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

First Draft, Chapters 1–6

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

FIRST DRAFT, CHAPTERS 1–6

U.S. Environmental Protection Agency
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DISCLAIMER

This draft document has been prepared by staff from the Health and Environmental Impacts and Air Quality Analysis Divisions of the Office of Air Quality Planning and Standards, and the Clean Air Markets Division, Office of Air Programs, U.S. Environmental Protection Agency. Any opinions, findings, conclusions, or recommendations are those of the authors and do not necessarily reflect the views of EPA. This document is being circulated to obtain review and comment from the Clean Air Scientific Advisory Committee (CASAC) and the general public. Comments on this draft document should be addressed to Dr. Anne Rea, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, C539-02, Research Triangle Park, North Carolina 27711 (email: rea.anne@epa.gov).

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ACRONYMS AND ABBREVIATIONS

ADR	Adirondack Mountains of New York
ANC	acid neutralizing capacity
AQCD	Air Quality Criteria Document
CAA	Clean Air Act
CAFO	confined animal feeding operation
CAIR	Clean Air Interstate Rule
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network
CH_4	methane
CMAQ	Community Multiscale Air Quality model.
CO_2	carbon dioxide
CSS	coastal sage scrub
DIN	dissolved inorganic nitrogen
DOI	U.S. Department of Interior
EGU	Electric Generating Units
EPA	U.S. Environmental Protection Agency
FIA	Forest Inventory and Analysis National Program
GHG	greenhouse gases
GIS	geographic information systems
GPP	gross primary productivity
H_2O	water vapor
H_2SO_4	sulfuric acid
ha	hectare
HFC	hydrofluorocarbon
Hg^{+2}	reactive mercury
Hg^0	elemental mercury
HNO_3	nitric acid
HONO	nitrous acid
HUC	hydrologic unit code
IDW	inverse distance weighted
IPM	Integrated Planning Model
ISA	Integrated Science Assessment
km	kilometer
LTER	Long Term Ecological Monitoring and Research
MEA	Millennium Ecosystem Assessment
$(NH_4)_2SO_4$	ammonium sulfate
N_2	gaseous nitrogen
N_2O	nitrous oxide
N_2O_3	nitrogen trioxide
N_2O_4	nitrogen tetroxide
N_2O_5	dinitrogen pentoxide
NAAQS	National Ambient Air Quality Standards

NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NEI	National Emissions Inventory
NEP	net ecosystem productivity
NH_3	ammonia gas
NH_4^+	ammonium ion
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	reduced nitrite
NO_3^-	reduced nitrate
NO_x	nitrogen oxides
NO_y	total oxidized nitrogen
NPP	net primary productivity
NRC	National Research Council
NTN	National Trends Network
NTR	organic nitrate
O_3	ozone
OAQPS	Office of Air Quality Planning and Standards
PAN	peroxyacyl nitrates
PFC	perfluorocarbons
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
REA	Risk and Exposure Assessment
RSM	response-surface model
S_2O_3	thiosulfate
S_2O_7	heptoxide
SAV	submerged aquatic vegetation
SF_6	sulfur hexafluoride
SO	sulfur monoxide
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_4	wet sulfate
SOM	soil organic matter
SO_x	sulfur oxides
SRB	sulfate-reducing bacteria
TP	total phosphorus
USGS	U.S. Geological Survey
VOC	volatile organic carbon
$\mu g/m^3$	micrograms per cubic meter

KEY TERMS

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., $PM_{2.5}$, NO_2, SO_2) occurring in the ambient air for which the National Ambient Air Quality Standards 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.

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.

Arid Region: A land region of low rainfall, where "low" is widely accepted to be less than 250 mm 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.

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%–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 oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N_2O or N_2) by denitrifying bacteria.

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

Ecological Dose: The concentration of a toxicant that inhibits a microbe-mediated ecological process by a designated percentage; for example, ED50 inhibits 50%.

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 human health and/or 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.

Ecosystem Services: The ecological processes or functions having monetary or non-monetary 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.

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), nitrous oxide (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 (HFCs), and perfluorocarbons (PFCs).

Key Elements of a Secondary National Ambient Air Quality Standard

(a) Indicator

(1) Atmospheric indicator (for a secondary NAAQS): The air pollutant(s) whose concentration(s) in the ambient air is (are) measured for purposes of determining compliance with the standard. This 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 oxides of

nitrogen, while the current indicator for the primary and secondary SO_x NAAQS is SO_2, representing all oxides of sulfur.

(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). As a result, a reduction in ANC can lead to acidification of stream water and thereby changes to fish community structure, a good indicator of overall stream health.

(b) Level (of a 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 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 a 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 a 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.

Nitrogen 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.

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

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

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

Sensitivity: The degree to which a system is affected, either adversely or beneficially, by an effect of NO_x and/or SO_x pollution (e.g., acidification, 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. This 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: This includes all biologically, chemically, and radiatively active nitrogen compounds in the atmosphere and biosphere, such as NH_3, NH_4^+, NO, NO_2, HNO_3, N_2O, NO_3^-, and organic compounds (e.g., urea, amines, nucleic acids).

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

Variable Factors: Influences which by themselves or in combination with other factors may alter the effects on public welfare of an air pollutant (section 108 (a)(2))

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

(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, man-made materials, animals, wildlife, weather, visibility, and climate; as well as damage to and deterioration of property, hazards to transportation, and the 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 precipitation.

1. INTRODUCTION

1.1 RATIONALE AND BACKGROUND FOR JOINT REVIEW

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), 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, 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 below in Section 1.2, EPA has historically defined the NAAQS for these pollutants in terms of the specific compounds NO_2 and SO_2, which serve as the indicators of the broader set of compounds that comprise NO_x and SO_x, respectively. The 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 below in Section 1.3. A joint review of these pollutants is being conducted because NO_x, SO_x, and their associated transformation products are linked from an atmospheric chemistry perspective, as well as from an environmental effects perspective, 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

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

since NAAQS were established in 1971 that a joint review of these two pollutants has been conducted. There is a strong basis for considering these pollutants together at this time, 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 policy-relevant questions that help to frame this review are presented below in Section 1.4, 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 in an ecologically meaningful way.

As discussed in the Act (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. An adverse public welfare effect from a policy perspective may not be the same as an adverse ecological effect from a scientific perspective. While adversity to ecological systems from a scientific perspective will be used to inform the Administrator's decision, the degree of change in an ecological indicator that corresponds to an adverse public welfare effect is ultimately decided by the Administrator. For example, levels of acid neutralizing capacity (ANC) below 100 may be a useful scientific indicator of ecological adversity for an array of ecological endpoints of concern. By considering this complete array of information on impacts, the Administrator makes the final determination on the specific level of ANC that will protect the public welfare from any known or anticipated adverse effects. Adverse public welfare effects are based on an assessment of how ecologically adverse impacts translate into adverse impacts on the public welfare. Adversity is not explicitly defined in the CAA: however, it can be inferred that adverse ecological impacts must have some corresponding impact on the well-being of human populations, through reductions in ecosystems services that might include direct services to humans (e.g., flood control) or indirect services (e.g., provision of habitat for endangered species).

This joint review is organized according to the Agency's current NAAQS review process, which consists of four major components and related documents: an Integrated Review Plan, an Integrated Science Assessment (ISA), a Risk and Exposure Assessment (REA), and a policy assessment and rulemaking notices. The Integrated Review Plan (EPA, 2007) provides the framework and schedule for this review and identifies policy-relevant questions to be addressed in the other components of the review. The second draft ISA (EPA, 2008), released for CASAC

and public review on August 11, 2008, provides an integrative assessment of the relevant scientific information and forms the scientific basis for the assessments presented in this draft REA document. This first draft REA 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, draft ISA), see http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html.

This risk and exposure assessment, when complete, 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, we will characterize the contributions of various sources and forms of atmospheric nitrogen to these risks. The final risk and exposure assessment will be organized as follows (See Attachment 1 for a more detailed working outline), which, to the degree possible, is also reflected in this document:

- **Chapter 1** provides an overview of this review; a history of past reviews and other relevant scientific assessments and Agency actions; a discussion of the scope of this joint NO_x and SO_x review; and a series of policy-relevant 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 case study locations, initial progress on identifying ecosystem services, and a discussion on addressing uncertainly 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 the 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.
- **Chapter 4** focuses on acidification, with an overview of the relevant science and progress on assessing current conditions in select case study locations for both aquatic and terrestrial acidification. (Note: For this draft, this information is included in Attachments 2, 3, and 4)

- **Chapter 5** focuses on nitrogen nutrient enrichment, with an overview of the relevant science and progress on assessing current conditions in select case study locations for both aquatic and terrestrial nitrogen nutrient enrichment. (Note: For this draft, this information is included in Attachments 2, 5, and 6)
- **Chapter 6** addresses additional effects, including a qualitative discussion on the interactions between sulfur and methylmercury production; nitrous oxide; and carbon sequestration.
- **Chapter 7** synthesizes the case study results and presents them in the context of a scientific structure that links fundamental scientific elements needed for a secondary standard based on a suite of ecological indicators.
- **Chapter 8** explores more specifically how a secondary NAAQS might be structured to address the targeted ecological effects discussed in the risk assessment.
- **Chapter 9** includes a brief list of ongoing analyses for the second draft of this risk assessment.

Due to the very tight schedule under which this review is being conducted, some of the analyses we anticipated for this first draft risk and exposure assessment are as yet incomplete. Currently, the case study analyses have been initiated, but not completed. Our progress on identifying sensitive areas for each targeted effect and the case study analyses are included as Attachments 2 through 6. As the analyses progress, summaries of the case study analyses will be presented in Chapters 4 and 5 of the second draft risk and exposure assessment. This first draft also includes in Chapter 9 a brief list of ongoing analyses to be presented in the second draft risk and exposure assessment. Please note that Chapters 7 and 8 are not available for public review at this time. We anticipate that, if available, Chapters 7 and 8 will be released no later than the week of September 15, 2008. Otherwise, they will be included in the second draft risk and exposure assessment. The second draft of this document will also describe the assessment of risks and exposures associated with just meeting potential alternative standards.

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 *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 air quality criteria (52 FR 27580). In November 1991, EPA released an updated draft air quality criteria document for CASAC and public review and comment (56 FR 59285). The draft document provided a comprehensive assessment of the available scientific and technical information on health and welfare effects associated with NO_2 and other oxides of nitrogen. 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 Air Quality Criteria Document (AQCD) for the 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 air quality criteria document 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 of 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, 1995).

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 SO_x criteria document (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 *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 have 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 SO_x concentrations and effects needed for setting a standard (38 FR 25679).

In 1979, EPA announced that it was revising the Air Quality Criteria Document (AQCD) for sulfur oxides concurrently with that for particulate matter and would produce a combined particulate matter and sulfur oxides criteria document. Following its review of a draft revised criteria document in August 1980, CASAC concluded that acid deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (1) emissions of relevant pollutants (e.g., SO_2 and oxides of nitrogen), (2) formation of acidic wet and dry deposition products, and (3) effects on terrestrial and aquatic ecosystems. CASAC also noted that acid deposition involves, at a minimum, several different

criteria pollutants: oxides of sulfur, oxides of nitrogen, and the fine particulate fraction of suspended particles. CASAC felt that any document on this subject should address both wet and dry deposition, since dry deposition was believed to account for at least one half of the total acid deposition problem.

For these reasons, CASAC recommended that a separate, comprehensive document on acid deposition be prepared prior to any consideration of using the NAAQS as a regulatory mechanism for the control of acid deposition. CASAC also suggested that a discussion of acid deposition be included in the AQCDs for nitrogen oxides and 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 acid 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). These documents, though they were not considered criteria documents and did not undergo CASAC review, represented the most comprehensive summary of relevant scientific information completed by EPA at that point.

On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and secondary standards. This proposal regarding the secondary SO_2 NAAQS was due to the Administrator's conclusions that (1) based upon the then-current scientific understanding of the acid 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, the Congress created the National Acid Precipitation Assessment Program (NAPAP) in response to growing public concern about acidic deposition. The NAPAP was given a broad 10-year mandate to examine the causes and effects of acidic deposition and to explore alternative control options to alleviate acidic 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 acid deposition problem, it soon became clear that a program to address acid 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 acid deposition problem that reflect a comprehensive approach envisioned by Congress. The primary and most important of the provisions, Title IV of these Amendments, established the Acid Rain Program to reduce emissions of SO_2 by 10 million tons and NO_x emissions by 2 million tons from 1980 emission levels in order 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 acid 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 in order 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 (Clean Air Act Amendments of 1990, Pub. L. 101-549, § 404) requiring EPA to conduct a study on the feasibility and effectiveness of an acid 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, EPA submitted its report, entitled *Acid Deposition Standard Feasibility Study: Report to Congress* (U.S. EPA, 1995) in fulfillment of this requirement. The Report concluded that establishing acid 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 that time.

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." That change has particular relevance to this 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 tropospheric ozone and stratospheric ozone depletion.

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 in order 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; visibility impairment; and foliar injury from ozone.

In a Federal Register notice in 2001, EPA announced receipt of these requests and asked for comment on the issues raised in them. 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 these requests for rulemaking (65 FR 48699).

The most recent 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 NAPAP's above, 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 acidic 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 Analyses

The sum of mono-nitrogen oxides, NO_2 and NO, typically are referred to as nitrogen oxides (NO_x) in the atmospheric science community. More formally, the family of nitrogen oxides includes any gaseous combination of nitrogen and oxygen, e.g., NO_2, NO, nitrogen dioxide (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 terms "oxides of nitrogen" and "nitrogen oxides" refer to all forms of oxidized nitrogen compounds, including nitric oxide (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."

By contrast, within the scientific community, the terms "oxides of nitrogen" and "nitrogen oxides" typically refer only to the mono-nitrogen oxides, NO and NO_2, and their sum is commonly abbreviated as NO_x. 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, as well as gaseous and particulate nitrate species such as nitric acid (HNO_3), peroxyacyl nitrates (PAN), and particle-phase ammonium nitrates.

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 gas (NH_3) and ammonium ion (NH_4^+), the sum of which is referred to as 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 (gas and particulate phases) or as wet (precipitation-derived ion phase) (see **Figure 1.3-1**).

In many areas, multiple forms of nitrogen from a variety of atmospheric and other sources enter ecosystems. The scientific community has long recognized that reactive nitrogen can impact ecosystems; it is the total amount of reactive nitrogen entering the ecosystem that is most relevant when assessing these impacts. That is, 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 reactive nitrogen inputs to the ecosystem.

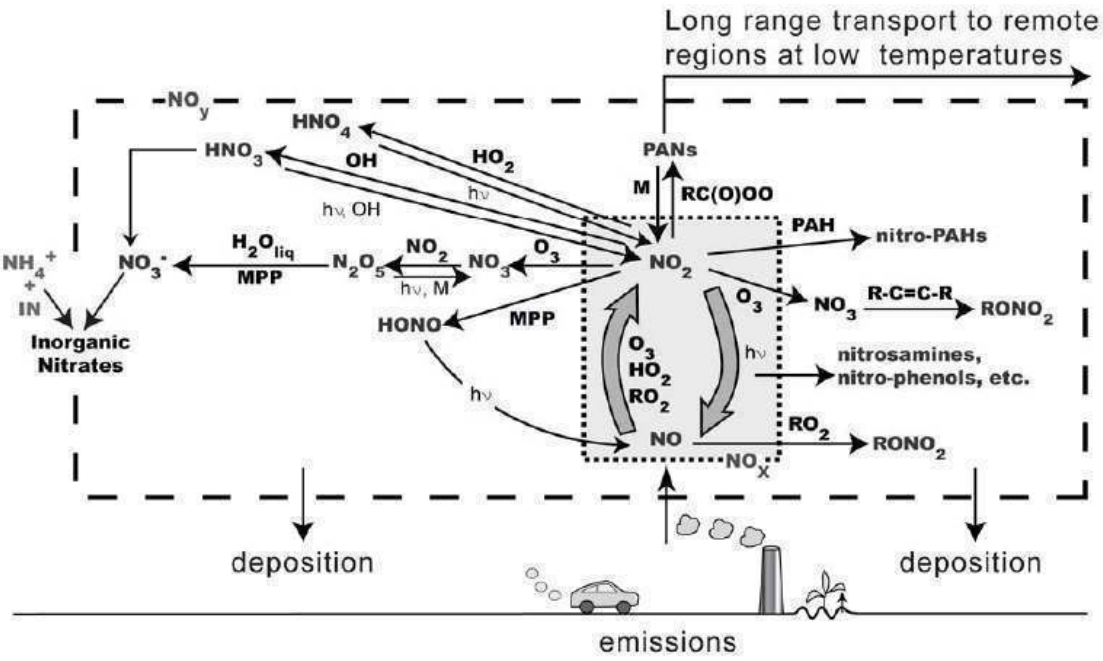

Figure 1.3-1. Schematic diagram of the cycle of reactive, oxidized nitrogen species in the atmosphere. (IN refers to inorganic particulate species [e.g., Na^{+},Ca^{++}], MPP to multiphase processes, hv to a solar photon, and R to an organic radical. Particulate-phase organic nitrates are also formed from the species on the right side of the figure) (U.S. EPA, 2007.)

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 (e.g., SO_2, sulfur monoxide [SO], sulfur trioxide [SO_3], thiosulfate (S_2O_3),heptoxide (S_2O_7), and particulate (e.g., ammonium sulfate $(NH_4)_2SO_4$) species (**Figure 1.3-2**). Acidification can result from the atmospheric deposition of SO_x and NO_x; in acid deposition, these species combine with water in the atmosphere to form sulfuric acid (H_2SO_4) and HNO_3. Acidification is an environmental effect primarily due to sulfur in which acid precipitation lowers the natural pH of waterbodies and damages terrestrial ecosystems. Over the past few decades, acidification of waterbodies has been recognized as an environmental issue throughout Europe and North America, and steps have been taken to control SO_x and NO_x emissions and to identify the recovery of the impacted ecosystems. Due to known acute effects on plants, SO_2 served as the chemical indicator for SO_x species in previous NAAQS reviews.

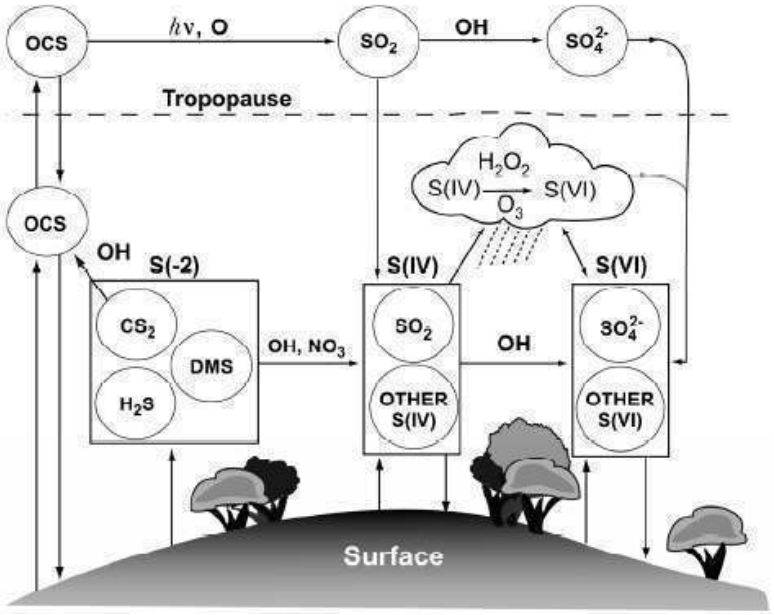

Figure 1.3-2. Schematic diagram of the cycle of sulfur species in the atmosphere.

1.3.3 Overview of Nitrogen- and Sulfur-related Ecological Effects

Nitrogen and sulfur interactions in the environment are highly complex. Both are essential, and sometimes limiting, nutrients needed for growth and productivity. Excess nitrogen or sulfur can lead to acidification, nutrient enrichment, and eutrophication. 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. In addition, these gas-phase NO_x species may contribute to nitrogen saturation in some areas of the United States. The second draft ISA indicates there is little new evidence for direct effects of exposure to gas-phase NO_x or SO_x on vegetation at current concentrations in the United States (U.S. EPA, 2008).

Emissions of NO_x and SO_x compounds into the air react through a complex series of gas-phase and heterogeneous reactions to produce additional intermediate compounds and final products. These reactions with NO_x and SO_x often occur under the same meteorological influences as those acting on formation of ozone (O_3) and secondary aerosols. These nitrogen- and sulfur-containing compounds are removed from the air by deposition—wet (rain, snow),

cloud and fog, and dry (gases and particles)—onto surfaces. Prevailing winds can transport these compounds hundreds of miles and across state and national borders.

Deposition of chemical species derived from NO_x and SO_x to the environment can affect ecosystem biogeochemistry, structure, and function. This can result from acidification that occurs when NO_x and SO_x emissions react in the atmosphere to form strong acids (i.e., sulfuric (H_2SO_4) and nitric (HNO_3) acid), which are then deposited onto the landscape. Acidification causes a cascade of effects that alter both terrestrial and aquatic ecosystems. These effects include slower growth, the injury or death of forest vegetation, and localized extinction of fish and other aquatic species.

The second draft ISA highlights evidence from two well-studied areas to provide more detail on how acidification affects ecosystems: the Adirondacks (New York) and Shenandoah National Park (Virginia) (U.S., EPA, 2008, Section 3.2) In the Adirondacks, the current rates of nitrogen and sulfur deposition exceed the amount that would allow recovery of the most acid sensitive lakes. In the Shenandoah National Park, past 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 suggest that the number of acidic streams will increase under the current deposition rates, but that re-acidification can be prevented if deposition is kept between 9–15 kg N ha^{-1} yr^{-1} and 0–6 kg S ha^{-1} yr^{-1} (U.S. EPA, 2008; Section 3.2). The second draft ISA highlights forests in the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians as the regions most sensitive to terrestrial acidification effects from acidifying deposition (U.S. EPA, 2008; Section 3.2). In the risk and exposure assessment, we target these areas for the air quality modeling presented in Chapter 3 and the case study analyses in Chapter 4.

In addition to acidification, NO_x acts with other forms of reactive nitrogen (including ammonia-based nitrogen) to increase the total amount of nitrogen available in terrestrial ecosystems and high elevation lakes. Reactive nitrogen deposition may contribute to the total reactive nitrogen load of some wetland and aquatic ecosystems that receive reactive nitrogen through multiple pathways (i.e., agricultural land runoff and wastewater effluent) (U.S. EPA, 2008; Section 3.3). Nitrogen deposition alters primary productivity that leads to changes in community composition and eutrophication. In aquatic ecosystems, deposition loads of

approximately 1.5–2 kg N ha^{-1} yr^{-1} are reported to cause alterations in diatom communities of freshwater lakes and impair water quality in the western United States (U.S. EPA, 2008; Section 3.3). In estuarine ecosystems, additional nitrogen from atmospheric and non-atmospheric sources contributes to increased phytoplankton and algal productivity, which leads 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 (HABs). The second draft ISA indicates that the contribution of atmospheric deposition to total nitrogen loads can be greater than 40% in highly eutrophic estuaries. The Chesapeake Bay is an example of a large, well-studied estuary that receives 21%–30% of its total nitrogen load from the atmosphere (U.S. EPA, 2008; Section 3.3).

In terrestrial ecosystems, there are multiple chemical indicators for the alteration of the biogeochemical cycling of nitrogen that is caused by reactive nitrogen deposition. Nitrate leaching is a well-documented effect that indicates the ecosystem is receiving more nitrogen than it uses; the onset of leaching is calculated to be between 5.6 and 10 kg ha^{-1} yr^{-1} for Eastern forests (U.S. EPA, 2008; Section 3.3). Nitrogen deposition can result in impacts 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 3 kg N ha^{-1} yr^{-1} (Pacific Northwest and southern California); 5 kg N ha^{-1} yr^{-1} correlates to the onset of declining biodiversity within grasslands (Minnesota and the E.U.), and at 10 kg N ha^{-1} yr^{-1} causes community composition of Alpine ecosystems and forest encroachment into temperate grasslands (U.S. EPA, 2008; Section 3.3). In the risk and exposure assessment, we target some of the aquatic and terrestrial ecosystems highlighted in the ISA for the air quality modeling presented in Chapter 3 and the case study analyses in Chapter 5.

In terrestrial and wetland ecosystems, 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 emission. 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 addressed qualitatively in Chapter 6.

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 produced an effect, one or several of those interacting factors were not in the range required for meaningful 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. The relationship between sulfur and methylmercury production is also addressed qualitatively in chapter 6.

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

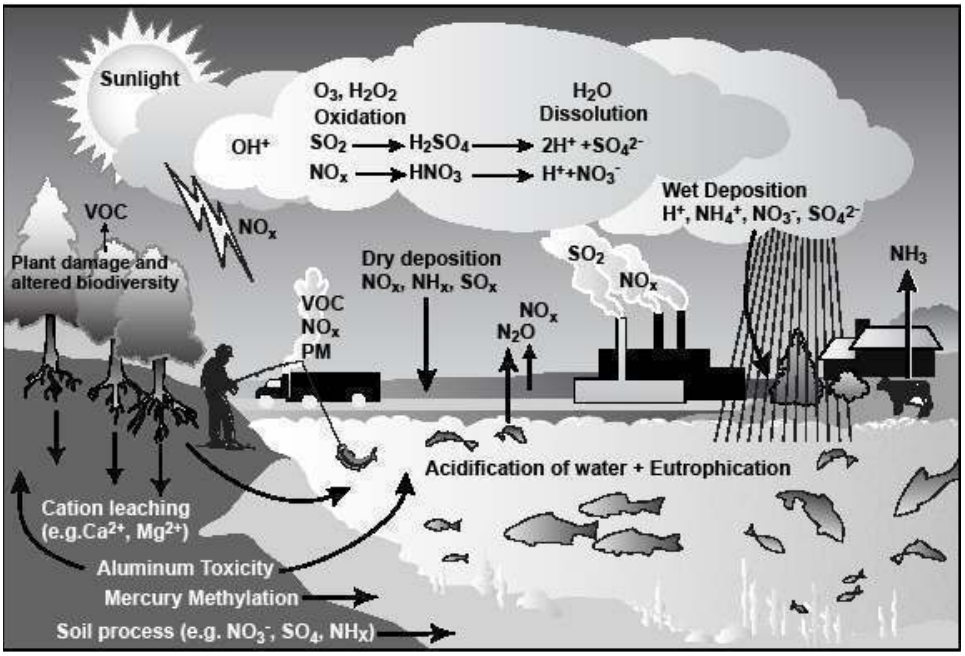

Figure 1.3-3. Nitrogen and sulfur cycling and interactions in the environment.

1.4 POLICY RELEVANT QUESTIONS

For this secondary NAAQS review of NO_x/SO_x, the main policy-relevant questions include the following:

- What are the known or anticipated welfare effects influenced by ambient NO_x and SO_x, and for which effects is there sufficient information available to be useful as a basis for considering distinct secondary standard(s)?
- What is the nature and magnitude of ecosystem responses to NO_x and SO_x that are understood to have known or anticipated adverse effects, and what is the variability associated with those responses (including ecosystem type, climatic conditions, environmental effects, and interactions with other environmental factors and pollutants)?
- To what extent do receptor surfaces influence the deposition of gases and particles (dry deposition), since dry deposition can contribute significantly to total deposition?
- Can effects from NO_x be distinguished from effects due to total reactive nitrogen?
- What ecologically relevant metrics adequately capture the relationships between ecosystem exposures and responses for the known or anticipated welfare effects we are trying to protect against?
- To what extent do the current standards provide protection from the public welfare effects associated with NO_x and SO_x?

To the extent the evidence suggests that the current standards do not provide appropriate protection from known or anticipated adverse welfare effects associated with NO_x and SO_x, we will consider ecologically meaningful revisions to the current standards. 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, we anticipate that ecologically meaningful NAAQS would need to be structured so as to take into account such complexity. To provide some context for addressing key policy relevant questions that are salient in this review, we have developed a possible structure for standards that could be based on meaningful ecological indicators that would provide for protection against the range of potentially adverse ecological effects that are associated with the deposition of NO_x and SO_x. In so doing, we have 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 depicts an example of a possible structure for an ecological effects based secondary NAAQS for NO_x and SO_x, together with the various elements that in combination would serve to define such a standard. While presented here for purposes of providing a context for understanding the additional policy-relevant questions, outlined below, that will help to frame our consideration of potential revisions to the current standards, the scientific foundations for this figure are more fully presented and discussed in the chapters below.

Chapter 3 provides information on current ambient levels of NO_x and SO_x and current deposition of nitrogen and sulfur, focusing on spatial and temporal patterns of deposition and impacts of ambient emissions on deposition. Chapters 4, 5, and 6 provide information on ecological effects and relevant ecological indicators of those effects. Chapter 7 synthesizes information across different endpoints and identifies impacts linked to ecosystem services that can help to inform the decision as to what levels of ecological indicators are protective against adverse public welfare effects. Linkages between ambient concentrations and deposition and between deposition and ecological indicators are discussed in Chapter 8, and the overall framework for linking atmospheric concentrations to ecological indicators through deposition is illustrated using the Adirondacks case study results for aquatic acidification effects. We anticipate that in the next draft, we will restructure the chapters such that Chapter 3 will discuss the linkages between ambient concentrations and deposition, while Chapters 4 and 5 will discuss the linkages between ecological indicators and deposition. In the next draft, Chapter 8 will focus on the legal support for a jointly structured, ecological effects based standard, as well as illustrations of the standard associated with different levels of protection against ecological impacts.

As shown in Figure 1.4-1, this secondary NAAQS structure accounts for variable atmospheric and ecological factors that are critical aspects of the complex relationships that need to be reflected in ecologically meaningful standards. We anticipate that the deposition and ecological effect functions shown in Figure 1.4-1 may be based on complex formulas that incorporate factors related to atmospheric transformations, climate conditions, land uses, and ecosystem characteristics. A discussion of these formulas, along with an example, is provided in Chapter 8.

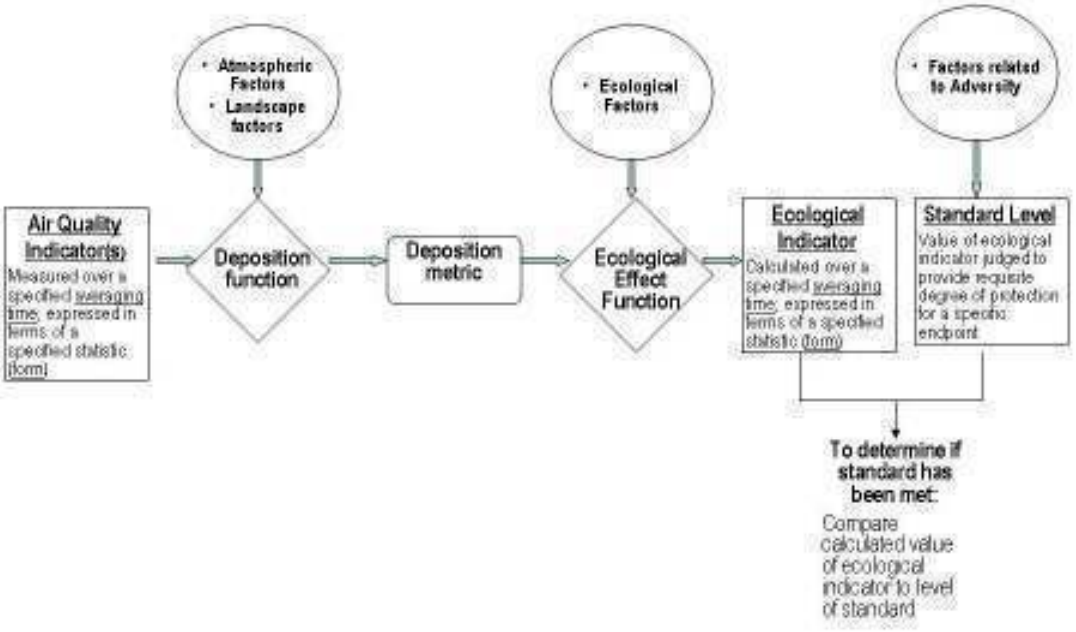

Figure 1.4-1. Possible structure of a secondary NAAQS for NO_x and SO_x based on an ecological indicator.

In considering potential alternative standards that may be structured as illustrated above, the following questions should be addressed:

- Does the available information provide support for considering different air quality indicators for NO_x and SO_x?
- Does the available information provide support for the development of appropriate deposition functions, and what atmospheric and environmental factors are most relevant for such a function?
- Does the available information provide a basis for identifying relevant ecological indicators for the range of ecological effect endpoints being considered in the review?
- Does the available information provide support for the development of appropriate ecological effect functions that meaningfully relate to the ecological effect endpoints being considered, and what ecological factors are most relevant for such functions?
- For which ecological effect endpoints being considered is a joint NO_x/SO_x standard most appropriate, and for which endpoints would separate standards be more appropriate?

- Taking into consideration factors related to defining adversity for various ecological endpoints being considered, 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 adverse impacts attributable to NO_x/SO_x, and what are the uncertainties in the estimated reductions?

In order to be able to answer these questions, we believe that 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 chemical species in the atmosphere
- Identifying the atmospheric pathways that govern the chemical transformation, transport, and deposition of NO_x 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 total deposition of reactive nitrogen, and between NO_x and total nitrogen loadings that are related to ecological effects.

These issues are addressed below in the discussions presented in Chapters 2 through 6.

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2. OVERVIEW OF RISK AND EXPOSURE ASSESSMENT

2.1 INTRODUCTION

This REA 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. In addition, these diverse ecosystems are not distributed evenly across the United States. To target acidification and nitrogen and sulfur enrichment, this risk and exposure assessment addresses four main ecosystem effects on terrestrial and aquatic systems identified in the ISA:

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

In addition to these four effects, we have qualitatively addressed the influence of sulfur enrichment on methylmercury production and the effects associated with N_2O and carbon sequestration.

Because these ecosystem effects are not evenly distributed across the United States, we have identified case studies 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 2007 draft ISA (U.S. EPA, 2007). Taking into account the recommendations of the ISA authors, we have selected ecological indicator(s) and case study locations (U.S. EPA, 2007). The choice of case study locations are summarized in **Table 2.1-1** based on ecosystem characteristics, indicators, and ecosystem service information developed as part of the risk and exposure assessment. Detailed explanations of this information are presented in Attachments 2 through 6. In the second draft risk and exposure assessment, we will evaluate the case study results for use in a broader characterization of national conditions to represent key components of our nation's ecology, recognizing that some ecosystems, and the effects on them, may be too unique to be characterized broadly.

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

Targeted Effect Area	**Characteristics of Sensitivity (Variable Ecological Factors)**	**Biological/ Chemical Indicator**	**Ecological Indicator**	**Ecological Effects**	**Ecosystem Services Impacted**	**Case Study Locations**
Aquatic Acidification	Geology, surface water flow, soil depth, weathering rates	[Al] pH ANC	Species richness, abundance, composition, ANC	Species losses of fish, phytoplankton, zooplankton; changed community composition, ecosystem structure and function	Fisheries, recreation, tourism	Adirondack Mountains (NY) Blue Ridge Mountains, Shenandoah National Park (VA)
Terrestrial Acidification	Geology, surface water flow, soil depth, weathering rates	Soil base saturation [Al] [Ca] C:N ratio	Tree health Red spruce, sugar maple, ANC	Decreased tree growth, Increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure and function	Food, natural habitat, tourism	Kane Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)
Aquatic Nutrient Enrichment	N-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)	Eutrophication Index (EI)	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Fish populations, water quality, and habitat quality	Potomac River Basin, Chesapeake Bay Neuse River Basin, Pamlico Sound

Targeted Effect Area	**Characteristics of Sensitivity (Variable Ecological Factors)**	**Biological/ Chemical Indicator**	**Ecological Indicator**	**Ecological Effects**	**Ecosystem Services Impacted**	**Case Study Locations**
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	Species changes, nitrogen enrichment of soil, changes in fire regime, changes in nutrient cycling	Loss of habitat, loss of biodiversity, recreation, water quality	Coastal Sage Scrub and mixed conifer forest (San Bernadino and Sierra Nevada Mountain Ranges, California)
Sulfur and Mercury Methylation Potential	Wetland type, presence of sulfate reducing bacteria, water pH, dissolved organic carbon, suspended particulate matter,	Interaction between: dissolved organic carbon, temperature, anoxia, and sulfide land cover, precipitation response, and limnography	MeHg concentrations in fish and shell fish	Neurotoxic effects in fish and throughout food web	Fishing, shell fishing, sports fishing, food, recreation, biodiversity	Little Rock Lake, WI (ISA case study)

To address the policy-relevant questions that guide the scope of this review, the risk and exposure assessment evaluates the relationships between atmospheric concentrations, deposition, biologically relevant exposures, ecosystem effects, and ecosystem services. To evaluate the nature and magnitude of ecosystem responses associated with adverse effects, this risk and exposure assessment examines various ways to quantify the relationship 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 on ecosystem change and services. The intent of the assessment is to determine the exposure metrics that incorporate temporal considerations (i.e., biologically relevant timescales), pathways, and ecologically relevant indicators necessary to maintain the functioning of these ecosystems. To the extent feasible, we also evaluate the overall load to the system for nitrogen and sulfur, as well as the variability in ecosystem responses to these pollutants. In addition, we evaluate the contributions of atmospherically deposited nitrogen and sulfur relative to total loadings in the environment. Since oxidized nitrogen is the listed criteria pollutant, for the atmospheric contribution to total nitrogen, we examine the contribution of 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 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) having different ambient air indicators to provide the required protection.

2.2 SEVEN-STEP APPROACH

The seven basic steps guiding the 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, which received CASAC approval. Therefore, we are carrying this approach forward for the risk and exposure assessment. The seven steps address the selection of 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 are documented in the ISA. 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, we have chosen to execute some of these steps in a qualitative or semi-quantitative fashion. Our progress towards characterizing current conditions (complete Steps 1 through 4) for each targeted effect area and case study analysis is presented in Attachments 2 through 6.

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

- **Step 1.** Plan for assessment using documented effects: biological, chemical, and ecological indicators, and potential ecosystem services.
- **Step 2.** Map sensitive areas that show 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.** Where feasible, scale-up case study assessment area findings to sensitive areas.
- **Step 6.** Assess the current ecological conditions for those sensitive areas.
- **Step 7.** Assess alternative levels of protection under different scenarios of deposition from ambient sources.

2.3 ECOSYSTEM SERVICES

Humankind benefits from a multitude of resources and processes that are supplied by ecosystems. Collectively, these benefits are known as ecosystem services and include products, such as clean drinking water, and processes, such as the decomposition of wastes. Ecosystem services are distinct from other ecosystem products and functions because there is human demand for them. Ecosystem services are generally defined as the benefits individuals and organizations obtain from ecosystems. 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 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, 2005).

Figure 2.3-1 is the World Resources Institute's schematic demonstrating the connections between the categories of ecosystem services and human well-being.

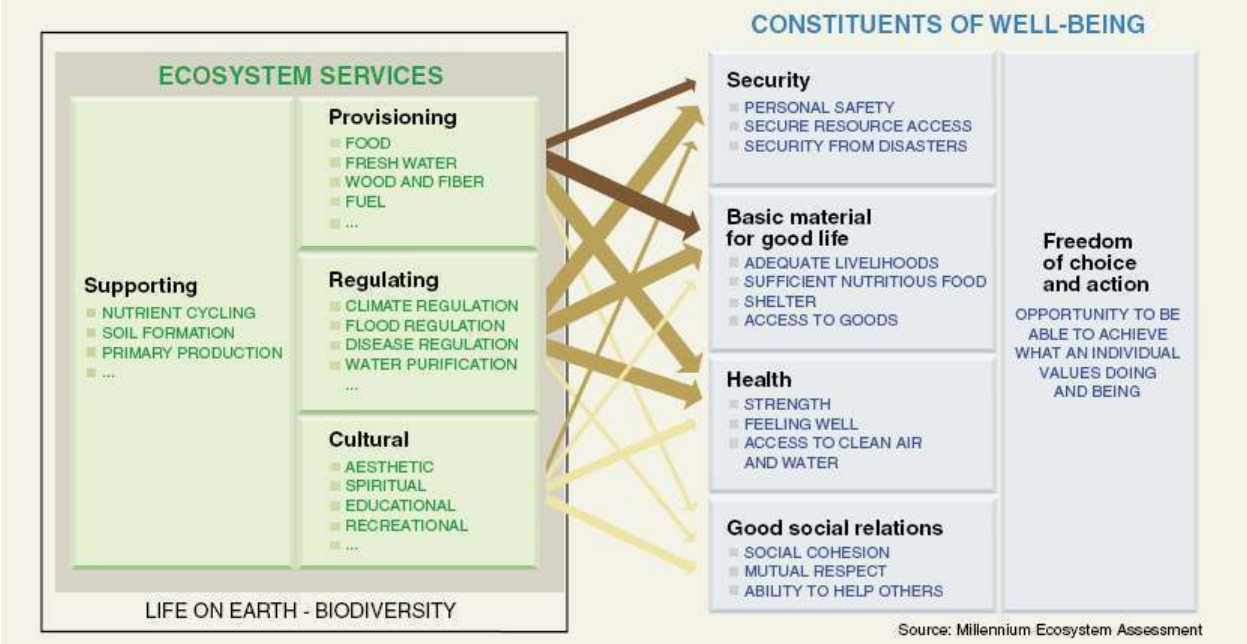

Figure 2.3-1. Millennium ecosystem assessment categorization of ecosystem services and their links to human well-being (MEA, 2005a).

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 our security, health, social relationships, and access to basic material goods (MEA, 2005b).

Historically, ecosystem services have been undervalued and overlooked. More recently, degradation and destruction of ecosystems has piqued interest in assessing the value of their

services. The economic approach to valuation is laid out 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 these values: market-based approaches, revealed preference methods, and stated preference methods (U.S. EPA, 2006). Because economic valuation of services can be difficult, non-monetary valuation using biophysical measurements and concepts can also be used to value services. One non-monetary valuation methodology uses relative value indicators (such as a flow chart indicating uses of a waterbody - boatable, fishable, swimmable); another assigns values to ecosystem goods and services through the use of the common currency of energy. 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 review, valuation will be used where possible based on available data in the case study locations.

The ecosystems of interest in this risk assessment are heavily impacted by anthropogenic air pollution. These effects 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 (e.g., nutrient cycling), provisioning service (e.g., timber production), and regulating services (e.g., climate regulation). 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.

We plan to develop, where possible, for each area of interest linkages to ecosystem services from indicators of each effect (i.e., biological, chemical, ecological) identified in Step 1 of the risk and exposure assessment. This link will be developed based on existing literature and will focus on the services identified in the peer-reviewed literature. These linkages 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, this linkage is one of the critical elements that will allow for valuation of benefits of EPA-regulated air pollutants (SAB C-VPESS, 2007). **Figure 2.3-2** illustrates an example of a path from nitrogen deposition in an

ecosystem to valuation that links ecological endpoints to changes in services and finally to valuation.

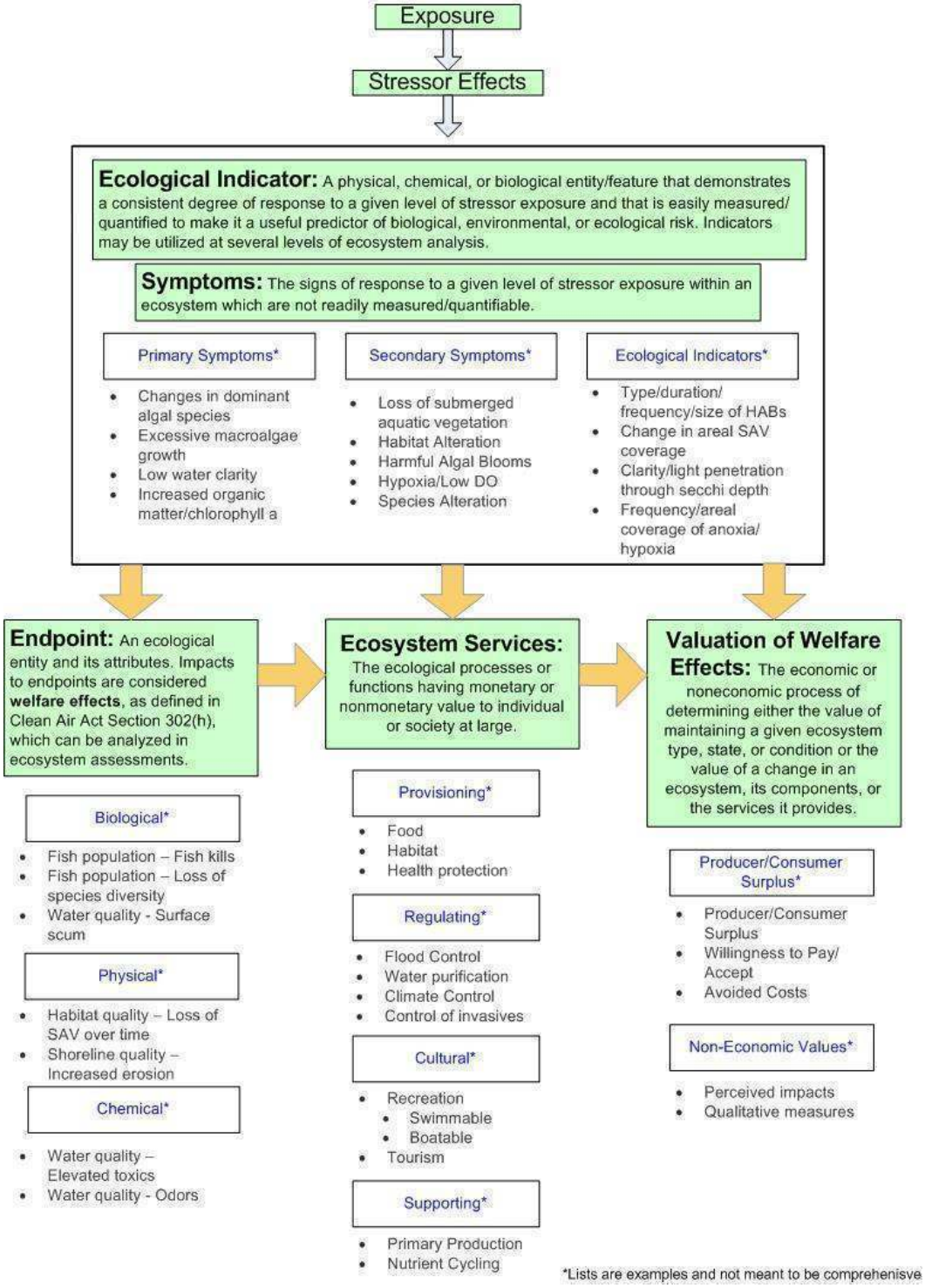

Figure 2.3-2. Pathway from nitrogen deposition to valuation for an aquatic system.

We have begun identifying the primary ecosystem service(s) for both acidification and enrichment and for major ecosystem types and components (i.e., terrestrial ecosystems, soils, aquatic ecosystems) under consideration in this risk and exposure assessment (see Table 2.1-1). The impacts associated with various ecosystem services for each targeted effect area are summarized in **Table 2.3-1**. Some of the potential linkages between impacts and effects in relation to specific ecosystem services are summarized for each targeted effect area below. This information will be more fully addressed in the second draft risk and exposure assessment.

2.3.1 Aquatic Acidification

The Aquatic Acidification Case Study will focus on ecosystem services such as fisheries**,** recreation, and tourism. Fisheries (decreased species richness) will be quantitatively linked to acidification through monitoring data and modeling of ANC, and recreation activities will likely be qualitatively related to acidification symptoms through user surveys.

2.3.2 Terrestrial Acidification

The Terrestrial Acidification Case Study will focus on ecosystem services such as food, natural habitat, and tourism. Sugar maple and red spruce abundance and growth (i.e., crown vigor, biomass, and geographic extent) will be quantitatively linked to acidification symptoms through the Forest Inventory and Analysis National Program (FIA) database analyses and analysis of estimated sales of maple sugar products.

2.3.3 Aquatic Nutrient Enrichment

The Aquatic Nutrient Enrichment Case Study will focus on ecosystem services such as fisheries, recreation, and tourism. Fisheries (closings, decreased species richness) will likely be quantitatively linked to eutrophication symptoms through monitoring data, and recreation activities will likely be qualitatively related to eutrophication symptoms through user surveys.

2.3.4 Terrestrial Nutrient Enrichment

The Terrestrial Nutrient Enrichment Case Study for Coastal Sage Scrub (CSS) will focus on ecosystem services such as biodiversity; threatened and endangered species and rare species (both national and state); landscape view; water quality; and fire hazard mitigation. Linkage methods from endpoint to services may include measurement of changes in biodiversity and

abundance and distribution of threatened and endangered species, comparison of past and present photography, and measurement of the distribution of soil moisture with depth and possible nitrate leakage.

The Terrestrial Nutrient Enrichment Case Study for Mixed Conifer Forests will focus on ecosystem services such as visual and recreational aesthetics provided by the community and water quality. Linkage methods from endpoint to services may include measurement of the densification of stands, shifts in tree dominance, shifts in lichen communities, foliar nitrogen increases, and increasing nitrate concentrations in streams.

2.3.5 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, which provide food for human populations. For some socio-economic groups (especially involving groups with low incomes), fishing is a subsistence activity that makes a very significant contribution to household food intake. Sport fishing often involves important recreational services, and for many groups (e.g., Native Americans and Alaska native Villagers), fishing and consuming local fish or shellfish is of cultural and spiritual significance. A synthesis of the ecological service and valuation aspects of fishing and shellfishing activities, with a focus on issues related to 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 2.3-1. Ecological Impacts Associated with Acidification, Nutrient Enrichment, and Increased Mercury Methylation and Their Associated Ecosystem Services

Targeted Effect Area	**Provisioning Services**	**Regulating Services**	**Cultural Services**	**Supporting Services**
Aquatic Acidification	▪ Fish kills ▪ Decline in fish population ▪ Decline in aquatic species richness, abundance, and health	Decline in habitat	Fish kills Decline in fish population Decline in aquatic species richness, abundance, and health	
Terrestrial Acidification	▪ Decline in forest productivity	▪ Increase forest soil erosion ▪ low water retention	▪ Decline in forest aesthetics ▪ Increase forest soil erosion ▪ low water retention	
Aquatic Nutrient Enrichment	▪ Fish kills ▪ Fish/water contamination ▪ Decline in fish population	▪ Decline in shoreline quality (erosion)	▪ Fish kills ▪ Fish/water contamination ▪ Decline in fish population ▪ Decline in shoreline quality (erosion) ▪ Poor water clarity and color ▪ Unpleasant odors	▪ Surface scum
Terrestrial Nutrient Enrichment				

Targeted Effect Area	Provisioning Services	Regulating Services	Cultural Services	Supporting Services
Coastal Sage Scrub (CSS)		▪ Decline in habitat, shrub abundance, species of concern ▪ Increase abundance of non-natives ▪ Increase in wildfires	▪ Decline in habitat, shrub abundance, species of concern ▪ Increase abundance of non-natives ▪ Increase in wildfires	
Mixed Conifer Forest		▪ Change in habitat suitability ▪ Increased tree mortality ▪ Increase in fire intensity ▪ Decline in surface water quality	▪ Change in habitat suitability ▪ Increased tree mortality ▪ Decline in mixed conifer forest aesthetics	▪ Change in forest's nutrient cycling, causing other nutrients to become limiting
Sulfur and Mercury Methylation	▪ Fish kills ▪ Fish/water contamination ▪ Decline in fish population		▪ Fish kills ▪ Fish/water contamination ▪ Decline in fish population	

2.4 UNCERTAINTY

A risk assessment of this scope, with four targeted effect areas, includes several components that rely on numerous analytical tools and techniques, data sources, and analyses, each containing some degree of uncertainty. The environmental effects of nitrogen and sulfur deposition vary widely in both terrestrial and aquatic ecosystems and may be either direct or indirect. The natural resistance of an ecosystem will also affect the severity of its response. In addition to the natural variability in any given ecosystem, there are likely to be sources of uncertainty related to the input parameters necessary to evaluate current conditions associated with nitrogen and sulfur deposition. For example, empirical data will contain uncertainties associated with measurements and analyses, whereas modeling results propagate uncertainties due to the scale and representativeness of the model input data. Due to the inherent complexity of the environmental processes involved with nitrogen and sulfur, uncertainty is difficult to define and capture quantitatively, especially within the scope of this review.

Some of the categories of uncertainty include (1) air quality/deposition and ecological modeling (with their associated parameterizations and input data), (2) characterization of sensitive ecosystems, and (3) the case study selection process along with the applicability of case study results to larger geographic areas. The magnitude of these uncertainties will vary depending on the associated data quality and availability. Each aspect and component of the risk assessment may be uncertain and, depending on its position in the analytical chain, may cascade through subsequent steps in the analysis and thus have a multiplicative effect on the overall uncertainty in final risk estimates.

Some key sources of uncertainty in each stage of the risk assessment are the following:

- Gaps in scientific knowledge of physical, chemical, atmospheric, and ecological processes
- Variability in estimated relationships between atmospheric concentrations and deposition that is not captured by existing models and analytical techniques
- Insufficient measurements in time and space to properly characterize ambient conditions for variables such as deposition, soil chemistry, and species composition
- Errors in measurements
- Use of surrogate variables and simplification of complex functions

- Biases due to omissions or other research limitations.

The various sources of uncertainty will be discussed, as appropriate, within each section of the risk assessment.

2.5 REFERENCES

MEA (Millennium Ecosystem Assessment Board). 2005a. *Ecosystems and Human Well-being: Current State and Trends, Volume 1*. Edited by R. Hassan, R. Scholes, and N. Ash. Washington: Island Press. Available at http://www.millenniumassessment.org/documents/document.766.aspx.pdf.

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3. SOURCES, AMBIENT CONCENTRATIONS, AND DEPOSITION

This chapter discusses current emissions sources of nitrogen and sulfur, as well as atmospheric concentrations, policy-relevant background, non-ambient loadings to ecosystems, and estimates of deposition for nitrogen and sulfur nationwide. Both measured and modeled data are used to evaluate current contributions of nitrogen and sulfur compounds to the case study locations described in detail in Attachments 2 through 6. The impacts of spatial and temporal parameters on ambient concentrations and their associated deposition are evaluated in Section 3.2.1. The relative contributions of ambient concentrations on deposition are evaluated in Section 3.2.2 using a response surface model analysis. The deposition fields described here will be used as modeling input for the individual case study modeling described in Attachments 2 through 6.

3.1 SCIENCE OVERVIEW

Prior to analyzing the effects of nitrogen and sulfur deposition to the environment, we must first evaluate the ambient emissions, transformations, and transport of nitrogen and sulfur in the atmosphere. As noted in the introduction, 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 (e.g., NH_3 and NH_4^+, collectively termed NH_x) can also play an important role in the emission, transformation, 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. Sulfur oxides (SO_x) refer to all oxides of sulfur, including SO, SO_2, SO_3, and disulfur monoxide (S_2O); however, only SO_2 is present in concentrations relevant for atmospheric chemistry and ecological exposures.

3.1.1 Sources of Nitrogen and Sulfur

3.1.1.1 NO_x

The total amount of NO_x emitted is 20.8 million tons/yr; NO_x emissions by state are shown in **Figure 3.1-1**.

Figure 3.1-1. Annual NO_x emissions by state for 2002 (U.S. EPA, 2002).

Combustion sources are the primary emitters of NO_x; their main emissions are in the form of NO and NO_2. The major combustion sources of NO_x are on-road motor vehicles and electrical utilities, with contributions from stationary engines, off-road vehicles, and industrial facilities. Nationally, anthropogenic sources account for approximately 87% of total NO_x emissions. Mobile sources (both on-road and off-road) account for about 60% of total anthropogenic emissions of NO_x, whereas stationary sources (e.g., electrical utilities and industry) account for the remainder (2007 ISA Annex2 Table 2-1). Highway vehicles represent the major mobile source component. In the United States, approximately half the mobile source emissions are contributed by diesel engines and half are emitted by gasoline-fueled vehicles and other sources (2007 ISA Annex2 Section 2.1.1 and Table 2-1). Apart from these anthropogenic sources, there are also natural sources of NO_x, including lightning, wildfires, and microbial activity in soils (2007 ISA Annex2 Section 2.1.2).

The distribution of NO_x emissions across major source categories is shown in the pie charts in **Figure 3.1-2**. Charts are provided to show the distribution of emissions on a national total basis, as well as for the eastern and western United States, due to differences in source emissions profiles. For this display, we have defined the eastern United States to include Texas, Oklahoma, Kansas, Nebraska, the Dakotas, and all states to the east. All other states are included

as part of the western United States. Note that emissions from Alaska and Hawaii are not included in any of these charts.

In both the East and West, a number of emissions sectors contribute relatively large amounts to the overall NO_x inventory. In general, NO_x emissions in the East are far greater than in the West. Most of the NO_x in the West is emitted from sources in California (not shown). The on-road sector is the largest contributor, followed by emissions from utilities (Electric Generating Units [EGUs]). The non-road, aircraft/locomotive/marine, and non-EGU point emissions contribute generally similar amounts to the overall NO_x inventory. Although NO_x emissions from fires are a relatively small fraction of the annual total emissions in the West, fires are episodic events, and thus, emissions can be quite high during those events.

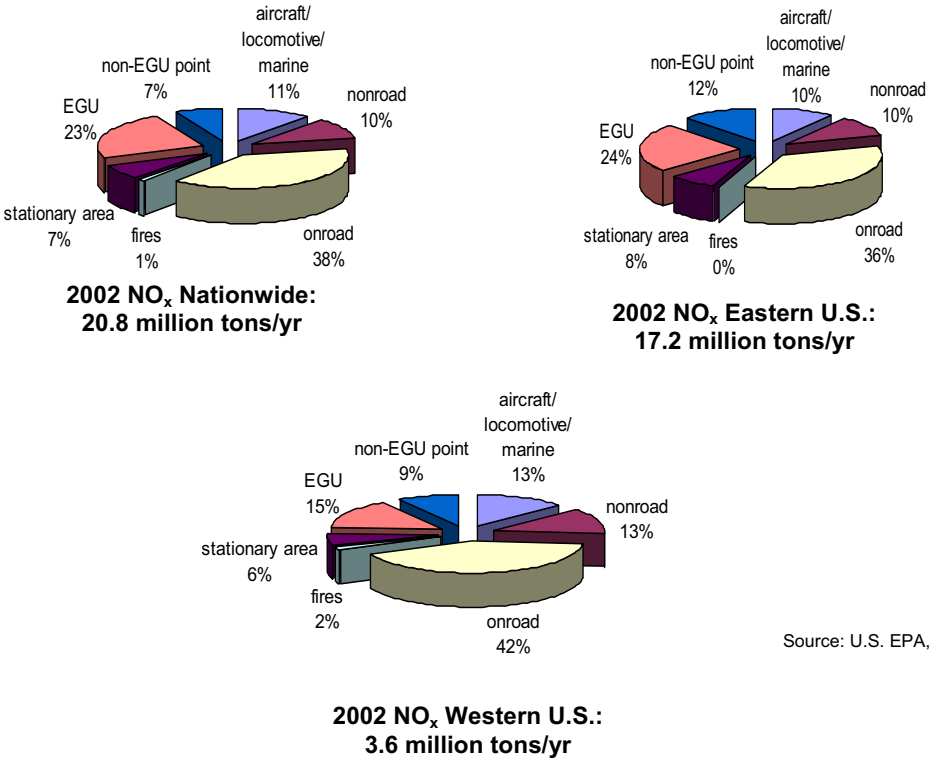


Figure 3.1-2. The distribution of NO_x emissions across major source categories in 2002.

3.1.1.2 NH_x

Total emissions of NH_x are 4.0 million tons/year; **Figure 3.1-3** shows annual ammonia emissions by state during 2002.

Figure 3.1-3. Annual emissions of NH_3 by state during 2002 (U.S. EPA, 2002).

The primary anthropogenic sources of NH_x emissions are fertilized soils and livestock. Confined animal feeding operations (CAFOs) and other intensified agricultural production methods have resulted in greatly increased volumes of animal wastes, of which 30%–70% may be emitted as NH_3. Motor vehicles and stationary combustion are small emitters of NH_x. Some NH_3 is emitted as a by-product of NO_x reduction in motor vehicle catalysts.

Where possible, our 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 play an important role in the standard-setting process, as discussed in Chapter 8.

3.1.1.3 SO_x

Total emissions of SO_2 are 14.7 million tons/yr; **Figure 3.1-4** shows annual SO_2 emissions by state during 2002.

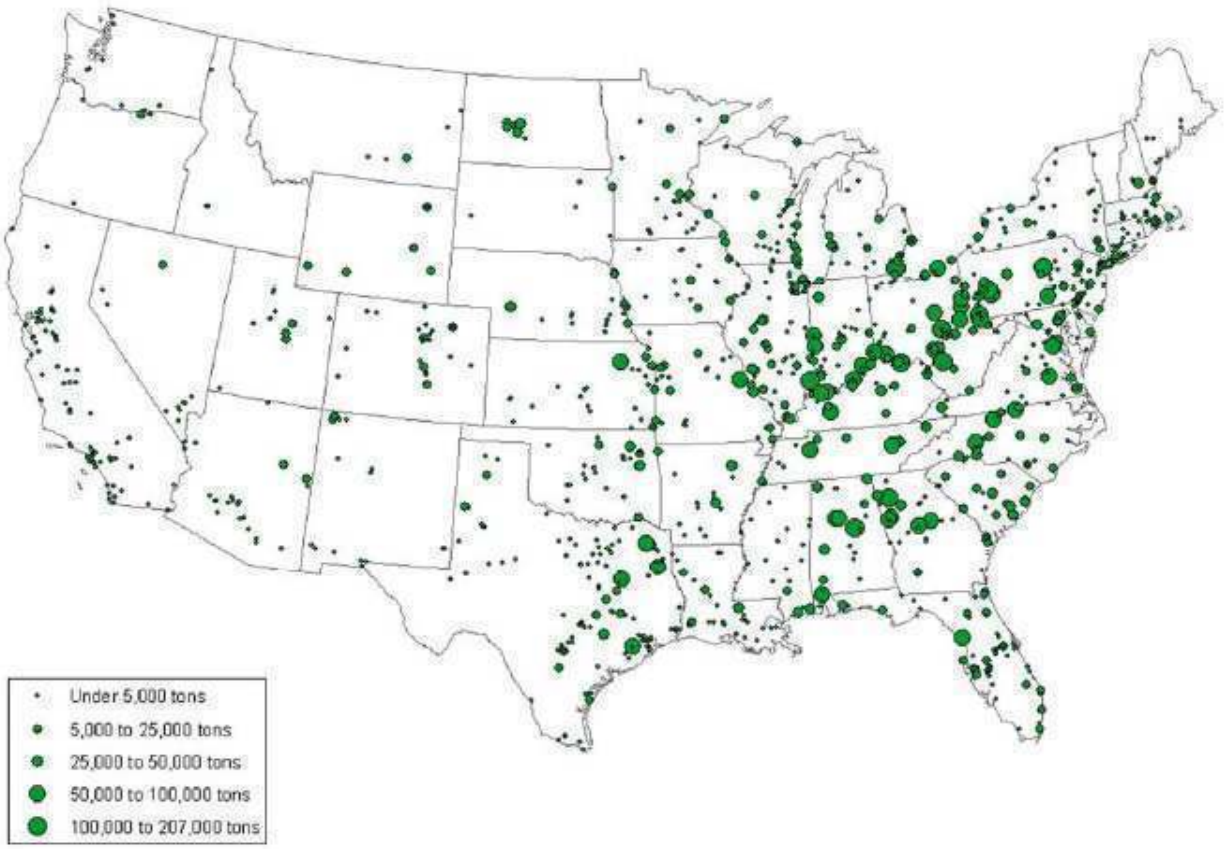


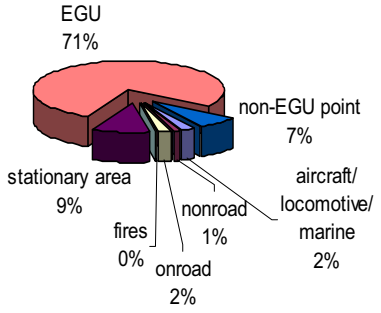
Figure 3.1-4. Annual SO_2 emissions in 2006 for acid rain program cooperating facilities (U.S. EPA, 2008).

Industrial emissions of SO_2 in the United States are mainly due to the combustion of fossil fuels by electrical utilities (~66 %) and industry (~29%); transportation-related sources contribute minimally (~5%) (2002 statistics) (U.S. EPA, 2006d). 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 this type of fuel.

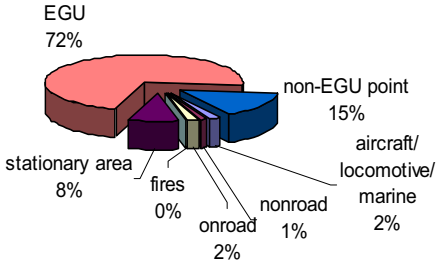
The largest natural sources of SO_2 are volcanoes and wildfires. Although SO_2 constitutes a relatively minor fraction (0.005% by volume) of total volcanic emissions (Holland, 1978), concentrations in volcanic plumes can be up to tens of ppm. Volcanic sources of SO_2 in the United States are limited to the Pacific Northwest, Alaska, and Hawaii. Sulfur is a component of amino acids in vegetation and is released during combustion. Gaseous sulfur emissions from this source are mainly in the form of SO_2.

Emissions of SO_2 from burning vegetation are generally in the range of 1%–2% of the biomass burned (Levine and Pinto, 1998).

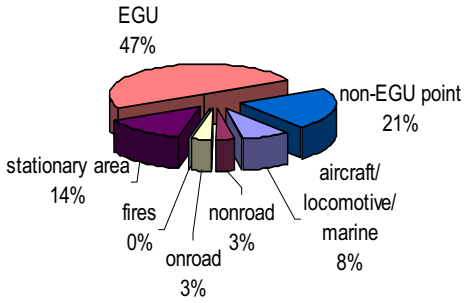
The distribution of SO_2 emissions across major source categories are shown in the pie charts in **Figure 3.1-5**. As with the pie charts for NO_x, charts are provided to show the distribution of emissions on a national total basis, as well as for the eastern and western United States. Note that emissions from Alaska and Hawaii are not included in any of these charts.



2002 SO_2 National Annual: 14.7 million tons/yr



2002 SO_2 Eastern U.S.: 13.8 million tons/yr



2002 SO_2 Western U.S.: 920,000 tons/yr

Source: U.S. EPA,

Figure 3.1-5. The distribution of SO_2 emissions across major source categories in 2002 (U.S. EPA, 2002).

Similar to emissions of NO_x, emissions of SO_2 are much greater in the East than in the West. The breakout of SO_2 emissions by source sector indicates that EGU emissions dominate in both the East and the West, but they are a much greater fraction of the inventory in the East (72%) compared to the West (47%). In the West, stationary area sources and non-EGU point sources also have a greater contribution to SO_2 than in the East. Note that SO_2 emissions from fires are understated in the National Emissions Inventory (NEI) due to an error in the emissions calculations.

3.1.2 Ambient Concentrations and Policy-Relevant Background

Policy-relevant background concentrations are those concentrations that would occur in the United States in the absence of anthropogenic emissions in continental North America (defined here as the United States, Canada, and Mexico). For NO_2, policy-relevant background concentrations are less than 300 parts per trillion (ppt) over most of the continental United States and less than 100 ppt in the eastern United States on an annual average basis (U.S. EPA, 2008). In urban areas near monitoring locations, 24-hour ambient NO_2 concentrations averaged less than 20 parts per billion (ppb), with a 99 percentile value of less than 50 ppb. Annual average NO_2 concentrations over the continental United States are less than 5 ppb for nearly all urban, rural, and remote sites. According to the ISA (U.S. EPA, 2008), background SO_2 concentrations are less than 10 ppt throughout most of the continental United States, except in areas of the Pacific Northwest, where natural SO_2 sources are particularly strong due to volcanic activity. Maximum policy-relevant background SO_2 concentrations are 30 ppt. In general, policy-relevant background concentrations of SO_2 contribute less than 1% of current concentrations, except in the Pacific Northwest, where policy-relevant background concentrations can contribute up to 80% (U.S. EPA, 2008).

The analyses for the REA examine the contribution of total reactive nitrogen and sulfur above the policy-relevant background concentrations.

3.1.3 Non-ambient Loadings of Nitrogen and Sulfur

Not all loadings of nitrogen and sulfur compounds to ecosystems are due to atmospheric deposition. Other inputs, such as run-off from agricultural soils to waterbodies and point-source discharges, also contribute to acidification and nutrient enrichment. In this assessment, we examine 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.

3.1.4 Deposition

3.1.4.1 Nitrogen

As noted in the ISA (U.S. EPA, 2008), 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. 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 (U.S. EPA, 2008).

From 2004–2006, mean nitrogen deposition was greatest in the Ohio River Valley, specifically in Indiana and Ohio, which had values as high as 9.2 and 9.6 kg ha^{-1} y^{-1}, respectively. Nitrogen deposition was lower in other parts of the East, including the Southeast, and in northern New England. The greatest deposition in the central United States occurred in Kansas and Oklahoma, which reported 7.0 and 6.5 kg ha^{-1} y^{-1}, respectively. **Figure 3.1-6** shows the total nitrogen deposition for 2002; **Figures 3.1-7 and 3.1-8** show the total oxidized and reduced nitrogen deposition in the United States in 2002, respectively.

In most regions of the United States, wet deposition of nitrate (NO_3) and NH_4^+ are the primary pathways of nitrogen deposition. Next most common is deposition in dry forms, as dry HNO_3, NH_4^+, and nitrate ions. This varies regionally as some of the arid Western areas have higher rates of dry deposition than the more humid East.

Atmospheric nitrogen loads to the Great Waters and estuaries in the United States are estimated to range from approximately 2%–38% of total atmospheric deposition. In the Chesapeake Bay, where nitrogen deposition and its ecological effects have been extensively studied, direct deposition of atmospheric nitrate is estimated to contribute from 20%–30% of total nitrogen and to 14% of the ammonium loadings.

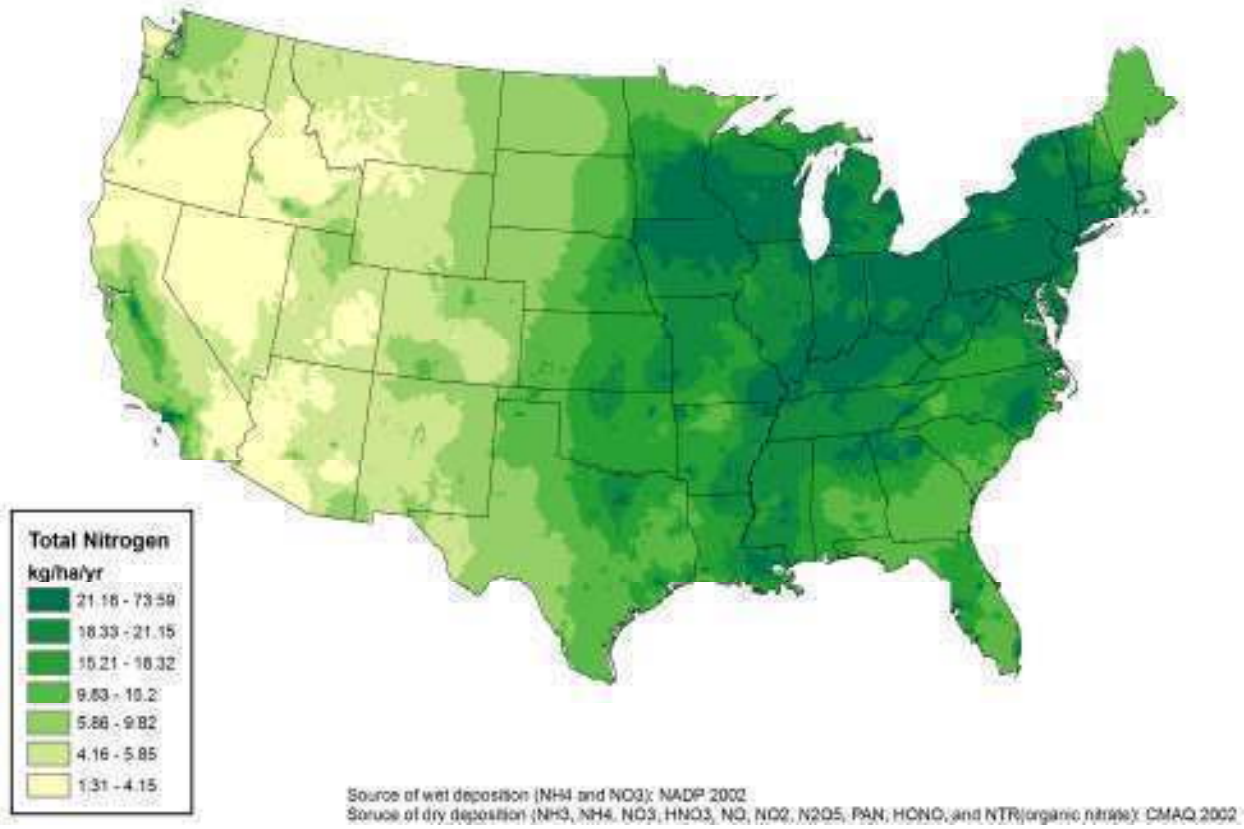


Figure 3.1-6. Total wet and dry nitrogen deposition in the United States in 2002.

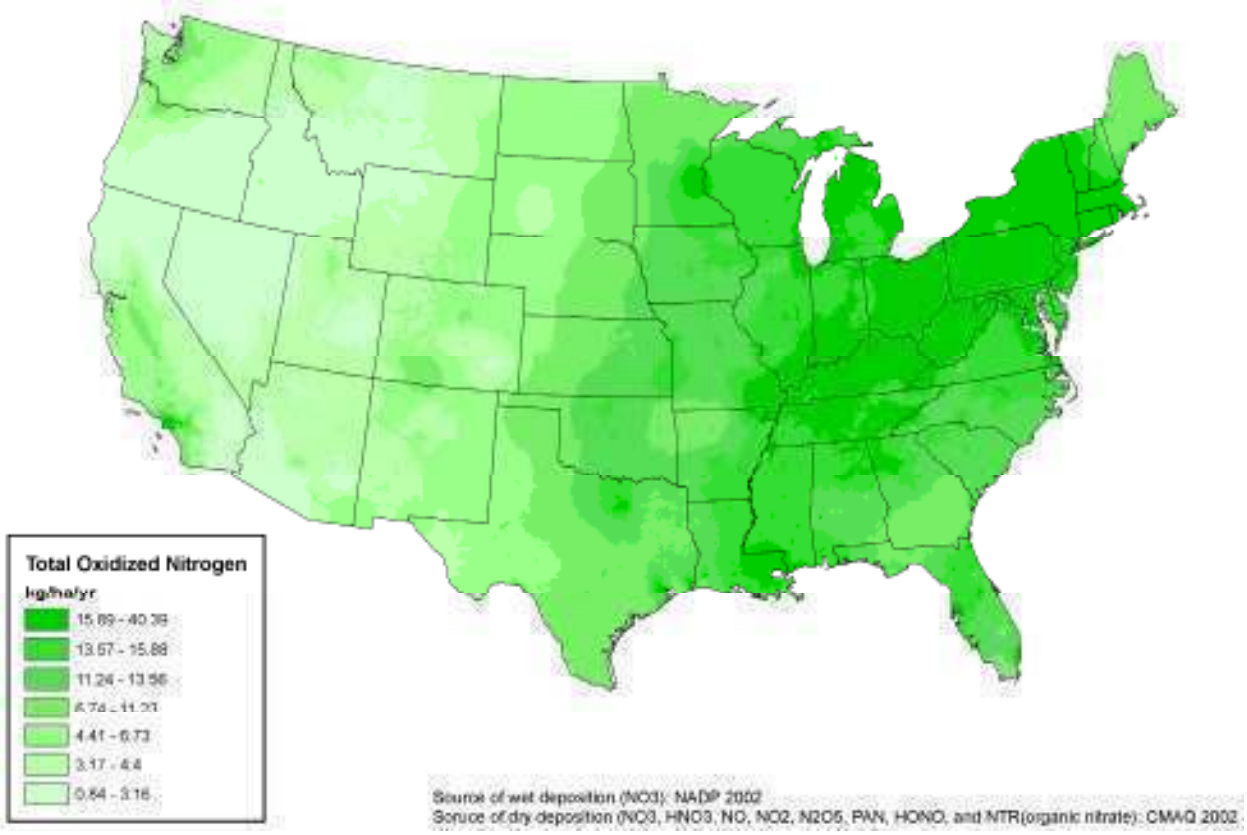


Figure 3.1-7. Total wet and dry oxidized nitrogen deposition in the United States in 2002.

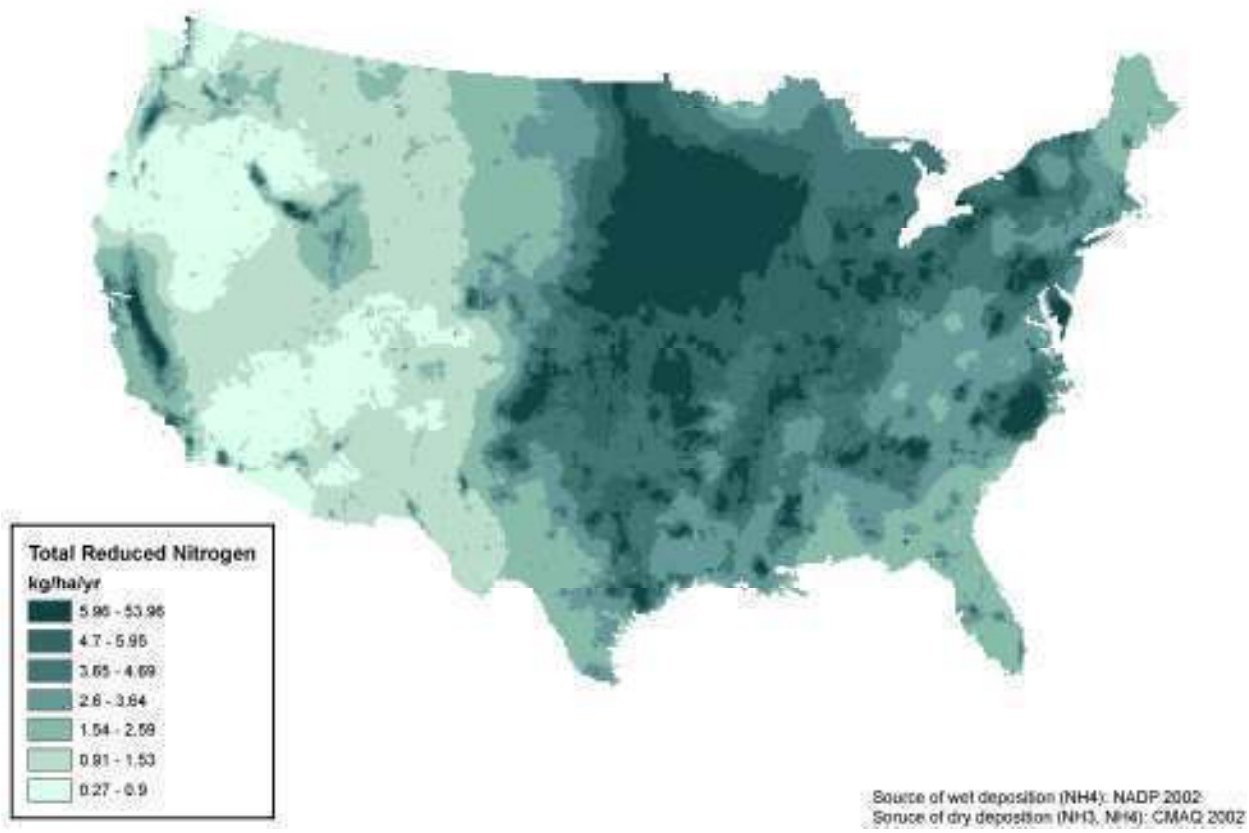


Figure 3.1-8. Total wet and dry reduced nitrogen deposition in the United States in 2002.

3.1.4.2 Sulfur

Average sulfur deposition was highest in the eastern United States during 2004–2006, with the maximum in the Ohio River Valley. In this region, measured sulfur deposition was 21.3 kg ha^{-1} y^{-1} at one monitoring station; most recording stations reported 3-year averages greater than 10 kg ha^{-1} y^{-1} (U.S. EPA, 2008) Total sulfur deposition in the United States west of the 100th meridian was relatively low, with all recording stations reporting less than 2 kg ha^{-1} $y^{-1}$and many reporting less than 1.0 kg ha^{-1} y^{-1}. Total wet and dry sulfur deposition for 2002 are shown in **Figure 3.1-9**.

The primary form of sulfur deposited is wet sulfate (SO_4); smaller contributions to deposition are made by dry sulfur dioxide and dry sulfate.

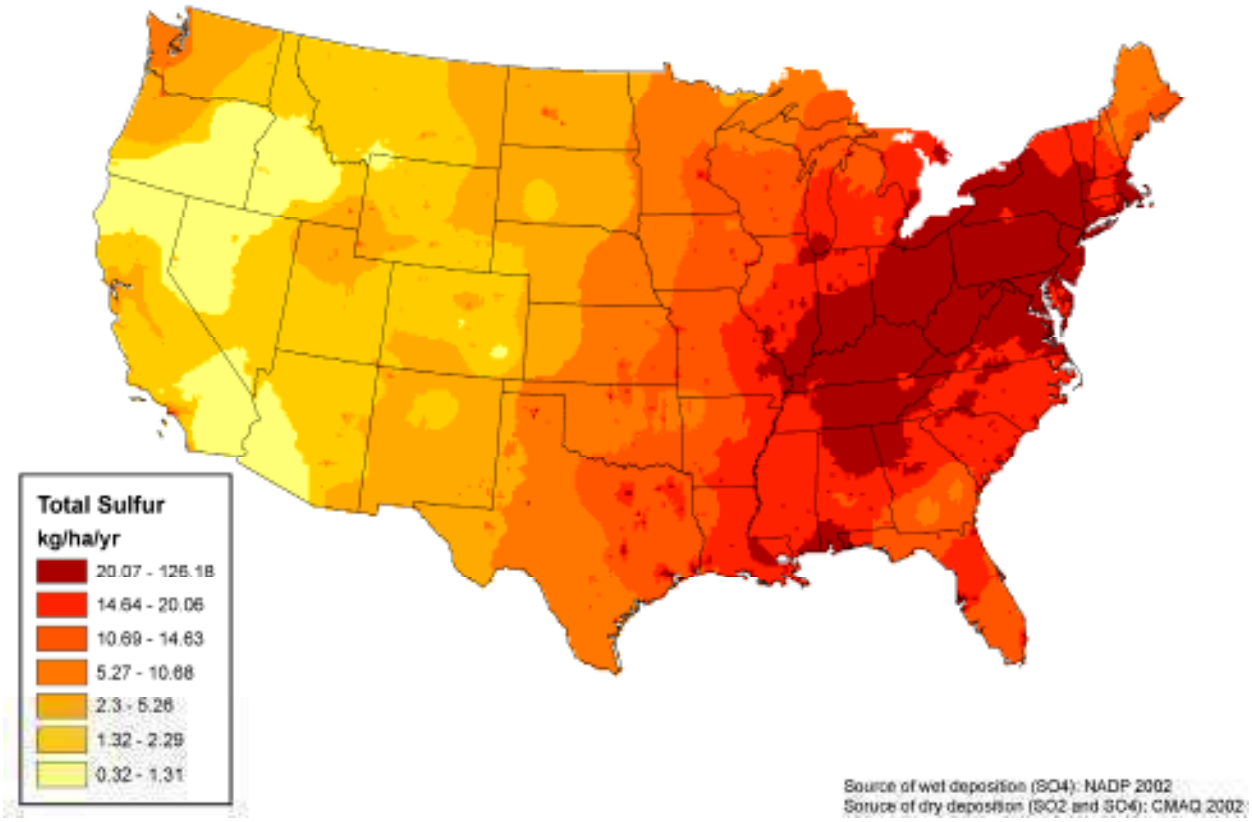


Figure 3.1-9. Total wet and dry sulfur deposition in the United States in 2002.

3.2 DATASETS

To create composite nitrogen and sulfur deposition datasets of both wet and dry constituents, two data sources were used:

- 2002 measured wet deposition from the National Atmospheric Deposition Program (NADP) National Trends Network (NTN).
- 2002 estimated dry deposition from the Community Multiscale Air Quality (CMAQ) model.

The NADP data is collected at several hundred point locations across the contiguous United States. From these points, analysts at the NADP network generated continuous surfaces at a 2.5-kilometer (km) grid cell resolution by using an inverse distance weighted (IDW) algorithm. The species of sulfur collected was SO_4, while for nitrogen it was NO_3 for oxidized nitrogen and NH_4 for reduced nitrogen.

The CMAQ data was 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. For total dry oxidized nitrogen, the species were NO_3, HNO_3, NO, NO_2, N_2O_5, PAN, nitrous acid (HONO), and organic nitrate (NTR), while for total dry reduced nitrogen, the species were NH_3 and NH_4.

Both input datasets contained deposition values in kilograms per hectare (kg/ha)/yr. The NADP data was 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 deposition values could be added together on a grid cell by grid cell basis. In order to calculate total nitrogen, the two chemical species from the NADP (i.e., NO_3 and NH_4) were added together and then added to the total dry nitrogen estimated values from CMAQ.

3.2.1 Spatial and Temporal Characterization of Concentrations and Deposition for Case Study Areas

3.2.1.1 Purpose and Intent

The purpose of this section of Chapter 3 is to describe the spatial and temporal patterns of nitrogen and sulfur deposition and NO_x and SO_x concentrations[2] in and near five of the case study areas.[3] In this analysis, we characterize and compare the magnitude, spatial gradients, and intra-annual and inter-annual variation in nitrogen and sulfur deposition and NOx and SO_x concentrations for each case study area. In addition to improving our overall understanding of the behavior of nitrogen and sulfur deposition, the results and findings of this analysis are intended to provide information on the following:

- The relative portion of oxidized nitrogen versus reduced nitrogen
- The relative amounts of wet and dry deposition of nitrogen and sulfur
- The magnitude of NO_x and SO_x concentrations.

[2] For the purpose of this analysis, NO_x is defined to be NO_y, which includes the following species: NO, NO_2, HNO_3, and PAN. SO_x is defined as SO_2.

[3] The case study areas are identified as case study locations in Chapter 2, Table 2.1-1.

We refer to wet/dry oxidized/reduced nitrogen and wet/dry sulfur deposition as the components of total reactive nitrogen and total sulfur deposition, respectively.

The inter-relationships of physical, chemical, and meteorological processes and land use that affect the spatial and temporal patterns of deposition and concentration are complex. The state of the science regarding these processes is described in the ISA. The main goal of chapter 3 is to help readers understand the characteristic patterns of deposition in the case study areas and how these patterns might influence the overall levels of adverse effects under current conditions. It is beyond the scope of this chapter to fully explain the characteristics revealed by the analysis of modeled and measured deposition and concentrations. Further exploration of these behaviors should be the subject of future research efforts.

3.2.1.2 Data and Tools

Both air quality model predictions and ambient measurements[4] are used in this analysis. The modeled data were obtained from annual simulations of the CMAQ model (Byun and Ching, 1999; Byun and Schere, 2006; Dennis et al., 1996) version 4.6.1. The measured data include wet deposition of SO_4, NO_3, and NH_4 from the NADP network and SO_2 measurements from Clean Air Status and Trends Network (CASTNet). We chose to use both measured and modeled data since each dataset provides information and value not fully captured by the other. The relative strengths and limitations of these datasets are described as part of the uncertainty discussion in Section 3.2.1.5.

Modeled Data

The CMAQ model is a comprehensive, three-dimensional grid-based Eulerian air quality model designed to simulate the formation and fate of gaseous and particle (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. For this analysis, we are using results from several existing CMAQ runs. These runs were made for modeling regions (i.e., modeling domains) covering the eastern and western United States, as shown in **Figure 3.2-1**. The horizontal spatial resolution of the CMAQ grid cells in these domains is approximately 12 x 12

[4] We use the " modeled data" to refer to the model predictions and "measured data" to refer to ambient measurements.

km. For the eastern domain, we have model outputs from annual CMAQ runs using meteorology and emissions for each of the 5 years from 2002 through 2006. (Note that the current analysis is based on a 2002 CMAQ model run; in the second draft risk and exposure assessment, we will present results based on 2002–2006 model runs.) We also have 12-km CMAQ data from the western domain for 2002. These annual CMAQ runs feature year-specific meteorology, as well as year-specific inventories for key emissions source sectors such as utilities, on-road vehicles, non-road vehicles, wildfires, and natural biogenic sources. Emissions for other sectors of the inventory for each of the years modeled rely on inventories for 2002. The inputs for these CMAQ runs were developed based on the data, procedures, and tools in the 2002 Multi-Pollutant Air Quality Modeling Platform. Details on the development and evaluation of this platform are described elsewhere.[5]

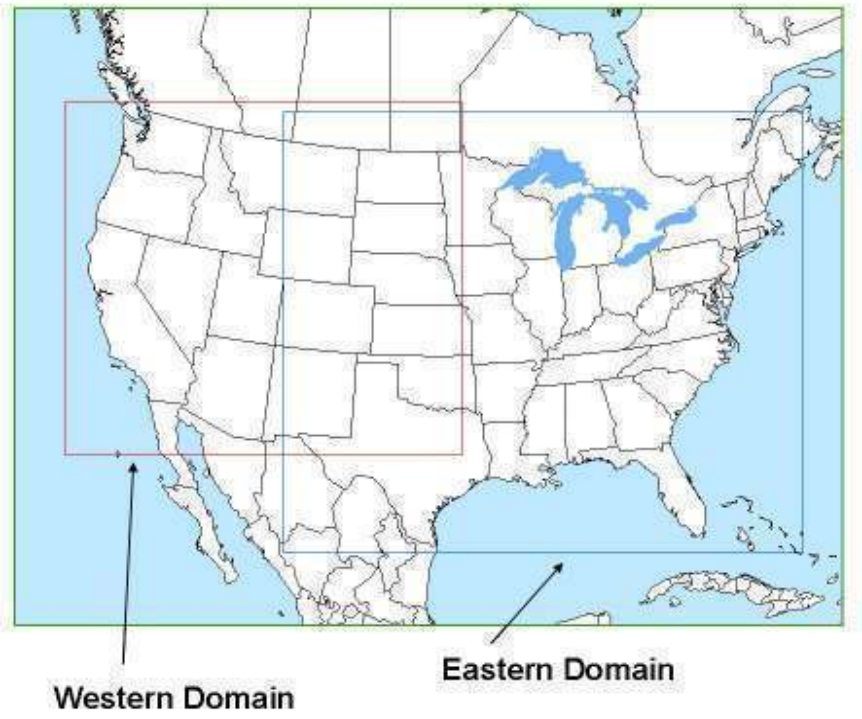


Figure 3.2-1. CMAQ 12-km eastern and western modeling domains.

The CMAQ runs produce hourly concentrations and wet and dry deposition of individual pollutant species in each grid cell within the domain. Concentration predictions for NO_x as NO_y[6] and SO_x as SO_2, both in units of ppb, are produced as part of our standard model output. The

[5] *Placeholder for citation for the 2002 Platform Report.*
[6] NOy is defined as the sum of CMAQ predictions for NO, NO_2, HNO_3, and PAN.

CMAQ deposition data for nitrogen and sulfur species 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. These composite deposition variables are derived from the species identified in **Table 3.2-1**, as applied in the formulas shown in **Table 3.2-2**. The CMAQ deposition data are in units of kg/ha. We are also including in the analysis gridded precipitation data that were input to the CMAQ runs to help understand the temporal and spatial behavior of wet deposition.

Table 3.2-1. CMAQ Nitrogen and Sulfur Deposition Species

CMAQ Species	**Chemical Name**
ANO_3	Particle Nitrate
HNO_3	Nitric Acid
N_2O_5	Nitrogen Pentoxide
HONO	Nitrous Acid
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
PAN	Peroxyacyl Nitrate
NTR	Organic Nitrate
ASO_4	Particle Sulfate
SO_2	Sulfur Dioxide

Table 3.2-2. Formulas for Calculating Nitrogen and Sulfur Deposition

Deposition Type	**Formula**
Oxidized Nitrogen	$0.2258*ANO_3 + 0.2222*HNO_3 + 0.4667*NO + 0.3043*NO_2 + 0.2592*N_2O_5 + 0.1157*PAN + 0.2978*HONO + 0.1052*NTR$
Reduced Nitrogen	$0.7777*NH_4 + 0.8235*NH_3$
Sulfur	$0.3333*ASO_4 + 0.5000*SO_2$

Measured Data

[Placeholder for description of Grimm-Lynch data base containing gridded wet deposition data for NO_3, SO_4, and NH_4+NH_3. (Grimm and Lynch, 2004).]

[Placeholder for description of CASTNet SO_2 data base.]

[Placeholder for discussion of why existing NO_2 measurements are not appropriate for this analysis……i.e., no monitors in rural areas.]

3.2.1.3 Analytical Techniques

As noted above, this analysis focuses on five case study areas, four in the East and one in the West. Two of the eastern Case Study Areas, the Adirondack Mountains of New York (ADR) and western Virginia (VIR) were selected in order to examine the effects of acidification. The ADR includes 44 lakes and ponds and the VIR includes 61 streams that are being modeled using the MAGIC water quality model. The other two eastern case study areas in the East are the Potomac and Neuse river basins, which were selected to analyze the effects of nutrient enrichment.

[Placeholder for description of the western case study area]

The characterization of deposition and concentrations for each of these areas is presented in terms of the following:

- The relative amount of oxidized nitrogen versus reduced nitrogen deposition
- The relative amount of wet versus dry deposition of nitrogen and sulfur
- The magnitude and spatial gradients of annual total nitrogen and sulfur deposition and each of the component species
- The intra-annual variation in nitrogen and sulfur deposition and each of the component species based on seasonal and monthly deposition data
- The inter-annual variation in nitrogen and sulfur deposition
- The magnitude, spatial gradients, and intra-annual variation of annual average NO_y and SO_2 concentrations.

[(7) Placeholder for analysis of the influence of inter-annual variability in meteorology on deposition – this analysis will be added in the second draft of this document.]

Approach for Analyzing CMAQ Deposition—Eastern United States Case Study Areas

To analyze the CMAQ data, we developed procedures for mapping the CMAQ 12-km grid cells to each of the case study areas. The first step in this process was to identify the

hydrologic unit codes (HUCs)[7, 8, 9] within each area. We then used GIS to overlay the CMAQ grid cells on these HUCs in order to link specific grid cells to each HUC. A grid cell was linked to a HUC if any part of the grid cell touched a portion of the HUC. Note that a grid cell may be linked to more than one HUC using this approach. The map in **Figure 3.2-2** shows the four eastern case study areas, along with the HUCs in each area and the outer boundary of the CMAQ grid cells that cover the area.

[7] HUCs 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.

[8] We used finest-resolution HUC information available, which was 11-digit HUCs for the ADR, 12-digit HUCs for the VIR area, and 8-digit HUCs for the Potomac and Neuse.

[9] In our analyses for the ADR and VIR areas, we selected the HUCs that contain the lakes/ponds and streams to be modeled with MAGIC. For the Potomac and Neuse, we included all the HUCs within the watersheds for each of these areas.

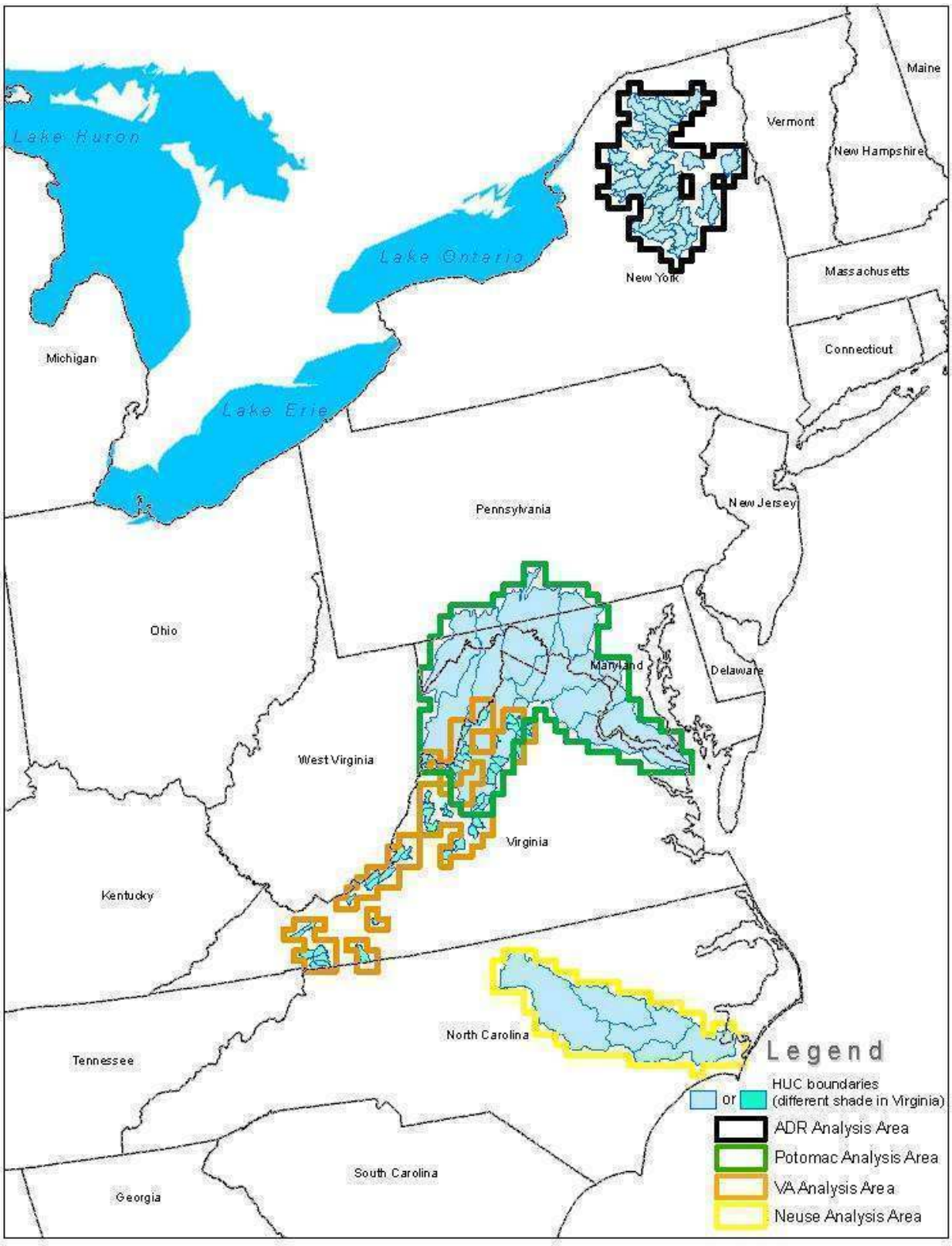


Figure 3.2-2. Case study areas in the eastern United States.

Using the set of selected grid cells, we calculated the monthly, seasonal,[10] and annual total deposition of wet and dry oxidized nitrogen, reduced nitrogen, and sulfur for each HUC in each area. This was done by summing the CMAQ deposition data for all the grid cells linked to the HUC. We also calculated the total deposition for each case study area as a whole using deposition data for the set of unique grid cells that cover the entire case study area. To analyze the intra-annual temporal patterns in nitrogen deposition, we computed the percentage of annual total deposition and precipitation that was predicted in each season and each month.

In addition to the HUC-level aggregations, we also prepared maps showing annual total deposition based on the gridded modeled data. These maps are used to (1) characterize the spatial gradients in nitrogen and sulfur deposition across each case study area and (2) compare the amount of deposition in each case study area to that in other adjacent parts of the region.

Approach for Analyzing CMAQ Deposition – Western United States Case Study Area

[Placeholder for this approach, if different from what we are doing for the East]

Approach for Analyzing Measured Deposition Data

[Placeholder for this approach]

Approach for Analyzing CMAQ Concentration Data

[Placeholder for this approach]

Approach for Analyzing Measured Concentration Data

[Placeholder for this approach]

3.2.1.4 Results and Findings

The results for each case study area are presented in the following manner. The characterization of nitrogen deposition is presented first, followed by the results for sulfur deposition. For nitrogen deposition, we describe the relative contribution of wet and dry oxidized and reduced nitrogen to annual total reactive nitrogen deposition in the case study area and examine how the contribution varies geographically across the area. We have a similar analysis

[10] Seasonal deposition and precipitation were calculated based calendar quarters (e.g., Jan/Feb/Mar is the winter season).

for wet and dry sulfur deposition. The analysis of contribution is followed by an analysis of spatial gradients in annual deposition. Next, we look at the seasonal and monthly (i.e., intra-annual) variation in each component of deposition for the case study area, along with the geographic variation in temporal patterns. We then investigate the inter-annual variability in deposition over the period 2002 through 2006 (in the second draft risk and exposure assessment).

[Placeholder: may also include analysis of influence of inter-annual met variability on deposition]

Adirondack Mountains Case Study Area

A map of the ADR is provided in **Figure 3.2.1**-3. This map shows the location of the 44 lakes and ponds and the HUCs which include these sites. The sites shaded in yellow represent 15 sites selected for analysis of the geographic variation deposition across the ADR.

