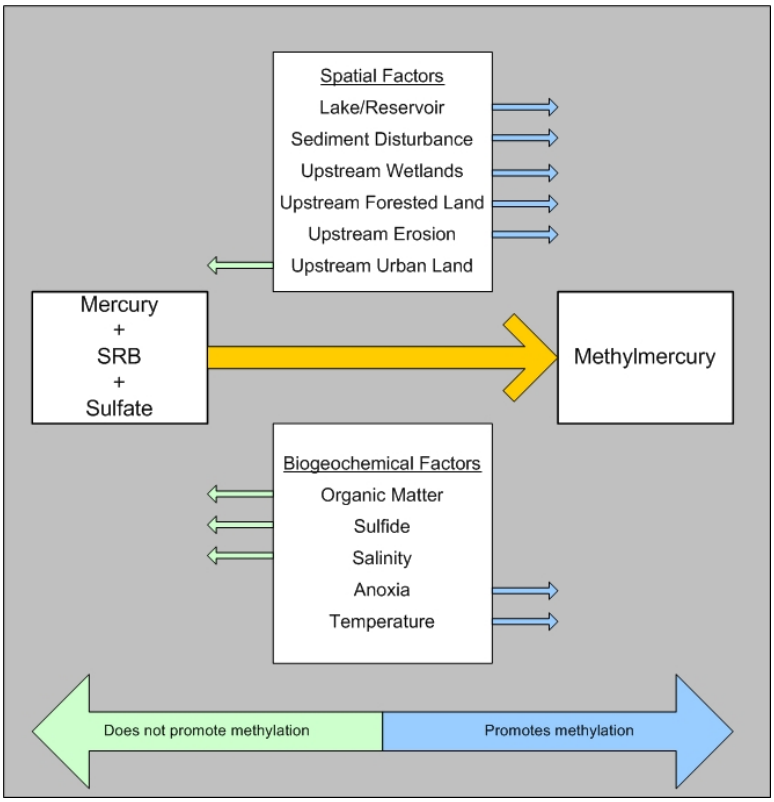

Figure 6.2-4. Spatial and biogeochemical factors influencing methylmercury production.

As research evolves and the computational capacity of models expands to meet the complexity of mercury methylation processes in ecosystems, the role of interacting factors may be better parsed out to identify ecosystems or regions that are more likely to generate higher

concentrations of methylmercury**. Figure 6.2-5** illustrates the type of current and forward-looking research being developed by the U.S. Geological Survey (USGS) to synthesize the contributing factors of mercury and to develop a map of sensitive watersheds. The mercury score referenced in **Figure 6.2-5** is based on SO_4^{2-} concentrations, acid neutralizing capacity (ANC), levels of dissolved organic carbon and pH, mercury species concentrations, and soil types to gauge the methylation sensitivity (Myers et al., 2007).

> It is evident that decreases in sulfate deposition will likely result in decreases in methylmercury concentration.

Interdependent biogeochemical factors preclude the existence of simple sulfate-related mercury methylation models (see **Figure 6.2-4**). It is clear that decreasing sulfate deposition is likely to result in decreased methylmercury concentrations. Future research may allow for the characterization of a usable sulfate-methylmercury response curve; however, no regional or classification calculation scale can be created at this time because of the number of confounding factors.

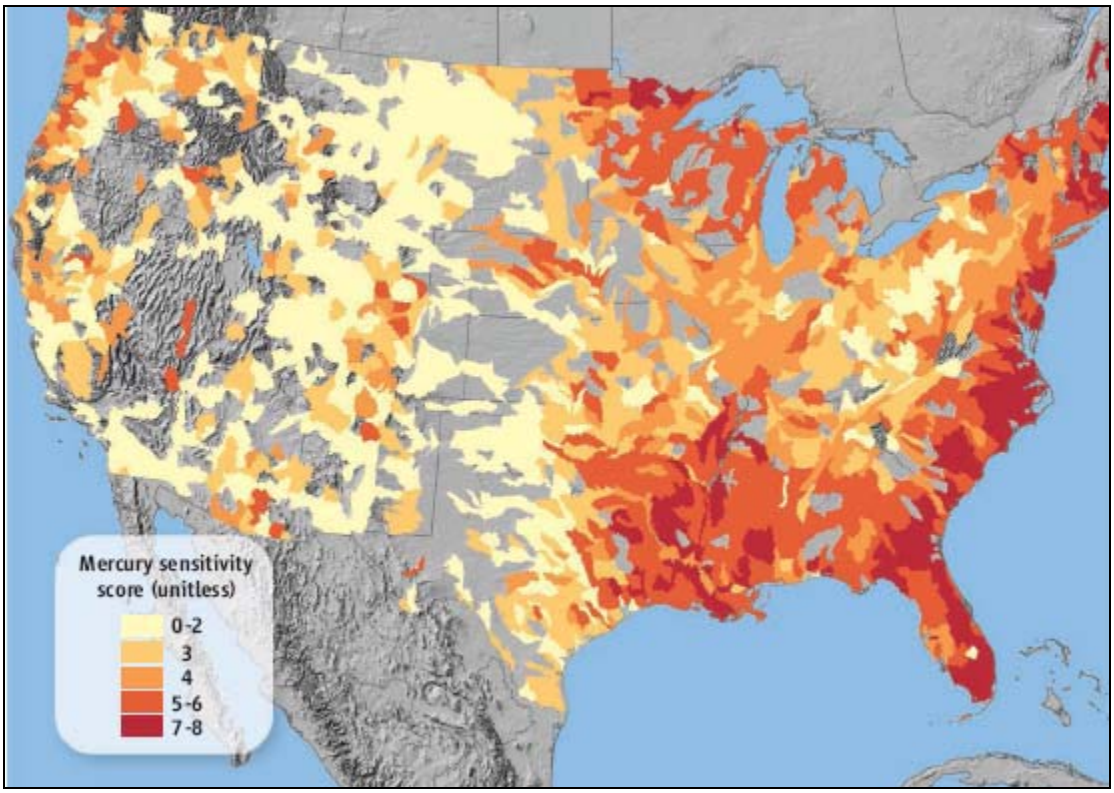

Figure 6.2-5. Preliminary USGS map of mercury methylation–sensitive watersheds derived from more than 55,000 water quality sites and 2,500 watersheds (Myers et al., 2007).

Decreases in SO_4^{2-} deposition have already shown promising reductions in methylmercury. Observed decreases in methylmercury fish tissue concentrations have been linked to decreased acidification and declining SO_4^{2-} and mercury deposition in Little Rock Lake, WI (Hrabik and Watras, 2002), and to decreased SO_4^{2-} deposition in Isle Royale in Lake Superior, MI (Drevnick et al., 2007). Although the possibility exists that reductions in SO_4^{2-} emissions could generate a pulse in methylmercury production because of decreased sulfide inhibition in sulfate-saturated waters, this effect would likely involve a limited number of U.S. waters (Harmon et al., 2007). Also, because of the diffusion and outward flow of both mercury-sulfide complexes and SO_4^{2-}, increased mercury methylation downstream may still occur in sulfate-enriched ecosystems with increased organic matter and/or downstream transport capabilities.

Remediation of sediments heavily contaminated with mercury has yielded significant reductions of methylmercury in biotic tissues. Establishing quantitative relations in biotic responses to methylmercury levels as a result of changes in atmospheric mercury deposition, however, presents difficulties because direct associations can be confounded by all of the factors discussed in this section. Current research does suggest that the levels of methylmercury and total mercury in ecosystems are positively correlated, so that reductions in mercury deposited into ecosystems would also eventually lead to reductions in methylmercury in biotic tissues. Ultimately, an integrated approach that involves the reduction of both sulfur and mercury emissions may be most efficient because of the variability in ecosystem responses. Reducing SO_x emissions could have a beneficial effect on levels of methylmercury in many waters of the United States. This will be addressed, as appropriate, in the policy assessment portion of this review.

6.3 NITROGEN ADDITION EFFECTS ON PRIMARY PRODUCTIVITY AND BIOGENIC GREENHOUSE GAS FLUXES

6.3.1 Effects on Primary Productivity and Carbon Budgeting

This section discusses the mechanisms by which atmospheric nitrogen deposition alters productivity and carbon sequestration in all nonagricultural ecosystems in the United States for which data is available. Rates of photosynthesis and net primary productivity (NPP) of ecosystems typically correlate with metrics of nitrogen availability (Field and Mooney, 1986;

Reich et al., 1997a, 1997b; Smith et al., 2002) along with other factors. The addition of nitrogen from an exogenous source will alter the productivity of nitrogen-limited ecosystems. In a meta-analysis that included terrestrial, freshwater, and marine ecosystems, Elser et al. (2007) found that there were similar patterns of nitrogen and phosphorus limitation among ecosystem types. This finding is in contrast with the existing paradigm that nitrogen-limitation dominates in terrestrial and marine ecosystems, and phosphorus-limitation dominates in freshwater ecosystems.

It is important to distinguish between effects on primary productivity and effects on carbon sequestration. Nitrogen addition to a given ecosystem may increase primary productivity. In some ecosystems, especially forests, this causes increased carbon sequestration (U.S. EPA, 2008, Section 3.3.3.1). However, in other ecosystems (e.g., tundra and wetlands) carbon lost from the ecosystem by respiration (i.e., heterotrophic + autotrophic) may offset the carbon gained by production. For example, a long-term nitrogen fertilization study in an arctic tundra ecosystem found that nitrogen addition increased aboveground plant production and carbon accumulation in the upper organic soil layer. However, nitrogen addition also stimulated soil carbon decomposition in the lower organic layer and in mineral soil. The carbon loss from the lower soil layer offset the carbon accumulation in biomass and the upper soil layer and caused a net ecosystem carbon loss (Mack et al., 2004). Similarly, Bragazza et al. (2006) investigated peatlands across a gradient of nitrogen deposition levels and found higher atmospheric nitrogen deposition resulted in higher carbon loss by increasing heterotrophic respiration and dissolved organic carbon leaching.

6.3.1.1 Terrestrial Ecosystems

Productivity

Experimental nitrogen additions to forest ecosystems have elicited positive growth responses in some, but not all, organisms (DeWalle et al., 2006; Elvir et al., 2003; Emmett, 1999; Högberg et al., 2006). A meta-analysis by LeBauer and Treseder (2008) of 126 nitrogen addition studies showed that most ecosystems are nitrogen-limited with an average increase of 29% in aboveground growth response to nitrogen. The response ratio was significant within temperate forests, tropical forests, temperate grasslands, tropical grasslands, wetlands, and tundra, but not within deserts (LeBauer and Treseder, 2008).

Multiple long-term forest experiments have demonstrated transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Högberg et al., 2006; Magill and Aber, 2004; McNulty et al., 2005). Forest growth enhancement can potentially exacerbate other nutrient deficiencies, such as calcium, magnesium, or potassium (K^+). An additional line of evidence comes from the experimental nitrogen removal studies: removal of nitrogen and sulfur from throughfall increased tree growth in Europe (Beier et al., 1995; Boxman et al., 1998).

Caspersen et al. (2000) found little evidence for growth enhancement due to nitrogen deposition after evaluating tree growth rates in five states (i.e., Minnesota, Michigan, Virginia, North Carolina, and Florida). Magnani et al. (2007) reported a strong positive correlation between estimated average long-term net ecosystem productivity (Levine et al., 1999) and estimated 1990 nitrogen wet deposition (Holland et al., 2005) for 20 forest stands mostly in Western Europe and the conterminous United States, although there have been critiques of the method and the magnitude of these reported effects (De Schrijver et al., 2008; De Vries et al., 2008; Sutton et al., 2008).

Nitrogen deposition can affect the patterns of carbon allocation between aboveground and belowground production. Increased nitrogen availability increases the shoot-to-root ratio, which can be detrimental to the plant because of decreased resistance to environmental stressors, such as drought and windthrow (Braun et al., 2003; Fangmeier et al., 1994; Krupa, 2003; Minnich et al., 1995). Nitrogen saturation also leads to the replacement of slow-growing spruce-fir forest stands by fast-growing deciduous forests that cycle nitrogen more rapidly (McNulty et al., 1996; 2005). In the western United States, atmospheric nitrogen deposition has been shown to cause increased litter accumulation and carbon storage in aboveground woody biomass, which in turn may lead to increased susceptibility to more severe fires (Fenn et al., 2003).

Carbon Sequestration

Nitrogen addition stimulates aboveground plant growth in most ecosystems (LeBauer and Treseder, 2008), which may in turn increase carbon sequestration in plant biomass. This is observed for many forest ecosystems (U.S. EPA, 2008, Section 3.3.3). On the other hand, nitrogen deposition may alter autotrophic and heterotrophic respiratory losses of carbon from ecosystems. When the respiratory loss is stimulated by nitrogen, it will offset some proportion of the gains made by increasing productivity (U.S. EPA, 2008, Section 3.3.3). For example, it is

known that nitrogen deposition increases the concentration of nitrogen in leaf tissue, and autotrophic maintenance respiration is positively correlated with tissue nitrogen content (Reich et. al., 2008).Carbon loss by heterotrophic respiration may be increasing in some ecosystems, while decreasing in others. The increased nitrogen availability could favor microbial decomposition by removing nitrogen constrains on microbial metabolism and stimulating soil organic carbon (SOC) decomposition, as observed in nitrogen-limited peat bogs and tundra (Mack et al., 2004; Bragazza et al., 2006). However, decomposition studies conducted in a forest ecosystem showed that higher litter nitrogen could stabilize soil organic carbon by fostering humus formation in the late decomposition stage (Berg and Laskowski, 2006). Because of the complexity of interactions between nitrogen and carbon cycling, the effects of nitrogen on carbon budgets (quantified input and output of carbon to the ecosystem) are variable.

Many nitrogen fertilization studies have investigated the effect of nitrogen addition on ecosystem carbon sequestration. Adams et al. (2005) examined whether nitrogen fertilization affects carbon sequestration of four Douglas-fir plantation sites in the Pacific Northwest. Those sites were initially established as part of the Regional Forest Nutrition Research Project (RFNRP) and received either three or four additions of 224 kilograms (kg) nitrogen(N)/hectare (ha) as urea (672 to 896 kg N/ha total) over 16 years. They found that the nitrogen-fertilized sites (161 megagrams [Mg] C/ha) had an average of 20% more carbon in the aboveground tree biomass compared to unfertilized sites (135 Mg C/ha), and nitrogen-fertilized soils (260 Mg C/ha) had 48% more soil carbon compared to unfertilized soils (175 Mg C/ha). Canary et al. (2000) studied carbon sequestration of another three RFNRP sites. They also found that nitrogen fertilization, a total of 896 to 1120 kg N/ha over a 16-year-period, increased carbon sequestration of Douglas-fir plantations. However, the response magnitudes were smaller than those reported by Adams et al. (2005). Nitrogen fertilization increased tree biomass carbon by 19% (200.2 Mg C/ha for control, and 238.6 Mg C/ha for nitrogen fertilized site) and soil carbon by 6.2% (123 Mg C/ha for control, and 131 Mg C/ha for nitrogen fertilized site).

In the ISA (U.S. EPA, 2008, Section 3.3.3.1), a meta-analysis was conducted of 17 observations from nine studies in U.S. forests to examine the effect of nitrogen fertilization on forest ecosystem carbon content (EC). In that study, EC was defined as the sum of carbon content of vegetation, forest floor, and soil (Johnson et al., 2006). Details on those publications, including study site, ecosystem type, nitrogen addition level, chemical form of nitrogen, and

experimental condition, appear in Annex C of the ISA (U.S. EPA, 2008). To avoid possible confounded variability caused by site conditions, this meta-analysis only included studies of those control and treatment sites that experienced the same climatic, soil, and vegetation conditions. The EPA meta-analysis revealed that while there was a great deal of variation in response, overall nitrogen addition, ranging from 25 to 200 kg N/ha/yr, increased EC by 6% for U.S. forest ecosystems. Different from Magnani et al. (2007), this study did not find any correlation between the amount of nitrogen addition and the response magnitudes of ecosystem carbon sequestration.