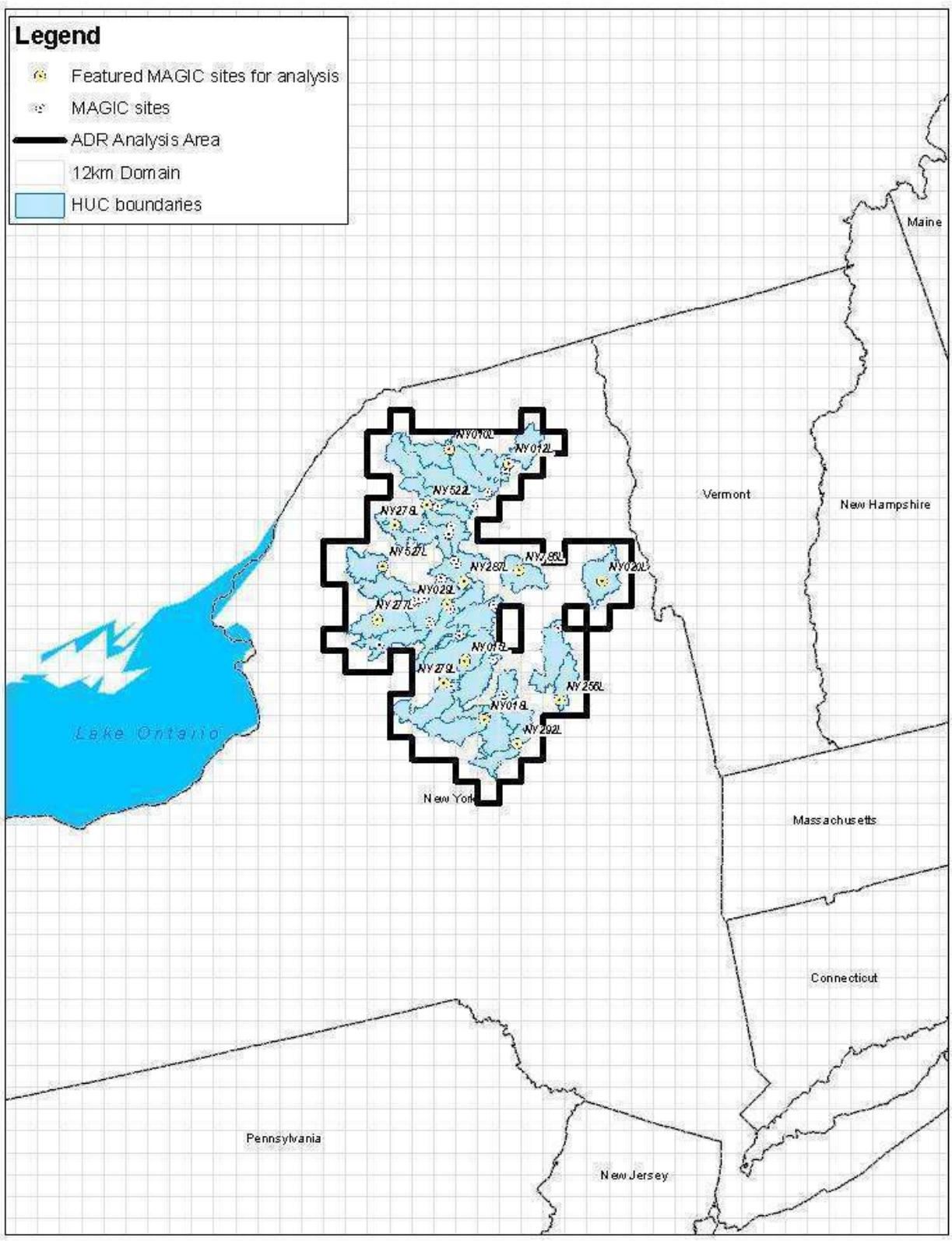


Figure 3.2-3. Adirondacks Case Study Area.

Relative Contribution of Wet and Dry Oxidized and Reduced Nitrogen Deposition

In **Figure 3.2-4,** we show the contribution to annual nitrogen deposition from wet and dry oxidized nitrogen and reduced nitrogen for the ADR as a whole, based on the 2002 CMAQ modeling data. Deposition of total reactive nitrogen in this case study area is dominated by oxidized nitrogen (69% oxidized nitrogen vs 31% reduced nitrogen). Oxidized nitrogen deposition is fairly evenly divided between wet and dry. In contrast, wet deposition is the largest contributor to reduced nitrogen (25% wet vs 6 %dry). Overall, the predicted total wet deposition (oxidized and reduced) is greater than dry deposition by 61% vs 39%. **Figure 3.2-5** indicates that the relative proportion of wet/dry oxidized/reduced nitrogen are generally similar across the ADR. Oxidized nitrogen deposition is greater than reduced nitrogen deposition in all locations with oxidized nitrogen contributing in the range of approximately 65%–75% of the total reactive nitrogen deposition. There does appear to be some geographic differences in wet vs dry deposition. Total wet deposition (oxidized nitrogen + reduced nitrogen) is in the range of 60% to 70% (with dry 30% to 40%) in the western portion of the ADR. In the eastern ADR, the portion of wet is somewhat less at 50% to 55%. Looking at oxidized nitrogen alone, it appears that wet oxidized nitrogen is generally a larger fraction of total reactive nitrogen compared to dry oxidized nitrogen in the southern/western portions of the ADR (35% to 40% wet oxidized nitrogen vs 25% to 30% dry oxidized nitrogen). However, in other portions of this case study area, wet and dry oxidized nitrogen are either roughly equivalent or dry deposition is a larger fraction to total reactive nitrogen deposition. For reduced nitrogen, wet deposition is much larger than dry reduced nitrogen in all portions of the ADR.

[Placeholder for contribution analysis based on measured data and a comparison between measured and modeled in terms of wet Ox vs wet Re N dep]

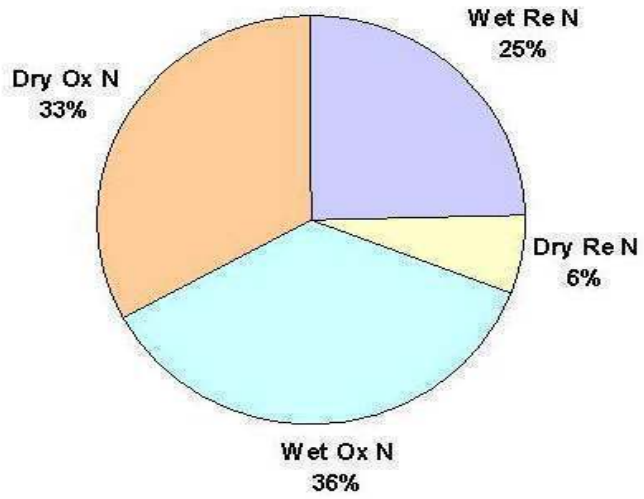


Figure 3.2-4. Contribution to annual total 2002 modeled deposition for the Adirondack Case Study Area.

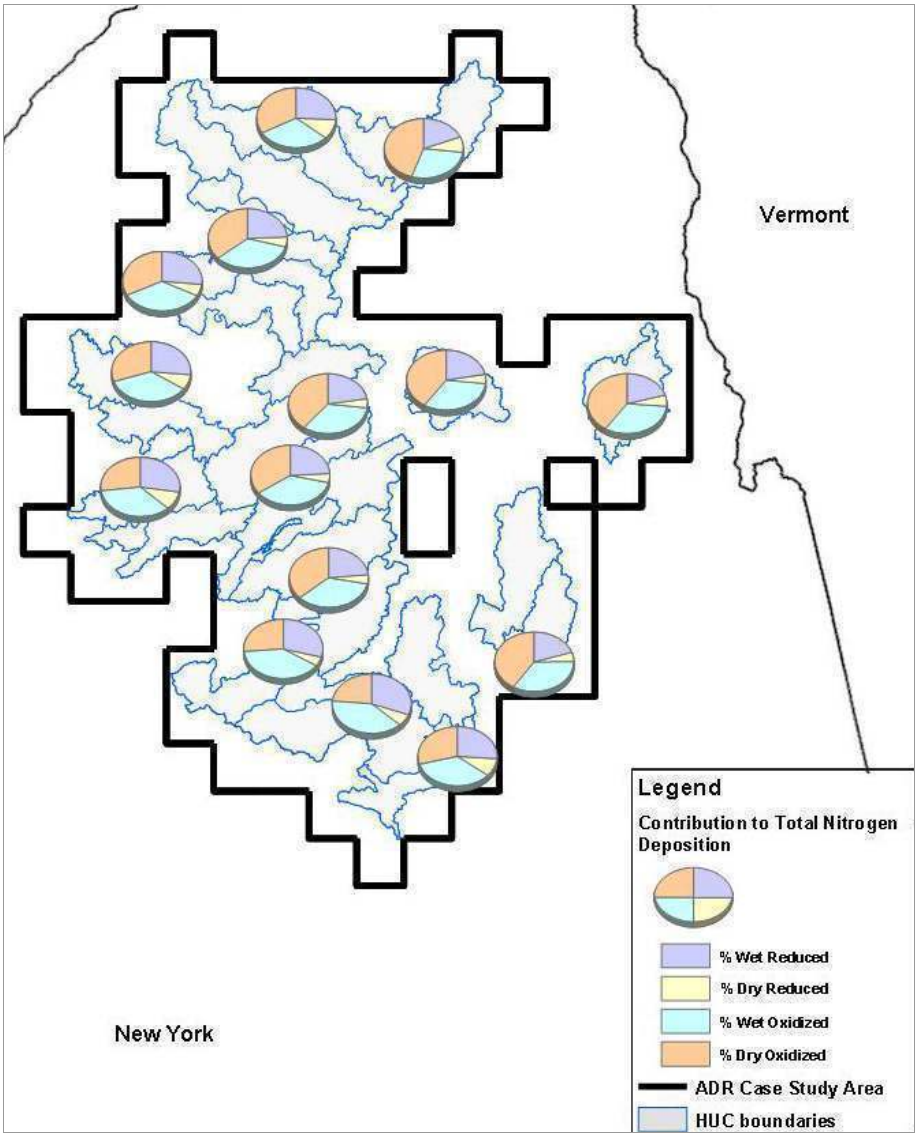


Figure 3.2-5. Contribution from wet/dry reduced and oxidized nitrogen to modeled 2002 annual total nitrogen deposition in the Adirondack Case Study Area.

Spatial Gradients in Annual Nitrogen Deposition Across the ADR

The annual total 2002 modeled total reactive nitrogen deposition in the ADR, as shown in Figure 3.2.1-6, reveals a clear spatial gradient in total reactive nitrogen deposition across the region. For example, total reactive nitrogen deposition is greater than 14 kg/ha in the southwest ADR compared to less than 8 kg/ha in the east. The spatial gradient in total reactive nitrogen deposition is largely driven by wet deposition as evident by comparing the wet nitrogen deposition map in Figure 3.2.1-7 to the dry nitrogen deposition map in Figure 3.2.1-8. The west to east gradient in wet nitrogen deposition appears to be much stronger than the gradient in dry

deposition. From **Figure 3.2-9**, it is evident that the relatively high total reactive nitrogen deposition in the southwestern portion of the ADR is part of a broad area of high deposition that stretches westward from this case study area along the southern shore of Lake Ontario toward western Pennsylvania and beyond.

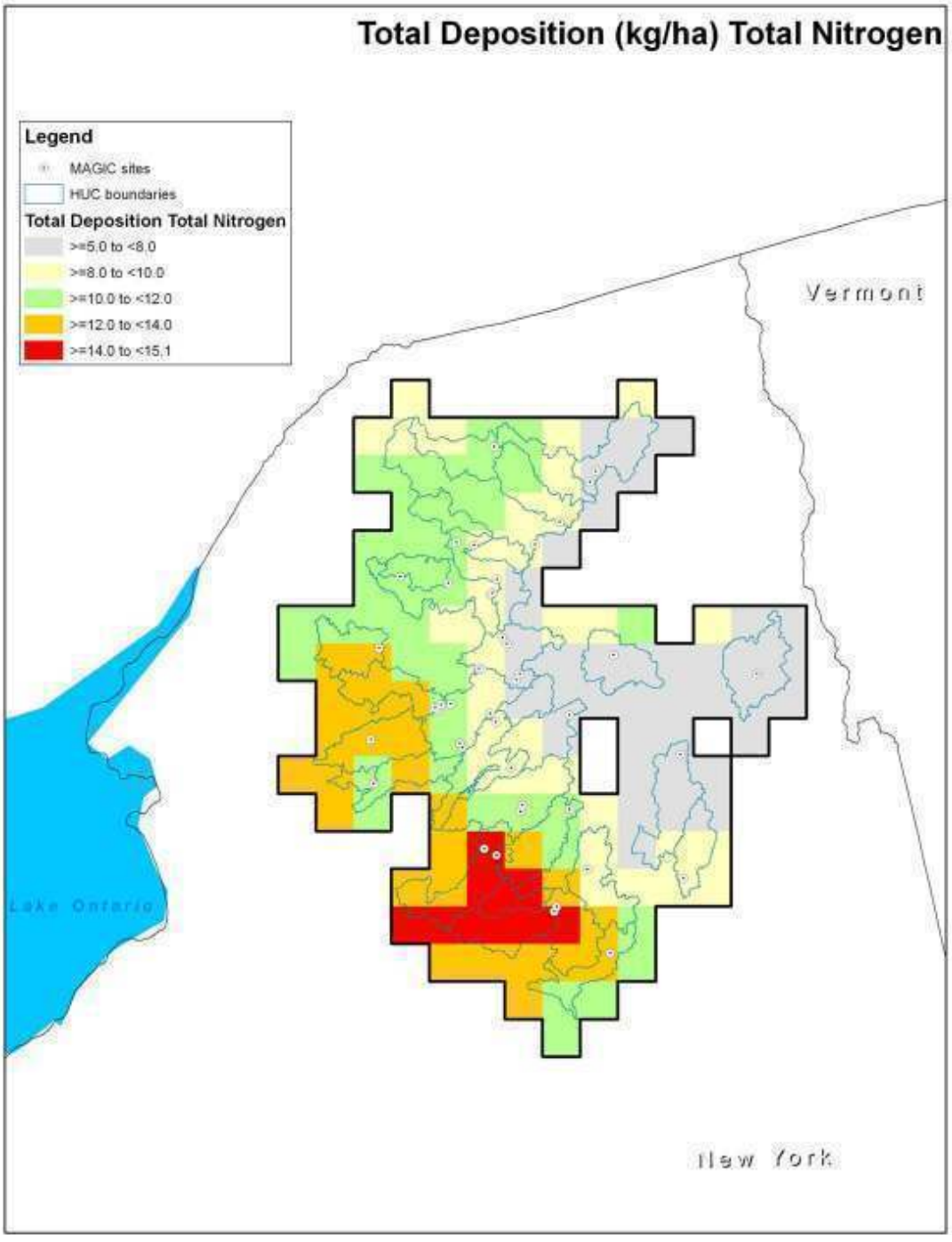


Figure 3.2-6. Modeled 2002 annual total nitrogen deposition across the Adirondack Case Study Area.

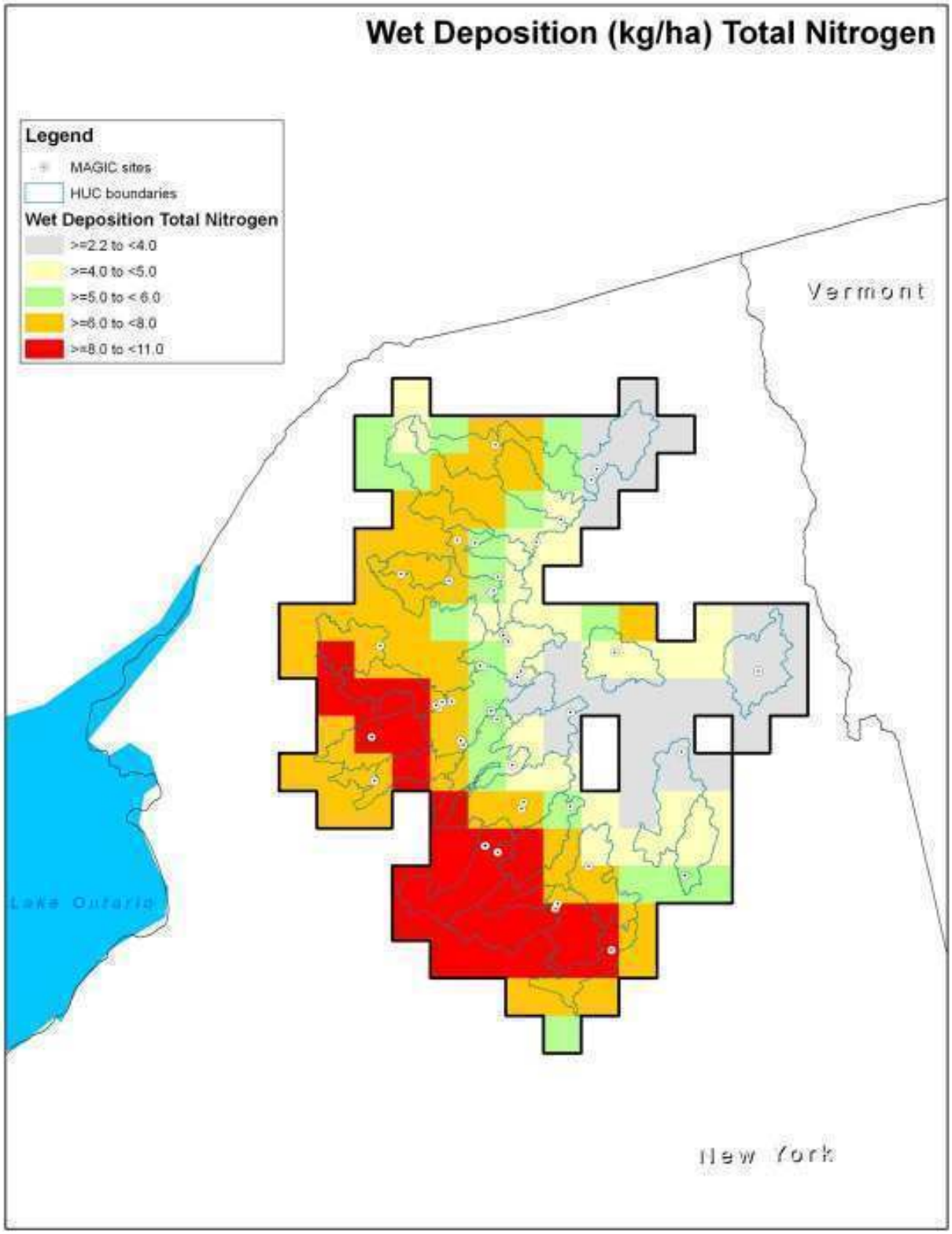


Figure 3.2-7. Modeled 2002 annual wet deposition of nitrogen across the Adirondack Case Study Area.

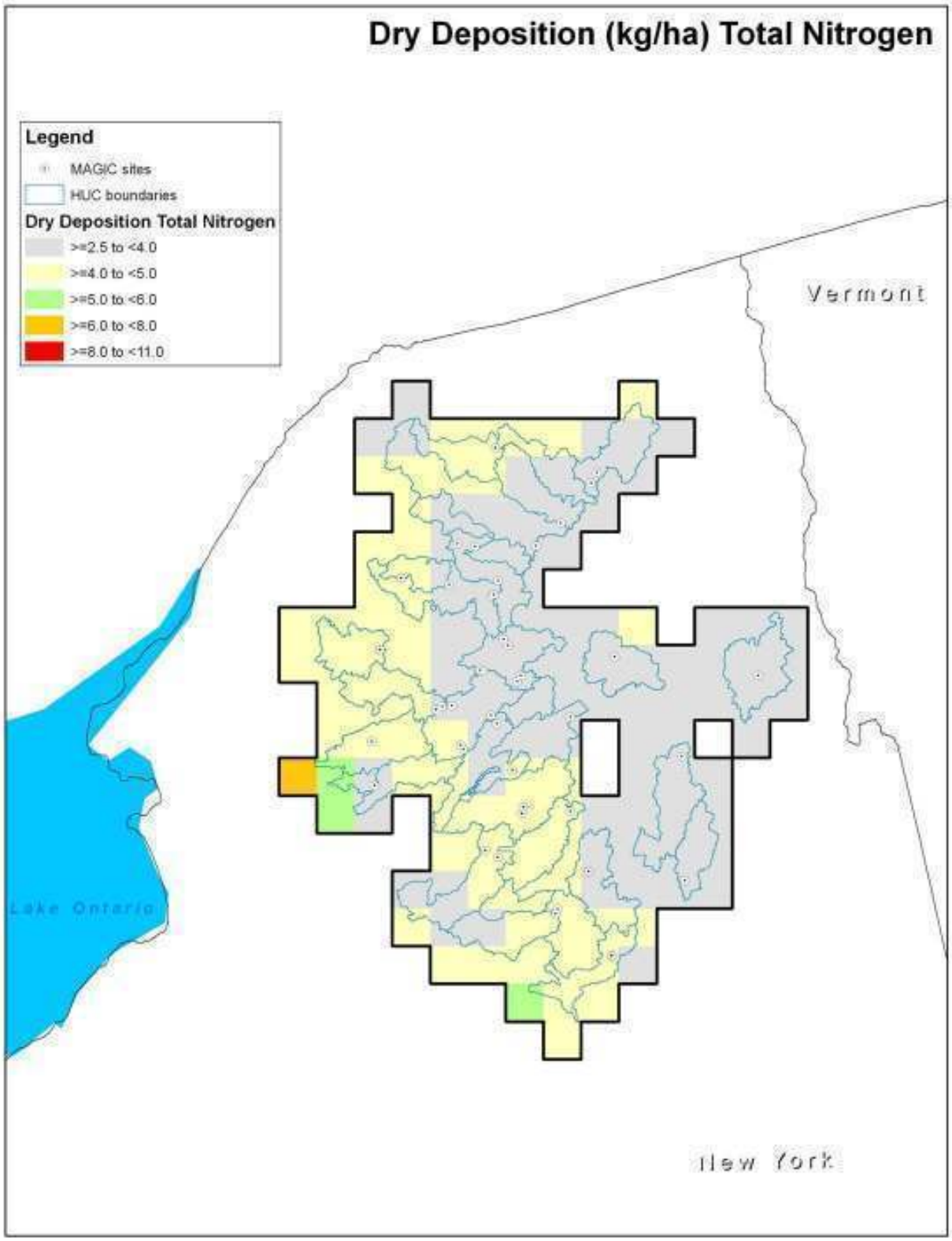


Figure 3.2-8. Modeled 2002 annual dry deposition of nitrogen across the Adirondack Case Study Area.

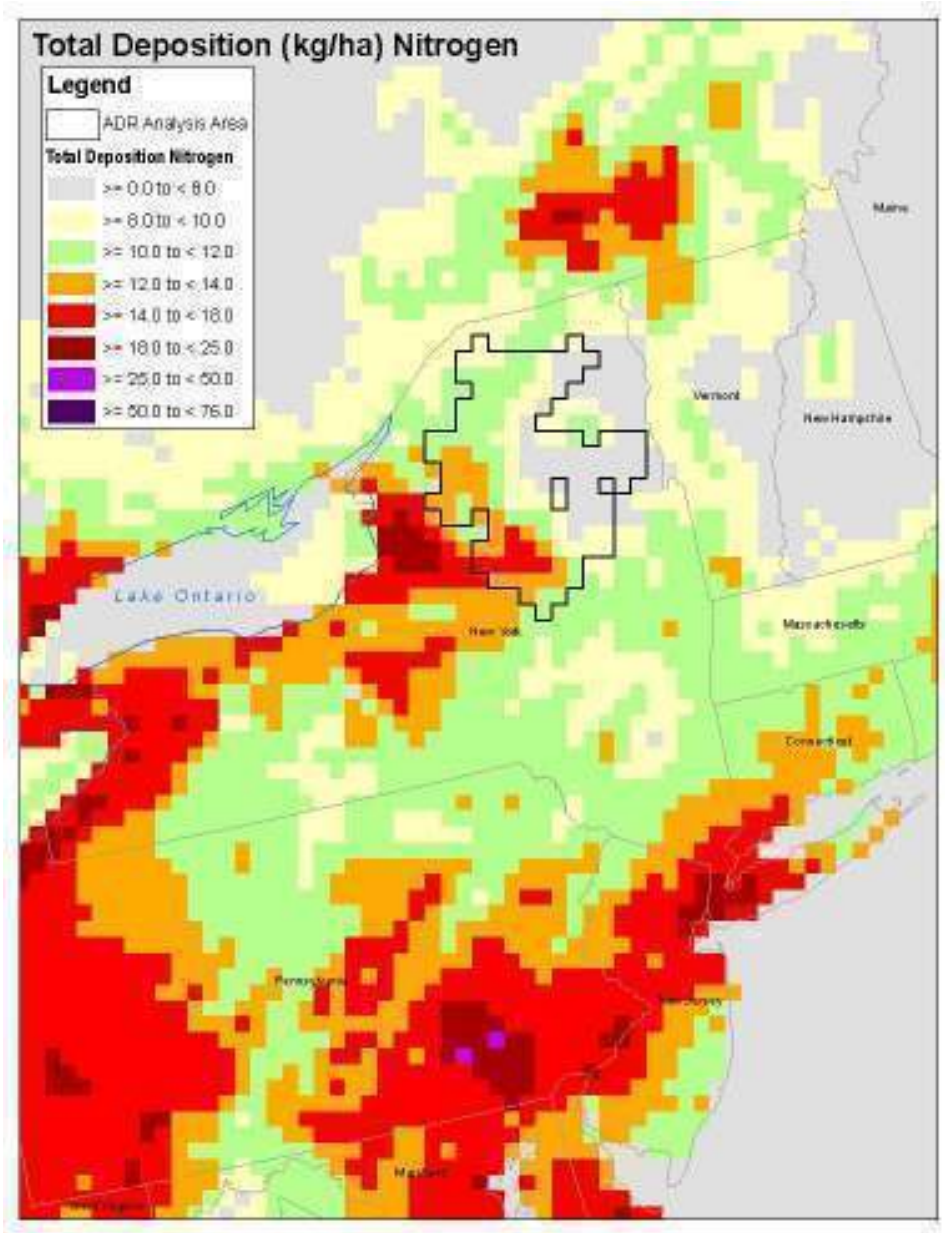


Figure 3.2-9. Modeled 2002 annual total nitrogen deposition across the Northeast.

The spatial patterns in wet and dry oxidized and reduced nitrogen are shown in **Figures 3.2-10a–d**. Wet oxidized and wet reduced nitrogen are similar in terms of west to east gradients, as expected since wet deposition of both oxidized and reduced nitrogen are largely driven by precipitation. In contrast, dry oxidized nitrogen deposition is largest in a southeast to northwest band across the mid-portion of the ADR. The amount of dry reduced nitrogen is small compared to the other components of nitrogen deposition with little spatial variation.

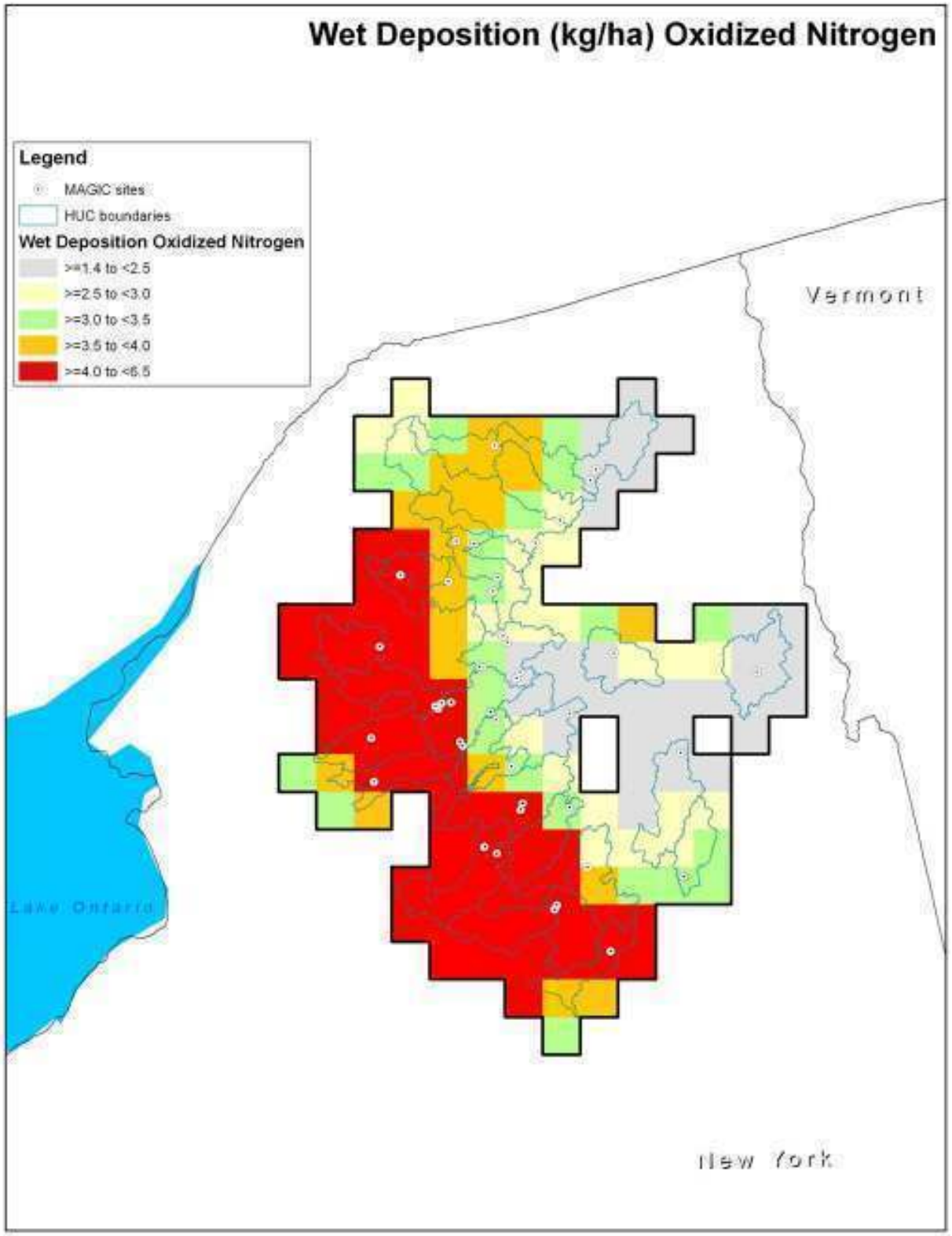


Figure 3.2-10a. Modeled 2002 annual wet oxidized nitrogen deposition across the Adirondack Case Study Area.

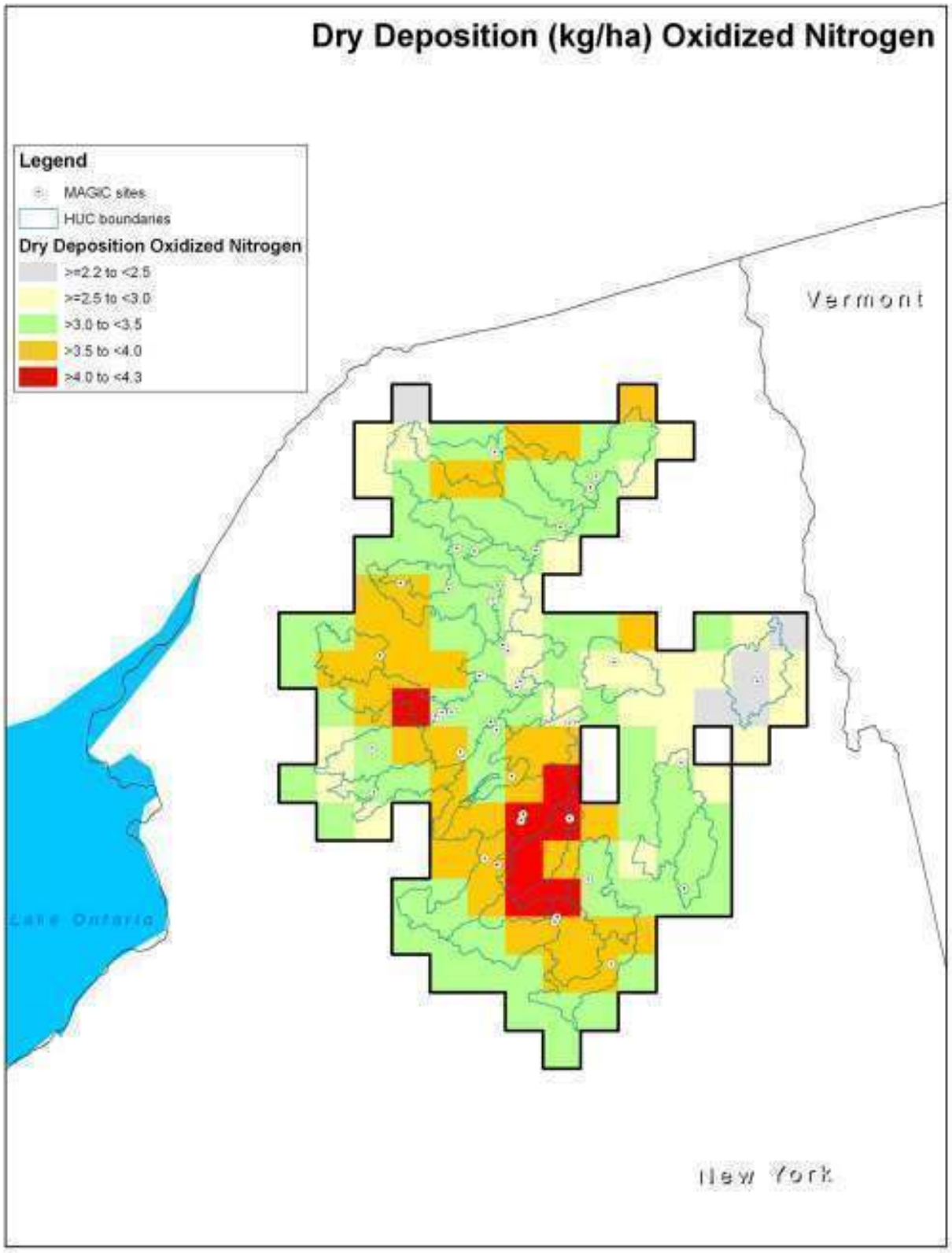


Figure 3.2-10b. Modeled 2002 annual dry oxidized nitrogen deposition across the Adirondack Case Study Area.

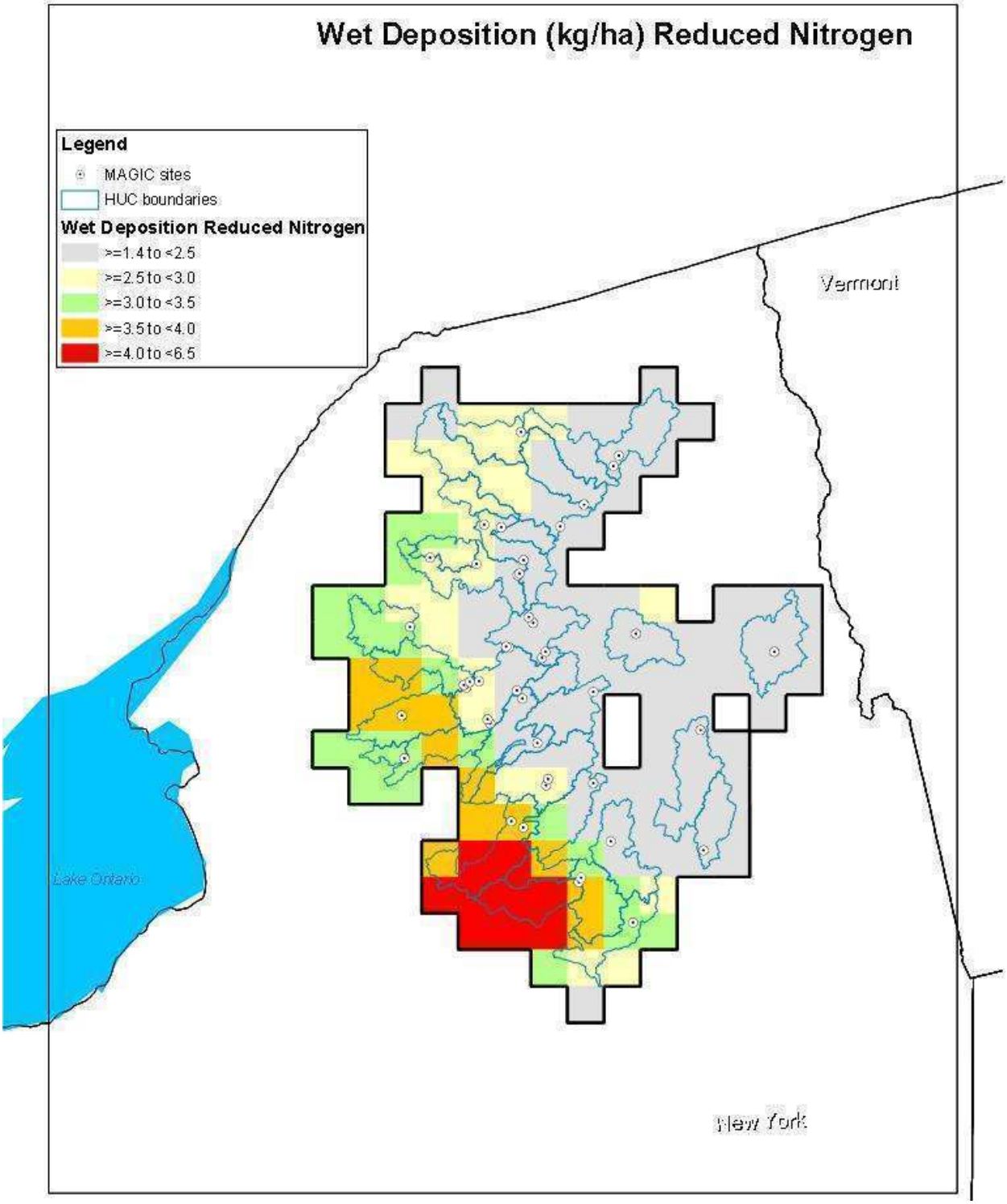


Figure 3.2-10c. Modeled 2002 annual wet reduced nitrogen deposition across the Adirondack Case Study Area.

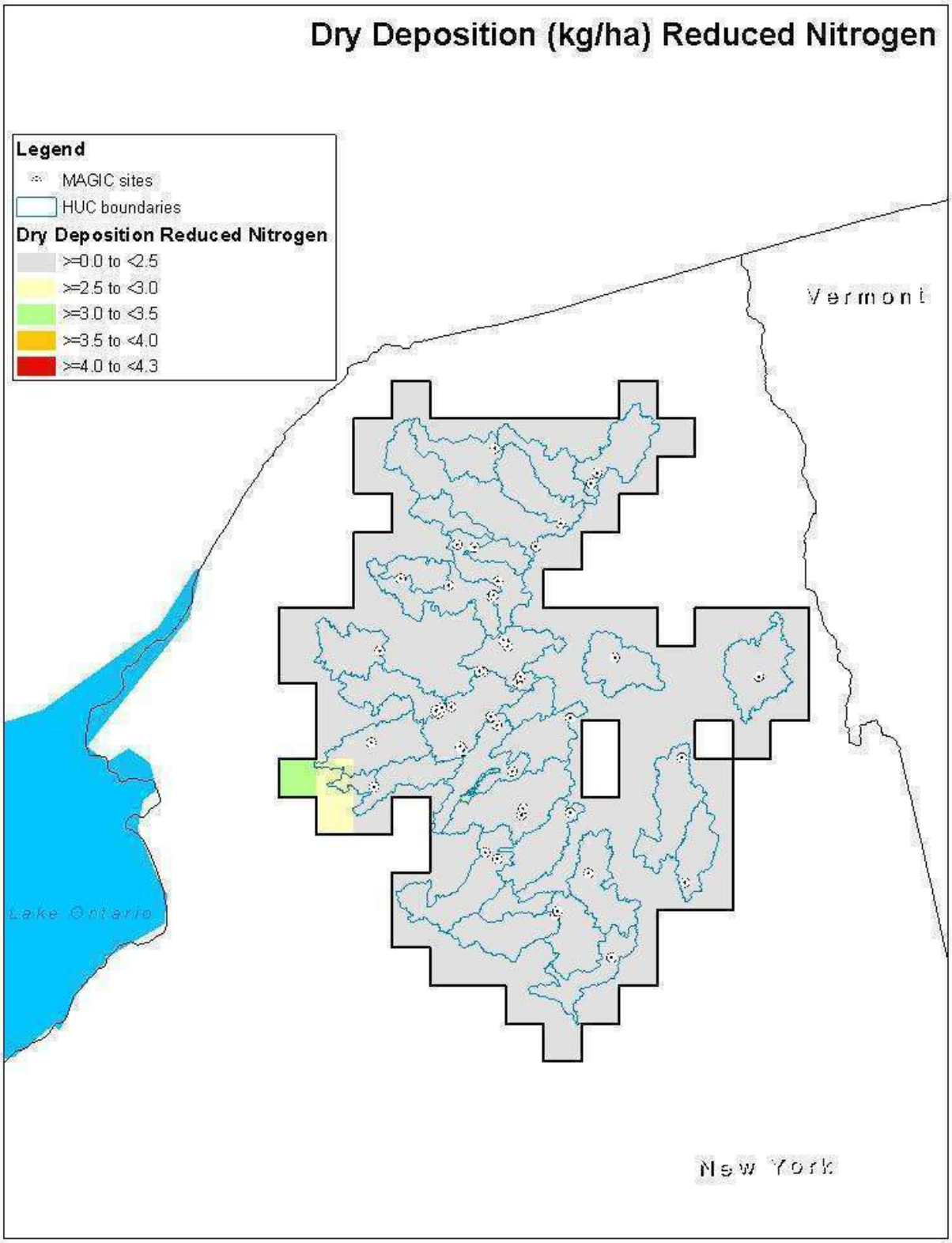


Figure 3.2-10d. Modeled 2002 annual dry reduced nitrogen deposition across the Adirondack Case Study Area.

[Placeholder for spatial patterns in measured vs modeled wet nitrate dep.]

Intra-Annual Variation in Nitrogen Deposition in the ADR

The seasonal variation in modeled 2002 total reactive nitrogen deposition is shown in **Figure 3.2-11**. Note that the data in this figure represent the percentage of annual total deposition that was predicted to occur in each season. For example, 29% of the 2002 modeled total reactive nitrogen deposition was predicted in the spring, with 27% in winter and 25% in the fall. The least amount of total reactive nitrogen deposition was in the summer, with 19% of the annual total. Although there seem to be relatively little seasonal differences in total reactive nitrogen deposition, this is not the case when broken out by wet and dry deposition for oxidized nitrogen and reduced nitrogen. The season percent of annual total modeled deposition of wet/dry oxidized nitrogen and reduced nitrogen, along with precipitation, are shown in **Figures 3.2-12 and 3.2-13**, respectively. The figures indicate that wet deposition of both oxidized and reduced nitrogen tend to track the temporal pattern in precipitation, with reduced nitrogen a closer match to precipitation than oxidized nitrogen. The clearest signal in the data is the minimum in wet deposition of both oxidized nitrogen and reduced nitrogen in the summer of 2002. The seasonal variations in dry deposition of both oxidized nitrogen and reduced nitrogen are very different from that of wet deposition. Dry oxidized nitrogen is fairly consistent from season to season, whereas reduced nitrogen shows a definite seasonal pattern that peaks in the summer. Thus, although there is relatively little intra-annual variation in total reactive nitrogen deposition, there are considerable seasonal differences in several of the individual components.

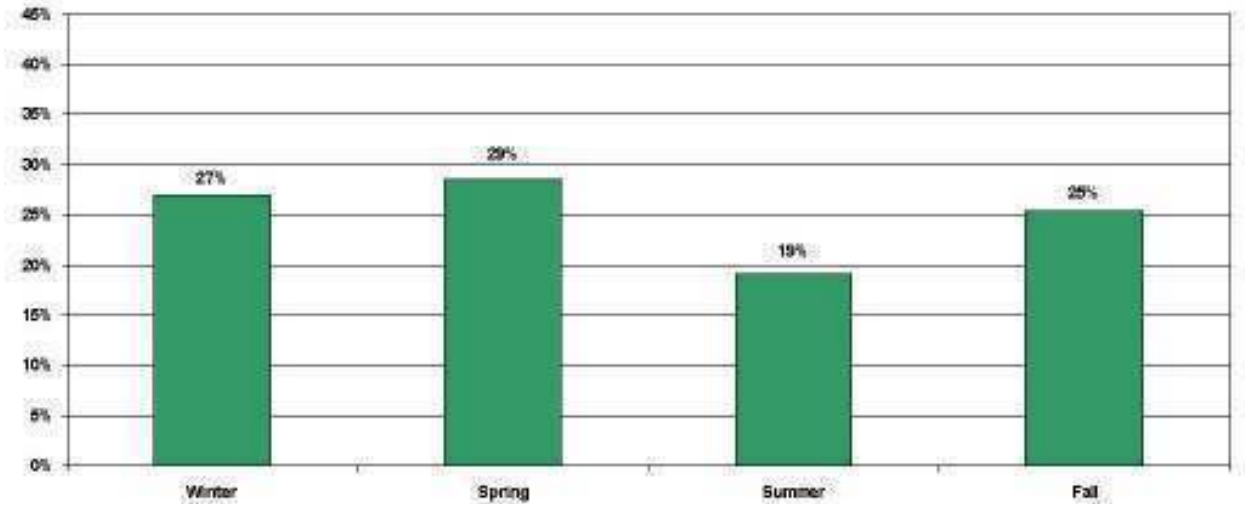


Figure 3.2-11. Percent of annual total nitrogen deposition by season for the Adirondack Region, based on 2002 CMAQ modeling.

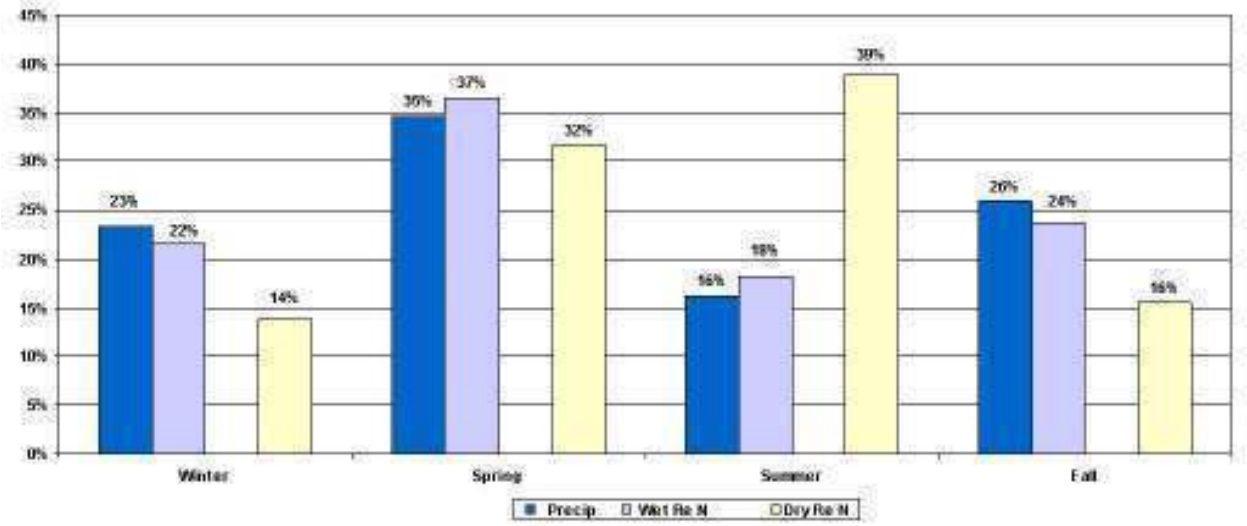


Figure 3.2-12. Percent of annual precipitation and reduced nitrogen deposition by quarter for the Adirondack Region, based on 2002 CMAQ modeling.

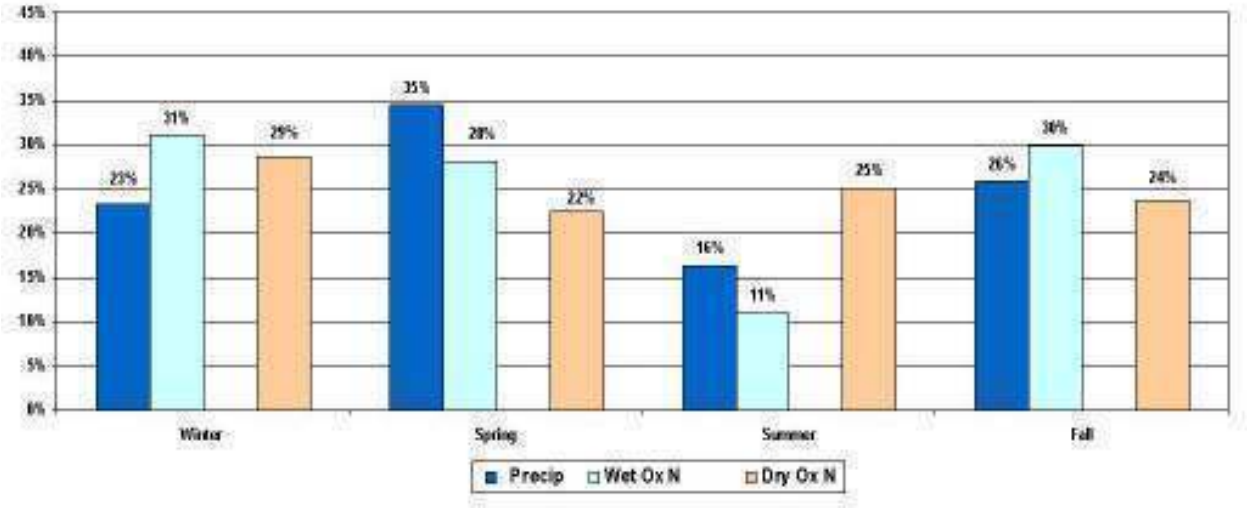


Figure 3.2-13. Percent of annual precipitation and oxidized nitrogen deposition by quarter for the Adirondack Region, based on 2002 CMAQ modeling.

Additional insight into the temporal behavior of nitrogen deposition as modeled for 2002 is revealed by examining the time series of monthly data for the ADR, as shown in **Figures 3.2-14 and 3.2-15** for oxidized nitrogen and reduced nitrogen, respectively. The monthly data indicate that both wet and dry reduced nitrogen exhibit clear temporal patterns. Dry reduced nitrogen increases from January to a peak in July, followed by a steady decline to December. In contrast, the monthly pattern in dry oxidized nitrogen is fairly flat through most of 2002, as evident from Figure 3.2-14. The monthly wet reduced nitrogen tracks the monthly precipitation rather closely, with the highest deposition in late spring from April through June. The monthly

temporal pattern of wet oxidized nitrogen does not follow precipitation to the same degree as wet reduced nitrogen.

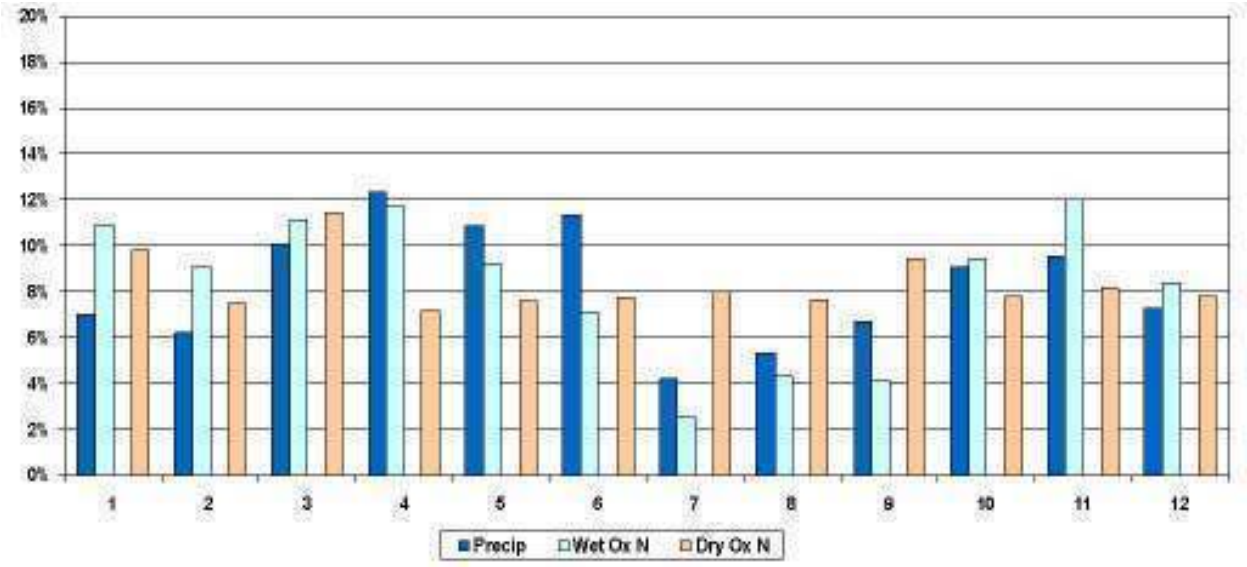


Figure 3.2-14. Percent of 2002 annual precipitation and oxidized nitrogen deposition by month for the Adirondack Region, based on 2002 CMAQ modeling.

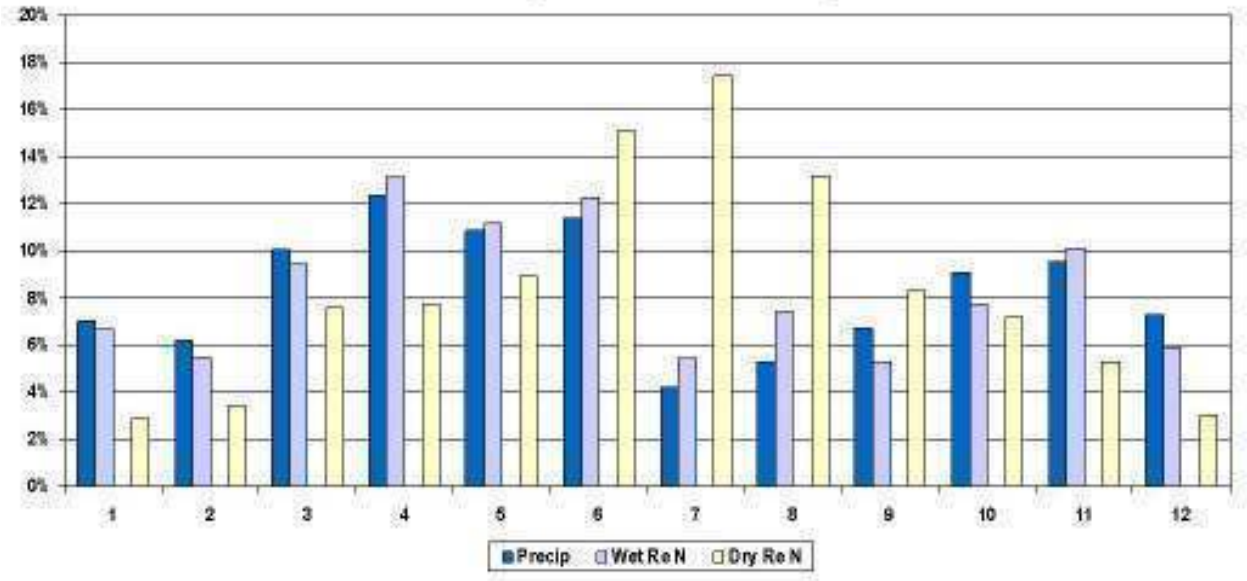


Figure 3.2-15. Percent of 2002 annual precipitation and reduced nitrogen deposition by month for the Adirondack Region, based on 2002 CMAQ modeling.

The monthly wet oxidized nitrogen and wet reduced nitrogen data at the 15 selected sites in the ADR are shown in **Figures 3.2-16 and 3.2-17**, respectively. The highest wet deposition in nearly all areas occurs in March and April for both wet oxidized nitrogen and reduced nitrogen,

1 although some sites also showed elevated levels of wet reduced nitrogen deposition extending
2 into June. A secondary peak in wet oxidized and reduced nitrogen is evident in October and
3 November at most locations. The minimum wet deposition tends to occur in July or July through
4 September.

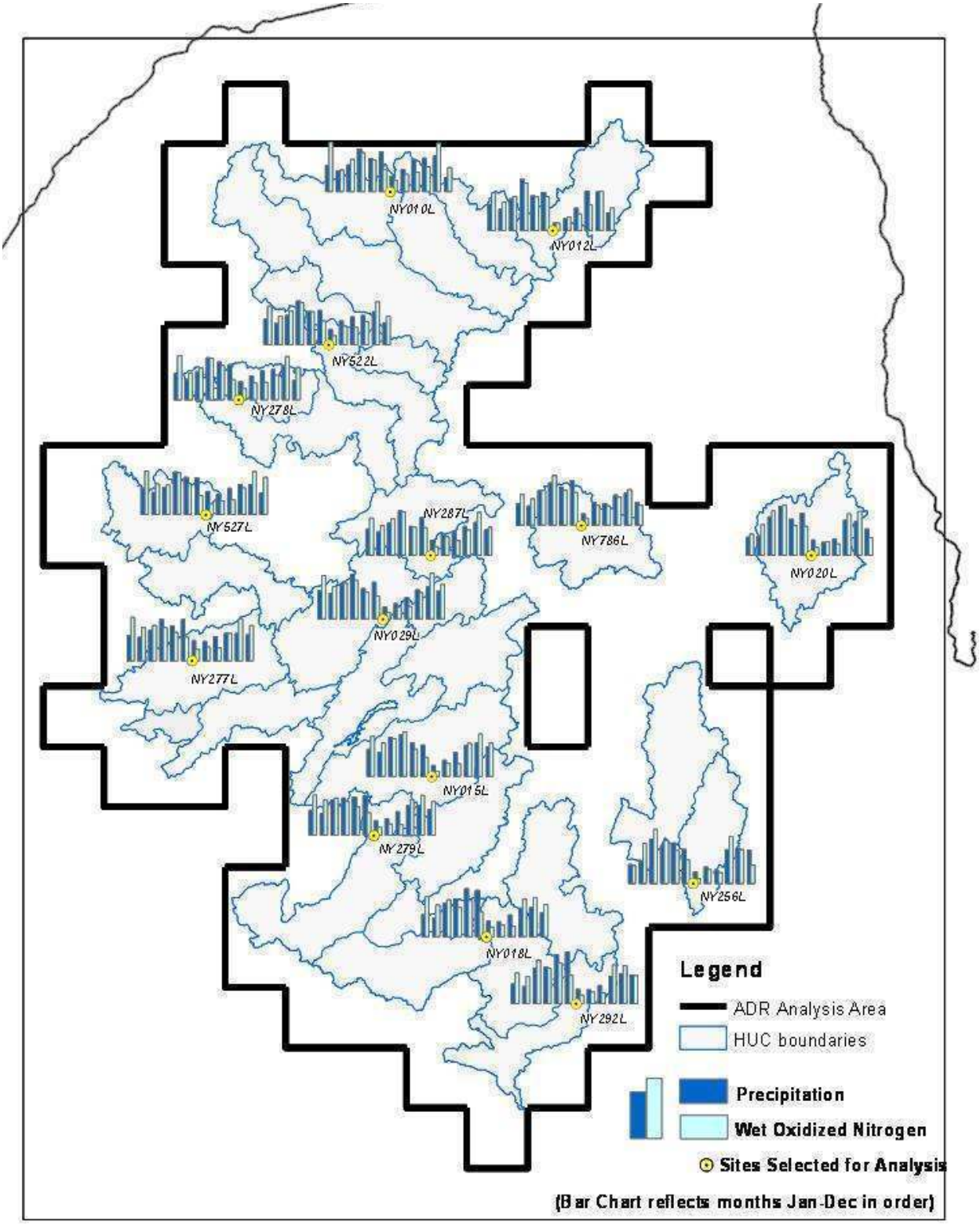


Figure 3.2-16. Percent by month of 2002 annual wet oxidized nitrogen deposition for selected sites in the Adirondack Case Study Area.

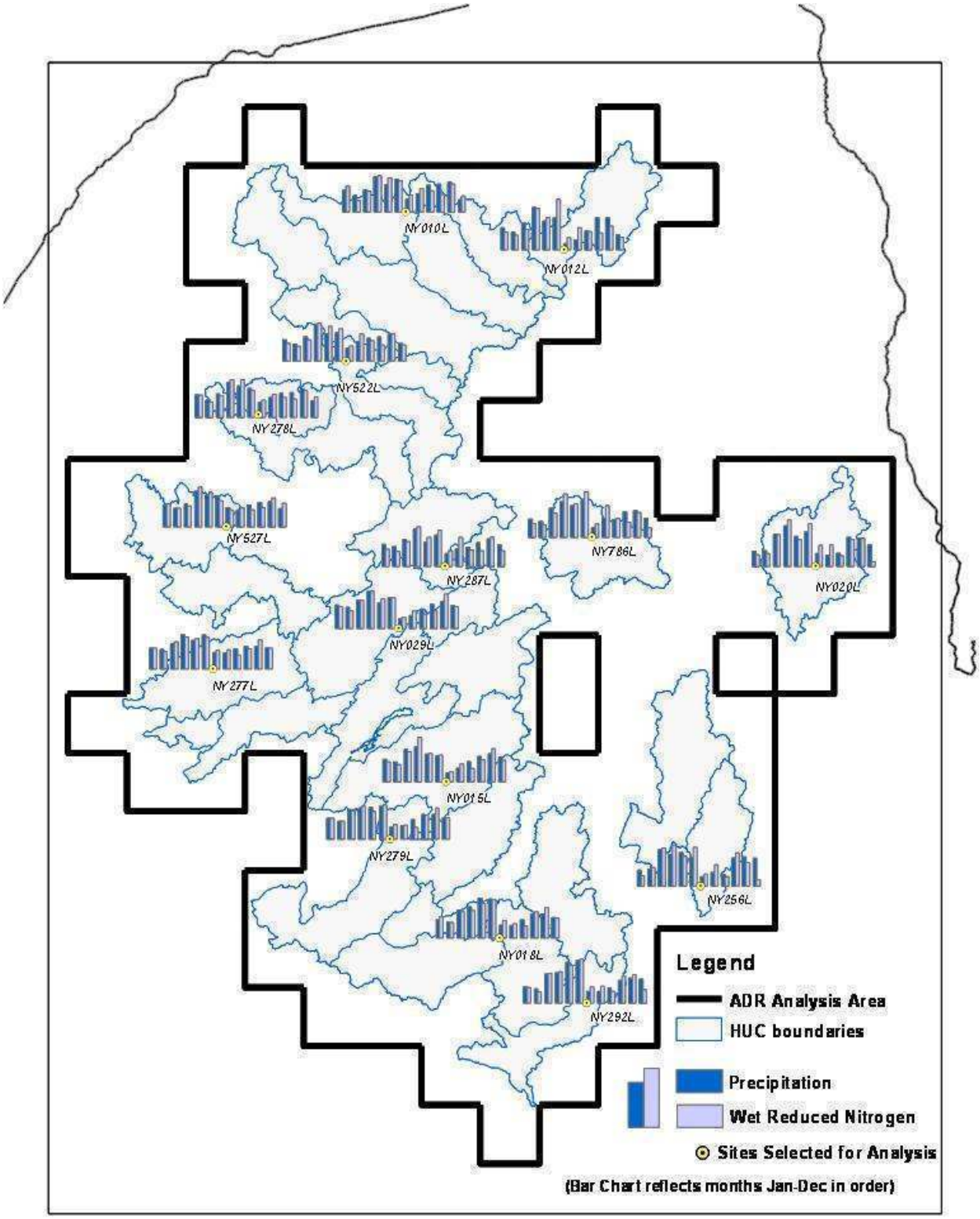


Figure 3.2-17. Percent by month of 2002 annual wet reduced nitrogen deposition for selected sites in the Adirondack Case Study Area.

The monthly dry oxidized nitrogen and dry reduced nitrogen data at the 15 selected sites in the ADR are shown in **Figures 3.2-18 and 3.2-19**, respectively. The temporal patterns of dry oxidized nitrogen and dry reduced nitrogen are quite different. The dry oxidized nitrogen temporal pattern is generally flat, except for notable peaks in January and March. In contrast, dry reduced nitrogen deposition is at a minimum January and December. Values begin to increase in March and reach a peak in June and July, followed by a steady month-to-month decline to December. The dry oxidized nitrogen and dry reduced nitrogen monthly temporal patterns are each fairly consistent across the ADR.

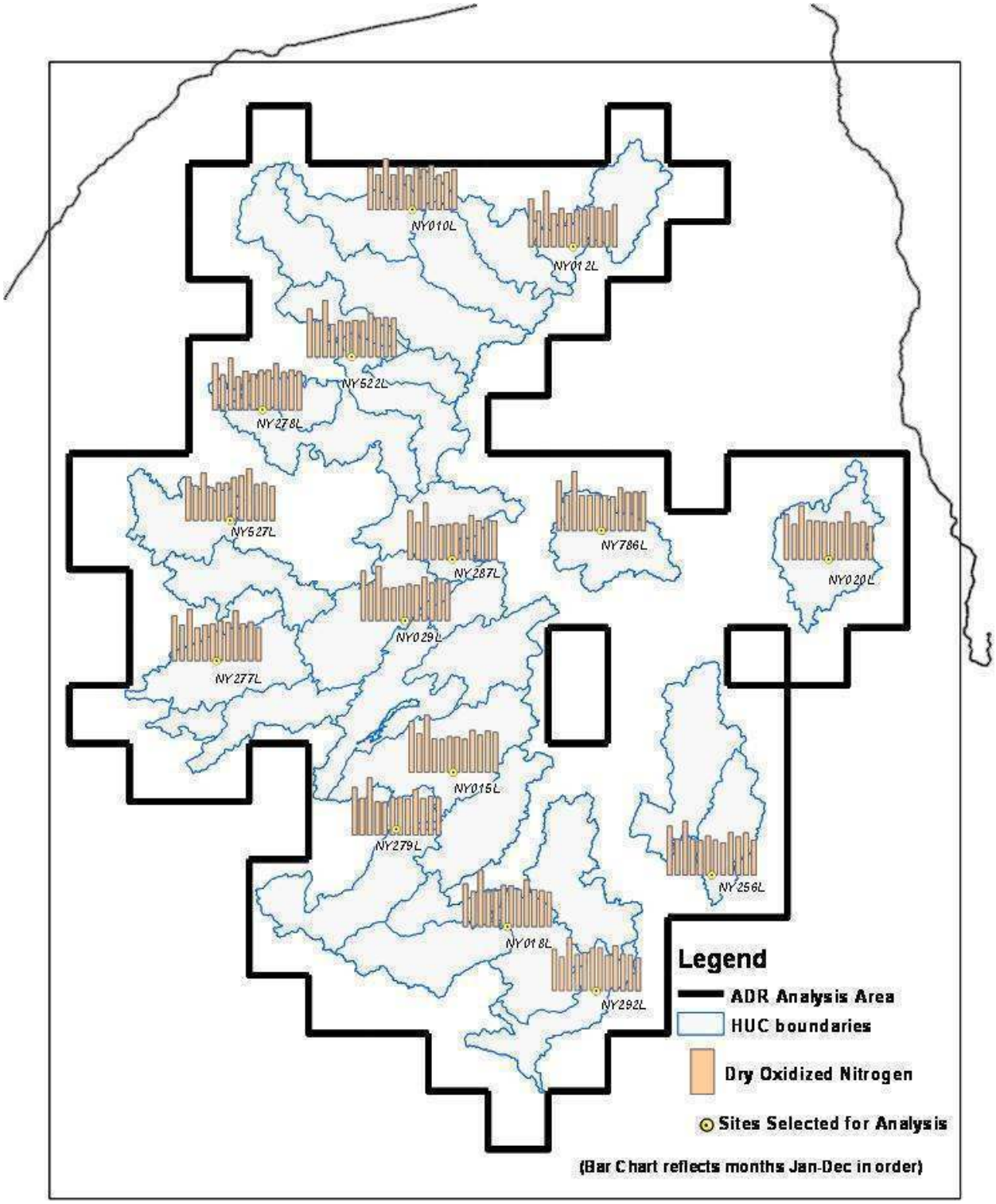


Figure 3.2-18. Percent by month of 2002 annual dry oxidized nitrogen deposition for selected sites in the Adirondack Case Study Area.

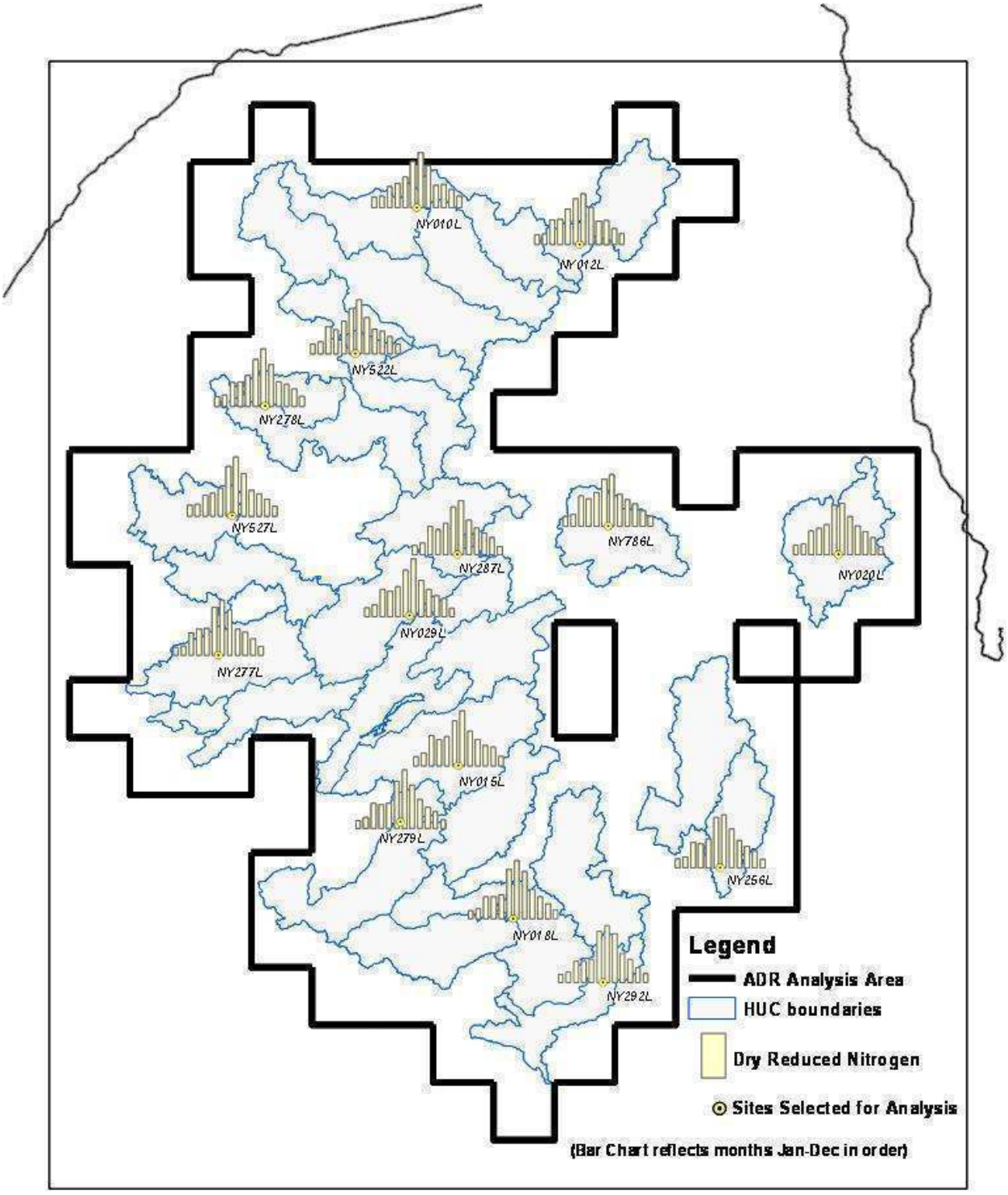


Figure 3.2-19. Percent by month of 2002 annual dry reduced nitrogen deposition for selected sites in the Adirondack Case Study Area.

[Placeholder for temporal analysis of wet dep based on measured data and a comparison between measured and modeled wet Ox vs wet Re N dep]

Relative Contribution of Sulfur Deposition

The contributions of wet and dry sulfur deposition to annual total sulfur deposition are shown in **Figure 3.2-20**. The portion of wet sulfur deposition is much greater than dry, with 64% wet versus 36% dry. The relative amount of wet and dry sulfur deposition is fairly uniform across the ADR, as shown in **Figure 3.2-21**.

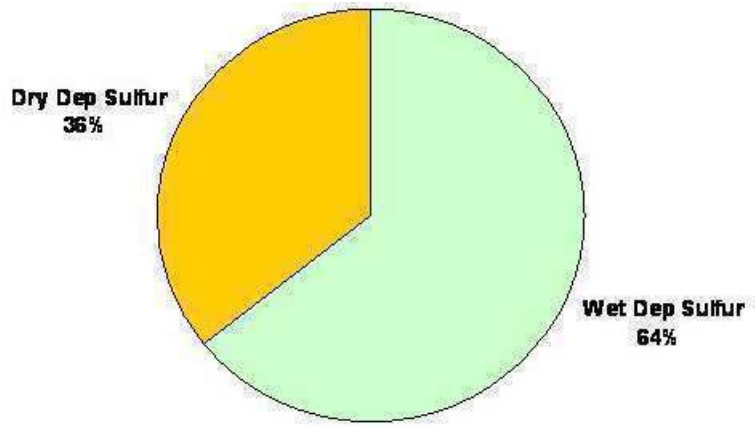


Figure 3.2-20. Percentages by component of 2002 annual sulfur deposition for the Adirondack Region.

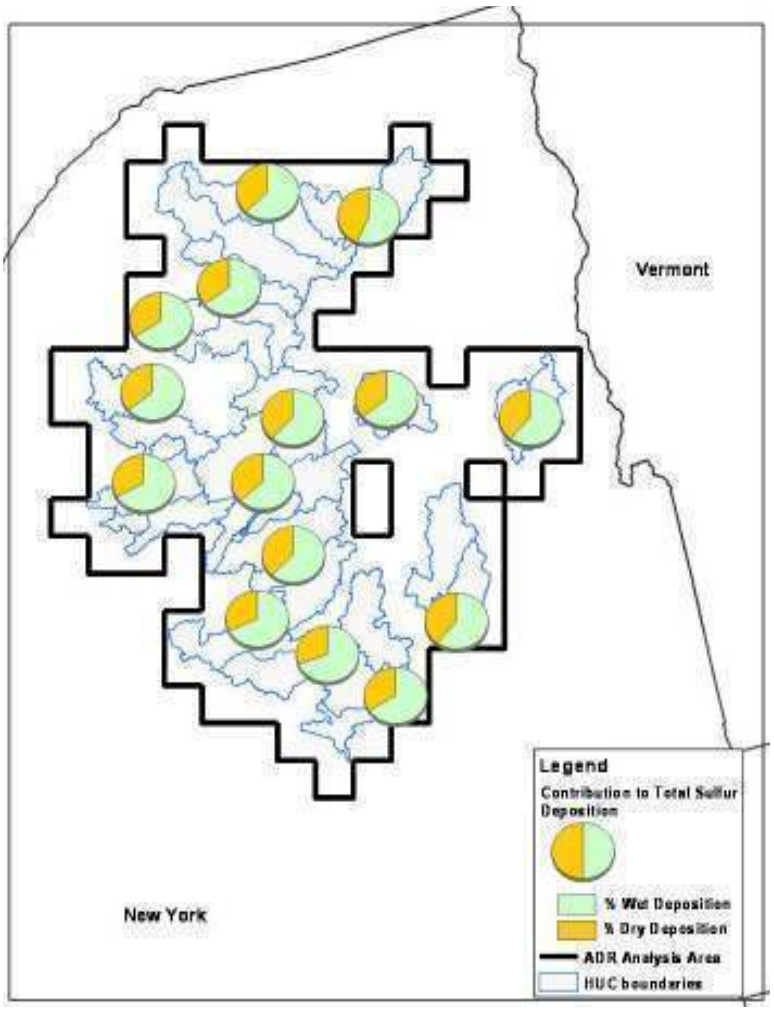


Figure 3.2-21. Contribution to 2002 modeled annual total sulfur deposition.

Spatial Gradients in Annual Sulfur Deposition Across the ADR

The annual total 2002 modeled sulfur deposition across the ADR is shown in **Figure 3.2-22**. The spatial pattern in sulfur deposition is similar to the pattern in nitrogen deposition (see Figure 3.2-19). Specifically, the highest amount of sulfur deposition is predicted in the southern and western portions of the case study area. Like nitrogen deposition, sulfur deposition is greater than 14 kg/ha in the southwest ADR compared to less than 8 kg/ha in the east. The spatial gradient in total sulfur deposition is largely driven by wet deposition as evident by comparing the wet sulfur deposition map in **Figure 3.2-23** to the dry sulfur deposition map in **Figure 3.2-24**. The spatial gradient in wet sulfur deposition appears to be much stronger than the gradient in dry sulfur deposition. Like nitrogen deposition, the relatively high total sulfur deposition in the southwestern portion of the ADR is part of a broad area of high sulfur deposition that stretches

westward from the case study area along the southern shore of Lake Ontario toward western Pennsylvania and beyond, as seen in **Figure 3.2-25**.

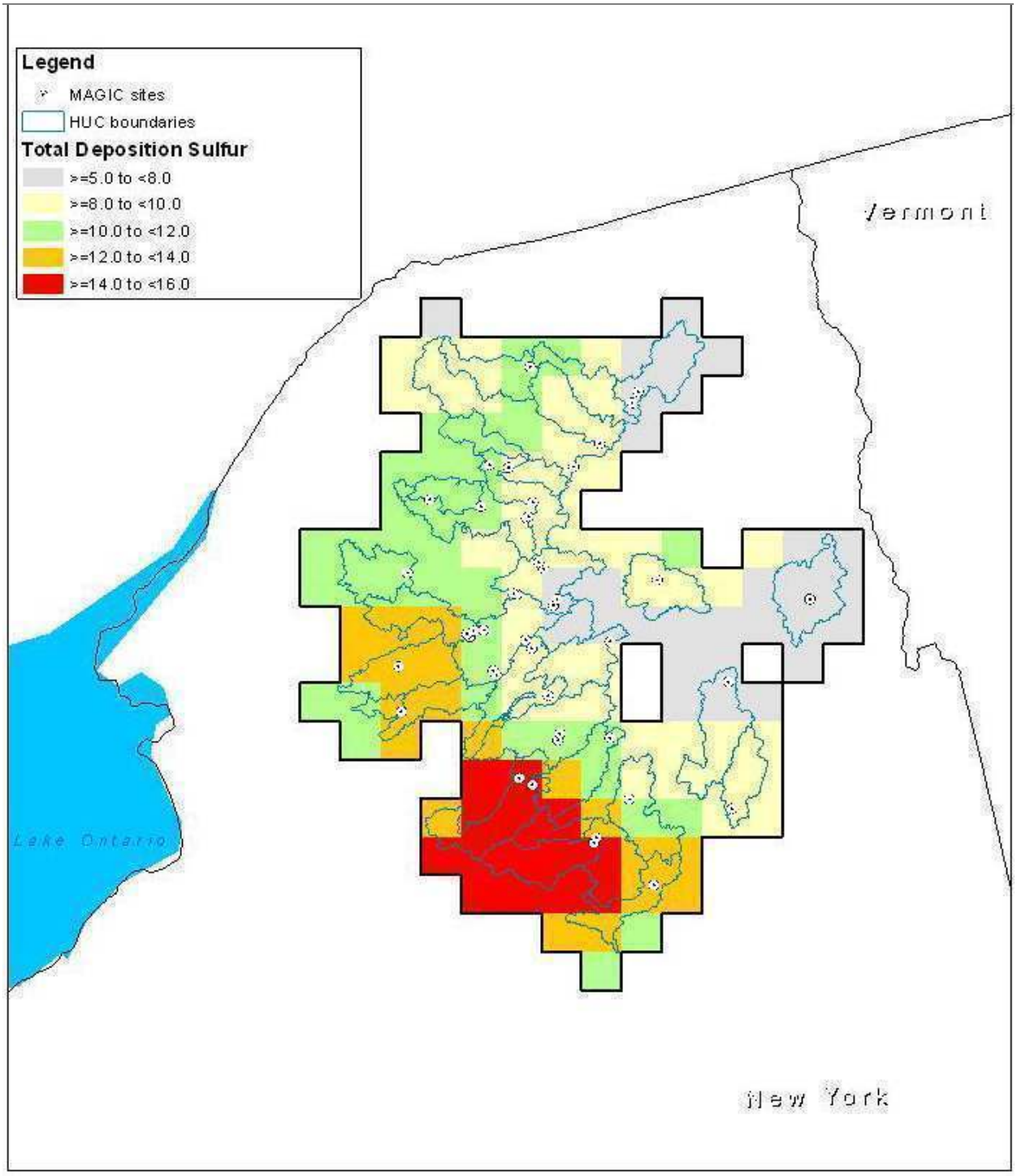


Figure 3.2-22. Modeled 2002 annual total sulfur deposition across the Adirondack Case Study Area.

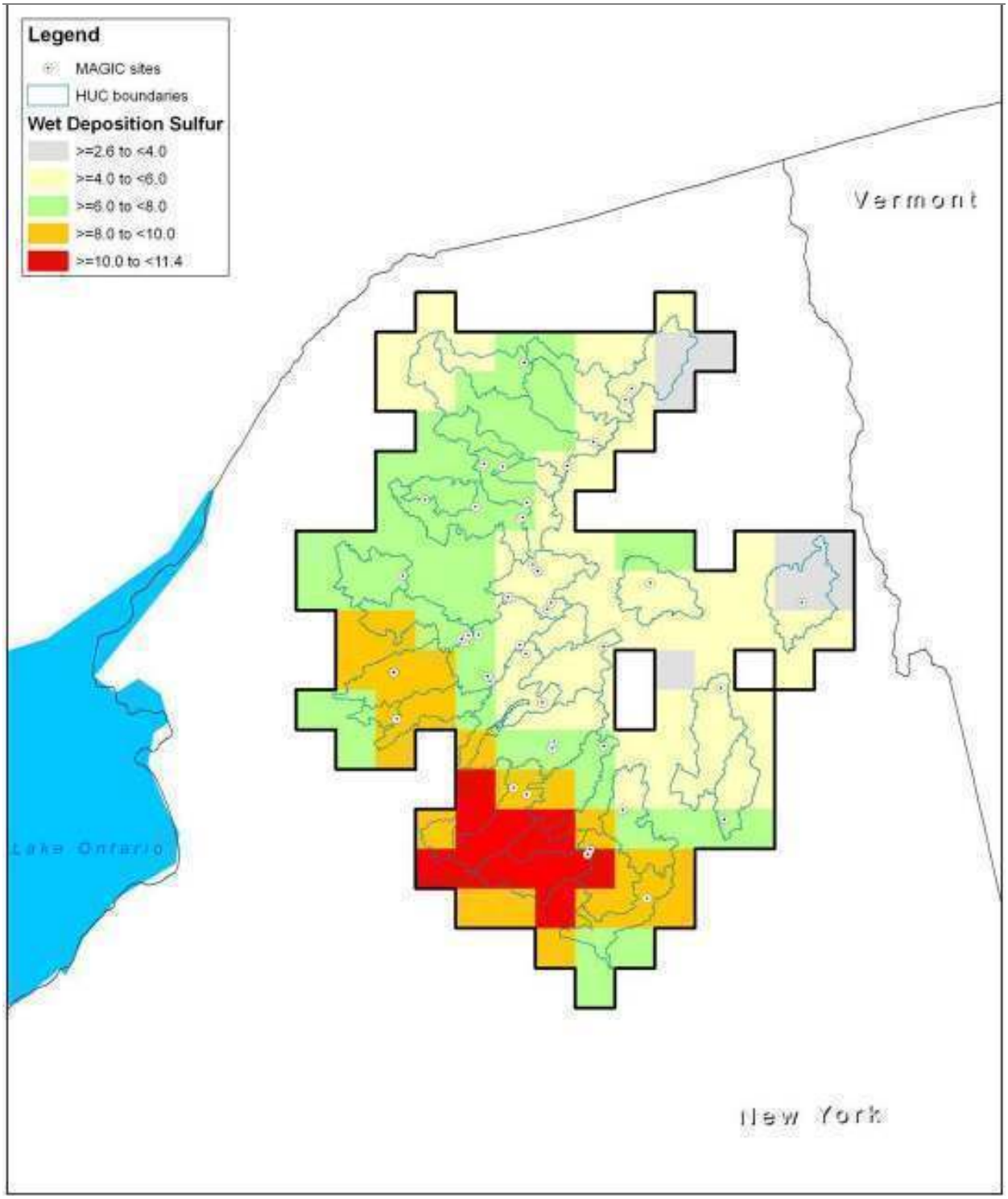


Figure 3.2-23. Modeled 2002 annual wet sulfur deposition across the Adirondack Case Study Area.

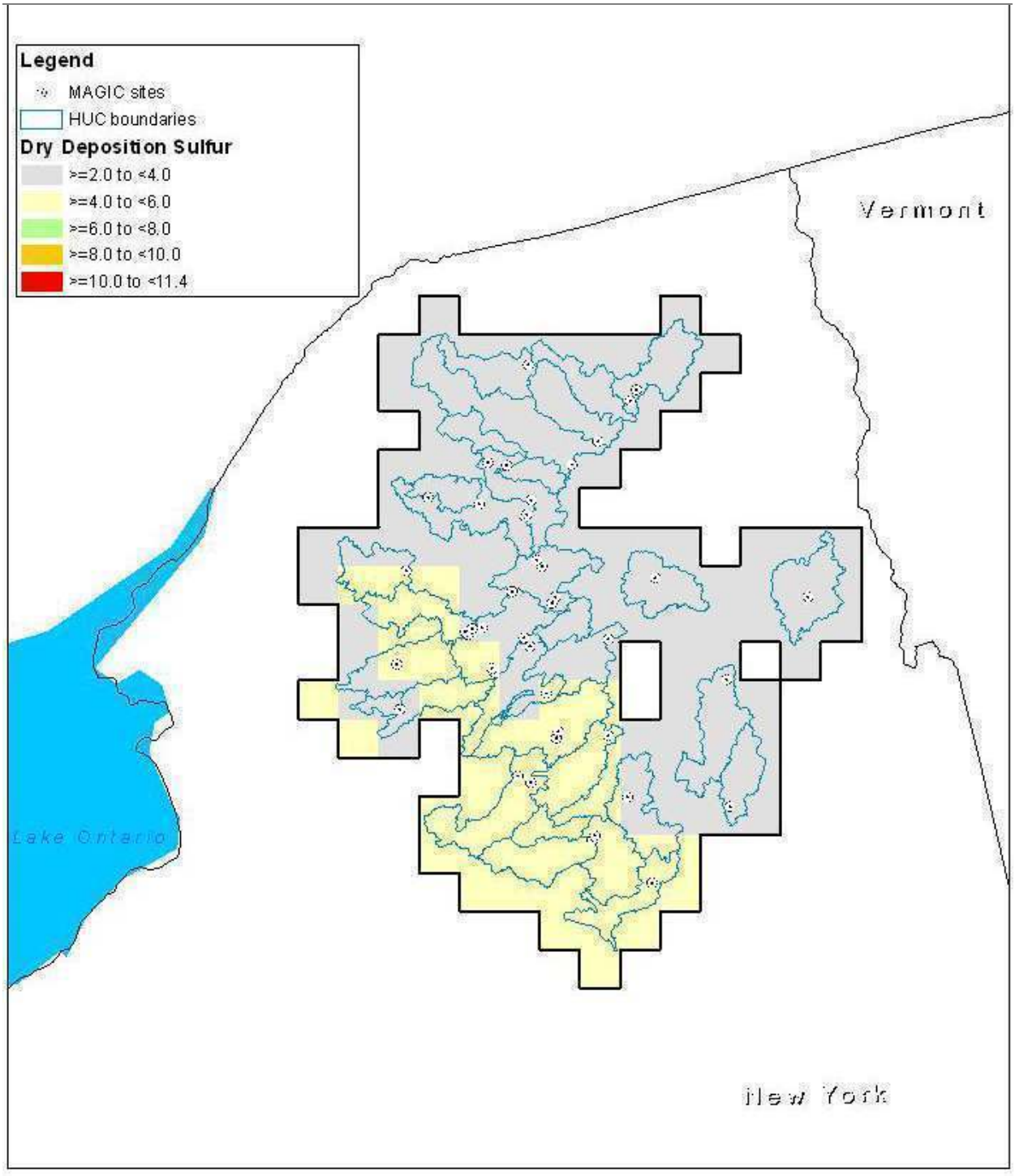


Figure 3.2-24. Modeled 2002 annual dry sulfur deposition across the Adirondack Case Study Area.

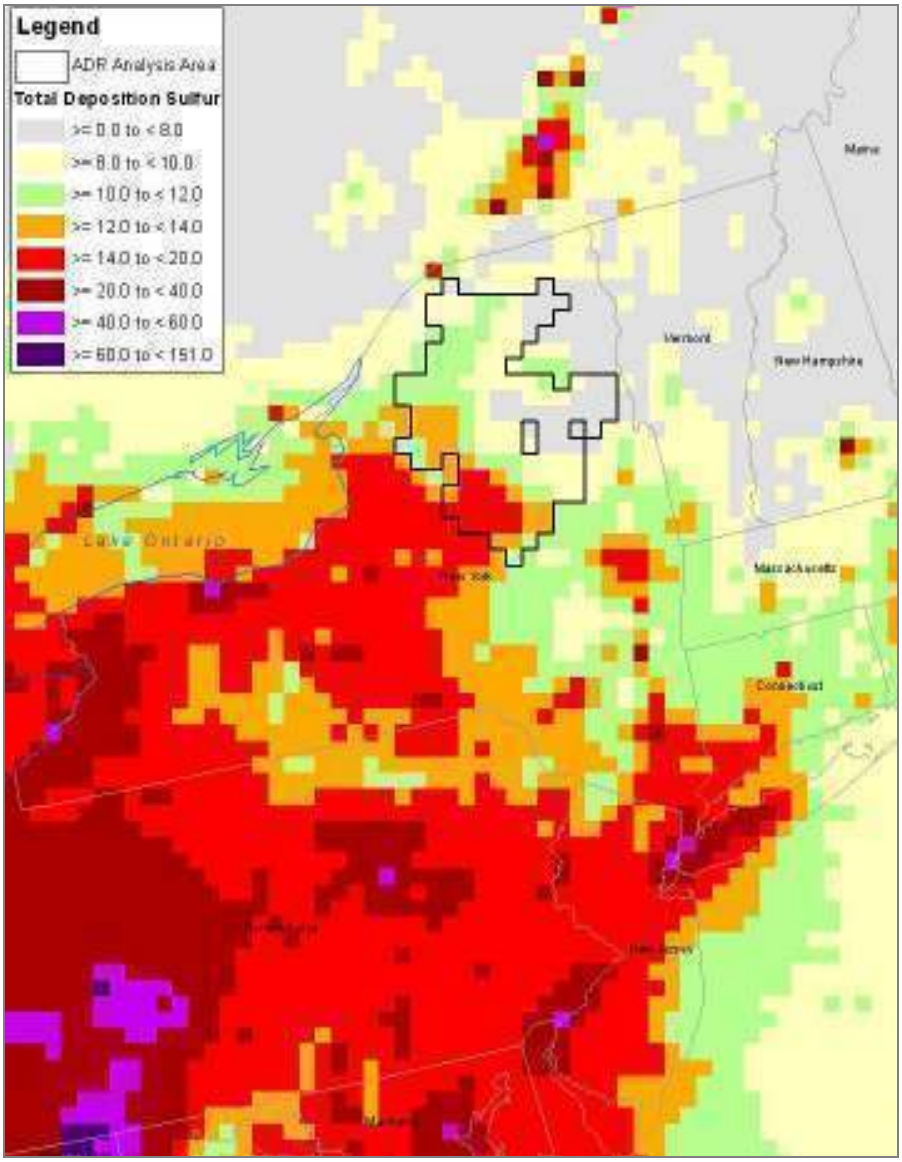


Figure 3.2-25. Modeled 2002 annual total sulfur deposition across the Northeast.

Intra-Annual Variation in Sulfur Deposition in the ADR

In **Figure 3.2-26**, we show the seasonal patterns in modeled 2002 total sulfur deposition in the ADR. In general, the relative amount of predicted sulfur deposition that falls in each season is fairly similar during 2002. Like total nitrogen, the greatest portion of annual sulfur deposition is predicted to occur in the spring (30%). The least amount of sulfur deposition is in the summer at 20% of the annual total. **Figure 3.2-27** provides a breakout of the seasonal amounts in terms of wet and dry sulfur deposition. The seasonal percentages of precipitation are provided for reference. The data in Figure 3.2-27 indicate that wet sulfur deposition is greatest

during the spring, which is also the season with the highest predicted precipitation. Over 37% of the annual wet sulfur deposition occurs in this season. In each of the other seasons, wet sulfur deposition is in the range of 19%–23%. Dry sulfur deposition is greatest in the winter (43% of annual total) followed by the fall (28%). The spring and summer have the least amount of dry sulfur deposition, with about 15% of the annual total in each of these seasons.

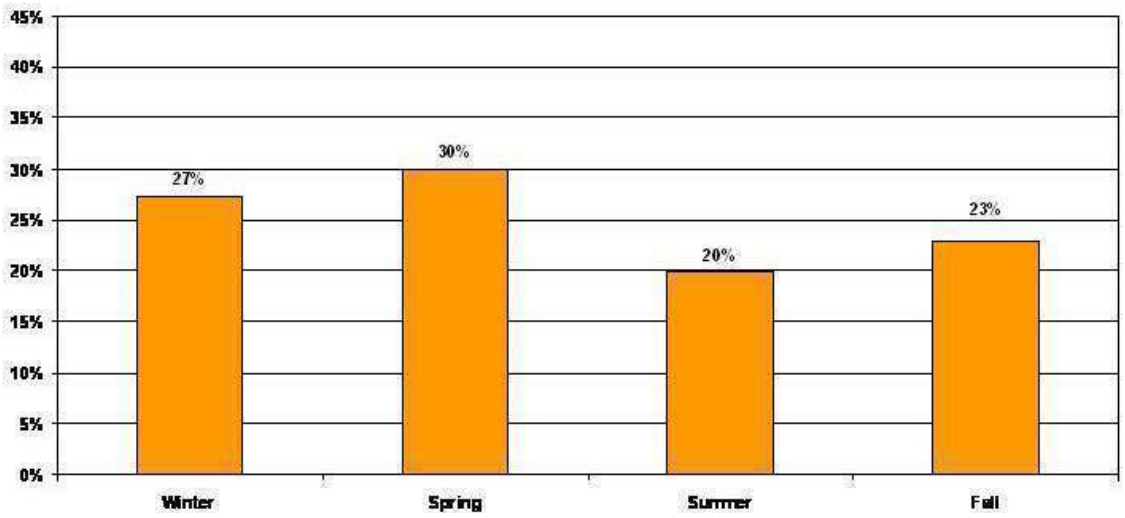


Figure 3.2-26. Percent of annual total sulfur deposition by season for the Adirondack Region, based on 2002 CMAQ modeling.

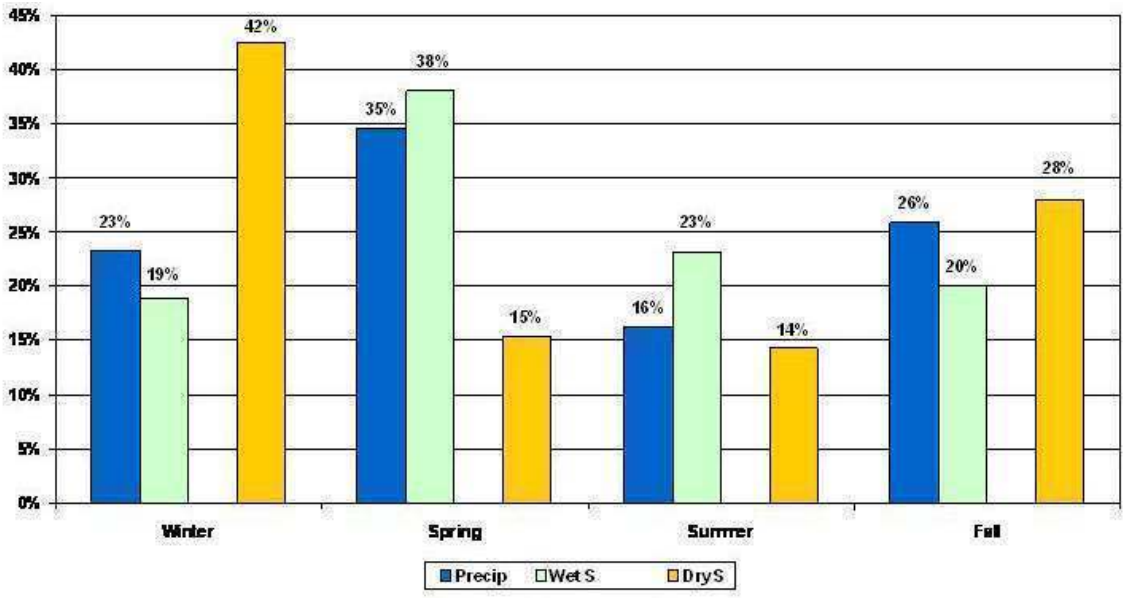


Figure 3.2-27. Percent of annual precipitation and wet and dry sulfur deposition by quarter for the Adirondack Region, based on 2002 CMAQ modeling.

The 2002 modeled monthly wet and dry sulfur deposition data for the ARD, as a whole, are displayed in **Figure 3.2-28**. These data show that wet sulfur deposition increases from a low in January to a peak in May. There is a sharp drop in wet sulfur deposition in July associated with a similar decline in precipitation. Moderately high amounts are predicted in August, September, and October followed by a decline toward the end of the year. In contrast to the temporal pattern exhibited by wet sulfur deposition, dry sulfur deposition is highest in January through March. There is a sharp decline between March and April with generally low values (i.e., 5% or less in each month) from May though September. Dry sulfur deposition increases in October and reaches a secondary peak in November.

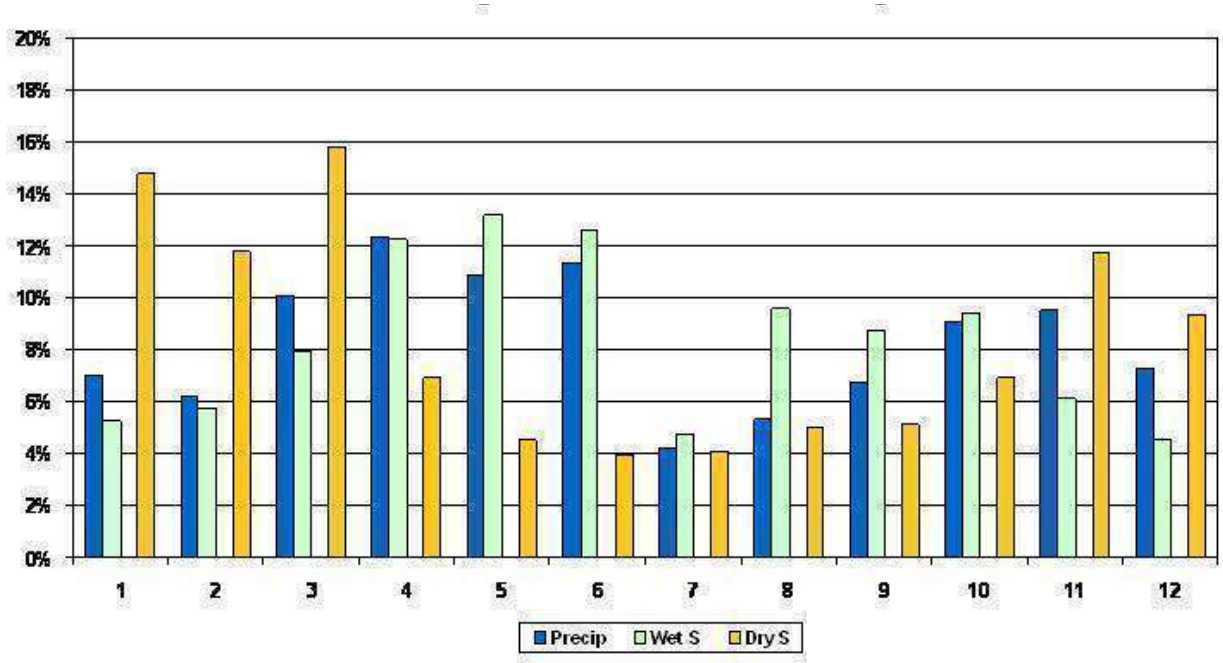


Figure 3.2-28. Percent of 2002 annual precipitation and sulfur deposition by month for the Adirondack Region, based on 2002 CMAQ modeling.

The monthly modeled dry and wet sulfur deposition data at the 15 selected sites in the ADR are shown in **Figures 3.2-29 and 3.2-30**, respectively. The temporal trend during the first half of the year in wet sulfur deposition at individual sites seems to be fairly consistent with the overall pattern of low values in the winter and high values in the spring. All sites exhibit the sharp drop in wet sulfur deposition in July. There are, however, geographic differences in the temporal patterns of wet sulfur deposition in the second half of the year. At the southern ADR sites wet sulfur deposition begins gradually increasing in August with a peak in October. In the northern half of this case study area, wet sulfur deposition shows a sharp increase from July to

August, followed by a steady decline to the end of the year. The temporal trends in the southern portion of the ADR area during the second half of 2002 are consistent with the trends in precipitation during this time period. In the northern ADR, the trends in wet sulfur deposition are not as consistent with the trends in precipitation. The monthly dry sulfur deposition data (see Figure 3.2.1-30) show a "concave" pattern. The highest amounts are in January through March followed by a sharp drop in April. Dry deposition continues to decline to a minimum in June/July followed by a gradual increase to a secondary peak in November. Unlike the temporal trends in wet sulfur deposition, the temporal behavior for dry sulfur deposition is geographically fairly consistent across the ADR. The pattern in dry sulfur deposition also differs from the monthly trend in dry oxidized and reduced nitrogen (see Figures 3.2-18 and 3.2-19). In fact, the trend in dry sulfur deposition, which is at a minimum in the summer, shows the opposite pattern of dry reduced nitrogen deposition, which peaks during this season.

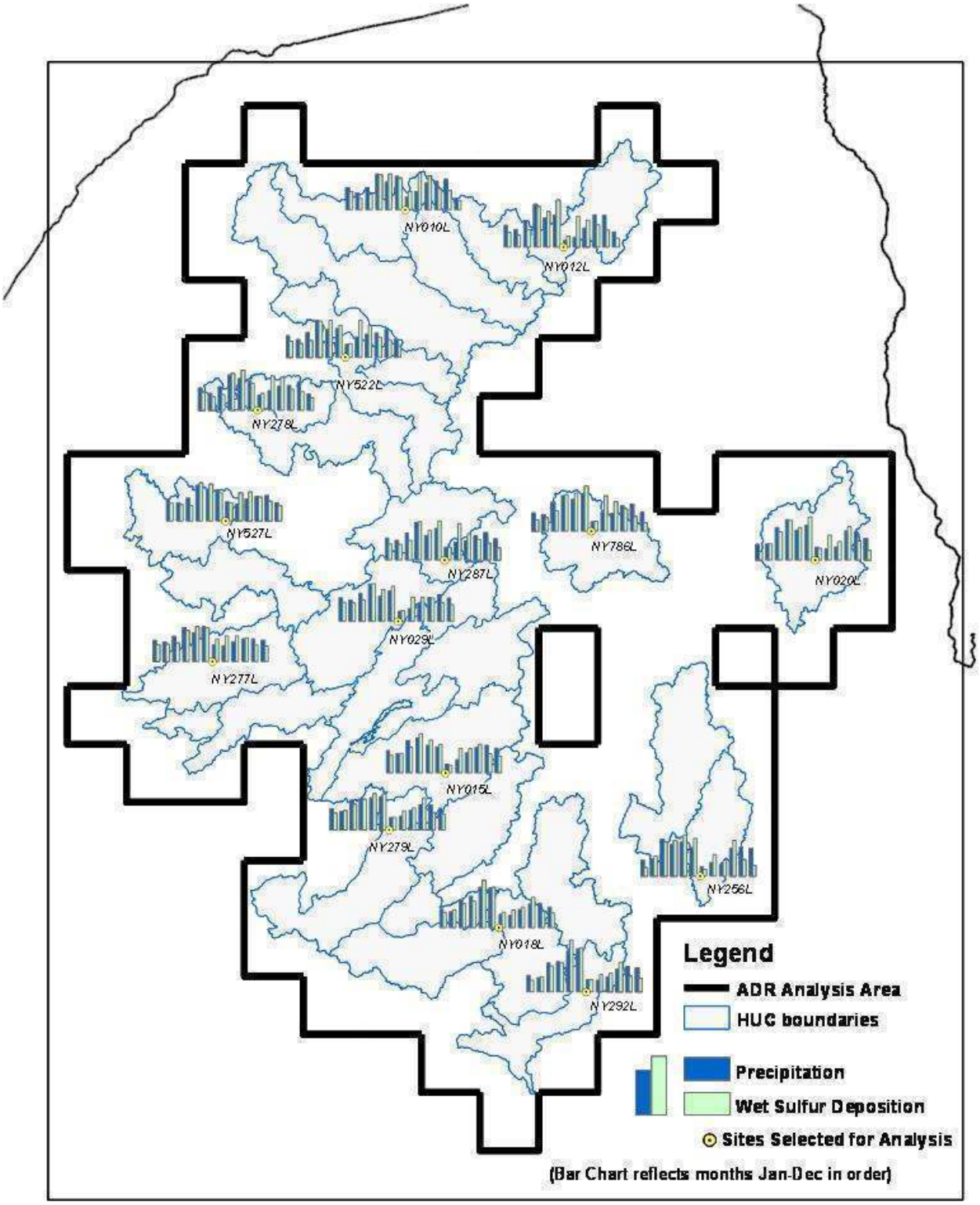


Figure 3.2-29. Percent by month of 2002 annual wet sulfur deposition for selected sites in the Adirondack Case Study Area.

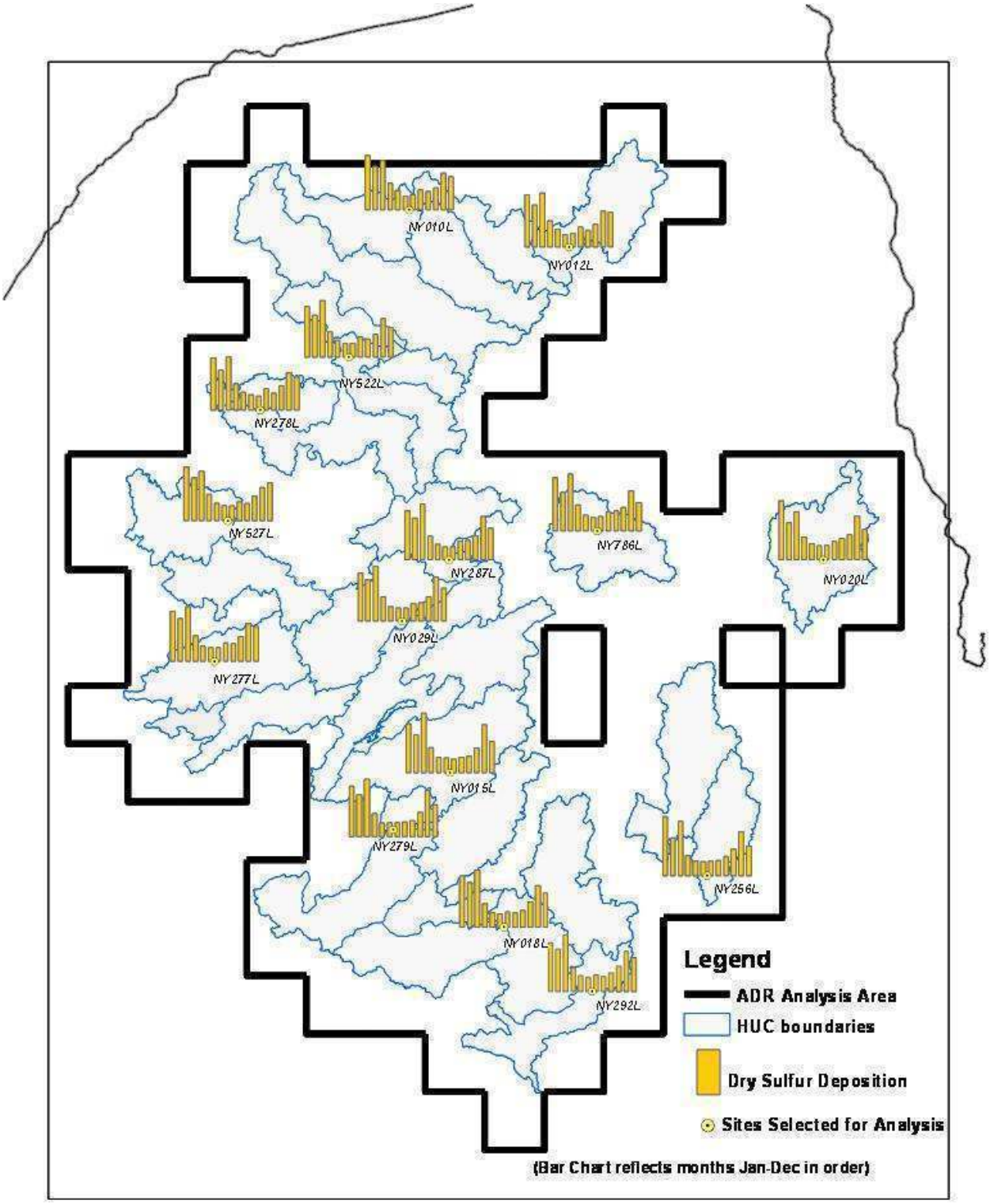


Figure 3.2-30. Percent by month of 2002 annual dry sulfur deposition for selected sites in the Adirondack Case Study Area.

Inter-Annual Variation in Nitrogen and Sulfur Deposition

[Placeholder for this section.]

Virginia Case Study Area

Potomac Case Study Area

Neuse Case Study Area

Western Case Study Area

3.2.1.5 Uncertainty

[Placeholder for this section]

3.2.2 Contributions of Emissions of NO_x and NH_3 to Deposition of Nitrogen

3.2.2.1 Purpose and Intent

The public welfare effects associated with ambient NO_x and SO_x do not occur due to direct exposure to ambient concentrations of NO_x and SO_x. Instead, ecosystem effects occur due to ecological exposures to loadings of all forms of nitrogen and sulfur 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, reducing 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 total reactive nitrogen, it is important to understand for that fraction of total nitrogen attributable to atmospheric deposition, the contribution of NO_x relative to reduced forms of nitrogen (NH_3 and NH_4). This section describes the analysis of the contribution of NO_x relative to reduced forms of nitrogen. The analysis uses a Response Surface Model (described below) to estimate the percent contribution

of NO_x and NH_3 emissions to total nitrogen deposition and to the oxidized and reduced forms of nitrogen deposition.

3.2.2.2 Data and Tools

EPA has recently developed a response-surface model (RSM) representation of the CMAQ model using multidimensional kriging techniques. CMAQ is a three-dimensional regional grid-based air quality model designed to simulate PM and O_3 concentrations and deposition over large spatial scales (e.g., over the contiguous United States) over an extended period of time (e.g., up to a year). It includes state-of-the-science capabilities for conducting urban to regional scale simulations of multiple air quality issues, including tropospheric ozone, fine particles, toxics, acid deposition, and visibility degradation. The CMAQ model is a publicly available (supported by the Community Modeling and Analysis System [CMAS] Center; http://www.cmascenter.org/), peer reviewed, state-of-the-science model consisting of a number of science attributes that are critical for simulating the oxidant precursors and nonlinear organic and inorganic chemical relationships associated with the formation of sulfate, nitrate, and organic aerosols. It also simulates the transport and removal of directly emitted particles that are speciated as elemental carbon, crustal material, nitrate, sulfate, and organic aerosols.

The RSM is a reduced-form prediction model using statistical correlation structures to approximate model functions through the design of complex multi-dimension experiments. In other words, the RSM is a metamodel, or model of a model, representing the outputs of the CMAQ model using statistical predictions. The RSM technique has been successfully tested and evaluated for $PM_{2.5}$ and ozone, respectively (U.S. EPA, 2006a, b) The RSM provides an accurate representation of the more complex CMAQ atmospheric chemistry model and allows for instantaneous calculation of the change in ambient $PM_{2.5}$ resulting from a change in emissions within a predefined set of sources, locations, and precursor emission types. The RSM allows for a more complete, systematic evaluation of the relative contribution of emission reductions (e.g., the percent impact on nitrogen deposition of NO_x versus NH_3 emissions, across these dimensions). The RSM includes 12 source/pollutant combinations and allows for application of emissions reductions in 9 urban areas and a region representing the rest of the continental United States.

The RSM used here is based on air quality modeling using CMAQ version 4.4 with a 36 km horizontal domain (148 x 112 grid cells) and 14 vertical layers. The modeling domain encompasses the contiguous United States and extends from 126 degrees to 66 degrees west longitude and from 24 degrees to 52 degrees north latitude. A complete description of CMAQ, meteorological, emission, and initial and boundary condition inputs used for this analysis are discussed in the technical support document for the EPA Clean Air Interstate Rule (CAIR) (U.S. EPA, 2005). The RSM outputs are based on projected 2010 pre-CAIR emissions inventories, and therefore reflect any uncertainties in those inventories. The range of emissions changes that are supported by the RSM extends from 0% to 120% of 2010 emissions levels.

The RSM can evaluate air quality changes that result from adjusting each of the following 12 emissions control factors on a regional basis:

1. NO_x EGU = NO_x EGU point source emissions based on the Integrated Planning Model (IPM) (see REF).
2. NO_x NonEGU Point and Area = NO_x IPM Non-EGU point source, area source, and agricultural source emissions
3. NO_x Mobile = NO_x non-road source and mobile source emissions
4. SO_x EGU = SO_x IPM EGU point source emissions
5. SO_x NonEGU Point = SO_x IPM Non-EGU point source emissions
6. SO_x Area = SO_x area source and agricultural source emissions
7. NH_3 Area = Ammonia area source and agricultural source emissions
8. NH_3 Mobile = Ammonia non-road source and mobile source emissions
9. POC/PEC Point (EGU and NonEGU) = Elemental carbon and organic carbon IPM EGU point source and IPM Non-EGU point source emissions
10. POC/PEC Mobile = Elemental carbon and organic carbon non-road source and mobile source emissions
11. POC/PEC area = Elemental carbon and organic carbon area source and agricultural source emissions
12. Volatile organic compound (VOC) All = IPM EGU point source, IPM non-EGU point source, area source, agricultural source, non-road source, and mobile source emissions.

Source groupings with small contributions to emissions were grouped with similar larger source groupings for efficiency. Non-EGU Area NO_x and SO_x sources were primarily smaller industrial combustion sources, such as coal, oil, and natural gas-powered boilers and internal combustion engines. Agricultural area sources were the only significant contributors to ammonia emissions. VOC sources were lumped together based on the chemistry incorporated in CMAQ version 4.4, indicating that VOCs are not expected to influence PM levels significantly.

Based on the 12 emissions control factors above, we developed the experimental design for these factors using a Latin Hypercube[11] method, which identified the necessary CMAQ modeling runs. Latin hypercube designs are very flexible in accommodating restrictions on the number of runs (as opposed to factorial designs, for example, which are fairly rigid). We implemented a design with 211 model runs (a base case plus 210 control runs). Any specific run had different levels of the 12 factors, for example, factor 1 (EGU NO_x) might be set at 0.1 (90% reduction), factor 2 (Non-EGU NO_x) at 0.3 (70% reduction), factor 3 (Mobile NO_x) at 0.75 (25% reduction), and so on. The complete list of model runs and corresponding emissions reduction scenarios (i.e., selection of policy factor controls) are available (U.S. EPA, 2006b). The CMAQ model was run for 4 months, 1 month from each season in 2002 (?),—February, April, July, October—to reduce computational time for such a large number of annual model runs. These months were chosen based on greatest predictability of the quarterly mean.

3.2.2.3 Analytical Techniques

To better inform our understanding of the roles of NO_x and NH_3 in deposition of nitrogen, we used the RSM described above to estimate the relative contribution of emissions of NO_x and NH_3 to deposition of nitrogen, including total as well as reduced and oxidized nitrogen. We focus on the percent contribution in the set of eight case study areas that are the focus of the risk and exposure analysis. All analyses were based on zero-out runs, e.g., setting the emissions of NO_x or NH_3 equal to zero and estimating the change in deposition at grid cells within the CMAQ domain). Note that zeroing out the RSM emissions factor for NO_x will not result in zero emissions of NO_x —the remaining emissions will include international sources and non-anthropogenic sources (e.g., lightning). Likewise, zeroing out the RSM emissions factor for NH_3 emissions will not result in zero emissions of NH_3, with remaining NH_3 emissions comprised of international emissions, non-anthropogenic emissions, and additionally, point sources of NH_3, which, while accounting for a low proportion of overall NH_3 emissions, can be significant in some limited locations.

We examine the contribution of NO_x, and NH_3 emissions to deposition in eight case study areas, including the Neuse River, Potomac River, Shenandoah National Park, Adirondacks, red spruce habitat, sugar maple habitat, coastal sage habitat, and in all coastal estuaries. The

[11] A Latin hypercube is the generalization of a Latin square to an arbitrary number of dimensions, whereby each sample is the only one in each axis-aligned hyperplane containing it.

CMAQ grid cells that cover each of these case study areas are displayed in **Figures 3.2-31 through 3.2-38**. For each of the case study areas, we constructed box plots for several metrics (**Figures 3.2-39 through 3.2-44**), covering several combinations of emissions and output variables. Box plots are a graphical method for displaying the central tendency and variability in a set of values. The box plots are arrayed for the eight case study areas in combined graphs to allow for comparison across case study areas, as well as illustrate the variability within each case study area. In each case, we examine the impact of ambient NO_x and NH_3 on deposition of total nitrogen, reduced nitrogen, and oxidized nitrogen. The percent impact on deposition was estimated to provide a more comparable relative metric across locations and seasons. An analysis of the spatial patterns of responses within each case study area is also presented.

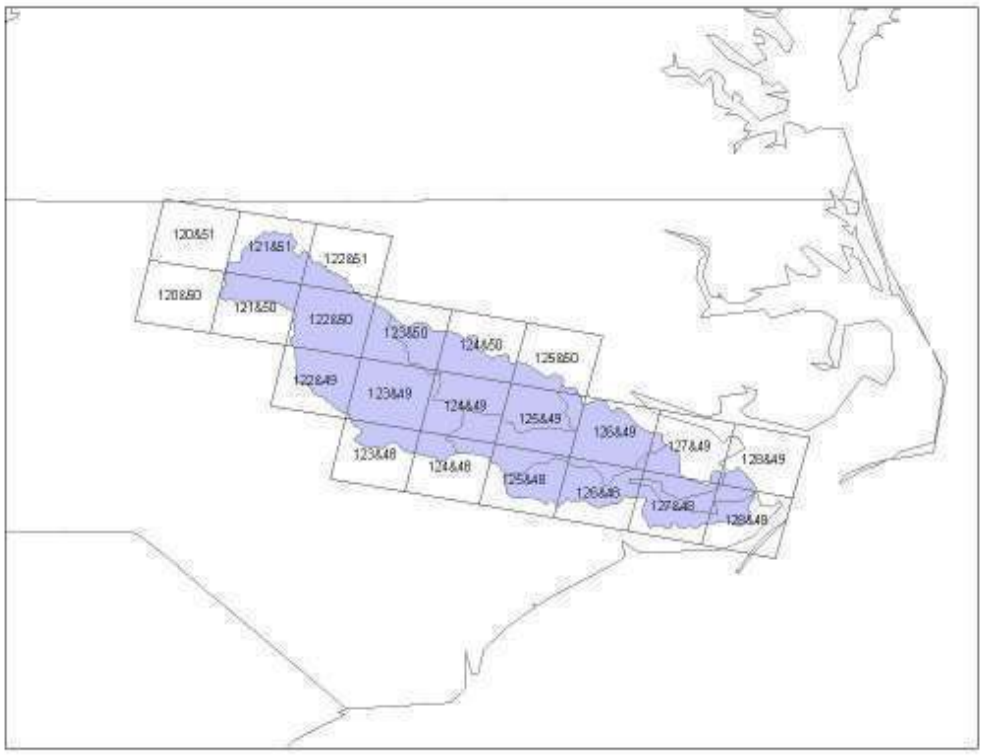


Figure 3.2-31. CMAQ 36 km grids in Neuse River Case Study Area.

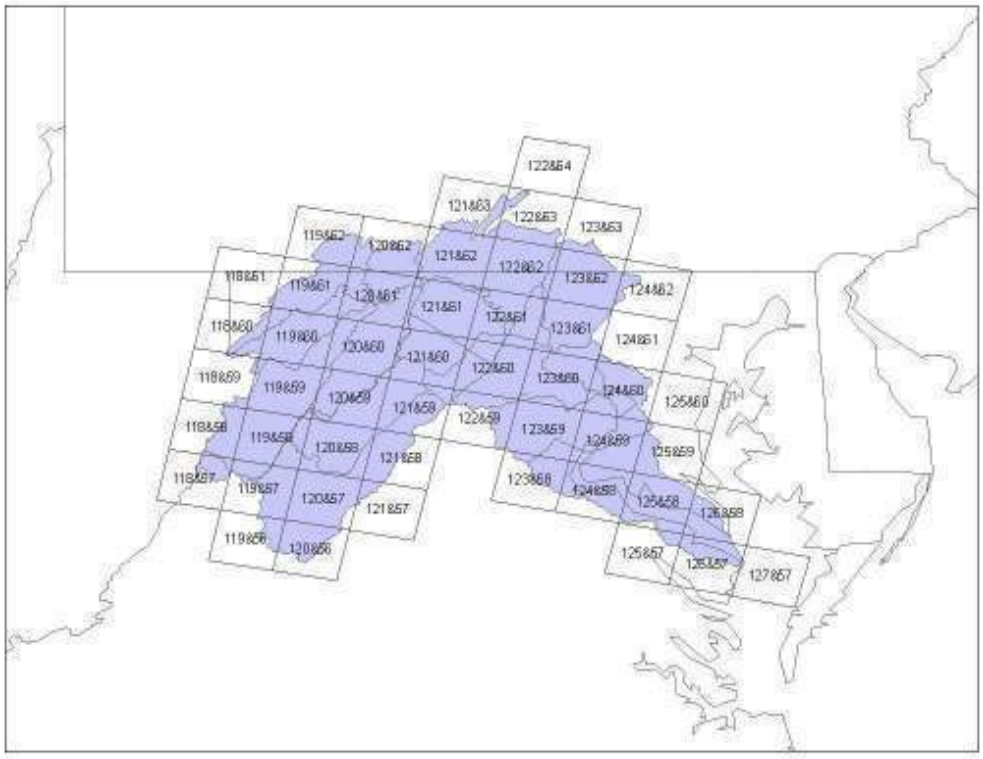


Figure 3.2-32. CMAQ 36-km grids in Potomac Case Study Area.

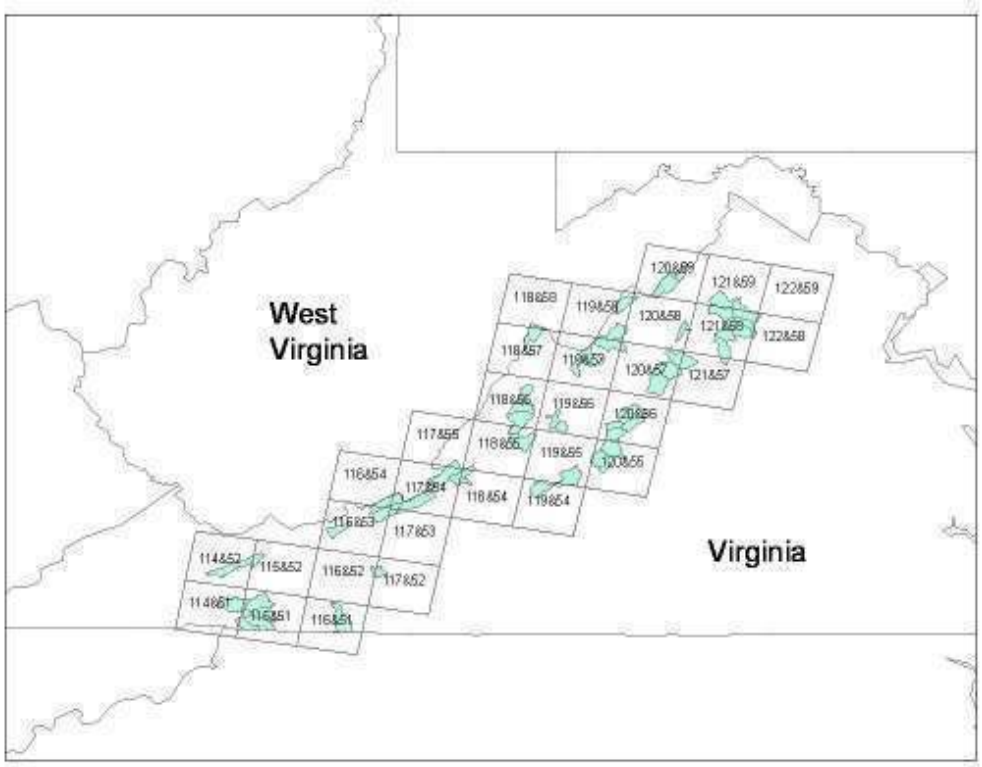


Figure 3.2-33. CMAQ 36-km grids in Shenandoah Case Study Area.

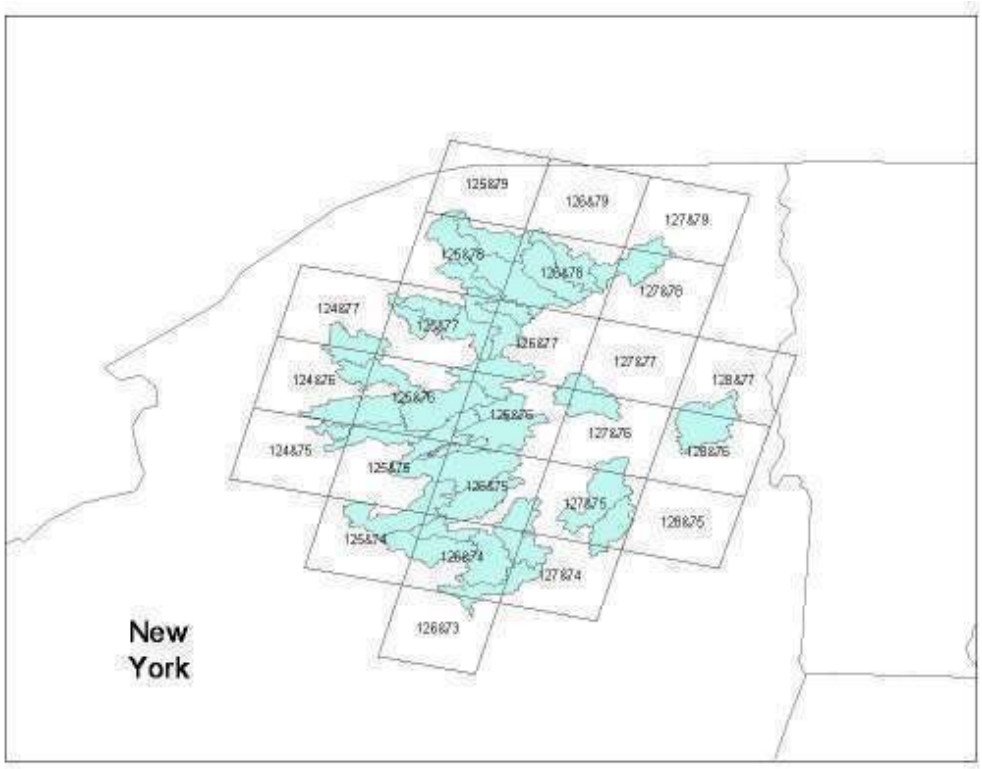


Figure 3.2-34. CMAQ 36-km grids in Adirondack Case Study Area.

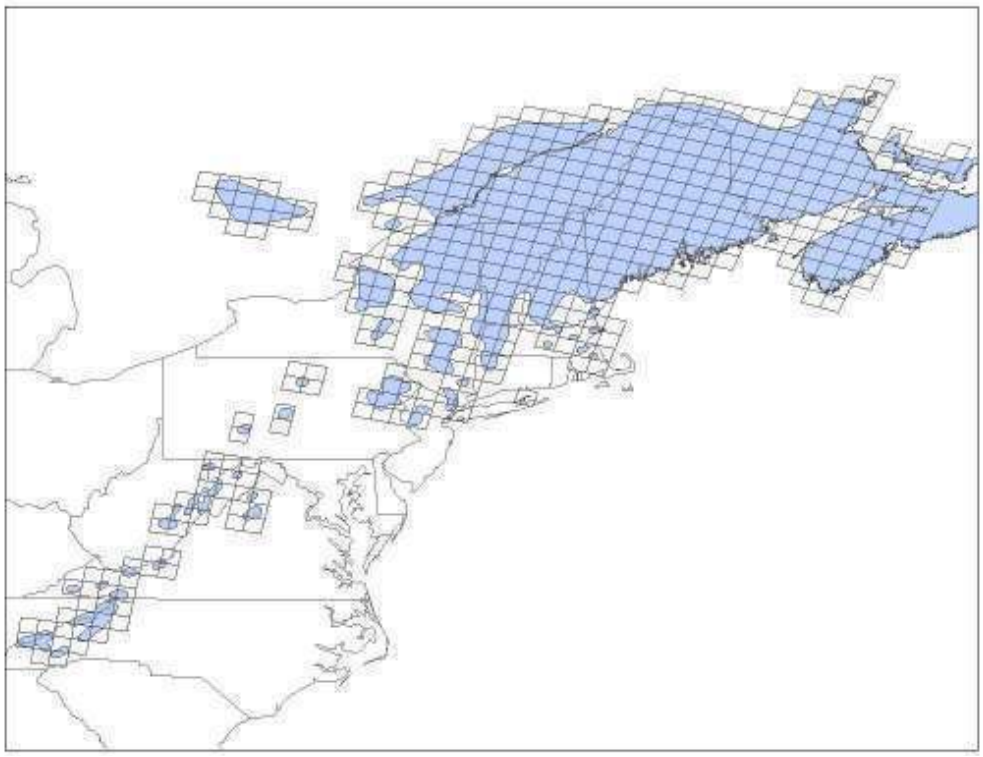


Figure 3.2-35. CMAQ 36-km grids in Red Spruce Case Study Area.

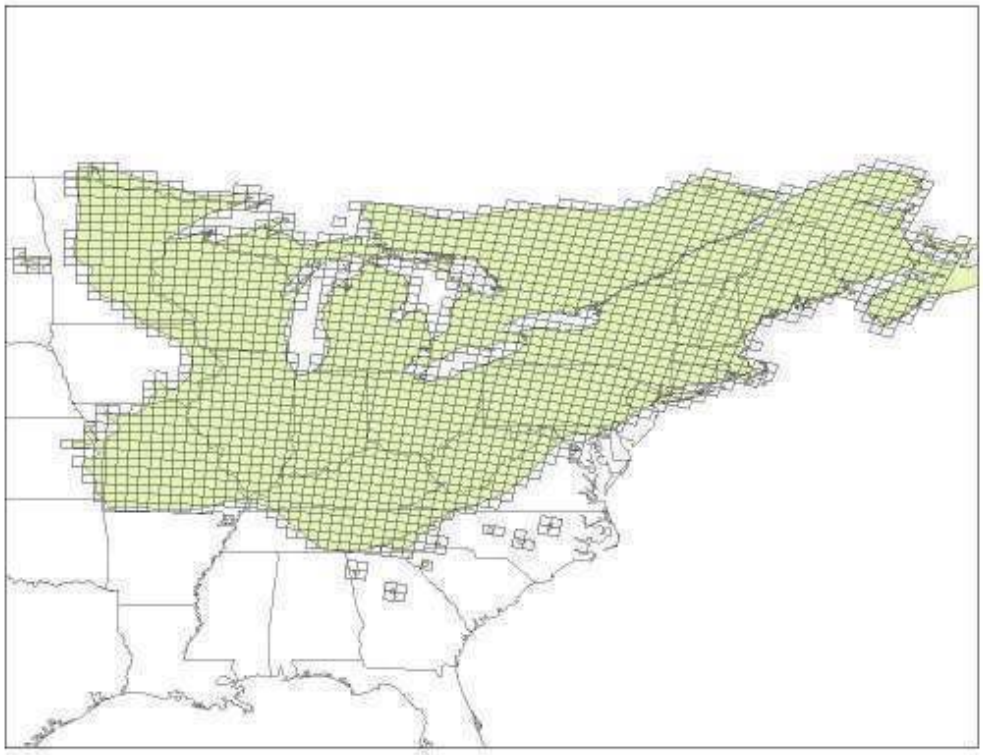


Figure 3.2-36. CMAQ 36-km grids in Sugar Maple Case Study Area.

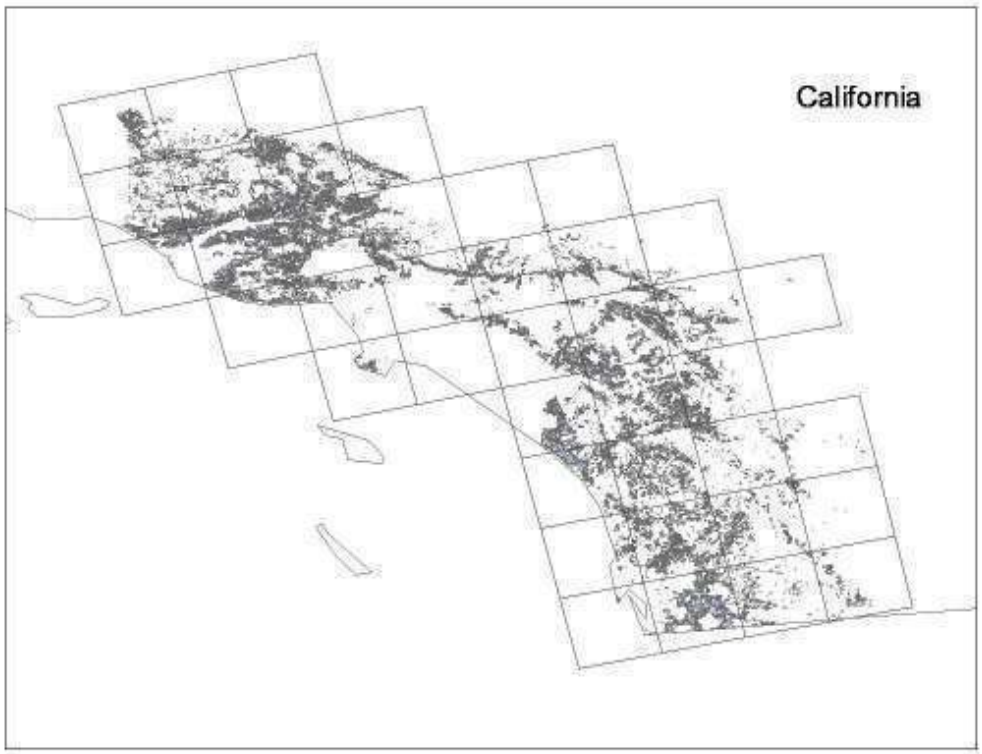


Figure 3.2-37. CMAQ 36-km grids in Coastal Sage Case Study Area.

Figure 3.2-38. CMAQ 36-km grids in Estuaries Case Study Area.

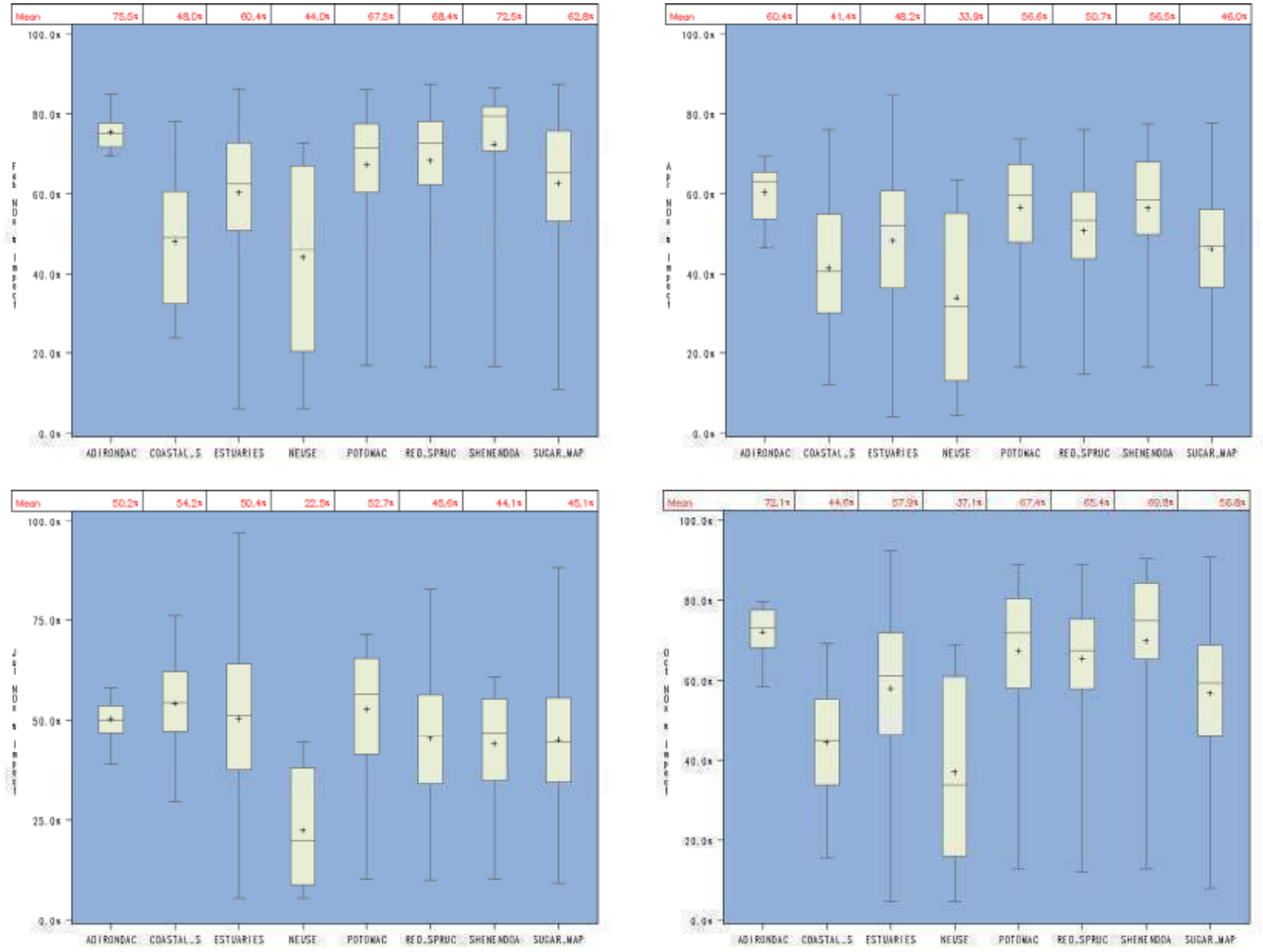


Figure 3.2-39. Percent impact of zero-out of NO_x emissions on total nitrogen deposition.

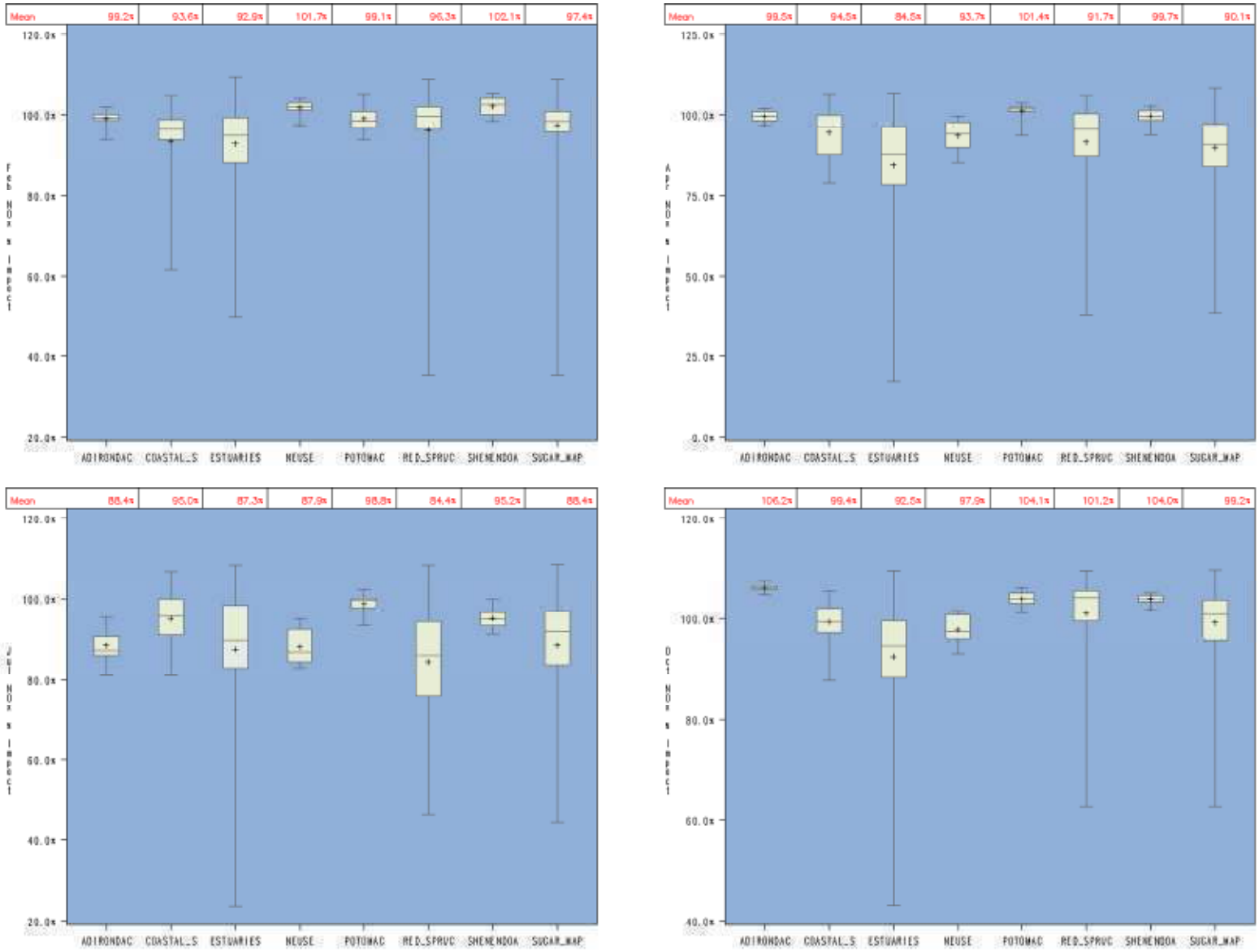


Figure 3.2-40. Percent impact of zero-out of NO_x emissions on oxidized nitrogen deposition.

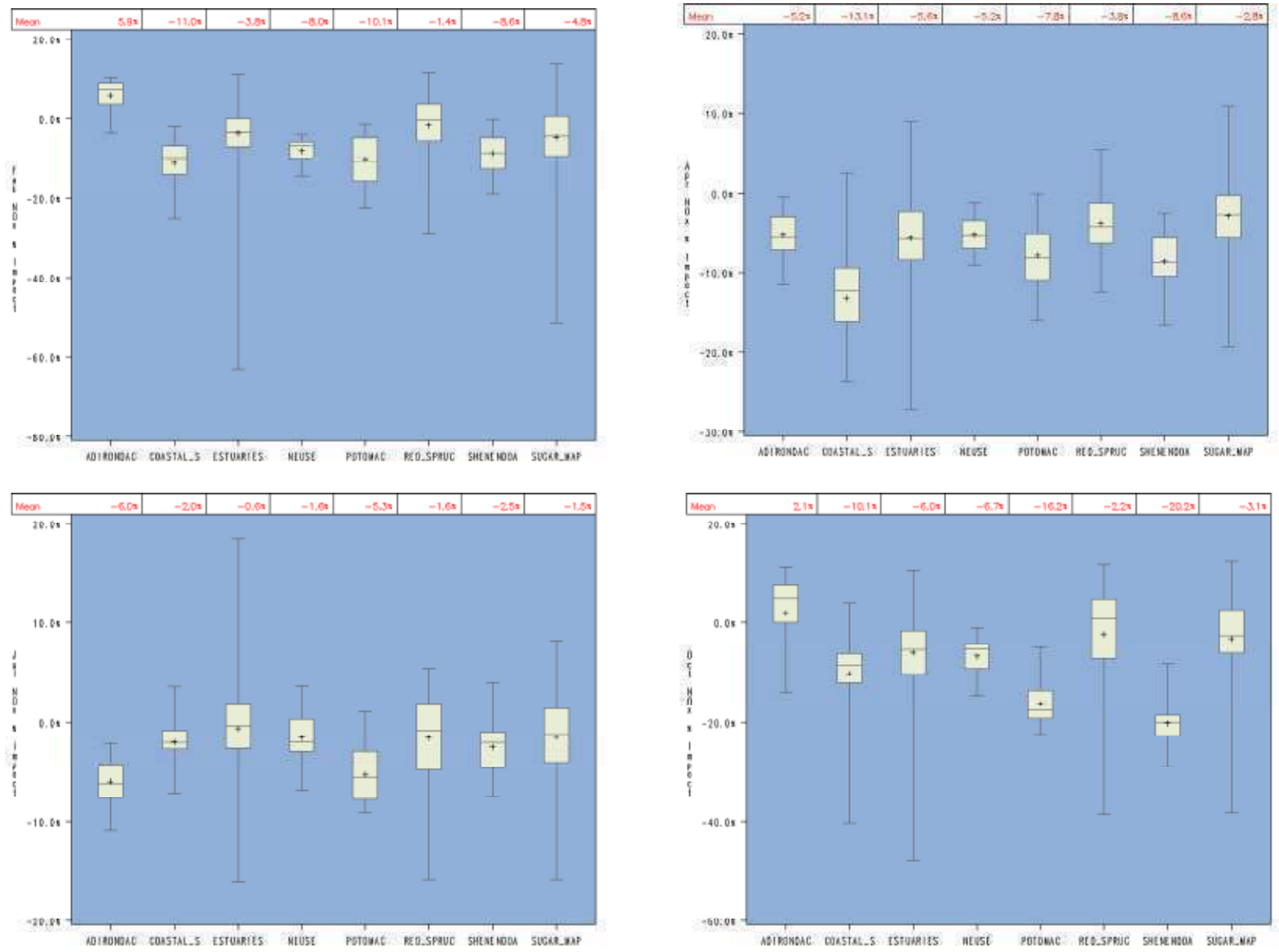


Figure 3.2-41. Percent impact of zero-out of NO_x emissions on reduced nitrogen deposition.

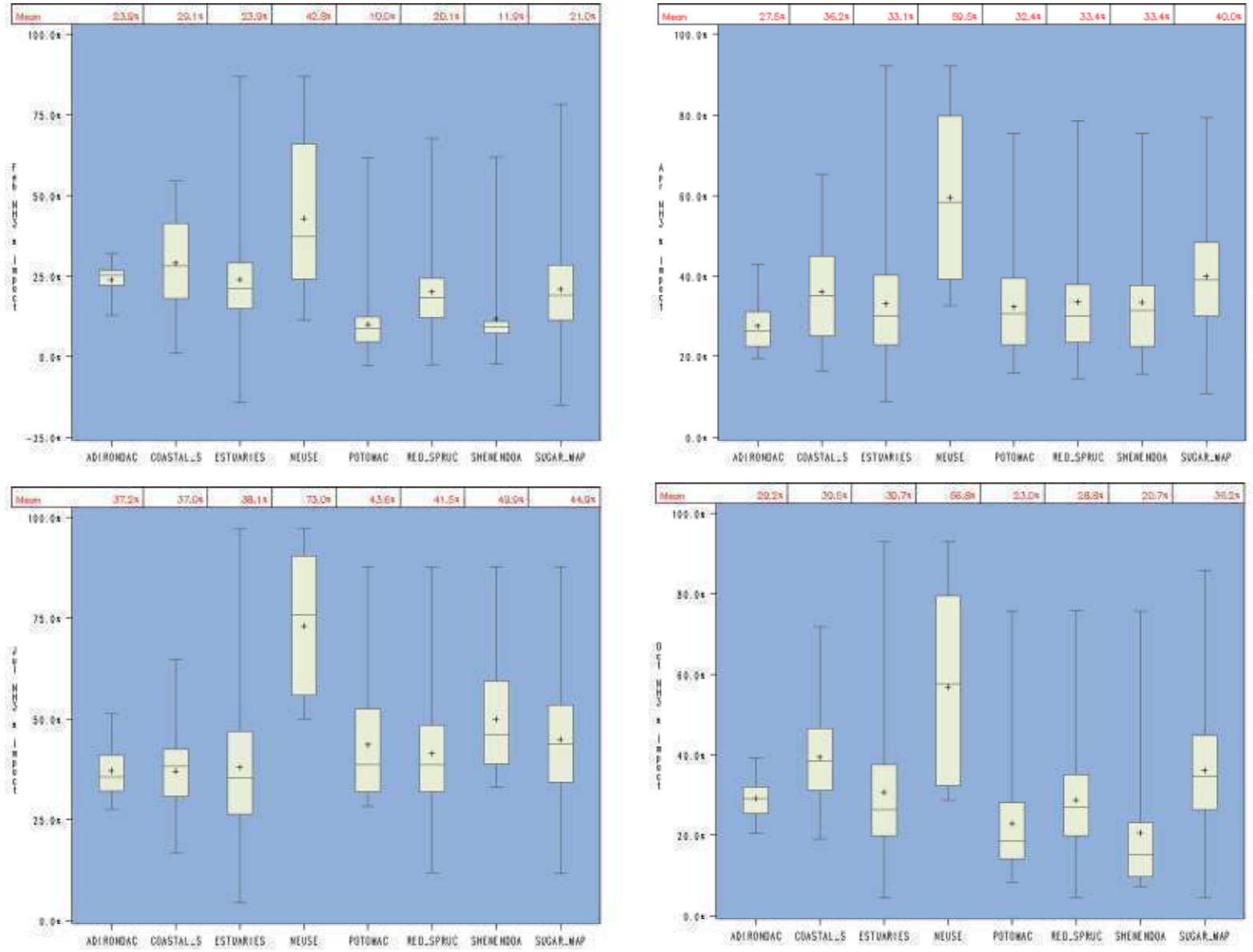


Figure 3.2-42. Percent impact of zero-out of NH_3 emissions on total nitrogen deposition.

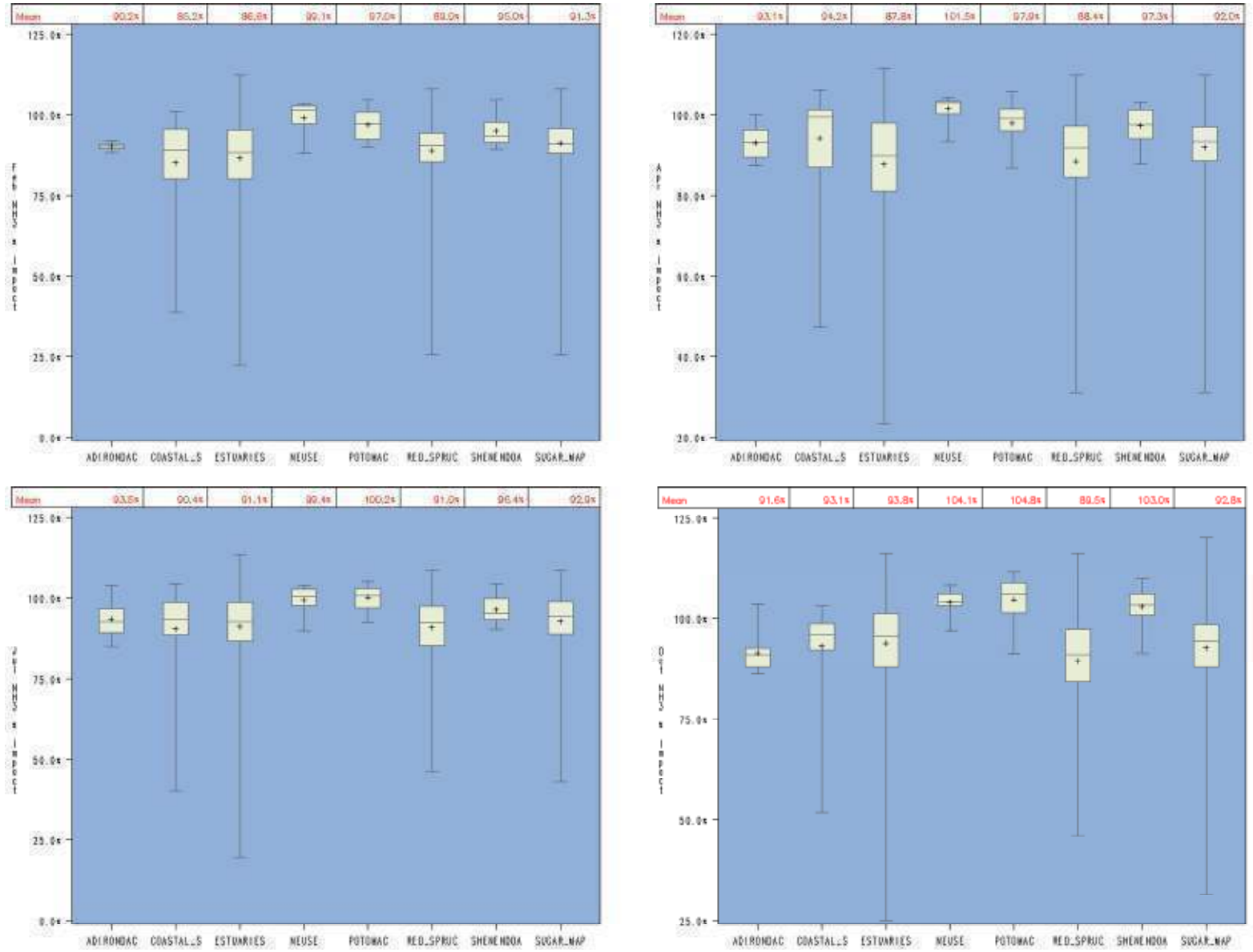


Figure 3.2-43. Percent impact of zero-out of NH_3 emissions on reduced nitrogen.

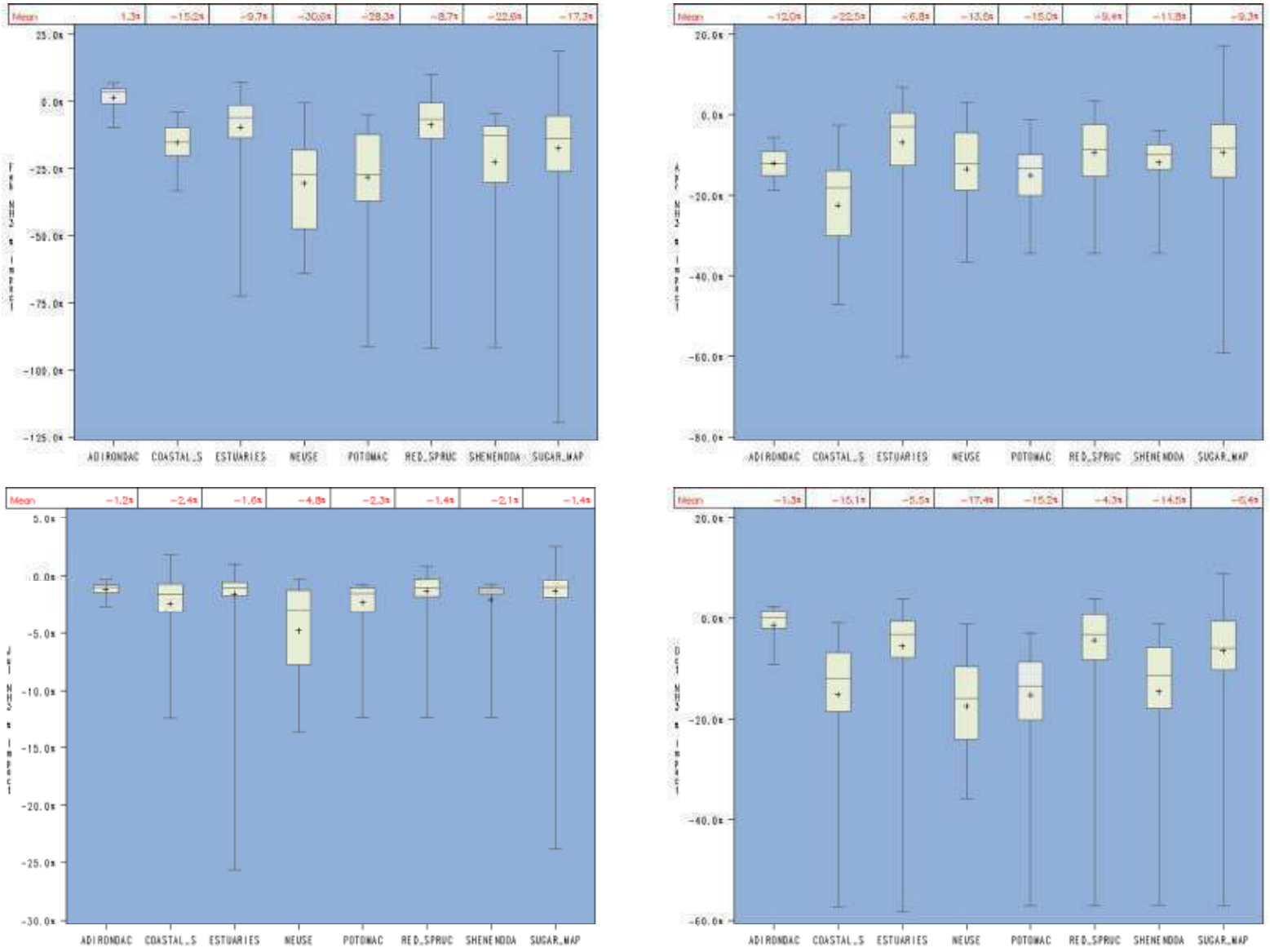


Figure 3.2-44. Percent impact of zero-out of NH_3 emissions on oxidized nitrogen deposition.

Relative (percent) impacts can be slightly greater than 100% due to the small level of error in the response surface modeling. The sum of the relative impacts across NO_x, NH_3 can be less than 100% due to nonlinearities in the atmospheric chemistry, e.g. reducing all pollutants by 100% would give different results than reducing each individually by 100% and summing the results. Because of the chemistry governing gas and particle-phase ammonia, SO_2 emissions can also have a small impact on deposition of nitrogen. However, because the focus of this section is on the relative importance of NO_x and NH_3, we do not provide results for SO_2 here.

3.2.2.4 Results and Findings

The first set of results, displayed in Figures 3.2-39 and 3.2-40, examine the relative impact of emissions of NO_x on the deposition of total reactive nitrogen. Figure 3.2-39 shows that NO_x emissions represent a significant contribution to deposition of total reactive nitrogen in each case study area, although the impact varies by season. The smallest impact of NO_x emissions, 22.5%, occurs in the Neuse River Case Study Area in July. The largest impact of NO_x emissions, 75.5%, occurs in the Adirondacks Case Study Area in February. In general, across case study areas, the largest NO_x percent impacts on total reactive nitrogen deposition occur in February, ranging from 44%–75% percent, while the smallest relative impacts, ranging from 22%–54%, occur in July. With the exception of the Coastal Sage Case Study Area, each area has its highest relative contribution from NO_x in February and lowest relative contribution in July. The Coastal Sage Case Study Area has the highest relative contribution in July and the lowest relative contribution in April. This may reflect differences in the climates between the eastern United States, where most of the other areas (with the exception of western portions of the Estuaries Case Study Area) are located, and the western California coast, where the Coastal Sage Case Study Area is located.

Figures 3.2-40 and 3.2-41 explore the relationship between NO_x emissions and total reactive nitrogen deposition in more detail, examining separately the relative impacts of NO_x on oxidized and reduced forms of nitrogen. It was anticipated that NO_x emissions will have a larger relative impact on oxidized nitrogen compared with reduced nitrogen (U.S. EPA, 2008). Figures 3.2-40 and 3.2-41 confirm this expectation. In each case study area and season, the relative

impact of NO_x emissions is over 84%, and in some cases, has a 100% impact,[12] indicating that all of the oxidized nitrogen is likely associated with NO_x emissions. Also, as expected, Figure 3.2-41 shows that in all case study areas and all seasons, NO_x emissions have less than a 20% impact on reduced nitrogen deposition. And, in most cases, the NO_x impact is actually negative, 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 possibility is that reducing NO_x reduces HNO_3, which limits ammonium nitrate (NH_4NO_3) formation (and for existing aerosol, a reduction in HNO_3 shifts the equilibrium toward the gas phase), thereby increasing the lifetime of NH_3. A net increase in NH_3 /NH_4^+ results. Because the deposition velocity of NH_3 is much higher than the deposition velocity for NH_4^+ aerosol, dry deposition of NH_x increases. The only instances where NO_x emissions contribute to decreased reduced nitrogen deposition are in the Adirondacks Case Study Area in February and October; however, these are very small impacts and may reflect statistical imprecision in the modeling. We will continue to explore these results for the final risk and exposure analysis.

Figure 3.2-42 examines the relative impact of emissions of NH_3 on the deposition of total reactive nitrogen. Figure 3.2-42 shows that NH_3 emissions represent a significant contribution to total reactive nitrogen in most case study areas, although the impact varies by season and by area. The smallest impact of NH_3, 10%, occurs in the Potomac Case Study Area in February. The largest impact of NH_3, 73%, occurs in the Neuse Case Study Area in July. The Neuse Case Study Area has the largest overall impact from NH_3 of any of the case study areas, across all four seasons. This may be due to the large concentration of CAFOs located in eastern North Carolina. In general, across case study areas, the largest NH_3 relative impacts on total nitrogen deposition occur in July from 37%–73%, while the smallest relative impacts, ranging from 10%–43%, occur in February. Each area has its highest relative contribution from NH_3 in July and its lowest relative contribution in February.

Figures 3.2-43 and 3.2-44 explore the relationship between NH_3 emissions and nitrogen deposition in more detail, examining separately the relative impacts of NH_3 on oxidized and

[12] In fact, the RSM modeling predicts a greater than 100% impact in some case study areas. This likely reflects that fact that the RSM is a statistical approximation to the CMAQ model. As with all statistical models, extrapolations to extreme cases can lead to larger than average statistical errors. In this analysis, where we are zeroing out emissions of individual pollutants, we are pushing the RSM model to its boundaries, and as such, the findings of greater than 100% impact are likely a statistical artifact. In this case, we interpret greater than 100% impacts as 100% impacts.

reduced forms of nitrogen. It is expected that NH_3 emissions will have a larger relative impact on reduced forms of nitrogen deposition. This modeling exercise, depicted in Figures 3.2-43 and 3.2-44, confirms this expectation. In each case study area and season, the relative impact of NH_3 emissions is over 85%, and in some cases, has a 100% impact, indicating that all of the reduced nitrogen is likely associated with NH_3 emissions. Also, as expected, Figure 3.2-44 shows that in all case study areas and all seasons, NH_3 has less than a 20% impact on oxidized nitrogen deposition. And, in most cases, the NH_3 impact is actually negative, meaning that NH_3 emissions contribute to greater deposition of oxidized nitrogen deposition. This relationship reflects the atmospheric reactions that lead to deposition of reduced and oxidized nitrogen. Reducing NH_3 limits NH_4NO_3 aerosol formation, increasing the lifetime of HNO_3. The ratio HNO_3;NO_3^- increases and since the deposition velocity of HNO_3 is much larger than that of NO_3^- aerosol, dry deposition of total oxidized nitrogen increases. The only positive impacts of NH_3 on oxidized nitrogen occur in the Adirondack Case Study Area in February; however, these are very small impacts and may reflect statistical imprecision in the modeling. We will continue to explore these results for the final risk and exposure analysis.

Spatial Analysis of Results

As noted above, there is a good deal of variability in the impacts of NO_x and NH_3 within and between case study areas. In order to explore this variability, the estimated impacts of NO_x and NH_3 on their deposition counterparts were mapped. For NO_x, the percentage impact on oxidized and total nitrogen deposition was mapped, and for NH_3, the percentage impact on reduced and total nitrogen deposition was mapped. Each of the impact maps uses the same color scale for ease of comparison across case study areas. Each map has four panels, one for each of the four months modeled, representing the four seasons. There are four maps for each case study area, for a total of 32% impact maps. The critical factors to consider in the maps of impacts on total nitrogen are the spatial uniformity of contribution in each case study area and the uniformity of contribution across seasons. For the maps displaying the impact of NO_x on oxidized nitrogen and the impact of NH_3 on reduced nitrogen, we expect to see most grid cells with close to 100% impact, reflecting the dominant impact of NO_x on oxidized nitrogen deposition and the dominant impact of NH_3 on reduced nitrogen. In some cases, the maps may show lower-impact percentages due to three types of emissions that are included in the baseline CMAQ modeling but not included as controllable emissions in the RSM modeling: (1)

international emissions, (2) non anthropogenic emissions, and (3) large point sources of ammonia.

Figures 3.2-45 through 3.2-48 present maps of the results for the Sugar Maple Case Study Area. With the Sugar Maple Case Study Area (Figure 3.2-45), it is clear that there is considerable heterogeneity in response to NO_x emissions reductions across the case study area, and between seasons. However, NO_x contributions are significant in a large number of grid cells in all seasons, suggesting that NO_x is an important part of overall nitrogen deposition in the Sugar Maple Case Study Area. Based on this analysis, NO_x appears to contribute the most consistently across the area during the winter and fall months, with lower contributions and more spatial heterogeneity during the spring and summer months. Likewise, as shown in Figure 3.2-46, the impact of ammonia emissions is greatest during the spring and summer months, with less impact during fall and winter months. Note that even during the fall and winter months, ammonia emissions have a large impact in those grid cells closest to major agricultural ammonia sources (e.g., the high poultry production area in northern Virginia and the high hog production area in southeastern Pennsylvania). With regard to the impact of NO_x emissions on oxidized nitrogen, as expected, Figure 3.2-47 shows that zeroing out domestic, anthropogenic NO_x emissions results in close to100% reduction in oxidized nitrogen deposition in most grid cells in the area, with the exception of some grid cells on the East Coast and in Canada, which likely reflects international emissions sources. Likewise, Figure 3.2-48 shows that zeroing out NH_3 emissions results in close to 100% reductions in reduced nitrogen deposition throughout the area. In a few grid cells near large point sources of ammonia, there is a less that 100% impact from zeroing out the area and mobile source NH_3 emissions, and off of the United States coast and in Canada, international emissions appear to contribute a portion of reduced nitrogen deposition.

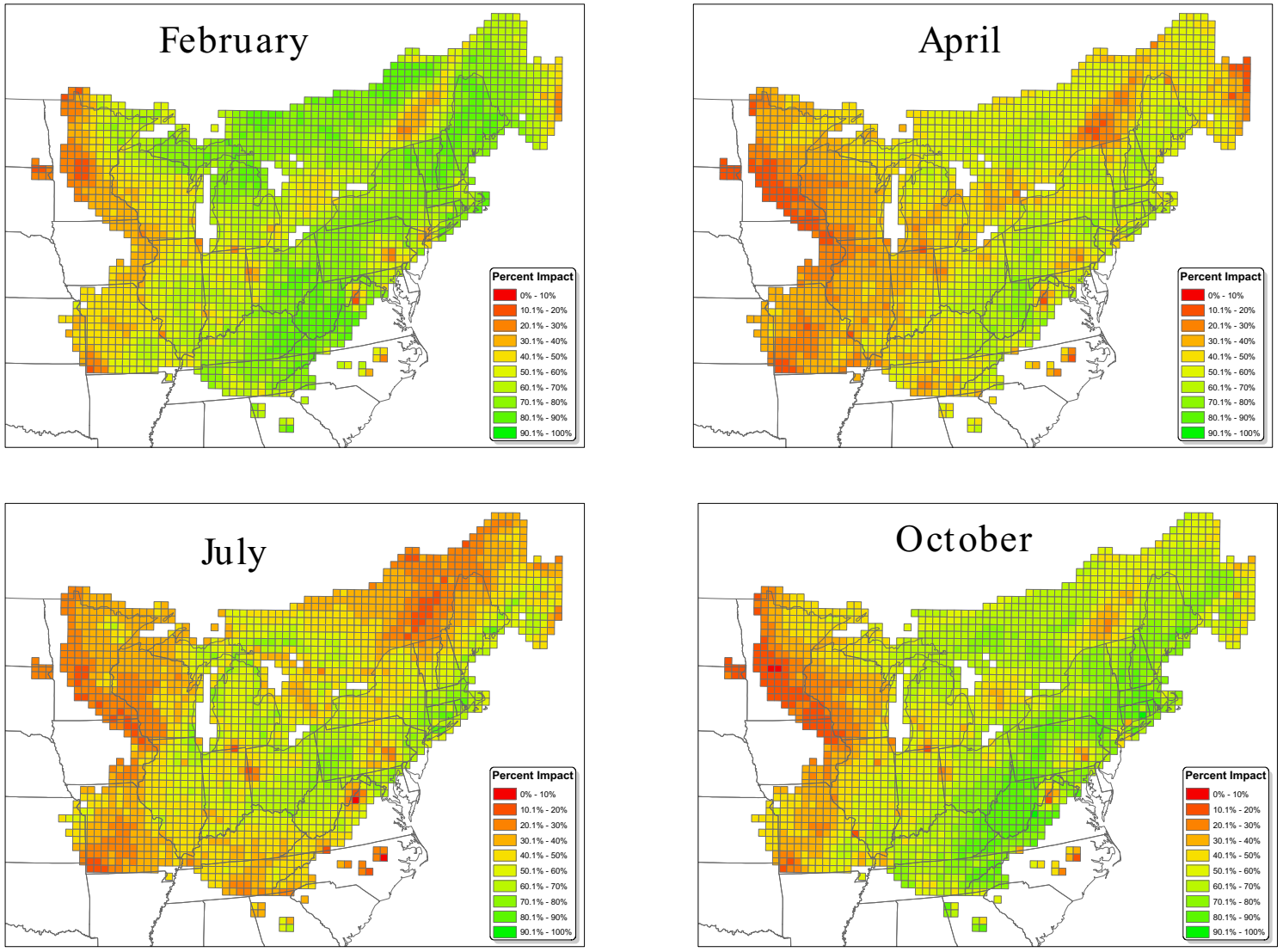


Figure 3.2-45. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Sugar Maple Case Study Area.

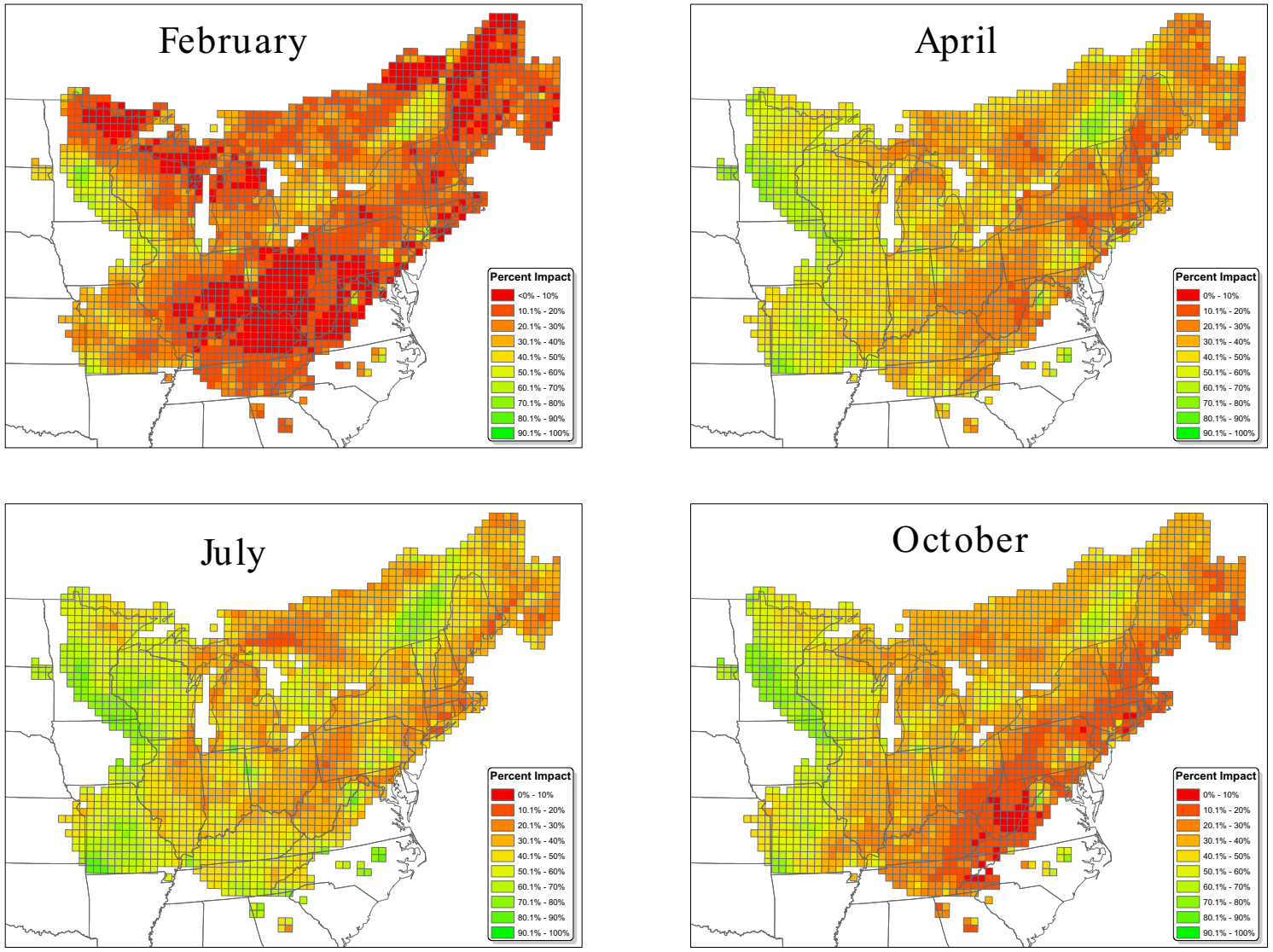


Figure 3.2-46. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Sugar Maple Case Study Area.

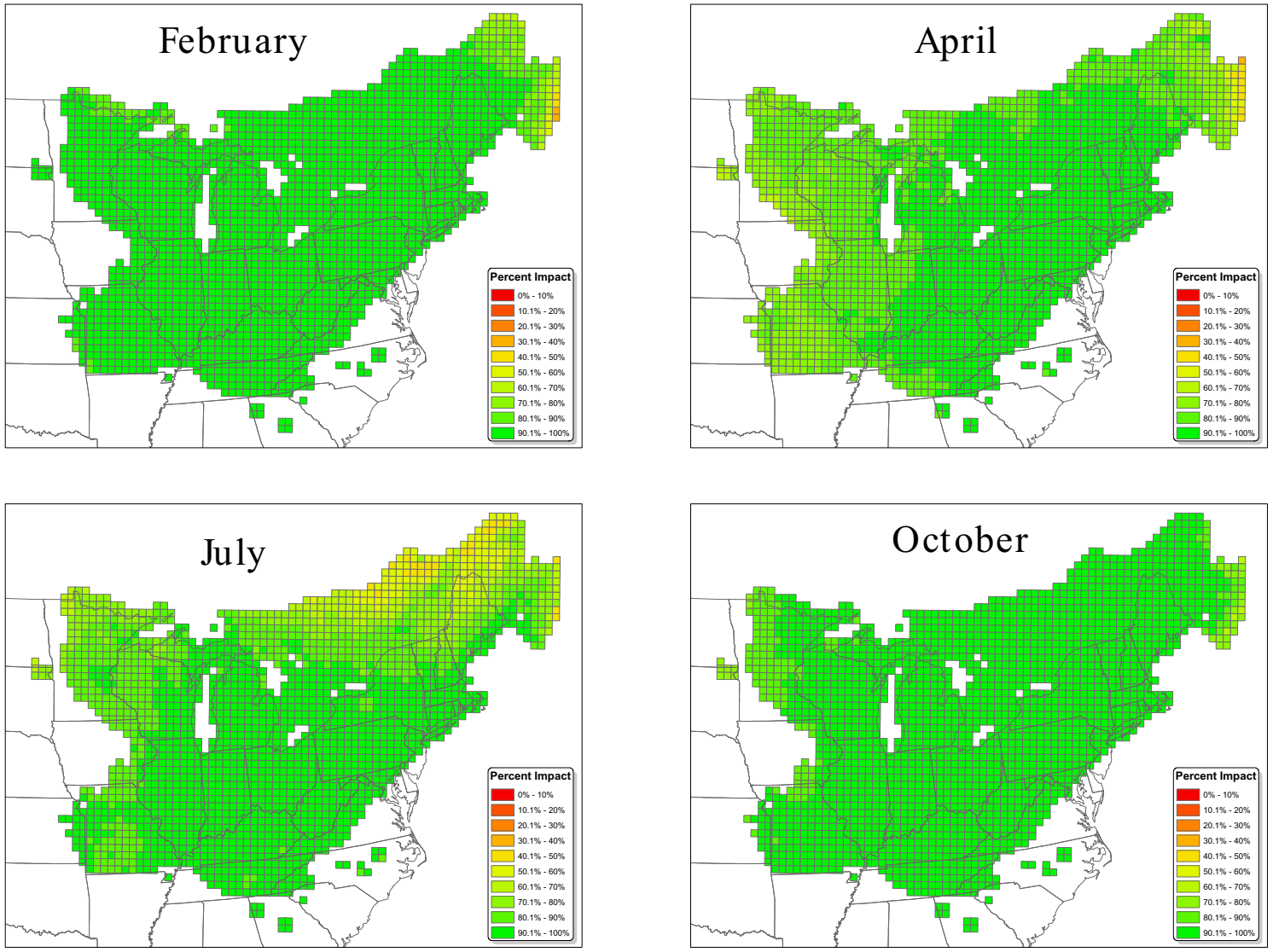


Figure 3.2-47. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Sugar Maple Case Study Area.

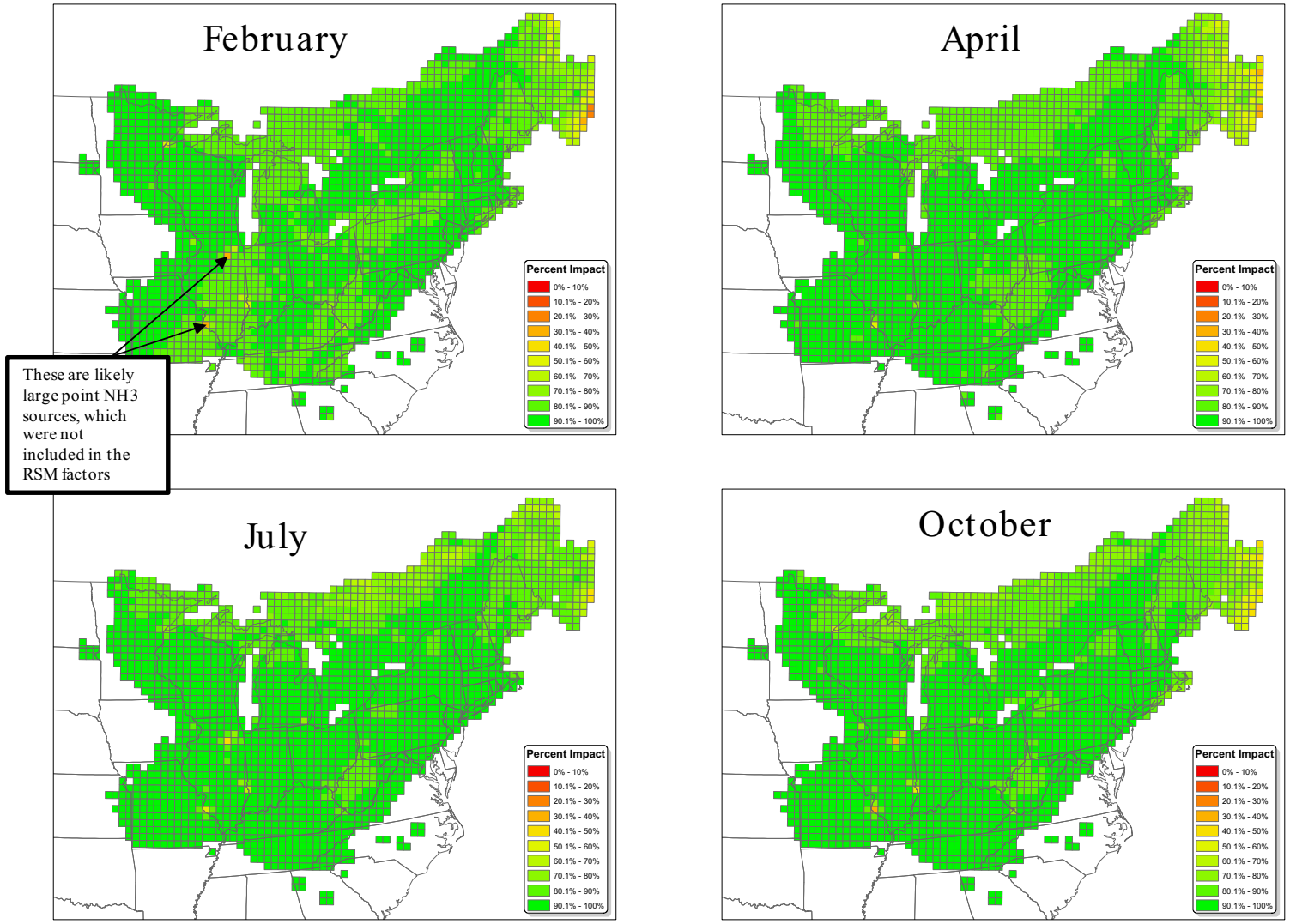


Figure 3.2-48. Percent impact of NH_3 anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Sugar Maple Case Study Area.

Figures 3.2-49 through 3.2-52 present maps of the results for the Red Spruce Case Study Area. For the most part, the Red Spruce Case Study Area overlaps the Sugar Maple Case Study Area. As such, similar patterns of total nitrogen deposition response can be seen in Figure 3.2-49. With the exception of July, the seasonal pattern of total nitrogen deposition response to NO_x is similar, with a large percent impact from zeroing out domestic, anthropogenic NO_x. The exceptions are in portions of Canada and in the heavy poultry production area of northern Virginia, where ammonia emissions are very high. In July, NO_x impacts are less relative to ammonia impacts, but are still significant in many grid cells. Examining Figure 3.2-51, as with the Sugar Maple Case Study Area, almost all of the oxidized nitrogen deposition is due to domestic NO_x emissions, with the exception of some grid cells in Canada and in the United States bordering Canada. Likewise, Figure 3.2-52 shows that almost all of the reduced nitrogen deposition is due to domestic NH_3 emissions, excepting some grid cells in Canada.

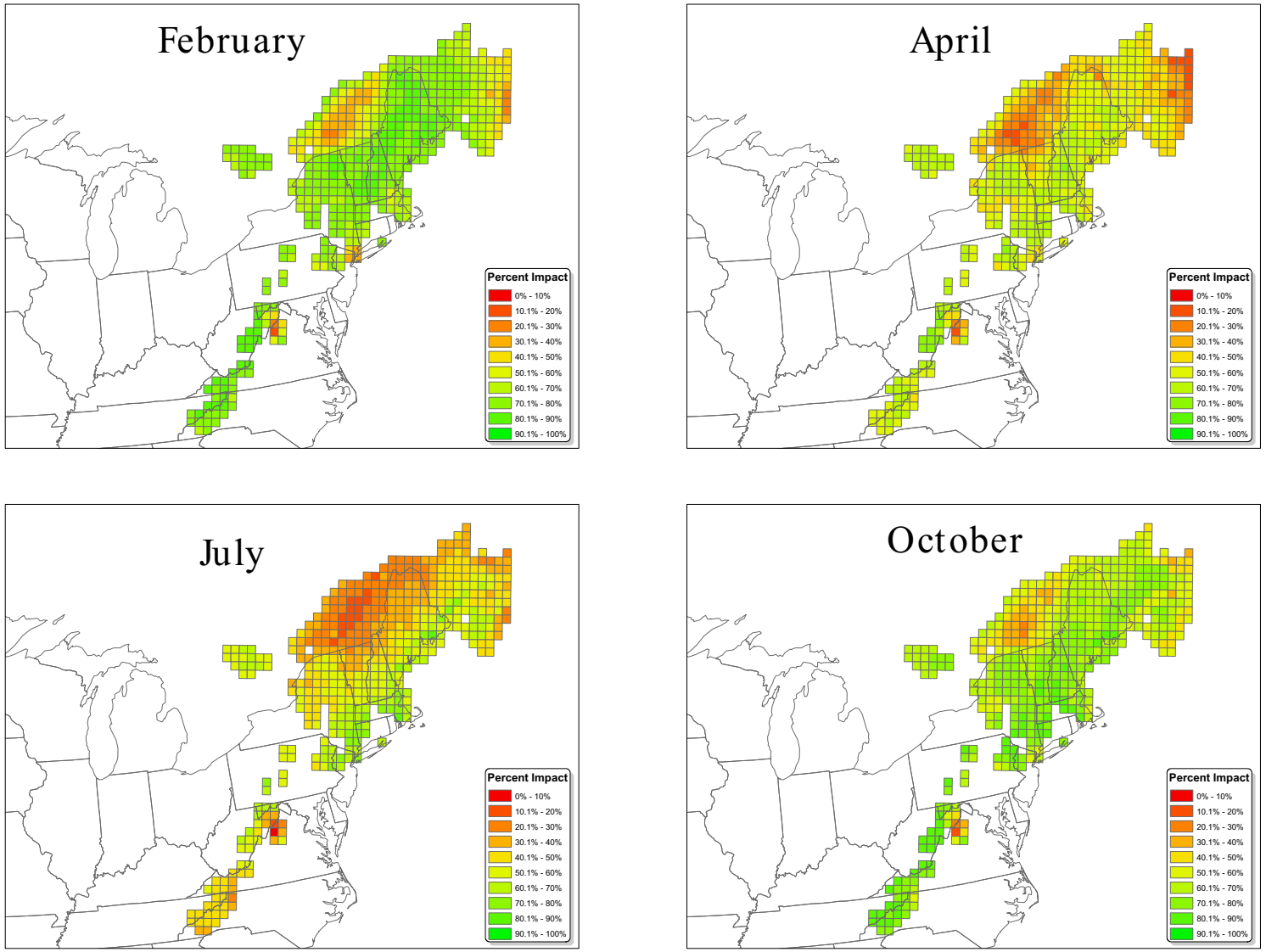


Figure 3.2-49. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Red Spruce Case Study Area.

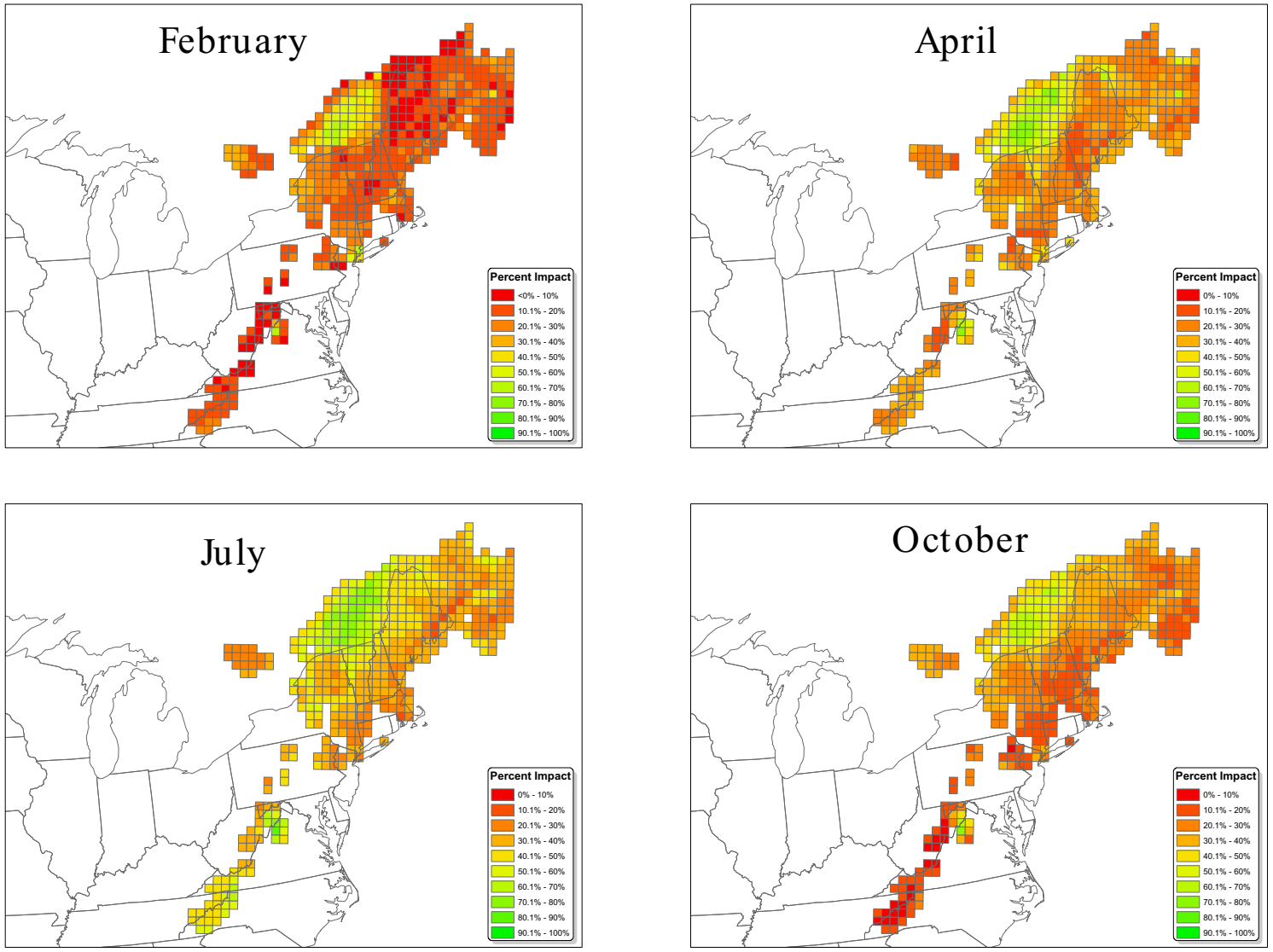


Figure 3.2-50. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Red Spruce Case Study Area.

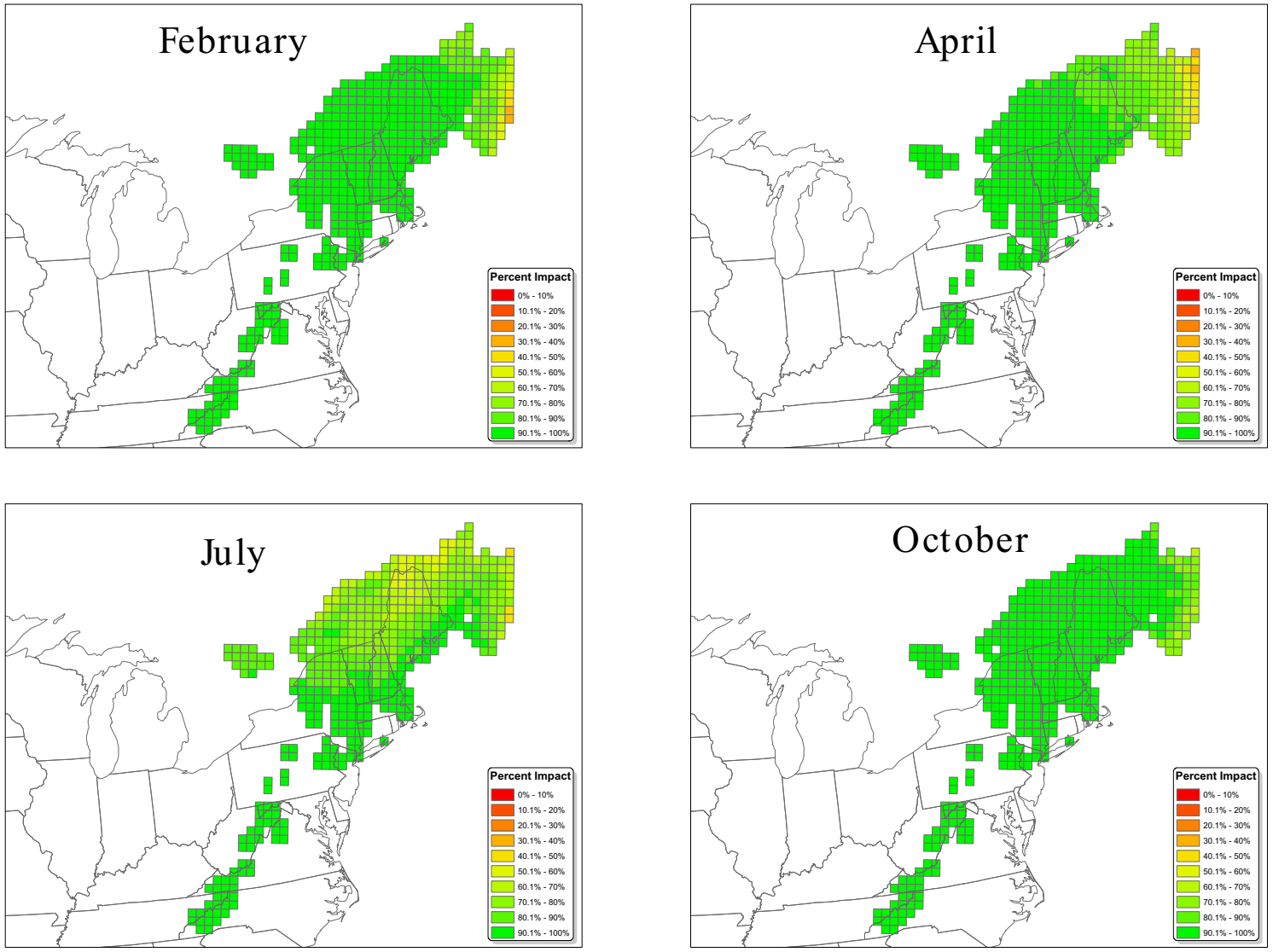


Figure 3.2-51. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Red Spruce Case Study Area.

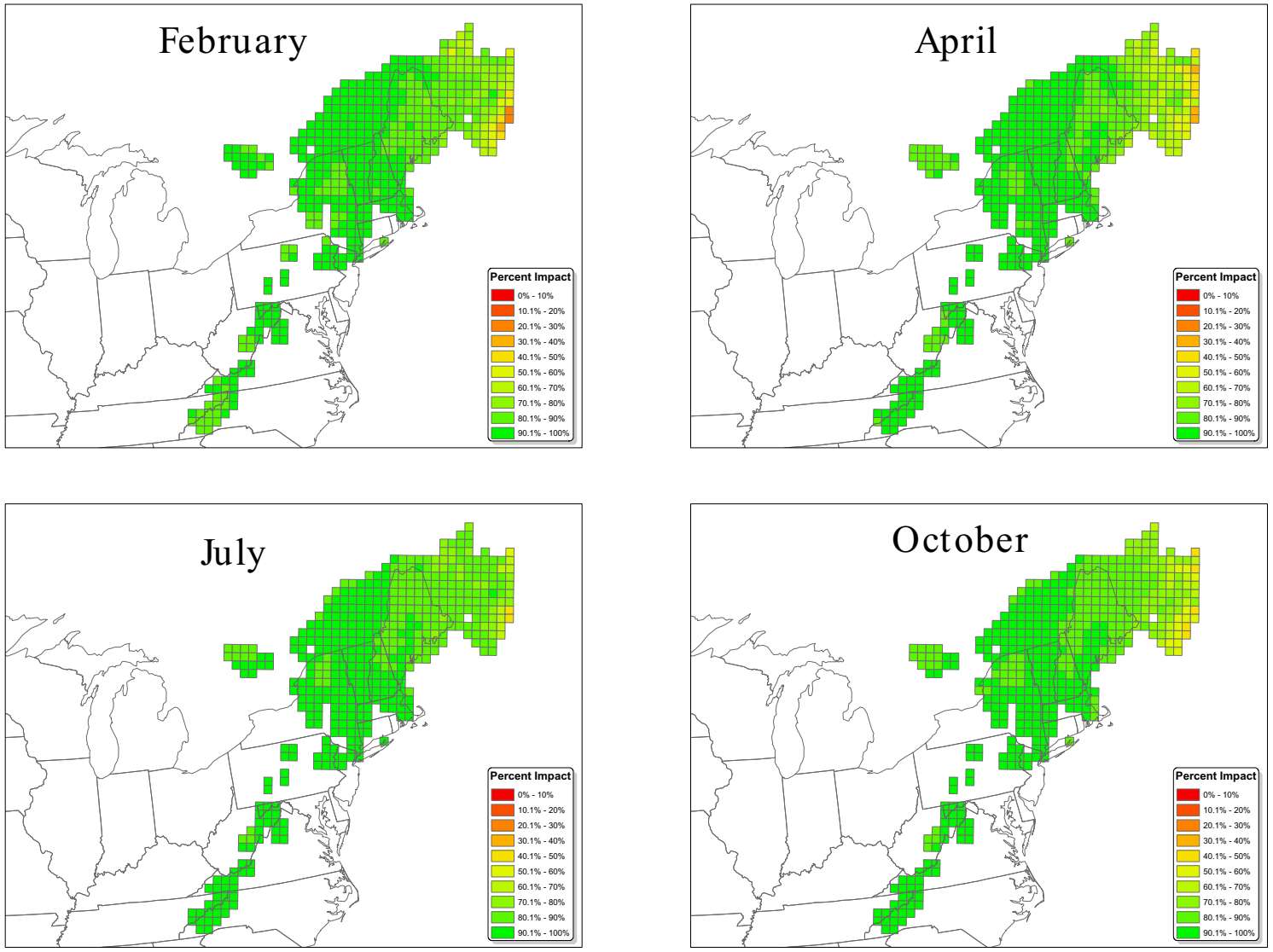


Figure 3.2-52. Percent impact of NH_3 anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Red Spruce Case Study Area.

Figures 3.2-53 through 3.2-56 present maps of the results for the Adirondacks Case Study Area. The Adirondacks Case Study Area is completely contained within the Red Spruce Case Study Area. Figure 3.2-53 shows that the specific grid cells in the Adirondacks Case Study Area show strong responses of total nitrogen deposition to domestic, anthropogenic NO_x emissions. With the exception of July, NO_x impacts are mostly greater than 50% throughout the case study area. In July, NO_x contributes more modestly, but still accounts for 40%–50% percent of total nitrogen deposition. Figure 3.2-55 shows that NO_x emissions account for almost all oxidized nitrogen deposition in the Adirondacks Case Study Area, while Figure 3.2-56 shows that NH_3 emissions account for almost all reduced nitrogen deposition.

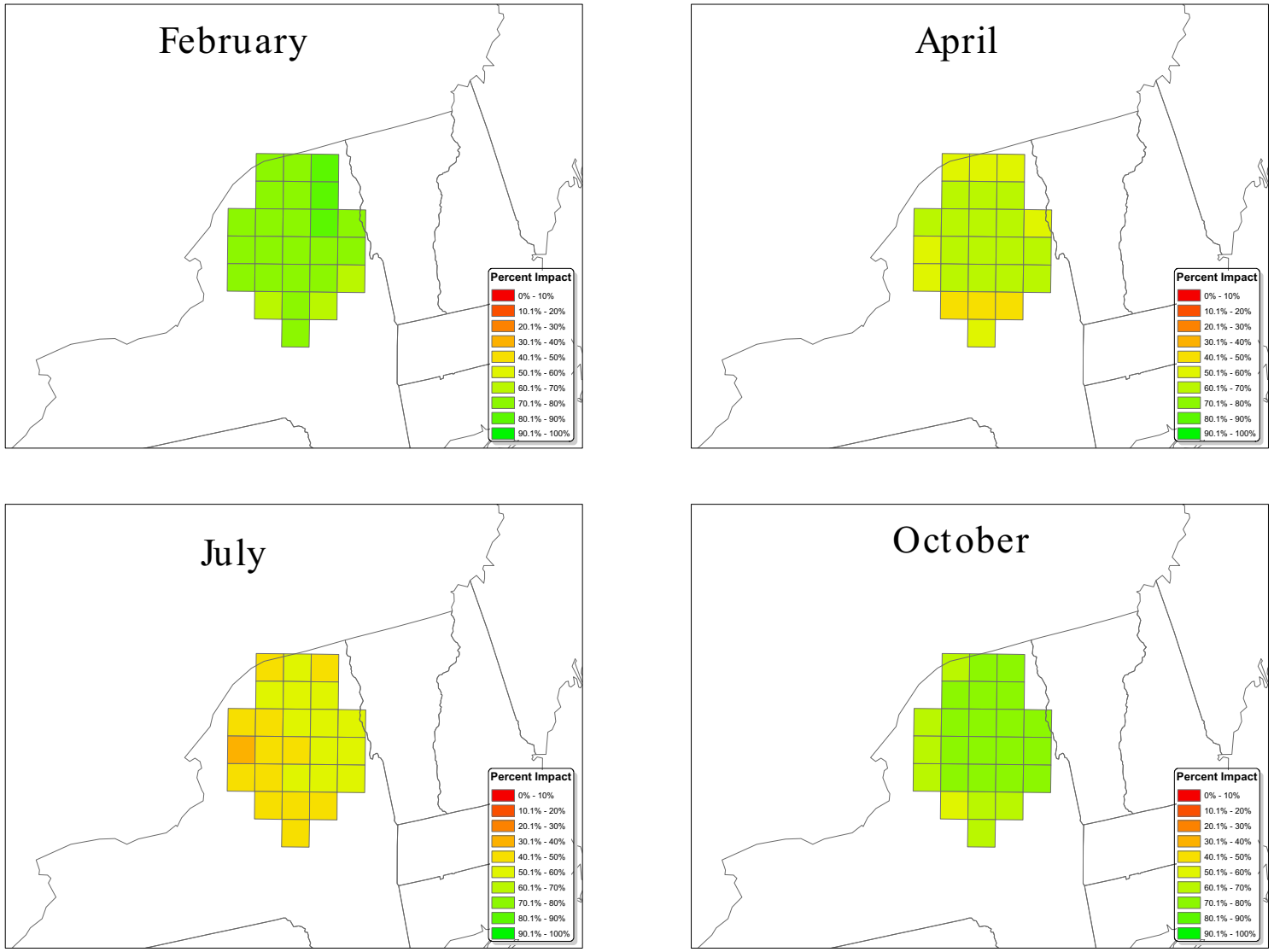


Figure 3.2-53. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Adirondacks Case Study Area.