Less is known regarding the effects of nitrogen deposition on carbon budgets of non-forest ecosystems. The EPA meta-analysis, including 16 observations from nine publications, showed that nitrogen addition from 16 to 320 kg N/ha/yr has no significant effect on net ecosystem exchange (NEE) of nonforest ecosystems (U.S. EPA, 2008, Sections 3.3.3.1 and 4.3.1.1). Details on those publications, including study site, ecosystem type, nitrogen addition level, chemical form of nitrogen, and experimental condition, are given in Annex C of the ISA (U.S. EPA, 2008).

ISA Conclusion

The ISA (U.S. EPA, 2008, Section 4.3.1.1) concluded that the evidence is *sufficient to infer a causal relationship* between nitrogen deposition and the alteration of biogeochemical cycling of carbon in terrestrial ecosystems. Nitrogen is often the most limiting nutrient to growth in ecosystems. Nitrogen deposition thus often increases primary productivity; thereby altering the biogeochemical cycling of carbon. Nitrogen deposition can cause changes in ecosystem carbon budgets. However, whether nitrogen deposition increases or decreases, ecosystem carbon-sequestration remains unclear. The meta-analysis conducted for the ISA indicated that nitrogen addition, ranging from 25 to 200 kg N/ha/yr, slightly increased ecosystem carbon content in forest ecosystem. However, nitrogen addition, ranging from 16 to 320 kg N/ha/yr, had no significant effect on NEE for nonforest ecosystems.

> The evidence is sufficient to infer a causal relationship between nitrogen deposition and the alteration of biogeochemical cycling of carbon in terrestrial ecosystems.

In terrestrial ecosystems, nitrogen deposition can accelerate plant growth and change carbon allocation patterns (e.g. shoot-to-root ratio), which can increase susceptibility to severe fires, drought, and wind damage. These effects have been studied in the western United States

and Europe (Adams et. al., 2005; Braun et. al., 2003; Canary et. al., 2000; Fenn et. al., 2003). The alteration of primary productivity can also alter competitive interactions among plant species. The increase in growth is greater for some species than for others, leading to possible shifts in population dynamics, species composition, community structure, and, in a few instances, ecosystem type.

6.3.1.2 Wetland Ecosystems

Productivity

The 1993 NO_x AQCD (U.S. EPA, 1993) reported that nitrogen applications, ranging from 7 to 3120 kg N/ha/yr, stimulated standing biomass production in wetlands by 6% to 413%. The magnitude of the changes in primary production depended on soil nitrogen availability and limitation of other nutrients. However, negative growth rates were observed for some wetland species that were adapted to low-nitrogen environments. For example, increasing nitrogen availability reduced population growth of *Sarracenia purpurea* (commonly known as the Purple pitcher plant or Side-saddle flower). Gotelli and Ellison (2002) reported that the extinction risk of *S. purpurea* within the next 100 years increased substantially if nitrogen deposition rate increased (1% to 4.7%) from the rate of 4.5 to 6.8 kg N/ha/yr. A study of *Sphagnum fuscum* (Rusty peat moss) in six Canadian peatlands showed a weak, although significant, negative correlation between NPP and nitrogen deposition when deposition levels were greater than 3 kg N/ha/yr ($y = 150 – 3.4(x)$; $r^2=0.01$, $p = 0.04$) (Vitt et al., 2003).

Carbon Sequestration

> The evidence is sufficient to infer a causal relationship between nitrogen deposition and the alteration of biogeochemical cycling of carbon in transitional ecosystems.

In the ISA (U.S. EPA, 2008, Sections 4.3.1.1 and 4.3.2.1), a meta-analysis was conducted that included wetlands with other nonforest ecosystems, and the results indicated *no effect* of nitrogen deposition on overall NEE of carbon. In other words, any gain in carbon capture by photosynthesis was offset by ecosystem respiration and carbon leaching. There were not enough studies to evaluate wetlands as a separate category. A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed that peat accumulation increases linearly with nitrogen deposition; however, in recent years this rate has begun to slow, indicating limited

capacity for nitrogen to stimulate accumulation (Turunen et al., 2004). Soil respiration has been studied in European countries under a natural gradient of atmospheric nitrogen deposition from 2 to 20 kg N/ha/yr. It was found that enhanced decomposition rates for material accumulated under higher atmospheric nitrogen supplies resulted in higher CO_2 emissions and dissolved organic carbon release (Bragazza et al. 2006).

ISA Conclusion

The ISA (U.S. EPA, 2008, Section 4.3.2.1) concluded that the evidence is *sufficient to infer a causal relationship* between nitrogen deposition and the alteration of biogeochemical cycling of carbon in transitional ecosystems. Nitrogen deposition often increases ecosystem productivity of wetlands, but it also leads to negative population growth rates of some wetland species that were adapted to low-nitrogen environments.

There was little evidence for an apparent effect on ecosystem carbon sequestration on wetlands.

6.3.1.3 Aquatic Ecosystems

Productivity

In a meta-analysis of more than 600 experiments, Elser et al. (2007) found that nitrogen limitation occurs frequently in freshwater ecosystems, in contrast to the traditional paradigm that freshwater ecosystems are mainly phosphorus-limited. Numerous other studies have also provided strong evidence indicating that nitrogen deposition has played an important role in influencing the productivity of oligotrophic, high-elevation lakes in the western United States and Canada, as well as in the Canadian Arctic (Das et al., 2005; Lafrancois et al., 2003; Saros et al., 2005; Wolfe et al., 2001, 2003, 2006). A comprehensive study of available data from the northern hemisphere surveys of lakes along gradients of nitrogen deposition showed increased inorganic nitrogen concentrations and productivity to be correlated with atmospheric nitrogen deposition (Bergström and Jansson, 2006).

Estuaries and coastal waters tend to be nitrogen-limited and are, therefore, inherently sensitive to increased atmospheric nitrogen loading (D'Elia et al., 1986; Elser et al., 2007; Howarth and Marino, 2006). There is a strong scientific consensus that nitrogen is the principal

cause of coastal eutrophication in the United States (see the Aquatic Nutrient Enrichment Case Study in Chapter 5 and Appendix 6 of this Risk and Exposure Assessment; NRC, 2000).

Carbon Sequestration

Little information is reported regarding the effects of nitrogen deposition on carbon budgets of freshwater, estuarine, and near coastal ecosystems.

ISA Conclusion

The ISA (U.S. EPA, 2008, Section 4.3.3) concluded that the evidence is *sufficient to infer a causal relationship* between nitrogen deposition and the alteration of biogeochemical cycling of carbon in aquatic ecosystems. The productivity of many freshwater ecosystems is nitrogen-limited. Nitrogen deposition can alter species assemblages and cause eutrophication of aquatic ecosystems where nitrogen is the growth-limiting nutrient. In estuarine ecosystems, nitrogen from atmospheric and nonatmospheric sources contributes to increased phytoplankton and algal productivity, leading to eutrophication.

> The evidence is sufficient to infer a causal relationship between nitrogen deposition and the alteration of biogeochemical cycling of carbon in aquatic ecosystems.

Ecosystem carbon sequestration is determined by the difference between input (net carbon fixed by photosynthesis) and output (autotrophic and heterotrophic respiration). Although many studies have shown nitrogen increases productivity in aquatic ecosystems, there is a limited understanding on how nitrogen affects NEE or ecosystem respiration of aquatic ecosystems. Quantification of how nitrogen deposition increases or decreases carbon sequestration of freshwater, estuarine, and near-coastal ecosystems remains unclear.

6.3.2 Biogenic Emissions of Nitrous Oxide

6.3.2.1 Science Overview

Nitrous oxide emissions from the United States are currently thought to be dominated by agricultural (managed) soils (>75%; U.S. EPA, 2008); however, it is important to note that this value does not include non-managed ecosystem emissions. Emissions from forests are thought to be >1%; however, at this point the United States, national emissions inventory does not calculate N_2O emissions from wetlands and rivers, which could be substantial. Total U.S. biogenic emissions from managed and non-managed systems have yet to be calculated. Globally, biogenic

sources are the dominant contributors (>90%) to atmospheric N_2O. Terrestrial soil is the largest source of atmospheric N_2O, accounting for 60% of global emissions (IPCC, 2001). Nitrous oxide production in soil is mainly governed by microbial nitrification and denitrification (Dalal et al., 2003). The contribution of each process to total N_2O production varies with environmental conditions. Denitrifying bacteria reduce NO_3^-or nitrite (NO_2^-) into N_2O or nitrogen (N_2) under anaerobic conditions. In submerged soils, such as wetland soil, denitrification should be the dominant process to N_2O emissions (Conrad, 1996). Increasing NO_3^- input generally increases the denitrification rate under suitable conditions of temperature and organic carbon supply. High soil NO_3^- concentrations also inhibit the reduction of N_2O to N_2 and result in a high N_2O/N_2 ratio (Dalal et al., 2003). Under aerobic environments, autotrophic nitrifying bacteria obtain energy by reducing ammonium (NH_4^+). Nitrous oxide is an intermediate product of the oxidation of NH_4^+ to NO_2^- or the decomposition of NO_2^-. The increase in N_2O emissions following NH_4^+ addition has been observed in many laboratory and field experiments (Aerts and De Caluwe, 1999; Aerts and Toet, 1997; Keller et al., 2005).

EPA conducted a meta-analysis, including 99 observations from 30 publications, to evaluate the effects of nitrogen addition on N_2O emissions from nonagricultural ecosystems (U.S. EPA, 2008, Section 3.3.4.2). Details on those publications, including study site, ecosystem type, nitrogen addition level, chemical form of nitrogen, and experimental condition appear in Annex C of the ISA (U.S. EPA, 2008). Overall, the results of the meta-analysis indicated that nitrogen addition, ranging from 10 to 562 kg N/ha/yr, increased N_2O emissions by 230% (statistically significant) across all ecosystems. Ecosystem type, chemical form of nitrogen, and nitrogen addition level affected the response magnitude of N_2O emissions. Compared to other ecosystems, tropical forests emitted more N_2O under nitrogen enrichment condition (+735%). However, this difference was only significant between tropical and coniferous forests. NO_3^- caused a higher stimulation (+494%) of N_2O emissions than NH_4^+ did (+95%). Although the mean response ratio increased with the amount of nitrogen addition, the differences among the three levels (<75, 75–150, and >150 kg N/ha/yr) were not significant.

There were no clear dose-response relationships between GHG emission/uptake and the amount of nitrogen addition to nonagricultural ecosystems, a result consistent with observations in agricultural ecosystems (FAO/IFA, 2001). However, Butterbach-Bahl et al. (1998) found that increasing NH_4^+ wet deposition led to a linear increase in N_2O emissions and a decrease in CH_4

oxidation at a red spruce forest site. The dose-response relationship was observed at a small scale characterized by homogenous conditions (such as a specific site), in contrast to the large heterogeneous scale investigated in the EPA meta-analysis. This inconsistency is likely caused because GHG production is influenced by multiple interactions of soil, climate, and vegetation (IPCC, 2001).

6.3.2.2 ISA Conclusion

> The evidence is sufficient to infer a causal relationship between total reactive nitrogen deposition and (a) the alteration of biogeochemical flux of N_2O in terrestrial ecosystems and (b) N_2O flux in wetland ecosystems.

The ISA concluded that the reviewed evidence is *sufficient to infer a causal relationship* between total reactive nitrogen deposition and the alteration of N_2O emissions from terrestrial ecosystems (U.S. EPA, 2008, Section 4.3.1.1). Averaged across 80 observations from terrestrial ecosystems, the meta-analysis conducted by EPA indicated that nitrogen addition, ranging from 10 to 562 kg N/ha/yr, increased N_2O emissions by 215% in terrestrial ecosystems. The response of N_2O emissions to nitrogen addition for coniferous forest, deciduous forest, and grasslands was statistically significant.

The ISA also concluded that the evidence reviewed was *sufficient to infer a causal relationship* between total reactive nitrogen deposition and the alteration of N_2O flux in wetland ecosystems (U.S. EPA, 2008, Section 4.3.2.1)**.** Averaged across 19 observations from wetland studies, the meta-analysis conducted by EPA indicated that nitrogen addition, ranging from 15.4 to 300 kg N/ha/yr, increased wetland N_2O production by 207% (U.S. EPA, 2008, Section 4.3.2.1).

6.3.3 Methane Emissions and Uptake

6.3.3.1 Science Overview

Atmospheric methane (CH_4) originates mainly (70% to 80%) from biogenic sources (Le Mer and Roger, 2001). Methane is produced in an anaerobic environment by methanogenic archaea (a type of single-celled organism) bacteria during decomposition of organic matter. Once produced in soil, CH_4 can then be released to the atmosphere or oxidized by methanotrophic bacteria in the aerobic zone (Le Mer and Roger, 2001). Methane production and oxidation processes occur simultaneously in most ecosystems. Wetland soils are generally CH_4 sources,

accounting for about 20% of global CH_4 emissions. Nonflooded upland soils are the most important biological sink for CH_4, consuming about 6% of the atmospheric CH_4 (Le Mer and Roger, 2001). Numerous studies have demonstrated that nitrogen is an important regulatory factor for both CH_4 production and oxidation (Bodelier and Laanbroek, 2004).

The EPA conducted a meta-analysis, including 61 observations from 27 publications, to evaluate the relationship between nitrogen addition and CH_4 flux. Details on those publications, including study site, ecosystem type, nitrogen addition level, chemical form of nitrogen, and experimental condition, appear in Annex C of the ISA (U.S. EPA, 2008). The impacts of nitrogen addition on CH_4 source and sink strength were estimated by CH_4 emissions and CH_4 uptake, respectively.

> The evidence is sufficient to infer a causal relationship between nitrogen deposition and the alteration of biogeochemical flux of CH_4 in terrestrial ecosystems and the alteration of CH_4 flux in wetland ecosystems.

Nitrogen addition, ranging from 30 to 240 kg N/ha/yr significantly increased CH_4 emissions by 115% when averaged across all ecosystems. Methane uptake was significantly reduced by 38% under nitrogen addition, ranging from 10 to 560 kg N/ha/yr. Methane uptake was reduced for all investigated ecosystems (i.e., coniferous forest, deciduous forest, grassland, and drained wetland), but this inhibition was significant only for coniferous and deciduous forests, with a reduction of 28% and 45%, respectively.

Several studies found that CH_4 uptake rates decreased with increasing nitrogen input (Butterbach-Bahl et al., 1998; King and Schnell, 1998; Schnell and King, 1994). However, this meta-analysis did not find significant correlation between the amount of nitrogen addition and the response ratio of CH_4 uptake/emission. The lack of a dose-response relationship likely occurred because CH_4 production is influenced by multiple interactions of soil nitrogen content, soil moisture, pH, and temperature (Le Mer and Roger, 2001), and varies greatly over small spatial and temporal scales (IPCC, 2007).

6.3.3.2 ISA Conclusion

The ISA (U.S. EPA, 2008, Section 4.3.1.1) concluded that the evidence is *sufficient to infer a causal relationship* between nitrogen deposition and the alteration of biogeochemical flux of CH_4 in terrestrial ecosystems. Averaged across 41 observations from terrestrial ecosystems, including four forms of nitrogen (NH_4^+, NO_3^-, NH_4NO_3, and urea) and the addition rates, ranging

from 10 to 560 kg N/ha/yr, the meta-analysis conducted by EPA indicated that nitrogen addition reduced CH_4 uptake, but this inhibition was significant only for coniferous and deciduous forests (U.S. EPA, 2008, Section 4.3.1.1).

The ISA (U.S. EPA, 2008, Section 4.3.2.1) also concluded that the evidence is *sufficient to infer a causal relationship* between nitrogen deposition and the alteration of CH_4 flux in wetland ecosystems. Wetlands are generally net sources of CH_4, but some wetlands can be net sinks, depending on environmental conditions such as drainage and vegetation (Crill et al., 1994; Saarnio et al., 2003). A meta-analysis was performed on a dataset of 17 observations to assess the effects of nitrogen additions on wetland CH_4 fluxes. This dataset included four forms of nitrogen (NH_4^+, NO_3^-, NH_4NO_3, and urea) and the addition rates ranged from 30 to 240 kg N/ha/yr. The results indicated that nitrogen addition increased CH_4 production from the wetlands but had no significant effect on CH_4 uptake of wetlands (U.S. EPA, 2008, Section 4.3.2.1).

In conclusion, nitrogen addition to ecosystems can affect primary productivity and biogenic GHG fluxes. Due to the complexity of interactions between nitrogen and carbon cycling, the effects of nitrogen on carbon budgets (i.e., quantified input and output of carbon to the ecosystem) are variable. Nitrogen deposition can affect the patterns of carbon allocation because most growth occurs aboveground, and nitrogen deposition also has been found to alter biogeochemical cycling of carbon in transitional ecosystems, such as wetlands, and in aquatic ecosystems. Causal relationships also exists between total reactive nitrogen deposition and (a) the alteration of biogeochemical flux of N_2O in terrestrial and wetland ecosystems and (b) the alteration of biogeochemical flux of CH_4 in terrestrial and wetland ecosystems.

6.3.4 Emission Factors

By adapting the methodology of the Intergovernmental Panel on Climate Change (IPCC) guidelines (Mosier et al., 1998), a nitrogen addition-induced GHG emission/uptake factor (*F*) can be estimated by the following equation:

$$F = (G_N - G_C) / N \tag{2}$$

where

G_N is annual flux of GHG from fertilized treatment (kg carbon or kg N/ha/yr)
G_C is annual flux of GHG from control (kg carbon or kg N/ha/yr)
N is annual nitrogen input (kg N/ha/yr).

A dataset of nitrogen effects on GHG emissions from ecosystems around the world was developed for the EPA ecosystem carbon content (EC), N_2O, and CH_4 meta-analyses (U.S. EPA, 2008, Section 4.3). Using this dataset, emission/uptake factors were calculated for the three GHGs. Only field studies that measured growing season or annual GHG fluxes were included in that calculation. Averaged across nitrogen addition treatments ranging from 25 to 200 kg N/ha/yr, the estimated carbon uptake factor (same as C:N response ratio) is 24.5± 8.7 kg CO_2-C/ha/yr per 1 kg N/ha/yr added to forest ecosystem (n=14), which is much lower than a C:N response of 175 to 225:1 reported by Magnani et al. (2008), but close to the C:N response ratio of 40:1 reported by Högberg (2007) and the C:N response ratio of 50 to 75:1 reported by Sutton et al. (2008). Averaged across nitrogen addition treatments ranging from 10 to 450 kg N/ha/yr, the mean N_2O emissions increased by 0.0087 ± 0.0025 kg N_2O-N/ha/yr per 1 kg N/ha/yr added to the natural ecosystem (n=42), which is comparable to the default N_2O emission factor of 0.0125 kg N_2O-N/ha/yr for agricultural field given by IPCC (2000). Averaged across nitrogen addition treatments ranging from 10 to 450 kg N/ha/yr, the mean CH_4 uptake decreased by 0.015±0.004 kg CH_4-C/ha/yr per 1 kg N/ha/yr added to the ecosystem (n=23). There are no emission factors published for which to compare this number. The emission factor for CH_4 was not calculated because there were few field studies that investigated growing season or annual CH_4 emissions under nitrogen addition.

6.3.5 Uncertainty

There is substantial evidence that nitrogen addition causes altered rates of biogenic GHG flux. However, there are limitations to the application of these data to calculate nitrogen deposition effects on net GHG fluxes for the United States. The first obstacle is that ecosystems are heterogeneous across the United States and clear dose-response curves are not available for large heterogeneous landscapes. Micrometeorological factors, including temperature, soil moisture, and precipitation, can vary substantially between ecosystems across the large spatial area of the United States. These factors influence the microbial response to nitrogen addition and introduce variation into the dose-response relationship. Another way to evaluate nitrogen effect on GHG flux is by emission factors (see Section 6.3.4 of this chapter). Emission factors are calculated by combining data from a range of nitrogen addition levels to produce one quantified rate. This method is a coarse evaluation that introduces several uncertainties: (1) the range of

nitrogen addition by studies that are included if the emission factor exceeds those which would be caused by deposition, and (2) the emission factor does not take into account how shifting micrometeorology causes variation in flux rates.

6.4 DIRECT PHYTOTOXIC EFFECTS OF GASEOUS SO_X AND NO_X

The current secondary NAAQS for SO_x and NO_x were set to protect against direct damage to vegetation by the gaseous forms of these pollutants. Uptake of these gaseous pollutants in a plant canopy is a complex process involving adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants penetrate into leaves through to the stomata, although there is evidence for limited pathways via the cuticle. Pollutants must be transported from the bulk air to the leaf boundary layer in order to get to the stomata. The entry of gases into a leaf is dependent upon the physical and chemical processes of gas phase and surfaces as well as the stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as humidity, temperature, and light intensity. When the stomata are closed, as occurs under dark or drought conditions, resistance to gas uptake is very high and the plant has a very low degree of susceptibility to injury. In contrast, mosses and lichens do not have a protective cuticle barrier to gaseous pollutants or stomates and are generally more sensitive to gaseous sulfur and nitrogen than vascular plants (U.S. EPA, 2008).

Outlined below are the effects of the major SO_x and NO_x gases that have phytotoxic effects on vegetation.

6.4.1 SO_2

Currently, SO_2 is the only criteria pollutant with a secondary NAAQS distinct from the primary standard. This standard is intended to protect acute foliar injury resulting from SO_2 exposure. The standard is a 3-hour average of 0.50 ppm and was promulgated in 1970 to protect against acute foliar injury in vegetation. The last AQCD for ecological effects of SO_x was completed in 1982 and concluded that controlled experiments and field observations supported retaining this secondary standard (U.S. EPA, 1971, 1982a, 1982c).

Acute foliar injury usually happens with hours of exposure, involves a rapid absorption of a toxic dose, and involves collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and is usually a result of variable SO_2 exposures over the growing season. The appearance of foliar injury can vary significantly between species and growth conditions

affecting stomatal conductance. Currently, no regular monitoring occurs for SO_2 foliar injury effects in the United States.

Besides foliar injury, long-term lower SO_2 concentrations can result in reduced photosynthesis, growth, and yield of plants. These effects are cumulative over the season and are often not associated with visible foliar injury. As with foliar injury, these effects vary among species and growing environment. SO_2 is also considered to be the primary factor causing the death of lichens in many urban and industrial areas, with fruticose lichens being more susceptible to SO_2 than many foliose and crustose species (Hutchinson et al., 1996). Damage caused to lichens in response to SO_2 exposure includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of nitrogen fixation, reduced K^+ absorption, and structural changes (Belnap et al., 1993; Farmer et al., 1992; Hutchinson et al., 1996). The 1982 SO_x AQCD summarized the concentration-response information available at the time (U.S. EPA, 1982b). Effects on growth and yield of vegetation were associated with increased SO_2 exposure concentration and time of exposure. However, that document concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified.

Because of decreases in ambient SO_2 concentrations and focus on O_3 vegetation effects research, few studies have emerged to better inform a metric and levels of concern for effects of SO_2 on growth and productivity of vegetation. The few new studies published since the 1982 SO_x AQCD continue to report associations between exposure to SO_2 and reduced vegetation growth. However, the majority of these studies have been performed outside the United States and at levels well above ambient concentrations observed in the United States. In light of limited new data, there is little evidence of phytotoxic effects on vegetation below the level of the current standard. However, the current evidence to date supports the appropriateness of the current standard level to protect vegetation from phytotoxic effects at higher exposure levels.

6.4.2 NO, NO_2, and Peroxyacetyl Nitrate (PAN)

It is well known that in sufficient concentrations, NO, NO_2, and PAN can have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (U.S. EPA, 1993). However, the 1993 NO_x AQCD concluded that concentrations of NO, NO_2, and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation

(U.S. EPA, 1993). The current ISA (U.S. EPA, 2008, Section 3.4) stated that very little new research has been done on these phytotoxic effects at concentrations currently observed in the United States.

The functional relationship between ambient concentrations of NO or NO_2 and a specific plant response, such as foliar injury or growth, is complex. Factors such as inherent rates of stomatal conductance and detoxification mechanisms and external factors, including plant water status, light, temperature, humidity, and the particular pollutant exposure regime, all affect the amount of a pollutant needed to cause symptoms of foliar injury. Plant age and growing conditions, and experimental exposure techniques also vary widely among reports of experimental exposures of plants to NO_2. An analysis conducted in the 1993 NO_x AQCD of over 50 peer-reviewed reports on the effects of NO_2 on foliar injury indicated that plants are relatively resistant to NO_2, especially in comparison to foliar injury caused by exposure to O_3 (U.S. EPA, 1993). With few exceptions, visible injury was not reported at concentrations below 0.20 ppm, and these occurred when the cumulative duration of exposures extended to 100 hours or longer. Reductions in rates of photosynthesis have also been recorded in experimental exposures of plants to both NO and NO_2, but usually at concentrations significantly higher than would normally be encountered in ambient air (U.S. EPA, 2008).

Since the 1993 NO_x AQCD was completed, the current ISA (U.S. EPA, 2008) found most new research on NO_2 exposure to vegetation has taken place in Europe and other areas outside the United States. For example, foliar nitrate (NO_3^-) reductase activity was increased in Norway spruce (*Picea abies*) trees growing near a highway with average exposures of about 0.027 ppm compared to trees growing 1,300 meters away from the highway with NO_2 exposures less than 0.005 ppm (Ammann et al., 1995). This was consistent with other studies on Norway spruce in the field and laboratory (Von Ballmoos et al., 1993; Thoene et al., 1991). Muller et al. (1996) found that the uptake rate of NO_3^- by roots of Norway spruce seedlings was decreased by the exposure to 0.1 ppm of NO_2 for 48 hours. Similarly, soybean plants grown in Australia had decreased NO_3^- uptake by roots and reduced growth of plants exposed to 1.1 ppm of NO_2 for 7 days (Qiao and Murray, 1998). In a Swiss study, poplar cuttings exposed to 0.1 ppm of NO_2 for approximately 12 weeks resulted in decreased stomatal density and increased specific leaf weight, but did not result in other effects such as leaf injury or a change in growth (Gunthardt-Goerg et al., 1996). However, NO_2 enhanced the negative effects of ozone on these poplars,

including leaf injury, when the pollutants were applied in combination (Gunthardt-Goerg et al., 1996).

Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant, which has been shown to cause injury to vegetation (See reviews by Cape, 2003, 1997; Kleindienst, 1994; Smidt, 1994; Temple and Taylor, 1983). Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species include spinach, Swiss chard, lettuces, and tomatoes. Petunias have also been characterized as sensitive to PAN exposures and have been used as bioindicators of in areas of Japan (Nouchi et al., 1984). Controlled experiments have also shown significant negative effects on the net photosynthesis and growth of petunia (*Petunia hybrida* L.) and kidney bean (*Phaseolus vulgaris* L.) after exposure of 30 ppb of PAN for four hours on each of three alternate days (Izuta et al., 1993). As mentioned previously, it is known that oxides of nitrogen, including PAN, could be altering the nitrogen cycle in some ecosystems, especially in the western United States, and contributing nitrogen saturation (Bytnerowicz and Fenn, 1996; Fenn et al., 2003, see Section 3.3). However, PAN is a very small component of nitrogen deposition in most areas of the United States. Although PAN continues to persist as an important component of photochemical pollutant episodes, there is little evidence in recent years suggesting that PAN poses a significant risk to vegetation in the United States (U.S. EPA, 2008).

6.4.3 Nitric Acid (HNO_3)

Relatively little is known about the direct effects of HNO_3 vapor on vegetation. However, the current ISA (U.S. EPA, 2008) highlighted recent research identifying HNO_3 as the cause for decline of sensitive lichen species in areas with relatively high HNO_3 deposition. Further, HNO_3 has a very high deposition velocity compared to other NO_x pollutants and may be an important source of nitrogen for plants (Hanson and Lindberg, 1991; Hanson and Garten, 1992; Vose and Swank, 1990). This deposition could contribute to nitrogen saturation of some ecosystems near sources of photochemical smog (Fenn et al., 1998). For example, in mixed conifer forests (MCFs) of the Transverse Range (i.e., Los Angeles basin mountain ranges), HNO_3 has been estimated to provide 60 percent of all dry deposited nitrogen (Bytnerowicz et al., 1999).

HNO_3 deposition has been suspected as the cause of a dramatic decline in lichen species in the Los Angeles basin (Nash and Sigal, 1999). This suggestion was strengthened by an

experiment that transplanted *Ramalina* lichen species from clean air habitats (Mount Palomar and San Nicolas Island) to analogous polluted habitats in the Los Angeles basin and repeatedly observed death of the lichens over a few weeks in the summer (Boonpragob and Nash, 1991). Associated with this death was massive accumulation of H^+ and NO_3^- by the lichen thalli (bodies) (Boonpragob et al., 1989). Recently, Riddell et al. (2008) exposed the healthy *Ramalina menziesii* thalli to moderate (8–10 ppb) and high (10–14 ppb) HNO_3 concentrations in month-long fumigations and reported a significant decline in chlorophyll content and carbon exchange capacity compared to thalli in control chambers. Thalli treated with HNO_3 showed visual signs of bleaching and were clearly damaged and dead by day 28. The damage may have occurred through several mechanisms including acidification of pigments and cell membrane damage (Riddell et al., 2008). The authors concluded that *Ramalina menziesii* has an unequivocally negative response to the HNO_3 concentrations common to ambient summer conditions in the Los Angeles air basin and that it is very likely that HNO_3 has contributed to the disappearance of this sensitive lichen species from the Los Angeles air basin, as well as other locations with arid conditions and high HNO_3 deposition loads (Riddell et al., 2008).

At high ambient concentrations, HNO_3 can also cause damage to vascular plants (U.S. EPA, 2008). Seedlings of ponderosa pine and California black oak subjected to short-term exposures from 50–250 ppb of HNO_3 vapor for 12 hours showed deterioration of the pine needle cuticle in light at 50 ppb (Bytnerowicz et al., 1998a). Oak leaves appeared to be more resistant to HNO_3 vapor, however, with 12-hour exposures in the dark at 200 ppb producing damage to the epicuticular wax structure (Bytnerowicz et al., 1998a). The observed changes in wax chemistry caused by HNO_3 and accompanying injury to the leaf cuticle (Bytnerowicz et al., 1998a) may predispose plants to damage by various environmental stresses such as drought, pathogens, and other air pollutants. Because elevated concentrations of HNO_3 and ozone co-occur in photochemical smog (Solomon et al. 1988), synergistic interactions between the two pollutants are possible (Bytnerowicz et al., 1998b). It should be noted that the experiments described above were observed at relatively short-term exposures at above ambient concentrations of HNO_3. Long-term effects of lower air concentrations that better approximate ambient HNO_3 concentrations should be investigated.

6.5 SUMMARY AND KEY FINDINGS

This Risk and Exposure Assessment focused on acidification and nutrient enrichment as welfare effects; however, additional effects have been documented. For example, in 1982, EPA acknowledged that particulate species of nitrates can reduce visibility. Also, materials damage such as corrosion, erosion, and soiling of paint and buildings has also been long documented. Both visibility and materials damage are being addressed in the PM NAAQS review in progress.

The ISA concluded that, based on research evidence, a causal relationship can be inferred between sulfur deposition (as sulfate, SO_4^{2-}) and increased mercury methylation in wetlands and aquatic environments. However, because the rate of methylation varies spatially and with biogeochemical factors, the correlation of sulfate deposition and methyl mercury could not be quantified for the purpose of interpolating the association across waterbodies or regions. The evidence indicates that decreases in sulfate deposition will likely result in decreases in methyl mercury concentration which is important given that in 2006, there were 3,080 fish consumption advisories for mercury in the United States, including 48 states, one territory, and two tribes. USGS mapping of mercury methylation-sensitive watersheds is underway as a means to better understand the extent of sensitivity.