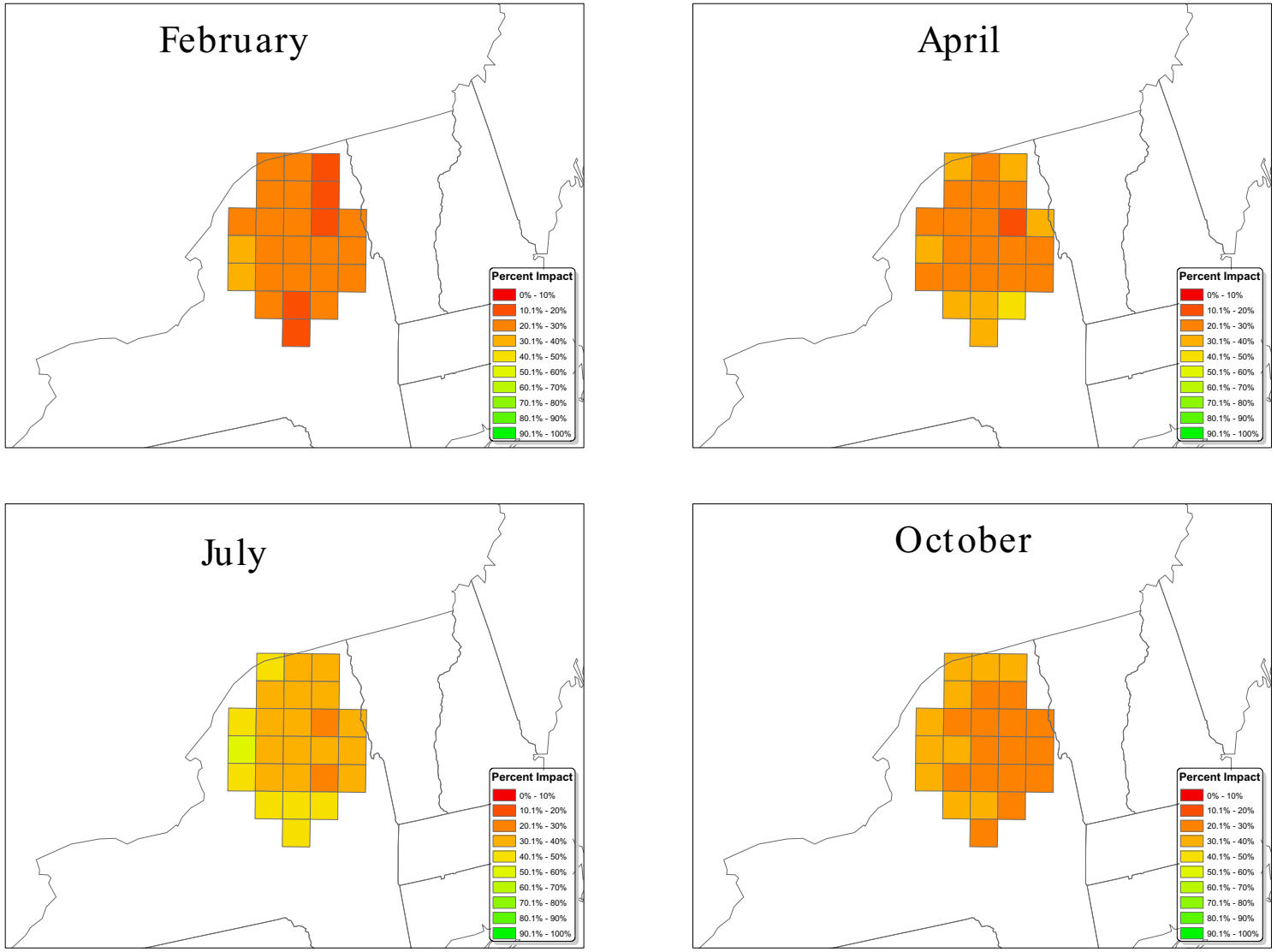


Figure 3.2-54. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Adirondacks Case Study Area.

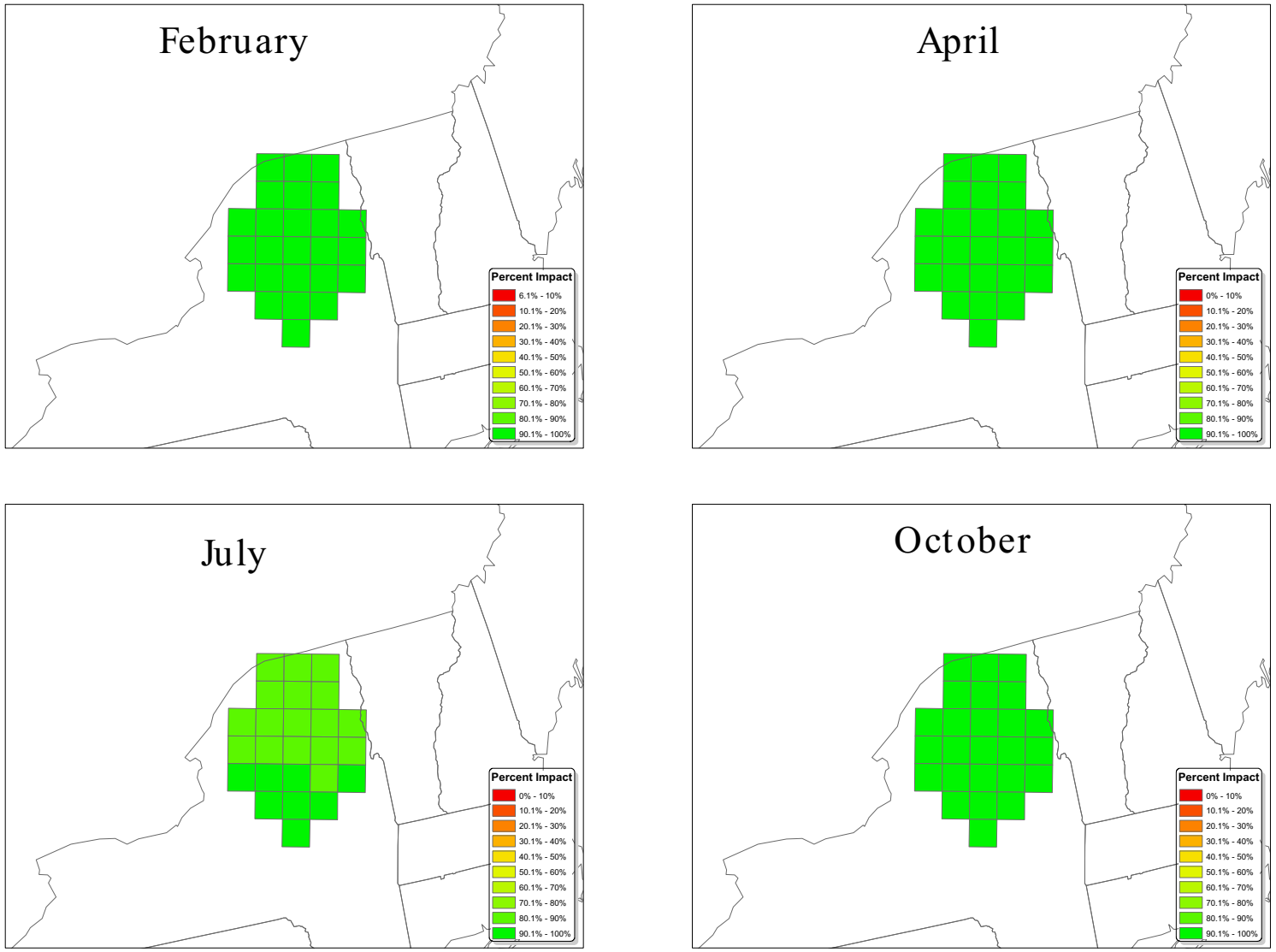


Figure 3.2-55. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Adirondacks Case Study Area.

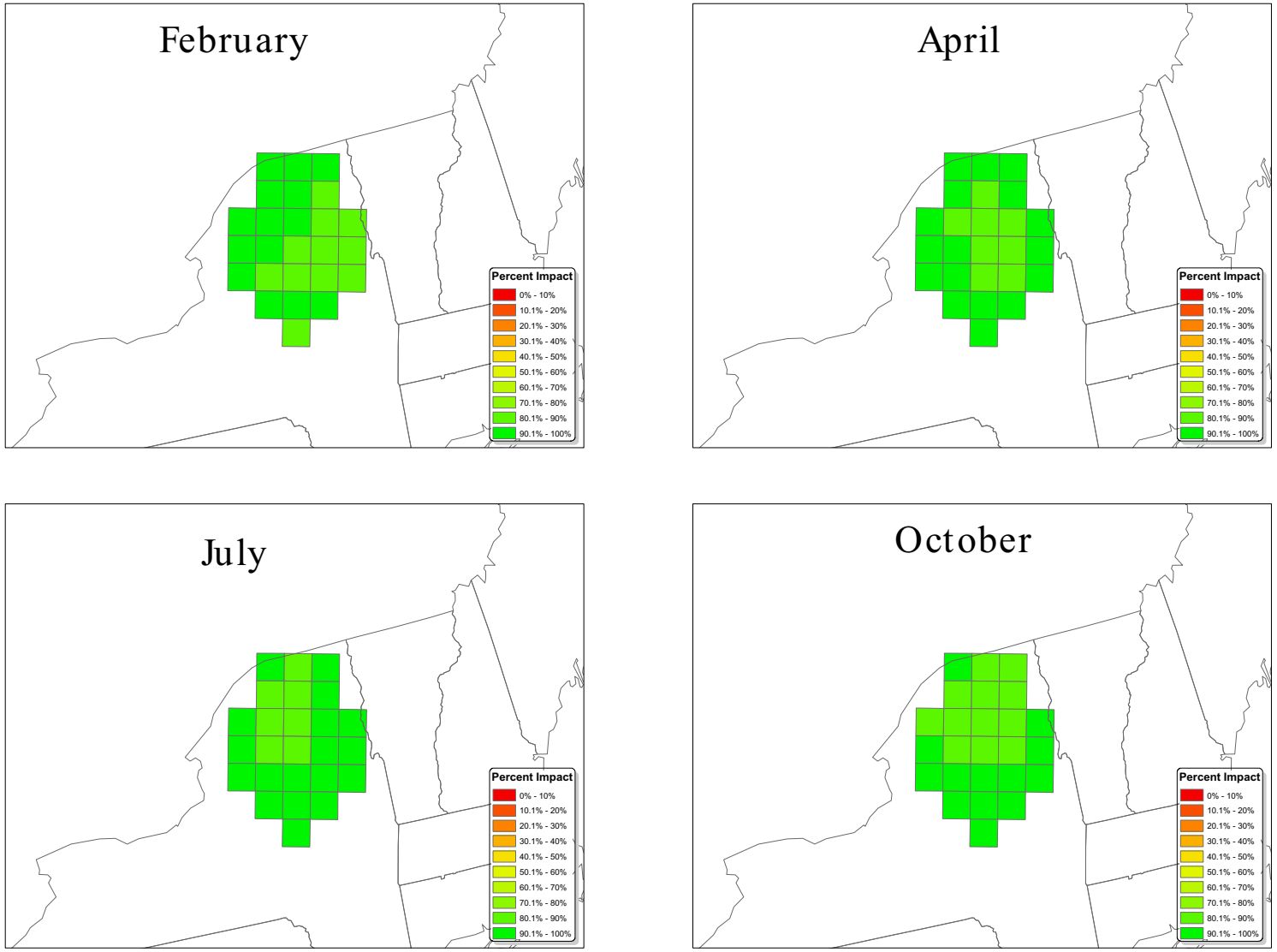


Figure 3.2-56. Percent impact of NH_3 anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Adirondacks Case Study Area.

Figures 3.2-57 through 3.2-60 present maps of the results for the Potomac Case Study Area. Figure 3.2-57 shows that the Potomac Case Study Area has a significant fraction of total nitrogen deposition from domestic, anthropogenic NO_x emissions, but also has a number of grid cells where NO_x emissions have a less than 40% impact. This is likely due to the location of high NH_3 emitting sources in or near Potomac Case Study Area grid cells; for example, poultry production in northern Virginia and hog and cattle production in southern Pennsylvania. However, for many of the grid cells nearest to the Chesapeake Bay, NO_x emissions contribute significantly (50% impact or greater) to total nitrogen deposition. As with the Adirondacks Case Study Area, Figure 3.2-59 shows that almost all of the oxidized nitrogen deposition is associated with NO_x emissions, while Figure 3.2-60 shows that almost all of the reduced nitrogen deposition is associated with NH_3 emissions.

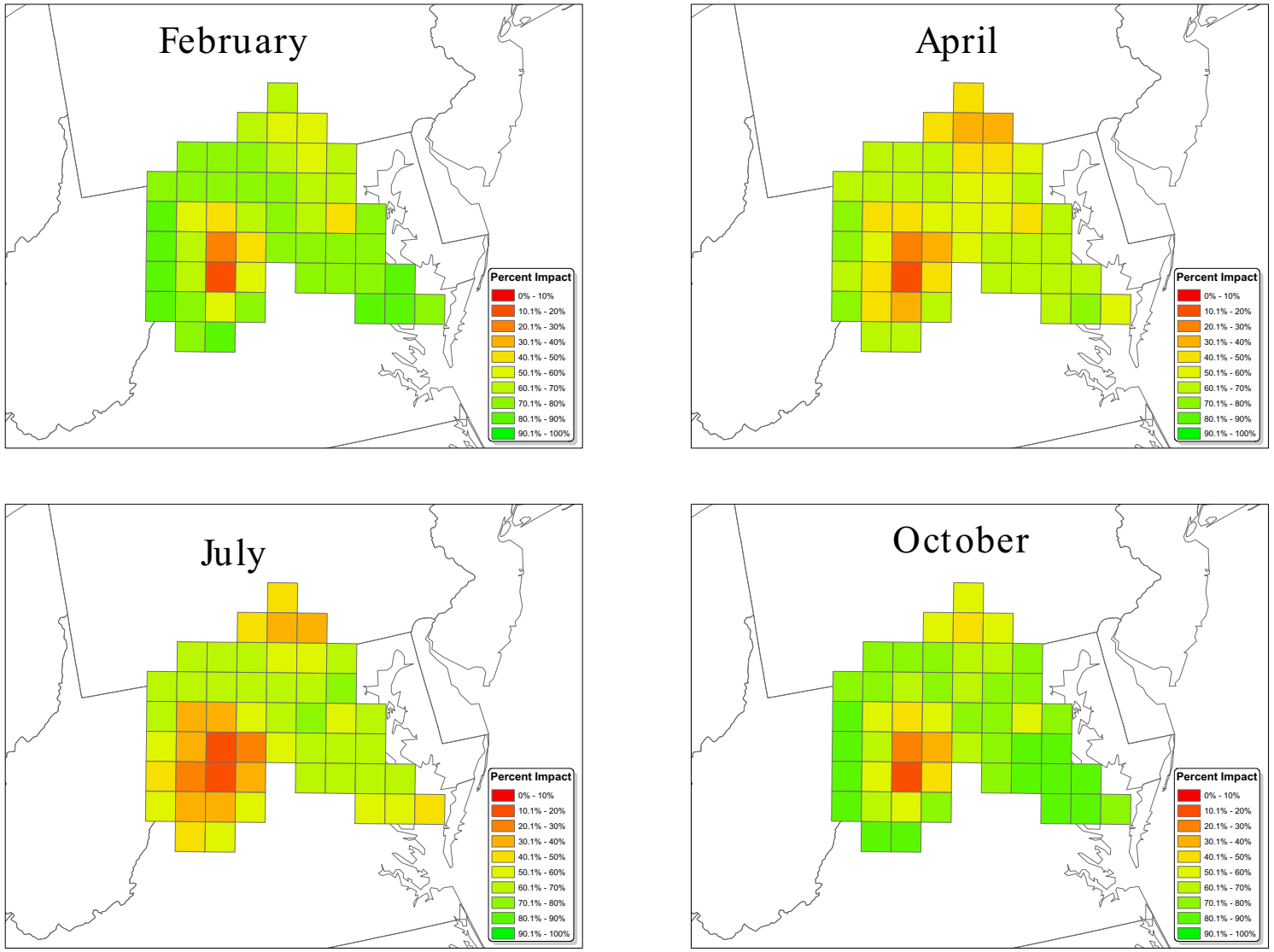


Figure 3.2-57. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Potomac Case Study Area.

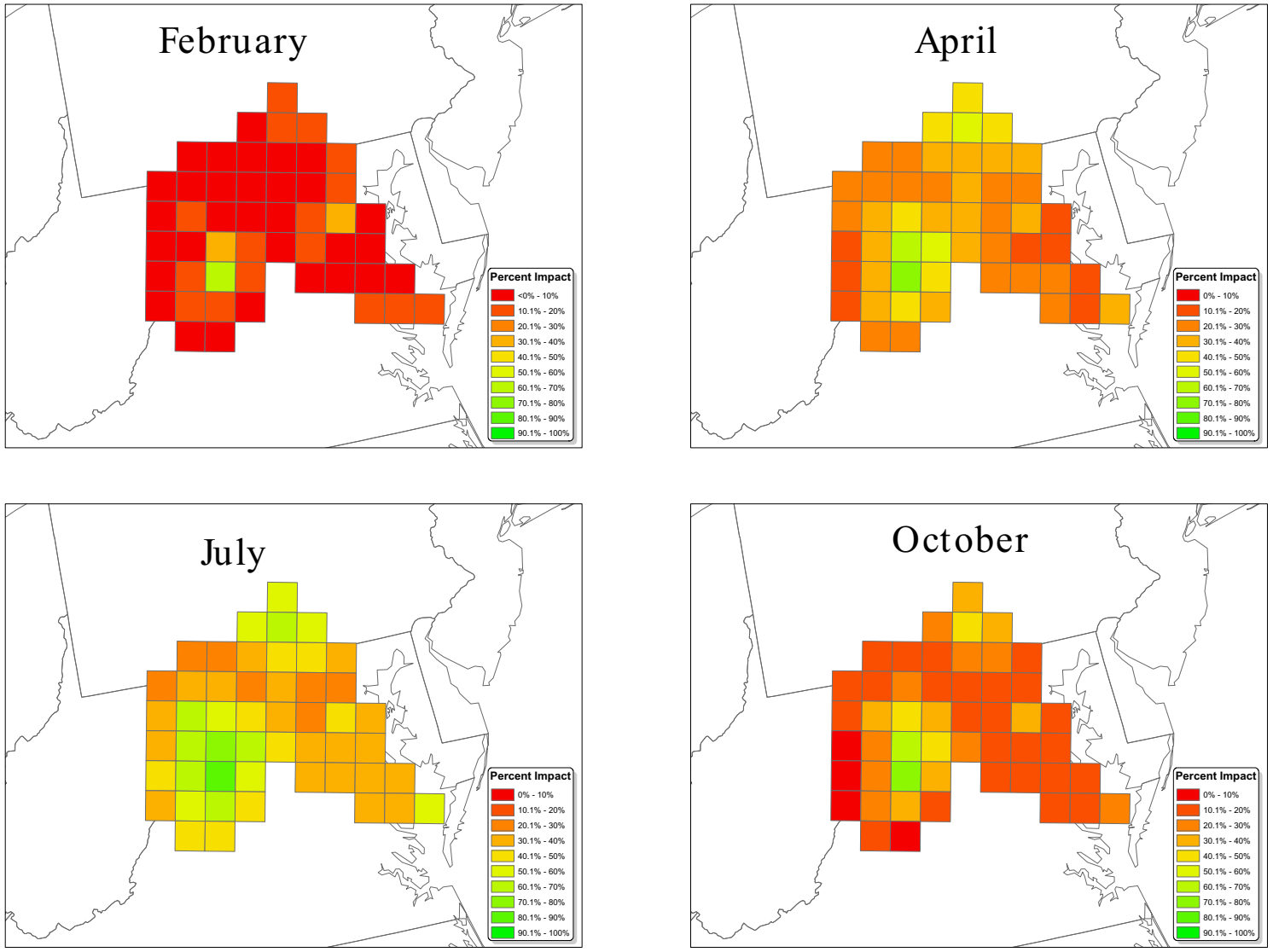


Figure 3.2-58. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Potomac Case Study Area.

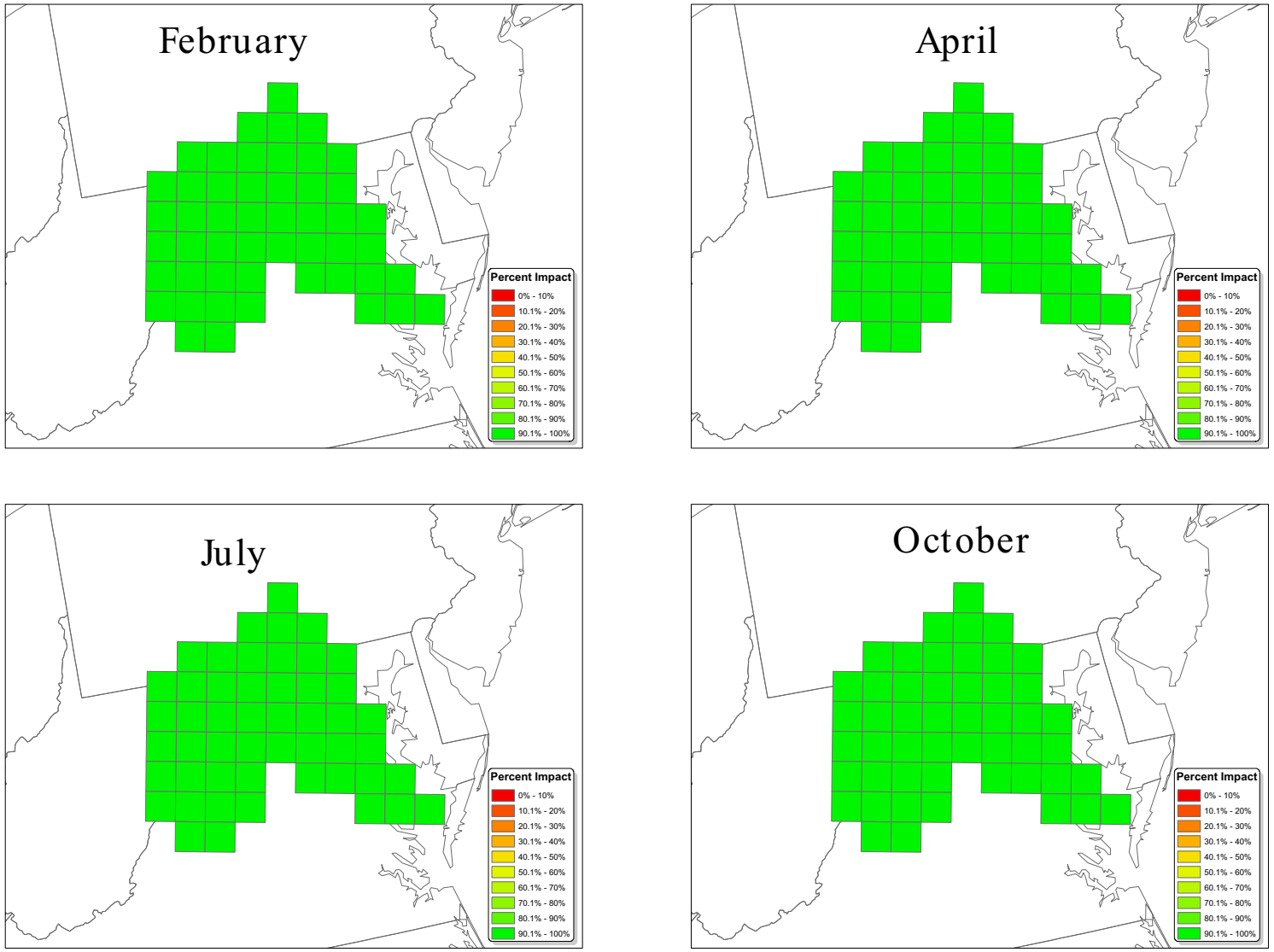


Figure 3.2-59. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Potomac Case Study Area.

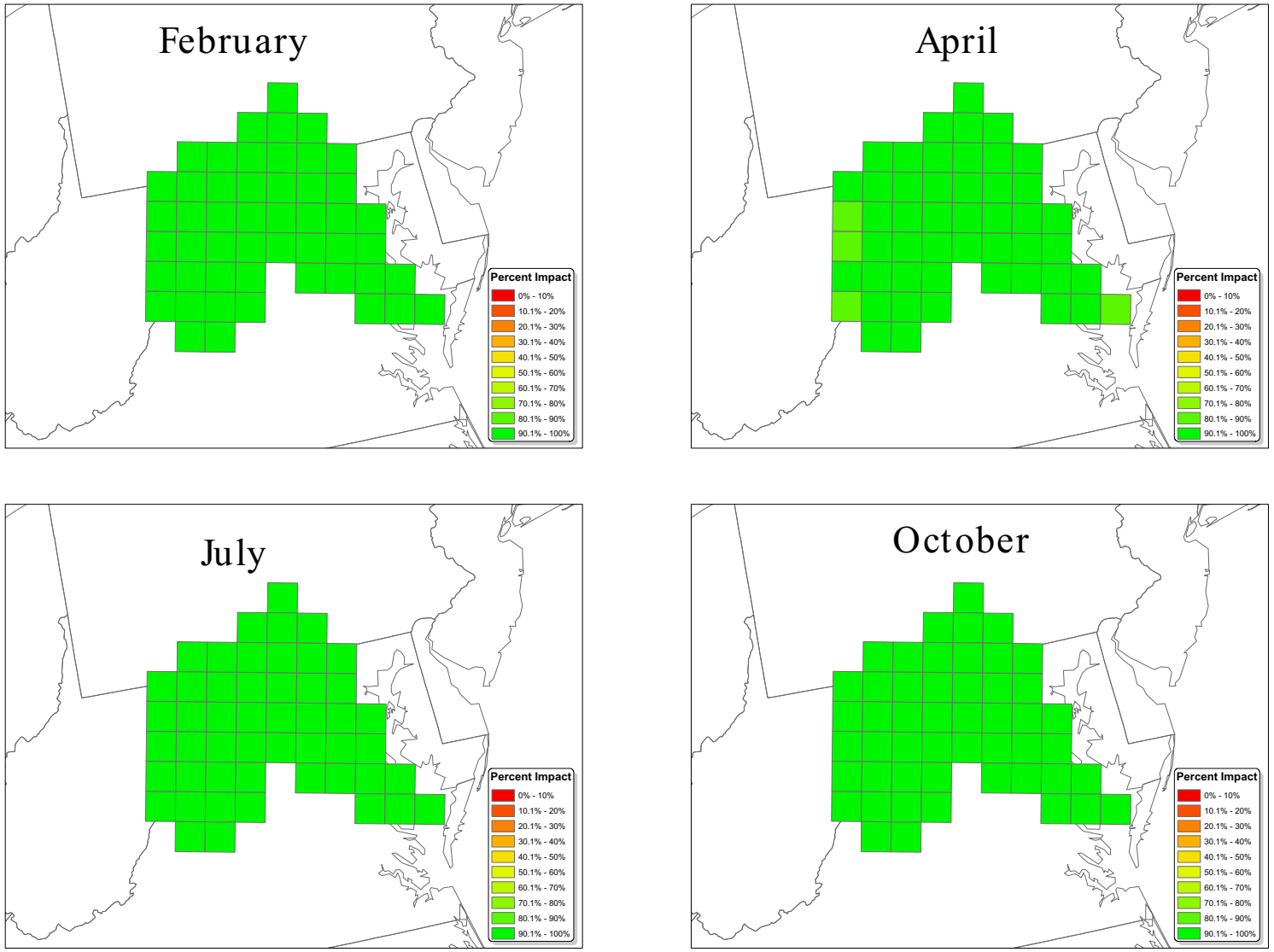


Figure 3.2-60. Percent impact of NH_3 anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Potomac Case Study Area.

Figures 3.2-61 through 3.2-64 present maps of the results for the Shenandoah Case Study Area. The Shenandoah Case Study Area overlaps a portion of the Potomac Case Study Area, and thus, shares similar characteristics. Figure 3.2-61 shows that there are a number of grid cells, especially in the northernmost and southernmost portions of the Shenandoah Case Study Area, that have relatively low percentage impacts on total nitrogen deposition from NO_x emissions, reflecting the higher contribution from NH_3 sources in northern Virginia and on the North Carolina/Virginia border. However, NO_x emissions still contribute significantly in many grid cells, especially during the winter and fall. As with the Adirondacks and Potomac areas, Figure 3.2-63 shows that almost all of the oxidized nitrogen deposition is associated with NO_x emissions, while Figure 3.2-64 shows that almost all of the reduced nitrogen deposition is associated with NH_3 emissions.

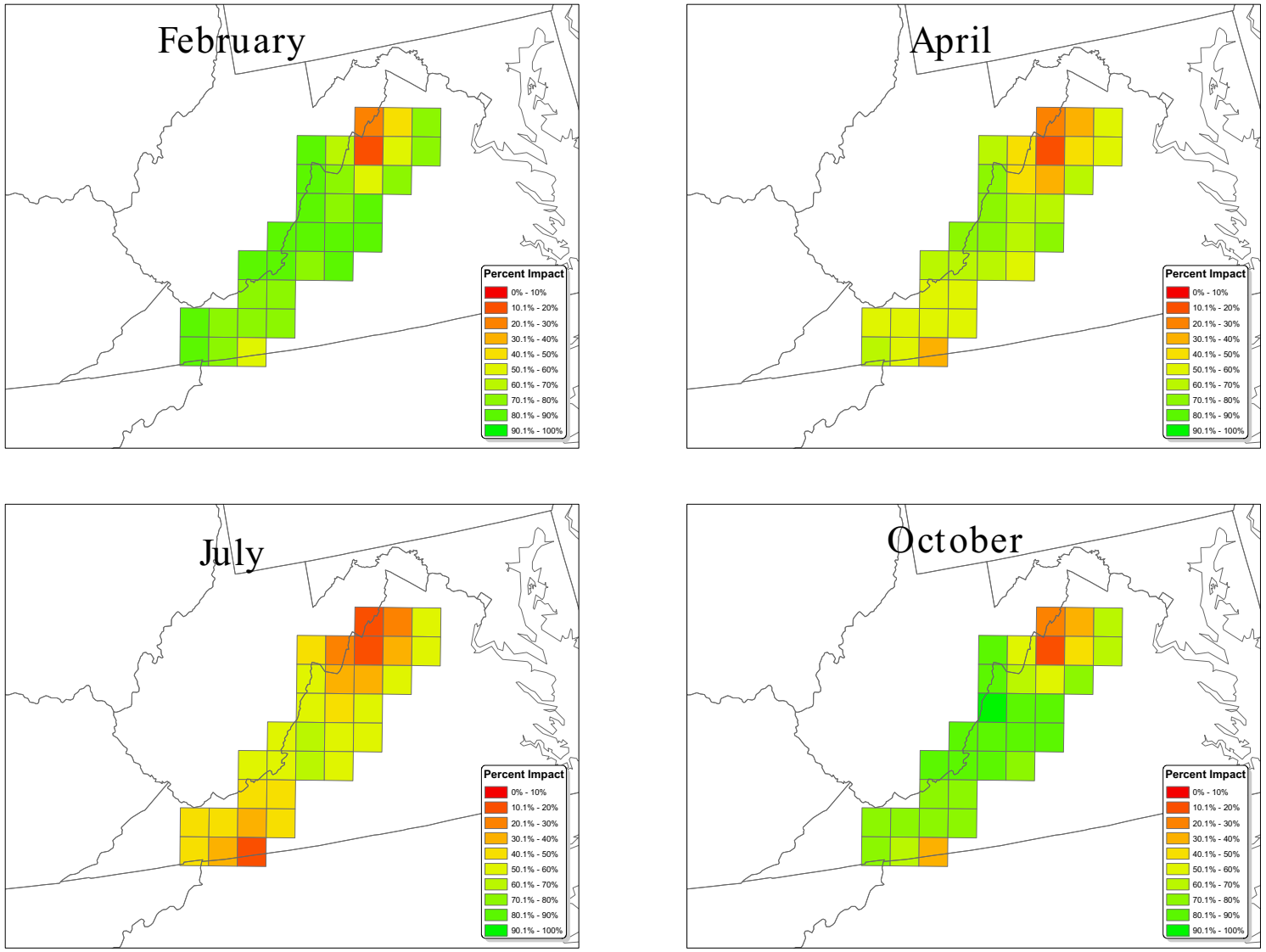


Figure 3.2-61. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Shenandoah Case Study Area.

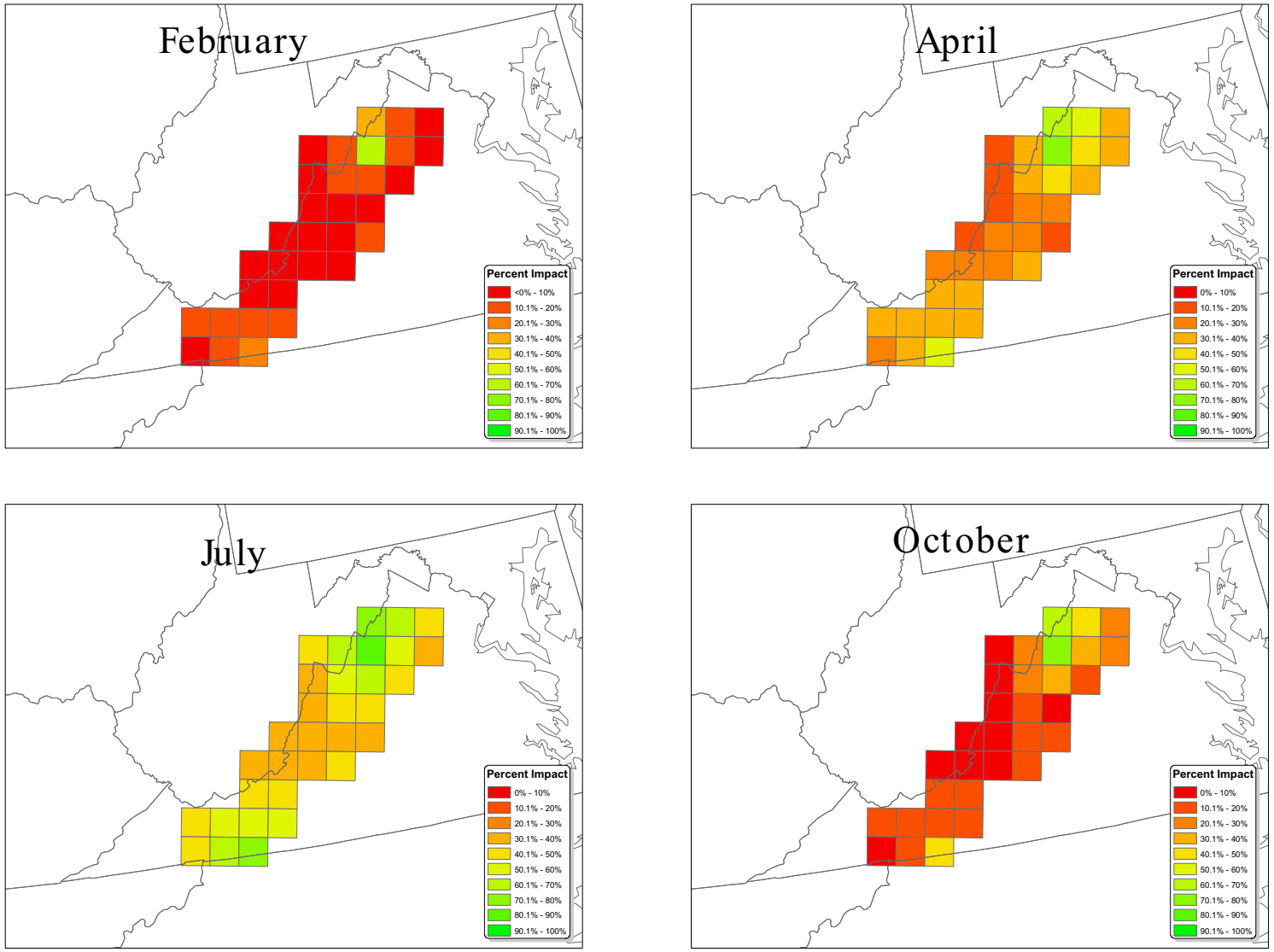


Figure 3.2-62. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Shenandoah Case Study Area.

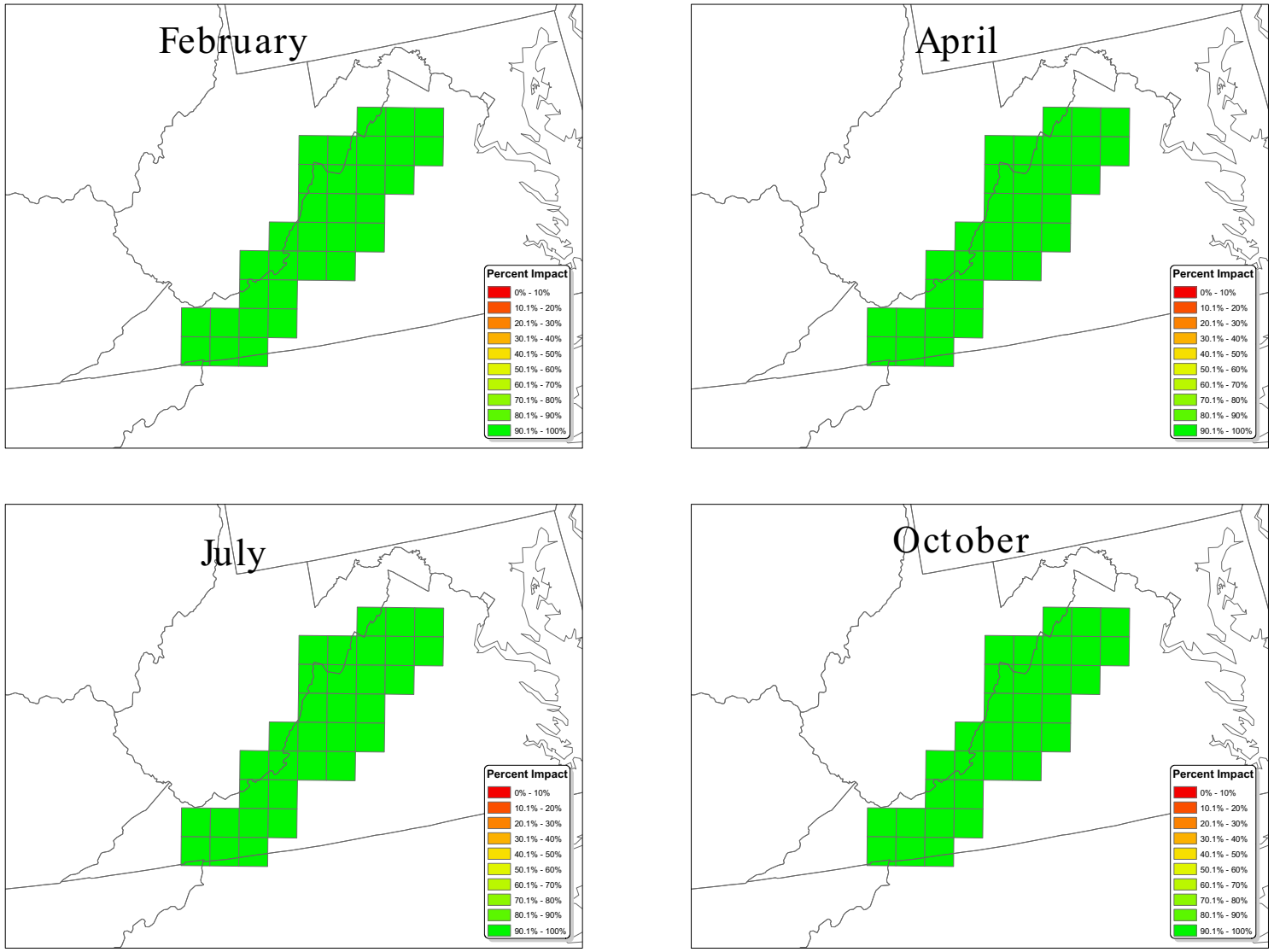


Figure 3.2-63. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Shenandoah Case Study Area.

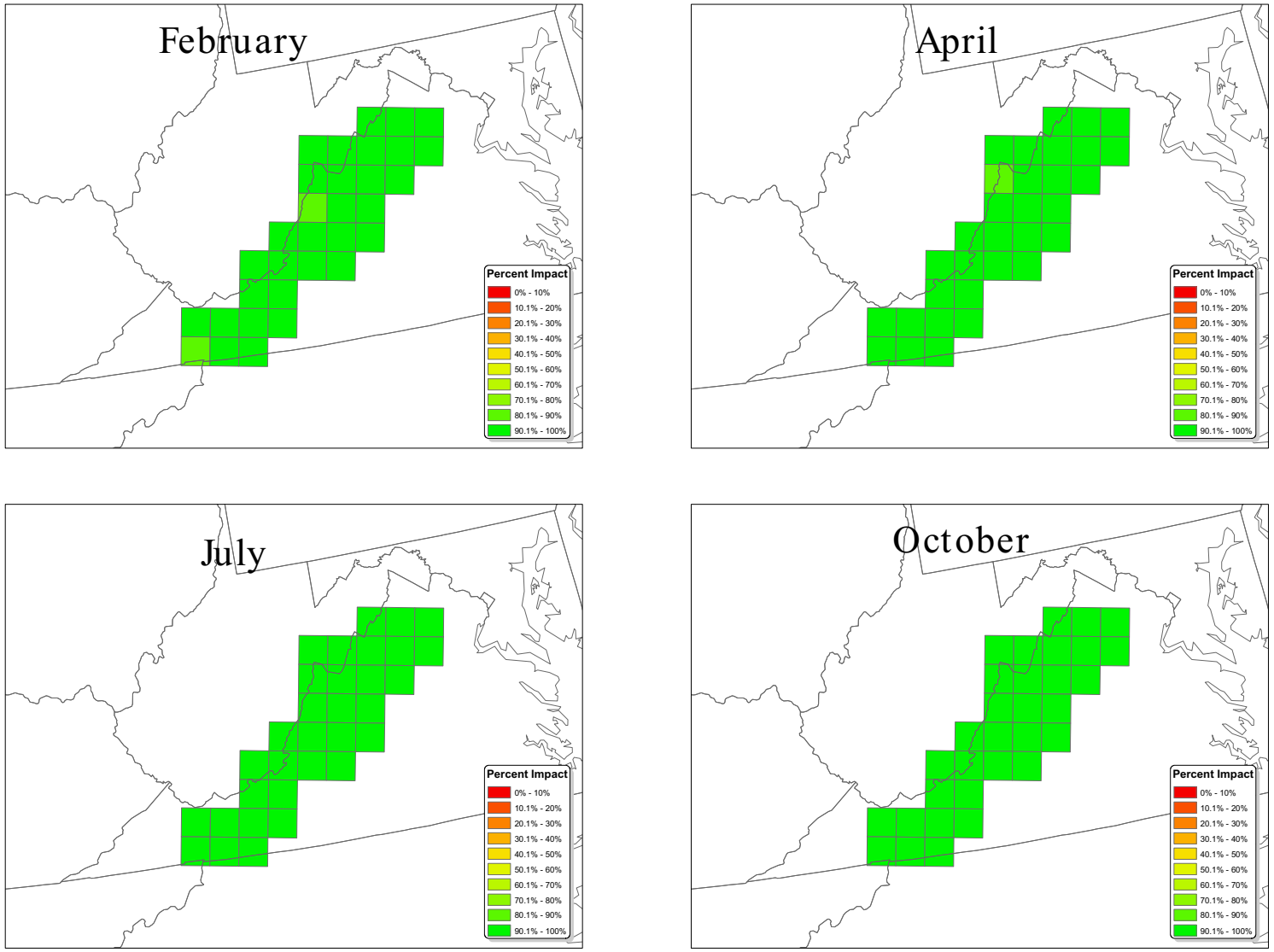


Figure 3.2-64. Percent impact of NH_3 Anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Shenandoah Case Study Area.

Figures 3.2-65 through 3.2-68 present maps of the results for the Neuse Case Study Area. Figure 3.2-65 shows that the Neuse Case Study Area is highly dominated by NH_3 emissions, especially in the central grid cells, which are located over the counties in North Carolina with high levels of CAFOs, primarily for hogs and turkeys. NO_x still contributes significantly in the western and eastern portions of this case study area, but the impact of NH_3 emissions is much more pronounced relative to the other case study areas. As with most of the other eastern case study areas, Figure 3.2-67 shows that almost all of the oxidized nitrogen deposition is associated with NO_x emissions, while Figure 3.2-68 shows that almost all of the reduced nitrogen deposition is associated with NH_3 emissions.

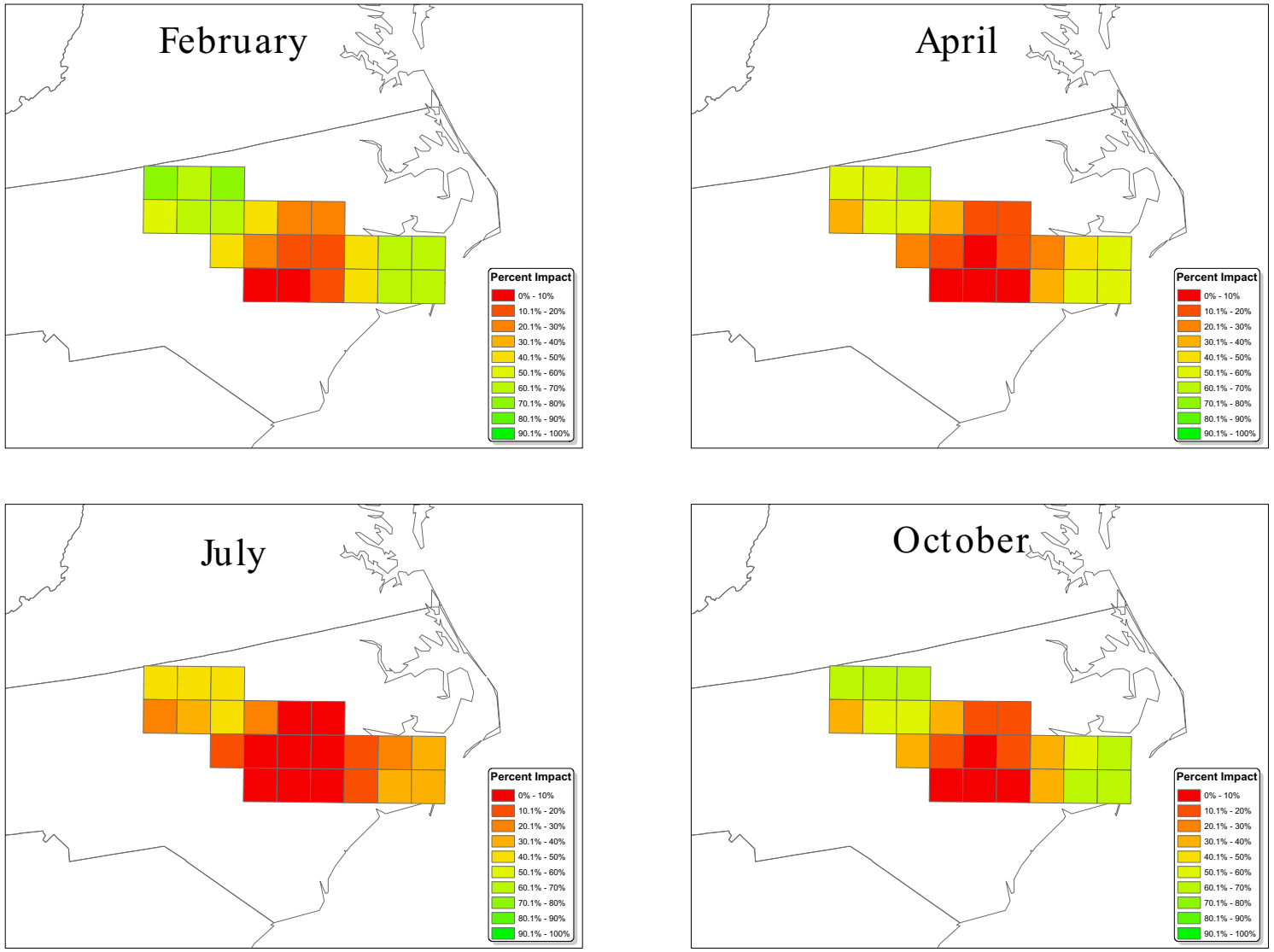


Figure 3.2-65. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Neuse Case Study Area.

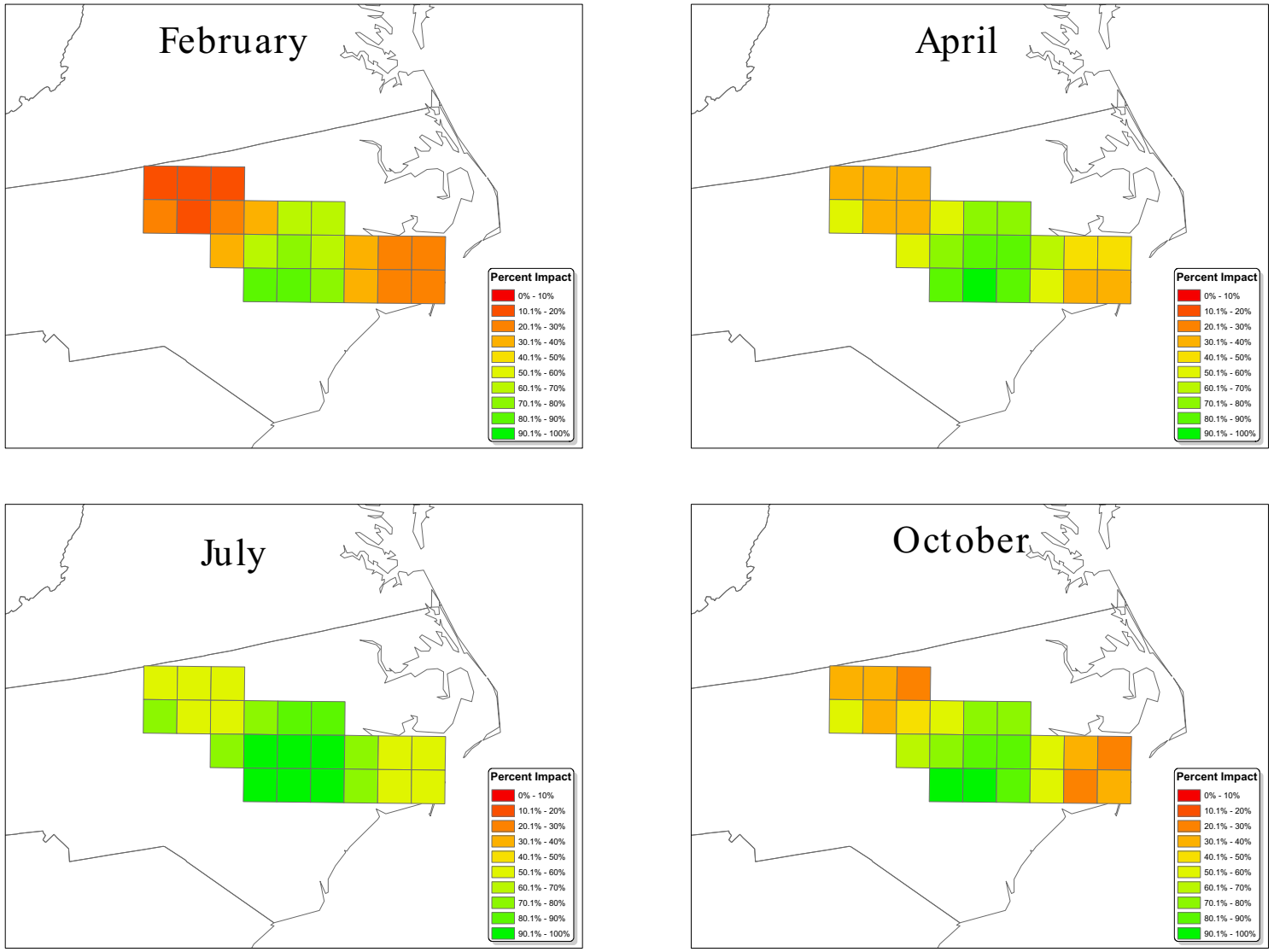


Figure 3.2-66. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Neuse Case Study Area.

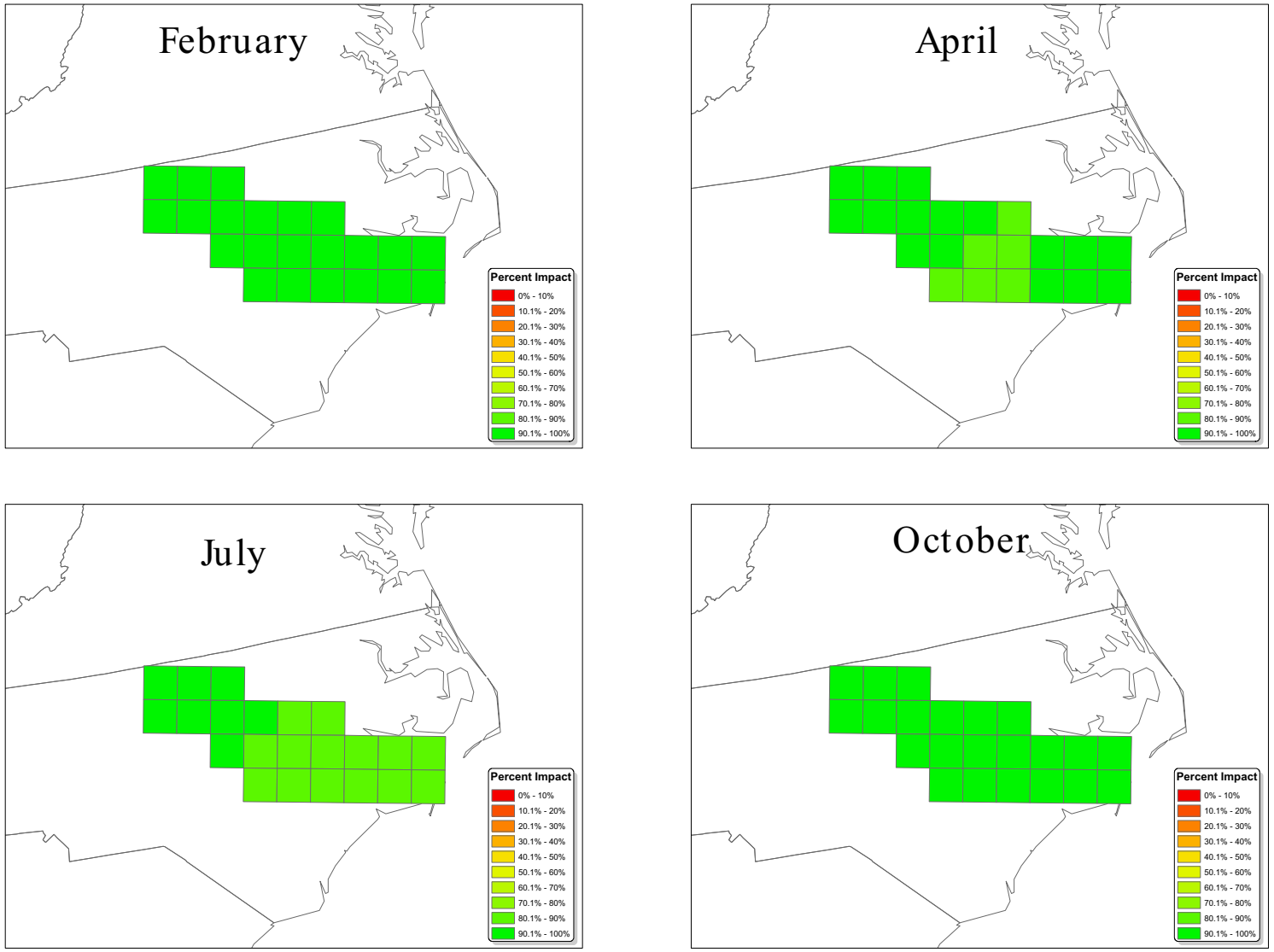


Figure 3.2-67. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Neuse Case Study Area.

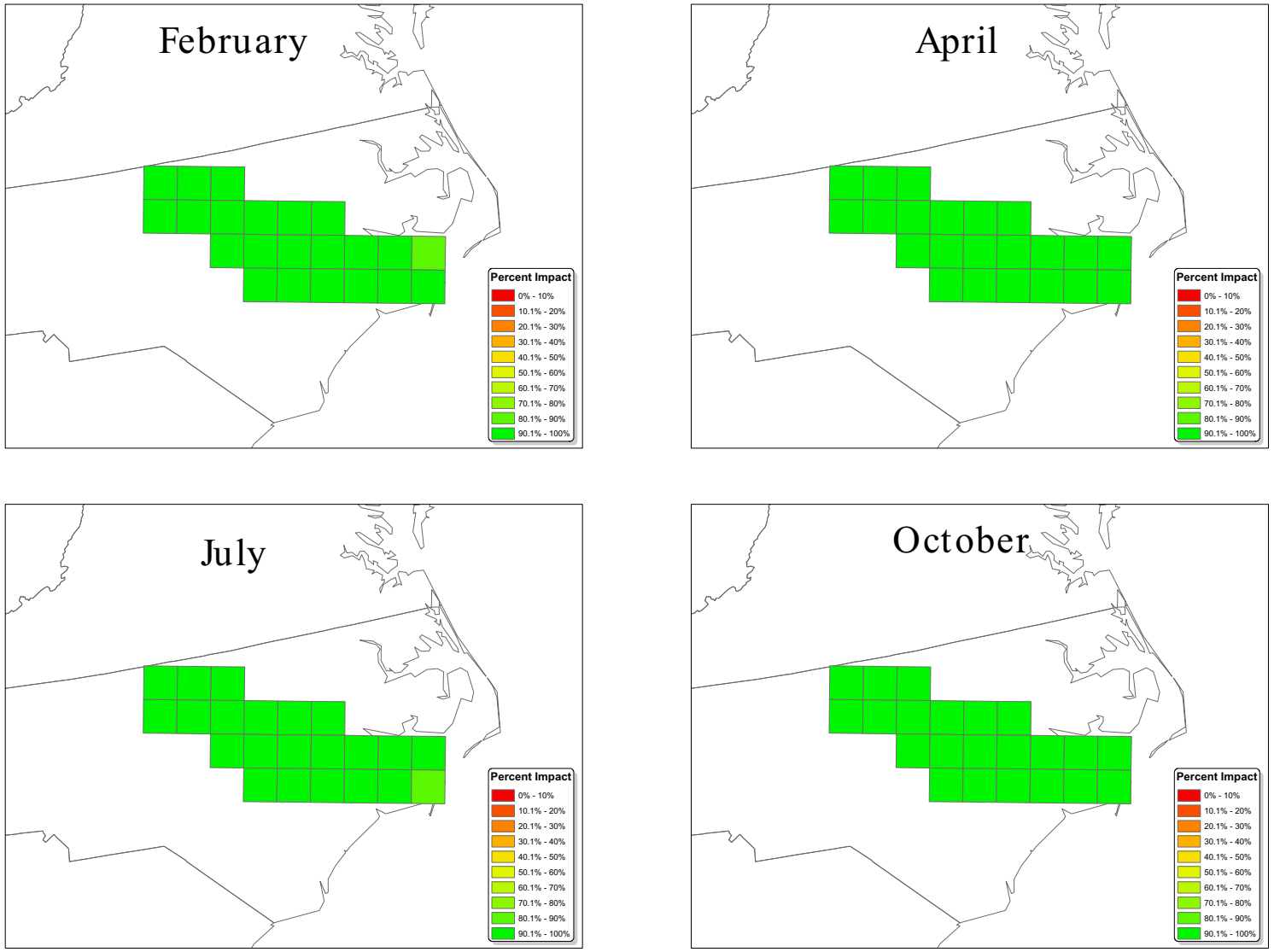


Figure 3.2-68 Percent Impact of NH_3 Anthropogenic United States Emissions Zero-out on Reduced Nitrogen Deposition in the Neuse Case Study Area.

Figures 3.2-69 through 3.2-72 present maps of the results for the Coastal Sage Case Study Area. Figure 3.2-69 shows the response of total nitrogen to NO_x emissions in the Coastal Sage Case Study Area. The Coastal Sage Case Study Area is the only case study area located completely in the western United States. As opposed to the eastern case study areas, the most significant contributions of NO_x are during July, rather than during the fall and winter. Domestic, anthropogenic NO_x contributes a significant amount to at least some grid cells in each season, but there is heterogeneity in response in each season. The northern portion of this case study area appears less responsive to domestic, anthropogenic NO_x than the southern portion. Examining the responses of oxidized nitrogen deposition in Figure 3.2-71, it appears that international NO_x emissions are contributing a small fraction to oxidized nitrogen deposition along the coast of California. Figure 3.2-72 shows that reduced nitrogen appears to have some international NH_3 component, but in a few grid cells, it seems to also be impacted by either a point source of NH_3 or non-anthropogenic sources.

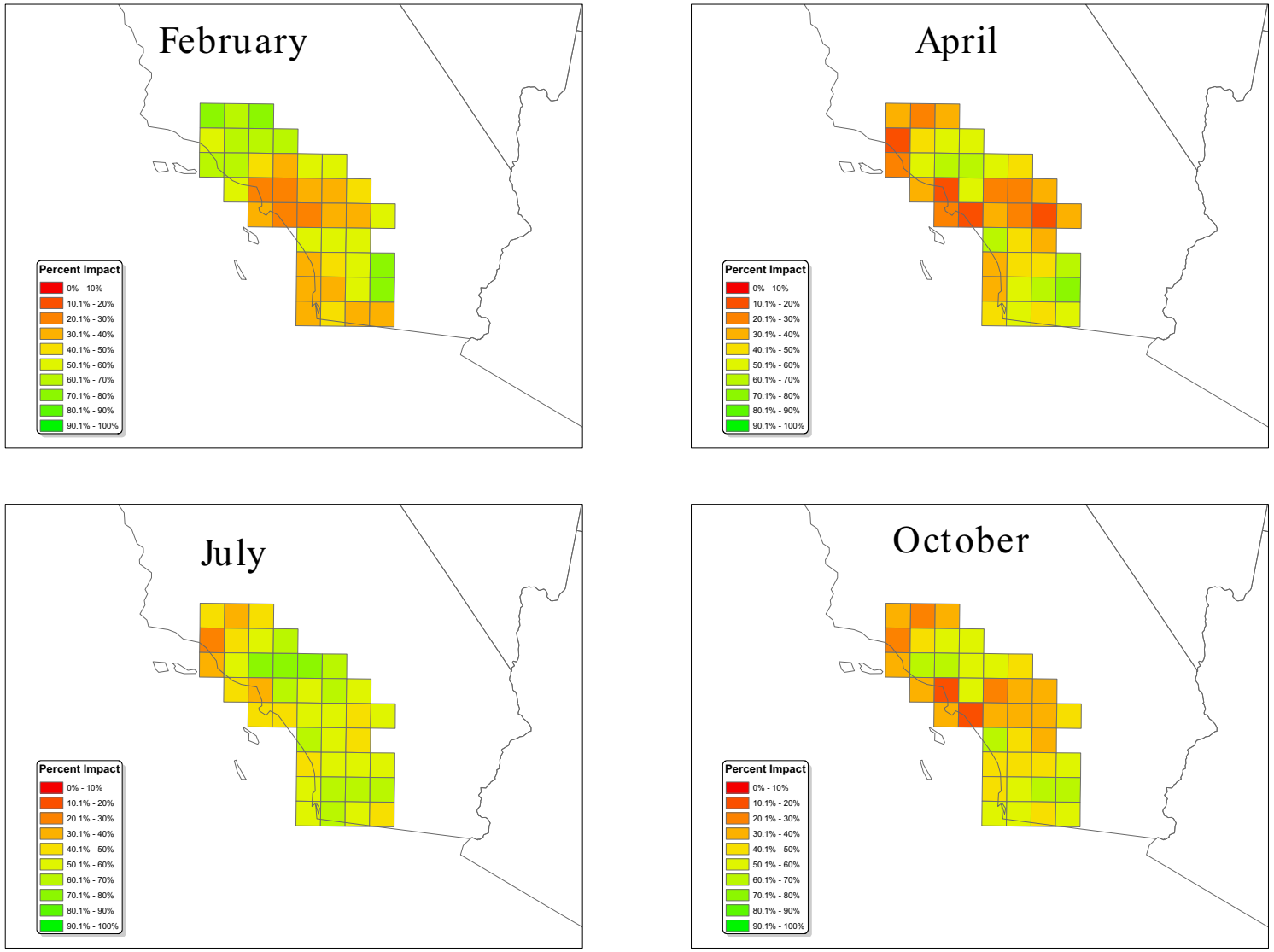


Figure 3.2-69. Percent impact of NO_x Anthropogenic United States emissions zero-out on total nitrogen deposition in the Coastal Sage Case Study Area.

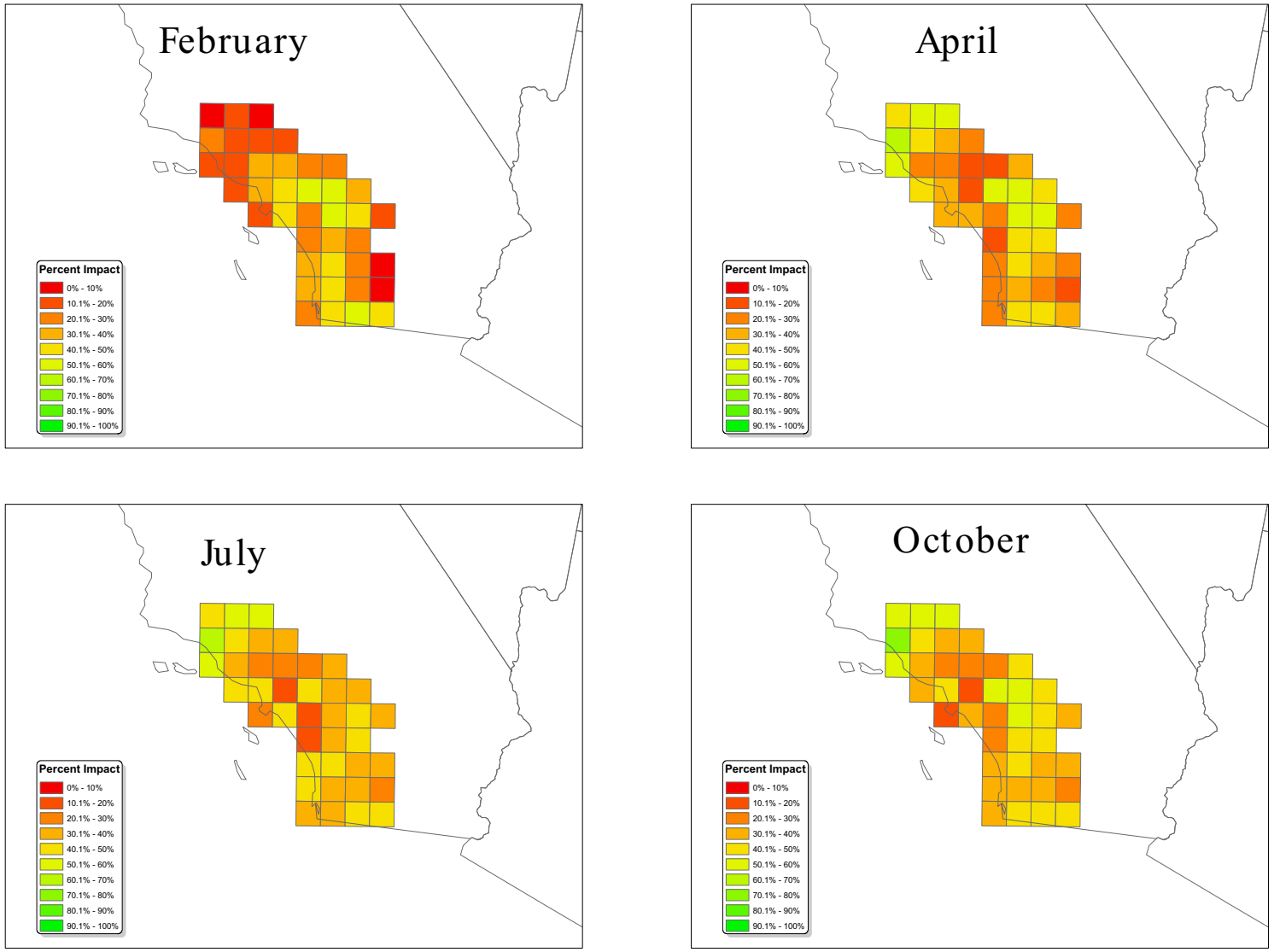


Figure 3.2-70. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Coastal Sage Case Study Area.

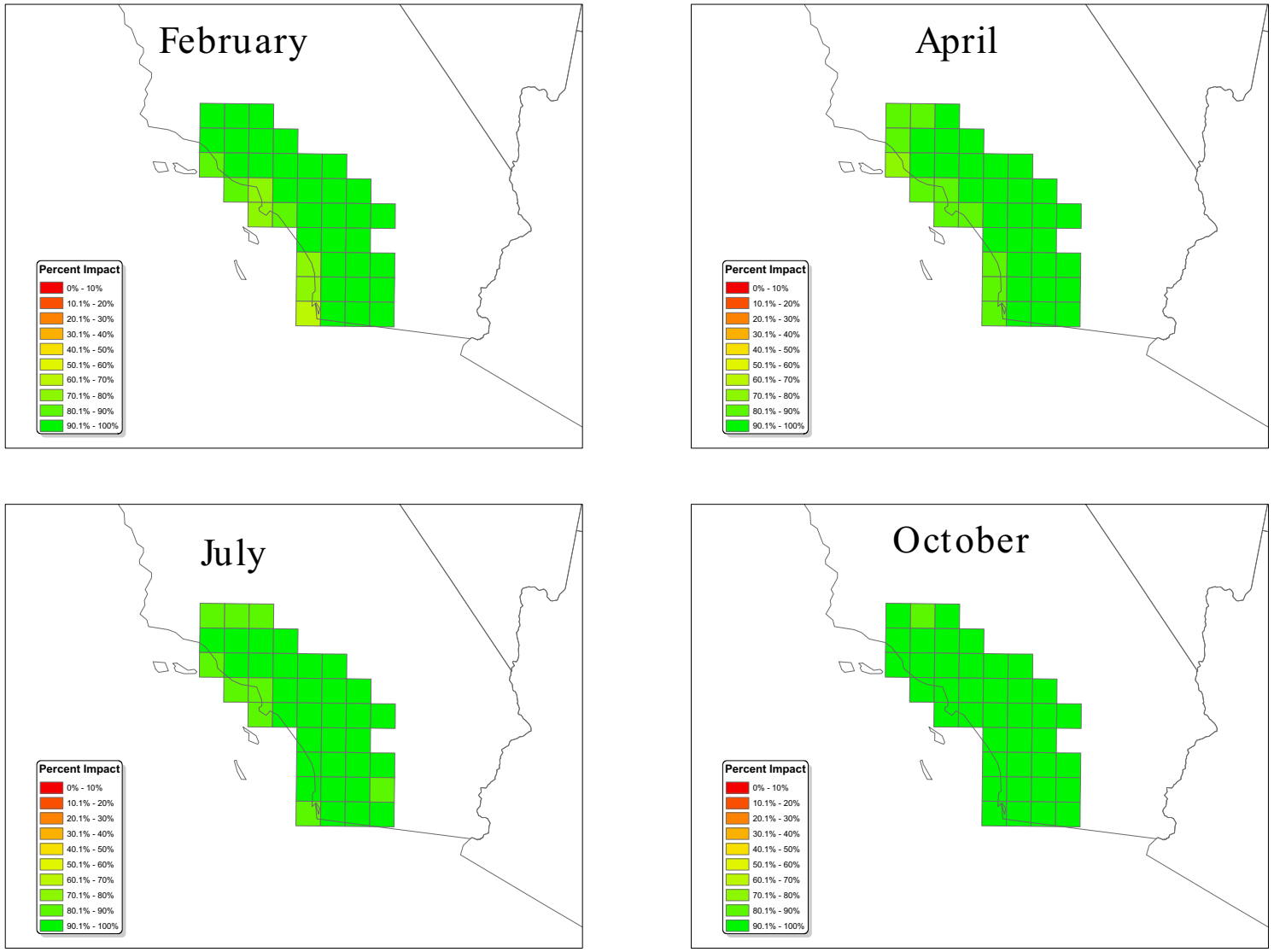


Figure 3.2-71. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Coastal Sage Case Study Area.

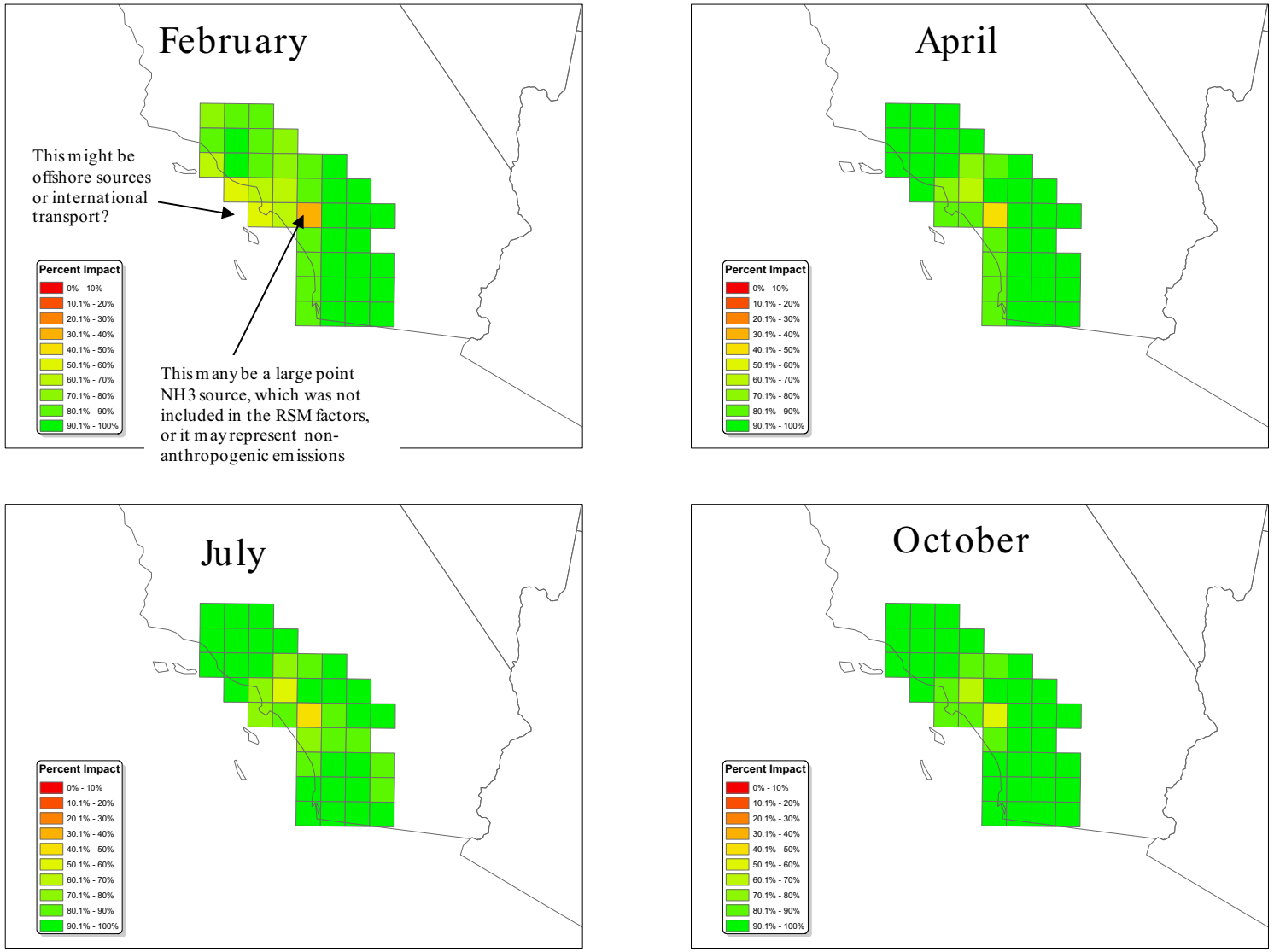


Figure 3.2-72. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Coastal Sage Case Study Area.

Figures 3.2-73 through 3.2-76 present maps of the results for the Estuaries Case Study Area. Figure 3.2-73 shows the response of total nitrogen to domestic, anthropogenic NO_x emissions in the Estuaries Case Study Area. The Estuaries Case Study Area covers a wide set of locations across the United States. In general, domestic, anthropogenic emissions of NO_x have a higher percentage impact on total nitrogen deposition to estuaries in the eastern United States relative to estuaries in the western United States. Examining the oxidized nitrogen deposition maps in Figure 3.2-75, part of the reason for this is the larger role of international NO_x emissions on the West Coast. In general, there is a significant impact of NO_x emissions on total nitrogen in most estuaries in at least some months; however, the degree of impact is highly variable. The majority of oxidized nitrogen deposition is due to domestic anthropogenic emissions, even in western coastal locations, whereas the majority of reduced nitrogen emissions is due to domestic, anthropogenic NH_3 emissions.

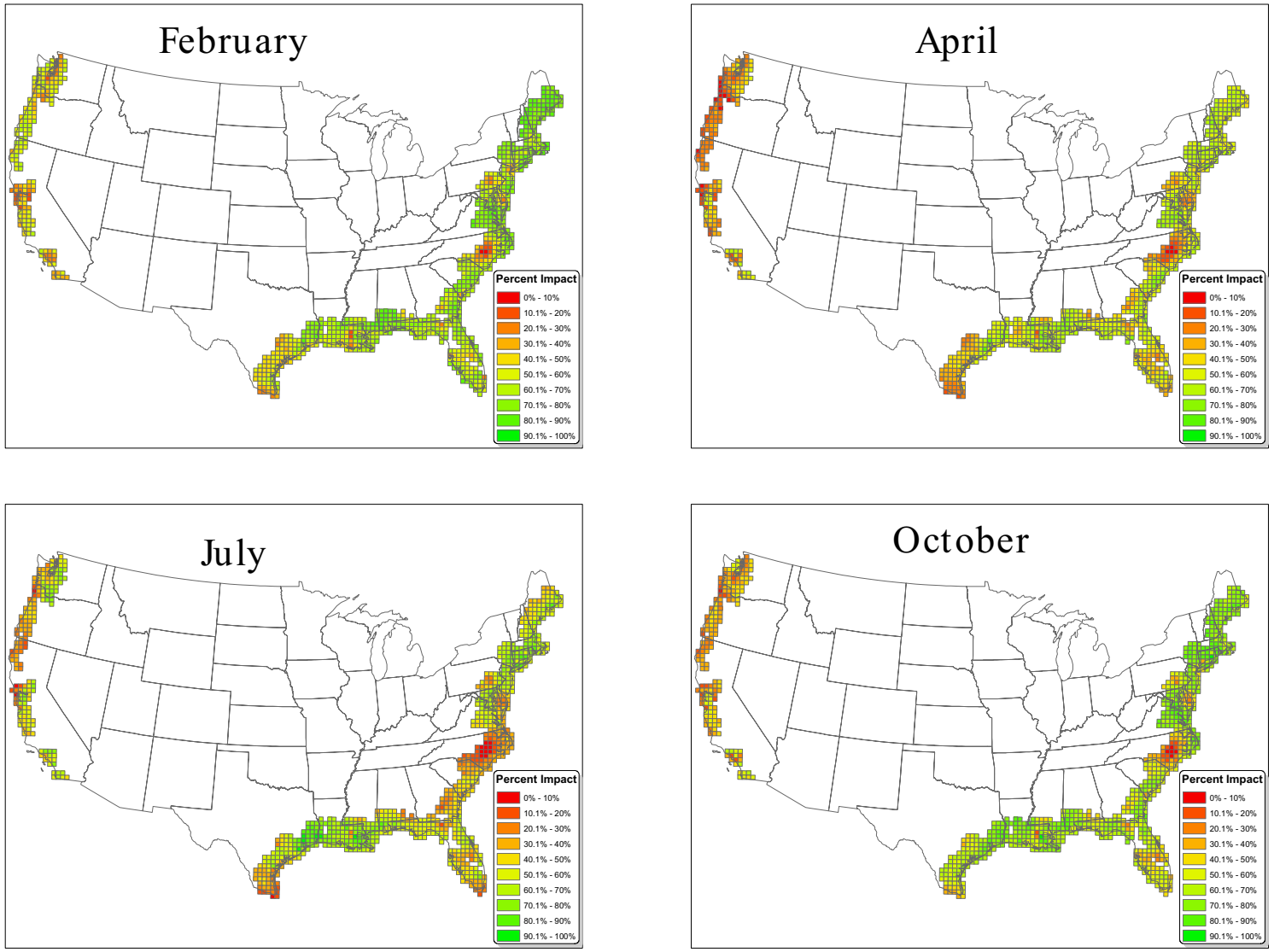


Figure 3.2-73. Percent impact of NO_x anthropogenic United States emissions zero-out on total nitrogen deposition in the Estuaries Case Study Area.

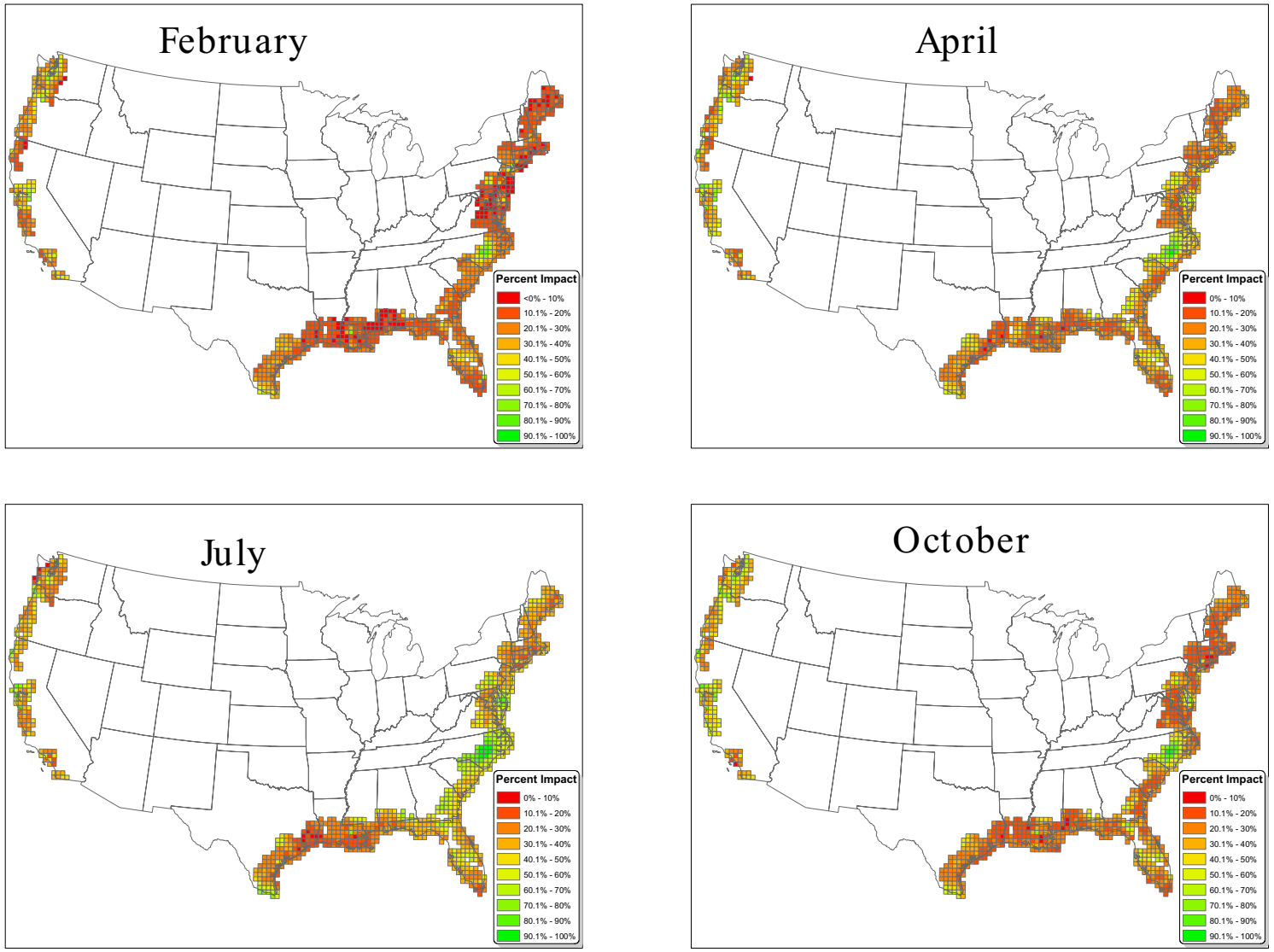


Figure 3.2-74. Percent impact of NH_3 anthropogenic United States emissions zero-out on total nitrogen deposition in the Estuaries Case Study Area.

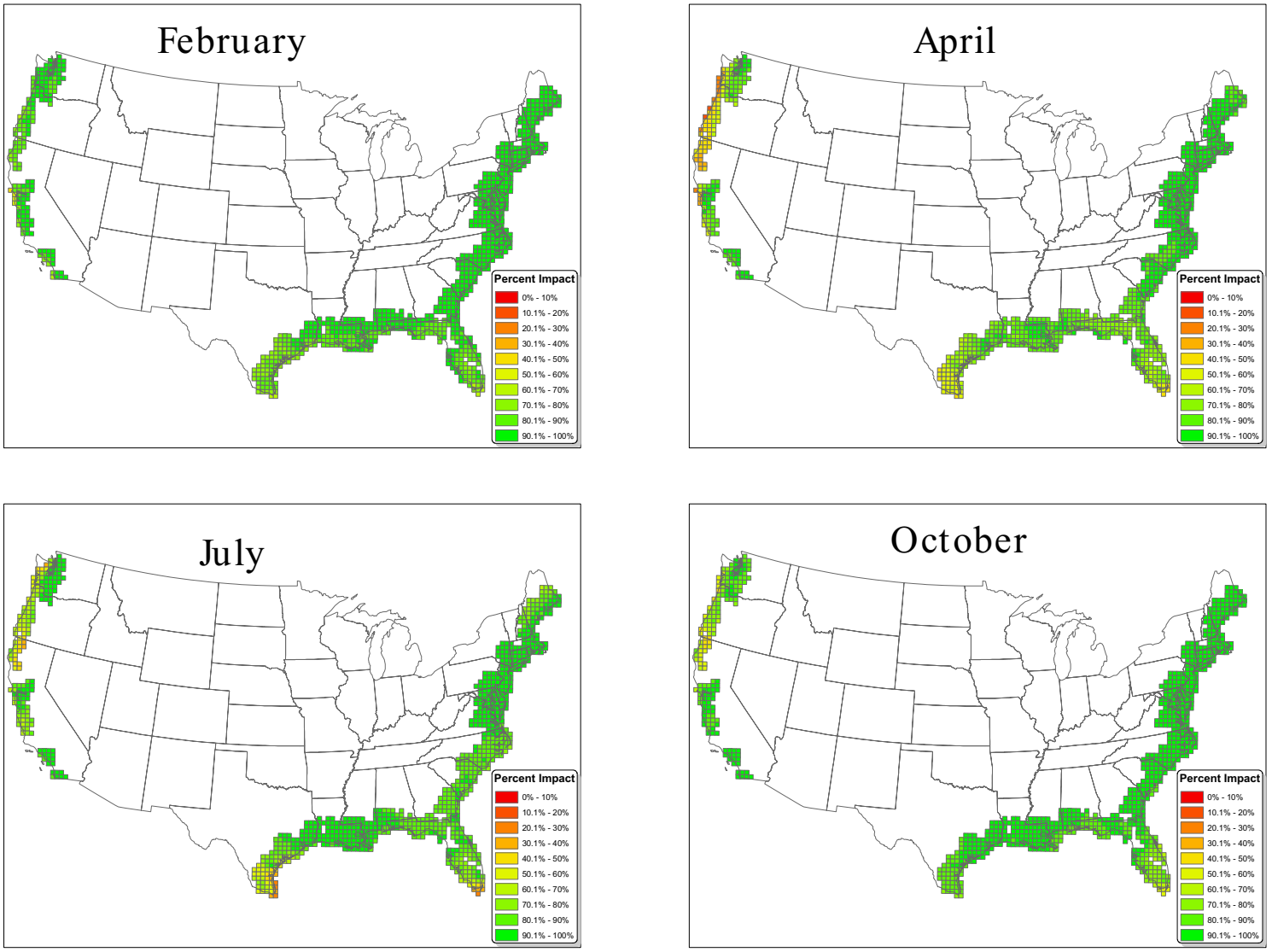


Figure 3.2-75. Percent impact of NO_x anthropogenic United States emissions zero-out on oxidized nitrogen deposition in the Estuaries Case Study Area.

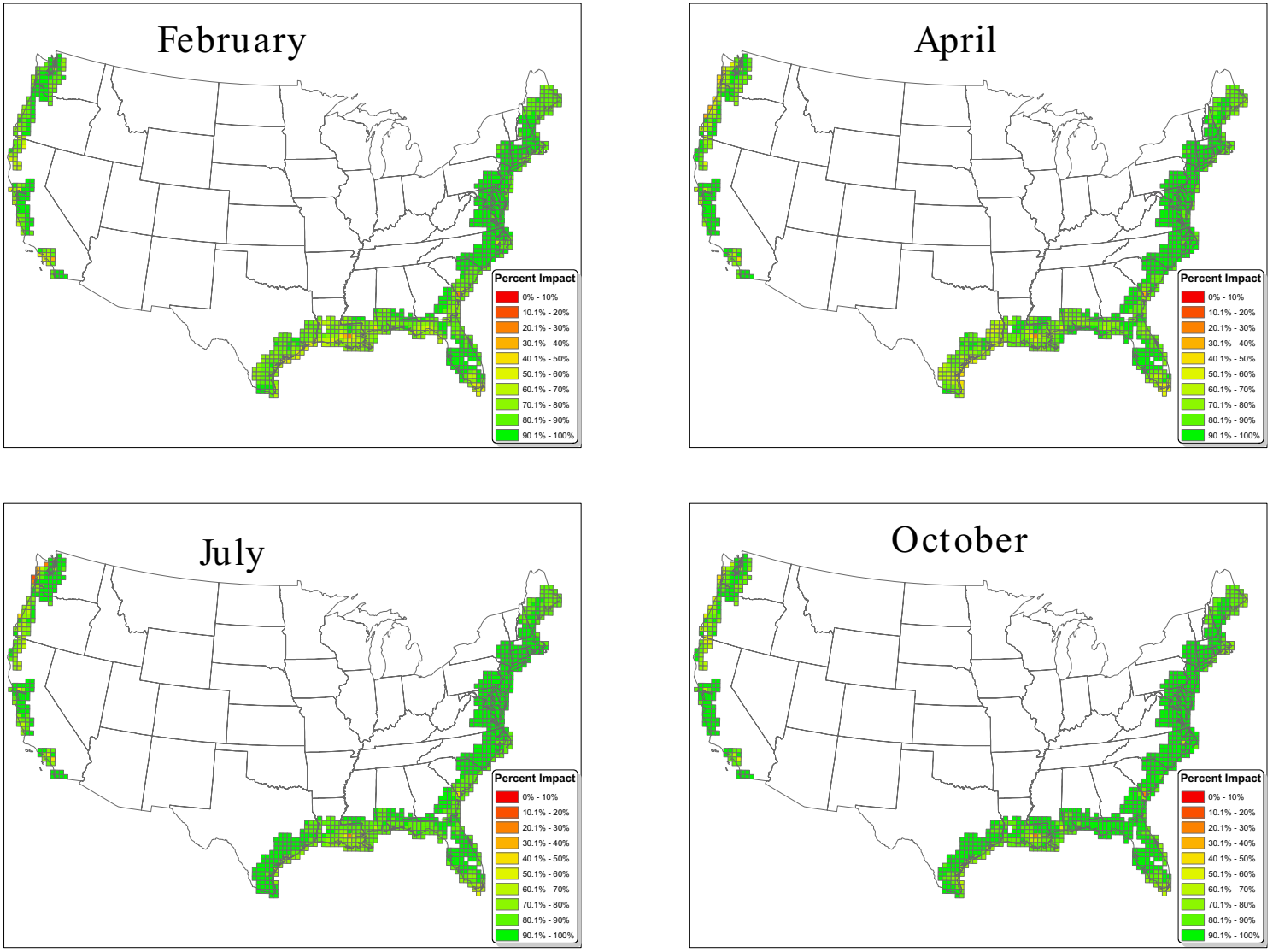


Figure 3.2-76. Percent Impact of NH_3 anthropogenic United States emissions zero-out on reduced nitrogen deposition in the Estuaries Case Study Area.

Over all of the case study areas, domestic, anthropogenic NO_x emissions have significant impacts on total nitrogen deposition and account for almost all of the oxidized nitrogen emissions. As such, standards that focus on NO_x will, in many locations, reduce both oxidized nitrogen deposition and the total nitrogen deposition. The separability between the impacts of NH_3 and NO_x on the different forms of deposition (e.g., NO_x affect mainly oxidized nitrogen deposition, while NH_3 affects mainly reduced nitrogen deposition) indicates the possibility of using forms of the standard that maintain the separation of oxidized and reduced nitrogen. We will continue to refine this analysis in the second draft risk and exposure assessment.

3.2.2.5 Uncertainty

To be drafted

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4. ACIDIFICATION

For this first draft of the Risk and Exposure Assessment document, we are including an outline of the intended content of this chapter for future drafts (see Attachment 1, *Working Outline*). Because the analyses are incomplete at this time, we refer the reader to Attachment 2 (*National Sensitive Areas Analysis*) for a discussion of the approach we are undertaking to identify areas sensitive to acidification caused by nitrogen and sulfur deposition. We have selected case study areas and have begun the analyses for aquatic and terrestrial acidification. Attachment 3 (*Aquatic Acidification Case Study*) and Attachment 4 (*Terrestrial Acidification Case Study*) detail the case study selection rationale, analysis approach, and results to date. At this time, we are requesting review of these four attachments in lieu of a formal Chapter 4.

We recognize that there may be some discrepancies in the use of terms between the case study reports and the risk assessment document. For example, in the case studies, the word "indicator" may reflect a biological, chemical, or ecological indicator, or it may be used to describe the indicator of a standard (typically an atmospheric concentration), whereas in risk assessment's described structure of a secondary standard, we attempt to make careful distinctions between air quality indicators, ecological indicators, and the atmospheric and ecological variables that affect them. In the second draft risk assessment, the results of the case study analyses will be synthesized into a common framework, and we will make the terminology consistent with risk assessment's standard structure.

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5. NUTRIENT ENRICHMENT

For this first draft of the Risk and Exposure Assessment document, we are including an outline of the intended content of Chapter 5 for future drafts (see Attachment 1, *Working Outline*). Because the analyses are incomplete at this time, we refer the reader to Attachment 2 (*National Sensitive Areas Analysis*) for a discussion of the approach we are undertaking to identify areas sensitive to nutrient enrichment caused by nitrogen deposition. We have selected case study areas and have begun the analyses for aquatic and terrestrial nutrient enrichment. Attachment 5 (*Aquatic Nutrient Enrichment Case Study*) and Attachment 6 (*Terrestrial Nutrient Enrichment Case Study*) detail the case study selection rationale, analysis approach, and results to date. At this time, we are requesting review of these four attachments in lieu of a formal Chapter 5.

We recognize that there may be some discrepancies in the use of terms between the case study reports and the risk assessment document. For example, in the case studies, the word "indicator" may reflect a biological, chemical, or ecological indicator, or it may be used to describe the indicator of a standard (typically an atmospheric concentration), whereas in the risk assessment's described structure of a secondary standard, we attempt to make careful distinctions between air quality indicators, ecological indicators, and the atmospheric and ecological variables that affect them. In the second draft risk assessment, the results of these case study analyses will be synthesized into a common framework, and we will make the terminology consistent with the risk assessment's standard structure.

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6. ADDITIONAL EFFECTS

6.1 SULFUR AND MERCURY METHYLATION

The biogeochemical cycle of mercury is closely tied to the sulfur cycle because the presence of sulfate in wetland and lake sediments is necessary for mercury to be incorporated into the food web. Adverse effects of mercury, including behavioral, reproductive, neurochemical, and hormonal effects, have been demonstrated in piscivorous mammals and birds (U.S. EPA, 1996; Scheuhammer et al., 2007), and methylmercury has been shown to be the form of mercury that accumulates in the tissues of fish and piscivorous species (Becker and Bigham, 1995; Bloom, 1992; Harris et al., 2003; Scheuhammer et al., 2007). Sulfate-reducing bacteria (SRB) play a key role in mercury methylation, and changes in sulfate deposition have resulted in changes in both mercury methylation and mercury concentrations in fish.

6.1.1 Science Background

Sulfur deposition likely increases mercury methylation in regions that receive relatively high levels of atmospheric sulfur and mercury deposition and that exhibit characteristics conducive to methylation. These regions include surface waters with low ANC and low pH and with large upstream or adjoining wetlands (Chen et al., 2005; Scheuhammer and Blancher, 1994; Scheuhammer et al., 2007). These sensitive ecosystems are prevalent in areas of the northeastern United States and southeastern Canada. Studies of mercury concentrations in feathers, blood, and eggs of the common loon (*Gavia immer*) indicate decreasing concentrations from west to east in this region (Evers et al., 1998, 2003). This pattern is generally consistent with patterns of deposition of both mercury and sulfur.

Several interrelated factors seem to be related to mercury uptake, 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). In addition, the proportion of upland to wetland land area within a watershed, as well as wetland type and annual water yield, appear to be important (St. Louis et al., 1996).

Mercury in the Environment

Mercury is a naturally occurring element, is very ubiquitous, and cycles through air, water, soils, and living organisms. Mercury concentrations have increased approximately 2 to 5 times since the onset of the industrial revolution and appear in even the most remote locations on the Earth (Munthe et al., 2007; U.S. EPA, 2006). In the northeastern United States, where population growth and industry have heavily influenced the region for a century, mercury concentrations are approximately four- to six-fold higher than in pre-Industrial Revolution times (Evers et al., 2007). Additionally, ecosystems with local emissions sources can exhibit mercury concentrations that exceed 10 times pre-Industrial Revolution levels (Munthe et al., 2007).

In the United States, the primary source of mercury to ecosystems is atmospheric deposition due to coal combustion (e.g., coal-fired electric utilities*)*. Other sources include municipal waste combustion, medical waste incineration, chlor-alkali plants, and industrial boilers. Depending on the particulate association and oxidation state, atmospheric mercury particles can remain suspended in the atmosphere for more than 2 years (Evers et al., 2007; U.S. EPA, 2006).

In the atmosphere, mercury is primarily inorganic. Approximately 95%–97% of atmospheric mercury is elemental mercury (Hg^0) and relatively nonreactive. Hg^0 is the least soluble of the inorganic mercury species and can be transported readily across long distances (Driscoll et al., 2007). Atmospheric transport is most likely the process that is responsible for the presence and accumulation of mercury in remote sites (Watras et al., 2006). Ionic forms of mercury are more soluble, generally react with water particles, and deposit within short ranges of emissions (Driscoll et al., 2007).

Atmospheric mercury deposition occurs by wet deposition, dry deposition, and to a lesser extent, direct stomatal uptake by plants. When deposited into terrestrial and aquatic ecosystems, elemental mercury is oxidized to reactive mercury (Hg^{+2}) (Ambrose et al., 2005; U.S. EPA, 2006). Inorganic mercury species do not directly pose a health threat to humans or animals; however, Hg^{+2} is much more likely to undergo transformation processes (Driscoll et al., 2007). Out of the deposited mercury pool, approximately 1%–2% is reduced and methylated to methylmercury, an organic lipophilic mercury species that is four times more capable of bioaccumulating in the tissues of humans, fish, birds, and other biota than is inorganic mercury

(Benoit et al., 2003; King et al., 2000; U.S. EPA, 2006). **Figure 6.1-1** shows the processes and oxidation states involved in mercury cycling in the environment.

Although it is clear that the primary source of mercury to most of the United States is of atmospheric origin and that mercury must be converted to methylmercury to accumulate to potential risk levels in biotic tissues, the mercury methylation process reflects a wide range of controlling factors that will differ from one part of the country to another. These site-specific factors present complications in extrapolating the findings of existing regionally focused risk assessments to other areas (Driscoll et al., 2007).

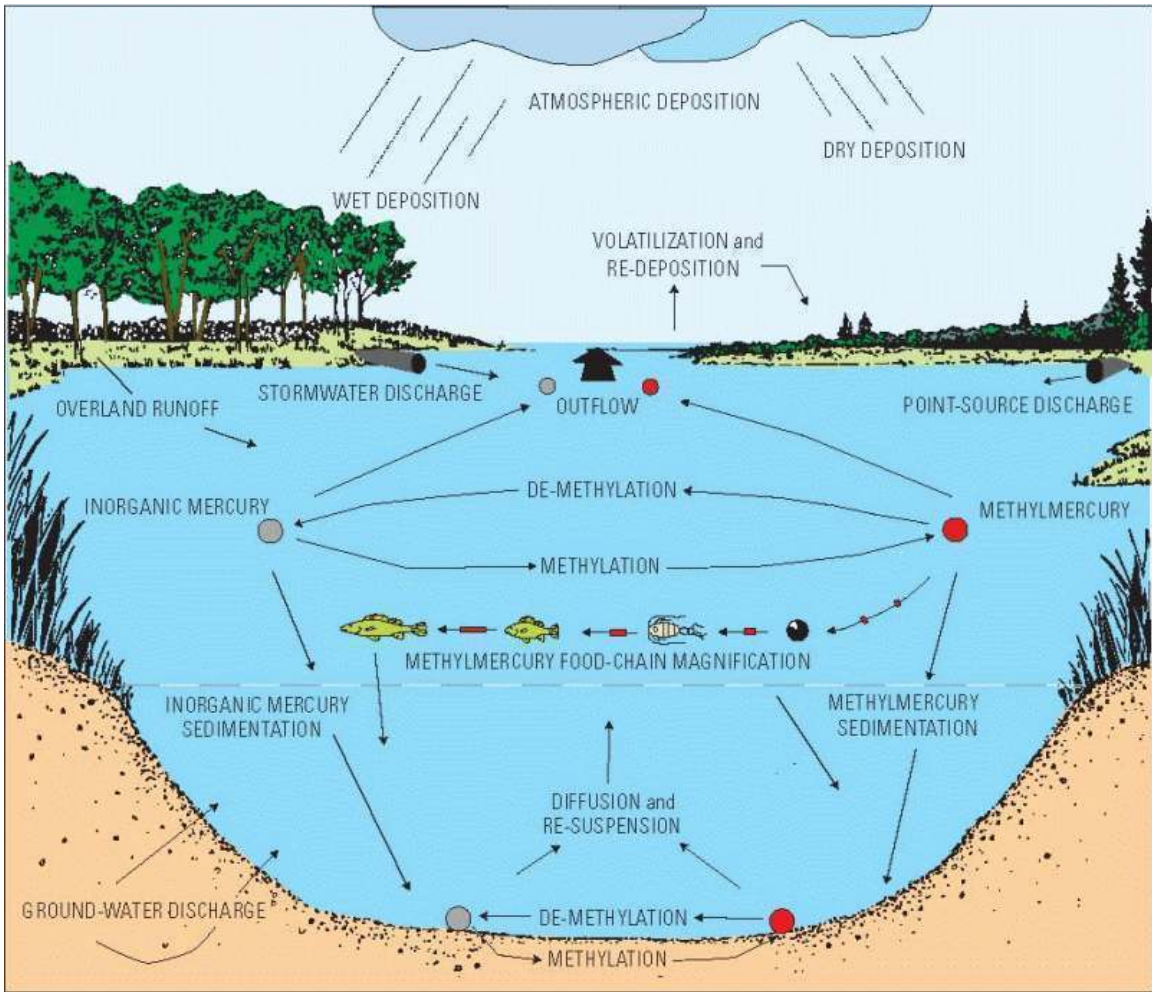

Figure 6.1-1. The mercury cycle in an ecosystem (USGS, 2006).