Nitrous oxide (N_2O) has not been considered in setting previous NO_2 NAAQS; however, the current ISA acknowledges that N_2O is a potent GHG, contributing 6.5% of total U.S. GHG emissions (in CO_2 equivalents). Although the Clean Air Act definition of "welfare effects" includes effects on climate, it is most appropriate to analyze the role of N_2O in the context of all of the GHGs. Therefore, it was not part of this Risk and Exposure Assessment.

The ISA concludes that the evidence is sufficient to infer a causal relationship between nitrogen deposition and the alteration of biogeochemical cycling of carbon in terrestrial, transitional, and aquatic ecosystems. Biogenic GHG fluxes, including N_2O and CH_4, are acknowledged in the ISA as being altered by nitrogen deposition in terrestrial and wetland ecosystems. There are no clear dose-response relationships between N addition and biogenic GHG fluxes, mainly due to the heterogeneity of ecosystems across the United States.

Finally, SO_x and NO_x gases have different degrees of phytotoxic effects on vegetation. A unique secondary NAAQS exists for SO_2 to protect against acute foliar injury, but it was determined in 1993 that concentrations of NO, NO_2, and PAN are rarely high enough to have phytotoxic effects on vegetation; therefore, no unique secondary standard exists. Relatively little

is known about the direct effects of HNO_3 vapor on vegetation, however, recent research on the decline of sensitive lichen species was highlighted in the ISA. HNO_3 also has a very high deposition velocity and may be an important source of nitrogen to plants. In the Transverse Range's MCF, HNO_3 has been estimated to provide 60% of all dry deposited nitrogen, and it has been suspected as the cause of a dramatic decline in lichen species. At high concentrations over the short-term, HNO_3 can damage vascular plants such as seedlings of ponderosa pine and California black oak. More research is needed to determine long-term exposure effects at lower concentrations.

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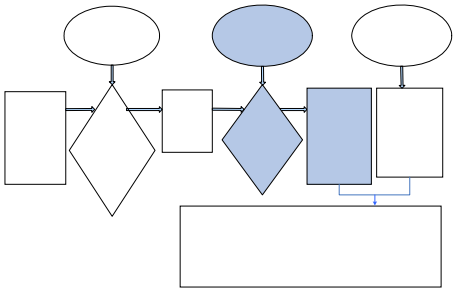

7.0 SYNTHESIS AND INTEGRATION OF CASE STUDY RESULTS

This chapter synthesizes the case study analyses associated with each targeted effect area by identifying the strengths, limitations, and uncertainties associated with the available data, modeling approach, and relationship between the selected ecological indicator and atmospheric deposition as described by the ecological effect function. The known data gaps and research needs associated with each targeted effect area are also identified. As noted in Chapter 2, there are different levels of uncertainty associated with the relationships between deposition, ecological effects, and ecological indicators. In addition, extrapolating from a case study area to a larger assessment area introduces additional uncertainty and potential error that needs to be addressed. Understanding the nature, sources, and importance of these uncertainties will help inform the standard-setting process. The Intergovernmental Panel on Climate Change (IPCC) *Fourth Assessment Report* (IPCC, 2007) addresses uncertainty across many disciplines and from diverse approaches using language associated with both qualitative and quantitative uncertainty that is based on expert judgment and statistical analysis. A similar approach will be used here, adapted specifically to the analyses covered in this review.

For this overview, the following terms are defined for each targeted effect area as follows:

- **Data Availability: *high, medium or low quality.*** This criterion is based on the availability and robustness of data sets, monitoring networks, availability of data that allows for extrapolation to larger assessment areas, and input parameters for modeling and developing the ecological effect function. The scientific basis for the ecological indicator selected is also incorporated into this criterion.

- **Modeling Approach:** ***high, fairly high, intermediate, or low confidence.*** This value is based on the strengths and limitations of the models used in the analysis and how accepted they are by the scientific community for their application in this analysis.
- **Ecological Effect Function:** ***high, fairly high, intermediate, or low confidence.*** This ranking is based on how well the ecological effect function describes the relationship between atmospheric deposition and the ecological indicator of an effect.

All of these parameters are necessary to evaluate the strength of the scientific basis for setting a national standard to protect against a given targeted effect.

7.1 AQUATIC ACIDIFICATION

7.1.1 Available Data

For many years, research has focused on characterizing the ecological response of aquatic systems due to acidifying deposition. Surface water monitoring data from 1990–2006 for sulfate and nitrate concentrations and ANC levels used for this analysis came from the U.S. Environmental Protection Agency (EPA)–administered Temporally Integrated Monitoring of Ecosystems (TIME)/Long Term Monitoring (LTM) network. At the core of the TIME project is the concept of probability sampling, whereby each sampling site is chosen to represent a particular segment of a target population so that the entire data set is representative of the broader population. The target populations in these regions include lakes and streams likely to be responsive to changes in acidifying deposition, defined in terms of ANC.

In addition, data from the EPA EMAP and Regional-EMAP (REMAP) surveys were used to characterize ecological conditions across populations of surface waters. EMAP and REMAP surveys have been conducted on lakes and streams throughout the country. EMAP surveys are probability surveys where sites are selected using a spatially balanced, systematic, randomized sample so that the results can be used to make estimates of regional extent of condition (e.g., number of lakes, length of stream). In both the Adirondack and Shenandoah case study areas, the sample sites selected for future monitoring were chosen based on the EMAP survey sites in the area that met the TIME target population definition. Each lake or stream is sampled annually (in summer for lakes; in spring for streams), and the results are extrapolated with known confidence to the target population(s) as a whole using the EMAP site population expansion factors or

weights (Larsen et al., 1994; Larsen and Urquhart, 1993; Stoddard et al., 1996; Urquhart et al., 1998). (Note: for more details about the TIME/LTM network and EMAP probability surveys, see Section 4.2.5 of Chapter 4 and Attachment B of Appendix 4)

The impact of acidifying deposition on aquatic systems is controlled by several environmental factors, such as geology, surface water flow, soil depth, and weathering rates, all of which influence the ability of a watershed to neutralize the additional acidifying deposition and prevent the lowering of surface ANC. ANC is a useful ecological indicator because it integrates the overall acid-base status of a lake or stream and reflects how aquatic ecosystems respond to acidifying deposition over time. There is also a relationship between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress; in particular, concentrations of hydrogen ion (as pH), calcium (Ca^{2+}), and aluminum (Al). In aquatic systems, there is a direct relationship between ANC and fish and phyto-zooplankton diversity and abundance (Baker et al., 1993).

The ANC of surface waters is widely used as a chemical indicator of acidic conditions because it has been found in many studies to be the best single indicator of the biological response and health of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006). Logistic regression of species presence/absence data against ANC provides a quantitative dose-response function that indicates the probability of occurrence of an organism for a given value of ANC. For example, the number of fish species present in a waterbody has been shown to be positively correlated with the ANC level in the water, with higher values supporting a greater richness and diversity of fish species (**Figure 7.1-1**). The diversity and distribution of phyto-zooplankton communities are also positively correlated with ANC.

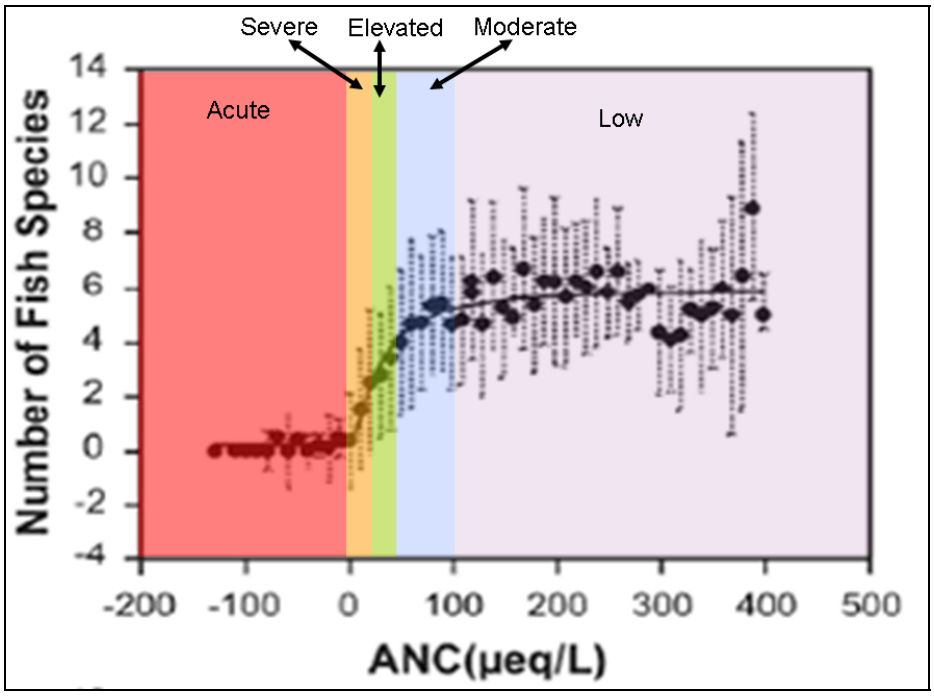

Figure 7.1-1. Number of fish species per lake or stream versus ANC level and aquatic status category (colored regions) for lakes in the Adirondack Case Study Area (Sullivan et al., 2006). The five aquatic status categories are described in **Table 7.1-1**.

For freshwater systems, ANC levels can be grouped into five major classes: <0, 0–20, 20–50, 50–100, and >100 microequivalents per liter (μeq/L), with each range representing a probability of ecological damage to the community. ANC values >100 μeq/L are generally not harmful (see **Figure 7.1-1**) to biota. With ANC <100 μeq/L, fish fitness and community diversity begin to decline, but the overall health of the community remains high as long as ANC concentrations do not fall below 50 μeq/L. ANC concentrations <50 μeq/L result in negative effects on sensitive biota. From 50 to 20 μeq/L, fish diversity and the overall fitness (i.e., health and reproduction) of most aquatic organisms in the waterbody are reduced. For ANC <20 μeq/L, all biota exhibit some level of negative effects, particularly because surface waters at this level are susceptible to episodic acidification and their associated harmful effects (i.e., toxic and lethal effects on fish). Fish and plankton diversity and the structure of the communities continue to decline sharply to levels where acidophilic species begin to outnumber all other species. Below an ANC level of 0 μeq/L, nearly complete loss of fish populations and extremely low diversity of planktonic communities occur. At these low levels, only acidophilic species are present, but even their population and community structure are sharply reduced. The five categories of ANC and

expected ecological effects are described in **Table 7.1-1** and are supported by a large body of research completed throughout the eastern United States (Sullivan et al., 2006).

Table 7.1.-1. Aquatic Status Categories

Category Label	ANC Levels	and Expected Ecological Effects
Acute Concern	<0 μeq/L	Complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acidophilic forms. The numbers of individuals in plankton species that are present are greatly reduced.
Severe Concern	0–20 μeq/L	Highly sensitive to episodic acidification. During episodes of high acidifying deposition, brook trout populations may experience lethal effects. The diversity and distribution of zooplankton communities decline sharply.
Elevated Concern	20–50 μeq/L	Fish species richness is greatly reduced (i.e., more than half of expected species can be missing). On average, brook trout populations experience sublethal effects, including loss of health, ability to reproduce, and fitness. Diversity and distribution of zooplankton communities decline.
Moderate Concern	50–100 μeq/L	Fish species richness begins to decline (i.e., sensitive species are lost from lakes). Brook trout populations are sensitive and variable, with possible sublethal effects. Diversity and distribution of zooplankton communities also begin to decline as species that are sensitive to acidifying deposition are affected.
Low Concern	>100 μeq/L	Fish species richness may be unaffected. Reproducing brook trout populations are expected where habitat is suitable. Zooplankton communities are unaffected and exhibit expected diversity and distribution.

One of the strengths of this case study is that there is a great deal of data available on surface water trends and ANC levels in the case study locations.

CONCLUSION: The available data used for the targeted effect of aquatic acidification are robust and considered *high quality.* There is *high confidence* about the use of these data and their value for extrapolating to a larger regional population of lakes.

7.1.2 Modeling Approach

The Model of Acidification of Groundwater in Catchments (MAGIC) was used to determine the past (pre-acidification), present (2002 and 2008), and future (2020 and 2050) acidic conditions in the case study areas. MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry

(Cosby et al., 1985a,b). The model simulates soil solution chemistry and surface water chemistry to predict annual average concentrations of the major ions in lakes and streams. Model inputs include deposition and physical and chemical surface water parameters. Weathering rates and initial (pre-industrial) base saturation values are calibrated by comparing model outputs and observed surface water chemistry. The benefits of MAGIC are that the input parameters are readily available and, once calibrated for a specific site, the model is easy to use.

The uncertainty in the water quality estimates (i.e., ANC) from MAGIC was derived by running multiple calibrations. These simulation uncertainty estimates were derived from the multiple calibrations at each site provided by the "fuzzy optimization" procedure employed in this project. For each of the modeled sites, 10 distinct calibrations were performed with the target values, parameter values, and deposition inputs for each calibration reflecting the uncertainty inherent in the observed data for the individual site. The effects of the uncertainty in the assumptions made in calibrating the model (and the inherent uncertainties in the data available) can be assessed by using all successful calibrations for a site when simulating the response to different scenarios of future deposition. The model then produces an ensemble of simulated values for each site (e.g., a median ANC).

Based on the MAGIC model simulations, the 95% confidence interval for the pre-acidification and current average ANC concentrations of 44 modeled lakes is 106.8 to 134.0 and 50.5 to 81.8 μeq/L, respectively, which is, on average, a 15 μeq/L difference in ANC concentrations, or 10%. The 95% confidence interval for pre-acidification and current average ANC concentrations of the 60 modeled streams is 91.9 to 110.9 and 53.4 to 62.4 μeq/L, respectively, which is, on average, a 8 μeq/L difference in ANC concentration, or 5%.

Results of predicted versus observed average water chemistry during the calibration period (i.e., reference year) are in **Figures 7.1-2 and 7.1-3** for MAGIC modeling. The model showed close agreement with measured values at all sites for the 1-year comparison of modeled values. For all sites' SO_4^{2-}, NO_3^-, and ANC simulations, the root mean squared error (RMSE) for predicted versus observed values, based on average ANC over a 5-year period, was 0.1 μeq/L, 0.05 μeq/L, and 3.5 μeq/L, respectively, for lakes in the Adirondack Case Study Area and 1.0 μeq/L, 0.06 μeq/L, and 1.0 μeq/L, respectively, for streams in the Shenandoah Case Study Area. RMSE is a frequently-used measure of the differences between values predicted by a model or an estimator and the values actually observed from the thing being modeled or estimated. Plots

of simulated and observed annual average ANC values for the period of 1980 to 2007 are graphed in **Figures 7.1-4 and 7.1-5** for two lakes in the Adirondack Case Study Area and two streams in the Shenandoah Case Study Area. The simulated and observed values are yearly average ANC values. Observed water chemistry data are from the LTM, ALTM, VTSSS, and TIME water quality measurement programs. The RMSE for ANC were 7.8 µeq/L and 5.1 µeq/L for lakes in the Adirondack Case Study Area and 11.8 µeq/L and 4.0 µeq/L for streams in Shenandoah Case Study Area. These direct comparisons show good agreement between simulated and observed water quality values.

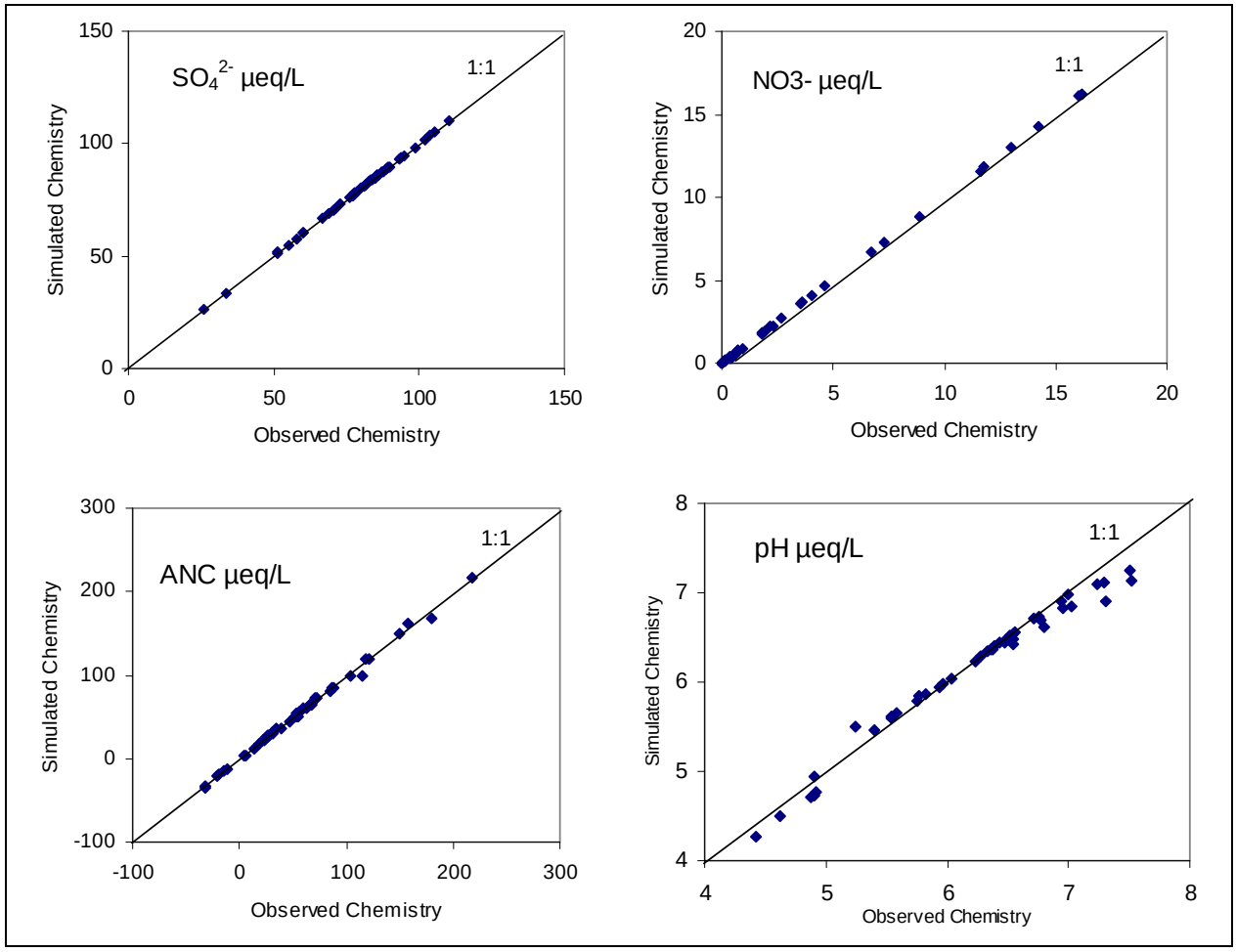

Figure 7.1-2. Simulated versus observed annual average surface water SO_4^{2-}, NO_3^-, ANC, and pH during the model calibration period for each of the 44 lakes in the Adirondack Case Study Area. The black line is the 1:1 line.

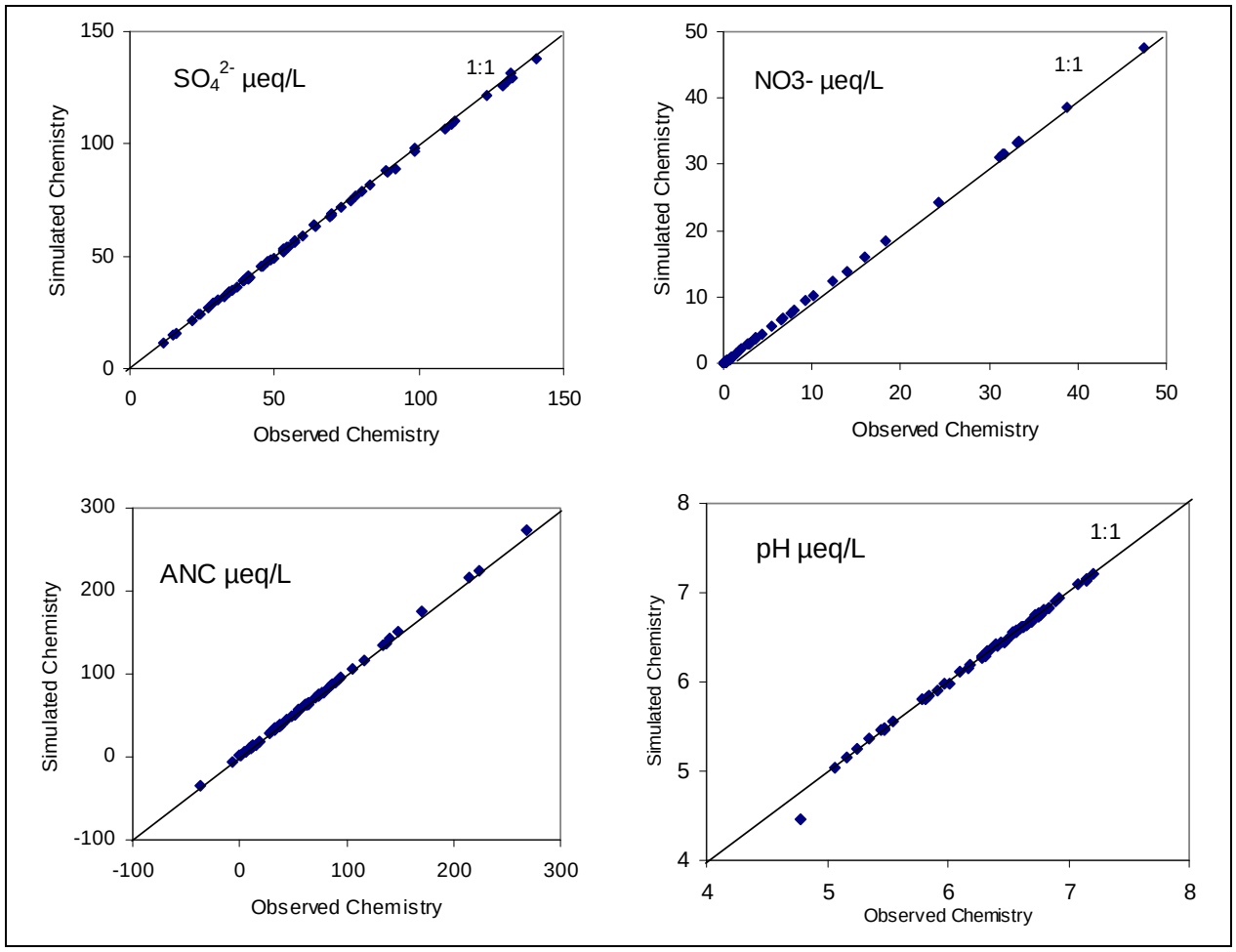

Figure 7.1-3. Simulated versus observed annual average surface water SO_4^{2-}, NO_3^-, ANC, and pH during the model calibration period for each of the 60 streams in the Shenandoah Case Study Area. The black line is the 1:1 line.

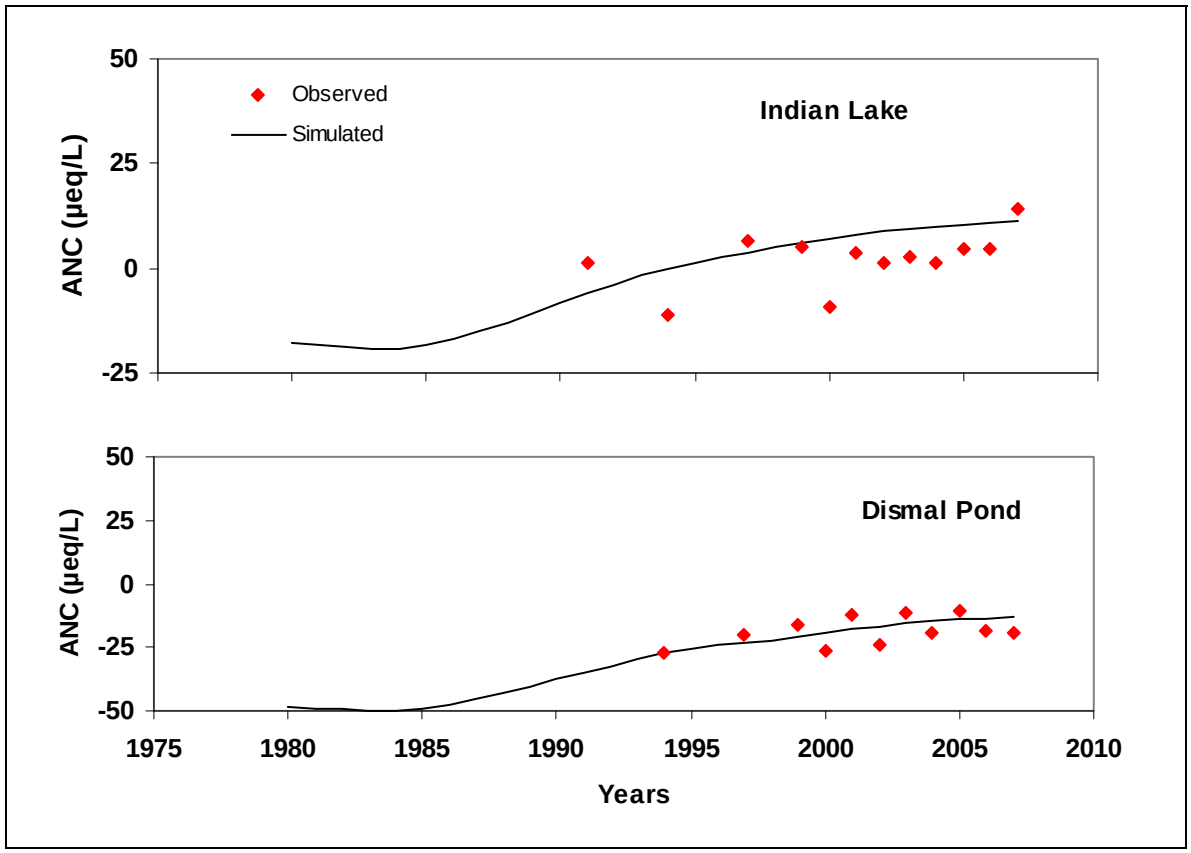

Figure 7.1-4. MAGIC simulated and observed values of ANC for two lakes in the Shenandoah Case Study Area. Red points are observed data, and the simulated values are the line. The Root Mean Squared Error (RMSE) for ANC was 7.81 µeq/L for Indiana Lake and 5.1 µeq/L for Dismal Pond.

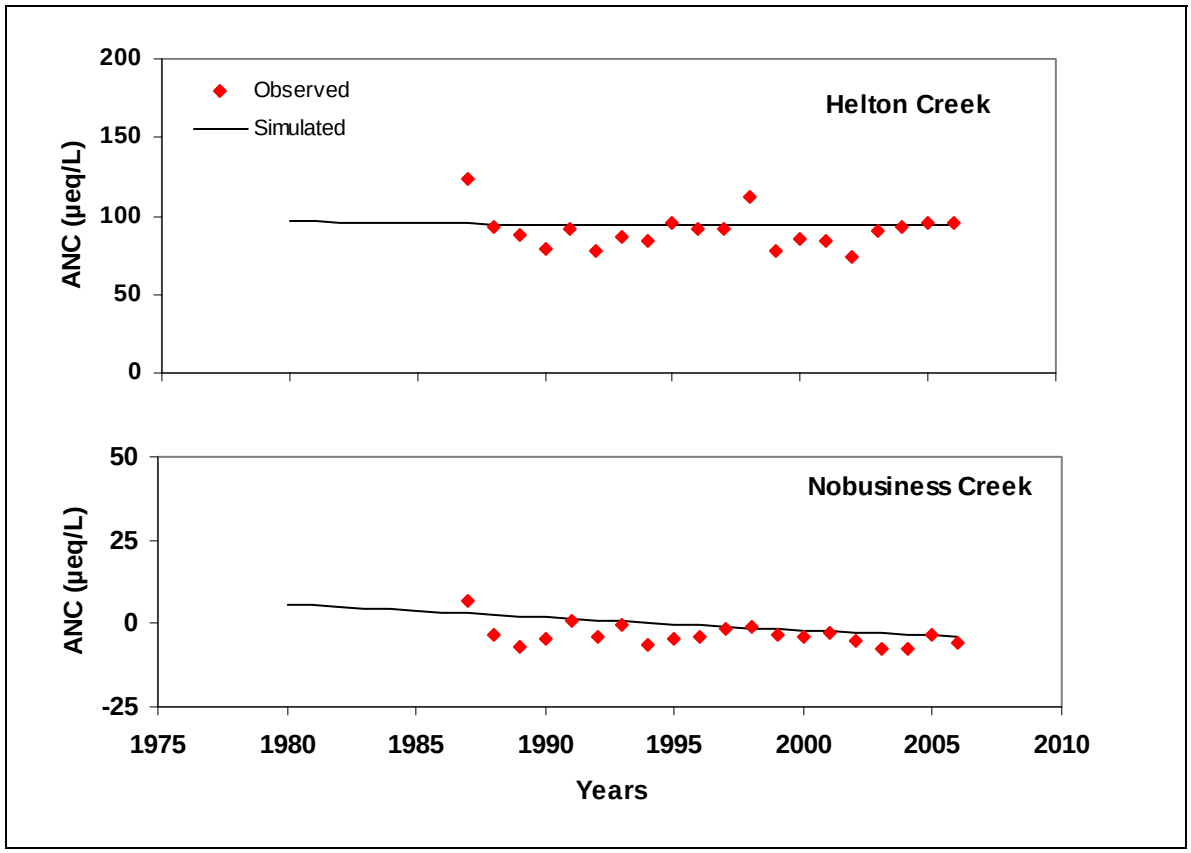

Figure 7.1-5. MAGIC simulated and observed values of ANC for two lakes in the Shenandoah Case Study Area. Red points are observed data, and the simulated values are the line. The Root Mean Squared Error (RMSE) for ANC was 11.8 µeq/L for Helton Creek and 4.0 µeq/L for Nobusiness Creek.

The critical load approach was used to connect current deposition of nitrogen and sulfur to the acid-base condition and biological risk to biota of lakes and streams. Calculating critical load exceedances (i.e., the amount of deposition above the critical load) allows the determination of whether current deposition poses a risk of acidification to a given group of waterbodies. This approach also allows for the comparison of different levels of ANC thresholds (e.g., 0, 20, 50, 100 µeq/L) and their associated risk to the biological community.

The critical load of acidity for lakes or streams was derived from present-day water chemistry using the steady-state critical load models. These models are based on the principle that excess base cation production within a catchment area should be equal to or greater than the acid anion input, thereby maintaining the ANC above a preselected level (Reynolds and Norris, 2001). This model assumes steady-state conditions and assumes that all SO_4^{2-} in runoff originates from sea salt spray and anthropogenic deposition. Given a critical ANC protection

level, the critical load of acidity is simply the input flux of acid anions from atmospheric deposition (i.e., natural and anthropogenic) subtracted from the natural (i.e., preindustrial) inputs of base cations in the surface water. An F-factor was used to correct the concentrations and estimate preindustrial base concentrations for lakes in the Adirondack Case Study Area. A detailed description of the F-factor approach is given in Section 1.2.2 of Attachment A of Appendix 4.

There is uncertainty associated with the parameters in the steady-state critical load model used to estimate aquatic critical loads. The strength of the critical load estimate and the exceedance calculation relies on the ability to estimate the catchment-average base cation supply (i.e., input of base cations from weathering of bedrock and soils and air), runoff, and surface water chemistry. The uncertainty associated with runoff and surface water measurements is fairly well known; however, the ability to accurately estimate the catchment supply of base cations to a waterbody is still poorly known. This is important because the catchment supply of base cations from the weathering of bedrock and soils is the factor that has the most influence on the critical load calculation and also has the largest uncertainty (Li and McNulty, 2007). Although the approach to estimate base cation supply in the case study areas (e.g., F-factor) approach has been widely published and analyzed in Canada and Europe, and has been applied in the United States (e.g., Dupont et al., 2005), the uncertainty in this estimate is unclear and is likely large. For this reason, an uncertainty analysis of the state-steady critical load model was completed to evaluate the uncertainty in the critical load and exceedances estimations.