6.1.2 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 the quantifiable prediction of mercury methylation is confounded by the interdependency of several variables, including the presence and types of SRB, sulfur species, mercury species, organic matter, and others (Benoit et al., 2003; Gilmour et al., 1992; Langer et al., 2001; Munthe et al., 2007; Watras and Morrison, 2008). SRB have been implicated as a significant mercury methylation vector as a by-product of converting sulfate to sulfide (Benoit et al., 2003; Branfireun et al., 1999; Compeau and Bartha, 1985; Gilmour et al., 1992). 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).

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 sulfate to SRB in the presence of methane and Hg^{+2}, usually in low oxygen sediments, leads to the following biomediated transformations:

$$Hg^{+2} \rightarrow HgS \rightarrow MeHg^{+}$$

Methylmercury concentrations are correlated with the amount of mercury in the ecosystem. Therefore, the presence of sulfate, inorganic mercury, and SRB are the primary requirements for the sulfate-reducing, bacterially mediated mercury conversion. Additional factors affecting conversion include 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 limnography, and runoff loading). Demethylation involves aerobic and anaerobic microbial processes, as well as processes involving exposure to sunlight (i.e., photodemethylation); therefore, increased methylation in natural environments should be considered as increased *net* mercury methylation (Benoit et al., 2003).

The role of sulfate in mercury methylation has been confirmed through a series of independent and interdependent studies. Early studies on Little Rock Lake, WI, first observed the link between sulfur enrichment, acidification, and methylmercury concentrations (Hrabik and Watras, 2002). The beneficial effect of decreased sulfate 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%–99% of 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 6.1-2** illustrates the general SRB methylation process.

Although mercury methylation occurs within the water column, there is generally a greater contribution of mercury methylation in sediments because of more concentrated availabilities of SRB, substrate, and sulfate concentration. Therefore, the conditions within and affecting sediment porewaters may collectively 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).

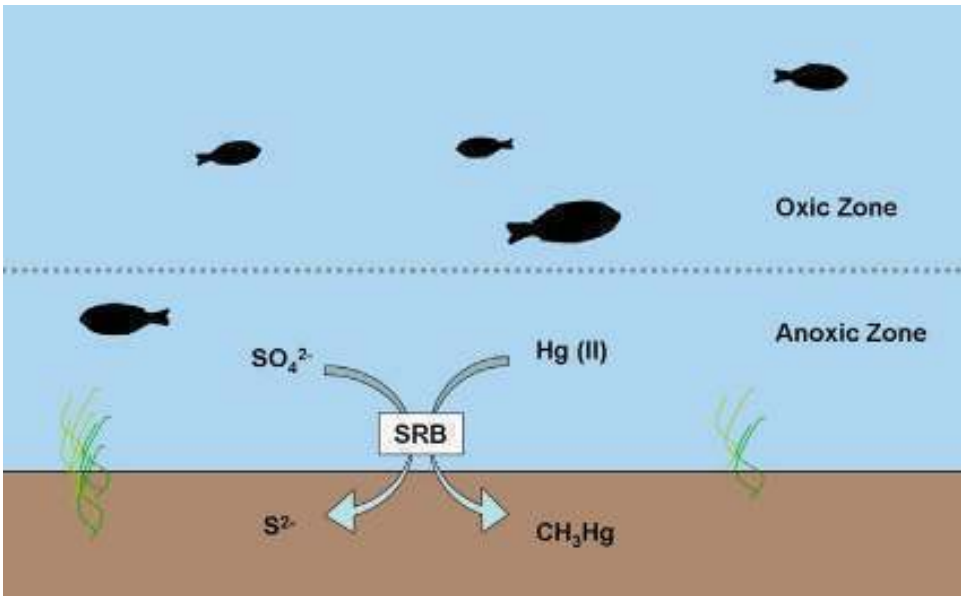

Figure 6.1-2. Biogeochemical process of mercury methylation.

6.1.2.1 Watershed Influences

The effect of watersheds on methylmercury production is dependent on many factors (e.g., dissolved organic carbon, temperature, anoxia, and sulfide); however, watershed influences also include the conditions and processes that impact these effects (e.g., land cover, precipitation response, and limnography). Watershed influences may also play a role in the uptake of methylmercury into fish and other aquatic species.

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 percentages of contributing wetlands 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).

6.1.2.2 Conclusions

There appears to be a relationship between sulfate deposition and mercury methylation; however, the rate of mercury methylation varies according to several factors. Therefore, no quantifiable correlation between sulfate deposition and methylmercury could be discerned for the purpose of interpolating the association across waterbodies or regions. Nevertheless, the association between sulfur and mercury cannot be neglected because of the implications of changes in methylmercury in ecosystems.

The research summarized here is continually evolving and, in the future, could potentially allow for more quantitative statements regarding the generation of methylmercury. As the computational capacity of models expands to meet the complexity of methylmercury in ecosystems, confounding factors may be parsed out to identify ecosystems or regions that are more likely to generate higher concentrations of methylmercury**. Figure 6.1-3** 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 6.1-3 is based on sulfate concentrations, ANC, dissolved organic carbon, pH, mercury species concentration, and soil types to gauge the methylation sensitivity (Myers et al., 2007).

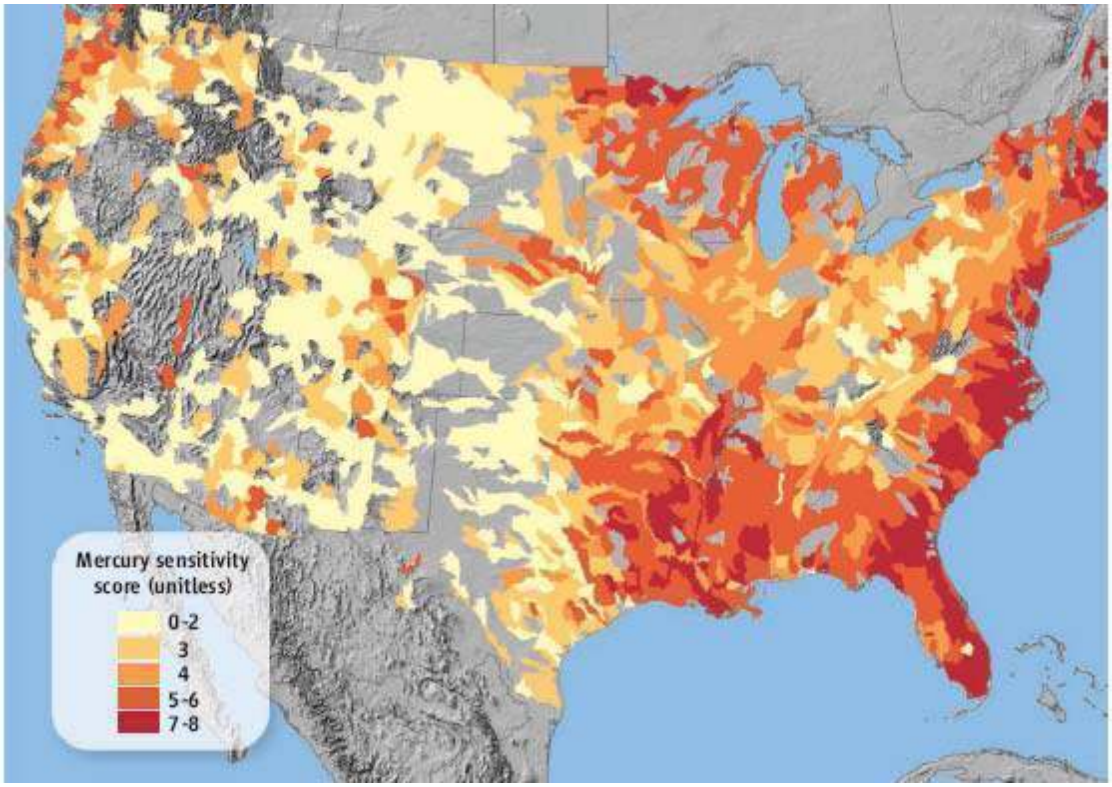

Figure 6.1-3. Preliminary USGS map of mercury methylation-sensitive watersheds, derived from more than 55,000 water-quality sites and 2,500 watershed (Myers et al., 2007).

This discussion highlights the interdependency of biogeochemical factors and precludes the existence of simple sulfate-related mercury-methylation models. However, it is evident that decreases in sulfate deposition will likely result in decreases in methylmercury concentration.

Future research may allow for the quantification of a sulfate-methylmercury response curve; however, no regional or classification calculation scale can be created at this time because of the number of confounding factors. According to the current state of research, associations with mercury methylation occur between the following:

- **Total mercury concentrations.** Mercury loading to ecosystems is required for the production of methylmercury. Increases in mercury concentrations are associated with increases in methylmercury.

- **Sulfate.** The majority of U.S. waters are sulfate-limited (Harmon et al., 2007); therefore, decreases in sulfate are likely to promote decreases in methylmercury.
- **Wetlands.** The presence of wetlands in or upstream of surface water systems is significantly correlated with methylmercury concentrations.
- **Average temperature.** Warmer temperatures stimulate the activity of sulfate-reducing bacteria.
- **Sulfide.** In sulfate-enriched systems, the rate of methylmercury generation may be retarded or inhibited by increased sulfide accumulation.
- **Land, sediment, and water-level disturbance.** Land-use changes, water-level fluctuations, and sediment disturbances can promote unintentional releases or bioavailability of organic matter, sulfate, and mercury.
- **Salinity.** Freshwater systems appear to yield higher percentages of methylmercury than salt waters. However, the importance of methylmercury in coastal and marine systems cannot be discounted because of the human presence in coastal environments and the abundance of fish and shellfish industries that rely on these systems. Also, salt water mercury fish consumption advisories demonstrate that methylmercury production in marine waters is present at levels that may be harmful to humans.

Figure 6.1-4 illustrates the complexity of mercury methylation in ecosystems.

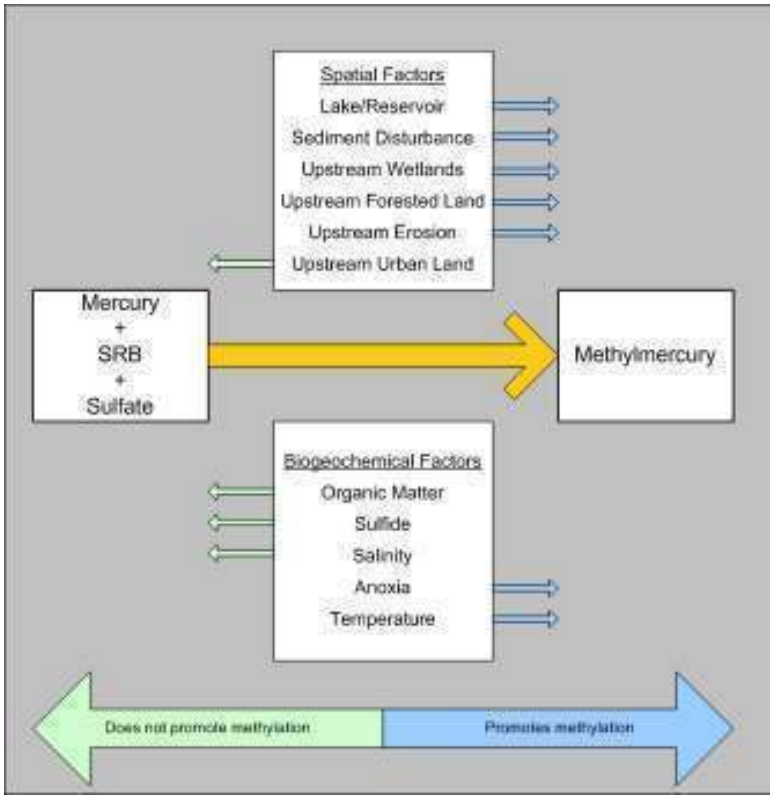

Figure 6.1-4. Spatial and biogeochemical factors influencing methylmercury production.

Management strategies for the reduction of methylmercury production are currently limited to reducing sulfur deposition, reducing mercury deposition, and preventing mercury sink disturbances. The latter strategy is not discussed here because of the lack of an overall ability to control these systems on a regional or federal scale and because it is beyond the scope of a secondary NO_x/SO_x NAAQS review.

Decreases in sulfate emissions have already shown promising reductions in methylmercury. Decreases in methylmercury fish tissue concentrations have been observed in Little Rock Lake, WI, and Isle Royale in Lake Superior, MI, (Hrabik and Watras, 2002; Drevnick et al., 2007). Although the possibility exists that reductions in sulfate emissions could generate a pulse in methylmercury production because of decreased sulfide inhibition in sulfate-saturated waters, the majority of U.S. waters are sulfate-limited (Harmon et al., 2007). Also, because of the diffusion and outward flow of both mercury-sulfide complexes and sulfate, increased mercury methylation downstream may still occur in sulfate-enriched ecosystems with increased organic matter and/or downstream transport capabilities.

Remediation of heavily mercury-contaminated sediments has yielded significant reductions of methylmercury in biotic tissues. Because the biotic responses to methylmercury levels as a result of atmospheric mercury deposition are much lower, direct associations have been confounded by all of the factors discussed here. Current research observations show that percentages of methylmercury and total mercury in ecosystems are positively correlated. If these observations continue to be confirmed, reductions in mercury deposited into ecosystems would 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.

6.2 NITROUS OXIDE (N_2O)

6.2.1 Science Overview

Nitrous oxide has not been considered in setting previous 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 criteria documents. 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 criteria document noted that N_2O may cause a small decrease in stratospheric ozone (U.S. EPA, 1982). Finally, the criteria document concluded that N_2O significantly contributes to the atmospheric greenhouse effect by trapping outgoing terrestrial radiation, and that the issue was being investigated, but that many years of research were still needed to reliably assess the issue. In 1993, the criteria document again identified N_2O as an oxidized nitrogen compound that is not generally considered to be an air pollutant, but does have an impact on stratospheric ozone and is considered to be among the more significant greenhouse gases (GHGs). These documents clearly considered N_2O to be within the scope of the listed nitrogen oxides' criteria for pollutants.

The second draft ISA acknowledges N_2O as a potent GHG and discusses N_2O sources and emissions in the United States, as well as the biogeochemistry of its microbial-mediated production via denitrification in natural ecosystems (U.S. EPA, 2008; Section 3.3). Based on the current U.S. Greenhouse Gas (GHG) Inventory (U.S. EPA, 2007), N_2O contributes approximately 6.5 % to total GHG emissions (in CO_2 equivalents) (**Figure 6.2-1**).

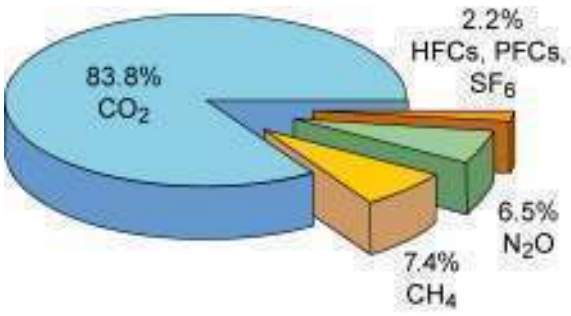

Figure 6.2-1. Percent of total U.S. emissions of greenhouse gases in CO_2 equivalents (U.S. EPA, 2007).

Since the definition of "welfare effects" includes effects on climate [CAA Section 302(h)], we will include N_2O 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.

Integrated Science Assessment Summary

Nitrous oxide is a GHG that contributes to global warming. Although the atmospheric concentration of N_2O (319 ppb) is much lower than CO_2 (379 ppm), its global warming potential is 296 times that of CO_2. Human activities have increased the atmospheric concentration of N_2O by 18% since preindustrial times (IPCC, 2007). The continuing increase of those GHG concentrations has been shown to threaten human and ecosystem health.

Anthropogenic nitrogen deposition to ecosystems not only changes the global nitrogen cycle, it also has profound impacts on biogeochemical processes associated with GHG emissions (Bodelier and Laanbroek, 2004; Dalal et al., 2003; Vitousek et al., 1997). The impacts of nitrogen addition on N_2O emissions were reviewed and quantitatively synthesized by meta-analysis in the ISA. The publications included in this meta-analysis are in Annex D of the draft ISA (U.S. EPA, 2008).

Biogenic sources are the dominating 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 the total N_2O production varies with environmental conditions. Denitrifying bacteria reduce nitrate (NO_3^-) or nitrite (NO_2^{-}) into N_2O or N_2 under anaerobic conditions. In submerged soils, such as wetland soil,

denitrification should be the dominant process to N_2O emission (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 N_2O reducing 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 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 Caluwe 1999; Aerts and Toet 1997; Keller et al., 2005).

The meta-analysis on the effects of nitrogen addition on N_2O emissions from non-agricultural ecosystems includes 99 observations from 30 publications (U.S. EPA, 2008). Nitrogen addition normally enhanced N_2O emissions, with some exceptions (Ambus et al., 2006; Ambus and Robertson, 2006; Borken et al., 2002; Curtis et al., 2006; Skiba et al., 1999). Although some natural ecosystems can be a N_2O sink (Chapuis-Lardy et al., 2007), very limited publications assessed the impact of nitrogen addition on N_2O uptake. Thus, only changes in N_2O production were estimated in this meta-analysis. Overall, the results of the meta-analysis indicated that nitrogen addition increased N_2O emissions by 215%. The response of N_2O emissions was influenced by ecosystem type and the form and amount of nitrogen addition.

Compared to other ecosystems, tropical forests emitted more N_2O under nitrogen enrichment conditions (+735%). This greater response may be because tropical forests are often phosphorus-limited rather than nitrogen-limited (IPCC, 2001). However, climatic conditions, especially temperature and precipitation, could also be key factors to drive N_2O emissions from tropical forest ecosystems.

Nitrate caused a higher stimulation (+494%) on N_2O emission than did NH_4^+ (+95%). By adding radiolabeled nitrogen-15 (^{15}N), labeled NO_3^- and NH_4^+ to soil, Russow and colleagues (2008) found that N_2O was mainly emitted by denitrification, and the contribution of denitrification to the total N_2O production increased from 54% in soil with normal soil organic matter (SOM) content to 76% in soil with high SOM content.

The ISA concludes that the reviewed evidence is *sufficient to infer a causal relationship* between reactive nitrogen deposition and the alteration of biogeochemical flux of N_2O in terrestrial ecosystems (U.S. EPA, 2008). Overall, the results of the meta-analysis discussed in Section 3.3.4 of the ISA indicated that nitrogen addition increased N_2O emissions by 215%. The

response of N_2O emission to nitrogen addition for coniferous forests, deciduous forests, and grasslands was significant. The ISA also concluded that the evidence reviewed was *sufficient to infer a causal relationship* between reactive nitrogen deposition and the alteration of N_2O flux in wetland ecosystems. In the meta-analysis of 19 observations from studies that evaluated the effects of nitrogen additions ranging from 15.4 to 300 kg N ha^{-1} yr^{-1}, nitrogen addition was shown to increase the production of N_2O by 207% (U.S. EPA, 2008)

6.2.2 Qualitative Analysis

The analysis of risk to public welfare from the increased generation of N_2O as a GHG is beyond the scope of this first draft risk and exposure assessment. A more complete analysis of the effects of increasing GHGs on public welfare should include N_2O as one of a suite of gases that affect global warming trends and would require a much broader treatment than could be given in the scope of this review. The EPA recently released an Advance Notice of Public Rulemaking on Regulating Greenhouse Gas Emissions under the Clean Air Act (http://www.epa.gov/ climatechange/emissions/downloads/ANPRPreamble.pdf), which discusses these effects in more detail.

6.3 CARBON SEQUESTRATION

This section discusses the mechanisms by which atmospheric nitrogen deposition alters carbon cycling in terrestrial and aquatic ecosystems. The interactions between increased nitrogen deposition and carbon sequestration in terrestrial and aquatic ecosystems are summarized in Sections 6.3.1 and 6.3.2. Although predicted values of atmospheric CO_2 concentrations in the future may alter the interaction between nitrogen and carbon cycling, further analysis on this topic is beyond the scope of this review.

6.3.1 Terrestrial Ecosystems

Because nitrogen availability often limits rates of net primary production in terrestrial ecosystems (Vitousek and Howarth, 1991), there is an implicit link between the carbon and nitrogen cycles (**Figure 6.3-1**). More than 50% of plant nitrogen is used for photosynthetic enzymes. Because nitrogen is necessary for photosynthesis, rates of photosynthesis and net primary productivity (NPP) typically correlate with metrics of nitrogen availability, such as leaf

nitrogen content and net nitrogen mineralization rate (Field and Mooney, 1986; Reich et al., 1997a, b; Smith et al., 2002).

Few studies have isolated the effect of chronic nitrogen deposition on plant growth and ecosystem carbon balances. It is difficult to untangle the effects of climate, disease, and land use from nitrogen deposition effects. Therefore, to address this question, we rely on fertilization studies, modeling, gradient studies, and time-trend analyses.

Carbon accumulation in terrestrial ecosystems occurs in the plants and in the soil. Carbon cycling is a complex process that can be quantified into ecosystem carbon budgets on the basis of net ecosystem productivity (NEP), defined as gross primary productivity (GPP) after subtracting the ecosystem respiration (i.e., vegetative + heterotrophic respiration). Factors that may increase terrestrial CO_2 sinks on a regional scale are increased NPP and decreased respiration of CO_2 from leaf or soil processes. These two mechanisms may be altered by atmospheric deposition of nitrogen, tropospheric ozone exposure, increased CO_2 concentrations, land-use change, and factors associated with climate warming (Beedlow et al., 2004; Melillo et al., 2002; Myneni et al., 1997; Schimel et al., 2001). This adds to the uncertainty regarding the sources and sinks of CO_2 in the terrestrial biosphere (Houghton, 2003). It should be noted that it is not known whether present terrestrial carbon sequestration can be sustained in view of limits of forest regrowth, nutrient availability, and uncertainty about changes in the frequency of disturbances such as fire (Schimel et al., 2001; Scholes and Noble, 2001).

6.3.1.1 Forests

Aboveground Processes

There is substantial evidence that nitrogen additions to trees cause increased leaf-level photosynthetic rates. However, the ISA (U.S. EPA, 2008) evaluated the potential for nitrogen deposition to increase aboveground carbon biomass and concluded that it is limited for reasons related to the biogeochemical cycling of nitrogen.

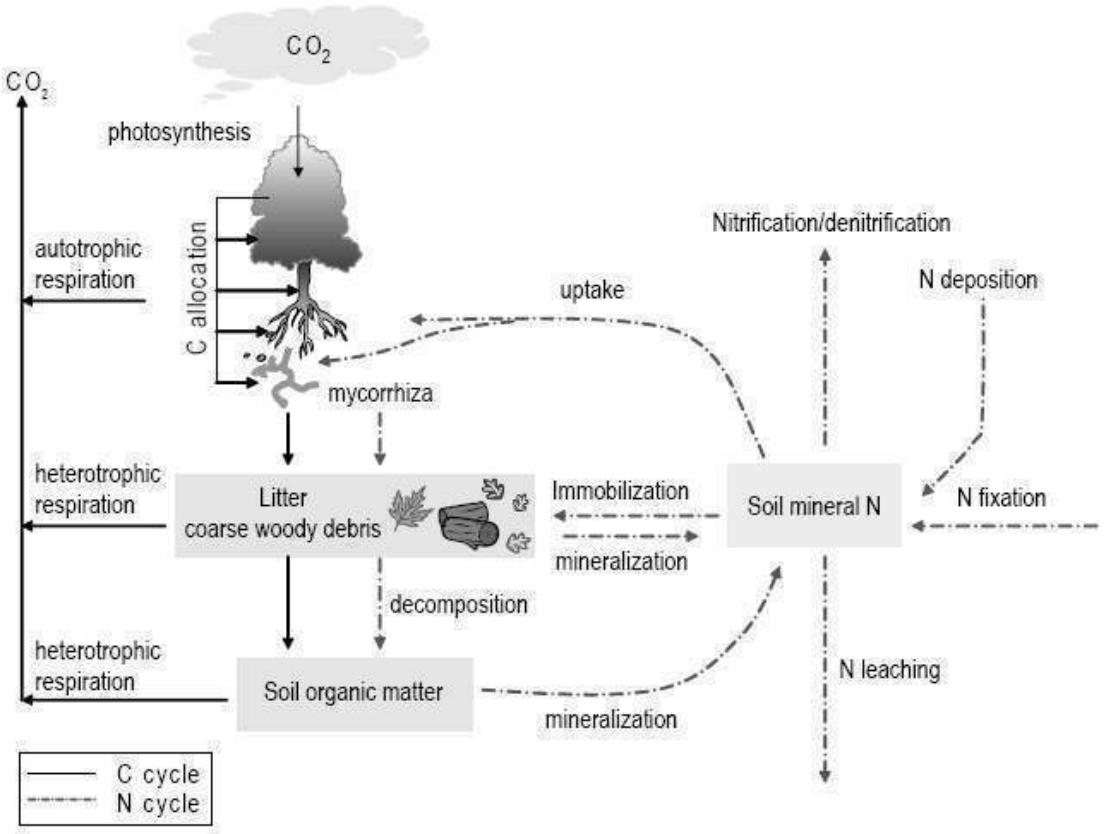

Figure 6.3-1. Interactions between the carbon and nitrogen cycles.

Forest growth enhancement, to the extent that it occurs, can potentially exacerbate other nutrient deficiencies, such as calcium, magnesium, or potassium. Multiple long-term 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 et al., 2004; McNulty et al., 2005).

Decreased growth and increased mortality have more commonly been observed in high-elevation coniferous stands than in lower-elevation hardwood forests, and these differences have been partially attributed to higher inputs of nitrogen at higher elevations and to response characteristics of coniferous, as opposed to deciduous, trees (Aber et al., 1998). Conifer forests that receive high inputs of reactive nitrogen appear to exhibit decreases in productivity and increases in mortality (Fenn et al., 1998). For example, fertilization experiments at Mount Ascutney, VT, suggested that nitrogen saturation may lead 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).

Belowground Processes

Soils contain the largest near-surface reservoir of terrestrial carbon; more than 50% of carbon captured annually by plants may be allocated below ground (Kubiske and Godbold, 2001). Although there remains considerable uncertainty in the potential response of soil carbon to increases in reactive nitrogen additions (Neff et al., 2002), a meta-analysis by Johnson and Curtis (2001) suggested that nitrogen fertilization caused an 18% increase in soil carbon content.

There is also evidence of a relationship between nitrogen deposition and root production. Nadelhoffer (2000) argued that it is likely that nitrogen deposition functions to decrease forest fine-root biomass, but to stimulate fine-root turnover and production. However, very high levels of nitrogen (>100 kg N ha^{-1} yr^{-1}) decreased root life span of *Pinus ponderosa* (Johnson et al., 2000).

Litterfall is usually the dominant source of soil organic carbon and a substantial source of organic nitrogen. Decomposition of litterfall is often facilitated by heterotrophic bacteria and mycorrhizae. The quantity of litter has been shown to increase with elevated nitrogen deposition (Schulze et al., 2000), resulting in increased microbial metabolism in soil. It is also well demonstrated that increased nitrogen availability reduces the ratio of carbon to nitrogen in leaf tissue. In turn, a lower carbon-to-nitrogen ratio in leaf litter has been shown to cause faster initial rates of decomposition (Melillo et al., 1982); however, the biochemistry of the leaf tissue is also important, and higher nitrogen litter can actually decompose more slowly in the long term (Berg, 2000).

Soil respiration is the dominant source by which plant-assimilated carbon is returned to the atmosphere via CO_2. Changes in the magnitude of soil CO_2 efflux due to changes in environmental conditions will likely influence the global atmospheric CO_2 budget (Schlesinger and Andrews, 2000). The effects of nitrogen addition on soil respiration are mixed. In the Harvard Forest Long Term Ecological Monitoring and Research (LTER) Site Chronic Nitrogen Amendment Study, nitrogen additions increased soil respiration for a hardwood stand, but not for a pine stand, during the first year of fertilization. However, continued nitrogen additions over a decade caused a 40% decrease in soil respiration for both stands, and this decrease was attributed mostly to a decrease in microbial respiration (Bowden et al., 2004).

Regional Trends in Net Ecosystem Productivity

Analyses of satellite observations of canopy greenness over the past 20 years across North America suggest enhancement of net ecosystem productivity in some regions, corresponding to observed changes in climate and forest management. Few such changes were observed in the northeastern United States (Hicke et al., 2002). In another study, evaluation of tree growth rates in five states (i.e., Minnesota, Michigan, Virginia, North Carolina, and Florida) found little evidence for growth enhancement due to any factor examined, including nitrogen deposition, CO_2 fertilization, or climate change (Caspersen et al., 2000). Potential effects of nitrogen deposition on boreal forests of North America are of concern, in part because of the large size of this terrestrial biome. Climate warming and nitrogen deposition may increase net primary productivity and carbon sequestration in the boreal forest, but they may also stimulate decomposition of soil organic matter, potentially leading to a net loss of carbon from the ecosystem (Kirschbaum, 1994; Mäkipää et al., 1999).

6.3.1.2 Arctic Tundra

In a long-term fertilization experiment (Mack et al., 2004), plots were fertilized from 1981 to 2000 to receive approximately 5 to 8 times the annual soil nitrogen uptake requirement for aboveground production in the arctic tundra ecosystem. Carbon storage increased above ground because of the accumulation of woody shrub biomass and litter, but this was offset by a larger decrease of carbon in belowground pools because of a pronounced decrease in the carbon contained in deep organic (>5 cm depth) and upper mineral soil layers (Shaver et al., 2001). This study clearly showed that increased nutrient availability enhanced decomposition of belowground carbon pools in deep soil layers more than it increased primary production, leading to a substantial net loss of carbon from this ecosystem.

Increasing temperatures may amplify these effects and further stimulate carbon losses from high-latitude systems, causing species shifts in the vegetation community, from tussock to increased shrub abundance, and leading to decreased ecosystem carbon storage. Finally, the decreased soil moisture and increased depth of thaw with temperature rise are predicted to have a positive effect on decomposition (Shaver et al., 2001), releasing more CO_2.

6.3.1.3 Grasslands

Belowground Factors

An investigation by Neff and colleagues (2002) of long-term effects (10 years) of nitrogen deposition (10 kg N ha^{-1} yr^{-1}) in a dry meadow ecosystem indicated that nitrogen additions significantly accelerated the decomposition of soil carbon fractions with decadal turnover times while further stabilizing soil carbon compounds in mineral-associated fractions with multi-decadal to century lifetimes. Despite these changes in the dynamics of different soil pools, no significant changes in bulk soil carbon were observed, highlighting a limitation of the single-pool approach for investigating soil carbon responses to changing environmental conditions (Neff et al., 2002). The authors noted that it remains to be seen if the effects that were caused by relatively high, decadal-term fertilizer additions are similar to those that would arise from lower, longer-term additions of nitrogen to natural ecosystems from atmospheric deposition.

Interactions with Fire

Several lines of evidence suggest that reactive nitrogen deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of ecosystem types (Fenn et al., 2003). Invasive grasses, which can be favored by high nitrogen deposition, promote a rapid fire cycle in many locations (D'Antonio and Vitousek, 1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of CSS to grassland in California (Minnich and Dezzani, 1998).

High grass biomass has also been associated with increased fire frequency in the Mohave Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). Fire was relatively rare in the Mojave Desert until the past two decades, but now occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

6.3.2 Aquatic Ecosystems

6.3.2.1 Wetlands

Aboveground Processes

In a literature summary, U.S. EPA (1993) showed that nitrogen applications, ranging from 7 to 3120 kg N $ha^{-1}yr^{-1}$, stimulated standing biomass production by 6%–413%. However, the magnitude of the changes in primary production depended on soil nitrogen availability and the limitation of other nutrients. The degree of nitrogen limitation to growth varies among wetlands across the United States (Bedford, 1999).

Although studies applying fertilizer treatment increase the primary production of plant species in intertidal wetlands, applications are several orders of magnitude larger than atmospheric deposition (Mendelssohn, 1979; Wigand et al., 2003). In comparison, nitrogen loads brought by tidal water and groundwater (565-668 kg N $ha^{-1}yr^{-1}$) are much larger than nitrogen depositing directly to the surface of coastal marshes, which suggests that direct nitrogen deposition may have limited impacts on this ecosystem (Morris, 1991). On the other hand, indirect atmospheric deposition that is nitrogen deposited to the watershed and transported via surface or groundwater could be the major source of the total nitrogen load to coastal marshes. For example, model calculation in Chesapeake Bay waters (U.S. EPA, 2000) suggests that 30% of the nitrogen delivered to wetlands via estuarine tides would originate from atmospheric deposition.

Belowground Processes

Bragazza and colleagues (2006) found that enhanced decomposition rates for material accumulated under higher atmospheric nitrogen supplies resulted in higher CO_2 emissions and dissolved organic carbon releases. The increased nitrogen availability favored microbial decomposition (1) by removing nitrogen constraints on microbial metabolism and (2) through a chemical amelioration of litter peat quality with a positive feedback on microbial enzymatic activity. Although some uncertainty remains about whether decay-resistant Sphagnum will continue to dominate litter peat, the data indicated that even without such changes, increased nitrogen deposition poses a serious risk to the valuable peatland carbon sinks.

Reduced vs. Oxidized Nitrogen

The form of added nitrogen may regulate wetland response to nitrogen deposition. Experimental applications of nitrate (i.e., oxidized nitrogen) appear to have been less effective at stimulating wetland plant productivity than applications of ammonium ion (i.e., reduced nitrogen) (U.S. EPA, 1993). However, an important caveat expressed by U.S. EPA (1993) was that the results of relatively short-term nitrogen fertilization experiments are not necessarily good predictors of long-term wetland community responses to increased nitrogen inputs.

6.3.2.2 Freshwater Aquatic Ecosystems

The biogeochemical cycles of nitrogen, phosphorus, and carbon are linked in freshwater ecosystems (**Figure 6.3-2**); therefore, nitrogen additions alter the balance of all three cycles. In nitrogen-limited aquatic systems, atmospheric inputs of nitrogen increase productivity and alter biological communities, especially phytoplankton.

Nitrogen Limitation

A freshwater lake or stream must be nitrogen-limited in order to be sensitive to nitrogen-mediated eutrophication. Recently, a comprehensive study of available data from the northern hemisphere surveys of lakes along gradients of nitrogen deposition shows increased inorganic nitrogen concentration and productivity to be correlated with atmospheric nitrogen deposition (Bergström and Jansson, 2006). These authors suggested that the majority of lakes in the northern hemisphere may have originally been nitrogen-limited, and that atmospheric nitrogen deposition has changed the balance of nitrogen and phosphorus in lakes so that phosphorus limitation is generally observed today. If this is correct, the role of atmospheric nitrogen deposition as an influence on aquatic primary production may have been underestimated throughout the entire history of limnology.

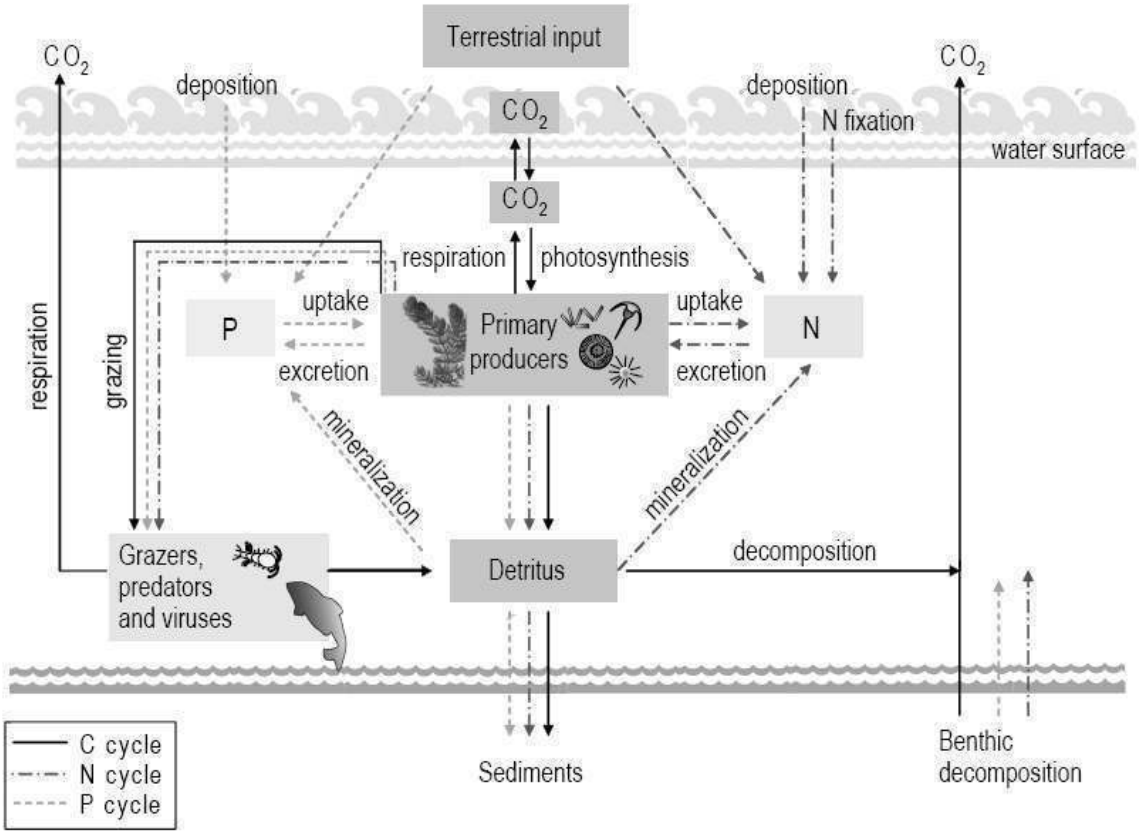

Figure 6.3-2. Nitrogen cycle in a freshwater ecosystem showing links to the phosphorous and carbon cycles.

Productivity investigations have included gradient studies in which the relationship between lake nitrogen concentration and primary productivity (reported as chlorophyll *a*, net primary productivity, or an index such as the lake chemistry ratio of dissolved inorganic nitrogen [DIN] to total phosphorus [TP] [DIN:TP]) was surveyed and correlated with atmospheric nitrogen deposition. Productivity studies have also included lake and stream bioassays in which nitrogen was added to waters in the field or the laboratory to measure the response. The most common, and easiest to document, indicators of change in algal productivity are measures of the concentration of chlorophyll *a* and water clarity. However, water clarity is also strongly influenced by the erosion of fine sediment to the lake or stream system. Chlorophyll *a* concentration is generally more directly tied to algal productivity than is water clarity.

Phytoplankton Biomass

Studies have shown an increase in lake phytoplankton biomass with increasing nitrogen deposition in several regions, including the Snowy Range in Wyoming (Lafrancois

et al., 2003), the Sierra Nevada Mountains in California (Sickman et al., 2003), and across Europe (Bergström and Jansson, 2006). Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric nitrogen deposition found strong relationships between nitrogen limitation and productivity where nitrogen deposition was low, and between phosphorus and nitrogen and phosphorus limitations where nitrogen deposition was higher (Bergström et al., 2005; Bergström and Jansson, 2006; Fenn et al., 2003).

A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America, including many of the studies described above, found algal growth enhancement from nitrogen amendments to be common in slightly less than half the studies (Elser et al., 1990). There was a mean increase in phytoplankton biomass of 79% in response to nitrogen enrichment (average of 46.3 $\mu eq\ L^{-1}$ N) (Elser et al., 1990). This meta-analysis was recently repeated with a much larger data set and similar results (Elser et al., 2007).

The most widely used index of biological change in response to nutrient addition is the measurement of chlorophyll *a* concentration in water. Surveys and fertilization experiments show increased inorganic nitrogen concentration and aquatic ecosystem productivity (as indicated by chlorophyll *a* concentration) to be strongly related.

The ISA (U.S. EPA, 2008) provides a broad summary on the interaction between nitrogen deposition and carbon sequestration.

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7. SYNTHESIS AND INTEGRATION OF CASE STUDY RESULTS TO INFLUENCE THE STANDARD SETTING PROCESS

This chapter is currently unavailable for release to CASAC and the public. We anticipate the release of this chapter on or about the week of September 15, 2008.

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8. CONSIDERATIONS IN THE STRUCTURE OF THE NO_X/SO_X SECONDARY STANDARD(S)

This chapter is currently unavailable for release to CASAC and the public. We anticipate the release of this chapter on or about the week of September 15, 2008.

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9. ANALYSES FOR SECOND DRAFT RISK ASSESSMENT

This first draft risk and exposure assessment for the secondary NAAQS review of NO_x and SO_x has focused on assessing the current conditions for the four targeted effect areas since the scope and methods plan was reviewed by CASAC in April 2008. For the second draft risk and exposure assessment, we plan to complete and update the current conditions assessments, as well as scale up to larger assessment areas where feasible. The following list previews our current plans for the second draft risk and exposure assessment, organized as currently presented in this document.

- Chapter 3: Sources Ambient Concentrations and Deposition
  - Add 2002–2006 CMAQ model year run to analyses to examine variability in meteorology relative to concentrations —creating dataset for Case Study Analyses
  - Create hybrid data set of 2002–2006 CMAQ/NADP data for case study modeling and scaling to larger assessment areas
  - Model 5 years of meteorology with one year of emissions to look year to year at meteorological effects on deposition
- Chapter 4 : Acidification
  - Use 2002–2006 CMAQ data set for modeling analysis
  - Scaling up to larger assessment areas: more Adirondack lakes and Shenandoah waterbodies
  - Methods for the Risk Assessment
    - Risk Modeling with MAGIC
    - Model Parameters for evaluating risk
  - Results
    - Adirondack - uncertainty
    - Shenandoah - uncertainty
  - Characterization of Risks Associated with Alternative Levels of Protection
  - Scaling up to Larger Assessment Areas
  - Uncertainty for Larger Assessment Areas

1 – Present Terrestrial Acidification Case Study results from Simple Mass Balance
2 Modeling expressed as base cation to Aluminum ratio and binning to soil ANC values
3 (to provide a range of critical limits)

4 ▪ Chapter 5 : Nutrient Enrichment

5 – Using 2002–2006 CMAQ data set for modeling analysis

6 – Scaling up to larger assessment areas

7 – Characterization of risks

8 ▪ Chapter 6 : Additional Effects

9 – Further evaluation as needed based on CASAC consultation

10

ATTACHMENT 1

WORKING OUTLINE

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August 15, 2008

Risk and Exposure Assessment to Support the Joint Review of the NO_2 and SO_2 Secondary National Ambient Air Quality Standards: Preliminary Draft

Working Outline

Draft

EPA Contract Number EP-D-06-003
Work Assignment 2-44
Project Number 0209897.002.044

Prepared for

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27709

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Risk and Exposure Assessment to Support the Joint Review of the NO_2 and SO_2 Secondary National Ambient Air Quality Standards: Preliminary Draft

1. Introduction
   - 1.1. Rationale for Background for Joint Review
   - 1.2. Policy-Relevant Questions
   - 1.3. History
     - 1.3.1 History of the Secondary NO_2 NAAQS
     - 1.3.2 History of the Secondary SO_2 NAAQS
     - 1.3.3 Conclusions from Previous NAAQS Reviews and alternative assessments (e.g. NAPAP, ADSFS, etc).
   - 1.4. Scope of the Risk and Exposure Assessment for the Current Review
     - 1.4.1 Species of Nitrogen Included in the Analyses
     - 1.4.2 Species of Sulfur Included in the Analyses
     - 1.4.3 Science Overview

2. Overview of Risk and Exposure Assessment
   - 2.1. Introduction
   - 2.2. Seven Step Approach
   - 2.3. Ecosystem Services
   - 2.4. Uncertainty

3. Sources, Ambient Concentrations and Deposition
   - 3.1. Science Overview
     - 3.1.1. Sources of Nitrogen and Sulfur (emissions)
     - 3.1.2. Ambient Concentrations and Policy Relevant Background
     - 3.1.3. Non-ambient Loadings of Nitrogen and Sulfur
     - 3.1.4. Deposition (CMAQ/NADP maps)
   - 3.2. Current Contributions to Ambient Conditions
     - 3.2.1. Spatial and Temporal Characterization of Ambient Concentrations and Deposition
       - 3.2.1.1. Purpose and Intent
       - 3.2.1.2. Data and Tools
       - 3.2.1.3. Analytical Techniques
       - 3.2.1.4. Results and Findings
       - 3.2.1.5. Uncertainty
     - 3.2.2. Contributions to Ambient Concentrations and Deposition
       - 3.2.2.1. Purpose and Intent
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ATTACHMENT 2

NATIONAL SENSITIVE AREAS ANALYSIS

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August 15, 2008

National Sensitive Areas Analysis

Draft

EPA Contract Number EP-D-06-003
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Prepared for

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ACRONYMS AND ABBREVIATIONS

cm	centimeters
CMAQ	Community Multiscale Air Quality
GIS	geographic information systems
Km	kilometer
NADP	National Atmospheric Deposition Program
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
FIA	Forest Inventory and Analysis National Program
EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Service
SO_4^{-2}	wet sulfate

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1. OBJECTIVE

The objective of this analysis is to define geographical areas sensitive to aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, and terrestrial nutrient enrichment. The first step in this process is to identify national geospatial datasets (or geographic information systems [GIS] layers) that contain measures of parameters that are known to affect any of these ecosystems. Each layer will play a role to a varying degree; not all layers contribute equally to ecosystem sensitivity. Each layer that makes a contribution must be classified so that categories of varying degrees of sensitivity can be created. These categories can either be defined by a simple threshold value (i.e., above or below which an area is sensitive), or by several values of increasing or decreasing sensitivity. When the layers are combined in a GIS system, the geographic areas that exceed the threshold values in each of the layers can be identified. This would yield the areas of highest potential sensitivity.

2. SELECTION OF GEOSPATIAL DATASETS

There are several broad criteria for selecting appropriate geospatial datasets, including the following:

- **Physical characteristics.** Physical characteristics are those that pertain to the physical environment of a given location (e.g., elevation, soil depth).
- **Chemical characteristics.** Chemical characteristics are those that pertain to the underlying chemical characteristics of the water or soil (e.g., soil pH).
- **Presence of sensitive receptors.** Overall sensitivity can be increased if there are biotas that are either known to be or depend on plant communities that are sensitive to acidification or nutrient enrichment.
- **Spatial resolution.** At a national scale of study, most, if not all, datasets will have an acceptable spatial resolution. The data will not be too coarse to show regional variation. Care must be used when combining data with different spatial resolutions (i.e., combining data designed to be used on a national scale with data designed to be used on a county scale) because the resultant data will only be as accurate as the least accurate of the inputs.

- **Spatial extent.** The goal of this analysis is to use data that geographically cover the entire continental United States. Where data only exists on a regional level, they may be considered if they can still represent the range of sensitivities.
- **Temporal resolution.** Every effort will be made to use data collected during the same general time period and, preferably as recently as possible, to reflect current conditions.
- **Completeness of metadata.** Only data with well-documented origins and collection techniques will be considered for inclusion in any analysis.

3. SENSITIVITY TO AQUATIC ACIDIFICATION

3.1 SELECTED INDICATOR GEOSPATIAL DATASETS

The publicly available geospatial datasets outlined in the following subsections have been identified as important contributors to aquatic acidification and meet the selection criteria.

3.1.1 Slope

- **Name:** Grayscale North America Shaded Relief
- **Contribution:** Streams or rivers tend to be more sensitive is to acidification in areas of steeper slopes because base cations are leached from soils and washed downstream.
- **Source:** U.S. Geological Service (USGS) National Atlas
- **Date:** September 2006
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** 1 kilometer (km) grid cells
- **Threshold Value(s):** 3%

3.1.2 Soil pH

- **Name:** Statsgo (Conus soils)
- **Contribution:** Areas that have low soil pH tend to also have low surface water pH.
- **Source:** Penn State University
- **Date:** 1998
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Soil unit (variable size)
- **Threshold Value(s):** pH less than or equal to 5.0

3.1.3 Soil pH

- **Name:** U.S. Forest Service Soils Survey
- **Contribution:** Areas that have low soil pH tend to also have low surface water pH.
- **Source:** U.S. Department of Agriculture (USDA) Forest Service (USFS), Forest Inventory and Analysis National Program (FIA)
- **Date:** 2001–2003
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Forest plot
- **Threshold Value(s):** pH less than or equal to 5.0

3.1.4 Soil Depth

- **Name:** Statsgo (Conus soils)
- **Contribution:** Areas that have thin soils tend to also have low surface water pH
- **Source:** Penn State University
- **Date:** 1998
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Soil unit (variable size)
- **Threshold Value(s):** Soil depth was divided into four quartiles, and the areas with the lowest soil depth (bottom quartile) were identified. The value defining the break point between the first and second quartiles was 51 inches in total depth.

3.1.5 Surface Water Alkalinity

- **Name:** Alkus
- **Contribution:** Classifies the continental United States into categories of acid neutralizing capacity (μeq/l). Areas with lowest acid neutralizing capacity are most sensitive to acidification.
- **Source:** U.S. Environmental Protection Agency (EPA), Office of Research and Development, Corvallis, OR
- **Date:** Pre-1992
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Unknown
- **Threshold Value(s):** 400 μeq/l or less are considered acid sensitive.

3.1.6 Geology

- **Name:** Karst
- **Contribution:** Karst topography is comprised of carbonate rocks, such as limestone and dolomite, which have a high ANC. This can be used to exclude these areas as being sensitive to acidification.
- **Source:** USGS National Atlas
- **Date:** 1998
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Unknown
- **Threshold Value(s):** All areas of karst, with the exception of fissure tubes (volcanic in origin), are used to exclude areas of acid sensitivity.
- **Geology:** ANC

3.2 OVERLAY RESULTS

The extraction of the areas of greatest acid sensitivity is a relatively simple process within the GIS. The two soil pH layers were averaged to yield a hybrid value. This hybrid layer was intersected with the other input layers to create a polygon that defines the area of highest potential sensitivity. The area can then be displayed in map form, as shown in **Figure 3.2-1**.

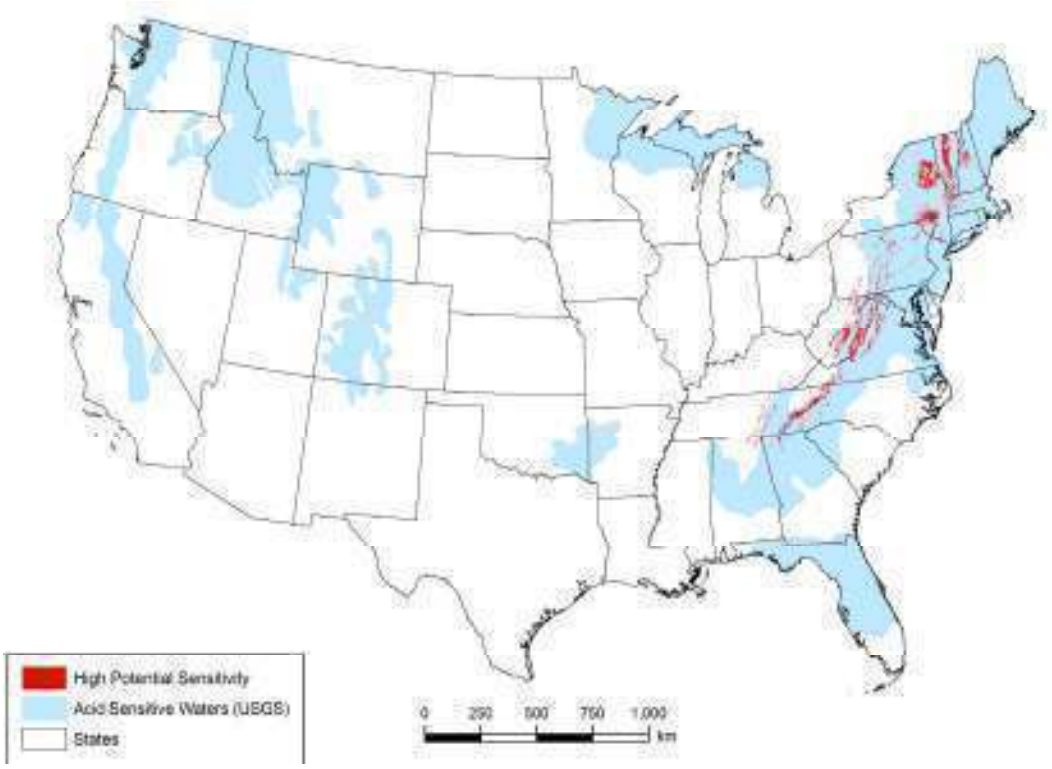

Figure 3.2-1. Area potentially sensitive to aquatic acidification.

4. SENSITIVITY TO TERRESTRIAL ACIDIFICATION

4.1 SELECTED INDICATOR GEOSPATIAL DATASETS

The publicly available geospatial datasets outlined in the following subsections have been identified as important contributors to terrestrial acidification and meet the selection criteria.

4.1.1 Range of Sugar Maple

- **Name:** Acersacr
- **Contribution:** Sugar maples are known to be sensitive to acidification and have an economic value, including the production of maple syrup and marketable timber.
- **Source:** USGS
- **Date:** 1971–1977
- **Spatial Extent:** Continental United States; however, only found regionally.
- **Spatial Resolution:** For use at scales of 1:10,000,000 or smaller.
- **Threshold Value(s):** Boundary defines range of the species.

4.1.2 Range of Red Spruce

- **Name:** Picerube
- **Contribution:** Red spruce are known to be sensitive to acidification, especially at higher elevations, and have economic value, including their use as marketable timber.
- **Source:** USGS
- **Date:** 1971–1977
- **Spatial Extent:** Continental United States; however, only found regionally.
- **Spatial Resolution:** For use at scales of 1:10,000,000 or smaller.
- **Threshold Value(s):** Boundary defines range of the species.

4.1.3 Geology

- **Name:** Karst
- **Contribution:** Karst topography is comprised of carbonate rocks, such as limestone and dolomite, which have a high ANC. The presence of karst can be used to exclude these areas as being sensitive to acidification.
- **Source:** USGS National Atlas
- **Date:** 1998
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Unknown
- **Threshold Value(s):** All areas of karst, with the exception of fissure tubes (volcanic in origin), are used to exclude areas of acid sensitivity.

4.1.4 Precipitation

- **Name:** Precipitation pH
- **Contribution:** Areas receiving acidic (low pH) precipitation are more likely to lose their buffering capacity over time, thus making them sensitive to acidification.
- **Source:** National Atmospheric Deposition Program (NADP).
- **Date:** 2006
- **Spatial Extent:** 312 monitoring stations variably distributed across the United States
- **Spatial Resolution:** For use on regional or national scale only.
- **Threshold Value(s):** Currently using a pH of less than or equal to 5.0 to define areas of acidic precipitation (subject to change).

4.1.5 Soil pH

- **Name:** Statsgo (Conus soils)
- **Contribution:** Areas that have low soil pH tend to also have low surface water pH
- **Source:** Penn State University
- **Date:** 1998
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Soil unit (variable size)
- **Threshold Value(s):** pH less than or equal to 5.0

4.1.6 Soil pH

- **Name:** U.S. Forest Service Soils Survey
- **Contribution:** Areas that have low soil pH tend to also have low surface water pH
- **Source:** USFS, Forest Inventory and Analysis National Program
- **Date:** 2001–2003
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Forest plot
- **Threshold Value(s):** pH less than or equal to 5.0

4.1.7 Wet Deposition of Sulfur Containing SO_4^{-2}

- **Name:** Wet Sulfate (SO_4^{-2}) Deposition
- **Contribution:** Greater deposition of sulfate in precipitation leads to lower precipitation pH. Over time this can reduce an area's buffering capacity.
- **Source:** NADP
- **Date:** 2006
- **Spatial Extent:** 312 monitoring stations variably distributed across the United States
- **Spatial Resolution:** For use on regional or national scale only, continental United States
- **Threshold Value(s):** None currently selected

4.1.8 Wet Deposition of Nitrogen Containing Chemical Species NO_3^- and NH_4^+

- **Name:** Wet nitrogen (both reduced and oxidized) deposition
- **Contribution:** Greater deposition of nitrate in precipitation leads to lower precipitation pH; over time this can reduce an area's buffering capacity

- **Source:** NADP
- **Date:** 2006
- **Spatial Extent:** 312 monitoring stations variably distributed across the United States
- **Spatial Resolution:** For use on regional or national scale only
- **Threshold Value(s):** None currently selected

4.1.9 Total Dry Deposition of Nitrogen Containing Both Oxidized and Reduced Chemical Species

- **Name:** DDTOTN_1A field from Community Multiscale Air Quality (CMAQ) dataset
- **Contribution:** Greater deposition of nitrogen deposited increases the likelihood of base cation depletion; over time, this can reduce an area's buffering capacity
- **Source:** CMAQ model
- **Date:** 2002
- **Spatial Extent:**12 km grid cells of the contiguous United States
- **Spatial Resolution:** For use on regional or national scale only, continental United States
- **Threshold Value(s):** None currently selected.

4.1.10 Total Dry Deposition of Sulfur

- **Name:** DDTOTS_1A field from CMAQ dataset
- **Contribution:** Greater deposition of sulfur increases the likelihood of base cation depletion; over time, this can reduce an area's buffering capacity
- **Source:** CMAQ model
- **Date:** 2002
- **Spatial Extent:** 12 km grid cells of the contiguous United States
- **Spatial Resolution:** For use on regional or national scale only. continental United States
- **Threshold Value(s):** None currently selected

4.1.11 Soil Depth

- **Name:** Statsgo (Conus soils)
- **Contribution:** Areas that have thin soils tend to also have low surface water pH
- **Source:** Penn State University
- **Date:** 1998

- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Soil unit (variable size)
- **Threshold Value(s):** RTI divided soil depth into fourth quartiles and used the areas with the lowest soil depth (bottom quartile) to define the areas of the highest sensitivity to acidification. The ended up as all measurements less than 51 centimeters (cm) in total depth.

4.2 LAYERS CONSIDERED, BUT NOT INCLUDED

4.2.1 Elevation

- **Name:** Grayscale North America Shaded Relief
- **Contribution:** Certain species, especially red spruce, become sensitive to acidification above an elevation of 750 meters
- **Source:** USGS National Atlas
- **Date:** September 2006
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** 1 km grid cells
- **Threshold Value(s)** - 750 meters
- **Exclusion Reason** - Not used because we already have range of red spruce

4.3 OVERLAY RESULTS

The areas of greatest terrestrial acidification sensitivity were defined by the following GIS process. The ranges of sugar maple and red spruce were combined to create a layer that consisted of ***either*** sugar maple or red spruce. The two soil pH layers were averaged to create a hybrid layer of top layer (20 cm) soil pH. From this hybrid layer, only those areas that had a surface pH of 5.00 or less were extracted. These layers were combined with the following:

- The lowest quartile of soil thickness
- The highest quartile of total nitrogen deposition (both wet from NADP and dry from CMAQ)
- The highest quartile of total sulfur deposition (both wet from NADP and dry from CMAQ)

- Areas of precipitation of pH 5.00 or less.

The area can then be displayed in map form.

Only areas common to all the inputs were retained. From this intermediate layer, areas of karst geology were removed. Karst geology typically has a high acid buffering capacity. The resultant layer contains the area of highest potential sensitive to terrestrial acidification and can be displayed in map form, as shown in **Figure 4.3-1**.

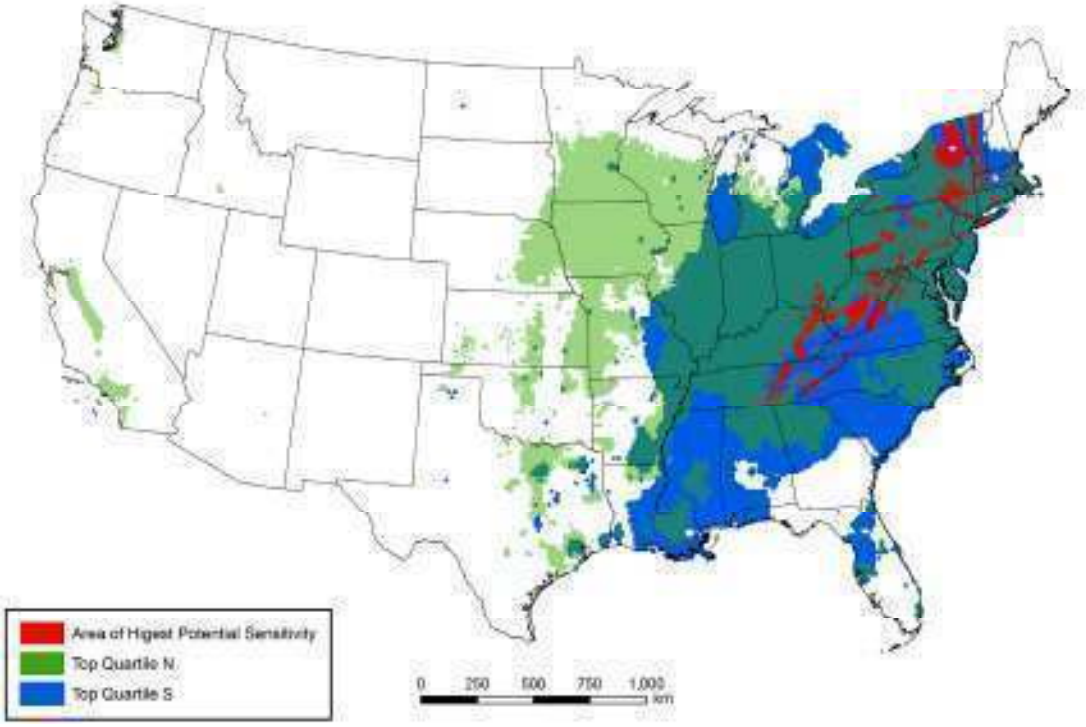

Figure 4.3-1. Areas potentially sensitive to terrestrial acidification.

5. SENSITIVITY TO AQUATIC NUTRIENT ENRICHMENT

5.1 SELECTED INDICATOR GEOSPATIAL DATASETS

The publicly available geospatial datasets outlined in the subsections below have been identified as important contributors to aquatic nutrient enrichment and meet the selection criteria.

5.1.1 Nitrogen in Surface Water

- **Name:** Total nitrogen (Kjeldahl).

- **Contribution:** Elevated nitrogen levels in surface water lead to increases in some aquatic plant species, resulting in a loss of dissolved oxygen (eutrophication)
- **Source:** EPA National Nutrient Database
- **Date:** Published in1998
- **Spatial Extent:** National
- **Spatial Resolution:** For use at national, regional, or state scales
- **Threshold Value(s):** Not yet determined

5.1.2 Wet Deposition of Nitrogen Containing Chemical Species NO_3^- and NH_4^+

- **Name:** Wet nitrogen (both reduced and oxidized) deposition.
- **Contribution:** Greater deposition of nitrogen (especially NO_3^-) in precipitation leads to increased nitrogen concentration of receiving water. Nitrogen acts as a nutrient in aquatic systems.
- **Source:** NADP
- **Date:** 2002
- **Spatial Extent:** 312 monitoring stations variably distributed across the United States
- **Spatial Resolution:** For use on regional or national scale only
- **Threshold Value(s):** None currently selected

5.1.3 Total Dry Deposition of Nitrogen Containing both Oxidized and Reduced Chemical Species

- **Name:** DDTOTN_1A field from CMAQ dataset
- **Contribution:** Greater deposition of nitrogen (especially NO_3^-) in precipitation leads to increased nitrogen concentration of receiving water. Nitrogen acts as a nutrient in aquatic systems.
- **Source:** CMAQ model
- **Date:** 2002
- **Spatial Extent:** 12 km grid cells of the contiguous United States
- **Spatial Resolution:** For use on a regional or national scale only
- **Threshold Value(s):** None currently selected

5.1.4 Eutrophic Estuaries

- **Name:** Coastal Assessment Framework
- **Contribution:** Identifies which estuaries are currently eutrophic or have the potential to become eutrophic
- **Source:** National Oceanic and Atmospheric Administration (NOAA)
- **Date:** 1999
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** For use on regional or national scale only
- **Threshold Value(s):** Boundary defines areas of eutrophication

5.1.5 Nutrient Criteria

- **Name:** Maximum Nutrient Concentrations by Region
- **Contribution:** Defines the maximum amount of nutrient load (total phosphorus, total nitrogen, chlorophyll *a*) for waterbodies by Level III ecoregion
- **Source:** EPA Office of Science and Technology
- **Date:** 2002
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Appropriate for use on a regional or national scale
- **Threshold Value(s):** Variable by region. May be possible to identify areas that exceed nutrient criteria with results from National Nutrient Database

5.1.6 Nitrogen-Limited Waters

- **Name:** Total nitrogen to total phosphorus ratios taken at the same time and at the same station
- **Contribution:** Nitrogen to phosphorus ratio is a measure of how much a waterbody is nutrient-limited. If a system is not nitrogen-limited, then it is phosphorus-limited. It is typically accepted that in water with a nitrogen to phosphorus ratio less than 7.2 nitrogen is the limiting factor. With higher ratios, phosphorus is the limiting nutrient.
- **Source:** EPA National Nutrient Database
- **Date:** Published in 1998
- **Spatial Extent:** National
- **Spatial Resolution:** For use at national, regional, or state scales

- **Threshold Value(s):** 7.2:1

5.2 INDICATOR GEOSPATIAL DATASETS CONSIDERED, BUT NOT USED

The publicly available spatial datasets outlined in the following subsections were considered for inclusion in the national sensitivity assessment, but were not used.

5.2.1 Presence of Nitrogen Sensitive Species

- **Name:** Johnson's Seagrass
- **Contribution:** Nutrient enrichment, caused by inorganic and organic nitrogen and phosphorus loading via urban and agricultural land run-off, can stimulate increased algal growth and smother Johnson's seagrass by shading rooted vegetation and diminishing the oxygen content of the water.
- **Source:** NOAA
- **Date:** 2000
- **Spatial Extent:** Ten portions of the Indian River Lagoon and Biscayne Bay, FL
- **Spatial Resolution:** For use on a statewide basis
- **Threshold Value(s):** Presence of species
- **Exclusion Reason:** Not a national distribution

5.3 OVERLAY RESULTS

The extraction of the areas of greatest aquatic nutrient enrichment sensitivity is a relatively simple process within the GIS. A simple intersection of the input layers yields a polygon that defines this area. The area can then be displayed in map form, as shown in **Figure 5.3-1**. **(Note: This overlay is currently in progress; therefore, the map provided in Figure 5.3-1 is a placeholder.)**

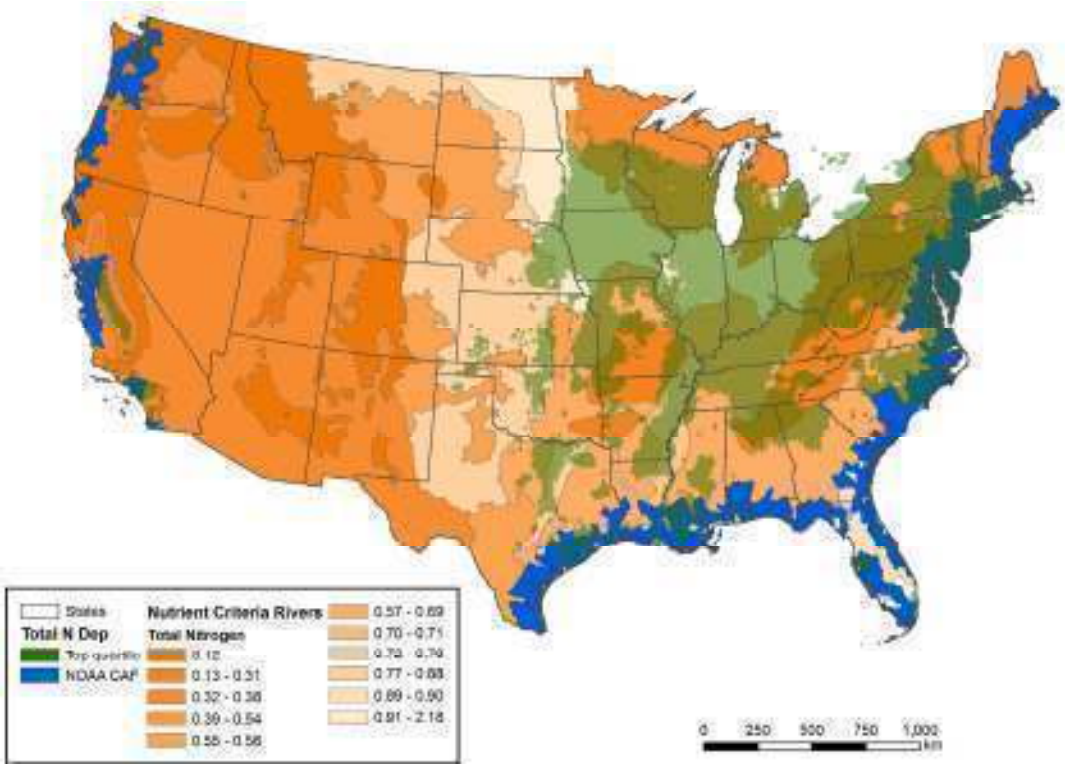

Figure 5.3-1. THIS FIGURE IS A PLACEHOLDER. Areas potentially sensitive to aquatic nutrient enrichment.

6. SENSITIVITY TO TERRESTRIAL NUTRIENT ENRICHMENT

6.1 SELECTED INDICATOR GEOSPATIAL DATASETS

The publicly available geospatial datasets outlined in the following subsections have been identified as important contributors to terrestrial nutrient enrichment and meet the selection criteria.

6.1.1 Presence of Acidophytic Lichens

- **Name:** Acidophytic Lichens
- **Contribution:** Lichen species that are known to be sensitive to increased levels of nitrogen loading will decrease in number. Other species are dependent upon lichens for both food and habitat.
- **Source:** List of acidophytic species from Fenn et al. (2008), Empirical and simulated critical loads for nitrogen deposition in California mixed conifer forests. *Environmental Pollution,* May. Geospatial data obtained from USFS FIA.

- **Date:** 2001–2006
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** For use at national or regional scales
- **Threshold Value(s):** Point (plot location) defines presence of the species.

6.1.2 Wet Deposition of Nitrogen Containing Chemical Species NO_3^- and NH_4^+

- **Name:** Wet nitrogen (both reduced and oxidized) deposition
- **Contribution:** Greater deposition of nitrogen (especially NO_3^-) in precipitation leads to increased nitrogen concentration of receiving water. Nitrogen acts as a nutrient in terrestrial systems.
- **Source:** NADP
- **Date:** 2006
- **Spatial Extent:** 312 stations variably distributed across the United States
- **Spatial Resolution:** For use on regional or national scale only
- **Threshold Value(s):** None currently selected

6.1.2 Total Dry Deposition of Nitrogen Containing both Oxidized and Reduced Chemical Species

- **Name:** DDTOTN_1A field from CMAQ dataset
- **Contribution:** Greater deposition of nitrogen (especially NO_3^-) in precipitation leads to increased nitrogen concentration of receiving water. Nitrogen acts as a nutrient in terrestrial systems.
- **Source:** CMAQ model
- **Date:** 2002
- **Spatial Extent:** 12 km grids of the contiguous United States
- **Spatial Resolution:** For use on regional or national scale only
- **Threshold Value(s):** None currently selected

6.1.3 Anthropogenic Land Cover

- **Name:** Urban and Agricultural Land Covers
- **Contribution:** Used to exclude areas that are not sensitive to terrestrial nutrient enrichment, such as agricultural areas and urbanized areas

- **Source:** USGS National Atlas
- **Date**: 2006
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** 1 km meter grid cells
- **Threshold Value(s):** Select out urban and agricultural land covers.

6.2 INDICATOR GEOSPATIAL DATASETS CONSIDERED, BUT NOT USED

The publicly available spatial datasets outlined in the following subsections were considered for inclusion in the national sensitivity assessment, but were not used.

6.2.1 Soil Nitrogen Content

- **Name:** Soil nitrogen concentration
- **Contribution:** Areas with a high nitrogen concentration may be at risk for nitrogen saturation.
- **Source:** Oak Ridge National Laboratory (not yet received)
- **Date:** Pre-1980
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Not yet known
- **Threshold Value(s):** Not yet determined
- **Exclusion Reason:** Data not received; quality uncertain

6.2.2 Presence of Nitrogen Sensitive Species Identified in Literature

- **Name:** To be created
- **Contribution:** Since there is not a single nationwide species that displays range loss because of additional nitrogen, it may be possible to assemble a "patchwork quilt" of study sites across the United States.
- **Source:** Literature
- **Date:** Recent
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Site-specific, but it may be possible to define a range
- **Threshold Value(s):** Presence of species

- **Exclusion Reason:** Source of nitrogen-sensitive species distribution not found

6.2.3 Presence of Mountains

- **Name:** Physiographic Provinces of the United States
- **Contribution:** Leeward sides of mountains tend to receive a greater amount of nitrogen deposition
- **Source:** USGS
- **Date:** 1946
- **Spatial Extent:** Continental United States
- **Spatial Resolution:** Published scale of 1:7,000,000; for use on regional or national scale only
- **Threshold Value(s):** Select mountain ranges only
- **Exclusion Reason:** Terrain is already taken into account by the CMAQ modeling

6.3 OVERLAY RESULTS

The extraction of the areas of greatest nutrient enrichment sensitivity involved the following steps within the GIS. The total nitrogen deposition grid (a sum of dry deposition from CMAQ and wet deposition from NADP) was reclassified into four quartiles. The quartile of highest total nitrogen deposition was then extracted. From this, areas of human use (urban and agricultural land covers) were removed. To this, a layer of acidophytic lichen distribution was added. The area of highest potential sensitivity can be displayed in map form, as shown in **Figure 6.3-1**.

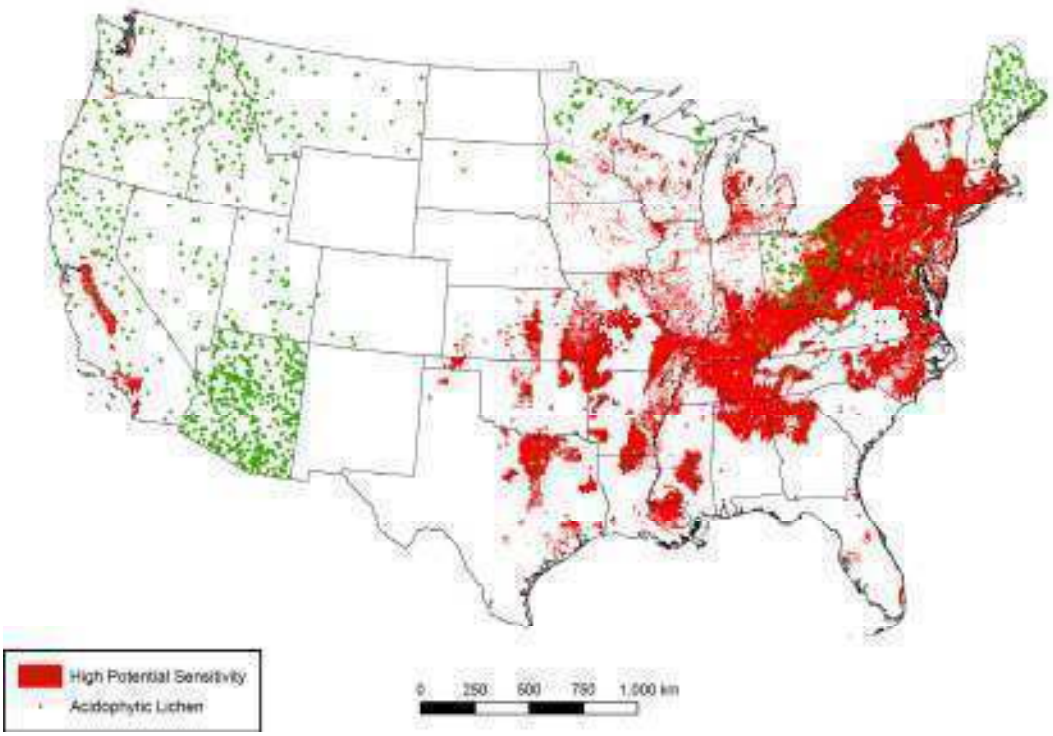

Figure 6.3-1. Areas potentially sensitive to terrestrial nutrient enrichment.

ATTACHMENT 3

AQUATIC ACIDIFICATION CASE STUDY

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August 15, 2008

Aquatic Acidification Case Study

Draft

EPA Contract Number EP-D-06-003
Work Assignment 2-44
Project Number 0209897.002.044

Prepared for

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27709

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CONTENTS

FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

$Al(OH)_3$	aluminum hydroxide
Al	aluminum
ANC	acid neutralizing capacity
ASTRAP	Advanced Statistical Trajectory Regional Air Pollution model
Ca^{2+}	calcium
CMAQ	Community Multiscale Air Quality
CO_2	carbon dioxide
EMAP	Environmental Monitoring and Assessment
EPA	U.S. Environmental Protections Agency
F-.	fluoride
H^+	hydrogen
K^+	potassium
kg/ha	kilograms/hectare
LTM	Long-term Monitoring Program
m	meter
Mg^{2+}	magnesium
Na^+	sodium
NAPD	National Atmospheric Deposition Program
NEG.ECP	New England Governors and Eastern Canadian Premier
NO_2	nitrogen dioxide
NO_3	nitrate
NO_x	nitrogen oxides
NSWS	National Lake/Stream Surveys
Si	silicon
SO_2	sulfur dioxide
$SO4_2^-$	sulfate
SO_x	sulfur oxides
SSWC	Steady-State Water Chemistry Model
TIME	Temporally Integrated Monitoring of Ecosystems Program

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1. PURPOSE

This case study is intended to estimate the ecological exposure and risk associated to aquatic ecosystems from acidification effects of the deposition of nitrogen and sulfur for two sensitive regions of eastern United States: the Adirondack Mountains and Shenandoah National Park and the surrounding areas of Virginia.

2. BACKGROUND

2.1 ACIDIFICATION

Emissions of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) compounds into the air react in the atmosphere through a complex mix of reactions and thermodynamic processes in gaseous, liquid, and solid phases to form various acidic compounds. These compounds are removed from the atmosphere through deposition: either wet (e.g., rain, snow), occult (e.g., fog, mist), or dry (e.g., gases and particles). Deposition of sulfur oxides (SO_x) and nitrogen oxides (NO_x) leads to ecosystem exposure. Among other effects on ecosystem structure and function, deposition of these compounds can lead to acidification of surface waters through the leaching of sulfate ($SO4_2^-$) and nitrate (NO_3^-) from soils. The effects depend on the magnitude of deposition, as well as a host of biogeochemical processes occurring in the soils and waterbodies.

When sulfur or nitrogen moves from soils to surface waters in the form of SO_4^{2-} or NO_3^-, an equivalent amount of cations, or countercharge, is also transported. If the countercharge is provided by cations (such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+).) other than hydrogen (H^+) and Aln^+, the base saturation and buffering capacity of the soil is reduced as the acidity of the soil water is neutralized. Continued SO_4^{2-} or NO_3^- leaching can deplete the base supply of the soil, thereby impairing the soil's ability to neutralize further acidic deposition. Further deposition and leaching of SO_4^{2-} leads to acidification of soil water, and by connection, surface water as the base cations are removed. Loss of soil base saturation is a cumulative effect that increases the sensitivity of the watershed to further acidic deposition.

Cumulative effects of sulfur deposition can also result from the adsorption of SO_4^{2-} to soil particles, a process that removes SO_4^{2-} from soil solution, and therefore, prevents leaching of cations and further acidification of soil. However, this potentially reversible process results in an

accumulation of sulfur in the soil, which can contribute to soil acidification if, and when, the SO_4^{2-} is eventually released back into solution. The degree to which SO_4^{2-} adsorbs on soil is dependent on soil characteristics. Soils in the United States that most effectively adsorb SO_4^{2-} occur south of the maximum extent of glaciation that occurred during the most recent ice age (Rochelle et al., 1987; Rochelle and Church, 1987). Sulfate adsorption is strongly pH dependent, and a decrease in soil pH resulting from acidic deposition can enhance the ability of soil to adsorb SO_4^{2-}.

2.2 INDICATORS OF ACIDIFICATION

Surface water chemistry is a primary indicator of acidification and the resulting adverse effects on the biotic integrity of freshwater ecosystems. There are numerous sensitive chemical receptors that can be used to assess effects of acidic deposition on lake or stream acid-base chemistry. These include surface water pH and concentrations of SO_4^{2-}, NO^{3-}, Al^{+}, 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 acid neutralizing capacity, or ANC. Each of these chemical indicators can provide useful information regarding both sensitivity to surface water acidification and the level of acidification that has occurred. Acidification effects on aquatic biota are most commonly evaluated using Al, pH, or ANC. Although ANC does not relate directly to the health of biota, the utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al. Furthermore, surface water acidification models do a better job estimating ANC than either pH or Al concentrations. For the purpose of this case study, ANC will be the focus of the indicator used.

ANC of surface waters was used as a metric to quantify the current acidic conditions and biological impacts of a subset of waterbodies in the study areas, because it provides an acid-base chemistry that reflects the relative balance between cations and strong acid anions and the cumulative effects of all of the ionic interactions that occur as atmospheric deposition and precipitation move from the atmosphere into the soil and drainage water to emerge in a stream or lake. For the purpose of this case study, ANC of surface waters is simply measured as the total amount of strong base ions minus the total amount of strong acid anions:

$$ANC = (Ca^{2+} + Mg^{2+} + K + Na + NH4) - (SO_4^{2-} + NO_3- + Cl^-) \quad (1)$$

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 water will have positive ANC. 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 higher pH and Ca^{2+} concentrations; lower ANC is generally associated with higher H^+ and Al^+ concentrations and a greater likelihood of toxicity to biota. This is the buffering capacity, or the ability of the system to resist acidification.

Field studies often rely upon the Gran titration approach. Process-based models, such as MAGIC and PnET-BGC, utilize the ANC calculated from the charge balance. For monitoring and assessment purposes, it is always best to determine both titrated and calculated ANC values. The difference between the two can be used to quantify uncertainty and reveal the influences of natural organic acidity and/or dissolved Al on the overall acid-base chemistry of the water.

Surface water pH is a common alternative to ANC as an indicator of acidification.

However, at pH values above about 6.0, pH is not a good indicator of either sensitivity to acidification or level of effect. In addition, pH measurements (especially at these higher values) are sensitive to levels of dissolved carbon dioxide (CO_2) in the water. In contrast, ANC is more stable and it reflects sensitivity and effect in a linear fashion across the full range of ANC values. Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated and calculated ANC values are commonly determined in field studies aimed at resource characterization or long-term monitoring.

2.3 SURFACE WATERS ACIDIFICATION IN EASTERN UNITED STATES

The regions of the United States with low surface water ANC values are the locations that are sensitive to acidic deposition. The majority of lakes and streams in the United States have ANC levels above 200 μeq/L and are not sensitive to the deposition of NO_x and SO_x air pollution at their existing ambient concentration levels. **Figure 2.3-1** 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.

Figure 2.3-1. Sensitive ecosystem to acidic deposition in the eastern United States.

Freshwater surveys and monitoring in the eastern United States has been conducted by many program since the mid-1980s, including the U.S. Environmental Protections Agency's (EPA's) Environmental Monitoring and Assessment (EMAP), National Lake/Stream Surveys (NSWS), Temporally Integrated Monitoring of Ecosystems (TIME) (Stoddard, 1990), and Long-term Monitoring (LTM) (Ford et al, 1993; Stoddard et al., 1998) programs. The purpose of these programs is to identify the current state and determine trends in regional populations of lakes or streams impacted by acidic deposition. Based on surface water data from these programs in the eastern United States, New England, the Adirondacks, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), northern Florida, and the Upper Midwest contain the greatest proportion of sensitive lakes and streams (i.e., ANC less than about 50 μeq/L) since the 1980s.

New England, the Adirondacks, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), and the Upper Midwest are estimated to contain 95% of the lakes and 84% of the streams in the United States that have been anthropogenically acidified through deposition. The Adirondacks had a large proportion of acidic surface waters (14%) in the NSWS; from 1984 to 1987, the Adirondack Lakes Survey Corporation sampled 1,469 Adirondack lakes greater than 0.5 hectares (ha) in size and estimated that many more (26%) were acidic (Driscoll et al., 1991). The proportions of lakes estimated by NSWS to be acidic were smaller in New England and the Upper Midwest (5% and 3%, respectively), but because of the large numbers of lakes in these regions, there were several hundred acidic waters in each of these two regions. The Valley and Ridge Province and Northern Appalachian Plateau had 5.5% and 6% acidic sites, respectively, based on data from the early 1990s. Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidic deposition in these areas is less clear. In 2002, Stoddard and colleagues (2003) took another comprehensive look at the level of acidification within all of these regions. Although improvement in ANC occurred, they still found that about 8% of lakes in the Adirondacks and 6%–8% of streams in 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 Adirondacks Mountains, the Northern Appalachian Plateau, and the Ridge/Blue Ridge region provide ideal case study locations to assess the risk to aquatic ecosystems from NO_x/SO_x acidic deposition.

3. CASE STUDIES

The Adirondacks Mountains in New York and the Ridge/Blue Ridge Mountains in the Shenandoah National Park and surrounding areas of Virginia were selected for the evaluation of the risk of ambient NO_x/SO_x concentrations to aquatic acidification and their biological impacts. Three main reasons support the selection of these two areas. First, both regions fall within the areas of the United State known to be sensitive to acidic deposition because of a host of environmental factors (e.g., geology) that make these regions predisposed to acidification. Second, these areas are representative of other sensitive areas to acidification, which will allow the results of this case study to be generalized. Third, a high degree of knowledge, research, and data have already been collected within these geographic regions (see Section 4 of the Integrated

Science Assessment [ISA]). For example, extensive water quality data exists (from monitoring networks in operation since the 1980s), along with numerous research studies that directly link the biological harm of individuals, populations, communities, and ecosystems to aquatic acidification. Sections below describe the case studies areas, past impacts of acidic deposition, and research linking biological and acidic conditions for each region.

3.1 ADIRONDACK MOUNTAINS

3.1.1 General Description

The Adirondack Mountains region is situated in northeastern New York State. It is characterized by dense forest cover and abundant surface waters, with 46 peaks that extend up to 1600 meter (m) in elevation. The Adirondack region has long been a nationally important recreation area for fishing, hiking, boating, and other outdoor activities. The Adirondack region, and the southwestern Adirondacks in particular, is sensitive to acidic deposition because it receives high precipitation, has shallow base-poor soils, and is underlain by igneous bedrock with low weathering rates and buffering capacity (Driscoll et al., 1991; Sullivan et al., 2006). The Adirondack region is also 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 United States policy on atmospheric emissions of SO_2 and NO_x (U.S. EPA, 1995; NAPAP, 1998).

3.1.2 Levels of Acidic Deposition

Wet deposition in the Adirondacks has been monitored by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) since 1978 at two sites (Huntington Forest and Whiteface Mountain) and seven other sites since 1980s. Since 1990, wet sulfate and nitrate deposition at these NADP/NTN sites in the Adirondacks has declined by about 45% and 40%, respectively (**Figure 3.1-1**). However, deposition is still 15 and 10 kg/ha of SO_4^{2-} and NO_3^- respectively.

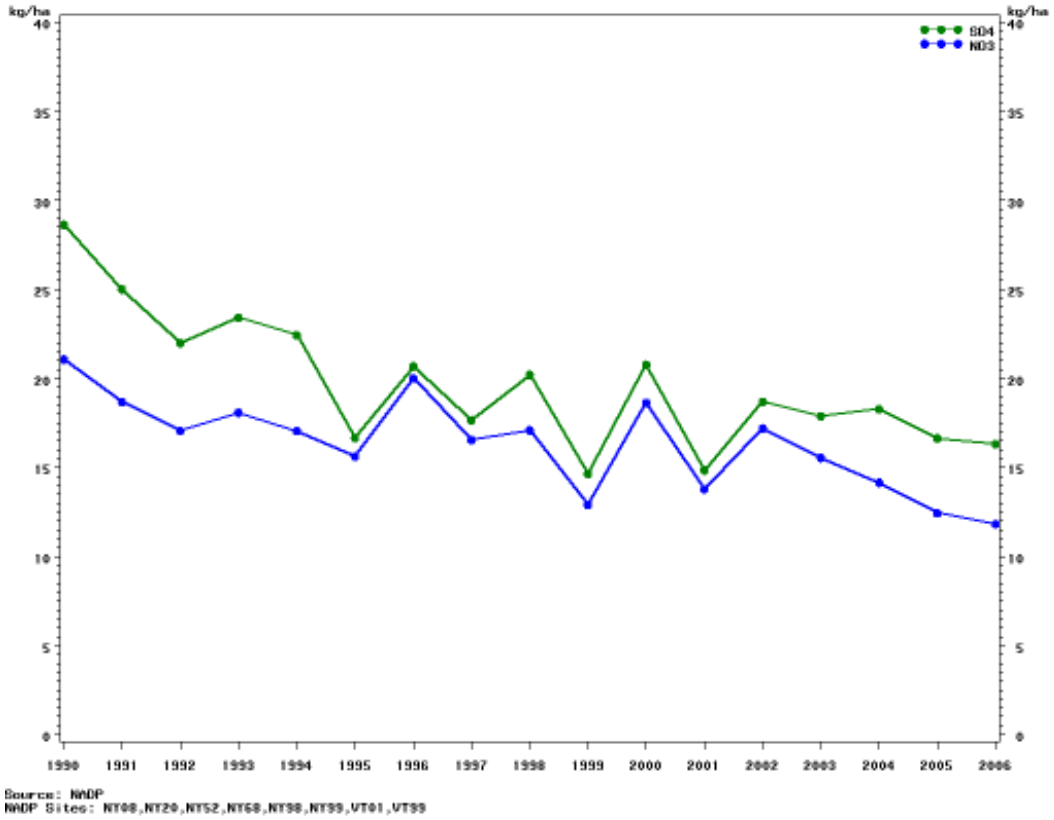

Figure 3.1-1. Annual average trends from 1990 to 2006 in wet SO_4^{2-} (green line) and NO_3^- (blue line) deposition from nine NADP/NTN sites in the Adirondack region.

3.2 SHENANDOAH NATIONAL PARK AND SURROUNDING AREAS OF VIRGINIA

3.2.1 General Description

Shenandoah National Park is located along the crest of the Blue Ridge Mountains in Virginia. Air pollution within Shenandoah National Park and surrounding areas, including concentrations of sulfur, nitrogen, and ozone (O_3), is higher than in most other national parks in the United States. This area is sensitive to acidic 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 buffering capacity. Shenandoah National Park region is also among the most severely acid-impacted regions in North America (Stoddard et al., 2003; Webb et al., 2004).

3.2.2 Levels of Acidic Deposition

Wet deposition in the Shenandoah National Park of Virginia has been monitored at 7 sites by the NADP/NTN since the 1980s. Since 1990, wet sulfate and nitrate deposition has declined by about 28% and 20%, respectively (**Figure 3.2-1**). However, deposition is still 15 and 10 kilograms/hectare (kg/ha) of SO_4^{2-} and NO_3^-, respectively.

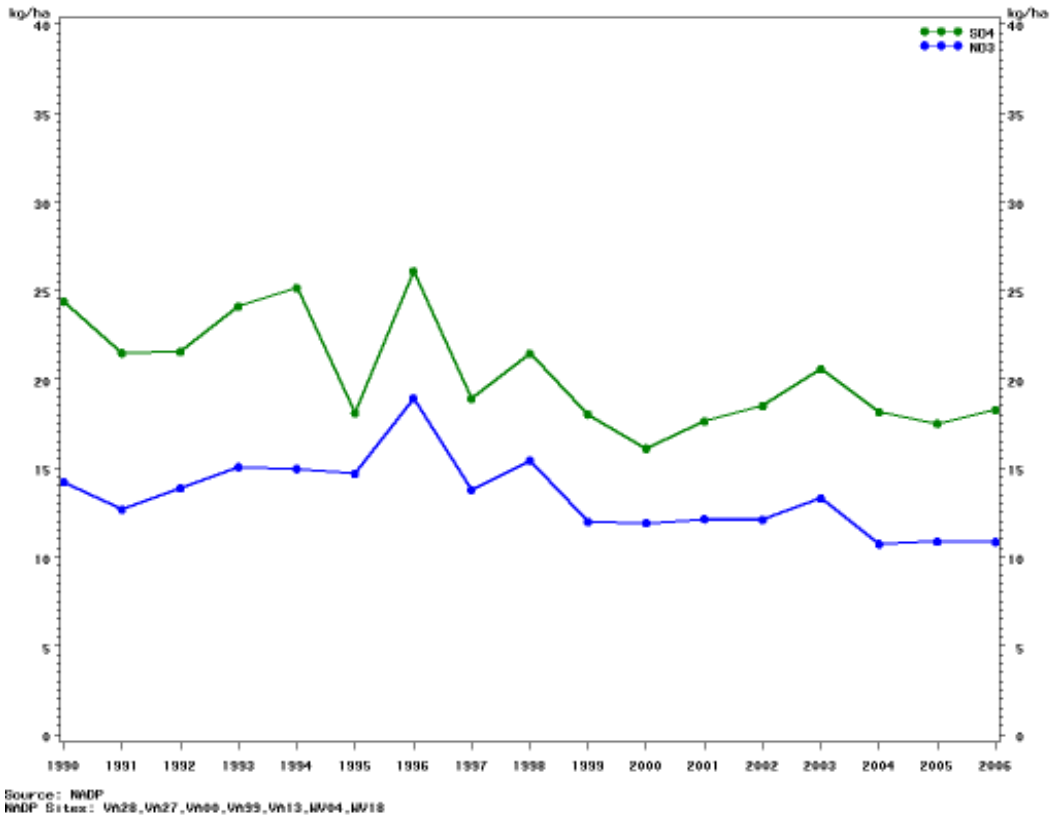

Figure 3.2-1. Annual average trends from 1990 to 2006 in wet SO_4^{2-} (green line) and NO_3^- (blue line) deposition from seven NADP/NTN sites in the Shenandoah National Park region.

4. APPROACH AND METHODS

4.1 APPROACH AND OBJECTIVES

For each of the case study areas, current conditions of the aquatic ecosystems to acidification impacts were evaluated by using multiple approaches that rely on monitoring data and modeled output. Current conditions were evaluated by a three-step process that assessed:

- The trends in sulfate, nitrate, and ANC concentrations in surface water to establish current pollution levels and trends that are linked to nitrogen and sulfur deposition,
- The percent of waterbodies that have different degrees of acidic conditions,
- The percent of waterbodies receiving current nitrogen and sulfur deposition loads above biological harmful levels.

4.1.1 Surface water trends

Trends in SO_4^{2-} and NO_3^-, and ANC concentrations measured in surface water, were used to establish the current condition of sensitive chemical receptors that are linked to the effects of acidic deposition on waterbodies acid-base chemistry. Each provides information regarding both sensitivity to surface water acidification and the level of acidification that has occurred today and in the past. Trends in these sensitive chemical receptors allow for the determination of whether the conditions of the waterbodies are improving and heading towards recovery or if the conditions are degrading. Measurements of SO_4^{2-} concentrations in surface waters provide important information on the extent of cation leaching in soils and how SO_4^{2-} concentrations relate to deposition and to the levels of ambient atmospheric sulfur. Assessments of acidic deposition effects dating from the 1980s to the present have shown SO_4^{2-} to be the primary anion in most acid-sensitive waters (Driscoll and Newton, 1985; Driscoll et al., 1988, 2001; Webb et al., 2004). Nitrate has the same potential as SO_4^{2-} to acidify drainage waters and leach potentially Aln^+ from watershed soils. In most watersheds, however, nitrogen is a limiting factor for plant growth; therefore, most nitrogen inputs through deposition are quickly incorporated into biomass as organic nitrogen with little leaching of NO_3^- into surface waters.

To assess surface water trends in sulfate, nitrate, and ANC concentrations, we used monitoring samples from the EPA-administered LTM program. Trends in SO_4^{2-}, NO_3^-, and ANC concentration were assessed using average yearly values for the period from 1990 to 2006. All the lakes included in this analysis were sampled weekly.

4.1.2 Level of Acidification and Biological Impacts

Ecological effects occur at four levels of biological organization: (1) the individual, (2) the population, comprised of many individuals, (3) the biological community, composed of many species, and (4) the ecosystem. Several metrics have been developed to describe the effects of

acidification at each of these levels of organization. For the individual, impacts are assessed in terms of fitness (i.e., growth, development, and reproduction) or sub-lethal effects on condition. Low-pH or ANC water can directly influence aquatic organism fitness or mortality by disrupting ion regulation and mobilizes Al, which is highly toxic to fish under acidic conditions (i.e., pH below 6 and ANC below 50 μeq/L). For example, research showed that as the pH of surface waters decreased below 6, many aquatic species, including fish, invertebrates, zooplankton, and diatoms, tended to decline (Schindler, 1988). Van Sickle and colleagues (1996) also found that blacknose dace (*Rhinichthy* spp.) were highly sensitive to low pH and could not tolerate inorganic Al concentrations above about 3.7 μM for extended periods of time. After 6 days of exposure to high inorganic Al, dace mortality increased rapidly to nearly 100%.

At the community level, species richness and community structure can be used to evaluate effects. Species composition refers to the mix of species that are represented in a particular ecosystem, while species richness refers to the total number of species in a stream or lake. Acidification alters species composition and richness in aquatic ecosystems. There are a number of species common to many oligotrophic waterbodies that are sensitive to and cannot survive, compete, or reproduce in acidic waters. In response to small to moderate changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species, resulting in changes in community composition and richness, but little or no change in total community biomass. The effects of acidification are continuous, with more species being affected at higher degrees of acidification. At a point, typically at a pH below 4.5 and an ANC below 0 μeq/L, complete to near loss of many classes of organisms occur, such as fish and aquatic insect populations, while others are reduced to only a few acidophilic forms.

Decreases in species richness have been observed in the Adirondacks and Catskills of New York (Baker et al 1993), the upper Midwest of the United States (Schindler et al., 1989), New England and Pennsylvania (Haines and Baker, 1986), and Virginia (Bulger et al., 2000). For example, studies in the Adirondack Mountains demonstrated the effect of acidification on species richness; of the 53 fish species recorded in Adirondack lakes, only 27 species were found in lakes with pH below 6.0. The 26 species missing from lakes with pH below 6.0 include important recreational species, such as Atlantic salmon, tiger trout (*Salmo trutta* X *Salvelinus fontinalis*), redbreast sunfish (*Lepomis auritus*), bluegill (*Lepomis macrochirus*), tiger musky (*Esox masquinongy* X *lucius*), walleye (*Sander vitreus*), alewife (*Alosa pseudoharengus*), and

kokanee (*Oncorhynchus nerka*) (Kretser et al., 1989), plus ecologically important minnows that are commonly eaten by sport fish. 346 of 1,469 lakes surveyed were devoid of fish. Among lakes with fish, there was a relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH >6.5 (Driscoll et al., 2001; Kretser et al., 1989).

4.1.3 ANC and Biological Impacts

ANC of surface waters was used as a metric to quantify the current acidic conditions and biological impacts of a subset of waterbodies in the study areas 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). It is a strong indicator of biological response because acid-base conditions in surface water have been shown to have direct effects on aquatic systems (i.e., individual species fitness loss or death, reduced species richness, and 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; Wedemeger et al. 1990). For example, Sullivan et al. (2006) found a logistic relationship between fish species richness and ANC class for Adirondack lakes (**Figure 4.1-1, a**), which indicates the probability of occurrence of an organism for a given value of ANC. In Shenandoah National Park, a statistically robust relationship between acid-base status of streams and fish species richness was also documented (**Figure 4.1-1, b**).