A probabilistic analysis using a range of parameter uncertainties was used to assess (1) the degree of confidence in the exceedance values and (2) the coefficient of variation (CV) of the critical load and exceedance values. The probabilistic framework is Monte Carlo, whereby each steady-state input parameter varies according to specified probability distributions and their range of uncertainty (see **Table 4.2-7** in Chapter 4). The purpose of the Monte Carlo methods was to propagate the uncertainty in the model parameters in the steady-state critical load model.

Within the Monte Carlo analysis, model calculations were run a sufficient number of times (i.e. 1,000 times) to capture the range of behaviors represented by all variables. The analysis tabulated the number of lakes where the confidence interval is entirely below the critical load, the confidence interval is entirely above the critical load, and the confidence interval straddles zero. Similar results are given for the number of sites, with all realizations above the

critical load, all realizations below the critical load, and some realizations above and some below the critical load. An inverse cumulative distribution function for exceedances was constructed from the 1000 model runs for each site, which describes the probability of a site to exceed its critical load. For each site, the probability of exceeding its critical load (i.e. probability of exceedance) is determined at the percent of the cumulative frequency distribution that lies above zero. The probability of exceedance, where the percentage of the cumulative frequency distribution lies above zero, was calculated for all sites and assigned to one of the following five classes:

- 0–5% probability: unlikely to be exceeded;
- 5–25% probability: relatively low risk of exceedance;
- 25–75% probability: potential risk of exceedance;
- •5–95% probability: relatively high risk of exceedance;
- >95% probability: highly likely to be exceeded.

This gives us a measure of the degree of confidence in whether the site exceeds its critical load. The CDF for Little Hope Pond is shown in **Figure 4.2-24** in Chapter 4.

The CV was also calculated on each site for both the critical load and exceedance calculations. The CV represents the ratio of the standard deviation to the mean and is a useful statistic for comparing the degree of variation in the data. The CV allows a determination of how much uncertainty (risk) comparison to its mean.

CONCLUSION: There is *fairly high confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for aquatic acidification.

7.1.3 Ecological Effect Function

The ecological effect function, which relates the contribution of atmospheric deposition of NO_x and SO_x to acidification in aquatic ecosystems, is described in detail in Section 4.2.7 of Chapter 4. Briefly, the acid balance of a lake or stream is controlled by acidifying deposition of nitrate, sulfate, watershed processes impacting the level of base cations present, and the sinks for nitrogen and sulfur in the watershed. The biotic integrity of freshwater ecosystems is then a function of the acid-base balance and the resulting acidity-related stress on the biota that occupy the water.

The calculated ANC of surface waters accounts for the inputs of base cations and acid anions, providing an indicator of the overall integrity of the ecosystem. The ANC concentration then provides a link between the surface water acidification and the ecological integrity of the aquatic community where a given level of ANC corresponds to an ecological effect (see **Table 7.1-1**). It also provides a link between the deposition of NO_x and SO_x and the acidification through the input of acid anions of NO_3^- and SO_4^-.

Given some "target" ANC concentration [ANC_{limit}]), which protects biological integrity, the amount of deposition of acid anions (AN) or depositional load (DL(N) + DL(S)) is simply the input flux of acid anions from atmospheric deposition that result in a surface water ANC concentration equal to the [ANC_{limit}] when balanced by the sustainable flux of base cations input and the sinks of nitrogen and sulfur in the lake and watershed catchment. The sustainable flux of base cations input and sinks of nitrogen and sulfur is equal to the uptake (N_{upt}), immobilization (N_{imm}), and denitrification (N_{den}) of nitrogen in the catchment; the in-lake retention of nitrogen (N_{ret}) and sulfur (S_{ret}); and the preindustrial flux of base cations ($[BC]_0^*$) to the watershed. Thus, the amount of deposition that will maintain an ANC level above an ANC_{limit} is described as

$$DL(N) + DL(S) = \{fN_{upt} + (1 - r)(N_{imm} + N_{den}) + (N_{ret} + S_{ret})\} + ([BC]_0^* - [ANC_{limit}])Q \quad (1)$$

where f and r are dimensionless parameters that define the fraction of forest cover in the catchment and the lake/catchment ratio, respectively, and Q is runoff. To convert surface water concentrations into surface water fluxes, multiply by runoff (Q) (in m/yr) from the site. Several major assumptions are made: (1) steady-state conditions exist, (2) the effect of nutrient cycling between plants and soil is ignored, (3) there are no significant nitrogen inputs from sources other than atmospheric deposition, (4) ammonium leaching is negligible because any inputs are either taken up by biota or adsorbed onto soils or nitrate compounds, and (5) long-term sinks of sulfate in the catchment soils are negligible.

It is not possible to define a maximal loading for a single total of acidity (i.e., both nitrogen and sulfur deposition) because the acid anions sulfate and nitrate behave differently in the way they are transported with hydrogen ions; one unit of deposition of sulfur will not have the same net effect on surface water ANC as an equivalent unit of nitrogen deposition. However, the individual maximum and minimum depositional loads for nitrogen and sulfur are defined when nitrogen or sulfur do not contribute to the acidity in the water. As shown in Equation 2, the

maximum depositional load for sulfur ($DL_{max}(S)$) is equal to the amount of sulfur the catchment can remove and still maintain an ANC concentration above the ANC_{limit}:

$$DL_{max}(S) = [([BC]_0^* - [ANC_{level}])Q]/ (1- p_s) \quad (2)$$

when nitrogen deposition does not contribute to the acidity balance and where p_s defines the fraction of in-lake retention of $S_{ret.}$ Given the assumption that the long-term sinks of sulfate in the catchment soils are negligible, the amount of sulfur entering the catchment is equal to the amount loaded to the surface water. For this reason, as shown in Equation 3, the minimal amount of sulfur is equal to zero:

$$DL_{min}(S) = 0 \quad (3)$$

In the case of nitrogen, $DL_{min}(N)$ is the minimum amount of deposition of total nitrogen (NH_x + NO_x) that catchment processes can effectively remove (e.g., $N_{upt} + N_{imm} + N_{den} + N_{ret}$) without contributing to the acidic balance:

$$DL_{min}(N) = fN_{upt} + (1-r)(N_{imm} + N_{den}) \quad (4)$$

The $DL_{max}(N)$ is the load for total nitrogen deposition when sulfur deposition is equal to zero:

$$DL_{max}(N) = fN_{upt} + (1-r)(N_{imm} + N_{den}) + [([BC]_0^* - [ANC_{level}])Q]/ (1-p_n) \quad (5)$$

where p_n defines the fraction of in-lake retention of N_{ret}.

In reality, neither nitrogen nor sulfur deposition will never be zero, so the depositional load for the deposition of one is fixed by the deposition of the other, according to the line defining in **Figure 7.1-6**.

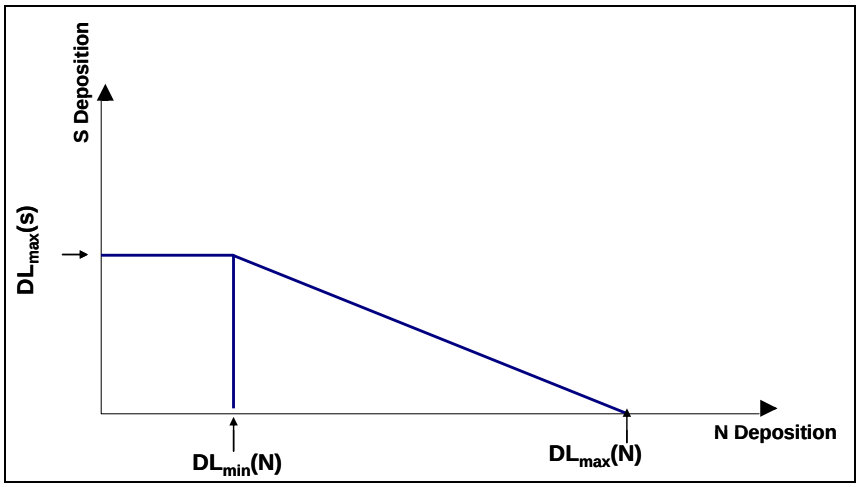

Figure 7.1-6. The depositional load function defined by the model.

The thick lines indicate all possible pairs of depositional loads of nitrogen and sulfur acidity that a catchment can receive and still maintain an ANC concentration equal to its ANC_{limit}. Note that in the above formulation, individual depositional loads of nitrogen and sulfur are not specified; each pair of depositions (S_{dep} and N_{dep}) fulfills Equations 1 through 5.

One important parameter, the preindustrial flux of base cations ($[BC]_0^*$), is difficult to quantify. Present-day surface water concentrations of base cations are elevated above their steady-state preindustrial concentrations because of base cation leaching through ion exchange in the soil due to anthropogenic inputs of SO_4^{2-} to the watershed. For this reason, present-day surface water base cation concentrations are higher than natural or preindustrial levels, which if not corrected for, would result in critical load values not in steady-state condition. Input parameters for this include atmospheric deposition, base cation uptake and retention, and weathering rates. Of these parameters, weathering rates are difficult to obtain on a nationwide basis.

CONCLUSION: There is *high confidence* associated with the ecological effect function developed for aquatic acidification.

7.1.4 Data Gaps and Research Needs

Based on the data and analyses presented in this chapter, Chapter 4, and Appendix 4, several data gaps arise that suggest further research is needed in the following areas:

- Developing relationships between critical loads for aquatic acidity and effects on ecosystem services, especially due to incremental changes in an ecological indicator such as ANC
- Developing nationwide weathering rates, or weathering rates for aquatic ecosystems sensitive to acidification
- Developing a better understanding of the uncertainty in critical loads for acidity and exceedance values
- Developing methods for calculating critical loads for surface water acidity when data are absent or of poor quality
- Evaluating ways to combine multiple critical load estimates for surface waters and soils on a national scale
- Estimating ways to determine critical load parameters across different media (e.g., surface waters, soils).

7.2 TERRESTRIAL ACIDIFICATION

7.2.1 Available Data

A meta-analysis of laboratory studies examining the relationship between base cation to aluminum ratio (Bc/Al) in soil solution and tree growth showed that tree growth was reduced by 20% relative to controls for 46 tree species (native and introduced) in North America (Sverdrup and Warfvringe, 1993). These data are summarized in **Figure 7.2-1**, which indicates that there is a 50% chance of negative tree response (i.e., >20% reduced growth) at a soil solution Bc/Al ratio of 1.2 and a 75% chance at a Bc/Al ratio of 0.6. These findings clearly demonstrate a relationship between Bc/Al ratio and tree health (i.e., as the Bc/Al is reduced, there is a greater likelihood of a negative impact on tree health).

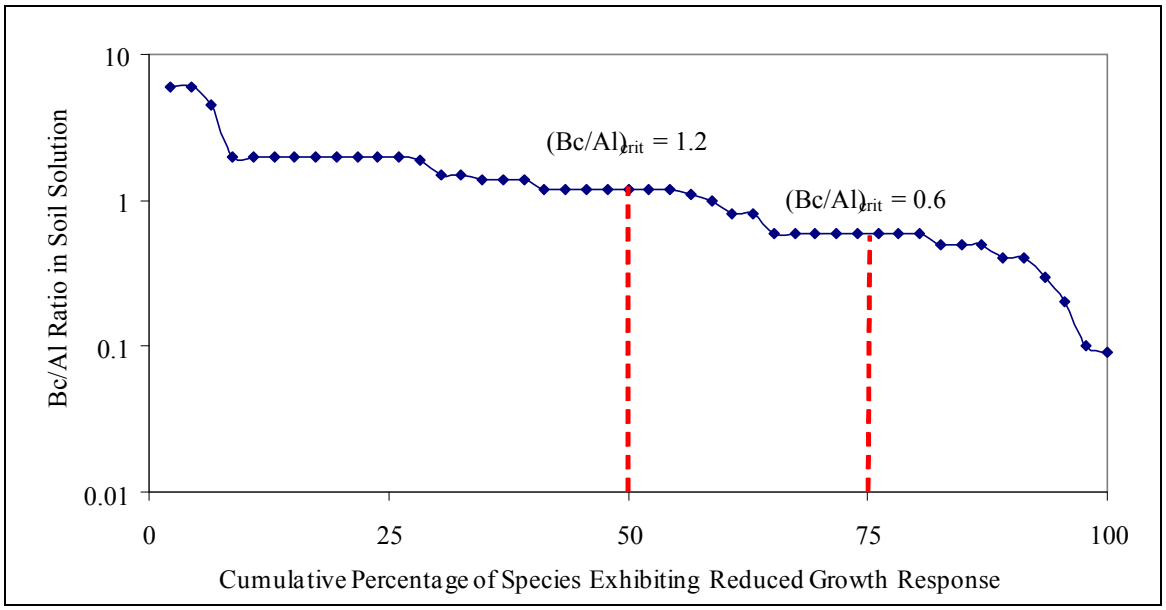

Figure 7.2-1. The relationship between the Bc/Al ratio in soil solution and the percentage of tree species (native and introduced; found growing in North America) exhibiting a 20% reduction in growth relative to controls (after Sverdrup and Warfvinge, 1993).

This review focused on sugar maple and red spruce because they occur in areas that receive high acidifying deposition and are known to be negatively affected by Ca^{2+} depletion and high concentrations of available Al, as measured by Bc/A1 ratios in soils. The ecological effects associated with acidifying deposition are summarized in **Table 7.2-1**. Bc/Al ratios in the soil solution were selected as the indicator to evaluate acidifying deposition loadings in terrestrial systems using the U.S. Forest Service Forest (USFS) Inventory and Analysis (FIA) database as a source of plot locations where sugar maple and/or red spruce are found growing.

Table 7.2-1. Summary of Linkages among Acidifying Deposition, Biogeochemical Processes that Affect Ca^{2+}, Physiological Processes that are Influenced by Ca^{2+}, and the Effect on Forest Function

Biogeochemical Response to Acidifying Deposition	Physiological Response	Effect on Forest Function
Leach Ca^{2+} from leaf membrane	Reduce the cold tolerance of needles in red spruce	Loss of current year needles in red spruce
Reduce the ratio of Ca^{2+}/Al in soil and soil solutions	Dysfunction in fine roots of red spruce blocks uptake of Ca^{2+}	Decreased growth and increased susceptibility to stress in red spruce

Biogeochemical Response to Acidifying Deposition	Physiological Response	Effect on Forest Function
Reduce the ratio of Ca^{2+}/Al in soil and soil solutions	More energy is used to acquire Ca^{2+} in soils with low Ca^{2+}/Al ratios	Decreased growth and increased photosynthetic allocation to red spruce roots
Reduce the availability of nutrient cations in marginal soils	Sugar maples on drought-prone or nutrient-poor soils are less able to withstand stresses	Episodic dieback and growth impairment in sugar maple

Source: Fenn et al., 2006.

Known areas of sensitivity to terrestrial acidification were identified in the *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur–Ecological Criteria (Final Report)* (ISA) (U.S. EPA, 2008), and a significant amount of the research work in the Allegheny Plateau region by the USFS has produced extensive peer-reviewed datasets of soil and tree characteristics (Bailey et al., 2004; Hallett et al., 2006; Horsley et al., 2000). The USFS-designated Kane Experimental Forest (KEF) has been the focus of several long-term studies since the 1930s. The seven plots in the forest with the highest concentrations of sugar maple trees were assessed for this case study of the effects of terrestrial acidification on sugar maple. A review of this information led to the selection of the Hubbard Brook Experimental Forest (HBEF) in New Hampshire's White Mountains as the location to examine the impacts of acidifying deposition on red spruce. This area has experienced high total nitrogen and sulfur deposition levels and low Ca^{2+}/Al soil solution ratios, and HBEF has been the site of extensive nutrient investigations and provided a large data set from which to work on the case study. The case study of the effects of terrestrial acidification on red spruce focused on Watershed 6 in the HBEF.

The analysis was expanded to a larger region based on the USFS FIA database permanent sampling plots' locations on forestland[1] (timberland[2] for New York, Arkansas, Kentucky, and North Carolina), each covering 0.07 ha. Only database information for nonunique[3], permanent

[1] Forestland is defined as, "land at least 10% stocked by forest trees of any size, or formerly having such tree cover, and not currently developed for non-forest uses, with a minimum area classification of 1 acre" (USFS, 2002a).

[2] Timberland is defined as, "forest land capable of producing in excess of 20 cubic feet per acre per year and not legally withdrawn from timber production, with a minimum area classification of 1 acre" (USFS, 2002b).

[3] Nonunique permanent sampling plot locations are those that have critical load attribute values (e.g., soils, runoff, atmospheric deposition) that are not distinct and are repeated within a 250-acre area of the plot location. This "confidentiality" filter is a requirement of the USFS to prevent the disclosure of data that can be directly linked to a location on private land. To comply with the necessary "confidentiality," full coverages of the data required for the critical load deposition calculations were given to the USFS, and the USFS matched and provided the data to each nonunique, permanent sampling plot.

sampling plots that supported the growth of sugar maple or red spruce and had the necessary soil, parent material, atmospheric deposition, and runoff data were included in the analyses. With these restrictions, 7,992 of the 14,669 sugar maple plots and 763 of the 2,875 red spruce plots were included in the analyses. Although only subsets of the plots were included in the analyses, the results are thought to accurately capture the range and trends in the datasets. Due to the randomness of the plot restrictions, it is unlikely that a bias was incorporated into the analyses.

In the analyses of critical loads for the full distribution ranges of sugar maple and red spruce, two fine-scale databases, the Soil Survey Geographic Database (SSURGO) of soils [USDA-NRCS, 2008] and U.S. Geological Survey (USGS) state-level geology [USGS, 2009] databases, were used as the sources for parent material mineralogy to allow for location-specific mineralogy descriptions. Although steps were taken to avoid misclassification, it is possible that parent material in some of the plots may have been misclassified.

CONCLUSION: The available data used to quantify the targeted effect of terrestrial acidification are robust and considered *high quality.* There is *high confidence* about the use of these data and their value for extrapolating to a larger regional population of forests.

7.2.2 Modeling Approach

The Simple Mass Balance (SMB) model, outlined in the International Cooperative Programme (ICP) Mapping and Modeling Manual[4] (UNECE, 2004), was used to evaluate critical loads of acidifying nitrogen and sulfur deposition in the KEF and HBEF case study areas. This model is currently one of the most commonly used approaches to estimate critical loads and has been widely applied in Europe (Sverdrup and de Vries, 1994), the United States (McNulty et al., 2007; Pardo and Duarte, 2007), and Canada (Arp et al., 2001; Ouimet et al., 2006; Watmough et al., 2006). It examines a long-term, steady-state balance of base cation, chloride, and nutrient inputs, "sinks," and outputs within an ecosystem, and base cation equilibrium is assumed to equal the system's critical load for ecological effects. A limitation of the SMB model is that it is a steady-state model and does not capture the cumulative changes in ecosystem conditions. However, as stated by the UNECE (2004), "Since critical loads are steady-state quantities, the use of dynamic models for the sole purpose of deriving critical loads is somewhat

[4] The *ICP Mapping and Modeling Manual* (UNECE, 2004) recommends that wet deposition be corrected for sea salt on sites within 70 km of the coast. Neither the HBEF nor KEF case study areas are located less than 70 km for the coast, so this correction was not used.

inadequate." In addition, if a dynamic model is "used to simulate the transition to a steady state for the comparison with critical loads, care has to be taken that the steady-state version of the dynamic model is compatible with the critical load model" (UNECE, 2004). Therefore, the selection of the SMB model was seen as the most suitable approach for this case study examining critical loads for sugar maple and red spruce.

CONCLUSION: There is *high confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for terrestrial acidification.

7.2.3 Ecological Effect Function

Note: Both the aquatic and terrestrial acidification case study analyses used a critical loads approach to determine impacts from atmospheric deposition to acidity. There are similarities in the approach, although different data sets and assumptions were used.

A component of critical load determinations is the establishment of the critical load function (CLF), or the ecological effect function used for this targeted effect. The CLF expresses the relationship between the critical load and all combinations of total nitrogen and sulfur deposition ($N+S_{comb}$) of an ecosystem. To define the CLF, minimum and maximum amounts of total nitrogen and sulfur deposition that combine to create the critical load must be determined (UNECE, 2004). The maximum amount of sulfur in the critical load ($CL_{max}(S)$) occurs when total nitrogen deposition does not exceed the nitrogen sinks (i.e., nitrogen immobilization, nitrogen uptake and removal by tree harvest, and denitrification) within the ecosystem. These nitrogen sinks are accounted for by the minimum amount of nitrogen in the critical load ($CL_{min}(N)$). Above this $CL_{min}(N)$ level, total nitrogen deposition can no longer be absorbed by the system, and acidification effects can occur. The maximum amount of nitrogen in the critical load ($CL_{max}(N)$) occurs when there is no sulfur deposition, and all of the acidity is due to the deposition of nitrogen.

An example of a CLF is depicted in **Figure 7.2-2.** All combinations of total nitrogen and sulfur deposition that fall on the black line representing the CLF are at the critical load. Any deposition combination that falls below the line or within the grey area is below the critical load. All combinations of nitrogen and sulfur deposition that are located above the line or within the white area are greater than the critical load.

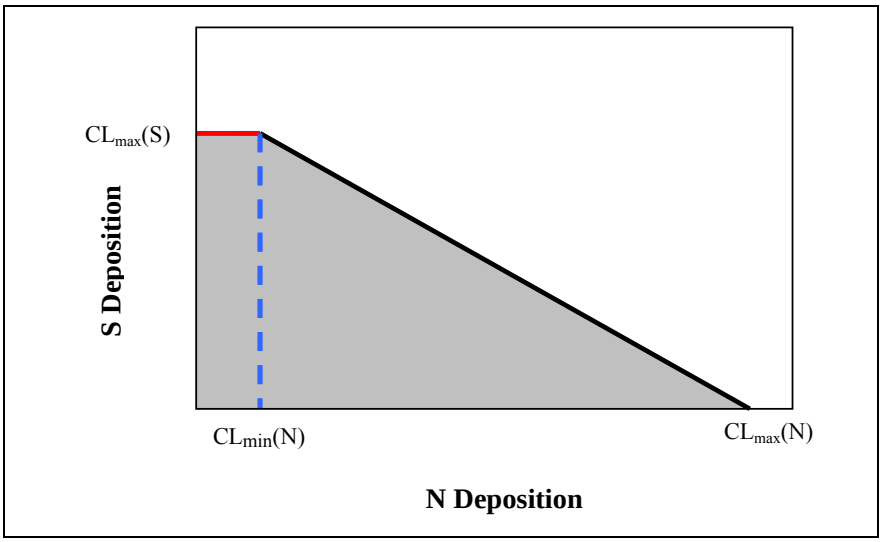

Figure 7.2-2. The critical load function created from the calculated maximum and minimum levels of total nitrogen and sulfur deposition (eq/ha/yr). The grey areas show deposition levels less than the established critical loads. The red line is the maximum amount of total sulfur deposition (valid only when nitrogen deposition is less than the minimum critical level of nitrogen deposition [blue dotted line]) in the critical load. The flat line portion of the curves indicates nitrogen deposition corresponding to the $CL_{min}(N)$ (i.e., nitrogen absorbed by nitrogen sinks within the system).

The majority of the data used to calculate critical loads for sugar maple and red spruce in the KEF and HBEF case study areas were specific to the case study areas and were compiled from published research studies and models, site-specific databases, or spatially-explicit GIS data layers. However, several of the parameters (e.g., denitrification, nitrogen immobilization, the gibbsite equilibrium constant, rooting zone soil depth) required the use of default values or values used in published critical load assessments. These assumptions are described in detail in Section 4.3.4.1 of Chapter 4. Default values were selected based on the literature. As with aquatic acidification, estimating base cation weathering rates is difficult. The clay-substrate method was used for estimating base cation weathering because it one of the most-commonly used methods for estimating this parameter.

As noted previously, it is possible that the parent material acidity—a component of the clay-substrate model to estimate base cation weathering—was misclassified for the critical loads analysis for the full distribution ranges of sugar maple and red spruce. Uncertainties associated with this potential misclassification are largest if and acidic parent material is misclassified as basic (median percent differences 60% to 61% for sugar maple and 71% to74% for red spruce),

compared to a basic parent material being misclassified as intermediate or vice versa (median percent differences 6% to 7% for sugar maple and 4% to5% for red spruce).

CONCLUSION: There is *fairly high confidence* associated with the ecological effect function developed for terrestrial acidification.

7.2.4 Data Gaps and Research Needs

Based on the data and analyses presented in this chapter, Chapter 4, and Appendix 5, several data gaps arise that suggest further research is needed in the following areas:

- Determining the most appropriate and accurate base cation weathering model to estimate terrestrial critical acid loads nationwide
- Expanding analyses to examine the relationships between tree growth and (1) critical load exceedance and (2) nitrogen deposition (i.e., further refine analyses of sugar maple and red spruce and expand analyses to include more tree species and a larger geographical area) to establish additional evidence of the connection between nitrogen and sulfur deposition and biological end points
- Exploring field-based tree growth as a tool to determine the most suitable Bc/Al soil solution indicator ratio
- Developing relationships between critical loads for terrestrial acidity and effects on ecosystem services.

7.3 AQUATIC NITROGEN ENRICHMENT

7.3.1 Available Data

Assessment of the atmospheric contribution to total nitrogen loads in an estuary requires a large-scale modeling approach. Although this assessment took the approach of looking at the main-stem river to an estuary (including the estuary) rather than an entire estuary system or bay, a number of datasets were still required. Five biological indicators were used to develop an assessment of the eutrophication status: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and submerged aquatic vegetation. The National Oceanic and Atmospheric Administration's (NOAA's) Assessment of Estuarine Trophic Status (ASSETS) produces a categorical eutrophication index (EI) that is an estimation of the likelihood that the estuary is experiencing specific discrete levels of eutrophication or will experience

eutrophication in the future based on five biological indicators: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and submerged aquatic vegetation. Taking these factors into consideration, many national databases were evaluated including the USGS's National Water Quality Assessment (NAWQA) program files, EPA's STORage and RETrieval (STORET) database, NOAA's Estuarine Drainage Areas data, and EPA's water quality standards nutrient criteria for rivers and lakes (see Appendix 6, Table 1.2-1).

The analytical approach consisted of a combination of SPAtially Referenced Regression on Watershed Attributes (SPARROW) modeling for nitrogen loads and assessment of estuary conditions under the NOAA ASSETS EI, which is highly scalable. Both components have been applied on a national scale—the national nutrient assessment using SPARROW (Smith and Alexander, 2000) and the NEEA using the ASSETS EI (Bricker et al., 1999, 2007), as well as on smaller scales. The data inputs for the SPARROW model were developed under separate studies and published by USGS, and only quality checks were performed, rather than full data validation. The ASSETS EI requires numerous data inputs and sources, resulting in a large amount of uncertainty associated with the calculations.

CONCLUSION: The available data used for the targeted effect of aquatic nitrogen enrichment are considered *medium quality.* There is *intermediate confidence* about the use of these data and their value for extrapolating to a larger regional area.

7.3.2 Modeling Approach

SPARROW is a watershed modeling technique designed and supported by USGS. The model relies on a nonlinear regression formulation to relate water quality measurements throughout the watershed of interest to attributes of the watershed. Both point and diffuse sources within the watershed are considered, along with non-conservative transport processes (i.e., loss and storage of contaminants within the watershed). SPARROW follows the rules of mass balance while using a hybrid statistical and process-based approach. SPARROW is a statistical model and provides measures of statistical uncertainty in model coefficient and water quality predictions. Utilization of the SPARROW model results in estimates of long-term, steady-state water quality in a stream. It uses a spatially distributed model structure based on a defined stream network allowing separate statistical estimations of land and water parameters that quantify the rates of pollutant delivery from sources to streams and the transport of pollutants to downstream locations within the stream network (i.e., reaches, reservoirs, and

estuaries) (Schwarz et al., 2006). The model is calibrated at each available monitoring station by comparing the modeled loads (i.e., a total of loads from each watershed segment and any upstream loads from previous calibrations) against monitored data at the station.

The link between the SPARROW model and the ASSETS EI occurs when the SPARROW output is used as the nitrogen load in the overall human influence index calculation of the ASSETS EI score. For the purposes of this study, a complete analysis from atmospheric deposition loading to ecological endpoint of the ASSETS EI score required an assessment of the relative changes in the deposition load, the resulting in-stream nitrogen load to the estuary, and the change in ASSETS EI score. An iterative assessment of the various possible ecological endpoints due to changing nitrogen loads has not been previously undertaken. A detailed listing of the uncertainties associated with predictive modeling and the use of a multi-indicator assessment tool are described in Section 5.2.8 of Chapter 5 and Section 5 of Appendix 6. These include data inputs to both SPARROW and ASSETS, uncertainty and sensitivity of SPARROW modeling to atmospheric inputs, heuristic estimates used in ASSETS, missing ranking in ASSETS scores, uncertainty ranges used, and the crossing of a categorical ranking system with a continuous nitrogen concentration scale.

CONCLUSION: There is *intermediate confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study analysis for excess aquatic nitrogen enrichment.

7.3.3 Ecological Effect Function

The relationship between atmospheric deposition and shifts in the ASSETS index values were assessed by applying percent decreases to the oxidized nitrogen loads in the estimated total nitrogen atmospheric deposition. The SPARROW model output for the 2002 current condition analysis was used to determine how the changing atmospheric inputs affected the overall total nitrogen load to the estuary of interest. These results were used to create the response curve relating instream total nitrogen concentrations to atmospheric deposition loads. A second response curve was defined for the alternative effects level analysis using historical data compilations of overall eutrophic condition scores and instream total nitrogen concentrations while holding the susceptibility portion of the overall human influence and the determined future outlook rankings constant. Then a “back--calculation” procedure was applied to the curves with

the intent of defining the atmospheric loads that are needed to improve the ASSETS EI from the current score of *Bad* (1) to *Poor* (2), *Moderate* (3), *Good* (4), or *High* (5).

The results of this analysis indicated reductions in atmospheric deposition alone could not solve coastal eutrophication problems due to multiple non-atmospheric nitrogen inputs, leading to questions and concerns regarding the utility of this approach in areas not dominated by atmospheric deposition and the appropriateness of the selected ecological indicator.

CONCLUSION: There is *low confidence* associated with the ecological effect function developed for excess aquatic nitrogen enrichment.

Note: In addition to the case studies for the Potomac and Neuse River estuaries, the ISA (U.S. EPA, 2008) presents scientific studies that show that increased atmospheric nitrogen deposition in high alpine lakes and streams can cause a shift in community composition and reduce algal biodiversity. Elevated nitrogen deposition results in changes in algal species composition, especially in sensitive oligotrophic lakes. Two opportunistic diatom species, *Asterionella formosa* and *Fragilaria crotonensi* (McKnight et al., 1990; Lafrancois et al., 2004; Saros, 2005) now dominate the flora of at least several alpine and montane Rocky Mountain lakes, with similar field data showing shifts in dominant algal species in other parts of the western United States. A hindcasting exercise has concluded that the change that occurred in Rocky Mountain National Park lake algae between 1850 and 1964 was associated with an increase of only about 1.5 kg N/ha in wet nitrogen deposition (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred in about 1.5 kg N/ha deposition (Saros et al., 2003). A strong relationship exists between excess aquatic nitrogen enrichment of high alpine lakes in the Rocky Mountains and atmospheric deposition because atmospheric deposition is the only source of nitrogen to these systems.