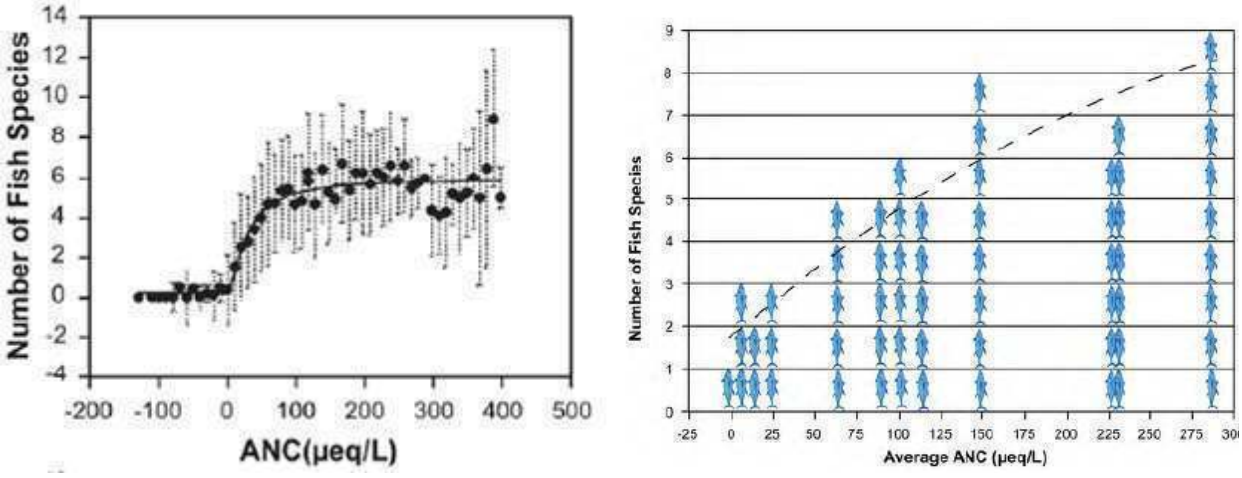

Figure 4.1-1. (a) Number of fish species per lake or stream versus acidity statues, expressed either as ANC. Adirondack lakes (Sullivan et al., 2006). (b) Number of fish species among 13 streams in Shenandoah National Park. Values of ANC are means based on quarterly measurements, 1987–1994. The regression analysis shoed a highly significant relationship ($p < 0.0001$) between mean stream ANC and the number of fish species. Streams having ANC consistently <75 μeq/L had three or fewer species.

However, because there is a continuum in the relationship between ANC levels and resulting biological effects, a range of ANC concentrations related to specific biological effects is needed to provide a comprehensive assessment of the current biological condition under current acidic deposition loads. For this reason, five categories of ANC concentrations were selected that relate to specific biological health conditions of aquatic communities, ranging from no impacts to complete loss of fish populations. These five classes are based on the relationships between ANC/pH and ecological attributes, including richness, diversity, community structure, and individual fitness of organisms. The below paragraph describes the biological impact given a range of ANC values and the scientific research that supports the grouping (see Section AX4 of the Annexes to the ISA for a more in depth description of the biological relationship used in this grouping).

For freshwater systems, ANC chemical levels are best grouped into five major classes: Acute Concern <0 μeq/L, Severe Concern 0–20 μeq/L, Elevated Concern 20–50 μeq/L, and Moderate Concern 50–100 μeq/L, and Low Concern >100 μeq/L, with each range representing a probability of ecological damage to the community (**Table 4.1-1**). Biota is generally not harmed when ANC values are above 100 μeq/L. The number of fish species also peak at ANC values above 100 μeq/L (Bulger et al., 1999; Driscoll et al., 2001; Kretser et al., 1989; Sullivan et al.,

2006). Below 100 µeq/L, it has been shown that fish fitness and community diversity begin to decline (**Figure 4.1-2**). At ANC levels between 100 and 50 µeq/L, the fitness of sensitive species (e.g., brook trout and other zooplankton) begins to decline. However, the overall health of the community remains high. When ANC concentrations are below 50 µeq/L, there are negative effects on sensitive biota. In Adirondack lakes, Kretser and colleagues (1989) showed a 50% reduction in the number of fish species below an ANC of 50 µeq/L. From 50 to 20 µeq/L, it has been shown that the overall fitness of most fish species are greatly reduced (Dennis and Bulger, 1995). Below 20 µeq/L, all biota exhibit some level of negative effects. At these levels, surface waters are susceptible to episodic acidification and their associated harmful 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). Below an ANC of 0 µeq/L, complete loss of fish populations and extremely low diversity of planktonic communities occur. Only acidophilic species are present, but their population numbers are sharply reduced. For example, under average ANC <0 µeq/l, lakes is the Adirondack region are generally fishless (Sullivan et al., 2006). A summary of the five categories of ANC and expected ecological effects can be found in **Table 4.1-1**.

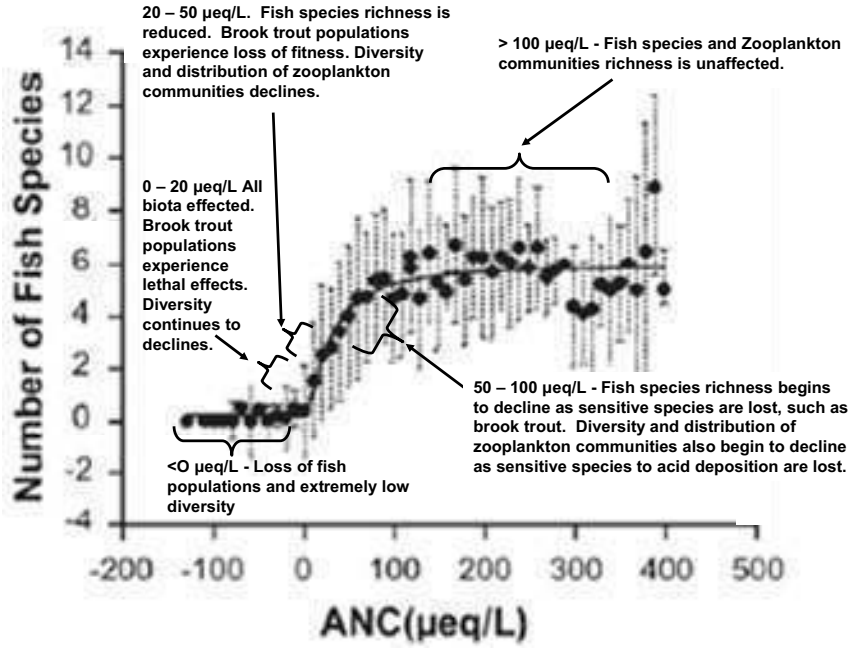

Figure 4.1-2. Number of fish species per lake or stream versus acidity statues, expressed as ANC in lakes in the Adirondacks of New York (Sullivan et al., 2006). Five classes: <0, 0–20, 20–50, and 50–100 µeq/L describe the biological effects at a range of ANC concentrations. See Table 4.1-1.

Table 4.1-1. Aquatic Status Categories

Category Label	**ANC Levels***	**Expected Ecological Effects**
Acute Concern	<0 micro equivalent per Liter (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 acid deposition, brook trout populations may experience lethal effects. Diversity and distribution of zooplankton communities declines sharply.
Elevated Concern	20 – 50 μeq/L	Fish species richness is greatly reduced (more than half of expected species are missing). On average, brook trout populations experience sub-lethal effects, including loss of health and reproduction (fitness). Diversity and distribution of zooplankton communities declines.
Moderate Concern	50 – 100 μeq/L	Fish species richness begins to decline (sensitive species are lost from lakes). Brook trout populations are sensitive and variable, with possible sub-lethal effects. Diversity and distribution of zooplankton communities begin to decline as species that are sensitive to acid 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.

4.1.3.1 Surface Water Assessment Using Monitoring Data

Current acid-base condition and the biological status of 175 lakes in the Adirondacks and 60 streams in the Shenandoah National Park and surrounding areas were assessed by grouping surface water ANC concentrations into the five aquatic status categories. This grouping allows for the evaluation of the range of current biological conditions under current nitrogen and sulfur deposition loads for this subpopulation of waterbodies. Surface water chemistry data were used from two EPA-administered surface water monitoring and survey programs: the TIME and the LTM programs. The years 2002 and 2006 were evaluated. Average yearly ANC concentrations were calculated from weekly values for LTM sites and monthly values for TIME sites. In the Adirondacks region, the 175 lakes consist of 60 LTM lakes and the regional EMAP probability sample of 115 lakes. The total number of target Adirondack lakes included in the EMAP frame was 1,829 (SE = 244). Details of the EMAP design were given by Larsen et al. (1994). In the

Shenandoah National Park and surrounding areas, the 60 lakes were from LTM program (**Figure 4.1-3**).

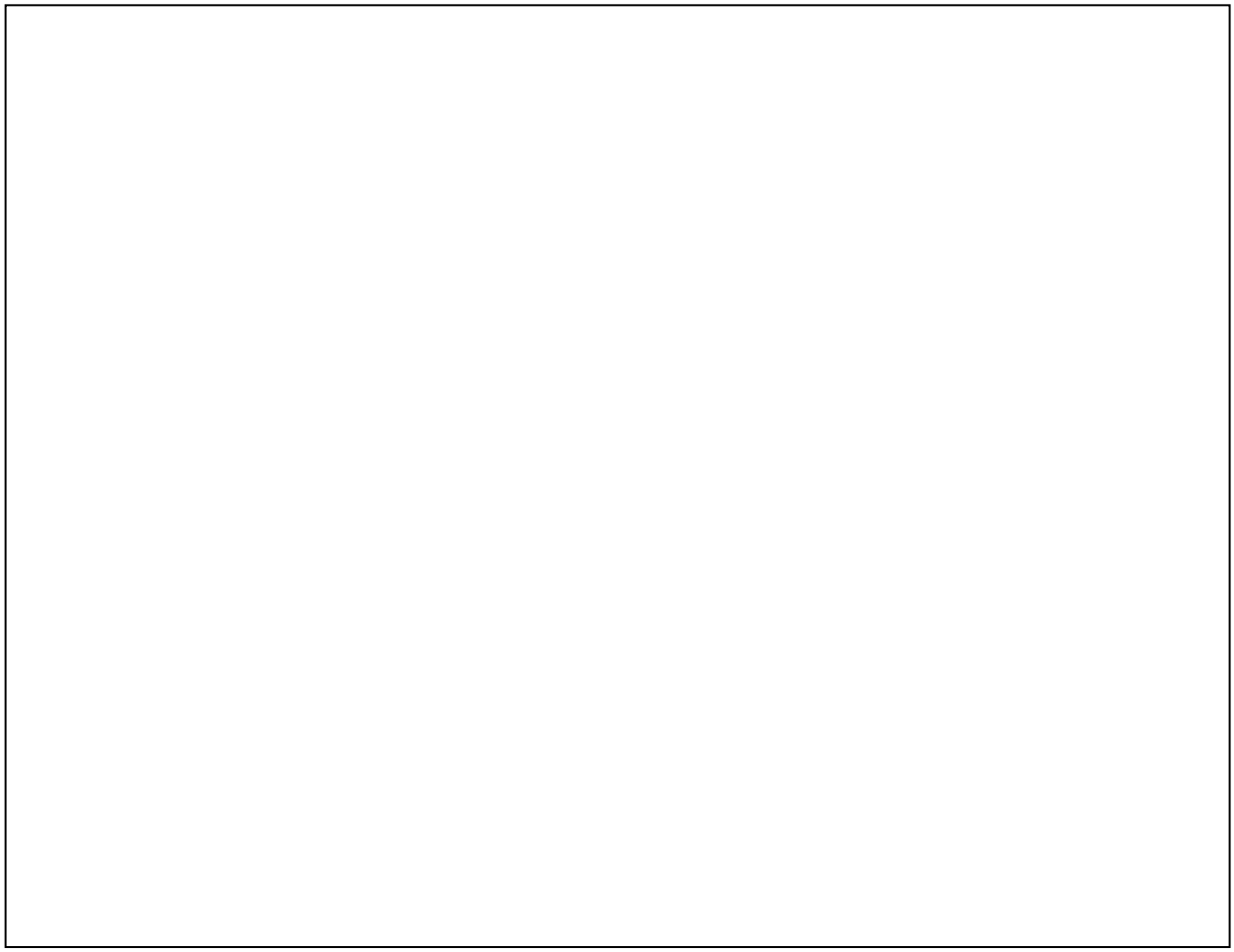

Figure 4.1-3. Site locations. *To be included in second draft REA*.

4.1.3.2 Surface Water Assessment Using Modeled Outputs

The MAGIC model was used to determine the natural conditions of the lakes in each 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). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of (1) a 2–10 submodel in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_{42-} adsorption, cation exchange, dissolution-precipitation-speciation of Al, and dissolution-speciation of inorganic carbon; and (2) a mass balance submodel in which the flux of major ions to and from the soil is assumed to be controlled by

atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. Thus, the degree and rate of change of surface water acidity depend both on flux factors and the inherent characteristics of the affected soils. The advantage of using a model like MAGIC is that it allows us to directly link known amounts of nitrogen and sulfur deposition to specific surface water ANC values and biological effects. See Section 4.3.1 for more details regarding the model MAGIC. .

Surface water ANC values for 44 lakes in the Adirondacks and 60 streams in the Shenandoah National Park and surrounding areas were modeled using 2002 levels of deposition. The resulting surface water ANC concentrations from the model were grouped accordingly to the five categories for the years from 2002 through 2007.

4.1.4 Critical Loads

Surface water chemistry data from LTM, TIME, and EMAP programs were used to calculate the critical load of 175 lakes in the Adirondacks and 60 streams in the Shenandoah National Park region. A critical load is simply the level of acidic deposition that a watershed can receive and still maintain an acid-base balance or ANC level that protects the biological community. In other words, it's the "buffering" capacity of a watershed to neutralize the addition of acidic deposition, such as SO_4^{2-} or NO_3^-, to the system and maintain a value of ANC that provides a level of biological protection. The buffering capacity of a watershed is determined by a host of biogeophysical factors, including base cation concentrations, base cation weathering rates, uptake by vegetation, rate of surface water flow, soil depth, and bedrock, which are best estimated by calculating a critical load. 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., >50 meq/m^2/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 addition acidic anions and protect aquatic life, making the system less susceptible to acidification.

ANC was used to link the water chemistry to the relevant community level biological changes or "protection." Three levels of biological protection or risk (i.e., ANC_{limit}) were used: ANC values of above 0 μeq/L (low protection), above 20 μeq/L (modest protection), and above 50 μeq/L (moderate protection). Detrimental effects are noted for waterbodies with these ANC levels, including decreased fitness and some loss in species diversity, with the effects being more severe near the 20 μeq/L ANC threshold. ANC values above 100 μeq/L are generally not considered because many waterbodies have ANC values naturally below that point and biota are not often harmed (see Figure 4.1-2). Thus, an ANC above 50 μeq/L gives moderate protection from species loss and fitness decline of aquatic organisms (Table 4.1-1). Below 20 μeq/L, all communities exhibit some negative effects (see Figure 4.1-2, Table 4.1-1), particularly because surface waters become susceptible to episodic acidification and associated harmful effects (where ANC goes below zero). An ANC of 0 μeq/L protects surface waters from becoming acidic, but overall, offers little to no protection of the biota (see Figure 4.1-2, Table 4.1-1).

The percent of waterbodies receiving current nitrogen and sulfur deposition loads above harmful levels were determined by subtracting the current deposition from each of the three calculated critical loads of ANC (0 μeq/L, 20 μeq/L, 50 μeq/L). Waterbodies with positive values (i.e., deposition – critical load) are protected, while negative values (i.e., deposition of nitrogen and sulfur exceed the critical load) are assumed to be adversely harmful to the biological community. Also, by repeating the assessment with three different threshold levels (above 0 μeq/L, above 20 μeq/L, and above 50 μeq/L), uncertainty can be accounted for in the level of protection of acidification. For both ANC levels of above 20 μeq/L and above 50 μeq/L, the number of waterbodies that maintain ANC conditions above these levels were determined using the same streams and lakes used to calculate susceptibility.

The Steady-State Water Chemistry Model (SSWC) was used to estimate critical load for each biological protective level. In order to assess current conditions for each waterbody, the calculated critical load for the three biological protection levels were compared to 2002 total wet and dry acidic deposition to determine which sites exceed their biological protection level. Estimates of wet and dry deposition for 2002 were based on measured values from the National Atmospheric Deposition Program (NADP) network combined with modeled values based on the Community Multiscale Air Quality (CMAQ) model, respectively. See Section 54.4 for more details.

4.2 MODELING APPROACH

4.2.1 MAGIC

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 the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of (1) a 2–10 submodel in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO42- adsorption, cation exchange, dissolution-precipitation-speciation of Al, and dissolution-speciation of inorganic carbon; and (2) a mass balance submodel in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. Thus, the degree and rate of change of surface water acidity depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and Al. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of aluminum hydroxide ($Al(OH)_3$). Aluminum speciation is calculated by considering hydrolysis reactions, as well as complexation with SO_4^{2-} and fluoride (F^-). The effects of CO_2 on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. Weathering and the uptake rate of nitrogen are assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included.

Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry (for complete details of the model, see Cosby et al., 1985 a, b; 1989). MAGIC was used to reconstruct the history of acidification and to simulate the future trends on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepisto et al., 1988; Whitehead

et al., 1988; Cosby et al., 1989, 1990, 1996; Hornberger et al., 1989; Jenkins et al., 1990a–c; Wright et al., 1990, 1994; Norton et al., 1992; Sullivan and Cosby, 1998; Sullivan et al., 2004).

The input data required in this project for aquatic and soils resource modeling with the MAGIC model (i.e., stream water, catchment, soils, and deposition data) were assembled and maintained in databases for each site modeled (electronic spreadsheets and text-based MAGIC parameter files). Model outputs for each site were archived as text-based time-series files of simulated variable values. The outputs were also concatenated across all sites and maintained in electronic spreadsheets.

4.2.1.1 Input Data and Calibration

The calibration procedure requires that streamwater chemistry, soil chemical and physical characteristics, and atmospheric deposition data be available for each watershed. The water chemistry data needed for calibration are the concentrations of the individual base cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and acid anions (Cl^{-}, SO_4^{2-}, NO_3^{-}) and the stream pH. The soil data used in the model include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable bases on the soil (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}). The atmospheric deposition inputs to the model include all major ions and must be estimates of total deposition, not just wet deposition.

The acid-base chemistry modeling for this project was conducted using 2002 as the Base Year. The effects models were calibrated to the available atmospheric deposition and water chemistry data and then interpolated or extrapolated to yield Base Year estimates of lake water chemistry in the year 2002, which served as the starting point for modeling of current water chemistry (i.e., 2002 to 2100, etc.).

4.2.1.2 Lake and Stream, and Soil data for Calibration

Several water chemistry databases were acquired for use in model calibration. Data were derived primarily from the EMAP and TIME survey and monitoring efforts. The required lake water and soil composition data for the modeling efforts included the following measurements:

- Stream water composition— pH, ANC, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-}, NO_3^{-}, and Cl^{-}
- Soil properties— thickness and total cation exchange capacity, exchangeable bases (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) bulk density, porosity, and pH where available; the stream water

chemistry database also included dissolved organic and inorganic carbon, H_4SiO_4, and inorganic monomeric Al (Ali).

4.2.1.3 Wet Deposition and Meteorology Data for Calibration

MAGIC requires, as atmospheric inputs for each site, estimates of the total annual deposition (eq/ha/yr) of eight ions, and the annual precipitation volume (m/yr). The eight ions are: Ca, Mg, Na, K, NH_4, SO_4, Cl, and NO_3. Total deposition of an ion at a particular site for any year can be represented as combined wet, dry, and occult (cloud and fog) deposition:

$$\text{TotDep} = \text{WetDep} + \text{DryDep} + \text{OccDep} \quad (2)$$

Inputs to the MAGIC model are specified as wet deposition (the annual flux in meq/m2/yr) and a dry and occult deposition factor (DDF, unitless), which is multiplied by the wet deposition in order to get total deposition:

$$\text{TotDep} = \text{WetDep} * \text{DDF} \quad (3)$$

Given an annual wet deposition flux (WetDep), the ratio of dry deposition to wet deposition (DryDep/WetDep), and the ratio of occult deposition to wet deposition (OccDep/WetDep) for a given year at a site, the total deposition for that site and year is uniquely determined.

In order to calibrate MAGIC, time-series of total deposition are needed for the calibration year of 2002 and the 140 years preceding the calibration for the historical reconstructions that are part of the calibration protocol. The procedure for providing a time-series of total deposition inputs to MAGIC is as follows.

The absolute values of wet deposition and DDF for each ion are provided for a Reference Year at each site. For this case study, the MAGIC Reference Year was 2002 at all sites. Given the Reference Year deposition values, the deposition data for the historical and calibration periods, and potentially any future deposition scenarios, can be calculated using the Reference Year absolute values and scaled time-series of wet deposition and DDF that give the values for a given year as a fraction of the Reference Year value. For instance, to calculate the total deposition of a particular ion in some historical or future year j:

$$\text{TotDep}(j) = [\text{WetDep}(0) * \text{WetDepScale}(j)\ ] * [\ \text{DDF}(0) * \text{DDF Scale}(j)] \quad (4)$$

where

WetDep(0) = the Reference Year wet deposition (meq/m2/yr) of the ion

WetDepScale(j) = the scaled value of wet deposition in year j (expressed as a fraction of the wet deposition in the Reference Year)

DDF(0) = the dry and occult deposition factor for the ion for the Reference Year

DDFScale(j) = the scaled value of the dry and occult deposition factor in year j (expressed as a fraction of the DDF in the Reference Year 2002).

The absolute value of wet deposition used for the Reference Year is time and space specific— varying geographically within the region, varying locally with elevation, and varying from year to year. It is desirable to have the estimates of wet deposition take into account the geographic location and elevation of the site, as well as the year for which calibration data are available. Therefore, estimates of wet deposition used for the Reference Year should be derived from a procedure (model) that has a high spatial resolution and considers elevation effects. As described below, the absolute wet deposition values used for the Reference Year in this project were derived from observed data based on the NADP.

The absolute value of the DDF used for the Reference Year specifies the ratio between the absolute amounts of wet and total deposition. This ratio is less variable in space and time than is the estimate of wet deposition. That is, if in a given year, the wet deposition goes up, then the total deposition usually goes up also (and conversely); and if the elevation or aspect of a given site results in lower wet deposition, the total deposition also will often be lower (and conversely). Therefore, estimates of the absolute vales of DDF may be derived from a procedure (model) that has a relatively low spatial resolution and/or temporally smoothes the data. Estimates of the absolute values of the DDF for the Reference Year at each site in this project were derived from the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model (Shannon, 1998), as described below.

The long-term scaled sequences used to specify time-series of deposition inputs for MAGIC simulations usually do not require detailed spatial or temporal resolution. Scaled sequences of wet deposition or DDF (normalized to the same reference year) at neighboring sites will be similar, even if the absolute wet deposition or DDF at the sites are different due to local aspect, elevation, etc. Therefore, if the scaled long-term patterns of any of these do not vary much from place to place, estimates of the scaled sequences (as for estimates of absolute DDF

values) may be derived from a model that has a relatively low spatial resolution. As described in the following sections, output from the ASTRAP model was used to constrict scaled sequences of both wet deposition and DDF for this project.

4.2.1.4 Wet Deposition Data (Reference Year and Calibration Values)

The absolute values of wet deposition used for defining the Reference Year and for the MAGIC calibrations must be highly site-specific. We used estimated wet deposition data for each site derived from the spatial interpolation model of Grimm and Lynch (2004), referred to here as the Grimm model. The Grimm model is based on observed wet deposition at NADP monitoring stations and provides a spatially interpolated value of wet deposition of each of the eight ions needed for MAGIC. The model also makes a correction for changes in precipitation volume (and thus wet deposition) based on the elevation at a given site. This correction arises from a model of orographic effects on precipitation volumes derived from regional climatological data.

The latitude, longitude, and elevation of the 100+ MAGIC modeling sites were provided as inputs to the Grimm model. The model outputs were quarterly and annual wet deposition and precipitation estimates for each modeling site. The annual data were used to define the Reference Year and for MAGIC calibration and simulation. The NADP data (and thus the estimates provided by Grimm's model) cover the period 1983 to 2002. This period includes the MAGIC Reference Year and the calibration years for all of the modeling sites in this project.

4.2.1.5 Dry and Occult Deposition Data and Historical Deposition Sequences

Absolute values of DDF and the scaled sequences of wet deposition and DDF are derived for this project from simulations using the ASTRAP model. The ASTRAP model was used to provide estimates of historical wet, dry, and occult deposition of sulfur and oxidized nitrogen at modeled sites of the two case studies regions. The ASTRAP sites included 10 existing NADP deposition. For each of the modeled sites, ASTRAP produced wet, dry, and occult deposition estimates of sulfur and oxidized nitrogen every 10 years, starting in 1900 and ending in 1990. The model outputs are smoothed estimates of deposition roughly equivalent to a 10-year moving average centered on each of the output years. The outputs of ASTRAP were used to estimate the absolute DDF for each site (using the DryDep/WetDep and OccDep/WetDep ratios from the

ASTRAP 19 output) and to set up the scaled sequences of historical wet deposition and historical DDF for the calibration of each site modeled in this project.

The wet, dry, and occult deposition estimates provided by ASTRAP for each year (for both sulfur and oxidized nitrogen) at each ASTRAP site were used to calculate the MAGIC DDF for each year and each site. This provided time series of DDF for sulfur and oxidized nitrogen for each ASTRAP site extending from 1850 to 1990. The value of DDF for 1990 was used as the absolute value of DDF for the Reference Year (i.e., no change was assumed for DDF from 1990 to 2002). The resulting time series of DDF values from 1900 to 2002 for each ASTRAP site were normalized to the 2002 values to provide historical scaled sequences of DDF at each ASTRAP site.

The time series of wet deposition estimates for each ASTRAP site were used to construct historical scaled sequences of wet deposition. The absolute wet deposition outputs of ASTRAP were normalized to their 1990 values and converted to scaled sequences of wet deposition from 1850 to 1990 for each ASTRAP site. It was then necessary to couple these historical scaled wet deposition sequences from 1990 to the MAGIC Reference Year 2002. This coupling was accomplished using scaled observed changes in wet deposition from 1850 to 2002 derived from the Grimm model.

4.2.1.6 Protocol for MAGIC Calibration and Simulation at Individual Sites

The aggregated nature of the MAGIC model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs), and the outputs (streamwater and soil chemical variables called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations adjusting the optimized parameters, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated.

There are eight parameters to be optimized in this procedure (the weathering and the selectivity coefficient of each of the four base cations), and there are eight observations that are used to drive the estimate (i.e., current soil exchangeable pool size and current output flux of each of the four base cations). If new assumptions or new values for any of the fixed variables or inputs to the model are adopted, the model must be re-calibrated by re adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

Estimates of the fixed parameters, the deposition inputs, and the target variable values to which the model is calibrated all contain uncertainties. A "fuzzy optimization" procedure was utilized in this project to provide explicit estimates of the effects of these uncertainties. The procedure consists of multiple calibrations at each site using random values of the fixed parameters drawn from a *range* of fixed parameter values (representing uncertainty in knowledge of these parameters) and random values of Reference Year deposition drawn from a *range* of total deposition estimates (representing uncertainty in these inputs). The final convergence (completion) of the calibration is determined when the simulated values of the criterion variables are within a specified "acceptable window" around the nominal observed value. This "acceptable window" represents uncertainty in the target variable values being used to calibrate the site.

Each of the multiple calibrations at a site begins with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized using an algorithm seeking to minimize errors between simulated and observed criterion variable. Calibration success is judged when all criterion values simultaneously are within their specified "acceptable windows", 21 (which may occur before the absolute possible minimum error is achieved). This procedure is repeated ten times for each site.

For this project, the "acceptable windows" for base cation concentrations in streams were taken as +/- 2 μeq/L around the observed values. "Acceptable windows" for soil exchangeable base cations were taken as +/- 0.2% around the observed values. Fixed parameter uncertainty in soil depth, bulk density, cation exchange capacity, stream discharge, and stream area were assumed to be +/- 10% of the estimated values. Uncertainty in total deposition was +/- 10% for all ions.

The final calibrated model at the site is represented by the ensemble of parameter values of all of the successful calibrations at the site. When performing simulations at a site, all of the calibrated parameter sets in the ensemble are run for a given historical or future scenario. The result is multiple simulated values of each variable in each year, all of which are acceptable in the sense of the calibration constraints applied in the fuzzy optimization procedure. The median of all the simulated values within a year is the "most likely" response for the site in that year. For this project, whenever single values for a site are presented or used in an analysis, these values are the median values derived from running all of the ensemble parameter sets for the site.

An estimate of the uncertainty (or reliability) of a simulated response to a given scenario can also be derived from the multiple simulated values within a year resulting from the ensemble simulations. For any year in a given scenario, the largest and smallest values of a simulated variable define the upper and lower confidence bounds for that site's response for the scenario under consideration. Thus, for all variables and all years of the scenario, a band of simulated values can be produced from the ensemble simulations at a site that encompasses the likely response (and provides an estimate of the simulation uncertainty) for any point in the scenario. For this project, whenever uncertainty estimates are presented, the estimate is based on this range of simulated values in any year arising from the simulations using the ensemble parameter sets. Three classes of uncertainty were examined for both case study areas that include uncertainty due to specification of

- Soils Data for calibration
- Stream Water Data calibration
- Deposition Data calibration.

4.2.1.7 Combined Model Calibration and Simulation Uncertainty

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 66 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

31 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 "confidence") width for the simulation at any point in time. All ten 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.

4.3 CRITICAL LOADS

4.3.1 The Steady-State Water Chemistry Model

The critical load of acidity for lakes or streams was derived from present-day water chemistry using the SSWC model. The SSWC model is 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 pre-selected 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., pre-industrial) inputs of base cations in the surface water.

Critical loads of acidity, CL(A), were calculated for each waterbodies from the principle that the acid load should not exceed the non-marine, non-anthropogenic base cation input and sources and sinks in the catchment minus a buffer to protect selected biota from being damaged:

$$CL(A) = BC^*_{dep} + BC_w - Bc_u - ANC_{limit} \quad (5)$$

where

BC^*_{dep} ($BC^*=Ca^*+Mg^*+K^*+Na^*$) = the sea-salt corrected (see section XX) non-anthropogenic deposition of base cations,

BC_w = the average weathering flux,

Bc_u ($Bc=Ca^*+Mg^*+K^*$) = the net long-term average uptake of base cations in the biomass (i.e., the annual average removal of base cations due to harvesting)

ANC_{limit} = the lowest ANC-flux that protects the biological communities.

Since the average flux of base cations weathered in a catchment and reaching the lake is difficult to measure or compute from available information, the average flux of base cations and the resulting critical load estimation were derived from water quality data (Sverdrup et al., 1990; Henriksen et al., 1992; Henriksen and Posch, 2001). Weighted annual mean water chemistry values were used to estimate average base cation fluxes, which were calculated from water chemistry data collected from the LTM/TIME monitoring networks (see Section 4.1.2.1).

The pre-acidification non-marine flux of base cations for each lake or stream, BC^*_0, is

$$BC^*_o = BC^*_{dep} + BC_w - Bc_u \quad (6)$$

Thus, critical load for acidity can be re-written as

$$CL(A) = BC^*_0 - ANC_{limit} = Q\cdot([BC^*]_0 - [ANC]_{limit}) \quad (7)$$

where the second identity expresses the critical load for acidity in terms of catchment runoff Q (in m/yr) and concentration ([x] = X/Q).

4.3.2 Pre-industrial Base Cation Concentration

Present-day surface water concentrations of base cations are elevated above their steady-state concentrations because of base cation leaching through ion exchange in the soil due to anthropogenic inputs of SO_4^- to the watershed. For this reason, present-day surface water base cation concentrations are higher then natural or pre-industrial levels, which if not corrected for, would result in critical load values not to be in steady-state condition. To estimate the pre-acidification flux of base cations, we started by calculating the present flux of base cations, BC^*_t, given by

$$BC^*_t = BC^*_{dep} + BC_w - Bc_u + BC_{exc} \quad (8)$$

where

BC_{exc} = the release of base cations due to ion-exchange processes.

Assuming that deposition, weathering rate, and net uptake have not changed over time, BC_{exc} we obtained by subtracting Equation 2 from equation 4:

$$BC_{exc} = BC^*_t - BC^*_0 \quad (9)$$

This present-day excess production of base cations in the catchment was related to the long-term changes in inputs of non-marine acid anions ($\Delta SO^*_2 + \Delta NO_3$) by the F-factor (see below):

$$BC_{exc} = F \cdot (\Delta SO^*_2 + \Delta NO_3) \quad (10)$$

For the pre-acidification base cation flux, we thus get from Equation (5):

$$BC^*_0 = BC^*_t - F \cdot (SO^*_{4,t} - SO^*_{4,0} + NO^*_{3,t} - NO^*_{3,0}) \quad (11)$$

The pre-acidification nitrate concentration, $NO^*_{3,0}$, is was assumed to be zero. Finally, the present exceedances of the critical load of acidity is defined as

$$Ex(A) = S^*_{dep} + N_{leach} - CL(A) \quad (12)$$

While sulfate is assumed to be a mobile anion ($S_{leach} = S^*_{dep}$), nitrogen is to a large extent retained in the catmint by various processes; therefore, N_{dep} can not be used directly in the exceedances calculation. Therefore, only present-day exceedances can be calculated from the leaching of N, N_{leach}, which is determined from the sum of measured concentration of nitrate and ammonia in the stream chemistry. No nitrogen-deposition data are required for exceedances

calculations; however, Ex(A) quantifies only the exceedances at present rates of retention of nitrogen in the catchment.

4.3.3 F-factor

An F-factor was used to correct the concentrations and estimate pre-industrial base concentrations. An F-factor is a ratio of the change in non-marine base cation concentration due to changes in strong anion concentrations (Henriksen, 1984; Brakke et al., 1990):

$$F = [BC^*]_t - [BC^*]_0 / [SO_4^*]_t - [SO_4^*]_0 + [NO3^*]_t - [NO3^*]_t \quad (13)$$

where the subscripts t and 0 refer to present and pre-acidification concentrations, respectively. If F=1, all incoming protons are neutralized in the catchment (only soil acidification); at F=0, none of the incoming protons are neutralized in the catchment (only water acidification). The F-factor was estimated empirically to be in the range 0.2–0.4, based on the analysis of historical data from Norway, Sweden, the United States, and Canada (Henriksen, 1984). Brakke and colleagues (1990) later suggested that the F-factor should be a function of the base cation concentration:

$$F = \sin (pie/2\ Q \cdot [BC^*]_t/[S] \quad (14)$$

where

Q = the annual runoff (m/yr)

[S] = the base cation concentration at which F=1; and for [BC*]t>[S] F is set to 1.

For Norway [S] has been set to 400 meq/m3 (ca. 8 mgCa/L) (Brakke et al., 1990).

The pre-acidification sulphate concentration in lakes, $[SO4^*]_0$, is assumed to consist of a constant atmospheric contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al., 1989). A XX pre-acidification sulfate concentration was used.

4.3.4 ANC Limit

Four classes of ANC limited were estimated: Suitable, ANC > 50 μeq/L; Indeterminate, ANC 20–50 μeq/L; Marginal, ANC 0–20 μeq/L; and Unsuitable, ANC < 0 μeq/L.

4.3.5 Sea Salt Corrections

The model applies a sea salt correction to the water chemistry concentrations. The equations below were applied to all lakes and streams, which was also applied to all the New England states and eastern Canadian provinces for the New England Governors and Eastern Canadian Premier (NEGECP) assessment. The equations correct for sea salt. An asterisk (*) indicates the value has been corrected for sea salt, Units are in ueq/L.

$$Ca^{*} = (Ca - (CL \cdot 0.0213)) \quad (10)$$

$$Mg^{*} = (Mg - (CL \cdot 0.0669)) \quad (11)$$

$$Na^{*} = (Na - (CL \cdot 0.557)) \quad (12)$$

$$K^{*} = (K - (CL \cdot 0.0.0206)) \quad (13)$$

$$SO_4^{*} = (SO_4 - (CL \cdot 0.14)) \quad (14)$$

5. RESULTS (NOT COMPLETE)

5.1 ADIRONDACK REGION OF NEW YORK

5.1.1 Surface Water Trends from 1990-2006

Since the mid-1990s, lakes in the Adirondack region have shown signs of recovery from nitrogen and sulfur deposition and acid rain. Emissions of SO_2 and NO_x have been reduced (Figure 3.1-1), and, as a result, sulfate and nitrate concentrations have decreased in surface waters by approximately 26% and 13%, respectively. This has led to improvement in the acid ANC of these waterbodies, which helps to neutralize or buffer the acidic deposition (**Figure 5.1-1**).

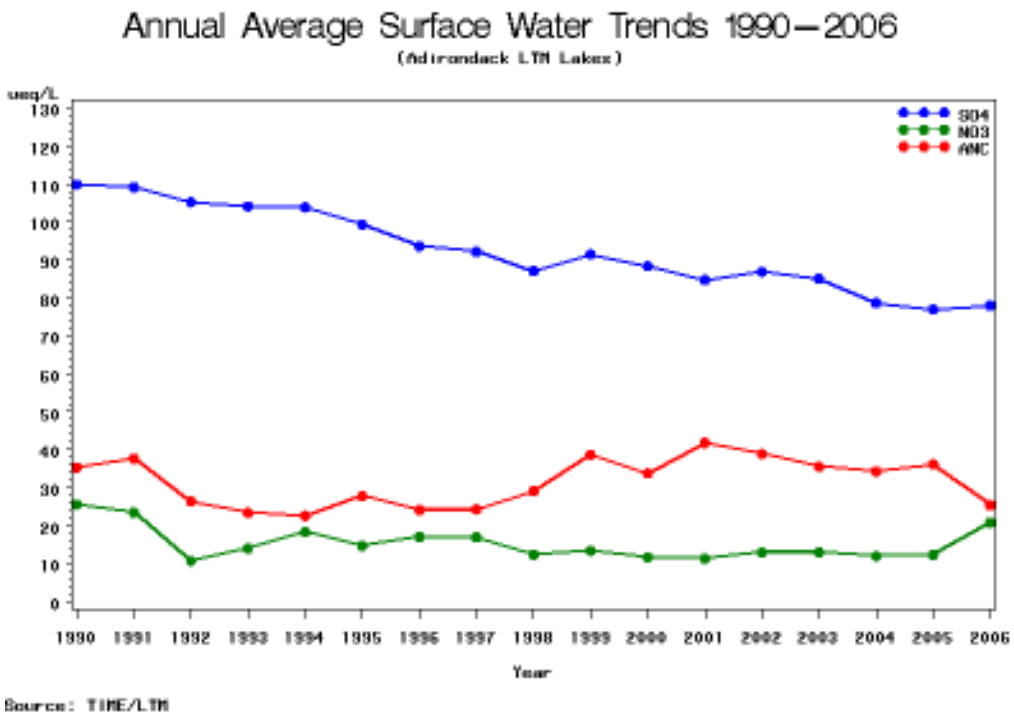

Figure 5.1-1. Trends in LTM monitored lakes in the Adirondacks of New York. Both sulfate and nitrate concentrations have decreased in surface waters by approximately 26% and 13%, respectively. This has led to improvement in the ANC of these waterbodies.

5.1.2 Condition of Surface Water Acidity

5.1.2.1 Modeled ANC Conditions

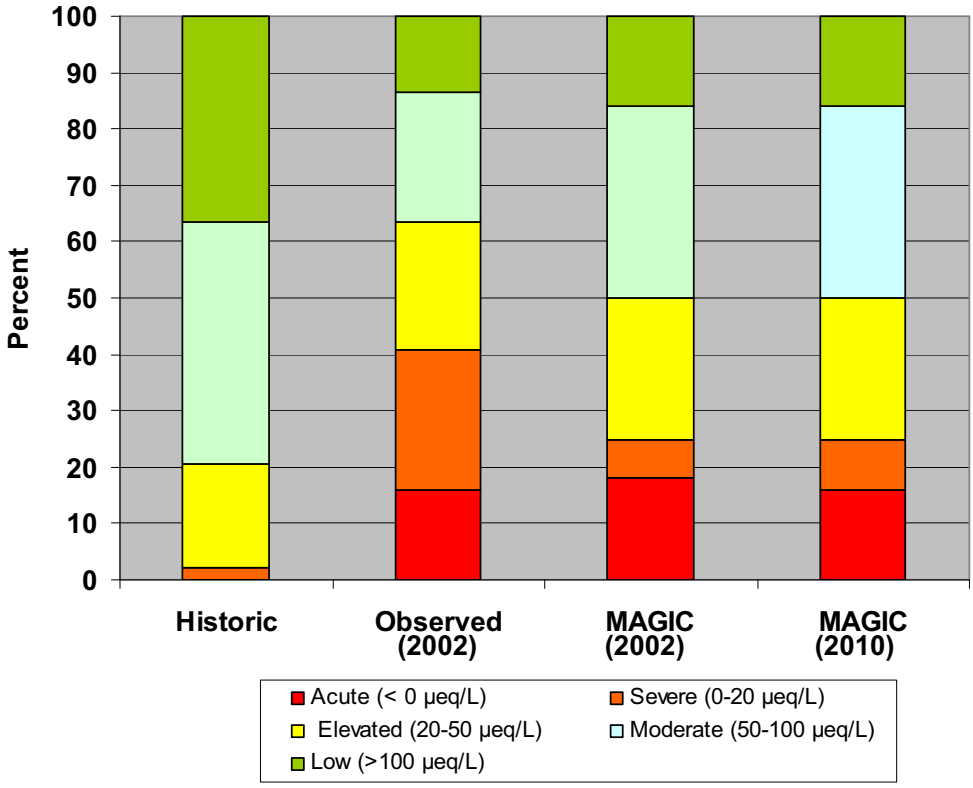

Figure 5.1-2. Predicted distribution of surface water ANC concentrations of 44 lakes across five assessment ANC categories based on results from MAGIC modeling (Historic and MAGIC 2002, 2010) and TIME/LTM monitoring data (Observed, 2002) for the Adirondacks Case Study Area. Individual bar graphs represent the percentage of the 44 studied lakes that fall into the five ANC categories. Categories of ANC include: Acute = <0 µeq/L, Severe = 0–20 µeq/L, Elevated = 20–50 µeq/L; Moderate = 50–100 µeq/L, Low = >100 µeq/L. Historical conditions represent the surface water ANC concentrations modeled by MAGIC before anthropogenic acidic deposition occurred (i.e., before 1860). Current condition is assessed as year 2002. Despite improvement in surface water ANC concentrations (Figure 5.1-1), both observed and modeled results show a higher percent of lakes that have acute and severe acidic conditions compared to their historical conditions.

5.1.2.2 Critical Load

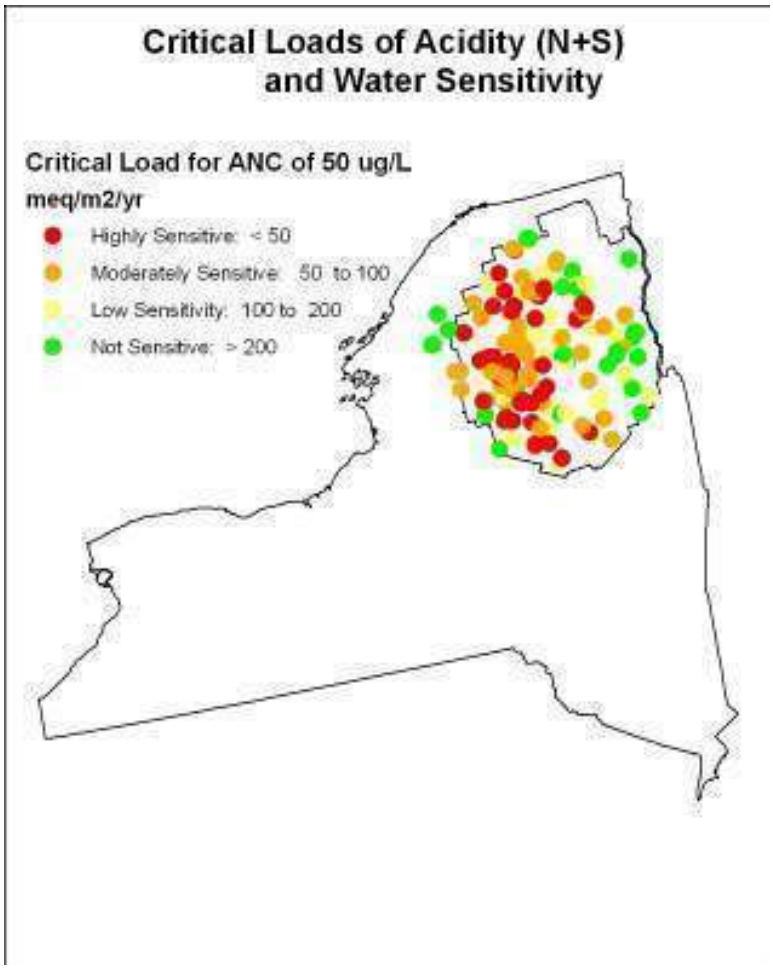

Figure 5.1-3. Critical loads of surface water acidity for an ANC concentrations of 50 μeq/L. Each dot represents an estimated amount of acidic deposition (i.e., critical load) that each lake's watershed can receive and still maintain an surface water ANC concentration of above 50 μeq/L. Watersheds with critical load values less than 100 meq/m^2/yr (red and orange dots) are most sensitive to surface water acidification while watersheds with values greater then 100 meq/m^2/yr (yellow and green dots) are the least sensitive sites.

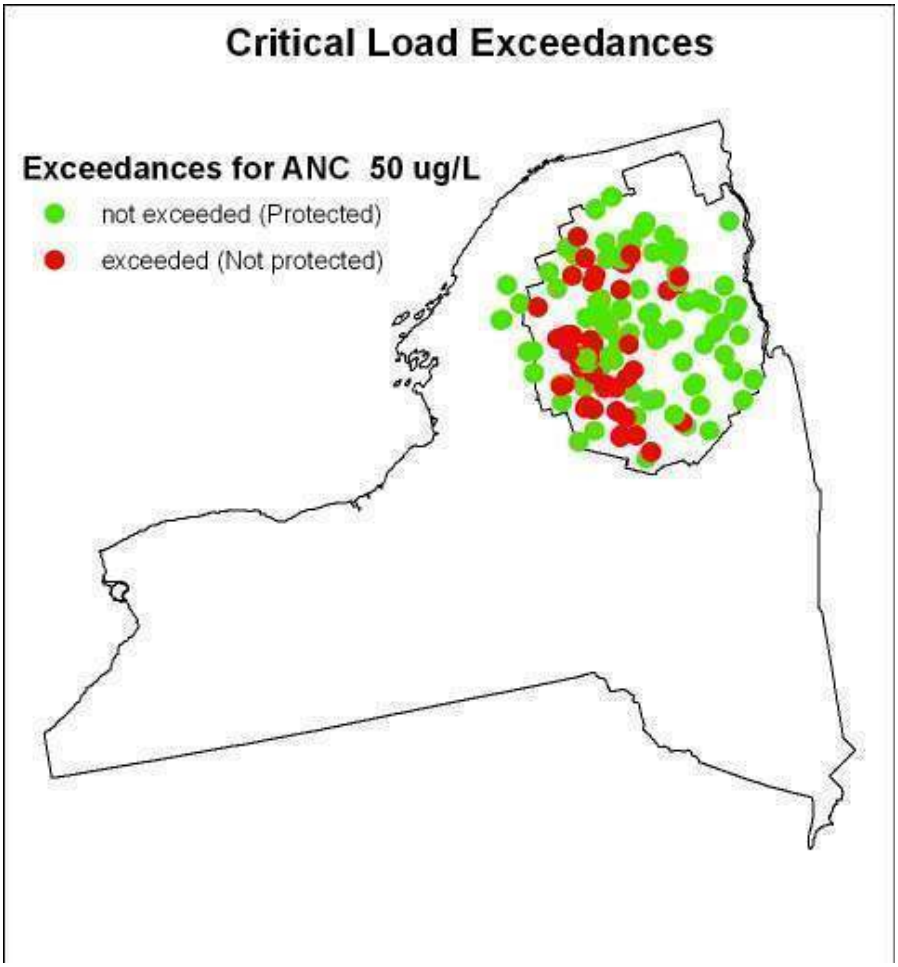

Figure 5.1-4. Critical load exceedances for ANC concentration of 50 μeq/L. Green dots represent lakes where current nitrogen and sulfur deposition is above their critical load and maintain an ANC concentration above 50 μeq/L. Red dots are lakes where current nitrogen and sulfur deposition exceeds their limit and are affected by current nitrogen and sulfur deposition load. An ANC limit of 50 μeq/L gives moderate protection from species loss and fitness decline of aquatic organisms (Table 4.1-1).

Table 5.1-1. Number and percentage of lakes that have current nitrogen and sulfur deposition loads that prevent surface water ANC concentration to be below an ANC of 50, and 20 ug/L for lakes in the Adirondack Mountains.

	50 ug/L	**20 ug/L**
LTM (N=60)	37 (62%)	24 (40%)
TIME (N=117)	25 (21%)	7 (6%)
MAGIC (N=44)	21 (48%)	7 (16%)

5.1.2.3 Uncertainty and Risk

5.2 SHENANDOAH NATIONAL PARK AND SURROUNDING AREAS, VIRGINIA

5.2.1 Surface Water Trends from 1990–2006

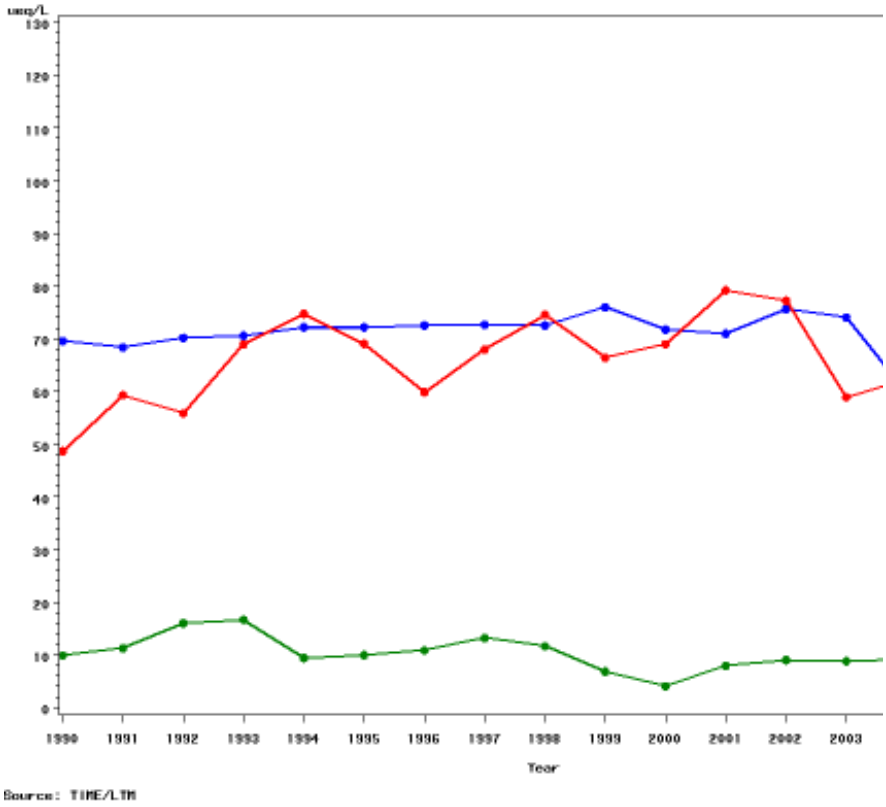

Figure 5.1-5. Trend in SO_4, NO_3, and ANC from LTM network.

5.2.2 Condition of Surface Water Acidity

5.2.2.1 Modeled ANC Conditions

5.2.2.2 Critical Load

5.2.2.3 Uncertainty and Risk

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ATTACHMENT 4

TERRESTRIAL ACIDIFICATION CASE STUDY

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August 15, 2008

Terrestrial Acidification Case Study

Draft

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TABLES

ACRONYMS AND ABBREVIATIONS

ANC	acid neutralizing capacity
Ca	calcium
CAL	critical load of acidity
CLF	critical load function
CLRTAP	Convention on Long-Range Transboundary Air Pollution
cm	centimeter
CMAQ	Community Multiscale Air Quality model
ESSC	Earth System Science Center
FIA	Forest Inventory and Analysis National Program
GIS	geographic information systems
ha	hectare
HBEF	Hubbard Brook Experimental Forest
HBES	Hubbard Brook Ecosystem Study
ISA	Integrated Science Assessment
kg	kilogram
km	kilometer
km^2	square kilometer
LTER	Long-Term Ecological Research
m	meter
m^2	square meter
MEA	Millennium Ecosystem Assessment
Mg	magnesium
mm	millimeter
mo	month
NO_3^-	nitrate
NO_x	nitrogen oxides
NRCS	National Resources Conservation Service
NSF	National Science Foundation
SMB	Simple Mass Balance
SO_4^{2}	sulfate
SO_2	sulfur dioxide
SO_x	sulfur oxides
SSURGO	Soil Survey Geographic Database
UNECE	United Nations Economic Commission for Europe
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
USGS	U.S. Geological Survey

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1. BACKGROUND

The selection and performance of case studies represent Steps 3 and 4, respectively, of the 7-step approach to planning and implementing a risk/exposure assessment of nitrogen oxides (NO_x) and sulfur oxides (SO_x) deposition on ecosystems, as presented in the April 2008 *Scope and Methods Plan for Risk Exposure Assessment* (U.S. EPA, 2008). Step 4 entails evaluating the current nitrogen and sulfur loads and effects to a chosen case study assessment area, including ecosystem services. In this case study, we will evaluate the current wet and dry nitrogen and sulfur deposition load to terrestrial ecosystems and the role atmospheric deposition can play in the acidification of a terrestrial ecosystem.

Deposition of NO_x and SO_x can result in acidification of certain terrestrial ecosystems. Because ecosystems may respond differently, it will be necessary to first perform risk exposure assessment case studies that are unique to the effect and ecosystem type. This report presents a proposed quantitative approach to analyzing the acidification effects of SO_x and NO_x deposition on red spruce and sugar maples.

Acidification

Acidification is the process of increasing the acidity of a system (e.g., lake, stream, forest soil). Within soils, acidification occurs through increases in hydrogen cations or protons. Terrestrial acidification occurs as a result of both natural biogeochemical processes and acidic deposition where mineral acids are added to the soils. Acidic deposition increases concentrations of sulfur and nitrogen in soil, which accelerates leaching of sulfate (SO_4^{2-}) and nitrate (NO_3^-) from soil to drainage water. Under natural conditions (i.e., low atmospheric deposition of sulfur and nitrogen), the limited mobility of anions in the soil controls the rate of base cation leaching. However, acidic deposition of sulfur and nitrogen provides anions that are more mobile in the soil environment than naturally occurring anions in the soil; these mineral acid anions can accelerate natural rates of base-cation leaching, particularly calcium (Ca) and magnesium (Mg). If soil base saturation (i.e., the concentration of exchangeable base cations as a percent of the total cation exchange capacity) is 20% to 25%, or lower, inorganic aluminum (Al) can become mobilized, leading to the leaching of Al into soil waters and surface waters (Reuss and Johnson, 1985). This is an extremely important effect of acidic deposition because inorganic Al is toxic to

tree roots, fish, algae, and aquatic invertebrates (U.S. EPA, 2007, Sections 4.2.1, 4.2.1.4, and 4.2.1.5).

1.1 INDICATORS, ENDPOINTS, AND ECOSYSTEM SERVICES

1.1.1 Indicators

There are a variety of indicators that can be used to measure the effects of acidification. **Table 1.1-1** provides a general summary and description of indicator groups. Within the Integrated Science Assessment (ISA), several of these indicators were further supported through references from the literature (**Table 1.1-2**).

Table 1.1-1. Key Indicators of Acidification Due to NO_x and SO_x

Key Indicator Group	**Examples of Indicators**	**Description**
Acid anions	SO_4^{2-}, NO_3^-	Trends in these concentrations reflect recent trends in atmospheric deposition (especially SO_4^{2-}) and in ecosystem responses to long-term deposition (notably NO_3^- and desorbed SO_4^{2-}).
Base cations	Ca^{2+}, Mg^{2+}, $\Sigma(Ca^{2+}+Mg^{2+})$, K^+, Na^+	These cations are mobilized by weathering reactions and cation exchange. They respond indirectly to decreases in SO_4^{2-} and NO_3^- because a reduced input of acids will lead to a reduction of neutralizing processes in the soil, thereby reducing the release of base cations to soil water and runoff water. (Base saturation is included within this category.)
Acidity	pH, (Gran) alkalinity, acid neutralizing capacity (ANC)	These indicators reflect the outcomes of interactions between the changing concentration of acid anions and base cations.
Carbon	carbon:nitrogen ratio	The carbon:nitrogen ratio of soil indicates alterations to the nitrogen biogeochemical cycle

Key Indicator Group	**Examples of Indicators**	**Description**
Metals	Al^{3+}, Fe^{3+}	These metals are mobilized as a response to the deposition of SO_4^{2-} and NO_3^-.
Biological	Forest health, community structure, species composition, taxonomic richness, Index of Biotic Integrity	Ecological effects occur at 4 levels: individual, population, community, and ecosystem. Metrics have been developed for each level to assess the adverse effects of acids.

Table 1.1-2. Literature Support for Selected Indicators of Acidification

Citation	**Main Finding**
Soil Base Saturation	
Reuss, 1983	If base saturation is less than 15% to 20%, exchange ion chemistry is dominated by inorganic Al.
Cronan and Grigal, 1995	Base saturation below about 15% in the soil B-horizon could lead to impacts from Al stress.
Lawrence et al.., 2005	Base saturation declines from 30% to 20% in the upper soil B-horizon showed decreases in diameter growth of Norway spruce.
Bailey et al., 2004	Sugar maple mortality found at Ca saturation less than 2% and Mg saturation less than 0.5% in the upper soil B-horizon.
Johnson et al., 1991; Joslin and Wolfe, 1992; Eagar et al., 1996	In soils with base saturation below about 20%, base cations reserves are so low that Al exchange dominates.
Al Concentrations	
Johnson et al.,1991; Joslin and Wolfe,1992; Eagar et al.,1996	See explanation above.
Cronan and Grigal,1995	There is a 50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. 100% risk for adverse effects on growth at molar ratio value below 0.2.
Johnson et al.,1994a, b	Ca:Al ratios above 1.0 across 4 years were found in a forestland experiencing high mortality.

Citation	Main Finding
DeWitt et al.,2001	Ca:Al ratios of Norway spruce stand below 0.5 showed reduced Mg concentrations in needles in the third year.
Carbon:Nitrogen Ratio	
Aber et al.,2003; Ross et al.,2004	Increased effects of nitrification occur only in soil with carbon:nitrogen ratio below about 20–25.

Source: U.S. EPA, 2007

Much of the literature surrounding terrestrial acidification focuses on Ca and Al as the primary indicators of detrimental effects for trees and other terrestrial vegetation. As such, we have focused our detailed discussion of indicators of terrestrial acidification on these two parameters and the interaction between them. The use of these indicators in combination and through the evaluation framework that will be described within this work ultimately combines all indicator categories described in Table 1-1 except the carbon category. Ca and Al are the focus of the analysis because these indicators have been shown to have quantitative links to tree health.

Schaberg and colleagues (2001) provide a more detailed description of the leaching effects caused by Al:

> Decreases in concentrations of exchangeable calcium are generally attributed to displacement by hydrogen ions, which can originate from either acid deposition or uptake of cations by roots (Johnson and others, 1994a, Richter and others, 1994). A regional survey of soils in northeastern red spruce forests in 1992-93 (fig. 2) has revealed that decreases in exchangeable calcium concentrations in the Oa horizon (a layer within the forest floor, where uptake of nutrients is greatest) can also result from increased concentrations of exchangeable aluminum, which originated in the underlying mineral soil (Lawrence and others, 1995). By lowering the pH of the aluminum-rich mineral soil, acid deposition can increase aluminum concentrations in soil water through dissolution and ion-exchange processes. Once in solution, the aluminum (although not a nutrient) is taken up by roots and transported through the trees to be eventually deposited on the forest floor in leaves and branches.

A continued buildup of aluminum in the Oa horizon can (1) decrease the availability of calcium for roots (Lawrence and others, 1995), (2) lower the efficiency of calcium uptake because aluminum is more readily taken up than calcium when the ratio of calcium to aluminum in soil water is less than 1 (Cronan and Grigal, 1995), and (3) be toxic to roots at high concentrations (Lawrence, et al. 1995).

These findings are further summarized in the ISA (U.S. EPA, 2007), as excerpted below.

Aluminum Concentration in Soil Solution: Ca to Al Ratio (U.S. EPA, 2007, Section 4.2.2.1.2)

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

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

The negative effect of Al mobilization on uptake of Ca by tree roots was proposed by Shortle and Smith (1988), and substantial evidence of this relationship has accumulated over the past 2 decades through field studies (McLaughlin and Tjoelker, 1992; Schlegel et al., 1992; Minocha et al., 1997; Shortle et al., 1997; Kobe et al., 2002) and laboratory studies (Sverdrup and

Warfvinge, 1993; see also review of Cronan and Grigal, 1995). Based on these studies, it is clear that high inorganic Al concentration in soil water can be toxic to plant roots. The toxic response is often related to the concentration of inorganic Al relative to the concentration of Ca, expressed as the molar ratio of Ca to inorganic Al in soil solution. As a result, considerable effort has been focused on determining a threshold value for the ratio of Ca to Al that could be used to identify soil conditions that put trees under physiological stress.

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

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

In summary, a molar ratio of Ca to Al in soil solution can be used as a general index that suggests an increasing probability of stress to forest ecosystems as the ratio decreases. The ratio value of 1.0 is proposed as a general damage threshold, but it cannot be interpreted as a universally applicable threshold in all natural systems. Tree species vary widely in their sensitivity to Al stress. In addition, Al concentrations in soil solution often exhibit pronounced spatial and temporal variability that is difficult to relate to root activity. Finally, the form of

Al present in solution plays an important role in determining toxicity. For example, organically complexed Al, which predominates in upper, organic-rich soil horizons, is essentially nontoxic (U.S. EPA, 2007).

Building on the explanation between Ca, Al, and tree health provided in the ISA, DeHayes and colleagues (1999) depict the relationship between nitrogen and sulfur deposition through acid rain and Ca within an ecosystem (**Figure 1.1-1)**. The authors used solid lines to denote known connections and dotted lines to present potential impacts. While the authors did not specify that increases in Al within the soils will occur with reductions in biologically available Ca pools, this impact is expected as detailed in the previous paragraphs. The final process represented in Figure 1.1-1 completes the linkage from the indicator of Ca (and therefore Al) to the effects on the ecosystem services for the terrestrial area. Continuing the example using Ca and Al indicators, Fenn and colleagues (2006) provided a description of the assessment endpoints and ecosystem services that may be impacted through acidification effects measured using these indicators (**Table 1.1-3**).

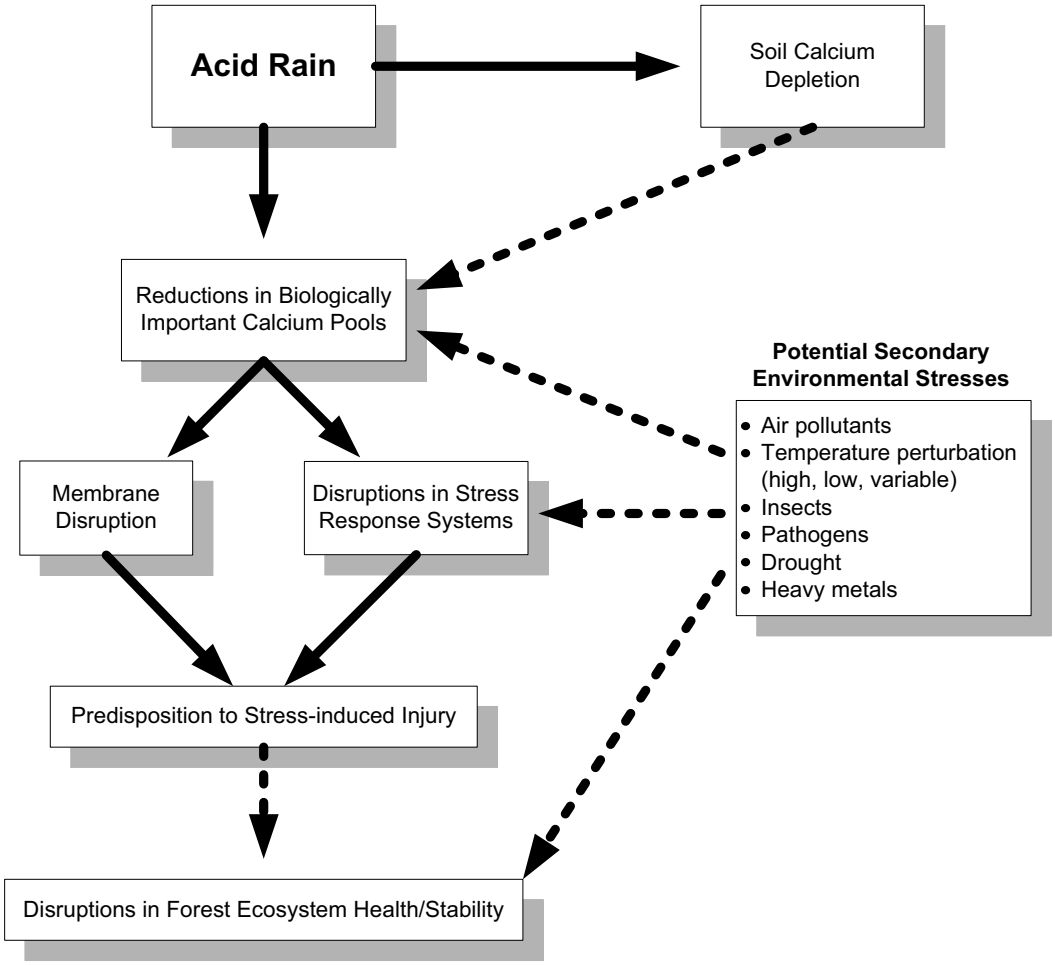

Figure 1.1-1. Conceptual impacts of acid deposition on ecosystem Ca health and sustainability (recreated from DeHayes et al., 1999).

Table 1.1-3. Summary of Linkages between Acid Deposition, Biogeochemical Processes that Affect Ca, Physiological Processes that are Influenced by Ca, and Effect on Forest Function

Biogeochemical Response to Acid Deposition	**Physiological Response**	**Effect on Forest Function**
Leach Ca 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 to Al in soil and soil solutions	Dysfunction in fine roots of red spruce blocks uptake of Ca	Decreased growth and increased susceptibility to stress in red spruce
Reduce the ratio of Ca to Al in soil and soil solutions	More energy is used to acquire Ca in soils with low Ca:Al ratios	Decreased growth and increased photosynthetic allocation to roots

Biogeochemical Response to Acid Deposition	Physiological Response	Effect on Forest Function
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

1.1.2 Endpoints

The tree species most commonly associated with the adverse acidification-related effects of nitrogen and sulfur deposition include red spruce (a conifer) and sugar maple (a deciduous tree species). Both species are found in the eastern United States (**Figure 1.1-2**).

Red spruce is found scattered throughout high-elevation sites in the Appalachian Mountains, including the southern peaks. Noticeable levels of the canopy red spruce died within the Adirondack, Green, and White mountains in the 1970s and 1980s. Acidic deposition has been implicated in this decline due to freezing injury (DeHayes et al., 1999). Within the southeastern United States, periods of red spruce growth decline were turned around after the 1980s, when a corresponding decrease in sulfur dioxide (SO_2) emissions was recorded in the United States (Webster et al., 2004). Al and Ca ratios in forest floor soil are also important to the overall health of red spruce trees in the Northeast. Red spruce has been shown to have an increased instance of foliar winter injury and bud mortality due to imbalanced Al and Ca levels in soils at locations in Vermont and surrounding states. A decrease in cold and winter weather tolerance leads to an increase in freezing injuries to red spruce, placing the species at a greater risk of declining overall forest health. Soil nutrient imbalances and deficiencies can reduce the ability of a tree to respond to stresses, such as insect defoliation, drought, and cold weather damage (DeHayes et al., 1999; Driscoll et al., 2003). From the overall research, important factors relating to the high mortality rates and decreased growth trends of red spruce include depletion of base cations in upper soil horizons by acidic deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidic deposition (U.S. EPA, 2007).

Sugar maple has been on the decline in the eastern United States since the 1950s. This species is found throughout the northeastern United States and the central Appalachian Mountain region. Studies on sugar maple have found that decline in growth is related to both acidic deposition and base-poor soils on geologies dominated by sandstone or other base-poor substrate

(Bailey et al., 2004; Horsley et al., 2000). These site conditions are representative of the kinds expected to be most susceptible to adverse impacts of acidic deposition because of probable low initial base cation pools and high base cation leaching losses (U.S. EPA, 2007). The probability of a decrease in crown vigor or occurrence of tree mortality increases on sites with low Ca and Mg as a result of leaching caused by acid deposition (Drohan and Sharpe, 1997). Additionally, plots of sugar maples in decline were found to have lower base cation concentrations and pH values, and Ca:Al ratios less than 1 (Drohan et al., 2002). These indicators have all been shown to be related to the deposition of nitrogen and sulfur.

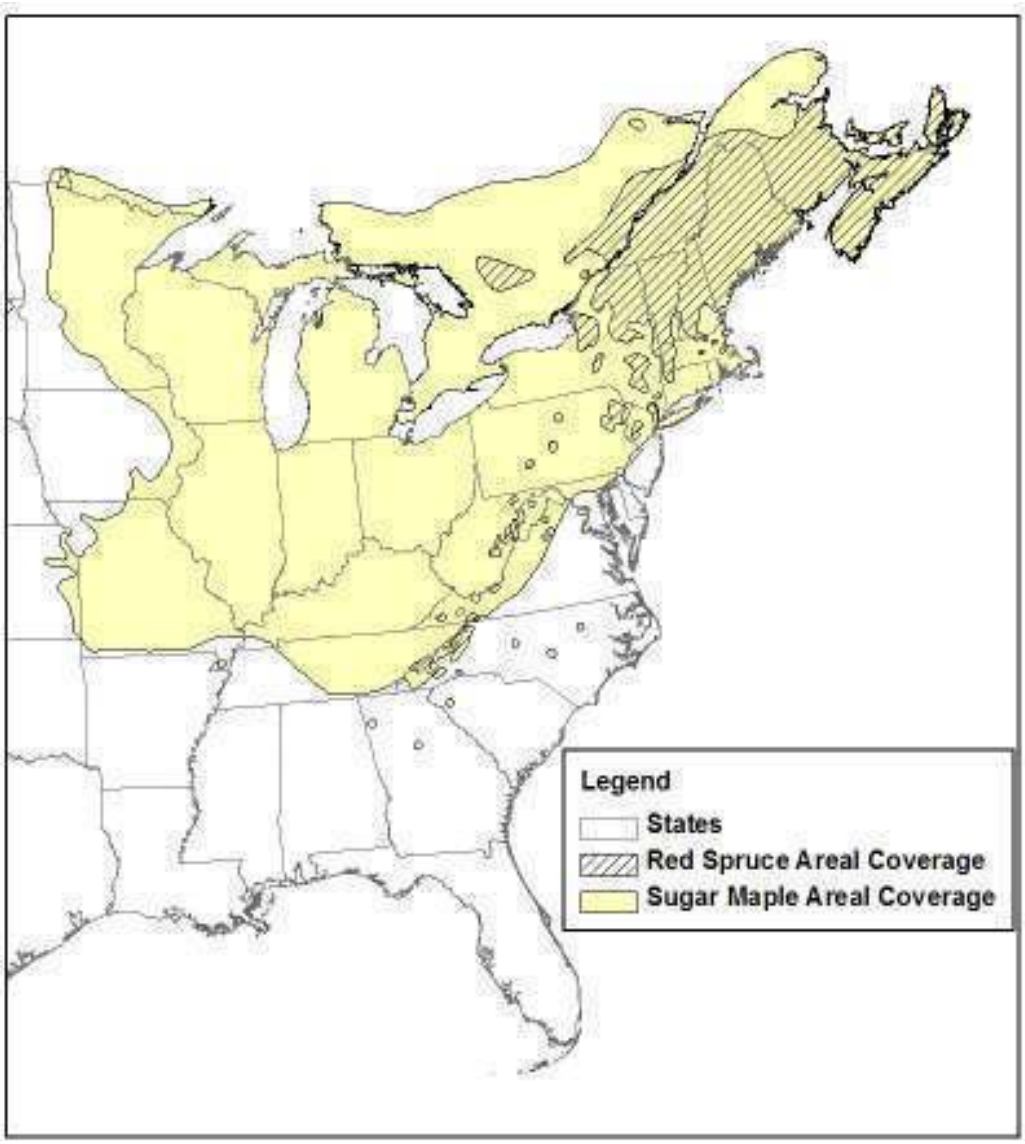

Figure 1.1-2. Areal coverages of red spruce and sugar maple tree species within the continental United States (USGS, 1999).

1.1.3 Ecosystem Services

Ecosystem services are generally defined as the benefits individuals and organizations obtain from ecosystems. In the Millennium Ecosystem Assessment, (MEA) ecosystem services are classified into four main categories:

- **Provisioning.** Includes products obtained from ecosystems.
- **Regulating.** Includes benefits obtained from the regulation of ecosystem processes.
- **Cultural.** Includes the nonmaterial benefits 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 (MEA, 2005).

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

- Decline in forest aesthetics – cultural
- Decline in forest productivity – provisioning
- Increase forest soil erosion and low water retention – cultural and regulating.

The terrestrial acidification case study approach will focus on food, natural habitat, and tourism. Sugar maple and red spruce abundance and growth (i.e., crown vigor, biomass and geographic extent) will be quantitatively linked to acidification symptoms through U.S. Department of Agriculture (USDA) Forest Service (USFS) Forest Inventory and Analysis National Program (FIA) database analyses and analysis of maple sugar production estimates sales.

1.2 CASE STUDIES

As described in the introduction to these case study assessments, selections of case study areas specific to terrestrial acidification began with geographic information systems (GIS) mapping. We used GIS analysis on datasets of physical, chemical, and biological properties indicative of terrestrial acidification potential to identify sensitive areas of the United States. (**Table 1.2-1**).

Table 1.2-1. Summary of Indicators, Mapping Layers, and Models for Targeted Ecosystems

Targeted Ecosystem Effect	**Indicator(s)**	**Mapping Layers**	**Model(s)**
Terrestrial Acidification Due to nitrogen and sulfur	Soil ANC Soil pH CEC Inorganic Al Ca:Al ratio	Special areas (e.g., Class I areas, the Adirondack Mountains) CMAQ (nitrogen & sulfur) by HUC Forest soils from USFS STATSGO soils USFS lichen USFS forest types	MAGIC; ILWAS; PnET-BGC

Note: ANC = acid neutralizing capacity, CEC = cation exchange capacity, USFS = U.S. Forest Service, HUC = hydrological unit, ILWAS = Integrated Lake-Watershed Acidification Study.

We also considered the potential case study areas identified by the Ecological Effects Subcommittee (EES) for examining the ecological benefits of reducing atmospheric deposition. Terrestrial acidification-relevant case study areas suggested by the EES are presented in **Table 1.2-2**. The ISA also recommended case study areas as candidates for risk/exposure assessments. (**Table 1.2-3** contains terrestrial acidification-relevant area.)

Table 1.2-2. SAB/EES Listing of Potential Assessment Areas for Evaluation of Benefits of Reductions in Atmospheric Deposition

Ecosystem/ Region	**Main CAA Pollutant(s)**	**Percentage(s) of Total Nutrient Load Attributable to Atmospheric Deposition**	**Quantitative Ecological and Economic Information**	**EES Comments**
Forested				
Adirondacks	Nitrogen; Sulfur; Mercury	Nearly 100%	Yes	High priority. Good quantitative ecological and economic data exist. Previous studies can be augmented readily.
Catskills	Nitrogen; Sulfur;	Nearly 100%	Yes	Medium priority. Economic data may be lacking. Issues similar to the Adirondacks.
Southern	Nitrogen;	Nearly 100%	Yes	Medium priority.

Ecosystem/ Region	Main CAA Pollutant(s)	Percentage(s) of Total Nutrient Load Attributable to Atmospheric Deposition	Quantitative Ecological and Economic Information	EES Comments
Appalachian Mountains	Sulfur;			Economic data on fisheries are available. Issues similar to the Adirondacks.
Rocky Mountains	Nitrogen	Nearly 100%	Yes	Medium priority. Levels of nitrogen loading much lower than for northeastern locations. Economic data may be lacking.

Table 1.2-3. Potential Assessment Areas for Terrestrial Acidification Identified in the Draft ISA

Area	Indicator	Detailed Indicator	Area Studies	Models	References in U.S. EPA, 2007
Hubbard Brook, New Hampshire	Terrestrial acidification; aquatic acidification	Forest ecosystem; soils; streams	Many studies for decades	PnET-BGC	Gbondo-Tugbawa and Driscoll, 2002; Gbondo-Tugbawa et al., 2002

Source: U.S. EPA, 2007

With the potential areas of assessment highlighted and the indicators (Ca and Al) and endpoints (i.e., tree health decline in sugar maple and red spruce) defined, we reviewed literature studies, federal reports, and additional sources of information, such as established experimental forests, to determine specific case study locations.

Selection of a case study location for sugar maples quickly focused on the Allegany Plateau in Pennsylvania, where a preponderance of the work in the literature has been focused. A significant amount of the work has been sponsored by the USFS (Horsley et al., 2000; Bailey et al., 2004; Hallett et al., 2006). Within this literature compilation, several forest sites were monitored and analyzed (Bailey et al., 2004). For this case study, we have settled on the Kane Forest study site. Kane was designated as an experimental forest by the USFS; it has been the focus of several long-term studies since the 1930s.

For red spruce, selection of a case study location involved a much larger geographic area because there was no overwhelming source of information. Using four studies that examined Ca and Al relationships to tree health, we compiled a list of forest sites and key information for each

(**Table 1.2-4).** After review of this information (i.e., tree population characteristics and reported impacts, as well as monitoring results), we again chose to go with an experimental forest site. The Hubbard Brook Experimental Forest (HBEF) experienced both high deposition levels and low Ca to Al ratios, although neither parameter was the extreme value amongst the compiled study sites. This forest has also been the subject of extensive nutrient investigations and provides a large data set from which to work.

Table 1.2-4. Compilation of Study Sites for Red Spruce within the Literature

Site Name	Elevation (m)	Latitude (degrees N)	Longitude (degrees S)	Size of Tree Population	Availability of Field Data	Ecological Importance	Reported Impacts	Reported Ca & Al Ratios	Deposition Load (kg/ha/yr)	Source(s)
Balsam High Top	1641	35.6656	–83.1962	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	Nearly 100% risk of adverse forest health effects	0.094*	Unknown	Bintz and Butcher, 2007
Clingman's Dome	2020	35.5629	–83.4987	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	Nearly 100% risk of adverse forest health effects	0.084*	Unknown	Bintz and Butcher, 2007
Double Spring Gap	1678	35.5652	–83.5429	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	Nearly 100% risk of adverse forest health effects	0.053*	Unknown	Bintz and Butcher, 2007
Mount LeConte	2010	35.6526	–83.4355	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	75% risk of adverse forest health effects	0.567*	Unknown	Bintz and Butcher, 2007
Mount Sterling	1772	35.7024	–83.1224	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	Nearly 100% risk of adverse forest health effects	0.07*	Unknown	Bintz and Butcher, 2007
Richland Balsam Mountain	1941	35.3676	–82.9904	Spruce-fir forest[+]	University study	Blue Ridge Parkway	Nearly 100% risk of adverse forest health effects	0.07*	Unknown	Bintz and Butcher, 2007
Spruce Mountain	1695	35.6084	–83.1790	Spruce-fir forest[+]	University study	Great Smoky Mountains National Park	Nearly 100% risk of adverse forest health effects	0.128*	Unknown	Bintz and Butcher, 2007
Sleepers River, Vermont		44.4092	–72.0158	Red spruce dominated with low exchangeable Al;Ca ratio	Not selected in studies		Site did not contain sufficient number of healthy, mature red spruce for study		Unknown	Shortle et al., 1997
Groton, Vermont	520	44.2100	–72.2000	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		No specific references at this time, but disturbances are known to have occurred	0.3^	5.3[#]	Shortle et al., 1997; Wargo et al., 2003
Howland, Maine	60	45.2000	–68.7300	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		No specific references at this time, but disturbances are known to have occurred	0.4^	3.1[#]	Shortle et al., 1997; Wargo et al., 2003

Site Name	Elevation (m)	Latitude (degrees N)	Longitude (degrees S)	Size of Tree Population	Availability of Field Data	Ecological Importance	Reported Impacts	Reported Ca & Al Ratios	Deposition Load (kg/ha/yr)	Source(s)
Bartlett, New Hampshire	525	44.1100	–71.2900	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS Experimental Forest (1,052 ha); red spruce covers highest slopes	Within the White Mountains	No specific references at this time, but disturbances are known to have occurred	0.8^	4.9#	Shortle et al., 1997; Wargo et al., 2003
Kossuth, Maine	100	45.4000	–67.9000	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		No specific references at this time, but disturbances are known to have occurred	0.8^	2.8#	Shortle et al., 1997; Wargo et al., 2003
Hubbard Brook, New Hampshire	755	43.9400	–71.7500	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS Experimental Forest (3,138 ha); red spruce abundant at higher elevations and on rock outcrops	Within the White Mountains	Acid-extractable Al in the forest floor increased over the past two decades at the HBEF, and ratios of Al to Ca in mineral soil solutions (but not forest floor solutions) were strongly correlated with exchangeable Al content in the forest floor.	0.8^	6.0#	Shortle et al., 1997; Wargo et al. 2003
Whiteface Mountain, New York	950	44.3900	-73.8600	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		Contained neither evidence of unusual mortality or current tree decline; winter injury events reported (Lazarus et al., 2004)	0.8^	7.9#	Shortle et al., 1997; Wargo et al., 2003
Crawford Notch, New Hampshire	670	44.1590	-71.3617	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location	Within the White Mountains	50% risk of adverse forest health effects; mortality of red spruce was significant but most of the remaining trees were in good to fair health	1.1^	5.5#	Shortle et al., 1997; Wargo et al., 2003
Big Moose Lake, New York	550	43.8300	-74.8500	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		50% risk of adverse forest health effects	1.2^	6.4#	Shortle et al., 1997; Wargo et al., 2003

Site Name	Elevation (m)	Latitude (degrees N)	Longitude (degrees S)	Size of Tree Population	Availability of Field Data	Ecological Importance	Reported Impacts	Reported Ca & Al Ratios	Deposition Load (kg/ha/yr)	Source(s)
Bear Brook, Maine	400	44.8700	-68.1100	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location		75% risk of adverse forest health effects	1.9^	3.8#	Shortle et al., 1997; Wargo et al., 2003
Cone Pond, New Hampshire	610	43.9000	-71.6000	Red spruce dominated with a gradient of forest floor exchangeable Al;Ca ratios	USFS study location	Within the White Mountains	Nearly 100% risk of adverse forest health effects	5.2^	5.4#	Shortle et al., 1997; Wargo et al., 2003
Mt. Abraham, Vermont		44.1201	-72.9357	Red spruce dominated with a high exchangeable Al;Ca ratio	Not selected in studies	Within the Green Mountains	Site did not contain sufficient number of healthy, mature red spruce for study; Forest floor solution Al:Ca ratio above the 50% risk level	7.1^		Shortle et al., 1997
Mt. Ascutney, Vermont	762	43.4333	-72.4500	Series of high elevation spruce-fir forest nitrogen addition plots=	USFS study location	Nitrogen additions to system	Reduction in live basal area on the high nitrogen addition plots versus control plots		Additions%	McNulty et al., 2005

* Molar Ca/Al Ratio (Bintz and Butcher, 2007).

^ Oa horizon Al/Ca Ratios (Wargo et al., 2003).

\# Estimated wet nitrogen deposition (Lilleskov et al., 2008).

% In addition to ambient nitrogen deposition, paired plots each received 15.7 kg N ha-1 year-1 (low nitrogen addition), 31.4 kg N ha-1 year-1 (high nitrogen addition) or no nitrogen addition (control) from 1988 to 2002.

\+ High elevation sites in the Southern Appalachians—The sites are located in the Great Smoky Mountains National Park and Richland Balsam Mountain on the Blue Ridge Parkway. Sites were selected because of the presence of a spruce-fir forest with a northwest slope aspect within 10 km of a trailhead at elevations between 1650 and 2025 m.

= Red spruce grew in large patches (> 1 hectare [ha]) at elevations above 725 m. Red spruce comprised > 80% of the total basal area in all plots; the remainder of the other tree species were divided among balsam fir, red maple, mountain maple, and birch.

1.2.1 Sugar Maple

1.2.1.1 Kane Experimental Forest (USFS, 2008b; USFS, 1999)

The Kane Experimental Forest **(Figure 1.2-1**) was established on March 23, 1932, although research there began as early as 1927 or 1928. The forest's primary mission has been forest management research, although watershed research was included in the beginning, and wildlife research is part of the current program. Ongoing long-term studies include individual tree and understory vegetation measurements; treatments include thinnings, regeneration cuts, uneven-age cuts, and long-term measurements of unmanaged forest.

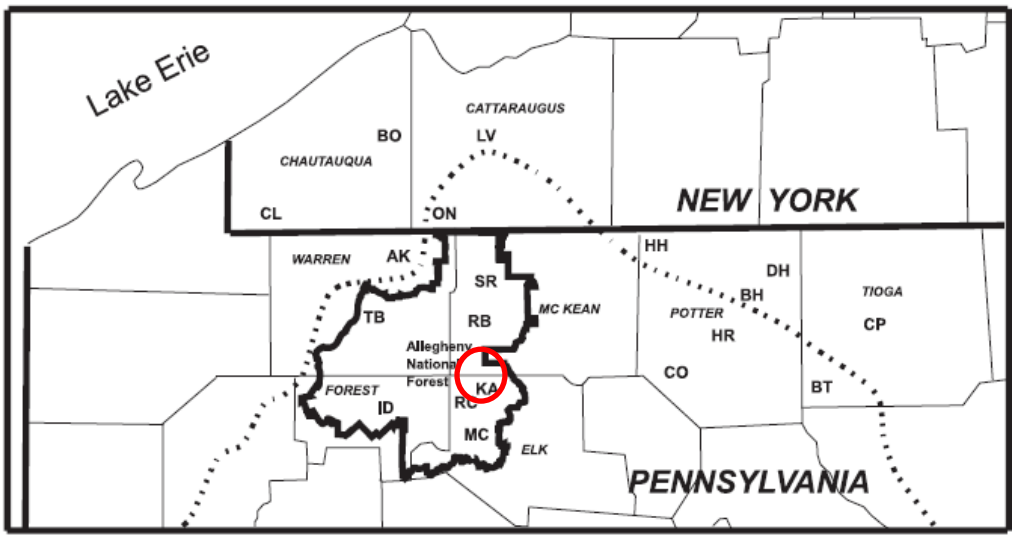

Figure 1.2-1. Kane Experimental Forest (Horsley et al., 2000).

The Kane Experimental Forest is on the eastern edge of the Allegheny National Forest, 3.5 miles south of Kane, PA. Main access is from Pennsylvania Route 321 or the Highland-Lamont Road, via Forest Service Road 138. The Experimental Forest is comprised of 1,737 acres of forestland; it ranges in elevation from about 1,800 to 2,100 feet above sea level, primarily on flat to gently sloping land. The Wolf Run and Ackerman Run drainages cross Kane Experimental Forest, as do the Mill Creek and Twin Lakes trails.

The climate of the Kane Experimental Forest is humid temperate. The forest receives approximately 110 centimeters (cm) of precipitation per year, mostly as rain, including 10 cm/month during the growing season. Precipitation can be quite acidic; Kane Experimental Forest receives high levels of both SO_4^{2-} and NO_3^- deposition. Between 1992 and 1998, the

average annual atmospheric deposition was 4.57 kilograms/hectare (kg/ha) for NO_3^-, 2.33 kg/ha for ammonium (NH_4^+), and 9.48 kg/ha for SO_4-S (Lewis and Likens 2007). The average annual temperature is 43° F. Overcast days are frequent, reducing the transpirational demand on plants.

The forest soils on the Allegheny Plateau are derived from shales and sandstones. In general, these soils are very stony and exist as extremely stony loams and sandy loams. They are strongly acidic. The major soil series are the well-drained Hazelton series, the moderately well-drained to somewhat poorly drained Cookport series, and the somewhat poorly drained Cavode series.

The forest stands on the Kane Experimental Forest are typical of the Allegheny Plateau. They resulted from a series of cuttings made in the original hemlock-beech-maple stands. The first cutting, made in the mid-to-late 1800s, removed the hemlock and the best hardwood trees to supply the local tanneries and sawmills. Most of the remaining hardwoods were cut between 1890 and 1925, but a few stands were clear-cut as late as 1937. Trees of nearly all sizes were removed in the later cuts; large trees were used for sawtimber products, whereas small trees were destructively distilled for charcoal and wood chemical products.

Currently, the Kane Experimental Forest contains second-growth stands ranging from 60 to about 100 years of age, a few third-growth stands 20- or 40-years-old, and one tract with remnant old growth. Most stands are even-aged in character, although they may actually contain several age classes because of the previous sequence of cuttings. The most common tree species are black cherry, maples, and beech, but many other species are present (e.g., yellow and sweet birch, eastern hemlock, cucumbertree, yellow poplar, white ash). Beech and striped maple seedlings dominate the understory of many unmanaged stands, joined by black cherry and black birch in managed stands. These forest stands represent the Allegheny hardwood or black cherry–maple; the northern hardwood, including the hemlock-hardwood and beech–birch–maple; and the upland hardwood, or red maple–dominated, forest types.

Several species of ferns, grasses, goldenrod, and aster occur in abundance as ground covers. Common spring ephemerals include trout lily, dwarf ginseng, and spring beauties. Wildlife species observed on the Kane Experimental Forest include white-tailed deer, wild turkey, black-throated green warblers, hermit thrushes, deer mice, chipmunks, red-backed salamanders, and wood frogs. The wildlife communities are typical of those found in managed second-growth forests of the Allegheny Plateau region.

Since the establishment of the Kane Experimental Forest, research has been conducted continuously on the forest; most research consists of relatively long-term studies. During the Civilian Conservation Corps days of the 1930s, studies of forest growth and development were initiated at the Kane Experimental Forest. Information from this early work has made important contributions to the present research program, and many of these long-term study areas are still yielding valuable information. Other past research includes thinning research, forest stocking, factors affecting the natural regeneration of Allegheny hardwoods, and the development of SILVAH, an early computerized decision-support system still widely used for forest management. Treatment techniques at the Kane Experimental Forest have included cutting, roto-tilling, irrigation, bending overstory trees, trenching, heating cables, fertilization, and shading.

Currently, the Northeastern Forest Experiment Station research team that maintains and administers the Kane Experimental Forest research conducts research on three problems: regeneration and forest renewal stand dynamics, silviculture, and sugar maple decline. Most of the research on the Kane Experimental Forest is focused on the stand dynamics and silviculture research problems. **Table 1.2-5** summarizes major studies at the Kane Experimental Forest related to the sugar maple and chemical criterion that can be used in calculating critical loads of nitrogen and sulfur.

Table 1.2-5. Major Studies at the Kane Experimental Forest

Authors	**Year**	**Title**	**Key Finding**
Horsley, S.B., R.P. Long, S.W. Bailey, R.A. Hallett, and T.J. Hall	2000	Factors Associated with the Decline-Disease of Sugar Maple on the Allegheny Plateau	The most important factors determining sugar maple health were foliar levels of Mg and Mn and defoliation history. The decline-disease of sugar maple appears to be the result of an interaction between Mg (and perhaps Mn) nutrition and stress caused by defoliation.

Authors	Year	Title	Key Finding
Bailey, S.W., S.B. Horsley, and R.P. Long	2005	Thirty Years of Change in Forest Soils of the Allegheny Plateau, Pennsylvania	Between 1967 and 1997, there were significant decreases in exchangeable Ca and Mg concentrations and pH at all depths. Exchangeable Al concentrations increased at all depths at all sites; however, increases were only significant in upper soil horizons. At most of the sites, losses of Ca and Mg on a pool basis were much larger than could be accounted for in biomass accumulation, suggesting the leaching of nutrients off-site.

1.2.2 Red Spruce

1.2.2.1 Hubbard Brook Experimental Forest (HBES, 2008; Pardo and Driscoll, 1996; USFS, 2008a)

The HBEF was established in 1955 as a major center for hydrologic research in New England. Located in White Mountain National Forest in central New Hampshire, the 3,138-ha bowl-shaped valley has hilly terrain, ranging from 222 to 1,015 meters (m) in altitude. The Hubbard Brook Ecosystem Study (HBES) was established by a cooperative agreement in 1963. In 1988, the HBEF was designated as a Long-Term Ecological Research (LTER) site by the National Science Foundation (NSF). **Figure 1.2-2** presents a map of the HBEF, with identification of four forest transect studies conducted by Siccama and colleagues, 2007.

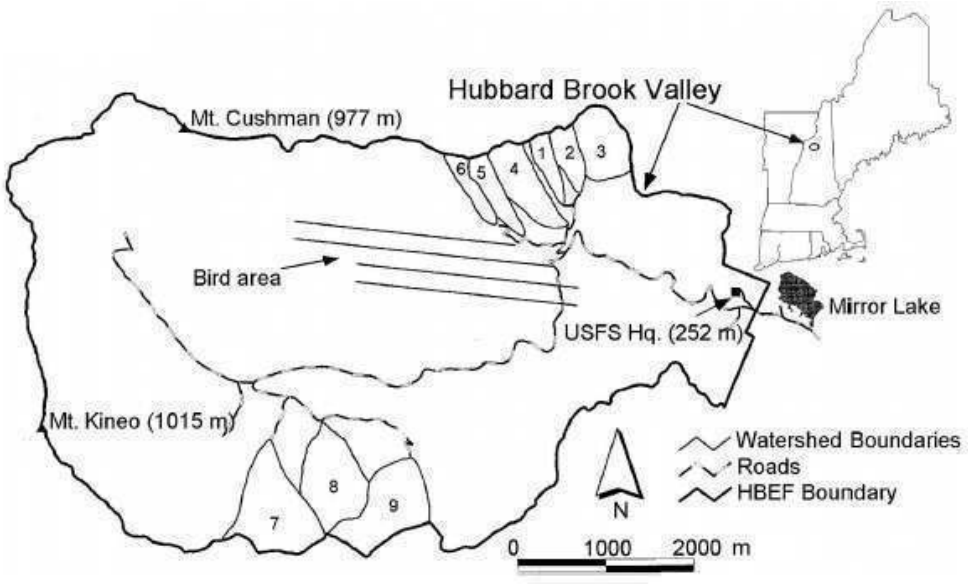

Figure 1.2-2. Hubbard Brook Experimental Forest (Siccama et al., 2007).

The soils, vegetation, and climate at the HBEF are characteristic of the northern hardwood forest complex, which spans much of the north-central and northeastern United States and southeastern Canada. Streamflow and chemistry reflect the landscape characteristics of the drainage area. Consequently, results from the relatively small watersheds at the HBEF are, to a first approximation, representative of a much larger regional area.

The HBEF is located in the southern part of the White Mountain National Forest in central New Hampshire (i.e., 43º56'N, 71º45'W; the geographic center of the HBEF). It lies in the towns of Ellsworth, Thornton, Warren, and Woodstock, all in Grafton County, and is near the village of West Thornton. The HBEF is an oblong basin about 8 km long by 5 km wide. Hubbard Brook is the single major stream draining the basin.

Although the climate of the HBEF varies with altitude, some major features include the following: (1) large and rapid changes in weather, (2) broad ranges in daily and annual air temperature, and (3) uniform monthly precipitation (i.e., about 100 millimeters/month [mm/mo]). In spite of the proximity of the HBEF to the ocean (116 km), the climate is predominantly continental. Annual precipitation at the HBEF averages about 1,400 mm, with one-third to one-quarter as snow. January averages about –9º C, and the average July temperature is 18º C. The average number of days without killing frost is 145; however, the growing season for trees is considered to be from May 15, the approximate time of full leaf development, to September 15, when the leaves begin to fall. The estimated annual evapotranspiration is about 500 mm.

Soils at the HBEF are predominantly well-drained Spodosols (Typic Haplorthods) derived from glacial till, with sandy loam textures. Principal soil series are the sandy loams of the Berkshire series, along with the Skerry, Becket, and Lyman series. These soils are acidic (i.e., pH about 4.5 or less) and relatively infertile (i.e., base saturation of mineral soil ~ 10%). Soil depths, including unweathered till, average about 2.0 m surface to bedrock, although this is highly variable. Depth to the C horizon averages about 0.6 m. At various places in the HBEF, the C horizon exists as an impermeable pan. Long-term measurements suggest that the forest floor is at steady-state.

The HBEF is entirely forested, mainly with deciduous northern hardwoods: sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and yellow birch (*Betula allegheniensis*), and some white ash (*Fraxinus americana*) on the lower and middle slopes. Other less abundant

species include mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), and trembling aspen (*Populus tremuloides*). Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white birch (*Betula papyrifera* var. *cordifolia*) are abundant at higher elevations and on rock outcrops. Hemlock (*Tsuga canadensis*) is found in riparian areas. Pin cherry (*Prunus pensylvanica*), a shade-intolerant species, dominated all sites for the first decade following a major forest disturbance. The region was settled by Europeans in the late 1800s; logging operations ending around 1915 to 1917 removed large portions of the conifers and better quality, accessible hardwoods. The present second-growth forest is even-aged and composed of about 80% –90% hardwoods and 10%–20% conifers. The total forest biomass has stopped accumulating since the early 1980s and is currently about 235 tons ha^{-1}. Present basal area is about 26 m^2 ha^{-1}, but varies according to elevation, habitat, and stand history.

Mean nitrogen loading in bulk deposition for the period 1965 to 1987 was 480 mol ha^{-1} yr^{-1}. Mean total nitrogen loading, including wet and dry deposition, was 570 mol ha^{-1} yr^{-1}. There was no significant trend in nitrogen deposition for the period 1965 to 1987.

Research at the HBEF has been in progress for more than 50 years. During the first 8 years following the establishment of the HBEF, the Northeastern Research Station, USFS, developed a network of precipitation and stream-gauging stations, and weather instrumentation, and vegetation monitoring sites on small, experimental watersheds. Data from these installations, combined with several initial studies, formed the hydrometeorologic foundation for much of the future research at the HBEF. The major emphasis in these early studies was to determine the impact of forest land management on water yield and quality and on flood flow.

The HBES originated in 1960 with the idea of the small watershed approach to studying element flux and cycling. Using the small watershed approach, studies of element-hydrologic interactions were conducted to form a basis for subsequent process-level and experimental research. In September 1987, the HBEF was awarded an LTER grant through the NSF. The overall objective of the project is to develop a better understanding of the response of northern hardwood-ecosystems to large-scale disturbances. Particular emphasis is placed on the areas of (1) vegetation structure, composition, and productivity; (2) dynamics of dead organic matter; (3) atmospheric-terrestrial-aquatic linkages; and (4) heterotroph population dynamics. Experimental manipulation has been used extensively in research at the HBEF. A number of whole watershed, stream, and lake manipulations have been conducted to test research hypotheses, obtain

quantitative information on pertinent environmental issues, and validate process-related formulations used in simulation models. Treatments applied at the HBEF include cutting and application of herbicides and fertilizers. **Table 1.2-6** summarizes major studies at the HBEF related to red spruce that calculated critical loads of nitrogen and sulfur.

Table 1.2-6. Major Studies at Hubbard Brook Experimental Forest

Authors	**Year**	**Title**	**Key Finding**
Driscoll, C.T., et al.	1989	Changes in the chemistry of surface waters: 25-year results at the Hubbard Brook Experimental Forest, NH	A decline in the sum of basic cations in surface water has paralleled the sulfate decline in atmospheric deposition, preventing any long-term decrease in stream acidity. There have been no significant long-term trends in precipitation inputs or stream outflow of NO_3^-.
Pardo, L.H. and C.T. Driscoll	1996	Critical loads for nitrogen deposition: case studies at two northern hardwood forests	Critical loads for nitrogen deposition with respect to acidity ranged from 0–630 eq ha^{-1} yr^{-1}; critical loads with respect to effects of elevated nitrogen (eutrophication and nutrient imbalances) ranged from 0–1450 eq ha^{-1} yr^{-1}.
Palmer S.M., C.T. Driscoll, and C.E. Johnson	2004	Long-term trends in soil solution and stream water chemistry at the HBEF; relationship with landscape position	Significant declines in strong acid anion concentrations were accompanied by declines in base cation concentrations in soil solutions draining the Oa and Bs soil horizons at all elevations. Persistently low Ca^{2+}/Al_i ratios (< 1) in Bs soil solutions at these sites may be evidence of continuing Al stress to trees.
Siccama, T.G, et al.	2007	Population and biomass dynamics of trees in a northern hardwood forest at Hubbard Brook Experimental Forest	Tree data from 1991–2001, including total aboveground biomass, in-growth of ≥ 10 cm DBH trees, mortality, biomass by type, aboveground net primary productivity, and net ecosystem productivity.

The specific study area in which we will carry out the critical loads analysis within HBEF has been narrowed to a portion of experimental Watershed 6. This watershed is maintained as the biogeochemical watershed for studies within the forest. It is 13.2 ha in area. Watershed 6 consists of typical northern hardwood species (e.g., sugar maple, beech, yellow birch) on the lower 90% of its area and by a montane boreal transition forest of red spruce, balsam fir, and white birch on the highest 10% of its area (**Figure 1.2-3**). Research within this watershed has provided data concerning throughfall (1989–1992), canopy leaf chemistry, forest inventories (2002), coarse literfall data (2002 near watershed), and forest floor mass, organic matter, and chemistry (1997) (www.hubbardbrook.org).

In 1965, a grid system of 208 grid cells, each 25 x 25 square meters (m^2), was instituted to serve as a plot system for analyses. Using this grid system and the 2002 Forest Inventory for the watershed, we identified nine grid units within the northeast portion of the watershed that contain large portions of red spruce trees (**Figure 1.2-4**). We intend to carry out the initial critical loads analysis across the area (0.56 ha) defined by these grid units. Further analyses can extend to larger portions of the watershed.