7.3.4 Data Gaps and Research Needs

Based on the data and analyses presented in this chapter, Chapter 5, and Appendix 6, several data gaps arise that suggest further research is needed in the following areas:

- Refining development of adequate indicators of effects of nitrogen enrichment
- Enhancing relationships between ecological indicators of nitrogen enrichment and atmospheric deposition used in this study

- Applying the methods used in this study to an atmospheric deposition-dominated estuarine system
- Reducing model and data uncertainty
- Expanding relationships between ecological indicators of nitrogen enrichment and ecosystem services associated with them
- Exploring alternative relationships between ecological indicators and atmospheric deposition other than what was used in this study giving consideration to methods that can be extrapolated outside of the case study area
- Improving knowledge of how individual chemical species of nitrogen contribute to eutrophication effects.

7.4 TERRESTRIAL NITROGEN ENRICHMENT

7.4.1 Available Data

For terrestrial nitrogen enrichment, there is a substantial amount of empirical evidence indicating that ecological alterations are occurring due to atmospheric deposition nationwide. The assessment of ecological effects due to terrestrial nitrogen enrichment was based on a weight-of-evidence approach that used the current scientific literature to determine benchmark values for ecological effects attributable to atmospheric nitrogen deposition in sensitive southern California coastal sage scrub (CSS) and mixed conifer forest (MCF) communities in the Sierra Nevada and San Bernardino mountains of California (see Section 7.4.1-1). This approach does not develop a separate ecological effect function relating atmospheric deposition to an ecological indicator.

There are sufficient data to relate an ecological effect to atmospheric nitrogen deposition. For the CSS community, the following ecological thresholds were identified:

- 3.3 kg N/ha/yr — the amount of nitrogen uptake by a vigorous stand of CSS; above this level, nitrogen may no longer be limiting
- 10 kg N/ha/yr — mycorrhizal community changes, CSS decline.

Fire is also an inextricable and significant component in CSS losses. Although CSS communities are fire resilient, nonnative grass seeds are quick to establish in burned lands, decreasing the water and nutrient amounts available to CSS for reestablishment (Keeler-Wolf,

1995). Additionally, when annual grasses have established dominance, these species alter and increase the fire frequency as they senesce earlier in the annual season, which increases dry, ignitable fuel availability (Keeley et al., 2005). With increased fire frequencies and faster nonnative colonizations, CSS seed banks are eventually eradicated from the soil, and the probability of reestablishment decreases significantly (Keeley et al., 2005).

For the MCF community in the Pacific Coast states, the following ecological thresholds were identified:

- 3.1 kg N/ha/yr — shift from sensitive to tolerant lichen species
- 5.2 kg N/ha/yr — dominance of the tolerant lichen species
- 10.2 kg N/ha/yr — loss of sensitive lichen species
- 17 kg N/ha/yr — leaching of NO_3^- into streams.

At the highest levels of atmospheric nitrogen deposition, native understory species were seen to decline (Allen et al., 2007). In addition to the decline in native understory diversity, changes in decreased fine-root mass, increased needle turnover, and the associated chemostructural alterations, MCF exposed to elevated pollutant levels have an increasing susceptibility to drought and beetle attack (Grulke et al., 1998, 2001; Takemoto et al., 2001). These stressors often result in the death of trees, producing an increased risk of wildfires. In addition to the documented signs of nitrogen saturation, it is interesting to note that both CSS and the MCF ecosystems had responses in epiphytic associations, as well as increased susceptibility to wildfire and invasion of exotic species.

Note that the effects of ozone and atmospheric nitrogen are difficult to separate, and lichen may be reacting to ozone effects and effects due to climate change.

The deposition loads used are presented in **Figure 7.4-1.**

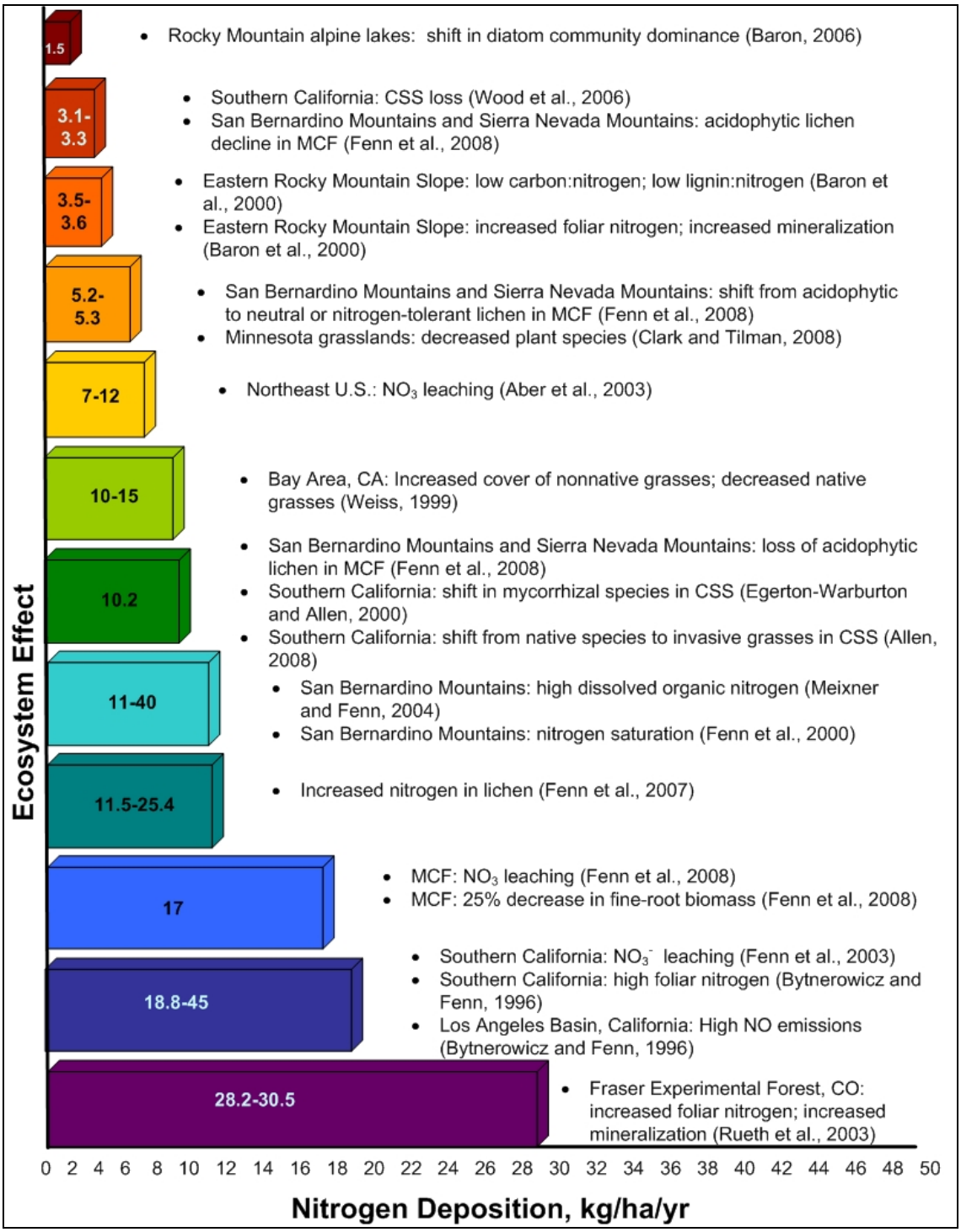

Figure 7.4-1. Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators with the inclusion of the diatom changes in the Rocky Mountain lakes

CONCLUSION: The available data used for the targeted effect of terrestrial nitrogen enrichment are considered *high quality;* however, there is a limited ability to extrapolate these data to a larger regional area.

7.4.2 Modeling Approach

As shown in **Figure 7.4-1**, a number of significant ecological endpoints have been identified. These results come from empirical results and from spatial databases. Dose/response relationships beyond benchmark values were investigated, but these have not yet been well quantified. Nitrogen deposition data was available at a 12-km resolution, and many of the ecosystems, especially CSS, are fragmented into smaller areas. The analysis was, therefore, somewhat limited by the discrepancy between resolution of the nitrogen deposition data and the distribution of habitats, as well as by the specific areas where ecological processes were measured. Further, some models have been tested, but with limited results. For example, the steady-state simple mass-balance model (UNECE, 2004) still has many unresolved uncertainties. Uncertainty exists in establishing the linkage between soil and biological impacts and the ability to account for forest management and wildfires (Fenn et al., 2008). The DayCent biogeochemical model is not a watershed-scale model and may not represent NO_3^- leaching accurately. However, application of DayCent yielded results more comparable to empirically based findings than the steady-state model (Fenn et al., 2008).

For these reasons, empirical data, in tandem with GIS analysis, were deemed more suitable to develop potential correlations between atmospheric nitrogen deposition and ecological endpoints. There is no response curve associated with the atmospheric nitrogen deposition loads for the observed ecological effects. As such, the endpoint cannot be shifted and associated with another response (as in the ANC response curve shown in **Figure 7.1-1**). In addition, while the data may be high quality for lichen, they may not have quantitative value for evaluating the response for other species or species in other regions of the United States. For these reasons, other than the spatial analysis of quantitative values of nitrogen effects and sensitivity, no additional modeling approaches were undertaken for this assessment.

CONCLUSION: No quantitative modeling was conducted for terrestrial nitrogen enrichment.

7.4.3 Ecological Effect Function

There are many factors that determine whether or not an ecological effect occurs in response to ambient concentrations of NO_x and SO_x. These may be ecological or atmospheric factors, both of which influence deposition or exposure and the subsequent ecological effects (i.e., acidification or nutrient enrichment). In the excess Terrestrial Nutrient Enrichment case

study, establishing a quantitative linkage between a given ecological indicator and deposition, as influenced by the variable ecological factors, was not addressed because deposition was used—rather than a traditional environmental indicator—as the direct metric for ecological response.

CONCLUSION: No ecological effect function was developed for excess terrestrial nitrogen enrichment.

7.4.4 Data Gaps and Research Needs

Based on the data and analyses presented in this chapter, Chapter 5 and Appendix 7, several data gaps arise that suggest further research is needed in the following areas:

- Elucidating the interactions among elevated levels of atmospheric nitrogen, fire intensity and frequency, and invasive grasses for CSS and elevated nitrogen and fire for MCF
- Increasing the understanding of CSS and MCF communities long-term response to elevated nitrogen and how benchmarks may change
- Developing indicators of CSS ecosystem health
- Using modeled data with a higher spatial resolution
- Increasing the understanding of the interactions between ozone, climate change and nitrogen deposition on CSS and MCF communities.

7.5 CONCLUSIONS

Although it is recognized that while there will always be inherent variability in ecological data and uncertainties associated with modeling approaches, there is a high level of confidence from a scientific perspective that known or anticipated adverse ecological effects are occurring under current ambient loadings of nitrogen and sulfur in sensitive ecosystems across the United States.

For aquatic and terrestrial acidification effects, a similar conceptual approach was used (critical loads) to evaluate the impacts of multiple pollutants on an ecological endpoint (compare **Figures 7.1-6 and 7.2-2**), whereas the approaches used for aquatic and terrestrial nutrient enrichment were fundamentally distinct. Although the ecological indicators for aquatic and terrestrial acidification (i.e., ANC and Bc/Al) are very different, both ecological indicators are well-correlated with effects such as reduced biodiversity and growth. While aquatic acidification is clearly the targeted effect area with the highest level of confidence (see **Table 7.5-1**), the relationship between atmospheric deposition and an ecological indicator is also quite strong for

terrestrial acidification. The main drawback with the understanding of terrestrial acidification is that the data are based on laboratory responses rather than field measurements. Other stressors that are present in the field but not present in the laboratory may confound this relationship.

The ecological indicator chosen for aquatic nutrient enrichment, the ASSETS EI, seems to be inadequate to relate atmospheric deposition to the targeted ecological effect, likely due to the many other confounding factors. Further, there is far less confidence associated with the understanding of aquatic nutrient enrichment because of the large contributions from non-atmospheric sources of nitrogen and the influence of both oxidized and reduced forms of nitrogen, particularly in large watersheds and coastal areas. However, a strong relationship exists between atmospheric deposition of nitrogen and ecological effects in high alpine lakes in the Rocky Mountains because atmospheric deposition is the only source of nitrogen to these systems. There is also a strong weight-of-evidence regarding the relationships between ecological effects attributable to terrestrial nitrogen nutrient enrichment; however, ozone and climate change may be confounding factors. In addition, the response for other species or species in other regions of the United States has not been quantified.

Table 7.5-1. Summary of the Levels of Confidence Associated with the Available Data, Modeling Approach, and the Relationship between the Selected Ecological Indicator and Atmospheric Deposition as Described by the Ecological Effect Function for Each Targeted Effect Area Considered in this Review

	Available Data	**Modeling Approach**	**Ecological Effect Function**
Aquatic Acidification	High quality	Fairly high confidence	High confidence
Terrestrial Acidification	High quality	High confidence	Fairly high confidence
Excess Aquatic Nitrogen Enrichment	Medium quality	Intermediate confidence	Low confidence
Excess Terrestrial Nitrogen Enrichment	High quality, limited ability to extrapolate	None	None

A summary of the information presented by this Risk and Exposure Assessment that may be useful for characterizing known or anticipated adverse effects to public welfare is shown in **Table 7.5-2**. This information may be useful to inform decision makers about what levels of

protection might be appropriate to protect public welfare from known or anticipated adverse impacts on ecosystems. Characterizing known or anticipated adverse effects to public welfare from a policy perspective will be addressed in the policy assessment for this review.

Table 7.5-2. Summary of Information Assessed in the Risk and Exposure Assessment to Aid in Informing Policy Based on Welfare Effects

Exposure Pathway (Current Deposition Levels) (NADP/CMAQ, 2002)	Affected Ecosystem (Case Study Areas)	Ecological Response (Targeted Effect)	Ecological Indicator	Ecological Effect	Ecosystem Service Affected
Adirondack Case Study Area: 10 kg N/ha/yr 9 kg S/ha/yr Shenandoah Case Study Area: 11 kg N/ha/yr 11 kg S/ha/yr	Adirondack Mountains, NY Blue Ridge Mountains and Shenandoah National Park, VA	Acidification in lakes and streams	Fish species richness, abundance, composition, ANC	Species losses of fish, phytoplankton, zooplankton; changed community composition, ecosystem structure, and function	Annual recreational freshwater fishing in New York State = more than 13 million days Approximately $66.4 million in implied value to NY anglers from a zero- out of nitrogen and sulfur deposition
Kane Experimental Forest Case Study Area: 14 kg N/ha/yr 210 kg S/ha/yr Hubbard Brook Experimental Forest Case Study Area: 8 kg N/ha/yr 7 kg S/ha/yr	Kane Experimental Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)	Acidification of forest soils	Tree health Red spruce, sugar maple Bc/Al ratio	Decreased tree growth Increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure, and function	Provision of wood products (sugar maple) 900 million board feet timber production

Exposure Pathway (Current Deposition Levels) (NADP/CMAQ, 2002)	Affected Ecosystem (Case Study Areas)	Ecological Response (Targeted Effect)	Ecological Indicator	Ecological Effect	Ecosystem Service Affected
Potomac River/Potomac Estuary Case Study Area: 13 kg N/ha/yr Neuse River/Neuse River Estuary Case Study Area: 14 Kg N/ha/yr	Potomac River Basin, Chesapeake Bay Neuse River Basin, Pamlico Sound	Nutrient enrichment in main stem river of an estuary	ASSETS EI	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Current saltwater recreational fishing 26.1 million activity days (North Carolina-Massachusetts)
Coastal Sage Scrub from 3 to 10 kg N/ha/yr Mixed Conifer Forest (San Bernardino Mountains and Sierra Nevada Range): from 3 to 10 kg N/ha/yr	Southern California Coastal Sage Scrub Mixed Conifer Forest (San Bernardino Mountains and Sierra Nevada Mountains, CA)	Nutrient enrichment in terrestrial ecosystems	Species composition	Species changes, nutrient enrichment of soil, changes in fire regime, changes in nutrient cycling	Annual benefits to California residents hunting, fishing, and wildlife viewing = approximately $4.6 billion; state expenditures for fire suppression = $300 million (2008)

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