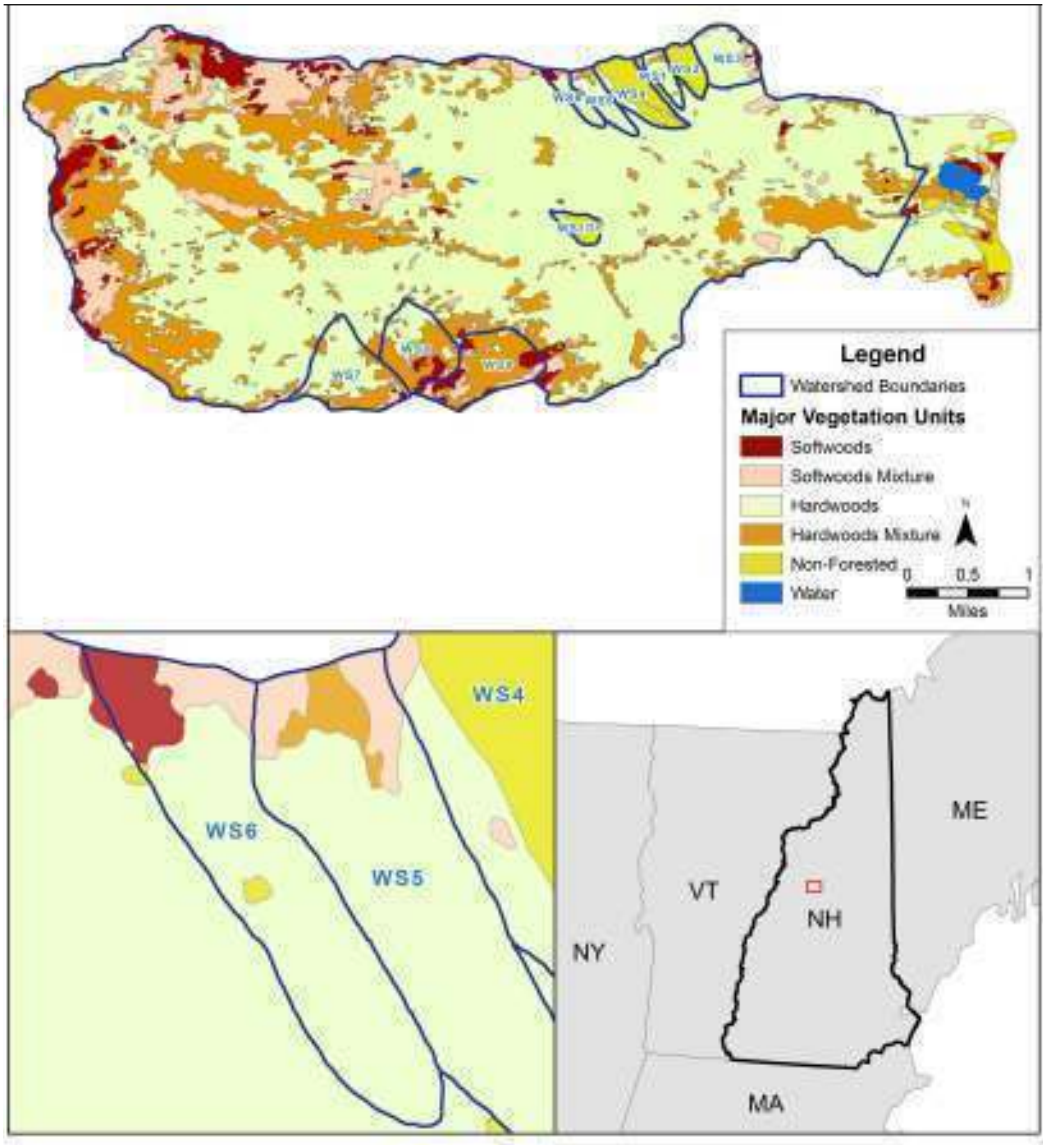

Figure 1.2-3. Hubbard Brook Vegetation and Experimental Watershed Number 6.

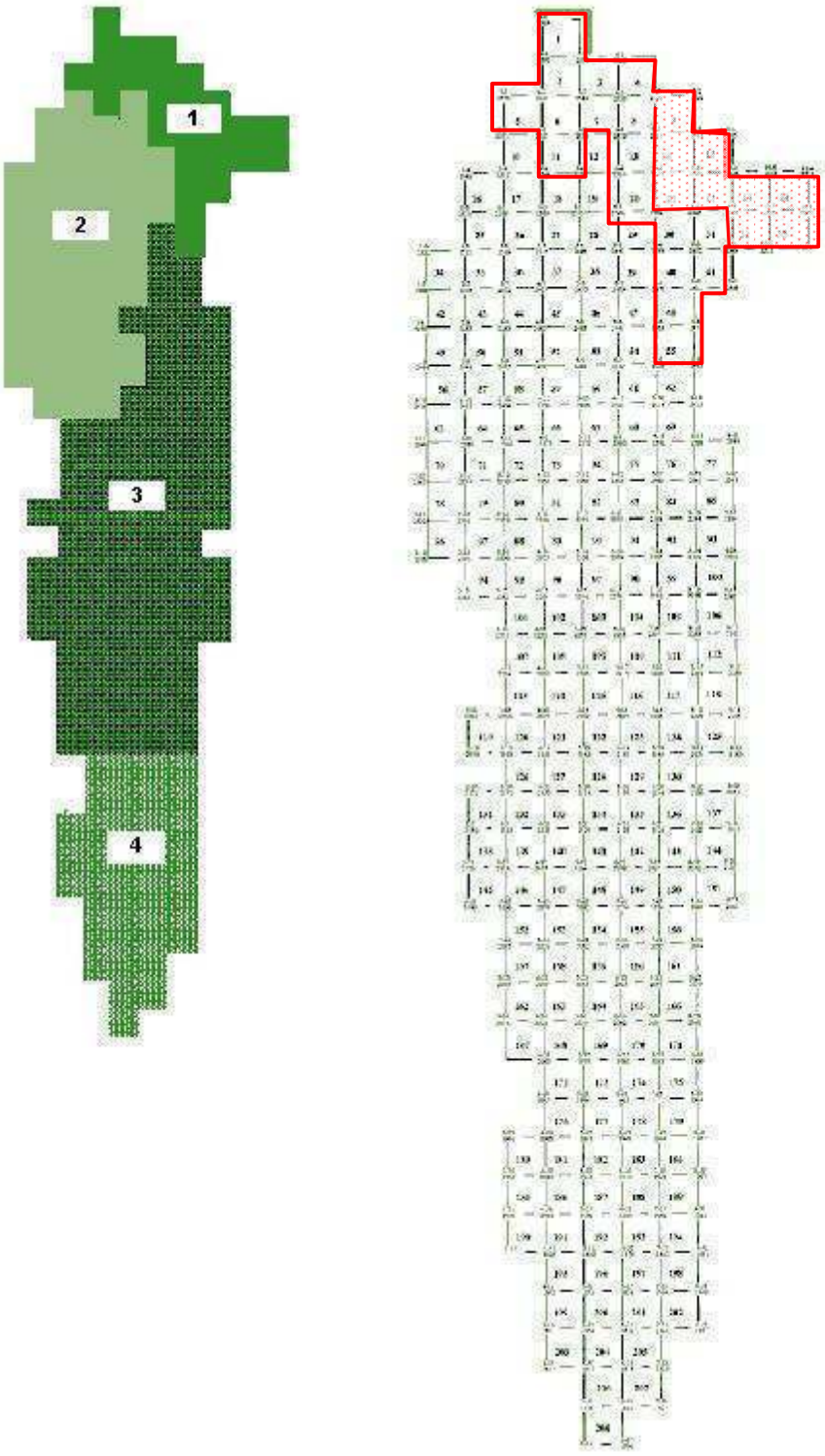

Figure 1.2-4. Grid unit representation of Experimental Watershed Number 6 (www.hubbardbrook.org). The red outline indicates the spruce/fir-dominated forest. The dotted grid cells represent the study area with high proportions of red spruce.

2. APPROACH AND METHODS

The ISA identified a key approach to quantifying the adverse effects of anthropogenic pollution as using critical loads. A critical load is "a quantitative estimate of ecosystem 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" (McNulty et al., 2007). Critical loads of sulfur and nitrogen acidity for an ecosystem have been specifically defined as "the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function" (Nilsson and Grennfelt, 1988). "The basic idea of the critical load concept is to balance the depositions that an ecosystem is exposed to with the capacity of this ecosystem to buffer the input (e.g., the acidity input buffered by the weathering rate), or to remove it from the system (e.g., nitrogen by harvest) without harmful effects within or outside the system" (UNECE, 2004).

European countries have been using critical acid loads for many years to assess nitrogen and sulfur deposition in forest ecosystems. These studies have served as the platform for informing policy related to the control and reduction of emissions of acidifying pollutants. The International Cooperative Programme on Modelling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends has published a series of manuals, the most recent in 2004, to provide guidance on calculating and mapping critical loads. The manuals help Parties to the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) meet their obligations of deriving data for effects and risk assessments using harmonized methods (UNECE, 2004). Canada has also completed critical loads studies in support of efforts to design emission-reduction programs (Jeffries and Lam, 1993; RMCC, 1990). Critical loads modeling was included in the *1997 Canadian Acid Rain Assessment* (Jeffries, 1997) for several regions in eastern Canada.

The establishment and analysis of critical loads within the United States is relatively new. The Conference of New England Governors and Eastern Canadian Premiers (NEG/ECP) funded studies that used critical loads–based methods to estimate sustainable acidic deposition rates and exceedences for upland forests representative of the New England states and the eastern Canadian Provinces in the early 2000s (NEG/ECP Forest Mapping Group, 2001). More recently, McNulty and colleagues (2007) completed a national critical loads assessment for U.S. forest soils at a 1 square kilometer (km^2) scale.

Within the ISA (U.S. EPA, 2007), EPA detailed an 8-step protocol to define the basic critical loads question in any analysis. Those steps are repeated here:

1. Identify the *ecosystem disturbance* that is occurring (e.g., acidification, eutrophication). Not all disturbances will occur in all regions or at all sites, and the degree of disturbance may vary across landscape areas within a given region or site.
2. Identify the *landscape receptors* that are subjected to the disturbance (e.g., forests, surface waters, crops). Receptor sensitivity may vary locally and/or regionally, and the hierarchy of those receptors that are most sensitive to a particular kind of disturbance may vary as well.
3. Identify the *biological indicators* within each receptor that are affected by atmospheric deposition (i.e., individual organism, species, population, or community characteristics). Indicators will vary geographically and perhaps locally within a given receptor type.
4. Establish the *critical biological responses* that define "significant harm" to the biological indicators (e.g., presence/absence, loss of condition, reduced productivity, species shifts). Significant harm may be defined differently for biological indicators that are already at risk from other stressors or for indicators that are perceived as "more valued."
5. Identify the *chemical indicators* or variables that produce or are otherwise associated with the harmful responses of the biological indicators (e.g., streamwater pH, lake Al concentration, soil base saturation). In some cases, the use of relatively easily measured chemical indicators (e.g., surface water pH or acid neutralizing capacity [ANC]) may be used as a surrogate for chemical indicators that are more difficult to measure (e.g., Al concentration).
6. Determine the *critical chemical limits* for the chemical indicators at which the harmful responses to the biological indicators occur (e.g., pH < 5, base saturation < 5%, inorganic Al concentration greater than 2 μM). Critical limits may be thresholds for indicator responses, such as presence/absence, or may take on a continuous range of values for continuous indicator responses, such as productivity or species richness. Critical limits may vary regionally or locally depending on factors such as temperature, existence of

refugia, or compensatory factors (e.g., high Ca concentration mitigates the toxicity of Al to fish and plant roots).

7. Identify the *atmospheric pollutants* that control (affect) the pertinent chemical indicators (e.g., deposition of SO_4^{2-}, NO_3^-, ammonium [NH_4^+], nitric acid [HNO_3]). Multiple pollutants can affect the same chemical variable. The relative importance of each pollutant in producing a given chemical response can vary spatially and temporally.
8. Determine the *critical pollutant loads* (e.g., kg ha^{-1} yr^{-1} total deposition of sulfur or nitrogen) at which the chemical indicators reach their critical limits. Critical pollutant loads usually include both wet and dry forms of pollutant deposition. The critical pollutant load may vary regionally within a receptor or locally within a site (e.g., as factors such as elevation or soil depth vary) and may vary temporally at the same location (e.g., as accumulated deposition alters chemical responses).

As shown in the eight steps above, a variety of indicators and responses can be incorporated into a critical load. Varying any one of these will result in a different critical load. As a result, there is no single definitive critical load for an ecosystem. For this case study, we will focus on forest acidification using the biological indicators of red spruce and sugar maple stands. We have determined that the chemical indicators will be the Ca to Al ratio in soil solution. The criteria chemical limits allow for the calculation of multiple critical loads depending on the risk level of interest. We examine this situation in further detail when discussing characteristics of the response curve of our analysis.

Several approaches can be taken to derive critical loads. Three of the most common are empirically derived estimates, mass balances, and dynamic models (Bull et al., 2001; Bobbink et al., 2003; Jenkins et al., 2003; McNulty et al., 2007; UNECE, 2004).

The UNECE CLRTAP has used empirical loads within their mapping framework. Empirical critical loads of nitrogen for specific receptor groups for natural and seminatural terrestrial ecosystems and wetland ecosystems were first presented in a background document for the 1992 workshop on critical loads held under the UNECE CLRTAP Convention at Lökeberg (Sweden) (Bobbink et al., 1992). After detailed discussion before and during the meeting, the proposed values were set at that meeting (Grennfelt and Thörnelöf, 1992). Updates to the empirical loads were completed for a 2007 update to the *2004 Manual on Methodologies and*

Criteria for Modeling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks, and Trends (henceforth referred to as the ICP Mapping and Modeling Manual) (UNECE, 2004). The ICP Mapping and Modeling Manual also provides separate critical loads for acidification of soils based on soil mineralogy and/or chemistry. For these critical loads, the guidance is presented as a range instead of a single value. Additionally, the guidance specifies modifying factors that allow the critical load value to be adjusted within the ranges presented (UNECE, 2004).

Mass balance methods are a form of simple chemical models that relate chemical criteria for the biological impact of deposition to the deposition levels going into the ecosystem. Use of a mass balance provides a simpler form of modeling than deterministic models, but still must rely on appropriate (soil) chemical criteria (and critical limits) with proven (empirical) relationships to biological effects. These models use the principles of the mass balance to determine a critical load on the basis of what is coming into, going out of, and being stored within the ecosystem. They offer steady-state estimates of critical levels for time frames based on the data used to evaluate the balance (UNECE, 2004).

Dynamic models simulate the processes of pollutant fate and transport into, out of, and within a system on a temporally varying basis. They require parameterization and, usually, calibration. “Since critical loads are steady-state quantities, the use of dynamic models for the sole purpose of deriving critical loads is somewhat inadequate. However, if dynamic models are 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).

2.1 CHOSEN METHOD

The terrestrial acidification case studies will be carried out using a critical loads assessment based on the critical loads formulation used and outlined most recently by McNulty and colleagues (2007) and the ICP Mapping and Modeling Manual (UNECE, 2004). This method, termed the Simple Mass Balance (SMB) method, has been developed and used as one of the principal methods for calculating critical loads of acidity of forest soils and ecosystems. The SMB method has been applied on a variety of systems and is used widely throughout Europe (McNulty et al., 2007; Sverdrup and de Vries, 1994; UNECE, 2004).

The SMB model examines a long-term, steady-state balance of nitrogen and sulfur inputs, sinks, and outputs within an ecosystem. With this model, equilibrium is assumed to equal the system's critical load. It is a single-layer model where assumptions stipulate that the soil layer is a homogeneous unit at least as deep as the rooting zone so that the nutrient cycle can be ignored. This allows the model to focus directly on growth and uptake processes. There are several additional assumptions that are included with application of the SMB model:

- All evapotranspiration occurs on the top of the soil profile
- Percolation is constant through the soil profile and occurs only vertically
- Physico-chemical constants are assumed to be uniform throughout the whole soil profile
- Internal fluxes (e.g., weathering rates, nitrogen immobilization) are independent of soil chemical conditions (such as pH) (UNECE, 2004).

The SMB relates deposition of nitrogen and sulfur to a critical load by incorporating mass balances for nitrogen and sulfur within the soils with the charge balance of ions in the soil leaching flux. With this method, the processes that add and remove nitrogen and sulfur from the soil, as well as the other charged elemental species, are accounted for. The leaching flux that drives this analysis provides the opportunity to specify the chemical criterion of importance to determine ecological effects using the critical loads analysis. More specifically, a critical level of leaching measured by the ANC is specified within the loading calculation. Details on the calculation of this critical level are provided below, along with discussion on the linkage to endpoints.

Although this method allows for the analysis of both nitrogen and sulfur deposition loads, it does not allow for the analysis of effects between the different reactive nitrogen species. However, this simplification of the nitrogen cycle is acceptable when looking at terrestrial acidification effects because the research to support the ecological endpoints of the effects due to each species of nitrogen has not been conducted. As stated by Hall in Chapter 5 of the UNECE 2004 Mapping and Modeling Manual, "the possible differential effects of the deposited nitrogen species (oxidized nitrogen [NO_y] or reduced nitrogen [NH_x]) are insufficiently known to make a differentiation between these nitrogen species for critical load establishment" (UNECE, 2004).

2.1.1 Critical Load Analysis Formulation

Creation of the SMB equation for acidity begins with a charge balance of ions in the soil leaching flux. Combining this charge balance with basic assumptions and mass balances around sulfur and nitrogen leaching from soils results in a simplified charge balance for the soil compartments. Critical loads for nitrogen and sulfur can then be calculated by defining a critical ANC leaching level ($ANC_{le,crit}$) within that charge balance (Equation 1). For complete development of the charge and mass balance equations, please refer to the ICP Mapping and Modeling Manual (UNECE, 2004).

The parameters in Equations 1 through 6 are expressed in units of eq ha^{-1} yr^{-1} except where noted. Equations 1 through 3 are presented as expressed by McNulty and colleagues (2007) where they specify that calculations are for a critical load of acidity (CAL) and not any other type of critical load.

$$CAL(S+N) = BC_{dep} - Cl_{dep} + BC_{w} - BC_{u} + N_{i} + N_{u} + N_{de} - ANC_{le,crit} \quad (1)$$

where

$CAL(S+N)$ = forest soil critical acid load for sulfur and nitrogen

BC_{dep} = base cation (i.e., Ca + K + Mg + Na) deposition

Cl_{dep} = chloride deposition; BC_w is base cation weathering

BC_u = uptake of base cations (i.e., Ca + K + Mg) in trees

N_i = nitrogen immobilization

N_u = uptake of nitrogen in trees

N_{de} = denitrification

$ANC_{le,crit}$ = forest soil acid neutralizing capacity of CAL leaching (Gregor et al., 2004).

Exceedence (eq ha^{-1} yr^{-1}) of the critical load is calculated by comparing the CAL to the current levels of nitrogen and sulfur deposition in Equation 2.

$$Ex(S+N)_{dep} = S_{dep} + N_{dep} - CAL(S+N) \quad (2)$$

where

Ex = exceedence of the forest soil critical nitrogen and sulfur loads

$(S+N)_{dep}$ = the deposition of S+N.

Higher exceedence values reflect greater exceedence of acidic deposition above the level associated with an increased likelihood of environmental harm (McNulty et al., 2007).

The specification of the critical chemical criterion for effects on the receptor occurs within the calculation of $ANC_{(le,crit)}$. Several formulations for $ANC_{(le,crit)}$ exist, depending on which criterion is being used to examine the critical load for the receptor: sensitivity to pH conditions or sensitivity to the toxic effects of Al. Generally, using criterion based on hydrogen ion concentrations are recommended for soils with a high organic matter content, while using criterion based on Al concentrations are considered most appropriate for mineral soils with a low organic matter content (UNECE, 2004). For our purposes of examining tree health, most of the previous research points to Al toxicity in relation to Ca depletion as the main indicator of tree mortality and decline. Therefore, we have chosen to calculate $ANC_{(le,crit)}$ (Equation 3) by setting the critical Al concentration through the $(BC/Al)_{crit}$ ratio. Further discussion on the criterion chosen is provided in the following sections.

$$ANC_{(le,crit)} = -Q^{2/3} \times \left(1.5 \times \frac{BC_{dep} + BC_w - BC_u}{K_{gibb} \times \left(\frac{BC}{Al} \right)_{crit}} \right)^{1/3} - 1.5 \times \frac{BC_{dep} + BC_w - BC_u}{\left(\frac{BC}{Al} \right)_{crit}} \qquad (3)$$

where

Q = annual runoff in $m^3\ ha^{-1}\ yr^{-1}$

BC_{dep} = base cation (i.e., Ca + K + Mg) deposition

BC_w = forest soil base cation weathering

BC_u = base cation uptake by trees

K_{gibb} = the gibbsite equilibrium constant, a function of forest soil organic matter content that affects Al solubility (Gregor et al., 2004)

BC/Al = the assumed critical base cation to Al ratio.

A depiction of the data and calculations for Equations 1 through 3 are presented in **Figure 2.1-1**. Color-coding reveals those values that are calculated, reported in literature, derived from monitoring data, or constants or assumed values specified in previous studies. This multistep process produces a single critical load value and a single value for any exceedence due to current deposition levels.

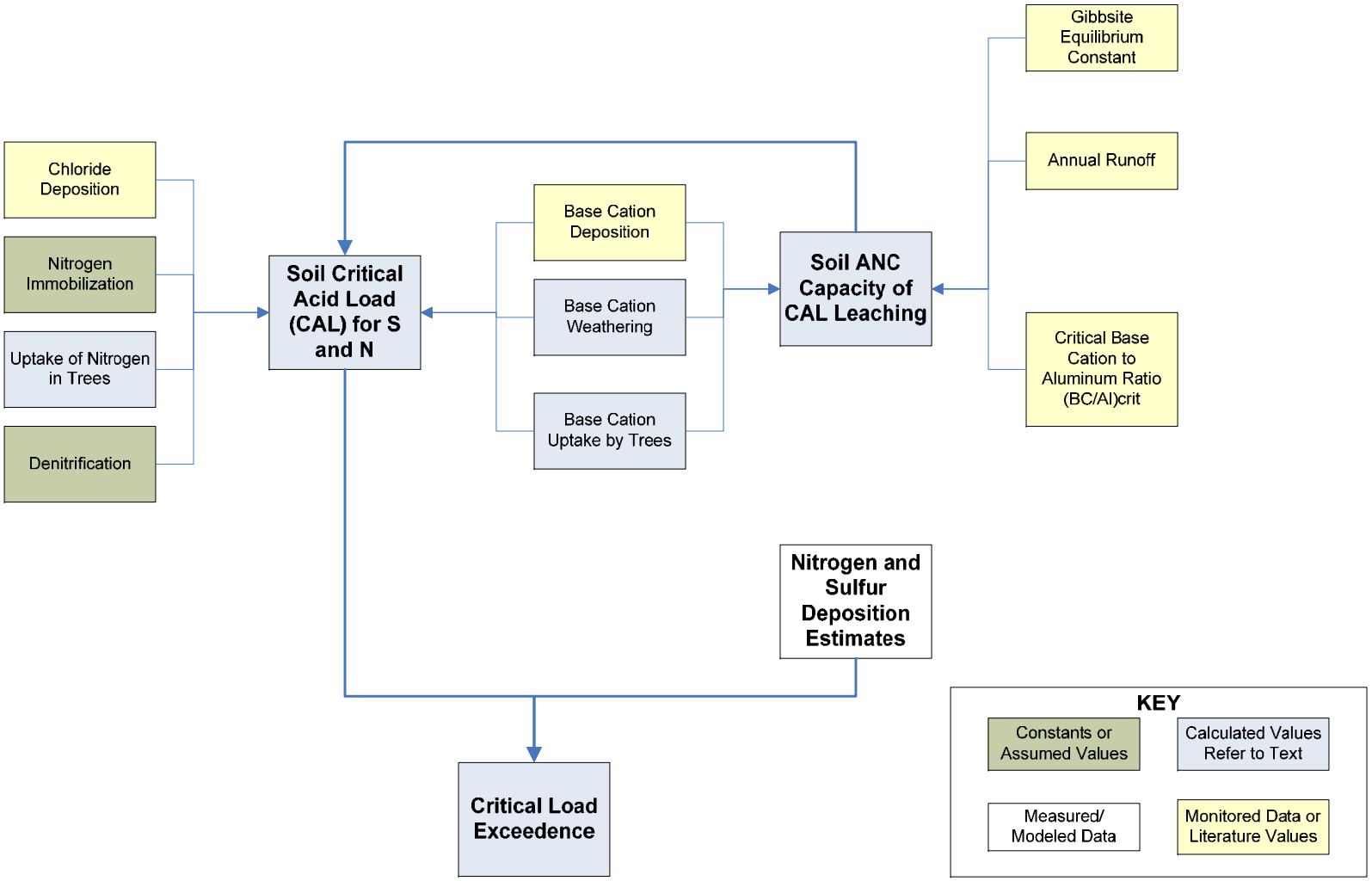

Figure 2.1-1. A diagram of the SMB method to calculate critical loads for acidity showing data derivations by model component.

To define a critical load function (CLF) against which all combinations of ambient nitrogen and sulfur deposition may be compared, you must calculate the maximum and minimum critical load levels for both nitrogen and sulfur. These maximum and minimum levels are defined in Equations 4 through 6 and are illustrated in **Figure 2.1-2** (UNECE, 2004). With respect to sulfur, there is no minimum critical level of sulfur deposition; the immobilization, uptake, and reduction of sulfur are not considered in this critical loads framework because these processes have been shown to be insignificant contributions to the cycling of nutrients within forests (Johnson, 1984). This results in no minimum critical level of sulfur deposition. The maximum critical load of sulfur ($CL_{max}(S)$) occurs when nitrogen deposition does not exceed the nitrogen sinks (Ni + Nu + Nde) within the ecosystem. At these low nitrogen deposition levels, all acidity from deposition is due to sulfur. As such, the critical load is calculated as previously defined, but considers only sulfur (Equation 4). The minimum critical deposition load for nitrogen ($CL_{min}(N)$), the load at which the system can no longer absorb nitrogen deposition and the acidification effects begin to take place, occurs when deposition equals the nitrogen sources and sinks within the system (Equation 5). Finally, the maximum critical load level for nitrogen ($CL_{max}(N)$) occurs when there is no sulfur deposition and all acidity due to deposition comes from nitrogen. Translated into an equation, this critical load can be calculated as the sum of $CL_{min}(N)$ and $CL_{max}(S)$ (corrected for denitrification).

$$CL_{max}(S) = BC_{dep} - Cl_{dep} + BC_{w} - BC_{u} - ANC_{le,crit} \quad (4)$$

$$CL_{min}(N) = N_{i} + N_{u} + N_{de} \quad (5)$$

$$CL_{max}(N) = CL_{min}(N) + \frac{CL_{max}(S)}{1 - f_{de}} \quad (6)$$

where

f_{de} = denitrification fraction ($0 < f_{de} < 1$); unitless.

The definitions of these maximum and minimum critical loads levels help define the combinations of nitrogen and sulfur deposition that will fall below, meet, or exceed the critical loads. All combinations of nitrogen and sulfur deposition that fall on the function line defined by the maximum and minimum levels, the Critical Load Function (CLF), (Figure 2.1-2) are at the critical load level. Any deposition combination that falls within the grey area is below the critical

load level, as defined by the receptor criterion used in calculating the $ANC_{le,crit}$. The white space within Figure 2.1-2 defines combinations of nitrogen and sulfur deposition that exceed the critical load.

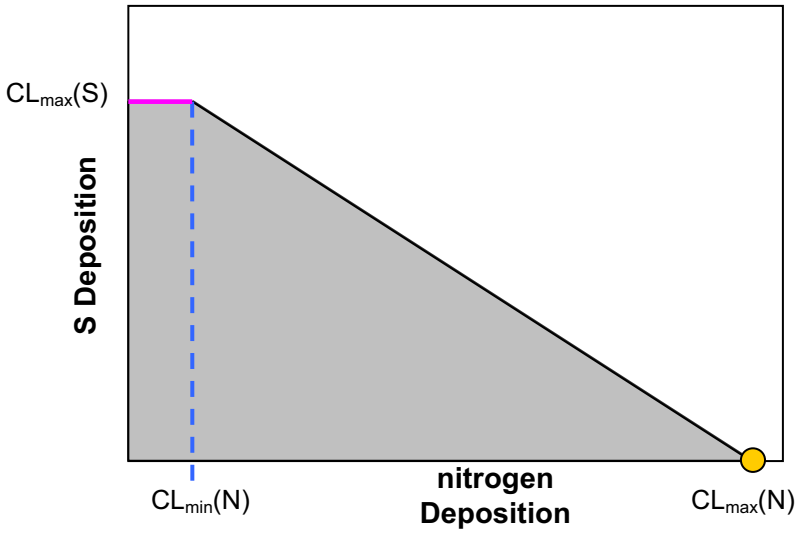

Figure 2.1-2. Illustration of the Critical Load Function (CLF) created from the calculated maximum and minimum levels of nitrogen and sulfur deposition (eq ha^{-1} yr^{-1}). The grey areas show deposition levels in compliance with the established critical loads. The pink line is the maximum critical level of sulfur deposition (valid only when deposition is less than the minimum critical level of nitrogen deposition [blue dotted line]). The gold circle represents the maximum critical level of nitrogen deposition (where there is no sulfur deposition). When there is no denitrification (e.g., upland forests), the slope of the line is 1.

Additional calculations for individual parameters used within the SMB are summarized and described below.

The base cation weathering rate (BC_w) can be estimated through a number of different methods (UNECE, 2004). Here we present the method used by McNulty and colleagues (2007) in their national analysis (Equations 7 through 9). This method, first developed by Sverdrup and colleagues (1990), relies on a combination of parent material and clay percentage to determine the soil weathering rate. This model parameter is one in which a large quantity of uncertainty can be introduced into the model; site-specific investigations will be conducted to verify that this method is appropriate before full implementation in the model.

$$\text{Acid Substrate: } BC_e = (56.7 \times \%\text{clay}) - (0.32 \times (\%\text{clay})^2) \quad (7)$$

Intermediate Substrate: $BC_e = 500 + (53.6 \times \%clay) - (0.18 \times (\%clay)^2)$ (8)

Basic Substrate: $BC_e = 500 + (59.2 \times \%clay)$ (9)

where

BC_e = empirical soil base cation weathering rate (eq ha^{-1} yr^{-1})

% clay = the percentage of clay within the soil substrate.

The empirical base cation weathering rate must then be corrected for air temperature and actual depth of the soil units used to determine the final BC_w. Equations 10 and 11 define these correction factors.

$$BC_c = BC_e \times e^{\left\{\left(\frac{A}{2.6+273}\right)-\left(\frac{A}{273+T_m}\right)\right\}} \quad (10)$$

$$BC_w = BC_c \times depth \quad (11)$$

where

BC_c = base cation weathering rate corrected for air temperature (eq ha^{-1} yr^{-1} m^{-1})

A = Arthenius constant (3600 K)

Tm = mean annual air temperature (ºC)

Depth = the depth of the mineral soil (m).

Nitrogen and base cation uptake were calculated in the same manner by McNulty and colleagues (2007) where differentiation is made in the concentration of either base cations or nitrogen in bark and bole (Equation 12). These calculations are conducted for each forest cover type and tree species on the site under investigation. Uptake values are only relevant if wood is being removed from the forest.

$$Uptake\,(eq\ ha^{-1}\ yr^{-1}) = AVI \times NC \times SG \times \%bark \times 0.65 \quad (12)$$

where

AVI = average forest volume increment (m^3 ha^{-1} yr^{-1})

NC = base cation or nitrogen nutrient concentration in bark and bole

SG = specific gravity of bark and bole wood (g cm^{-3})

%bark = percentage of volume growth that is allotted to bark

65% = tree volume that is removed from the site (Birdsey, 1992; Hall et al., 1998; Martin et al., 1998).

Because denitrification (the process by which NO_3^- is converted into gaseous nitrogen) usually occurs within water-saturated soil, an assumption of zero for denitrification in upland forests is valid. However, to provide a robust analysis, we have included the formula for denitrification provided by the ICP Mapping and Modeling Manual in Equation 13 (UNECE, 2004).

$$N_{de} = \begin{cases} f_{de}(N_{dep} - N_i - N_u) & \text{if } N_{dep} > N_i + N_u \\ 0 & \text{else} \end{cases} \quad (13)$$

where

f_{de} = denitrification fraction ($0 < f_{de} < 1$); unitless

N_{dep} = total nitrogen deposition.

The remaining model parameters (highlighted in yellow and green in Figure 2.1-1) will be compiled from site-specific literature and applicable previous critical loads assessments. Further details are also provided in the next section.

2.1.2 Data Requirements

To satisfy Equations 1 through 9 used to calculate the critical loads, data requirements must be met (**Table 2.1-1**). There are also additional data elements that can be used to create a more robust analysis (**Table 2.1-2**). Tables 2.1-1 and 2.1-2 also provide information on likely sources from which to obtain the data. These data sources will be further refined upon completion of the 2002 base-case scenario. All efforts will be made to develop site-specific data rather than rely on blanket estimates of parameters from the literature.

Table 2.1-1. Mandatory Data Requirements for Calculating Critical Loads for Nitrogen and Sulfur for Forest Ecosystems (as described in Duarte, 2005)

Mandatory Data Requirement	**Data Type**	**Data Source**
Wet deposition (N, S, Ca, Mg, K, Na)	Atmospheric/climate data	CMAQ
Dry deposition (N, S, Ca, Mg, K, Na)	Atmospheric/climate data	CMAQ
Runoff	Atmospheric/climate data	GSI; LE
Stand composition	Tree data	FIA; GSI; TS

Mandatory Data Requirement	**Data Type**	**Data Source**
Number of stems by species	Tree data	FIA; GSI; TS; HBFI
Nutrient concentration (N, Ca, Mg, K) by biomass fraction by species	Tree data	FIA; LE
Annual biomass removal rate by species	Tree data	GSI; LE; FIA
Percent of growth allocated to bark by species	Tree data	LE
Specific gravity of bark and bole wood by species	Tree data	LE
Mean annual increment by species	Tree data	FIA; TS; LE
Mean annual temperature (long-term)	Atmospheric/climate data	GSI
Soil depth	Soil data	SRG; TS
Soil texture	Soil data	SRG; TS
Parent material	Soil data	SRG; TS
Soil series	Soil data	SRG; TS
Organic matter percent in soil	Soil data	SRG; TS

CMAQ = estimates from the Community Multi-scale Air Quality Model; LE = literature estimates; GSI = general site information; FIA = the Forest Inventory Analysis; TS = targeted study for the site; HBFI = Hubbard Brook Forest Inventory; SRG = Soil Survey Geographic (SSURGO) Database soils data

Table 2.1-2. Optional Data Requirements for Calculating Critical Loads for Nitrogen and Sulfur for Forest Ecosystems

Optional Data Requirement	**Data Type**	**Data Source**
Latitude and longitude (center point)	Site description data	GSI
Elevation	Site description data	GSI
Polygon file and/or plot radius	Site description data	GSI
Throughfall	Atmospheric/climate data	LE
Precipitation volume (long-term)	Atmospheric/climate data	GSI
Mean annual evapotranspiration	Atmospheric/climate data	GSI; LE
Bulk deposition (N, S, Ca, Mg, K, Na)	Atmospheric/climate data	CMAQ; TS
Biomass by species	Tree data	GSI; LE; FIA
Diameter at breast height (DBH) by species	Tree data	FIA; GSI; TS; HBFI
Volume by species	Tree data	FIA; TS; LE
Number of soil pits per site	Soil data	GSI; LE
Soil bulk density	Soil data	SRG; TS

Optional Data Requirement	Data Type	Data Source
Extractable nutrients (Al, Ca, Mg, K, Na)	Soil data	SRG; TS
Cation exchange capacity	Soil data	SRG; TS
Mineralogy	Soil data	SRG; TS
Base saturation	Soil data	SRG; TS
Volumetric soil moisture	Soil data	SRG; TS

CMAQ = estimates from the Community Multi-scale Air Quality Model; GSI = general site information; LE = literature estimates; FIA = Forest Inventory and Analysis National Program; TS = targeted study for the site; SRG = SSURGO soils data.

Each study site has been the subject of a large number of studies since its creation. Therefore, many of the long-term average parameters needed for the site are available in summaries of this general site information. In other instances, targeted studies have examined certain site characteristics. For instance, Drohan and colleagues (2002) completed a targeted study of the soils in northern Pennsylvania, which included the Kane Experimental Forest. Literature estimates are available from other critical loads analyses, such as the national analysis completed by McNulty and colleagues (2007) or previous site-specific critical loads analysis, such as the work done by Pardo and Driscoll (1996) in the HBEF. The FIA by the USFS collects, analyzes, and reports information on the status and trends of America's forests, and, therefore, can be a great source for tree characteristics. Finally, the Soil Survey Geographic (SSURGO) Database by the USDA National Resources Conservation Service (NRCS) provides information on soil units intended for farm, landowner/user, township, or county natural-resource planning and management (NRCS, 2006).

2.1.3 Data Issues and Assumptions with Method

The use of the SMB critical loads analysis method on a national level has raised several issues concerning the assumptions and choices in process representation used for estimating model parameters. These issues are highlighted below to ensure that we adequately address them at the site-specific level at which we will conduct our case study analyses.

- Wet deposition data should be corrected for sea-salt interactions if your study site is within 70 km of the coast.
- Cloud deposition must be accounted for in order to not underestimate the exceedence.

- The base cation weathering rate estimation method must be validated for the site of interest. The mineral weathering rate is very significant for sites where there are concerns about acidification because of the role it plays in buffering acidic inputs. Underestimating the weathering rate will cause the critical load to be too low.
- Organic matter type should be calculated by soil map unit by combining CONUS-SOIL layers with STATSGO layers using the Earth System Science Center (ESSC) technique.
- The base cation and nitrogen uptake values calculated are only relevant if wood is being removed from the forest. In the McNulty analysis, for instance, areas designated as wilderness in the National Wilderness Preservation System were given uptake values set to zero. In site-specific studies, it may be possible to use county-level data as a crude estimate of biomass removal. Additionally, for Class I areas, it is necessary to have information about frequency and intensity of fire.
- In the national analysis (McNulty et al., 2007), denitrification was set to zero to represent upland forests. Denitrification losses are often considered to be negligible and are excluded from critical load calculations, but they should be included at sites where they are significant.
- In the national analysis (McNulty et al., 2007), nitrogen immobilization was set to 42.86 eq N ha^{-1} yr^{-1} based on average latitudes of forests in the United States. This value will be specified as a site-specific value for each of the case studies.

2.2 CRITICAL LOAD ASSESSMENT RESPONSE CURVE

In determining whether a critical load is exceeded, the key factors going into determining what the critical load is must be defined. The forest soil ANC is one of the most important factors in determining the critical load. This factor is determined based on the critical base cation to Al ratio [$(BC/AL)_{crit}$]. In most literature studies, this ratio is set to 1.0 for coniferous forests and 10.0 for deciduous forests (McNulty et al., 2007; NEG/ECP Forest Mapping Group, 2001; Pardo and Duarte 2007; UNECE, 2004). To provide more specific estimates for the tree species of interest in these case studies, we have conducted an extensive literature search to refine this ratio for determination of an appropriate critical load that can be related to tree growth or nutrition inhibition or tree die-off. A series of studies have been identified that provide the necessary link between the Ca to Al ratio (Ca:Al) in soils to tree impacts (**Table 2.2-**1).

A study by Cronan and Grigal (1995) compiled all relevant research up to that point in time on Al stress. A review of this literature resulted in the estimation of a 50:50 risk of adverse impacts on tree growth or nutrition when the soil solution Ca:Al ratio is as low as 1.0; a 75% risk when the soil solution ratio is as low as 0.5; and nearly a 100% risk when the soil solution Ca:Al molar ratio is as low as 0.2. Many studies since have referenced this study to set chemical criterion for monitoring comparisons and critical loads calculation. Additionally, other research has built on these ratios to support the findings. For instance, Shortle and colleagues (1997) found that as the Al:Ca binding ratio in the root zone of red spruce stands increased from 0.3 to 1.9, the foliar concentration of the biochemical stress marker putrescine also increased from 45 to 145 nm g^{-1}. This correlation of the putrescine concentration to the Al:Ca binding ratio (adj. r^2 0.68, $P < 0.027$) suggests that foliar stress may be linked to soil chemistry.

Table 2.2-1. Summary of Critical Endpoints for Al Effects on Tree Health

Study	**Species**	**Ca:Al Ratio**	**Risk Level**
Cronan and Grigal, 1995	Multiple species	1.0	50% risk
		0.5	75% risk
		0.2	100% risk
Thornton et al., 1987 (As cited in Cronan and Grigal, 1995)	Red spruce	1	Threshold of significant impact on tree growth or nutrient content
Thornton et al., 1986 (As cited in Cronan and Grigal, 1995)	Sugar maple	0.42 to 2.5	Threshold of significant impact on tree growth or nutrient content
Sverdrup and Warfvinge, 1993	Multiple species	0.2 to 2.8*	Point of 20% reduction in root growth
Johnson et al., 1994a, b	Not specified	> 1.0 for 4 years	High mortality
DeWitt et al., 2001	Norway Spruce	< 0.5	reduced Mg concentrations in needles in third year
Shortle et al., 1997	Red Spruce	Correlation between Al:Ca ratio to biological stress marker	Use Cronan and Grigal risk levels for comparison
Drohan et al., 2002	Sugar Maple	< 1.0	Declining plots

Study	Species	Ca:Al Ratio	Risk Level

* Ratio presented is BC:Al, not Ca:Al

For this analysis, we plan to vary the BC:Al critical ratio based on previous research (Cronan and Grigal, 1995; Drohan et al., 2002) to reflect different risk levels for tree mortality, thereby producing different $ANC_{le,crit}$ and resulting CLFs. For example, a critical load would be developed using the level of BC:Al shown to produce a 20% decline in growth in trees. A second critical load would be developed using the level of BC:Al shown to produce a 50% decline and so on. Other critical loads analyses have chosen to use set values for the $(BC:Al)_{crit}$. For instance, in the national analysis by McNulty and colleagues (2007), values were set at 1.0 for coniferous forests (Gregor et al., 2004) and 10.0 for deciduous forests (Watmough et al., 2004). By using various $(BC:Al)_{crit}$ values based on the anticipated level of risk to tree health, we are able to evaluate different CLFs against the baseline deposition levels and any policy or deposition reductions scenarios we are provided (**Figure 2.2-1**).

The literature values to this point have provided a mixture of critical levels related to either the Ca:Al ratio or the BC:Al ratio. As shown in Equations 1 through 3, the critical loads analysis has been developed in terms of BC:Al. The work by Cronan and Grigal (1995) presents these risk levels in terms of Ca:Al and not BC:Al. The Ca:Al ratio is not directly transferrable to BC:Al ratios, although work has been done to present the critical load framework in terms of Ca:Al (Heywood et al., 2006). These alterations of the basic SMB method require the estimation of Ca weathering and leaching rates, which introduce further sources of uncertainty to the model calculations in addition to the estimation of those rates for base cations. For this reason, we have chosen to proceed with BC:Al ratios related to risk levels. Sverdrup and Warfvinge (1993) have provided such ratio-risk level relationships. At this time, we present the ratios reported by Cronan and Grigal in the graphics for illustrative purposes. The actual analysis will be conducted using critical BC:Al levels derived by Sverdrup and Warfvinge. If the ratios for BC:Al are not to provide relatable risk levels, we will proceed with the methods developed by Heywood and colleagues (2006) to use the Ca:Al ratios reported by Cronan and Grigal (1995).

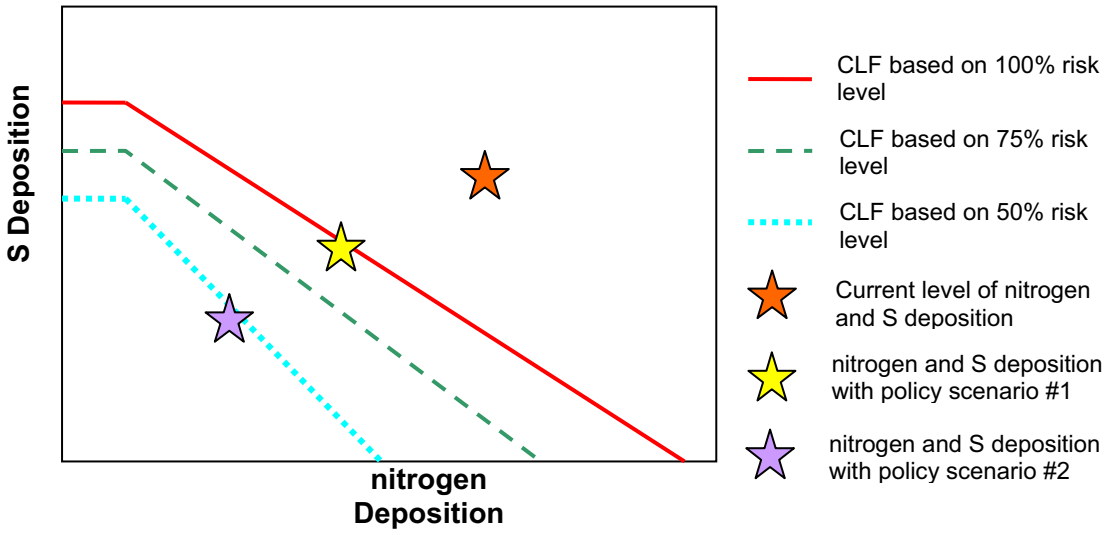

Figure 2.2-1. An example of the response curves that relate deposition scenarios to critical loads calculated based on varying levels of expected risk in tree mortality.

3. RESULTS

At this time we do not have current results for the 2002 base-case ("current condition") scenario. The intention of this draft report is to lay out the methods that will be used to conduct this base- case modeling run. We intend to perform the base-case scenario during the summer of 2008. The 2002 base-case scenario and future case study assessments, when combined, will result in a figure, such as the one in Figure 2.2-1, which can be used to assess the most feasible and beneficial nitrogen and sulfur reduction scenario.

3.1 CURRENT STATE OF SYSTEMS

In future drafts of the report, this section will summarize the results of the 2002 base-case scenario, which will rely on Community Multi-scale Air Quality Model (CMAQ) output for that year based on various sources' measured emissions rates. Critical loads research at each of the case study sites is either not available in the literature, or exists for a period other than the one of interest. For now, we present some results on the health of trees, deposition levels, and any available thresholds that will provide a basis of comparison for the 2002 base-case scenario.

3.1.1 Sugar Maple

Horsley et al. (2000) found that the most important factors associated with sugar maple health were foliar levels of Mg and Mn, as well as defoliation history. They propose that acid deposition may contribute to the low base cation status on upper slopes, but indicate that the relative contributions of geologic factors and acidic deposition to low base cation status and sugar maple decline remain unquantified in northern Pennsylvania. Bailey et al. (2005) found that between between 1967 and 1997, there were significant decreases in exchangeable Ca and Mg concentrations and pH at all depths in the soils of the Allegheny Plateau. Atmospheric deposition of various solutes, including NO_3^- and SO_4^{2-}, are presented in **Table 3.1-1**.

Table 3.1-1. Atmospheric deposition (kg ha^{-1} yr^{-1}) of solutes at the Kane Experimental Forest, PA, from the National Atmospheric Deposition Program/National Trends Network

Solute	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**
NO_3-N	4.66	4.68	5.31	4.01	4.53	4.62	4.16
NH_4-N	2.54	1.79	2.81	2.17	2.59	2.51	1.89
Inorganic N	7.20	6.48	8.12	6.19	7.12	7.13	6.05
SO_4-S	11.52	9.06	12.15	7.38	9.12	9.07	8.07
Ca^{2+}	1.37	1.16	1.30	0.98	1.27	1.32	0.88
Mg^{2+}	0.18	0.39	0.22	0.15	0.20	0.19	0.13
K^+	0.20	0.63	0.27	0.14	0.45	0.17	0.13
Na^+	0.62	0.64	0.54	0.46	0.81	0.52	0.34
Cl^-	1.56	1.98	1.63	1.22	1.73	1.47	1.20
H^+	0.72	0.62	0.82	0.53	0.60	0.63	0.59

Note: Values from 1993 and 1997 do not meet all NADP/NTN criteria for completeness (Lewis and Likens, 2007).

3.1.2 Red Spruce

There are two studies that can be used to summarize work at HBEF: one is a site-specific critical loads study conducted by Pardo and Driscoll (1996), and another is a statewide assessment of sustainable deposition by the Forest Mapping Group (NEG/ECP Forest Mapping Group, 2005).

In the Pardo study, critical loads were calculated over a time-series spanning 22 years, using long-term biogeochemical data collected at HBEF. Critical load calculations were made for both HBEF and Huntington Wildlife Forest using four charge and mass balance equations:

steady-state water chemistry method, nitrogen mass balance method, basic cation mass balance method, and steady-state mass balance method. Data types included stream water and precipitation chemistry, precipitation volume and stream water flux, biomass increment, soil pools and increment, and mineral weathering rate. Calculations for HBEF were made for three periods, 1965 to1976, 1977 to 1981, and 1982 to 1986, each having a different rate of biomass accumulation. Critical loads of N, with respect to acidity, for Huntington Wildlife Forest and HBEF ranged from 0-630 mol ha^{-1} yr^{-1}. Critical loads of nitrogen, with respect to elevated nitrogen (eutrophication and nutrient imbalances) ranged from 0-1450 mol ha^{-1} yr^{-1}. **Table 3.1-2** summarizes the critical loads calculated using each method.

Table 3.1-2. Critical Load Calculations for the Hubbard Brook Experimental Forest

Model	**Critical load type**	**1965–1976**	**1977–1981**	**1982–1986**	**1965–1986**
Steady-state water chemistry	Critical [NO_3^-] (μeq L^{-1})	11	-1	-4	5
Nitrogen mass balance	Critical nitrogen load (mol ha^{-1} yr^{-1})	1452	923	133	1033
Basic cation mass balance	Critical nitrogen load (eq ha^{-1} yr^{-1})	62	133	91	84
Modified basic cation mass balance	Critical nitrogen load (eq ha^{-1} yr^{-})	1405	770	-45	931
Steady-state balance	Critical nitrogen load low (eq ha^{-1} yr^{-})	498	630	606	552
	Critical nitrogen load high[1] (eq ha^{-1} yr^{-})	-433	-240	-236	-334

[1] Negative critical load values were set to 0 for analysis purposes in the original work (Pardo and Driscoll, 1996).

The Forest Mapping Group found that a 50% reduction in nitrogen and sulfur deposition can reverse damaging forest effects by 76% in New Hampshire. They also found that atmospheric deposition of nitrogen and sulfur during 1999 to 2003 (**Figure 3.1-1**) exceeded the critical load in approximately 18% of the forested area of New Hampshire. The critical loads estimated by the group (**Figure 3.1-2**) ranged widely in New Hampshire and Vermont (0 – 21 keq ha^{-1} y^{-1}) as a result of the diverse geology and climate of the region. It must be remembered that the Forest Mapping Group used an alternative form of the critical loads method, relying on

sustainable deposition, and thus, their findings will not be directly comparable to the results that will be calculated under the methods described for this case study.

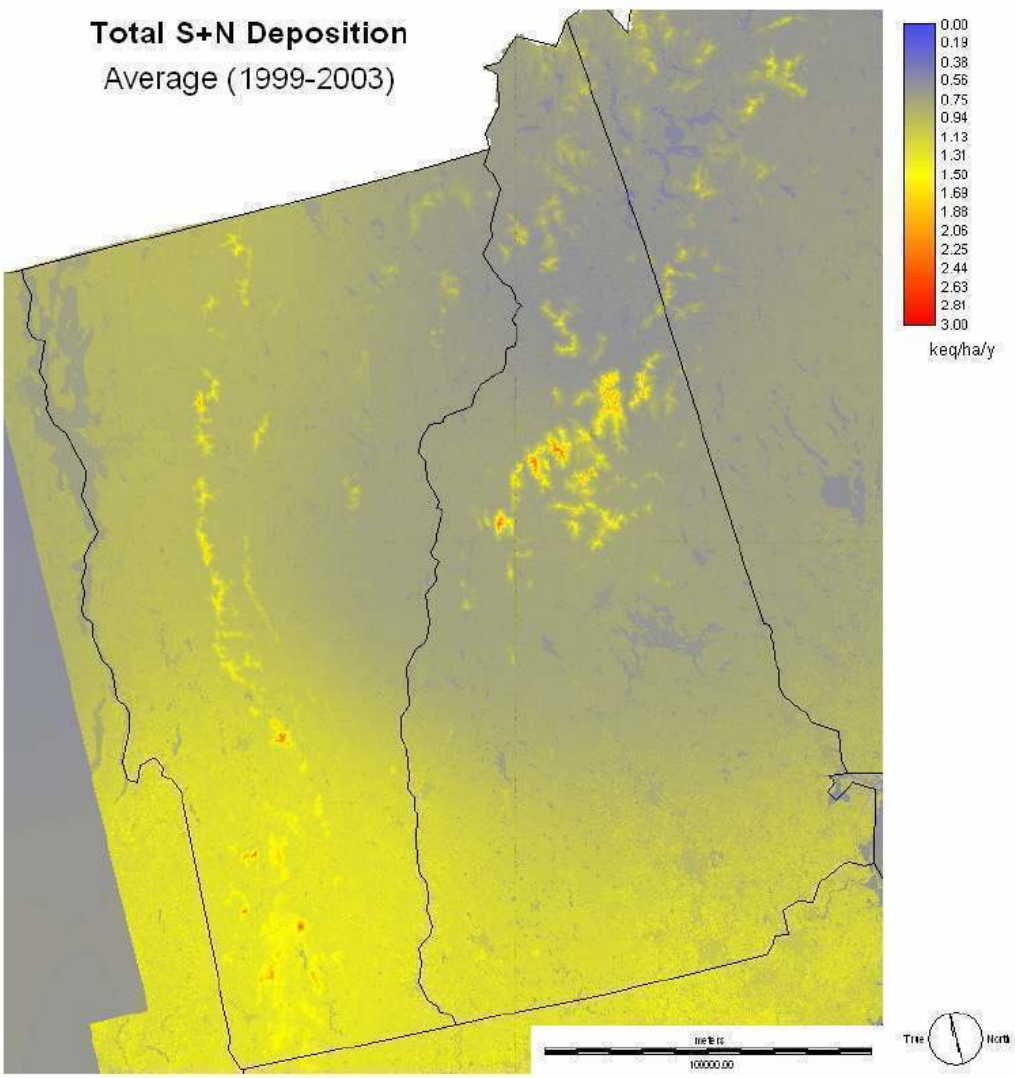

Figure 3.1-1. Average annual atmospheric deposition of sulfur and nitrogen (particle + SO_2 + precipitation + cloud water) to New Hampshire and Vermont (1999–2003). Nitrogen includes both ammonium and $\mathbf{NO_3^-}$ forms (NEG/ECP Forest Mapping Group, 2005).

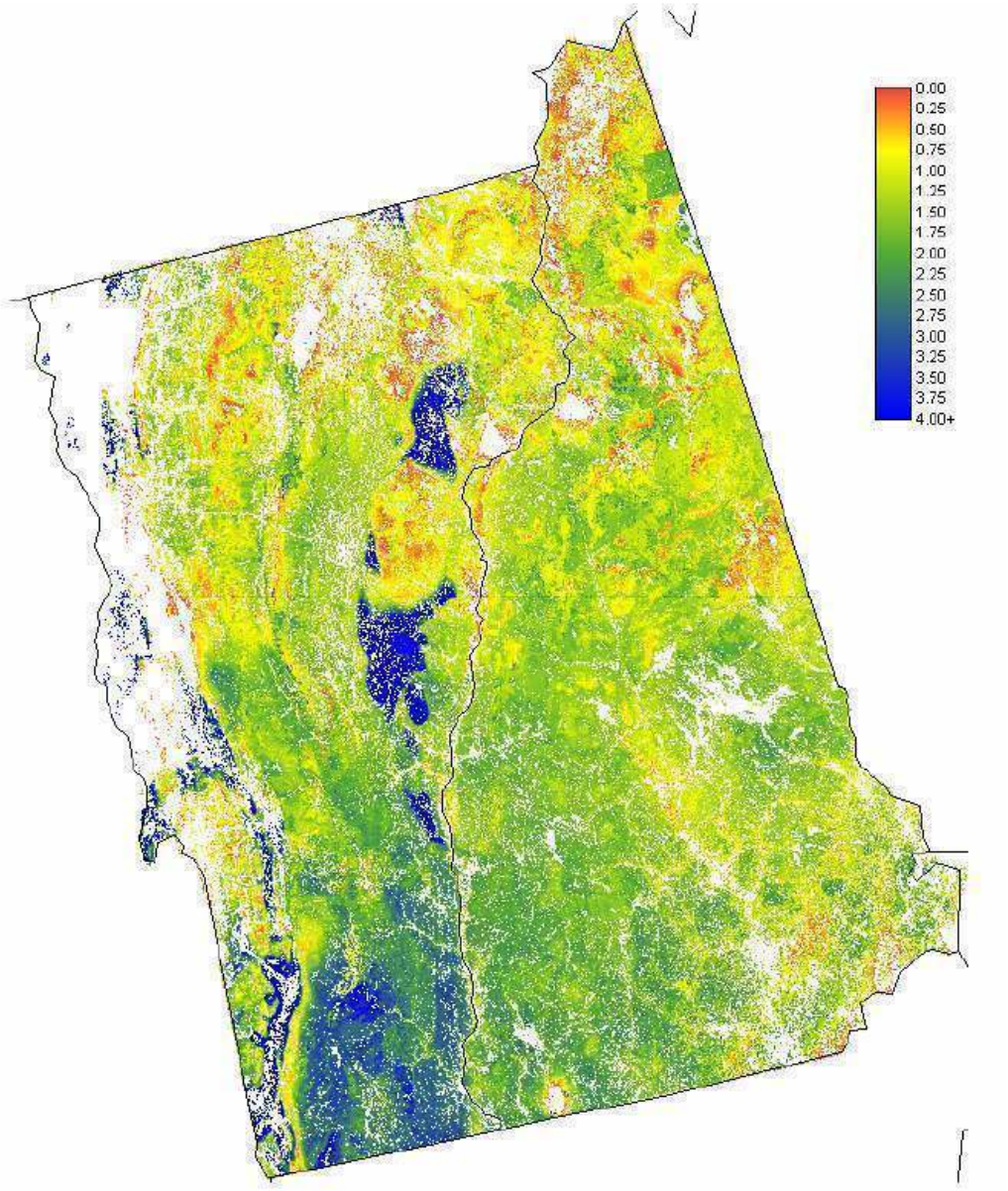

Figure 3.1-2. Critical loads of sulfur and nitrogen for upland forest areas of New Hampshire and Vermont (NEG/ECP Forest Mapping Group, 2005).

3.2 FUTURE CASE STUDY ASSESSMENTS

The future case study assessments will include the 2002 base-case scenario and the future policy scenarios designated by alternative CMAQ inputs to the critical loads model. The data requirements for the case study assessments will all be satisfied upon completion of the 2002 base-case scenario. The actual critical loads functions (shown in Figure 2.2-1) will be completed with the base-case scenario because the critical loads depend on model parameters for each site that are independent of the estimates of the nitrogen and sulfur depositions measures that will be

derived from the various CMAQ deposition scenarios (assuming that base cation deposition values will not be derived from CMAQ data, but rather estimated from site-specific literature, studies, and monitoring results for the time period of interest). The various deposition policy scenarios, in addition to the base case, can then be plotted against the CLFs for final analysis, as depicted in Figure 2.2-1.

If additional information is desired, there are methods presented in the UNECE ICP Mapping and Modeling Manual that allow for critical loads to be examined on the basis of decreases in only one of the deposition parameters instead of decreases in both nitrogen and sulfur. For further details on this type of analysis, please refer to the manual (UNECE, 2004).

4. IMPLICATIONS FOR OTHER SYSTEMS

Critical loads analyses have been widely used across all of Europe and are now required in some instances. Canada has also used critical loads for deposition policy scenarios. Within the United States, there has been one national analysis and several targeted analyses using different critical loads methods in the recent literature. Statewide assessments were conducted by the Forest Mapping Group within New England using a sustainable deposition approach to critical loads (NEG/ECP Forest Mapping Group, 2001). These applications illustrate that a critical loads method can be applied to a wide variety of geographic and climatic terrestrial ecosystems.

The scalability of the analysis can also be assessed through these previous analyses. The national analysis conducted for the United States (McNulty et al., 2007) required the use of several simplifying assumptions that left out key points highlighted by others, such as cloud deposition (NEG/ECP Forest Mapping Group, 2001) and correction for sea-salt interactions. These issues were listed in Section 2.1.3. The statewide analyses conducted by the Forest Mapping Group addressed most of the issues listed in that section showing that larger scale applications are possible. Ultimately, the scalability of a critical loads analysis depends on the data sources available, the assumptions made within the study design, and the internal scale of the model calculations.

The question remains on whether the chemical criterion of using the Ca to Al ratio to provide the link to biological indicators can be used within the same critical loads method in various systems across the country. The apparent answer is “yes.” This is because a plethora of studies have examined nutrient imbalances in soil solution and their effects on tree health and

foliar chemistry. Numerous other studies have linked the nutrient imbalances in soil solution to Al increases in soil solution. The nutrient imbalances and Al increases have also been shown to stem from acidic deposition. Although the links are not direct in most literature studies, the areas covered and the nutrients and cations studied provide enough information to discern the same effects across regions.

5. UNCERTAINTY

Because the SMB model examines a long-term, steady-state balance of nitrogen and sulfur inputs, sinks, and outputs within an ecosystem and does not represent dynamic soil processes, the results of the model are general system estimates and not temporally varying cause and effect results. Another concern with using this method is that the representation of internal fluxes (e.g., weathering rates, nitrogen immobilization) is independent of soil chemical conditions (such as pH) (UNECE, 2004). The use of these representations relies on the assumption that soil conditions do not vary over short periods and can be accurately represented by longer-term averages. Systems that experience rapid changes in soil and vegetation characteristics (i.e., due to large storm or erosion events) will be sources of greater uncertainty in the results than systems that remain relatively stable over a number of years.

Additionally, as widely used as the SMB is, there are still fundamental issues of uncertainty surrounding the calculation method. The uncertainty comes from the equation's dependence on assumptions that the researcher must make, as well as the need to pull data from a variety of sources. For example, it is difficult to obtain the most accurate estimate of the forest soil's weathering rate based on forest system disparities. Also, calculating the forest system's ANC relies on multiple variables that can be very difficult to estimate and often introduces a wide range of critical loads. Li and McNulty (2007) tested SMB's accuracy and reliability across a large scale in the United States. The results of the study indicated that uncertainty in using SMB to assess critical loads of acid deposition came primarily from varying assessments of base cation weathering and ANC, with each respectively contributing 49% and 46% to the total variability in CAL estimates. Uncertainty in base cation weathering was dominated by the base cation weathering base rate (74%), with additional large contributions from soil depth and temperature. The most important parameters to sensitivity in $ANC_{le,crit}$ were the base cation weathering base rate, soil depth, growth rate, stem wood density, and base cation weathering

percent. A 20% increase in each of these parameters led to a > 90% increase in $ANC_{le,crit}$. Overall, base cation weathering base rate, soil depth, and soil temperature were also critical parameters to the model (Li and McNulty 2007).

Thus, improvements to the model must be made to reduce the amount of error in obtaining estimates of the two most important factors—base cation weathering rate and the soil's ANC—in order to reduce the uncertainty in the range of CALs that are developed. There are a number of different methods that can be used to estimate the magnitude of weathering. The seven different approaches used to quantify soil weathering rates presented in the UNECE ICP Mapping and Modeling Manual (UNECE, 2004) are as follows:

- The use of soil type and general bedrock geology to approximate the cation release
- Assignment according to the proceedings of the Skokloster workshop (Nilsson and Grennfelt, 1988)
- Approximation using the Steady-State Water Chemistry model (Henriksen et al., 1992)
- The base mineral index correlation model, total analysis correlation model, and mineralogy correlation model (Equations 7 through 9)
- Calculation with the regional version of the PROFILE model.

Although the models vary in accuracy (i.e., with the soil type and bedrock geology method and the Skokloster workshop method requiring the least amount of data), which model the researcher would use to calculate soil weathering and the subsequent release of base cations depends on the amount and types of data available.

$ANC_{le,crit}$ can be calculated (Equation 3) by either setting the critical Al and hydrogen ion concentrations and converting them to critical fluxes or by defining the fluxes in relation to a critical molar ratio of Ca or base cations to Al. Setting critical Al and hydrogen ion concentrations is yet another variable that may introduce variability. Critical concentrations can be set for Al, hydrogen ion, or both, that are related to adverse effects on the chosen receptor. Different gibbsite equilibrium constant values can also affect the critical load; therefore, it is important that the value selected is related to the percentage of organic matter in the soil at the rooting zone of the selected receptor. Different critical molar ratio values affect the critical load, as does the choice of which ratio—$(Ca:Al)_{crit}$ or $(BC:Al)_{crit}$ —is applied.

For initial analyses, we will seek to control for and quantify uncertainty by using a combination of the mineralogy correlation model and site-specific literature estimates for the weathering rates and through variation of the $(BC:Al)_{crit}$ ratio within the CLF calculations. If use of these methods provides unacceptable results, the other methods listed above will be investigated.

6. CONCLUSIONS

The following topics will be developed more fully in later drafts after comment period:

- The critical loads method will be based on the SMB equation established
- Analyses using the SMB equation will be conducted on two sites dominated by either red spruce or sugar maples
- The SMB relies on estimates of the critical leaching level for ANC.
- Imbalances in Ca, Mg, and Al in forest soils have been shown to result from acidic deposition.
- Tree species have been shown to be sensitive to levels of Ca and Al in forest soil solutions.
- The base cation to Al or Ca to Al ratio can be used within the SMB method to provide chemical criteria of importance to the biological indicators of red spruce and sugar maples.
- Base cation to Al ratios of 1.0, 0.5, and 0.2 will be used to show risk levels for adverse effects of 50%, 75%, and 100%, respectively.

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ATTACHMENT 5

AQUATIC NUTRIENT ENRICHMENT CASE STUDY

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Aquatic Nutrient Enrichment Case Study

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ACRONYMS AND ABBREVIATIONS

ASSETS	Assessment of Estuarine Trophic Status
CAFO	confined animal feeding operation
CASTNet	Clean Air Status and Trends Network
CMAQ	Community Multiscale Air Quality model.
CO_2	carbon dioxide
DIN	dissolved inorganic nitrogen
EDA	Estuarine Drainage Areas
EPA	U.S. Environmental Protection Agency
GIS	geographic information systems
HAB	harmful algal bloom
HSPF	Hydrologic Simulation Program-FORTRAN
HUC	hydrologic unit code
INCA	Integrated Nitrogen in Catchments
ISA	Integrated Science Assessment
km	kilometer
km^2	square kilometer
MAGIC	Model of Acidification of Groundwater in Catchments
MD DNR	Maryland Department of Natural Resources
MEA	Millennium Ecosystem Assessment
m^{i2}	square mile
NAAQS	National Ambient Air Quality Standards
NCCR	National Coastal Condition Report
NEEA	National Estuarine Eutrophication Assessment
NOAA	National Oceanic and Atmospheric Administration
NO_x	nitrogen oxides
OEC	Overall Eutrophic Condition
OHI	Overall Human Influence
QA	quality assurance
QC	quality control
QUAL2K	Enhanced Stream Water Quality Model
RCA/ECOMSED	Row Column AESOP/Estuary and Coastal Ocean Model with Sediment Transport
RF1	Reach File version 1
RHESSys	Regional Hydeo-Economic Simulation System
SAV	submerged aquatic vegetation
SO_x	sulfur oxides
SPARROW	Spatially Referenced Regression on Watershed
STORET	STOrage and RETrieval
USGS	U.S. Geological Survey
WASP	Water Quality Analysis Simulation Program

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1. BACKGROUND

One classification of effects targeted for this risk and exposure assessment is nitrogen and sulfur enrichment of ecosystems in response to nitrogen oxides (NO_x) and sulfur oxides (SO_x) deposition. Enrichment effects are caused by nitrogen or sulfur deposition, but are dominated by nitrogen deposition, which is the focus of this case study. Nitrogen enrichment can result in eutrophication in aquatic systems (see Section 4.3 of the the U.S. Environmental Protection Agency's [EPA's] draft Integrated Science Assessment [ISA], U.S. EPA, 2007).

Because ecosystems may respond differently to enrichment, it will be necessary to first perform risk and exposure assessment case studies unique to the effect and ecosystem type. We will assess the feasibility of consolidating the effects and/or ecosystems in the risk and exposure assessment and, where feasible, perform a broader characterization. However, some ecosystems and their effects may be too unique to consolidate into a broad characterization.

Upon completion of all risk and exposure assessment case studies, the results of the assessments performed for unique combinations of effects and ecosystem types will be presented together to facilitate decision making on the total effects of nitrogen and sulfur deposition. Ecosystem services that relate to the effects will be identified and valued, if possible. Ecosystem services provide an additional way to compare effects across various ecosystems.

The selection and performance of case studies represent Steps 3 and 4, respectively, of the seven-step approach to planning and implementing a risk and exposure assessment, as presented in the April 2008 *Draft Scope and Methods Plan for Risk/Exposure Assessment: Secondary NAAQS Review for Oxides of Nitrogen and Oxides of Sulfur* (U.S. EPA, 2008). Step 4 entails evaluating the current nitrogen and sulfur loads and effects to a chosen case study assessment area, including ecosystems services. In this case study, we will evaluate the current nitrogen deposition load to aquatic ecosystems; in particular, estuarine systems and the role atmospheric deposition can play in the eutrophication of an aquatic ecosystem.

Eutrophication

Eutrophication is the process whereby a body of water becomes over-enriched in nutrients, resulting in increased productivity (e.g., of algae or aquatic plants) and sometimes also in decreased dissolved oxygen levels. Reactive nitrogen also promotes eutrophication in inland freshwater ecosystems and estuarine and coastal marine ecosystems, ultimately reducing

biodiversity due to a lack of oxygen needed for the survival of many species of aquatic plants and animals.

Freshwater Aquatic Ecosystems (U.S. EPA, 2007, Section 4.3.2.3.1)

A freshwater lake or stream must be nitrogen-limited to be sensitive to nitrogen-mediated eutrophication. Although conventional wisdom holds that most lakes and streams in the United States are limited by phosphorus, recent evidence illustrates examples of lakes and streams that are limited by nitrogen and show symptoms of eutrophication in response to nitrogen addition. For example, surveys of lake nitrogen concentrations and trophic status along gradients of nitrogen deposition show increased inorganic nitrogen concentration and productivity to be correlated with atmospheric nitrogen deposition (Bergström and Jansson, 2006). Additional information supporting the connection between nitrogen loading and eutrophication in freshwater systems is provided in the EPA's draft ISA (U.S. EPA, 2007).

Estuarine and Coastal Marine Ecosystems

Estuarine and coastal marine ecosystems are highly important to human and ecological welfare through the ecosystem services they provide (e.g., fisheries and recreation). "Because the productivity of estuarine and nearshore marine ecosystems is generally limited by the availability of N_r, an excessive contribution of N_r from sources of water and air pollution can contribute to eutrophication" (U.S. EPA, 2007). The National Estuarine Eutrophication Assessment (NEEA) examined more than 140 estuaries along the coasts of the conterminous United States. The assessment examined a range of symptoms of eutrophication, including algal blooms, hypoxia, and vegetation growth. Findings from the study concluded that 65% of the assessed systems had moderate to high overall eutrophic conditions (Bricker et al., 2007a). Increasingly, individual estuarine ecosystems have become the center of intensive studies on nutrient enrichment/eutrophication causes and effects. Within the Chesapeake Bay, studies of the frequency of phytoplankton blooms and the extent and severity of hypoxia revealed overall increases in these detrimental effects (Officer et al., 1984). Within the Pamlico Estuary in North Carolina, similar trends have been observed and studied by Paerl and colleagues (1998). Sources identified within these assessments range from atmospheric deposition to fertilizer applications and other land use-based applications.

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

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

1.1 INDICATORS, ENDPOINTS, AND ECOSYSTEM SERVICES

Major indicators for nutrient enrichment to aquatic systems from atmospheric deposition of reactive nitrogen require measurements based on available monitoring stations for wet deposition (National Atmospheric Deposition Program [NADP]/National Trends Network [NTN]) and limited networks for dry deposition (Clean Air Status and Trends Network [CASTNet]). Wet deposition monitoring stations can provide more information on an extensive range of nitrogen species than is possible for dry deposition monitoring stations. This creates complications in developing estimates for total nitrogen deposition levels because dry deposition data sources will likely be underestimated due to the use of fixed deposition velocities that do not reflect local conditions at the time of measurement, under-representation of monitoring sites in certain landscapes, and omission of some reactive nitrogen species in the measurements (U.S. EPA, 2007).

For aquatic ecosystems, the indicators for "nutrient enrichment" effects reflect a combination of inputs from all media (e.g., air, discharges to water, diffuse runoff, groundwater inputs). Major aquatic system indicators include nutrient loadings (Heinz Center for Science, 2007), indicators of excess algal standing crops or, in larger waterbodies, anoxia (i.e., absence of dissolved oxygen) and hypoxia (i.e., reduced dissolved oxygen) in bottom waters (see **Table 1.1-1**). For nitrogen, loadings or concentration values related to total nitrogen (a combination of nitrates, nitrites, organic nitrogen, and total ammonia) are encouraged for inclusion in numeric criteria as part of EPA-approved state water quality standards (U.S. EPA, 2000). Given the nature of the major indicators for atmospheric deposition and indicators for aquatic and terrestrial ecological systems, a data-fusion approach that combines monitoring indicators with modeling inputs and outputs is often used (Howarth, 2007).

Table 1.1-1. Key Indicators of Nutrient Enrichment Due to Reactive Nitrogen, Including NO_x

Key Indicator Group	**Examples of Indicators**	**Description**
Nitrogen deposition	Nitrate or ammonia	From wet or dry deposition monitoring stations and networks
Nitrogen throughfall deposition	Nitrate, ammonia, organic nitrogen	Special measurements in terrestrial ecosystem with corrections for nitrogen intercepted by plant canopies
Nitrogen loadings and fluxes to receiving waters	Total nitrogen or constituent species combined with flow data from gauged stations	Reflects a combination of inputs from all media (e.g., air, discharges to water, diffuse runoff, and groundwater inputs); relative role of air deposition should ideally be compared with air deposition data and also with available (preferably multimedia) models
Other indicators of aquatic system nutrient enrichment (eutrophication)	Algal standing crop (plankton and periphyton); anoxia/hypoxia for estuaries and large rivers	Reflects a combination of inputs from all media (e.g., air, discharges to water, diffuse runoff, and groundwater inputs); relative role of air deposition should ideally be compared with air deposition data and also with available (preferably multimedia) models

Nitrogen is an essential nutrient for estuarine and marine ecosystem fertility and is often the algal growth-limiting nutrient (U.S. EPA, 2007; Section 4.3.3.4). Excessive nitrogen contributions can cause habitat degradation, algal blooms, toxicity, hypoxia,, anoxia, fish kills,

and a decrease 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., 2007a).

Figure 1.1-1, excerpted from the National Oceanic and Atmospheric Administration's (NOAA's) NEEA Update, provides a brief description of each of the indicators. Further interactions between the indicators are described in the following text. For greater detail on each of the indicators, including previous findings and study areas, refer to the draft ISA and the NEEA Update.

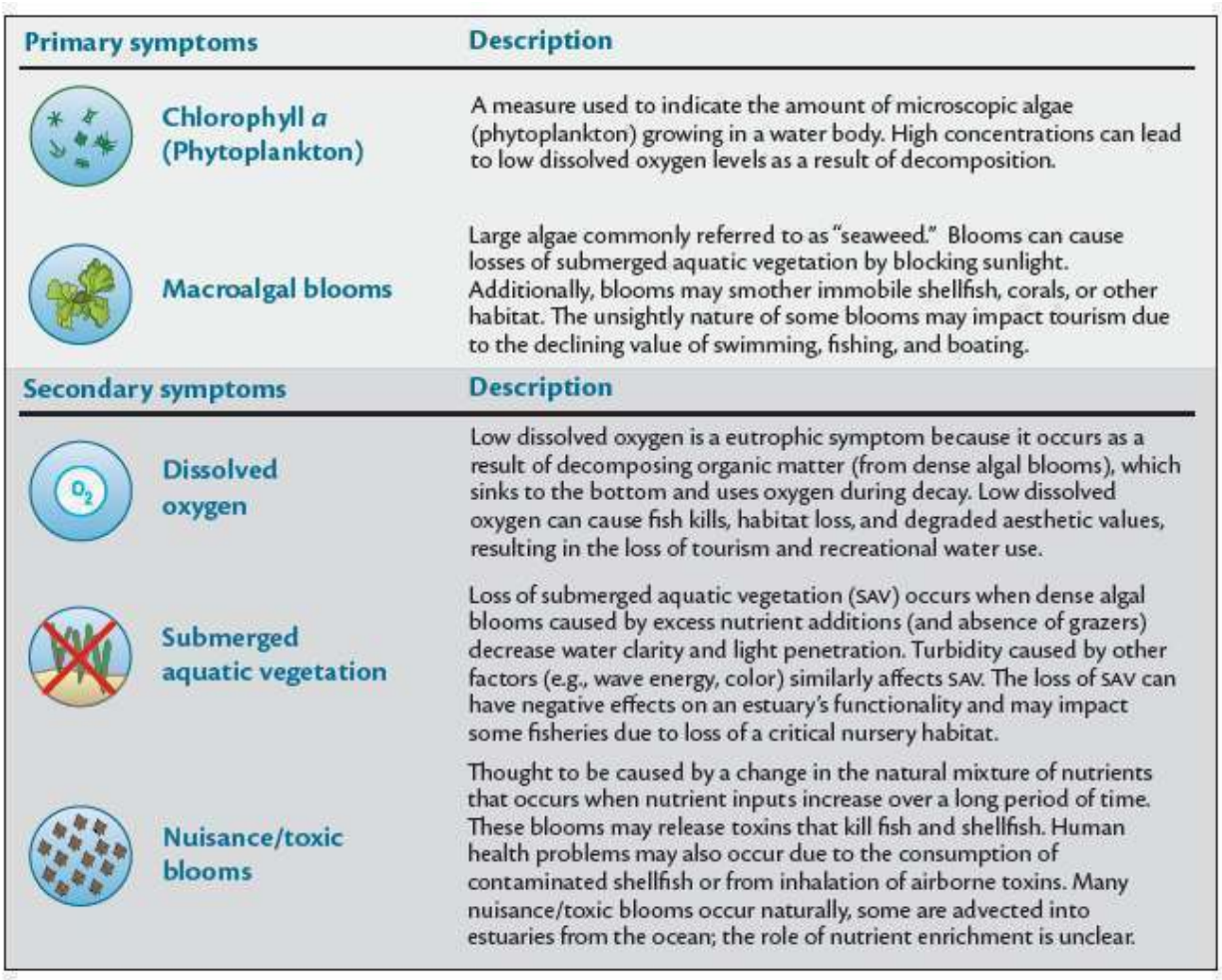

Figure 1.1-1. Descriptions of the five eutrophication indicators used in the NEEA (Bricker et al., 2007a).

Figure 1.1-2 provides a simplified progression of the indicators as the estuarine waters become more eutrophic. In the NEEA Update (Bricker et al., 2007a), an illustrated relationship

between the overall eutrophic condition, water quality and biological indicators, and influencing factors (nitrogen loads) is presented (**Figure 1.1-3**).

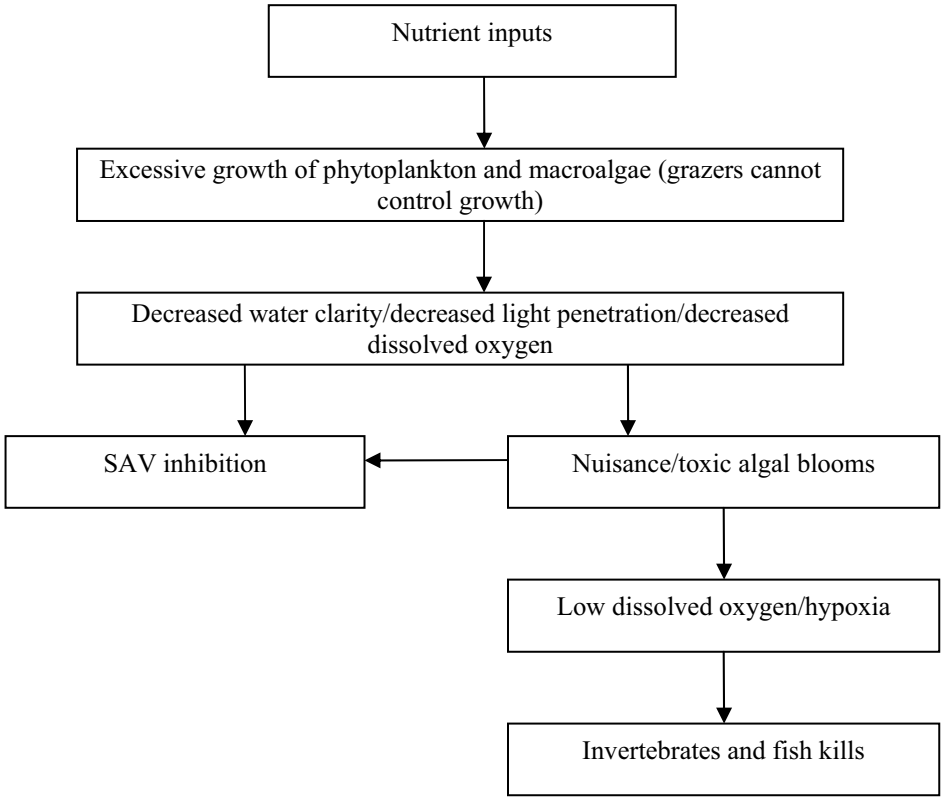

Figure 1.1-2. A simplified schematic of eutrophication effects on an aquatic ecosystem.

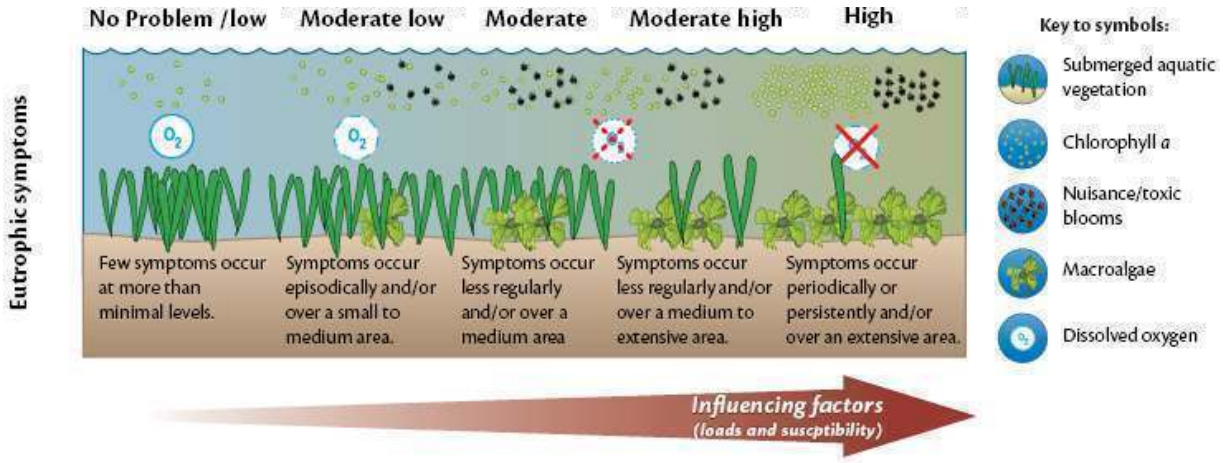

Figure 1.1-3. An illustrated representation of eutrophication measures through the use of indicators and influencing factors from the NEEA (Bricker et al., 2007a).

Indicators of eutrophication do not provide a direct link to the ecological benefits of the ecosystem. Because of this, the endpoints of eutrophication impacts and the ecosystem services affected must be identified and related to the quantifiable indicators. **Table 1.1-2** provides some examples of the endpoints associated with the indicators of eutrophication. As described in the introduction, the endpoints are ecological entities and their impacts. For instance, an indicator may be low dissolved oxygen, but the endpoint or impact of having low dissolved oxygen is a decrease in fish populations that are highly sensitive to dissolved oxygen conditions.

Table 1.1-2. Assessment Endpoints for Nutrient Enrichment Due to Deposition of Reactive Nitrogen, Including NO_x

Assessment Endpoint
Fish abundance/population
Water quality, color, clarity
Species richness/community structure
Habitat quality, including benthos and shoreline
Surface scum, odors

Continuing to link the indicators and endpoints to the ecological processes of value to society brings us to the ecosystem services related to eutrophication. Examples are provided in **Table 1.1-3.** Using the example of dissolved oxygen and the resulting decrease in fish population, we identify the ecosystem services of fish catch rate and fish kills, which support both food and materials and recreational uses of the ecosystem.

Table 1.1-3. Ecosystem Services for Aquatic Systems Affected by Nutrient Enrichment

Ecosystem Service
Fisheries ▪ Fish catch rate ▪ Fishable area ▪ Size/extent of fish kills
Recreation ▪ Boating ▪ Swimming ▪ Beach conditions

Ecosystem Service
Tourism ▪ Aesthetics
Risk of illness ▪ Drinking water quality ▪ Contaminated fish

The methods of connecting the endpoints and ecosystem services related to eutrophication are beyond the scope of this case study. Rather, the remaining discussion focuses on determining and detailing the indicator measures as a function of the changing atmospheric deposition inputs of reactive nitrogen, including NO_x.

Ecosystem services are generally defined as the benefits individuals and organizations obtain from ecosystems. In the Millennium Ecosystem Assessment (MEA), ecosystem services are classified into four main categories

- **Provisioning.** Includes products obtained from ecosystems.
- **Regulating.** Includes benefits obtained from the regulation of ecosystem processes.
- **Cultural.** Includes the nonmaterial benefits 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 (MEA, 2005).

A number of impacts on the endpoints of fish population, water quality, and habitat quality and the related ecosystem services exist, including the following

- Fish kills – provisioning and cultural
- Surface scum – cultural
- Fish/water contamination – provisioning and cultural
- Decline in fish population – provisioning and cultural
- Decline in shoreline quality (erosion) cultural and regulating
- Poor water clarity and color – cultural
- Unpleasant odors - cultural

The aquatic enrichment case study approach will focus on fisheries, recreation, and tourism. Fisheries (closings, decreased species richness) will likely be quantitatively linked to eutrophication symptoms through monitoring data, and recreation activities will likely be qualitatively related to eutrophication symptoms through user surveys.

1.2 CASE STUDIES

1.2.1 Case Study Selection

The selection of case study areas specific to eutrophication began with a review of spatial datasets of physical, chemical, and biological properties indicative of eutrophication potential in order to identify sensitive areas of the United States (**Table 1.2-1**).

Table 1.2-1. Summary of Indicators, Mapping Layers, and Models for Targeted Ecosystems

Targeted Ecosystem Effect	**Indicator(s)**	**Mapping Layers**	**Model(s)**
Aquatic nitrogen enrichment and eutrophication	▪ Nitrate and ammonia, total nitrogen (major reactive nitrogen species) ▪ Al toxicity data ▪ Chlorophyll *a* (e.g., algal standing crop) ▪ Anoxia/hypoxia (primarily estuaries and tidal rivers) ▪ Nitrogen loadings for sub-watersheds or larger basins and Estuarine Drainage Areas (EDAs) ▪ EPA *National Coastal Condition Reports* (NCCR) Water Quality Index; and NOAA Estuarine Coastal Eutrophication Index ▪ Diatom data for nitrogen-limited systems	▪ STOrage and RETrieval (STORET) retrievals ▪ U.S. Geological Survey (USGS) National Water Quality Assessment Program information ▪ USGS Spatially Referenced Regression on Watershed (SPARROW) attributes, information ▪ Water quality standards nutrient criteria for rivers and lakes ▪ EPA, NCCR, and NOAA estuarine eutrophication indicators ▪ NOAA EDAs ▪ EPA/NOAA airsheds for major Atlantic and Gulf estuaries Community Multiscale Air Quality (CMAQ) (nitrogen) by hydrological unit code	▪ USGS SPARROW ▪ PnET-BCG

We also considered the potential case study areas identified by the Ecological Effects Subcommittee (EES) of the Advisory Council on Clean Air Compliance Analysis for examining the ecological benefits of reducing atmospheric deposition. Nutrient enrichment relevant case study areas suggested by the EES are reproduced in **Table 1.2-2**. The draft ISA also recommended case study areas as candidates for risk and exposure assessments; **Table 1.2-3** contains nutrient enrichment relevant areas. For aquatic nutrient enrichment, special emphasis was given to the Chesapeake Bay 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.

For purposes of the risk assessment, two areas were selected for case study analysis to which a common methodology could be applied—Chesapeake Bay and the Pamlico Sound. We considered the following factors in choosing these case study areas:

- Availability of atmospheric deposition data
- Availability of existing water quality modeling that accounted for the role of atmospheric deposition
- A large, mainstem river that feeds the system with adequate hydrologic unit code (HUC) delineation and point- and nonpoint-source input data
- Scientific stature of the case study area
- Scalability and generalization opportunities for risk analysis results from the case studies.

These estuarine ecosystems have been the subjects of extensive research, which provides the data needed for a first phase of quantitative analysis of the role of nitrogen deposition in eutrophication. Other candidate estuarine systems will also be evaluated for potential future analyses, and freshwater ecosystems in the western United States will be the subject of case study analyses in a follow-on phase of this risk and exposure assessment.

Because the Chesapeake Bay and Pamlico Sound are fed by multiple river systems, we scaled the case study to one main stem river for each system: the Potomac River Basin for the Chesapeake Bay and the Neuse River Basin for the Pamlico Sound.

Table 1.2-2. Science Advisory Board/EES Listing of Potential Assessment Areas for Evaluation of Benefits of Reductions in Atmospheric Deposition with Respect to Aquatic Nutrient Enrichment

Ecosystem/ Region	**Main CAA Pollutant(s)**	**Percentage(s) Attributable to Atmospheric Deposition**	**Quantitative Ecological and Economic Information**	**EES Comments**
Coastal				
Waquoit Bay	Nitrogen	30%	Yes	High priority. Higher loading from non-depositional sources may confound analysis.
Chesapeake Bay	Nitrogen	20%–30%	Yes	High priority. Loading from diverse sources, particularly agricultural, may confound analysis.
Long Island Sound	Nitrogen; mercury	Nitrogen = 23%–35%; Mercury = ?	Yes	High priority. High nitrogen loading from wastewater treatment plants may confound analysis.
Barnegat Bay	Nitrogen	50% total; Direct deposition 30–39%	Yes	High priority. Direct linkage of ecological effects with atmospheric deposition; quantitative economic data exist.
Tampa Bay	Nitrogen; mercury	Nitrogen = 25%–30%	Yes	Medium priority. Examined in previous EPA efforts. Variability in loading data may confound analysis.
Gulf of Maine	Nitrogen	Low	?	Low priority. Linkage of nitrogen loadings and ecological impacts is not well established. Major source of nitrogen is open-ocean influx.
Casco Bay	Nitrogen; mercury	Nitrogen = 30%–40% Mercury = 84%–92%	Yes	Medium priority. Good data on ecological and economic impacts are available.

Ecosystem/ Region	**Main CAA Pollutant(s)**	**Percentage(s) Attributable to Atmospheric Deposition**	**Quantitative Ecological and Economic Information**	**EES Comments**
Rocky Mountains	Nitrogen	Nearly 100%	Yes	Medium priority. Levels of nitrogen loading much lower than for northeastern locations. Economic data may be lacking.

1

Table 1.2-3. Potential Assessment Areas for Aquatic Nutrient Enrichment Identified in the Draft ISA (U.S. EPA, 2007)

Area	Indicator	Detailed Indicator	Area Studies	Models	References in U.S. EPA, 2007	Source
Adirondacks	Aquatic nutrient enrichment; terrestrial nutrient enrichment; mercury methylation		PIRLA I and II; Adirondack Lakes Survey; Episodic Response Project; EMAP	MAGIC; PnET-BGC	Baker and Laflen, 1983; Baker et al., 1990b; Baker et al., 1990c; Baker et al., 1996; Benoit et al., 2003; Chen and Driscoll, 2004; Confer et al., 1983; Cumming et al., 1992; Driscoll et al., 1987a; Driscoll et al., 1991; Driscoll et al., 1998; Driscoll et al., 2001a; Driscoll et al., 2001b; Driscoll et al., 2003b; Driscoll et al., 2003c; Driscoll et al., 2007a; Driscoll et al., 2007b; Evers et al., 2007; GAO, 2000; Havens et al., 1993; Ito et al., 2002; Johnson et al., 1994b; Landers et al., 1988; Lawrence et al., 2007; NAPAP, 1998; Siegfried et al., 1989; U.S. EPA, 2003; Sullivan et al., 1990; Sullivan et al., 2006a; Sullivan et al., 2006b; U.S. EPA, 1995b; Van Sickle et al., 1996; Whittier et al., 2002; Wigington et al., 1996; Zhai et al., 2007	ISA
Chesapeake Bay	Aquatic nutrient enrichment; aquatic nitrogen limited eutrophication				Bricker et al., 1999; Bricker et al., 2007; Boesch et al., 2001; Boyer et al., 2002; Boyer and Howarth, 2002; Cooper and Brush, 1991; Fisher and Oppenheimer, 1991; Harding and Perry, 1997; Howarth, 2007; Kemp et al., 1983; Malone, 1991, 1992; Officer et al., 1984; Orth and Moore, 1984; Twilley et al., 1985	ISA

Area	Indicator	Detailed Indicator	Area Studies	Models	References in U.S. EPA, 2007	Source
Alpine and sub-alpine communities of the eastern slope of the Rocky Mountains, CO	Aquatic nutrient enrichment; terrestrial nutrient enrichment	Biomass production; NO_3 leaching; species richness			Baron et al., 1994; Baron et al., 2000; Baron, 2006; Bowman, 2000; Bowman and Steltzer, 1998; Bowman et al., 1993; Bowman et al., 1995; Bowman et al., 2006; Burns, 2004; Fenn et al., 2003a; Fisk et al., 1998; Korb and Ranker, 2001; Rueth et al., 2003; Seastedt and Vaccaro, 2001; Sherrod and Seastedt, 2001; Steltzer and Bowman, 1998; Suding et al., 2006; Williams and Tonnessen, 2000; Williams et al.,1996a; Wolfe et al., 2001	ISA
Beartooth Mountain, WY	Aquatic nutrient enrichment	Algae composition switch			Saros et al., 2003	ISA
Pamlico Estuary, NC	Aquatic nitrogen limited eutrophication	Hypoxia; phytoplankton bloom			Paerl et al., 1998	ISA
Rocky Mountain National Park, CO	Aquatic nutrient enrichment	Diatom shifts			Interlandi and Kilham, 1998	ISA
Lake Tahoe, CA	Aquatic nutrient enrichment	Primary productivity; chlorophyll *a*			Goldman, 1988; Jassby et al., 1994	ISA

1.2.2 Potomac River and Estuary

The Chesapeake Bay is the largest of 130 estuaries in the United States. It is a commercial and recreational resource for more than 15 million people who live in and near its watershed (i.e., drainage basin). The bay produces approximately 500 million pounds of oysters, crabs, and other seafood per year. The richness of its species can be seen in the value of the bay's annual fish harvest, which is estimated at more than $100 million. The Chesapeake Bay estuary receives approximately 50% of its water from the Atlantic Ocean in the form of salt water. The other half of the water (i.e., fresh water) drains into the bay from a large 165,800-square-kilometer (km^2) (64,000-square-mile [mi^2]) drainage watershed. Among the 150 major rivers and streams in the Chesapeake Bay drainage basin are the James, Potomac, York, Rappahannock, Patuxent, and Susquehanna. The Potomac watershed comprises about 22% of the land area and 30% of the population of the total Chesapeake Bay watershed. As a result, pollution loads from the Potomac River have a significant impact on the health of the bay. The Chesapeake Bay contains on average more than 68 trillion liters (18 trillion gallons) of water (http://www.waterencyclopedia.com/Ce-Cr/Chesapeake-Bay.html).

The Potomac River is approximately 413 miles (665 km) long, with a drainage area of approximately 14,670 mi^2 (38,000 km^2) and a population of approximately 5,350,000 people. It begins at Fairfax Stone, WV, and runs to Point Lookout, MD. In terms of area, this makes the Potomac River the fourth largest river along the Atlantic Coast of the United States and the twenty-first largest in the United States as a whole (http://www.fact-index.com/p/po/potomac_river.html). As shown in **Figure 1.2-1**, as well as in **Table 1.2-4 and Table 1.2-5**, 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 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 also been reported in the draft ISA to contribute from 5% to 15%–20% of the basin's total nitrogen load (U.S. EPA, 2000; Boyer et al., 2000 respectively).

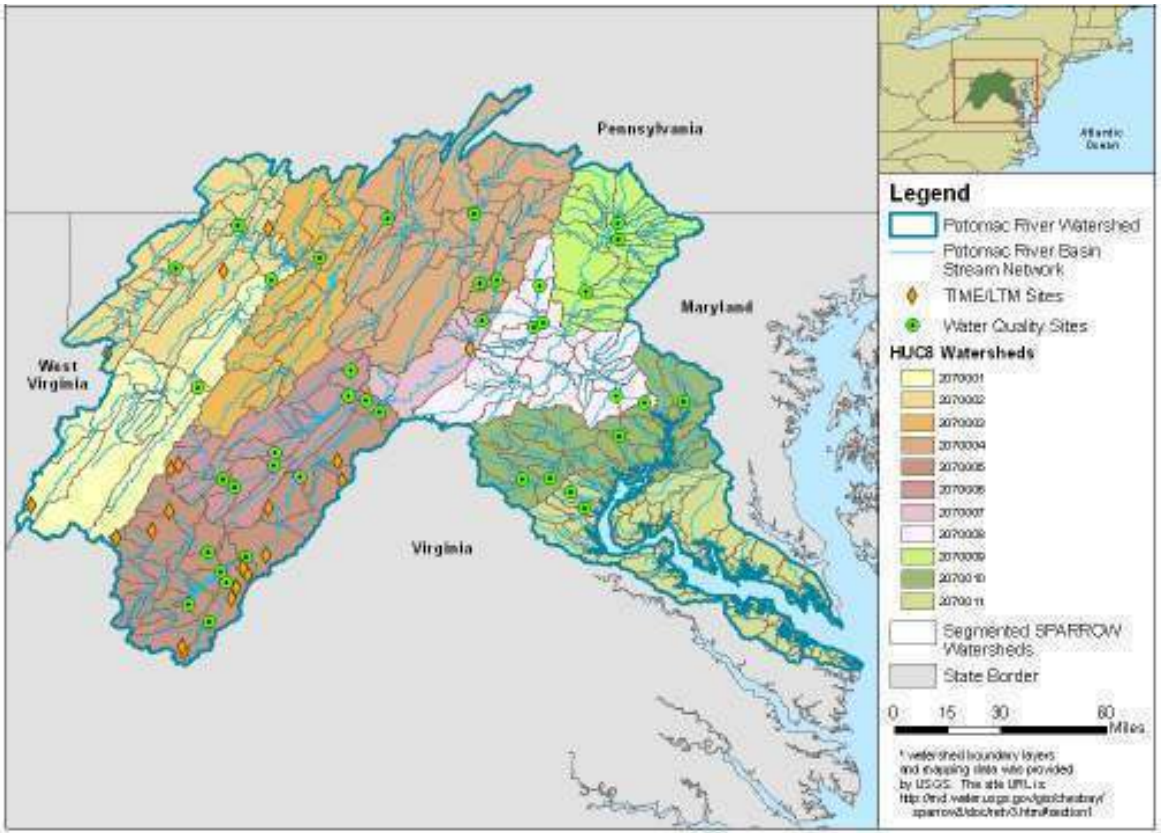

Figure 1.2-1. The Potomac River Watershed and Estuary.

Table 1.2-4. Physical Characteristics of the Potomac River Estuary (NEEA Estuaries Database)

Parameter	**Value**	**Metadata**
Estuary area (km^2)	1260	Estuary area, calculated from NOAA shapefiles
Tidal fresh zone area (km^2)	183	Tidal fresh area, calculated from NOAA shapefiles
Mixing zone area (km^2)	1077	Mixing zone area, calculated from NOAA shapefiles
Saltwater zone area (km^2)	0	Salt water area, calculated from NOAA shapefiles
Estuary volume (m^3)	6.4638E+9	Best estimate of volume from digital bathymetric chart if available; otherwise, NOAA planimetry
Estuary depth (m)	5.13	From digital bathymetric chart if available; otherwise, NOAA planimetry
Estuary perimeter (km)	1350	Perimeter of estuary, based on shapefile; can be used to calculate various aspect ratios
Percent estuary open (%)	1.33	Percent of the perimeter that is the “open” (or oceanic) boundary; somewhat subjective
Catchment area (km^2)	36804	

Parameter	Value	Metadata
Catchment mean elevation (m)	330	Calculated from catchment shapefiles + Hydro1K (a global 1-km grid of elevation)
Catchment maximum elevation (m)	1433	Calculated from catchment shapefiles + Hydro1K (a global 1-km grid of elevation)
Catchment/estuary area ratio	29.2	Area ratio, based on catchment and area data given above

Table 1.2-5. Hydrological Characteristics of the Potomac River Estuary (NEEA Estuaries Database)

Parameter	Value	Metadata
Tide height (m)	0.55	NOAA estimate of tide height, back-calculated from tide volume; in some cases, guessed from nearby systems
Tide volume (m^3)	6.93E+8	Tide height (m) x estuary area (km^2) x 10^6
Tides/day (#)	2	NOAA designation
Tide volume/day ($m^3.d^{-1}$)	1339130435	Calculated from tide volume and tides per day
Tide ratio	0.11	Tide height divided by estuary depth; a cleanup of a NOAA variable
Stratification ratio	0.02649	Total freshwater flux per day divided by tide volume per day
Percent freshwater (%)	14.5	Based on NOAA shapefiles of the three zones according to their designation
Percent mixed water (%)	85.5	Based on NOAA shapefiles of the three zones according to their designation
Percent seawater (%)	0	Based on NOAA shapefiles of the three zones according to their designation
Average salinity (psu)	11	Based on NOAA estimate of freshwater volume, but scaled to "local coastal salinity," below
Tidal exchange (days)	121	Exchange time as (Est_V/net fw_V per d) * (coastal_sal - avg_sal)/coastal_sal); a salinity-based estimate of exchange
Tidal freshwater flush (d)	36	NOAA-based calculation, using (daily tide + freshwater volume)/system volume
Daily freshwater/estuary area ($m.d^{-1}$)	27.063	NOAA estimate of daily flow/estuary area
Daily freshwater ($m^3.d^{-1}$) (best)	34100000	NOAA estimate above or (if not available) NCPDI estimate

Parameter	Value	Metadata
Flow/estuary area ($m.d^{-1}$) (best)	27.063	Best estimate/estuary area
Total freshwater Volume ($1.d^{-1}$)	0.00549	Best estimate/estuary volume (= hydraulic exchange rate)
Daily precipitation ($m^3.d^{-1}$)	3.64e+06	Direct precipitation on system, derived from PRISM Shapefile
Daily evaporation ($m^3.d^{-1}$)	2.26e+06	Direct evaporation from system, derived from LOICZ 0.5 degree database, originally from Wilmott
Daily precipitation/estuary area ($mm.d^{-1}$)	2.889	Daily precipitation/estuary area
Daily evaporation/estuary area ($mm.d^{-1}$)	1.794	Daily evaporation/estuary area
Flow ($m^3.d^{-1}$)	2.33e+07	NCPDI_1982–1991

1.2.3 Neuse River and Estuary

The Neuse River is the longest river in North Carolina, and the Neuse River Basin is the third largest river basin in the state (**Figure 1.2-2**). The Neuse River is a mainstem river to the Pamlico Sound—one of the two largest estuaries on the Atlantic Coast. The river originates in north-central North Carolina and flows southeasterly until it reaches tidal waters upstream of New Bern. At New Bern, the river broadens dramatically and changes from a free-flowing river to a sound. While the Neuse River itself is 248 miles long, there are 3,497 freshwater stream miles, 16,414 acres of freshwater reservoirs and lakes, 369,977 estuarine acres, and 21 miles of Atlantic coastline within the entire Neuse River Basin. The drainage area for the basin is approximately 14,210 mi^2 (36,804 km^2). There are 19 major reservoirs in the Neuse River Basin; most of these are located in the upper portion of the basin. The basin starts in the eastern Piedmont physiographic region, with approximately two-thirds of the basin located in the Coastal Plain (NCDENR, 2002).

The Neuse River Basin encompasses all or portions of 18 counties and 74 municipalities. The basin 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. Only 8% of the land falls into the urban/built-up category. Despite the large amount of cultivated cropland and the relatively small amount of urban area, the basin has seen a significant decrease (-180,000 acres) in cultivated cropland and forest and an increase (+227,000 acres) in developed

areas over the past 15 years (NRCS, 2001). The Neuse River Basin is divided into 14 sub-basins (6-digit NC Division of Water Quality sub-basins) (NCDENR, 2002). **Tables 1.2-6 through 1.2-8** provide physical, land use and population, and hydrological characteristics of the Neuse River Basin, respectively.

There are 332,457 estuarine acres classified for shellfish harvesting (Class SA [shellfishing]) in the Neuse River Basin. The Neuse River is important to the commercial blue crab (*Callinectes sapidus*) fishery in the eastern United States and accounted for approximately one-quarter of the blue crab harvest from 1994 to 2002 (Smith and Crowder, 2005). Eutrophication became a water quality concern in the lower Neuse River Basin in the late 1970s and early 1980s. Nuisance algal blooms prevalent in the upper estuary prompted investigations by the State. These investigations, as well as other studies, indicated that algal growth was being stimulated by excess nutrients entering the estuarine waters of the Neuse River. In 1988, a phosphate detergent ban was put in place, and the lower Neuse River Basin received the supplemental classification of nutrient-sensitive waters. Phosphorus loading was greatly reduced, and algal blooms in the river and freshwater portions of the estuary were reduced as a result of this action. However, the 1993 *Neuse River Basin-wide Water Quality Plan* (NC DENR, 1993) recognized that eutrophication continued to be a water quality problem in the estuary below New Bern. Extensive fish kills in 1995 prompted further study of the problem. Low dissolved oxygen levels associated with algal blooms were determined to be a probable cause of many of the fish kills. The algal blooms and correspondingly high levels of chlorophyll *a* prompted the State to place the Neuse River Estuary on the 1994, 1996, 1998, and 2000 303(d) List of Impaired Waters. It was determined that control of nitrogen was needed to reduce the extent and duration of algal blooms.

Atmospheric deposition is believed to play a role in nutrient loading to the Neuse River and Pamlico Sound. As excerpted from Whitall and Paerl, the following discusses the role of atmospheric deposition to nutrient loading for sensitive waterbodies:

> Excessive nitrogen loading to nitrogen-sensitive waters, such as the Neuse River Estuary (North Carolina) has been shown to promote changes in microbial and algal community composition and function (harmful algal blooms), hypoxia and anoxia, and fish kills. Previous studies have estimated that wet atmospheric deposition of nitrogen (WAD-N), as deposition of dissolved inorganic nitrogen

(DIN: NO^-_3, NH_3/NH^+_4) and dissolved organic nitrogen, may contribute at least 15% of the total externally supplied or "new" nitrogen flux to the coastal waters of North Carolina. In a 3-year study from June 1996 to June 1999, Whitall and Paerl calculated the weekly wet deposition of inorganic and organic nitrogen at 11 sites on a northwest–southeast transect in the watershed. The annual mean total (wet DIN + wet organics) WAD-N flux for the Neuse River watershed was calculated to be 956 mg $N/m^2/yr$ (15,026 Mg N/yr). Seasonally, the spring (March–May) and summer (June–August) months contain the highest total weekly nitrogen deposition; this pattern appears to be driven by nitrogen concentration in precipitation. There is also spatial variability in WAD-N deposition; in general, the upper portion of the watershed receives the lowest annual deposition and the middle portion of the watershed receives the highest deposition. Based on a range of watershed nitrogen retention and in-stream riverine processing values, we estimate that this flux contributes approximately 24% of the total "new" nitrogen flux to the estuary (Whitall and Paerl, 2001).

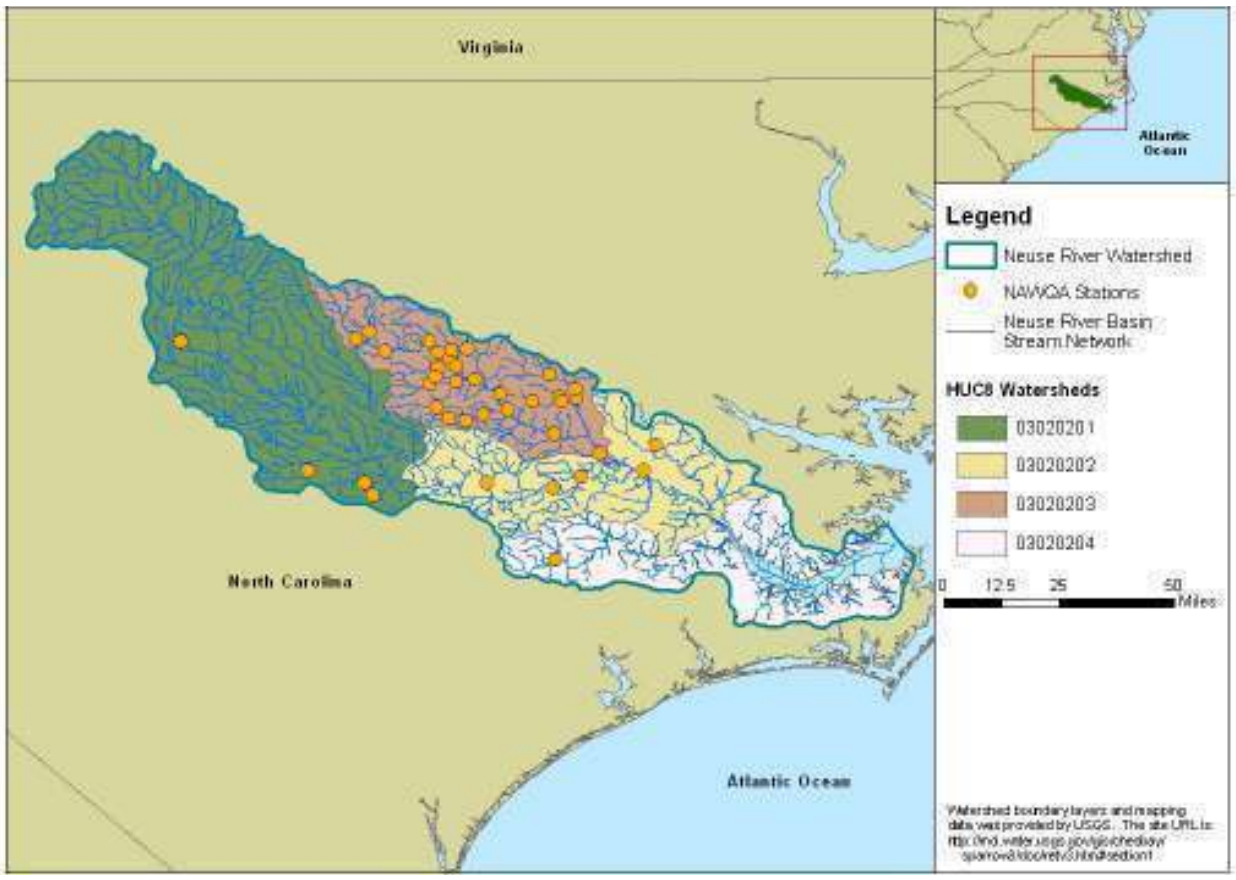

Figure 1.2-2. The Neuse River Watershed and Estuary.

Table 1.2-6. Neuse River and Estuary Physical Characteristics (NEEA Estuaries Database)

Parameter	**Value**	**Metadata**
Estuary area (km^2)	456	Estuary area, calculated from NOAA shapefiles
Tidal fresh zone area (km^2)	5	Tidal fresh area, calculated from NOAA shapefiles
Mixing zone area (km^2)	451	Mixing zone area, calculated from NOAA shapefiles
Saltwater zone area (km^2)	0	Saltwater area, calculated from NOAA shapefiles
Estuary volume (m^3)	1.304×10^9	Best estimate of volume from digital bathymetric chart if available; otherwise, NOAA planimetry
Estuary depth (m)	2.86	From digital bathymetric chart if available; otherwise, NOAA planimetry
Estuary perimeter (km)	523	Perimeter of estuary, based on shapefile; can be used to calculate various aspect ratios
Percentage estuary open (%)	2.1	Percentage of the perimeter that is the "open" (or oceanic) boundary; somewhat subjective
Catchment area (km^2)	14,066	
Catchment mean elevation (m)	56	Calculated from catchment shapefiles + Hydro1K (a global 1-km grid of elevation)
Catchment maximum elevation (m)	245	Calculated from catchment shapefiles + Hydro1K (a global 1-km grid of elevation)
Catchment/estuary area ratio	30.8	Area ratio, based on catchment and area data given above

Table 1.2-7. Neuse River Basin Land Use and Population (NEEA Estuaries Database)

Parameter	**Value**	**Metadata**
Urban (km^2)	1,328.66 (9.5%)	USGS Land Use and Land Cover (LUDA) for entire watershed 1972 with census 1990 information, base year early 1990s
Agriculture (km^2)	4,983.14 (35.6%)	USGS LUDA for entire watershed 1972 with census 1990 information, base year early 1990s
Forest (km^2)	6,648.5 (47.5%)	USGS LUDA for entire watershed 1972 with census 1990 information, base year early 1990s
Wetland (km^2)	1,020.46 (7.3%)	USGS LUDA for entire watershed 1972 with census 1990 information, base year early 1990s
Range (km^2)	5.17998 (0%)	USGS LUDA for entire watershed 1972 with census 1990 information, base year early 1990s

Parameter	Value	Metadata
Total (km^2)	13,985.93998	USGS LUDA for entire watershed 1972 with census 1990 information, base year early 1990s
Population (#)	1,015,059	Based on gridded (1-km) U.S. 1990 census data, corrected for catchments extending outside the United States (with LANDSCAN)
Population/estuary area ($\#.km^{-2}$)	2,226	Population based on gridded (1-km) U.S. 1990 census data, corrected for catchments extending outside the United States (with LANDSCAN). Estuary area, calculated from NOAA shapefiles.

Table 1.2-8. Neuse River and Estuary Hydrology (NEEA Estuaries Database)

Parameter	Value	Metadata
Tide height (m)	0.15	NOAA estimate of tide height, back-calculated from tide volume; in some cases, guessed from nearby systems
Tide volume (m^3)	6.84E+7	Tide height (m) x estuary area (km^2) x 10^6
Tides/day (#)	2	NOAA designation
Tide volume/day ($m^3.d^{-1}$)	132,173,913	Calculated from tide volume and tides per day
Tide ratio	0.05	Tide height divided by estuary depth; a cleanup of a NOAA variable
Stratification ratio	0.08318	Total freshwater flux per day divided by tide volume per day
Percent freshwater (%)	1.1	Based on NOAA shape files of the three zones according to their designation
Percent mixed water (%)	98.9	Based on NOAA shape files of the three zones according to their designation
Percent seawater (%)	0	Based on NOAA shape files of the three zones according to their designation
Average salinity (psu)	13	Based on NOAA estimate of freshwater volume, but scaled to “local coastal salinity,” below
Tidal exchange (days)	74	Exchange time as (Est_V/net fw_V per d)*(coastal_sal - avg_sal)/coastal_sal); a salinity-based estimate of exchange
Tidal freshwater flush (d)	73	NOAA-based calculation, using (daily tide + freshwater volume)/system volume
Daily freshwater/estuary area ($m.d^{-1}$)	22.368	NOAA estimate of daily flow/estuary area

Parameter	Value	Metadata
Daily freshwater ($m^3.d^{-1}$) (best)	10,200,000	NOAA estimate above or (if not available) NCPDI estimate
Flow/estuary area ($m.d^{-1}$) (best)	22.368	Best estimate/estuary area
Total freshwater volume ($1.d^{-1}$)	0.00843	Best estimate/estuary volume (= hydraulic exchange rate)
Daily precipitation ($m^3.d^{-1}$)	1.72e+06	Direct precipitation on system, derived from PRISM shapefile
Daily evaporation ($m^3.d^{-1}$)	926,000	Direct evaporation from system, derived from LOICZ 0.5 degree database, originally from Wilmott
Daily precipitation/ estuary area ($mm.d^{-1}$)	3.772	Daily precipitation/estuary area
Daily evaporation/ estuary area ($mm.d^{-1}$)	2.031	Daily evaporation/estuary area
Flow ($m^3.d^{-1}$)	7.95e+06	NCPDI_1982–1991

Ammonia emissions from fast-growing, intensive livestock feeding operations in the 1980s and 1990s are believed to contribute to nitrogen deposition in eastern North Carolina watersheds. In 1997, the North Carolina General Assembly established moratoria on the construction or expansion of certain swine farms and on lagoons and animal waste management systems for certain swine farms. One of the original purposes of these moratoria was to allow completion of certain studies related to swine farms and animal waste management systems. The 1998–2006 General Assemblies extended these moratoria because research on environmentally superior technologies was conducted. In 2007, Senate Bill 1465 was passed to establish swine waste management performance standards (North Carolina General Assembly, 2007). During that 10-year period, although the swine population was restricted from growth, there were no legislative constraints on the growth of poultry or other livestock. For example, poultry populations increased in two Neuse River Basin counties, according to the U.S. Department of Agriculture's 2002 Ag Census. Statewide, the census reported an increase in poultry farms from 5,094 in 1997 to 6,251 in 2002 statewide (USDA, 2002). (The 2007 Ag Census is not complete.) In Lenoir County in the Neuse River Basin, broilers increased from 297,000 in 1997 to 929,000 in 2002, but the total number of all-poultry farms only increased by 3, from 47 to 50. The county's turkey population decreased from 878,000 to 720,000 (USDA, 2002). In Wayne County, populations increased from 2.7 million to 3.8 million broilers and from 1.9 million to 2.0

million turkeys, and the overall number of poultry farms in Wayne County decreased from 147 in 1997 to 126 in 2002 (USDA, 2002). The continued contribution of poultry operations' growth to nitrogen deposition during the moratoria has not been assessed, particularly in terms of its deposition in the Neuse River Basin.

2. APPROACH AND METHODS

Due to the requirement that this case study span both terrestrial and aquatic systems to accommodate indirect (i.e., to the watershed) and direct (i.e., to the water surface) deposition effects, as well as the requirement that it span a variety of indicators, we determined that a modeling approach was necessary to examine the impacts due to aquatic nutrient enrichment from nitrogen and sulfur deposition.

There are several complicating factors to carrying out an analysis of eutrophication in waterbodies when one of the requirements is to include modeled output of atmospheric deposition from a high-level, detailed atmospheric model. This analysis is considered a multimedia analysis where the air, land, and water are involved. Typically, models or analysis methods existing in the literature focus on only one of those components. Links between the components with the desired output of eutrophication indicators are rare in the current literature or modeling environments. Additionally, the few instances that are available in the literature tend to focus on specific case study areas or on being highly empirical and difficult to scale or extend to alternate locations. All these facts must be considered when developing a method to examine the effects of N_r, including NO_x, deposition on aquatic nutrient enrichment.

2.1 MODELING

There are four basic steps necessary to undertake a modeling effort to examine the effects of nitrogen and sulfur deposition (RTI, 2007):

1. Choose the specific question/problem to address.
2. Choose the best models based on model formulation (e.g., are biological processes considered?), desired output, study area, data availability, and necessary uncertainty/sensitivity analyses for the models.

3. Determine and set up any processes/algorithms necessary to match atmospheric modeling output (assumed to be from Community Multiscale Air Quality [CMAQ]) to the chosen receiving water or terrestrial/watershed model.
4. Obtain the data needed for model parameterization.

The problem to be addressed in this analysis is assessment of the effects of deposition of N_r, including NO_x, on aquatic nutrient enrichment. We need to identify the impacts of both direct (i.e., deposition on the waterbody surface) and indirect (i.e., deposition within the watershed and transport to the waterbody) deposition. We need a method that will provide measures of the indicators of eutrophication that were previously described in Section 1.1.

A previous RTI International (RTI)* report (RTI, 2007) detailed the difficulty, along with the desire, to utilize atmospheric modeling in combination with the receiving-water and terrestrial/watershed models for analyzing the effects of reactive nitrogen, including NO_x, deposition. The multimedia approach to modeling is still in development; therefore, at this time, not many models are set up to immediately accept the output from an atmospheric model such as CMAQ. In the previous model investigation, RTI examined 35 receiving-water and terrestrial/watershed models, which represent a wide diversity of types of ecosystems; history, location, and spatial/temporal scale of application; scientific acceptance and organizational and agency support; complexity and requirements; state variables and processes; and management uses.

Several existing models accept atmospheric concentration or flux data, but the time-step, spatial resolution, and exact species required might all differ from the atmospheric model output. The RTI report (2007) provided a list of models that could fulfill the multimedia approach while utilizing CMAQ output as input for the atmospheric component to the model. These models include the Hydrologic Simulation Program-FORTRAN (HSPF), Regional Hydeo-Economic Simulation System (RHESSys), GT/MEL, Model of Acidification of Groundwater in Catchments (MAGIC), PnET-BGC, Integrated Nitrogen in Catchments (INCA), Spatially Referenced Regression on Watershed attributes (SPARROW), AQUATOX, Water Quality Analysis Simulation Program (WASP), Enhanced Stream Water Quality Model (QUAL2K), CE-QUAL family of models, and Row Column AESOP/Estuary and Coastal Ocean Model with Sediment Transport (RCA/ECOMSED). These models are very different from one another in

terms of the system components included, process representations, data requirements, and output parameters (for comprehensive details for each model refer to the RTI report [2007]).

After determining which models could utilize CMAQ data, we then looked at the ecosystem component encompassed by the models. The choice of case study areas that include estuaries dictated that the model chosen must provide nutrient loads to an estuary waterbody and examine the impacts of those loads within the estuary itself. Although AQUATOX and QUAL2K are receiving-water models, they do not function for estuaries nor do they account for indirect deposition over the contributing watershed. The WASP, CE-QUAL family of models, and RCA/ECOMSED are receiving-water models, which can be parameterized for estuaries, but they do not simulate terrestrial processes. Several of the other models account for indirect deposition and are strictly terrestrial models. These models include RHESSys and GT/MEL. Other models include both the indirect deposition and direct deposition, but only over streams and lakes within the watershed. These models are HSPF, MAGIC, PnET-BGC, INCA, and SPARROW.

From this analysis, it was apparent that a multiple step/model analysis would be required. We would need a step/model to examine the indirect deposition and a step/model to examine the estuarine effects. The challenge then became balancing analysis power against data, effort, and scalability requirements. Using the list of models above, we identified several that could be used to produce nutrient loads to the estuary, the obvious critical component of an eutrophication analysis. We determined that the best model for determining nitrogen loading to the estuary would track the atmospheric deposition of nitrogen through the watershed and to the estuary. This requirement eliminated models that did not provide stream networking (PnET-BGC, MAGIC) or that lumped land use categories together (INCA). The remaining models of HSPF and SPARROW are greatly different models. HSPF is a highly parameterized model that requires extensive data inputs and calibration. SPARROW is a hybrid statistical and process-based model that requires much less data for parameterization but still includes spatial variation and source investigation. We therefore chose to use SPARROW to estimate nitrogen loadings to the estuary.

We then sought to find the most applicable method for examining eutrophication effects in an estuary. The three identified models that could represent estuarine processes (i.e., WASP, CE-QUAL family of models, and RCA/ECOMSED) were systematically ruled out as

possibilities. RCA/ECOMSED is a proprietary model with extensive data requirements and requires a high level of expertise. The CE-QUAL family of models has primarily been used by the U.S. Army Corps of Engineers. The various versions of CE-QUAL all have extensive data requirements, and no indications of model integration have been uncovered in the literature. WASP provides the output desired, but requires parameterization for each system of study. Considering that the SPARROW model will provide total nitrogen loads to the estuary and the fact that we seek to provide a method that is scalable and applicable to a variety of future study sites, we chose not to use the WASP model.

With the elimination of the three identified dynamic modeling applications, a more descriptive method of evaluation was sought. We identified the NEEA method developed by NOAA as a likely candidate for eutrophication assessment.

2.2 CHOSEN METHOD

After examining several estuarine assessment options, the most comprehensive evaluation technique that could be applied on a wide scale was revealed to be an assessment of eutrophication as conducted in NOAA's NEEA. This assessment has been titled Assessment of Estuarine Trophic Status (ASSETS; Bricker et al., 2007a). This eutrophication index (EI) results in an estimation of the likelihood that the estuary is experiencing eutrophication or will experience eutrophication in the future.

The ASSETS EI incorporates indirect deposition over the watershed through evaluating the nitrogen loading to the estuary. Thus, a decision was required on how to derive the nitrogen load to the estuary based on the CMAQ modeled data. Because the ASSETS EI is a more screening-level approach, the nitrogen load to the estuary is only required to be an annual estimate of total nitrogen loading. For these reasons, we have chosen to use the SPARROW model to provide the estimates of nitrogen loading to the estuary.

The combination of SPARROW modeling and the ASSETS EI (**Figure 2.2-1**) provides a sound basis for conducting a eutrophication assessment. Both SPARROW and the ASSETS EI are supported by federal agencies and have been through several improvement iterations. As we will show in the following sections, the method provides a screening-level approach that includes an appropriate level of detail for determining the impacts on eutrophication in an estuary based on changes in atmospheric deposition loadings.

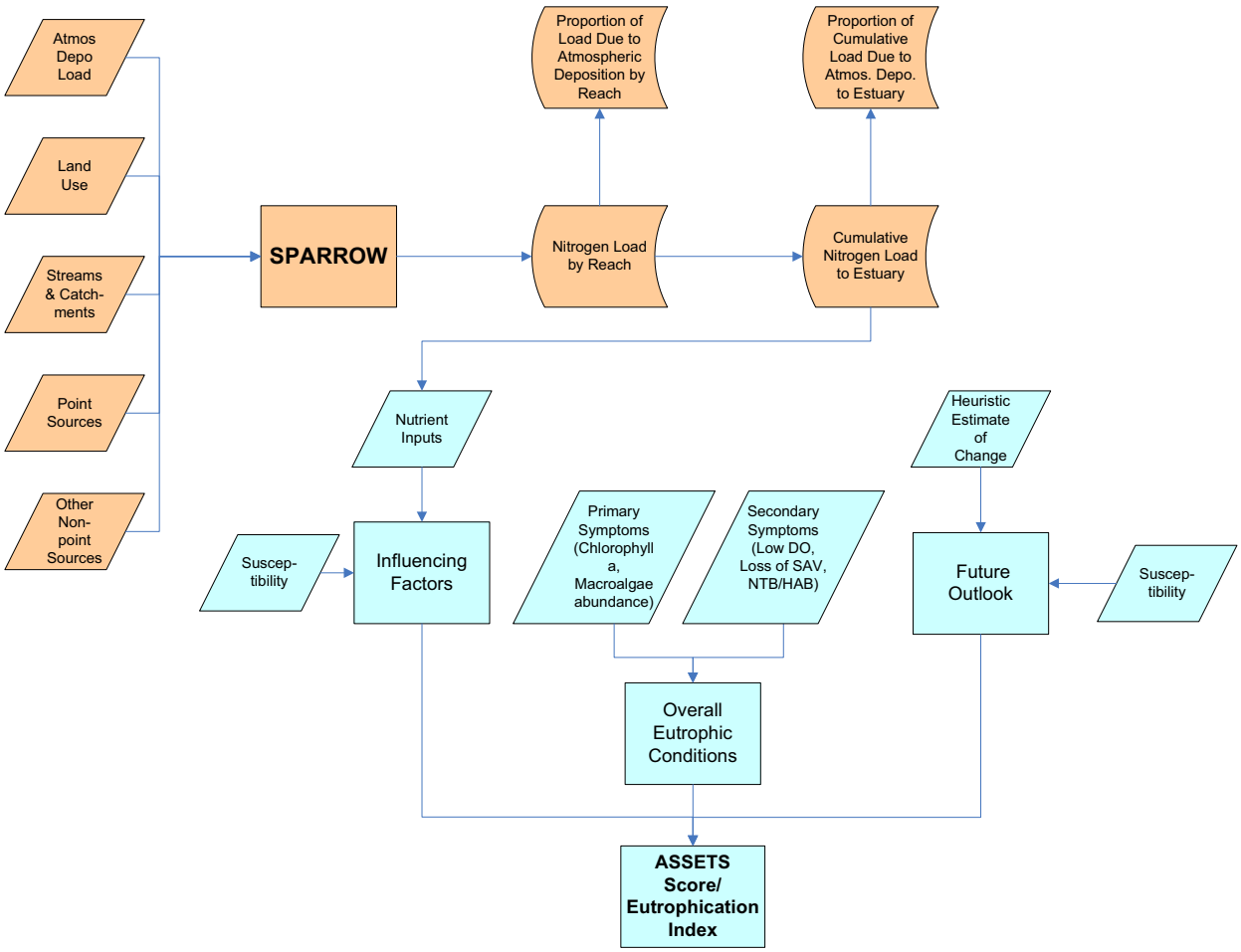

Figure 2.2-1. Modeling methodology for case study.

Both the Potomac and Neuse River Estuaries had ASSETS EI scores available, and both were the subject of past and ongoing SPARROW modeling of point and nonpoint sources, including atmospheric deposition.

2.2.1 SPARROW

2.2.1.1 Background and Description

SPARROW is a watershed modeling technique designed and supported by the U.S. Geological Survey (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 nonconservative transport processes (i.e., loss and storage of contaminants within the watershed). SPARROW follows the rules of mass balance while utilizing a hybrid statistical and process-based approach

(**Figure 2.2-2**). "Because the dependent variable in SPARROW models (i.e., the mass of contaminant that passes a specific stream location per unit time) is, in mathematical terms, linearly related to all sources of contaminant mass in the model, all accounting rules relating to the conservation of mass will apply" (Schwartz et al., 2006). Additionally, since SPARROW is a statistical model at its core, it provides measures of 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. In most applications, SPARROW estimates represent mean annual stream loadings of a contaminant.

Load leaving the reach	=	Load generated within upstream reaches and transported to the reach via the stream network	+	Load originating within the reach's incremental watershed and delivered to the reach segment

Figure 2.2-2. Mass balance description applied to the SPARROW model formulation.

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 downstream endpoints. "Spatial referencing and the mechanistic structure in SPARROW have been shown to improve the accuracy and interpretability of model parameters and the predictions of pollutant loadings as compared to those estimated in conventional linear regression approaches (e.g., Smith et al., 1997; Alexander et al., 2000)" (Schwartz et al., 2006). This spatially distributed model structure based on a defined stream network allows separate statistical estimation 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) (Schwartz et al., 2006). **Figure 2.2-3** 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 (the star labeled X). The SPARROW model is calibrated at each monitoring station (represented by stars in Figure 2.2-3) by comparing the modeled loads (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.

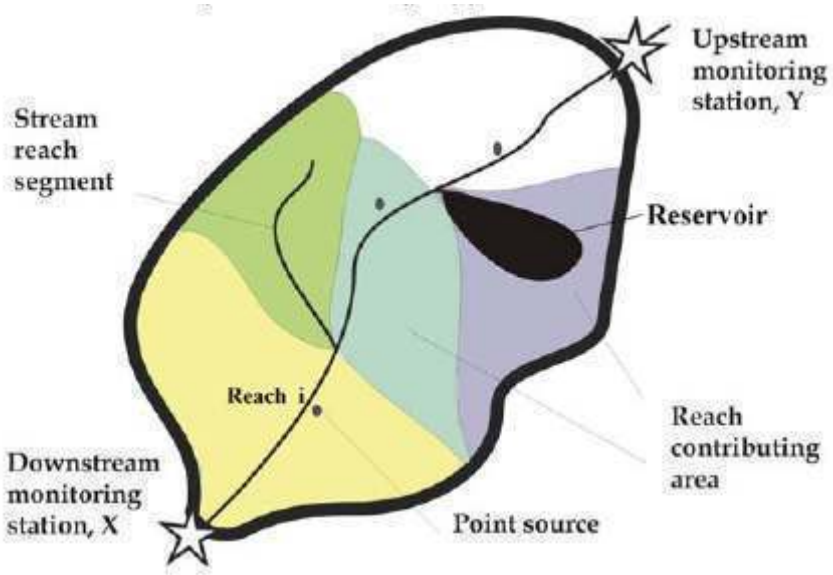

Figure 2.2-3. Conceptual illustration of a reach network.

Within this case study, we show the mathematical formulation of the basic version of SPARROW presented by McMahon and colleagues (2003) for consideration in Equations 1 to 3. "The additive contaminant source components and multiplicative land and water transport terms are conceptually consistent with the physical mechanisms that explain the supply and movement of contaminants in watersheds" (Schwartz et al., 2006). Preservation of mass, accounting for transport and decomposition at individual sources, is accomplished within SPARROW through the spatial referencing of all processes with respect to the stream network and the specific reach in which the process is carried out. Decomposition processes are represented through losses in delivery to the stream and within the stream reach itself (Equation 2) or within a reservoir (Equation 3).

$$Load_i = \sum_{n=1}^{N} \sum_{j \in J(i)} \beta_n S_{n,j} e^{(-\alpha Z_j)} H_{i,j}^{S} H_{i,j}^{R} \varepsilon_i \qquad (1)$$

where

Load = Nitrogen load or flux in reach *i,* measured in metric tons
n, *N* = Source index where *N* is the total number of individual *n* sources
J(i) = Set of all reaches upstream, including reach *i*
β_n = Estimated source coefficient for source *n*
$S_{n,j}$ = Nitrogen mass from source *n* drainage to reach *j*

α = Estimated vector of land to water delivery coefficients
Z_j = Land-surface characteristics associated with drainage to reach *j*
$H^S_{i,j}$ = Fraction of nutrient mass present in water body *j* transported to water body *i* as a function of first-order loss process associated with stream channels
$H^R_{i,j}$ = Fraction of nutrient mass present in water body *j* transported to water body *i* as a function of first-order loss process associated with lakes and reservoirs
ε_i = Multiplicative error term assumed to be independent and identically distributed across separate sub-basins defined by intervening drainage areas between monitoring stations.

$$H^S_{i,j} = \prod_m \exp(-k_m L_{i,j,m}) \quad (2)$$

where

k_m = First-order loss coefficient (km^{-1}) (A *k* value of 0.08, for example, indicates that nitrogen is removed at a rate of approximately 8% per km of channel length.)
m = Number of discrete flow classes
$L_{i.j.m}$ = Length of the stream channel between water bodies *j* and *i* in flow class *m.*

$$H^R_{i,j} = \prod_l \exp(-kq_l^{-1}) \quad (3)$$

where

k = Estimated first-order loss rate (or settling velocity; units = m/yr)
q_l^{-1} = Reciprocal areal hydraulic load of lake or reservoir (ratio of water-surface area to outflow discharge; units = yr/m) for each of the lakes and reservoirs (*l*) located between water bodies *j* and *i.*

SPARROW has been designed to identify and quantify pollution sources that contribute to the water quality conditions predicted by the model. Several different types of sources may be examined, and sources may be for an individual stream location or summarized for a grouping of stream locations. Examples of sources modeled within SPARROW include atmospheric deposition, point sources, animal agriculture, or land use–based supply of contamination. "The ability to develop quantitative information on pollution sources in SPARROW models stems from the ability to trace, for each contaminant category, the predicted in-stream flux through a given stream reach to the individual sources in each of the upstream reach watersheds contributing contamination to that reach" (Schwartz et al., 2006). **Figure 2.2-4** highlights some of these sources in a conceptualization of the SPARROW model process.

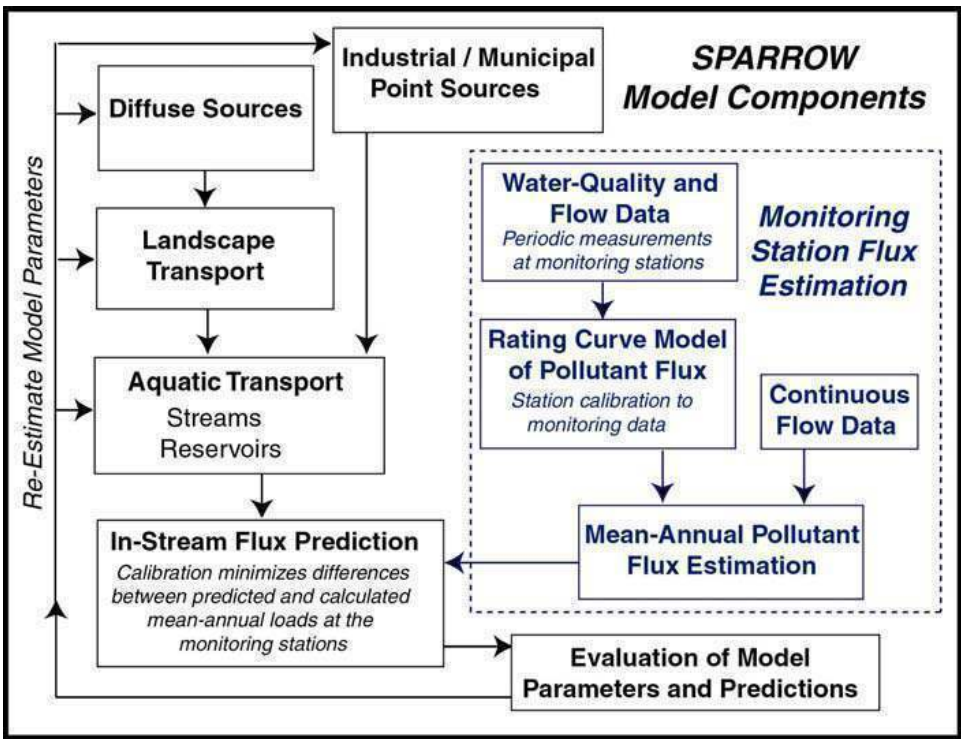

Figure 2.2-4. SPARROW model components (Schwartz et al., 2006).

Complete procedures, such as calculation of monitoring station flux estimation (Figure 2.2-4) and details on data formatting, will not be discussed in this paper. The reader is pointed to the documentation for the recently released SAS version of the SPARROW model available from the USGS SPARROW Web site (http://water.usgs.gov/nawqa/sparrow/sparrow-mod.html) for full details on the model. The reader may also review some of the previous SPARROW applications presented in **Table 2.1-1**. In the following sections describing SPARROW, we provide basic definitions of terms that aid in understanding SPARROW inputs and outputs and discuss some details that pertain to an application focused on atmospheric deposition inputs. Finally, we describe an alternate formulation of SPARROW that highlights contributions of ammonia to the total N_r load for use in the Neuse River Basin.

Table 2.1-1. Examples of SPARROW Applications

Location	**Citation**
National	Smith and Alexander, 2000
Major estuaries of the United States	Alexander et al., 2001
Chesapeake Bay	Preston and Brakebill, 1999; Brakebill and Preston, 2004

Location	Citation
State of Kansas waters	Kansas Department of Health and Environment, 2004
Connecticut River Basin	NEIWPCC, 2004
State of New Jersey waters	Smith et al., 1994
New England waters	Moore et al., 2004
New Zealand river basins	Alexander et al., 2002; Elliot et al., 2005
North Carolina coastal watersheds	McMahon et al., 2003
Tennessee and Kentucky watersheds	Hoos, 2005

2.2.1.2 Key Definitions for Understanding SPARROW Modeling

The following definitions have been summarized from the documentation accompanying the SAS application of the SPARROW model available from the USGS (Schwartz et al., 2006). Additional references are noted when used.

- **Bootstrapping.** This is the practice of estimating model coefficients by estimating those properties when sampling from an approximating distribution using replacement.
- **Delivered Yield (load per area).** This is the amount of nutrient that is generated locally for each stream reach and weighted by the amount of in-stream 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 in-stream 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 nutrient that is 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).
- **In-Stream Loss.** This refers to stream attenuation processes that act on contaminant flux as it travels along stream reaches. A first-order decay process implies that the rate of removal of the contaminant from the water column per unit of time is proportional to the concentration or mass that is present in a given volume of water. According to a first-order decay process, the fraction of contaminant removed over a given stream distance is estimated as an exponential function of a first-order reaction rate coefficient (expressed in

reciprocal time units) and the cumulative water time of travel over this distance. Within SPARROW, the in-stream loss rate is assumed to vary as a function of stream channel length and various flow classes.

- **Landscape Variables.** These variables describe properties of the landscape that relate to climatic, or natural- or human-related terrestrial processes affecting contaminant transport. These typically include properties for which there is (1) some conceptual or empirical basis for their importance in controlling the rates of contaminant processing and transport, and (2) broad-scale availability of continuous measurements of the properties for use in model estimation and prediction. Examples include precipitation, evapotranspiration, soil properties like organic content or permeability, topographic index, or slope. Particular types of land-use classes, such as wetlands or impervious cover, may also be potentially used to describe transport properties of the landscape.
- **Land-to-Water Delivery Factor.** This factor describes the influence of landscape characteristics in the delivery of diffuse sources of contamination to the stream. The interaction of particular land-to-water delivery factors with individual sources may also be important to consider in SPARROW models.
- **Monitoring Station Flux Estimation.** This refers to the estimates of long-term flux used as the response variable in the model. Flux estimates at monitoring stations are derived from station-specific models that relate contaminant concentrations from individual water quality samples to continuous records of streamflow and time. These estimates are what are used to calibrate the model in each application.
- **Non-linear Regression.** The SPARROW model equation is a nonlinear function of its parameters. As such, the model must be estimated using nonlinear techniques. The errors of the model are assumed to be independent across observations and have zero mean; the variance of each observation may be observation-specific. A general method commonly used for these types of problems, one in which it is not necessary to assume the precise distribution of the residuals, is nonlinear weighted least squares. This is the estimation method used by SPARROW.
- **Segmented Watershed Network.** This network relates to the system of joined stream reaches that define the watershed of interest. Previous SPARROW applications have

relied on the River Reach File 1 (RF1) hydrography developed by U.S. EPA (1996) and the 1:100,000 scale National Hydrologic Dataset (NHD; USGS, 1999). These datasets may be used in their original form or modified as needed depending on application requirements

- **Source.** SPARROW distinguishes between source categories (e.g., point sources, atmospheric sources, and animal agriculture) and individual sources (i.e., the rate of supply of contaminant of a particular category originating in the watershed and draining to a specific stream reach). A variety of sources based on knowledge of the watershed and inferences from literature may be examined with SPARROW.
- **Stream Reach.** The most elemental spatial unit of the infrastructure used to estimate and apply the basic SPARROW models. Stream reaches define the length of stream channel that extends from one stream tributary junction to another. Each reach has an associated contributing drainage catchment.
- **Total Yield (load per area).** The amount of nutrient, 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).

2.2.1.3 Concepts of Importance to Case Study SPARROW Application

Previous SPARROW applications have typically relied on atmospheric deposition measurements from NADP and have used wet nitrate deposition as a surrogate for nitrogen deposition over the watershed of interest. Within the case studies that we will conduct, we will use estimates of atmospheric deposition from CMAQ. Several differences in the final parameterization of the SPARROW model will most likely result from this variation in input data.

We must first describe the expected rules of model coefficient estimation based on source type. When using direct measures of contaminant mass as a source estimate, "the source-specific parameter (α_n) is expressed as a dimensionless coefficient that, together with standardized expressions of the land-to-water delivery factor, describes the proportion or fraction of the source input that is delivered to streams (note that source and land-to-water delivery coefficients that are standardized in relation to the mean values of the land-to-water delivery variables are necessary

to compare and interpret the physical meaning of source coefficients). This fraction would be expected to be < 1.0 but > 0, reflecting the removal of contaminants in soils and ground water" (Schwartz et al., 2006).

An example of a source of this type would include atmospheric deposition where the model input would be the mass of nitrogen deposited over the watershed. When using only wet nitrate deposition as an estimate of nitrogen deposition, the model would be expected to account for the additional nitrogen species (e.g., organic nitrogen, dry deposition of nitrate) to the extent that they are correlated with the measured inputs of nitrate (Alexander et al., 2001). This accounting is revealed by estimation within the model application of a land-to-water delivery fraction for wet nitrate deposition (i.e., product of the deposition coefficient and the exponential land-to-water delivery function) that exceeds 1.0.

Although available estimates for the estuarine watersheds indicate that wet nitrate deposition is highly correlated with dry plus ammonium and organic wet deposition, and estimates of the ratio of total (dry plus wet) deposition to nitrate wet deposition for the estuarine watersheds range from 3.2 to 4.0 with an average of 3.6 (Alexander et al., 2001), the use of NADP wet nitrate measurements requires the assumption that the spatial distribution of the various nitrogen species across a watershed does not vary. With the inclusion of explicit nitrogen species in atmospheric deposition measures, this assumption will not be required, and we expect to find the land-to-water delivery fraction for the atmospheric deposition source term estimation to be below 1.0. This variation will be explored within the case studies as will be the general model fit with the improved atmospheric deposition inputs.

2.2.1.4 Consideration of Ammonia in Total Reactive Nitrogen Load

As highlighted in Section 2.2.1.1, SPARROW can examine a wide range of sources. In work conducted by RTI under the Smithfield Agreement for North Carolina, a modified formulation of SPARROW was developed to specifically examine reactive nitrogen loadings of ammonia in North Carolina. The methodology compiled North Carolina-specific inputs for a land parcel-based method of examining land use contributions to the SPARROW model. These inputs include instream loss rates based on North Carolina flow data, methods for looking at edge-of-field delivery for agricultural land parcels, and specific contributions of ammonia to deposition totals based on the location of localized emissions and land use. For a complete

description of the previous Smithfield modeling effort, please refer to the methodology document (RTI, 2003).

We have considered using the data developed during this study to examine the local contributions of ammonia to atmospheric deposition of reactive nitrogen that may not be considered within the CMAQ-modeled data. We will be able to use previously compiled data of gaseous ammonia emissions (because of the moratorium on swine operations since the late 1990s, this previous data should still be valid for the 2002 timeframe) as an additional source term within a second SPARROW formulation that can be compared to the SPARROW formulation, relying only on the CMAQ and NADP atmospheric data. This additional analysis to separate atmospheric deposition of ammonia from local sources from other atmospheric sources of nitrogen to watersheds, including NO_x provided by the CMAQ/NADP data, will provide a weight of evidence analysis of the atmospheric modeling methods for watersheds with extensive animal operations.

2.2.2 ASSETS Eutrophication Index

2.2.2.1 Background and Description

The EI was defined by the NEEA Program and developed into a Pressure-State-Response framework termed ASSETS. It is categorical, where each of three indices results in a score that, when combined, result in a final overall score, also known as the ASSETS score or rating, which is representative of the health of the estuary. The indices are as follows:

- **Influencing factors.** 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.** An estimate of current eutrophic conditions derived from data for five symptoms known to be linked to eutrophication
- **Future outlook.** A qualitative measure of expected changes in the system.

The following excerpt from Whitall and colleagues describes the objectives in applying the ASSETS method:

> The ASSETS assessment method should be applied on a periodic basis to track trends in nutrient-related water quality over time in order to test

management related hypotheses and provide a basis for more successful management. The null hypothesis being tested in this approach is: The change in anthropogenic pressure as a result of management response does not result in a change of state. The hypothesis is tested, e.g., to verify whether decreased pressure improves State, or whether increased pressure deteriorates State. In many cases, a reduction in pressure will result in an improvement of State, but in some cases, such as naturally occurring harmful algal bloom (HAB) advected from offshore, it will not (Whitehall et al., 2007).

Influencing Factors

Influencing factors help to establish a link between a system's natural sensitivity to eutrophication and the nutrient loading and eutrophic symptoms actually observed. This understanding also helps to illustrate the relationship between eutrophic conditions and use impairments (Bricker et al., 2007a). Influencing factors are determined by calculating two factors of susceptibility and nitrogen load, where "susceptibility" provides a measure of a system's nutrient retention based upon flushing and dilution, and "nitrogen loads" are a ratio between the nitrogen input to the system from the oceans versus from the land (**Figure 2.2-5)**.

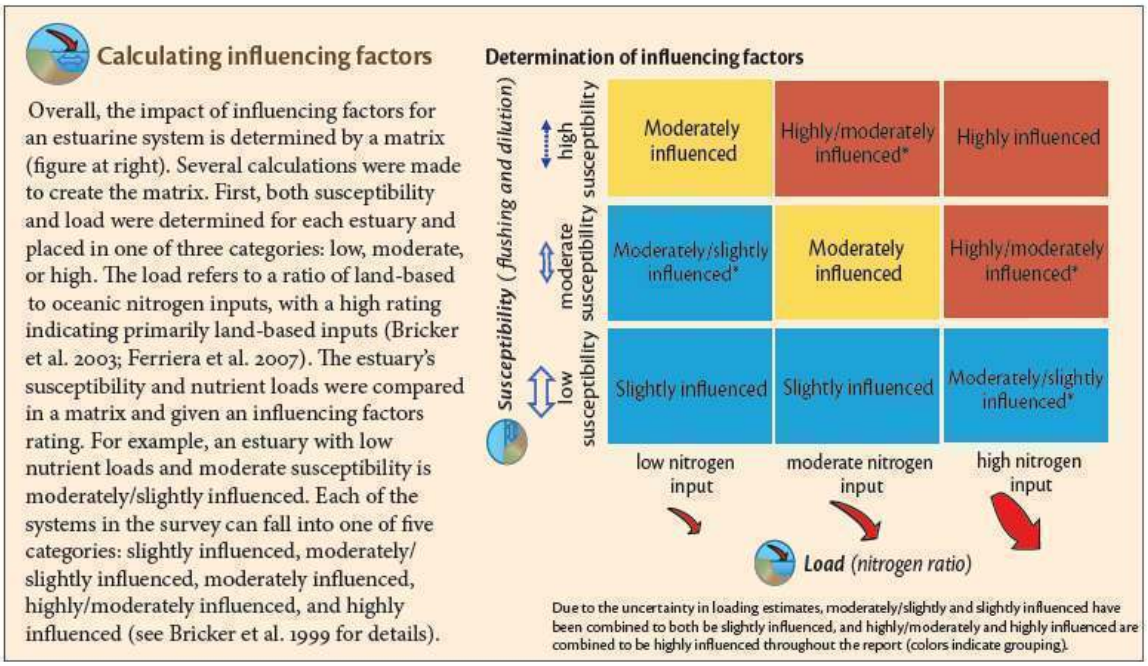

Figure 2.2-5. Influencing factors description and decision matrix (Bricker et al., 2007a).

The following factors take into account both the natural characteristics of and human impacts to systems.

- **Susceptibility.** For a coastal system, susceptibility depends on the flow of water into and out of the system. This flushing capability is determined by the physical properties (e.g. size, mouth) of the system as well as the influence of tidal waters and inflow of freshwater from tributaries. When water flushes into and out of the system easily and quickly (i.e. there is a short residence time) nutrients flush out of the system rapidly and there is not enough time for eutrophic symptoms to develop. Systems with short residence times have low susceptibility. The opposite also holds true. When water, and therefore nutrients, does not flush quickly from the estuary or coastal system there is time for eutrophication effects to develop.
- **Nitrogen Load.** For this assessment, the loading component is estimated as the ratio of nitrogen coming from the land (i.e., human-related) to that coming from the ocean and is given a rating of low, moderate, or high (Bricker et al., 2003; Ferreira et al., 2007). For example, a high rating means that > 80% of the nutrient load comes from land, whereas a low rating signifies a land-percentage of < 20%. This rating also provides insight into loading management because loads to systems with primarily ocean-derived nitrogen are not easily controlled. Understanding the sizes of current and expected future loads provides further insight into the application and success of management measures.

Overall Eutrophic Condition

To assess the eutrophic conditions of a system, the NEEA relies on five symptoms. Each of the five symptoms, divided into primary and secondary categories, is assessed based on a combination of the following factors: concentration or occurrence, duration, spatial coverage, frequency of occurrence, and confidence in the data (**Figure 2.2-6**). The two primary symptoms, chlorophyll a and macroalgal abundance (**Figure 2.2-7**), were chosen as indicators of the first possible stage in the process of water quality degradation leading to eutrophication. The secondary symptoms, which in most coastal systems will develop from the primary symptoms, include low dissolved oxygen levels, loss of SAV, and occurrences of nuisance/toxic algal blooms (**Figure 2.2-7**). At times the secondary symptoms may also be present or develop without expression of primary symptoms. Nutrient concentrations are not employed as a

symptom indicator because concentrations may vary between low and high values based on a number of factors, such as estuary susceptibility, which invalidates the use of nutrient concentrations alone as an indicator. As stated by Bricker and colleagues "Through the use of a simple model, the current framework was established to help understand the sequence, processes, and symptoms associated with nutrient enrichment. Despite its limitations, it represents an attempt to synthesize enormous volumes of data and derive a single value for eutrophication in each estuary, essentially representing a complex process in a simple way" (Bricker et al., 2007a).

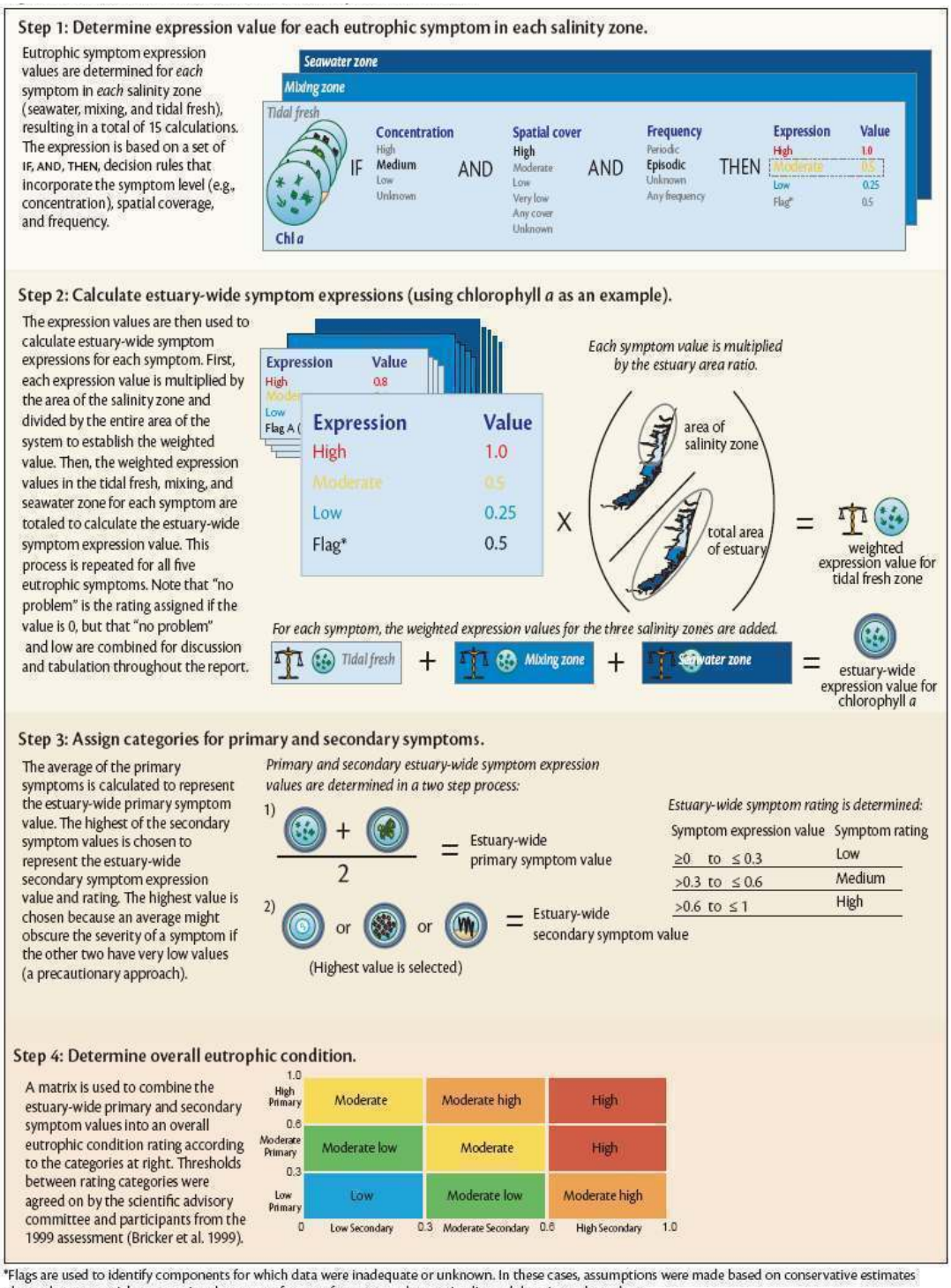

Figure 2.2-6. Overall eutrophic condition description and decision matrix (Bricker et al., 2007a).

Symptom	Parameters	Expression: Low	Expression: Moderate	Expression: High
Chlorophyll *a* (phytoplankton) Typical high concentration ($\mu g\ L^{-1}$) in an annual cycle determined as the 90th percentile value.	*Spatial coverage:* High >50%; Moderate 25–50%; Low 10–25%; Very low 0–10% *Frequency:* Episodic; Periodic; Persistent *Concentration:* High >20 $\mu g\ L^{-1}$; Medium 5–20 $\mu g\ L^{-1}$; Low 0–5 $\mu g\ L^{-1}$	*Low symptom expression:* Conc. / Coverage / Frequency low / any / any medium / mod. - v. low / episodic high / low - v. low / episodic	*Moderate symptom expression:* Conc. / Coverage / Frequency medium / high / episodic medium / moderate / periodic high / low - v. low / periodic high / moderate / episodic	*High symptom expression:* Conc. / Coverage / Frequency medium / high / periodic high / mod. - high / periodic high / high / episodic
Macroalgae Causes a detrimental impact on any natural resource.	*Frequency of problem:* Episodic (occasional/random) Periodic (seasonal, annual, predictable) Persistent (always/continuous)	No macroalgal bloom problems have been observed.	Episodic macroalgal bloom problems have been observed.	Periodic or persistent macroalgal bloom problems have been observed.
Dissolved oxygen Typical low concentration (determined as the 10th percentile value) in an annual cycle.	*Spatial coverage:* High >50%; Moderate 25–50%; Low 10–25%; Very low 0–10% *Frequency:* Episodic; Periodic; Persistent *State:* Anoxia 0 mg L^{-1}; Hypoxia 0–2 mg L^{-1}; Biol. stress 2–5 mg L^{-1}	*Low symptom expression:* State / Coverage / Frequency anoxia / mod. - low / episodic anoxia / very low / periodic hypoxia / low - v. low / periodic hypoxia / moderate / episodic stress / any / episodic stress / mod. - v. low / periodic	*Moderate symptom expression:* State / Coverage / Frequency anoxia / high / episodic anoxia / low / periodic hypoxia / moderate / periodic hypoxia / high / episodic stress / high / periodic	*High symptom expression:* State / Coverage / Frequency anoxia / moderate - high / periodic hypoxia / high / periodic
Submerged aquatic vegetation A change in SAV spatial area observed since 1990.	*Magnitude of change:* High >50%; Moderate 25–50%; Low 10–25%; Very low 0–10%	The magnitude of SAV loss is low to very low.	The magnitude of SAV loss is moderate.	The magnitude of SAV loss is high.
Nuisance/toxic blooms Causes detrimental impact on any natural resources.	*Duration:* Persistent, seasonal, months, variable, weeks, days, weeks to seasonal, weeks to months, or days to weeks *Frequency:* Episodic, periodic, or persistent	Blooms are either a) short in duration (days) and periodic in frequency; or b) moderate in duration (days to weeks) and episodic in frequency.	Blooms are either a) moderate in duration (days to weeks) and periodic in frequency; or b) long in duration (weeks to months) and episodic in frequency.	Blooms are long in duration (weeks, months, seasonal) and periodic in frequency.

*For further technical documentation of the methods, refer to Bricker et al. 1999 and Bricker et al. 2003.

Figure 2.2-7. Detailed descriptions of primary and secondary indicators of eutrophication (Bricker et al., 2007a).

Future Outlook

The future outlook relies on a similar combination of factors as the influence factors. That is, a rating of the system susceptibility and nutrient loading in the future. The aim of this index is to estimate future changes in the system through a combination of any physical, hydrologic, or pollutant loadings to the system itself or to its contributing watershed through such actions as watershed management plans, development restrictions, policy changes resulting in nutrient reductions, etc. The matrix in **Figure 2.2-8** is used to determine the future outlook rating.

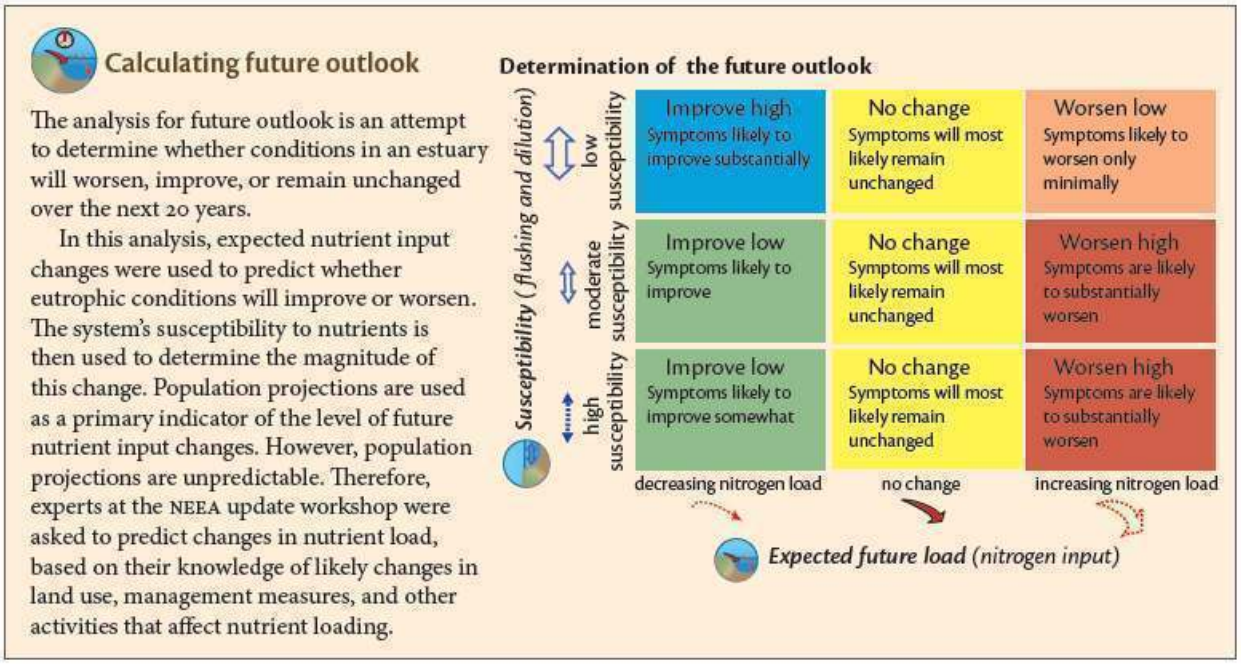

Figure 2.2-8. Future outlook description and decision matrix (Bricker et al., 2007a).

The last step is to combine the influencing factors, overall eutrophic conditions, and future outlook scores into a single overall score. The scores fall into one of five categories: High, Good, Moderate, Poor, or Bad.

2.2.2.2 Applications and Updates

The ASSETS method developed out of the NEEA was first reported in 1999. Since that time, it has been used in several assessments across the country and internationally and has undergone revision and validation (Bricker et al., 1999, 2003, 2007b; Ferreira et al., 2007; Whitall et al., 2007). The original NEEA ASSETS assessment relied on questionnaires to experts

for each estuary considered (Bricker et al., 1999). Later assessments determined that reliance on monitored data and less on reports from experts provided a more valid assessment tool (Bricker et al., 2006, 2007b). With the NEEA Update in 2007, an online database was completed in which data users and data holders could access and input data (Bricker et al., 2007b). Additional datasets have also been collected for smaller study areas (Bricker et al., 2006). These data systems provide a wealth of information from which analyses may be conducted.

The original formulation of the ASSETS EI within the NEEA used watershed nutrient model estimates from SPARROW (Bricker et al., 1999). Although the updated ASSETS methodology has further apportioned nitrogen sources using the WATERSN model (Whitall et al., 2007), SPARROW is still appropriate for this study because we can define atmospheric deposition inputs relative to other nitrogen sources.

2.2.3 Assessments Using Linked SPARROW and EI

The link between the SPARROW model and the ASSETS EI occurs when the SPARROW output is used as the nitrogen load in the influencing factors calculation of the ASSETS EI. For each case study and future policy scenario, a new influencing factors score will be calculated based on the SPARROW-predicted nitrogen load, which will vary due to the different simulated atmospheric nitrogen contributions. As the influencing factors score is only one component of the ASSETS EI, we will discuss risk assessment/management approaches that can be gained from this approach to vary the nitrogen load to the estuary.

Ferreira and colleagues (2007) provide an example of the eutrophication management approaches that can be undertaken using the ASSETS EI assessment method. Using this approach (**Figure 2.2-9**), trends in the changes in state of the system (i.e., overall eutrophic condition) are investigated based on changes in the pressures to the system (i.e., influencing factors). Typically, this analysis would be conducted by comparing ASSETS EI scores for the same system over different years. In the risk assessment analysis, we will examine how changes in pressure on the system (through changes in nitrogen loading to the estuary) affect the influencing factors score and overall ASSETS EI score for the estuary. Ideally, we would be able to predict a response curve such as the one shown in **Figure 2.2-10** for each estuary, using the various atmospheric deposition scenarios that will be carried out in the risk assessment.

However, apart from the baseline scenario for 2002, where we will use modeled atmospheric deposition of actual conditions, the analysis using the ASSETS EI will be theoretical.

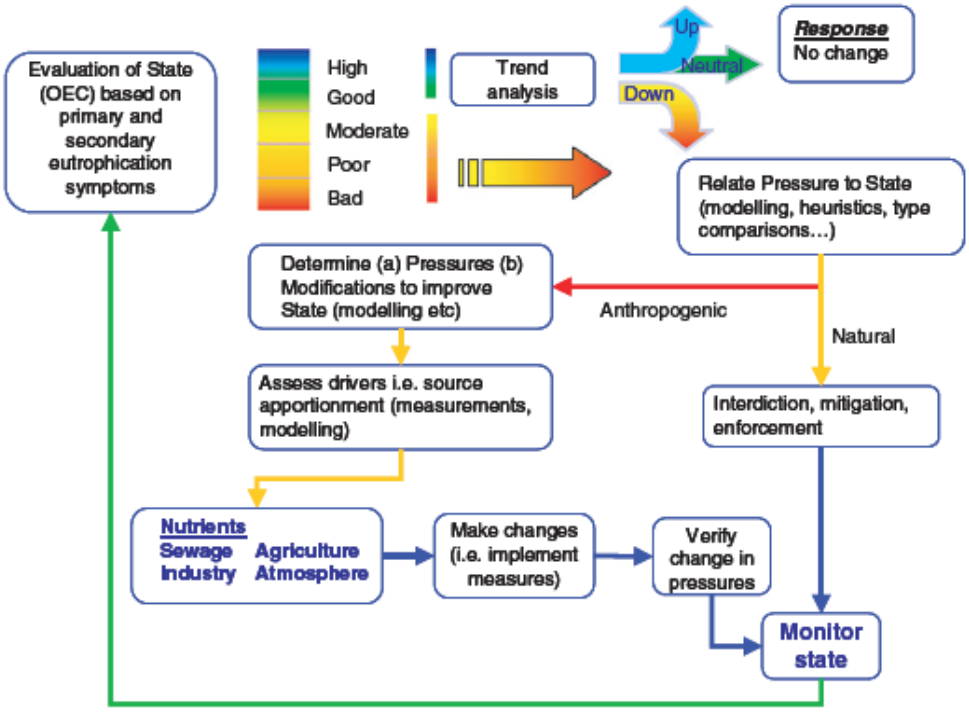

Figure 2.2-9. Conceptual approach to eutrophication management using the ASSETS EI assessment (Ferreira et al., 2007).

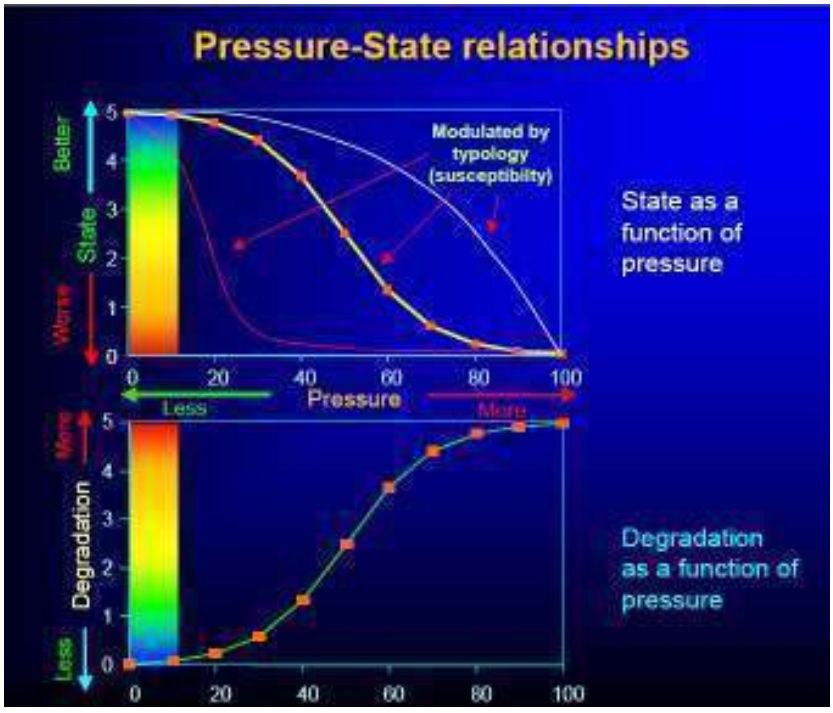

Figure 2.2-10. Example of response for case study analysis (Bricker et al., 2007b).

For the 2002 baseline scenario, we will calibrate the modeled watershed nitrogen load using the SPARROW model to monitoring data from the streams within the watershed. We will also gather monitoring data from the estuaries for the values of the primary and secondary symptoms used in the Overall Eutrophic Condition (OEC) during 2002. We will use this compilation of data to evaluate the ASSETS EI for 2002.

For the future policy scenarios, because we will be estimating nitrogen loadings to the estuary based on simulated atmospheric deposition scenarios instead of monitored conditions, we will not have direct measures of state on which to create the response curves (i.e., we will not have concurrent measurements of primary and secondary symptoms in the estuary because these are theoretical deposition scenarios). The influencing factors score will be calculated directly from the modeled watershed nitrogen loads and the susceptibility for the estuary, which will remain unchanged. However, consideration must also be given to whether the state (i.e., overall eutrophic condition) will change based on this change in nitrogen loading (i.e., pressure/influencing factor). Without monitoring data for each of the primary and secondary symptoms related to a specific nitrogen load calculated from the theoretical deposition scenarios, we cannot calculate a direct change in overall eutrophic condition score. Even with a comprehensive water quality model, any change in output would be subject to uncertainty when lacking monitoring data to calibrate the model, especially in such a complex process as eutrophication.

We propose to rely on expert judgment and expected thresholds within the ASSETS EI to determine if the overall eutrophication condition score, based the individual symptom measures, should change when the influencing factor score is changed. This proposed analysis method will be aided by the fact that calculation of the overall eutrophic condition score relies on a numerical ranking of primary and secondary indicators (i.e., 0 = low expression of indicator class; 1 = high expression of indicator class). By using the thresholds within the ASSETS scoring matrices, we can determine whether the previous symptom value was on the border between two categories, and therefore, have the possibility to change state categories as the influencing factors change. For example, a dissolved oxygen value of 1.9 mg/L would be on the verge between “hypoxia” and “biological stress” (Figure 2.2-7). With a large decrease in nitrogen loading, it is possible that this value would improve and cause the state rating to change to “biological stress” rather than to “hypoxia.” Changes in these values will then carry into the indicator scores. For each

system, we will determine whether the score for each indicator class lies on the boundary between two score classifications (e.g., a score of 0.6 for secondary symptoms lies on the boundary between *Moderate High* and *High* rankings when there is a *High* ranking of primary symptoms). If a score lies close to the boundary and the nitrogen load to the estuary is substantially increased or decreased due to atmospheric changes, we will know whether to increase the score to the next higher category or leave the score as is, respectively, for each situation. If changes in scores cannot be supported by weight of evidence, we will seek consultation with experts on each case study system through written inquiry.

Additionally, we will investigate whether historical trends tracked within the estuaries relate to any of the case study scenarios we will be evaluating. For instance, was there a previous year in which a nitrogen load to estuary was similar to a load predicted by the SPARROW model? If so, is there monitoring data from within the estuary on which we may assess the overall eutrophic condition related to that nitrogen load?

Overall results from this analysis will provide an estimated pressure-state curve as presented in Figure 2.2-10. These estimated curves can provide the opportunity to perform additional analyses where changes in ecosystem services related to changes in pressure and state may be examined.

3. RESULTS

3.1 CURRENT STATE OF SYSTEMS

At this time, the current state of systems refers to previous work that has been conducted using the modeling and assessment methods we will utilize to conduct the 2002 base-case scenario and future policy scenarios. Therefore, in this draft, Sections 3.1.1 and 3.1.2 summarize previous work and provide details on changes that will be incorporated in the future base-case scenario.

3.1.1 Potomac River and Estuary Summary

The previous work conducted on the Potomac River watershed and estuary was completed as part of a Chesapeake Bay SPARROW application that has been updated twice since its original formulation (Brakebill et al., 2001; Brakebill and Preston, 2004; Preston and Brakebill, 1999). The ASSETS EI was created for 2002 data in an eutrophication assessment

involving the Gulf of Maine (Bricker et al., 2006). We summarize the results from both of these studies in the following sections and address how the updated 2002 base-case scenario will vary in setup. **Table 3.1-1** summarizes both the previous work and the modifications that will be made for the future case study analyses.

3.1.1.1 SPARROW Assessment

The Version 3 Chesapeake Bay SPARROW application modeled the watershed for the time period of the late 1990s. Stream nitrogen load estimates from 87 sites were used to calibrate the model. The stream reach network used in this analysis relied on a modified version of the RF1 used in previous Chesapeake Bay SPARROW applications, but included 68 reservoirs that were not previously included. This analysis examined the sources of atmospheric deposition, fertilizer and manure application, point sources, septic systems, and land use. Details on the compilation of each of these GIS-based datasets can be found in the work by Brakebill and Preston (2004). Watershed characteristics that were in the model include precipitation, temperature, slope, soil permeability, and hydrogeomorphic regions.

The future SPARROW assessment for the 2002 base-case scenario will use the same source inputs and watershed characteristics, except in the case of atmospheric deposition. The Version 3 Chesapeake Bay SPARROW application relied on 1997 mean deposition values of wet-deposition atmospheric nitrate using the 191-point measurements in the NADP program across the country. To determine atmospheric deposition of wet nitrate for each watershed segment (**Figure 3.1-1**), interpolation was used in conjunction with a Triangulated Irregular Network (Brakebill and Preston, 2004). As described in Section 2.2.1.3, relying on wet nitrate deposition as a surrogate for total nitrogen deposition requires an assumption of spatial homogeneity between the nitrogen species. In the 2002 base-case scenario, we will utilize the CMAQ output as atmospheric deposition inputs to the model.

Figure 3.1-2 presents the results of the 1997 Chesapeake Bay SPARROW application by watershed segment. Results are presented for total and delivered yields (defined in Section 2.2.1.2) for the entire nitrogen load predicted by the model and for the nitrogen load derived from atmospheric sources. As shown by these results, the western watersheds in the mountains produce the greatest nitrogen load per area from atmospheric deposition, but it is the watersheds along the mainstem of the Potomac River that actual contribute the greatest amounts

of nitrogen from the atmospheric deposition to the estuary. Analyzing the delivered yields produces a total nitrogen loading to the Potomac River Estuary of 34 x 10^3 metric tons nitrogen/yr. The nitrogen load to the estuary due to atmospheric deposition is estimated at approximately 2 x 10^3 metric tons nitrogen/yr or 6% of the total loading. These results will be compared and contrasted to the 2002 base-case scenario that will be completed using CMAQ results. We will determine whether spatial patterns in these total and delivered yields vary when additional nitrogen species are included in the analysis as compared to this current analysis where only wet nitrate was considered.

The actual data inputs (except for atmospheric deposition) to the model will likely rely on a combination of data compiled for the Version 3 SPARROW application and for the recently released Phase 5 Chesapeake Bay Watershed Model (http://ches.communitymodeling.org/models/CBPhase5/index.php#container). The Phase 5 model relies on a slightly different watershed and stream reach segmentation network, but provides data in annual increments, including 2002. Upcoming work will combine the applicable data from these models to arrive at the best input dataset for the desired base-case scenario.

Table 3.1-1. Key Facts/Aspects of the Potomac Case Study

Category	**Description of Current/Demonstration Research**	**Source**	**Description for Final Case Study of Effects**
Spatial domain	SPARROW: Entire Chesapeake Bay watershed, including the Potomac River watershed ASSETS EI: Potomac estuary	Brakebill and Preston, 2004; Bricker, et al.,2006	Potomac River watershed and estuary; The spatial domain is contained with the 8-digit hydrologic units (HUC8): 02070001, 02070002, 02070003, 02070004, 02070007, 02070008, and 02070010. The catchments and stream reaches defined during the Chesapeake Bay application (Version 3) of the SPARROW model will be used as the basis for analysis. For these stream reaches, interpolation between the HUC8 results of CMAQ will be needed for atmospheric inputs to the model
Temporal domain	SPARROW (Version 3): Late 1990s with water quality calibration of surface water nitrogen calculated for 1997, point discharges for 1995–1997, land use data created based on 1992 NLCD with updates using Landsat from 1992 and 1997, agricultural data from the late 1990s and 1997 Agricultural Censuses, and atmospheric data as described below ASSETS EI: 2002 basis	Brakebill and Preston, 2004; Bricker, et al.,2006	2002 or surrounding years (depending on surface water calibration data obtained from National Water Quality Assessment Database & STORET and input datasets provided from the USGS Major River Basin Assessment currently underway)
Atmospheric nitrogen species	Wet-deposition atmospheric nitrate	Brakebill and Preston, 2004	Summation of available species from CMAQ to total nitrogen (TN)

Category	Description of Current/Demonstration Research	Source	Description for Final Case Study of Effects
Data origin of emission sources (modeling or monitoring)	1997 mean deposition values of wet-deposition atmospheric nitrate using the 191 point measurements in the NADP program; to get to atmospheric deposition for each watershed segment, interpolation was used in conjunction with a Triangulated Irregular Network.	Brakebill and Preston, 2004	CMAQ; If calibration data for surface water inputs is available for years prior to 2002, atmospheric inputs for these years may be mined from the sources used in the demonstration research.
Analytic tool	Separate analyses using SPARROW and the ASSETS EI	RTI, 2003; Bricker et al., 2007a;	Combined analysis using SPARROW and the ASSETS EI
Tool output indicators	SPARROW: Mean Annual TN Loading ASSETS EI: ASSETS overall score relating to likelihood of eutrophication		Change in ASSETS overall score based on changing input nitrogen loads from SPARROW modeling using various atmospheric deposition scenarios
Endpoint of indicators	No service-related endpoint completed		Habitat and water quality degradation (expressed in terms of eutrophication effects (i.e., anoxia, loss of SAV)
Linkage to endpoints (science that connects indicator value to endpoint)	N/A		Inherent in the numerical score of EI using expression of symptoms (e.g., SAV, dissolved oxygen, harmful algal blooms)
Ecosystem services	Fisheries, Recreation, Tourism		Fisheries, recreation, tourism

Category	Description of Current/Demonstration Research	Source	Description for Final Case Study of Effects
Linkage method from endpoint to services	N/A		Quantitative: fisheries (e.g., closings, decreased species richness) related to eutrophication symptoms through monitoring data Qualitative: recreational activities related to eutrophication symptoms through user surveys Gaps: wealth of monitoring data not applied to answer applicable questions; wide variety of surveys available to conduct

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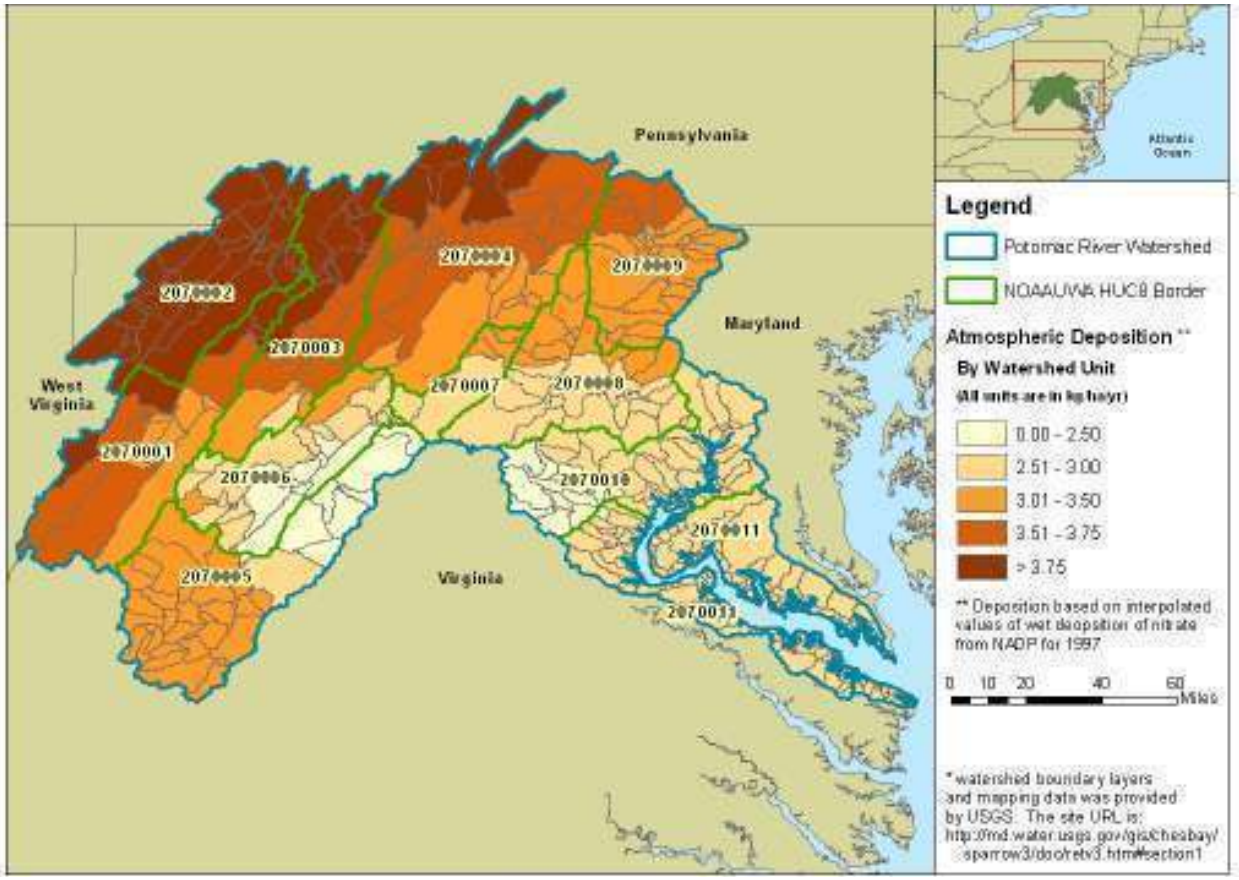

Figure 3.1-1. Atmospheric deposition inputs based on interpolation of wet nitrate measures from NADP for the late 1990s' Chesapeake Bay SPARROW application.

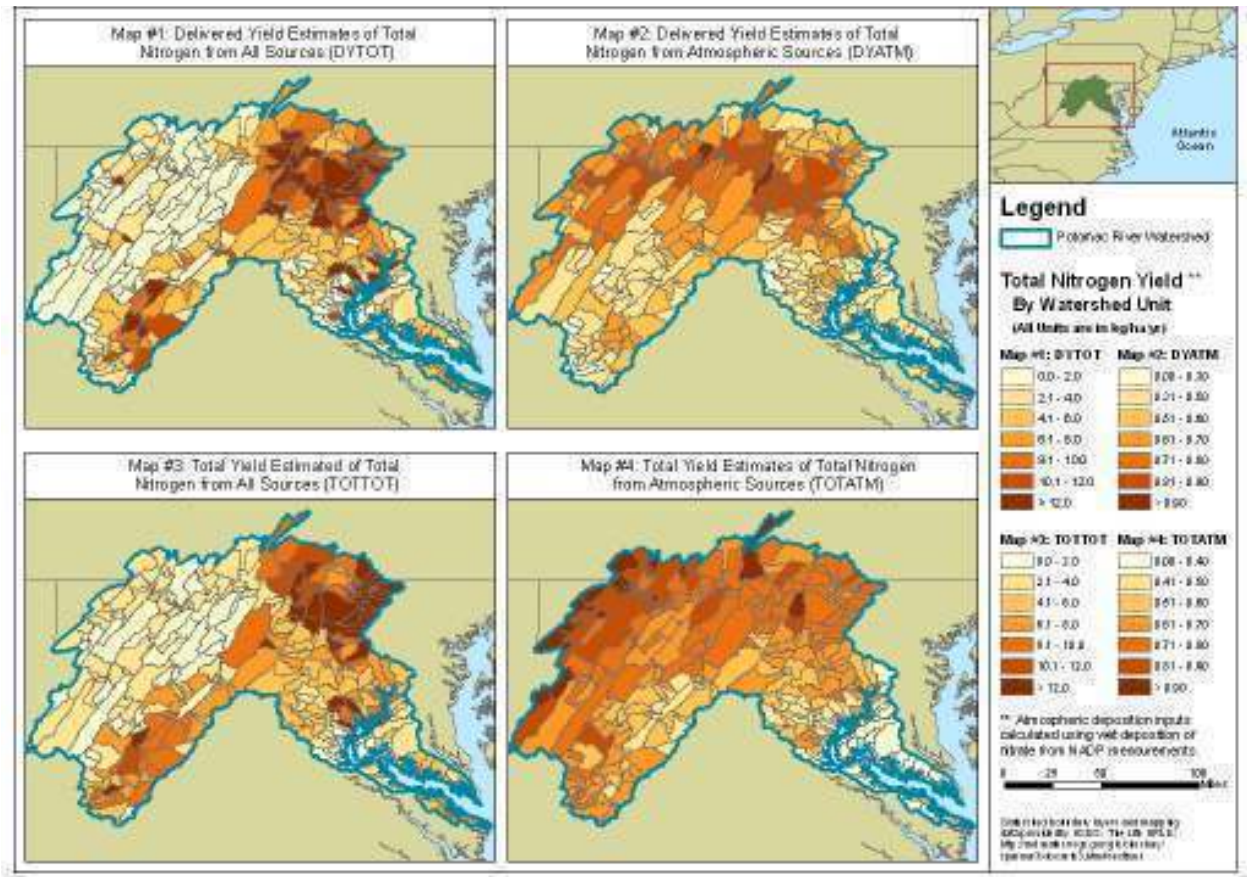

Figure 3.1-2. Total nitrogen yields from all sources and from atmospheric deposition only as predicted by the late 1990s' Chesapeake Bay SPARROW application.

3.1.1.2 ASSETS EI Assessment

An ASSETS EI was completed for the Potomac River Estuary (**Figure 3.1-3**) in a 2006 NOAA project on the Gulf of Maine (Bricker et al., 2006). The data used to complete the scoring was from 2002. As such, this ranking provides the necessary data for the basis of the future 2002 base-case scenario. The total nitrogen loading to the estuary relied on estimates from the Chesapeake Bay Watershed Model (Version 4.3), a model based on HSPF. The total nitrogen loading of 1.4 x 10^3 metric tons nitrogen/yr presented in the report is actually the nitrogen loading from only the Lower Potomac River watershed, as defined by Maryland's Department of Natural Resources (MD DNR; MD DNR, 2004). The report also presented results from a previous SPARROW modeling effort in the Potomac River watershed from 1987, where the total nitrogen load to the estuary was predicted to be 20.6 x 10^3 metric tons nitrogen/yr. As there is a considerable difference between the two loadings presented in the report and the loading predicted by the most recent SPARROW application in the Chesapeake Bay, the influencing

factors score will be reexamined upon verification of the total nitrogen load used to perform the ASSETS assessment.

The current assessment using the total nitrogen load in question shows that the system has a high susceptibility to pressures and a high score for nutrient inputs, resulting in a score of *High* for influencing factors. Individual scores for the primary and secondary indicators vary, but result in an overall score of *High* for the overall eutrophic condition. It is these two scores that will be assessed in the future risk assessment analyses with emphasis on verifying this current ranking for the influencing factors score. As shown in the future outlooks assessments, the score of *Improve Low* is based on the expectations that future nutrient pressures will decrease and there will be significant population and development increases. These assumptions will be verified before continuing the case study analysis.

Indices	Methods	Parameters/ Values / EAR			Index category	ASSETS grade
Pressure OHI index	Susceptibility	Dilutionpotential	High	High Susceptibility	High	OHI = 1 OEC = 1 DFO = 4 Bad
		Flushingpotential	Low			
	Nutrient inputs	High				
State OEC index	Primary Symptom Method	Chlorophyll a	High	High	High	
		Macroalgae	No Prob			
	Secondary Symptom Method	Dissolvedoxygen	Low	High		
		Submerged aquaticvegetation	Large Increase			
		Nuisance and Toxic Blooms	Problem (1)			
Response DFO index	Future nutrient pressures	Futurenutrientpressuresdecrease,significantpopulation/ development increases – Improve Low			Improve Low	

Figure 3.1-3. The ASSETS EI scores for the Potomac River Estuary (Bricker et al., 2006).

Below we provide a summary of the raw data that was used by Bricker and colleagues (2006) to create the final scores of the ASSETS EI presented in Figure 3.1-3. These data will be reviewed before use in the future policy scenarios. Several gaps in the raw data provided to this point exist, including measures of frequency of expression of the symptoms and macroalgae raw data.

The **Overall Human Influence** (OHI) score was developed based on the following data:

- The Potomac River has a high dilution potential, but a low flushing potential.
- Combined with a low export potential, this gives the system an overall susceptibility rating of *High*.

- Nitrogen loading for the system calculated the human influence to be 94.8% for 2002, which corresponds to a value of *High*.
- With high inputs and high susceptibility, the OHI value is high for 2002.

For the **Overall Eutrophic Condition (OEC),** water quality monitoring data used to determine primary and secondary symptoms comes from the Chesapeake Bay Program's online database (www.chesapeakebay.net), the Virginia Institute of Marine Science, and the "Eyes on the Bay" Web site maintained by the MD DNR (http://mddnr.chesapeakebay.net/hab/). Summaries of the raw data used to determine the primary and secondary symptoms by Bricker and colleagues (2006) are as follows:

Chlorophyll *a* (12 stations, 645 individual samples)

- Overall 90th percentile value for all 2002 data and all stations was 16.42 ug/L.
- Spatial coverage of chlorophyll *a* 90th percentile
- *Low* = 1% coverage
- *Medium* = 59%
- *High* = 9%.
- The highest spatial coverage above (which is for *Medium*) is adopted for the overall chlorophyll *a* value, and as such, the system gets an expression of *High*.

Dissolved Oxygen (11 stations and represents 1329 individual samples)

- Overall combined 10th percentile for all stations in 2002 was 4.2 mg/L, which also corresponds to that of biological stress.
- Dissolved oxygen levels approximate spatial percentages:
- No Problem = 23%
- Biological Stress = 28%
- Anoxia = 19%.

Salinity

A median salinity was calculated for the estuary using the Chesapeake Bay Program's data for the years 1997–2002.

Submerged Aquatic Vegetation

- Used the 2001 and 2002 coverage dataset produced at the Virginia Institute of Marine Science from aerial photography flown in 2001 and 2002
- Calculated the change in SAV coverage by subtracting the areal coverage of 2001 from the areal coverage for 2002
- In 2001, SAV in the Potomac River had a spatial coverage of approximately 529,557.04 square meters (m^2), whereas in 2002, there was an approximate 34-million m^2 increase up to 34,479,090.57 m^2.

Harmful Algal Bloom (HAB)

- Data collected from the "Eyes on the Bay" Web site 2002 HAB report search)
- HABs were a large problem during 2002. There were multiple different blooms throughout the year,
- Largest and longest bloom was that of Dinophysis accuminata, from February 2002 until about April 2002. (During the three months of the bloom, shellfish beds were closed, and no harvesting was allowed.)
- HABs carried the largest NEEA/ASSETS secondary symptoms value (*High*) and were combined with the overall primary symptom value to calculate the OEC.

The OEC for the Potomac River in 2002 was High and was calculated from a primary symptoms value of *High* (from chlorophyll *a* 90th percentile) and a secondary symptoms value of *High* (from HAB).

Bricker and colleagues (2006) provided a justification for a score of *Improve Low* for the **Determining Future Outlook** index by the following:

> For the Potomac River basin, nitrogen loading, phosphorus loading, and sediments all decreased between 1985 and 2002 (MD DNR, 2004). In contrast however, population growth in Maryland alone is projected to increase at an approximate 1% every year while the Potomac River basin itself includes many new suburban communities that are expected to continue to experience rapid suburban growth.

So even though nitrogen, phosphorus, and sediment loading are decreasing, significant population increases and development may mask the decreases in loading and cause there to be only small positive changes in future nutrient pressures. Thus, with high susceptibility and only small improvements in future nutrient pressures, the overall calculation for DFO in the Potomac River is Improve Low for 2002.

3.1.2 Neuse River and Estuary Summary

3.1.2.1 SPARROW Assessment

As described in Section 2.2.1.4, a modified SPARROW application was completed to account for Concentrated Animal Feeding Operations (CAFOs) and edge-of-field delivery rates to the Neuse River and estuary for a timeframe of the late 1990s–2002. Atmospheric nitrogen inputs were modeled from swine operations within North Carolina and were summarized from ambient monitoring stations for background atmospheric nitrogen inputs (**Figure 3.1-4**). The results of this modeling effort provide a preliminary assessment of the current state of the system, while parsing out swine inputs from other atmospheric nitrogen inputs that may be regulated by the National Ambient Air Quality Standards (NAAQS) for NO_x. Below we describe how we expect these results to vary when using the 2002 base-case scenario. **Table 3.1-2** provides a summary of the inputs and analysis methods that were used in the previous work and that will be used in the 2002 base-case scenario analysis.

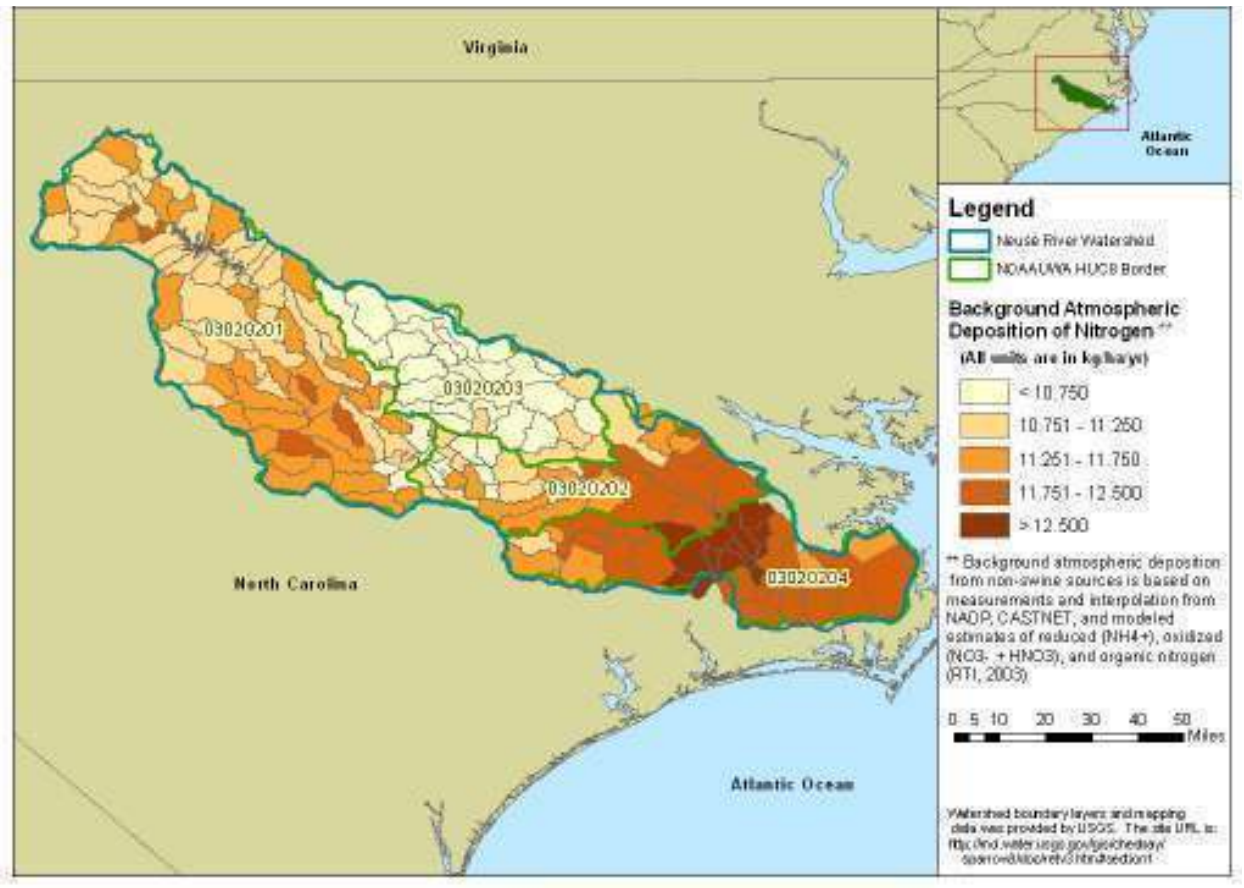

Figure 3.1-4. Background atmospheric total nitrogen deposition from NADP, CASTNET, and modeled data over the time period of 1996–2000 (RTI, 2003).

Table 3.1-2. Key Facts/Aspects of the Neuse Case Study

Category	**Description of Current/Demonstration Research**	**Source**	**Description for Final Case Study of Effects**
Spatial domain	SPARROW: Neuse River watershed defined on the 14-digit hydrologic unit (HUC14) scale; coastal HUCs with nondentritic drainage patterns could not be built; stream reaches based on EPA Reach File Version 3 Eutrophication Index: Neuse Estuary	RTI, 2003; Bricker et al., 2007a	SPARROW: HUC14 representation of the Neuse River watershed Eutrophication Index: Same definition of Neuse Estuary as used in NEEA Update
Temporal domain	Source data from 1995–2003; atmospheric data for 1996–2000	RTI, 2003	Updated input data for 2002 timeframe for all except swine emissions data, which will remain the same
Atmospheric nitrogen species	Wet and dry deposition data; reduced (NH_4^+), oxidized (NO_3^-+HNO_3), and organic forms of nitrogen; used ambient monitoring sites with spatial interpolation	RTI, 2003	Summation of available species from CMAQ to total nitrogen (TN)
Data origin of emission sources (modeling or monitoring)	15 wet deposition sites; 3 dry deposition sites; sources of data: CASTNET, NADP (Whitall and Paerl, 2001)	RTI, 2003	CMAQ; If calibration data for surface water inputs is available for years prior to 2002, atmospheric inputs for these years may be mined from the sources used in the demonstration research.
Analytic tool	Separate analyses using SPARROW and the ASSETS EI	RTI, 2003; Bricker et al., 2007a	Combined analysis using SPARROW and the ASSETS EI
Tool output indicators	SPARROW: Mean annual TN loading ASSETS EI: ASSETS overall score relating to likelihood of eutrophication		Change in ASSETS overall score based on changing input nitrogen loads from SPARROW modeling using various atmospheric deposition scenarios

Category	Description of Current/Demonstration Research	Source	Description for Final Case Study of Effects
Endpoint of indicators	Habitat and water quality degradation (expressed in terms of eutrophication effects (i.e., anoxia, loss of SAV)		Habitat and water quality degradation (expressed in terms of eutrophication effects (i.e., anoxia, loss of SAV)
Linkage to endpoints (science that connects indicator value to endpoint)	Previous work not applicable to ecosystem services due to atmospheric deposition effects because it was focused on swine operations. Similar endpoints and linkages can be modified for SPARROW output.	RTI, 2003	Inherent in the numerical score of the ASSETS EI using expression of symptoms (e.g., SAV, dissolved oxygen, harmful algal blooms)
Ecosystem services	Fisheries, recreation, tourism		Fisheries, recreation, tourism
Linkage method from endpoint to services	N/A		Quantitative: fisheries (e.g., closings, decreased species richness) related to eutrophication symptoms through monitoring data Qualitative: recreational activities related to eutrophication symptoms through user surveys Gaps: wealth of monitoring data not applied to answer applicable questions; wide variety of surveys available to conduct

Results indicate that 90% of the predicted in-stream concentrations for watershed outlet reaches fall within the range of 1.5 mg/L and 5.1 mg/L (total nitrogen), with the distribution especially for total nitrogen more skewed toward the lower end of the range. This distribution is generally indicative of eutrophic conditions, based on stream classification work by Dodds and colleagues (1998). We compiled model outputs and aggregated them to assess both spatial patterns and relative contributions from the different source categories considered. With default input and delivery assumptions, we estimate swine waste accounts for 30% of the nitrogen loading to coastal waters from inland, free-flowing streams and rivers in the study area.

For the entire study area (which included not only the Neuse River but also the Tar-Pamlico, Cape Fear, White Oak, and New river basins), swine facilities are predicted to contribute 28% of the atmospheric nitrogen inputs. Ammonia transported from swine facilities that deposits directly onto estuarine waters is estimated to deposit at rates of 0.01 to 0.04 kg/ha/yr for the different estuaries considered (i.e., Pamlico, Neuse, White Oak, and New), accounting for between 0.01% to 0.1% of the total estuarine loading. The rate of ammonia direct deposition to estuaries is estimated to be <1% of the estimated total nitrogen deposition rate accounting for non-swine sources, suggesting that local (i.e., indirect) ammonia gas transport and deposition is a more serious concern than ammonia transport directly to estuary waters. However, we cannot draw inferences about ammonium transport from swine facilities to estuaries because we did not attempt to model transport and deposition into the water system of swine waste as ammonium particles.

We completed a model run in which all swine input source terms for both runoff and deposition were set to zero, providing a hypothetical “zero swine discharge” scenario. This scenario reduced the area-wide total nitrogen delivery to estuaries by 125 million kg/yr, with variable reductions in more local stream concentrations and loadings, depending on the relative influence from swine facilities. The largest change at a 14-digit watershed outlet level was an in-stream improvement of 6.5 mg/L of total nitrogen, with the median improvement across all watershed outlet reaches being 0.14 mg/L. Our results demonstrate that ammonia deposition is a potentially significant component of surface water contributions in these North Carolina river basins.

Total nitrogen loads to the estuary calculated based on both the normal simulation and the "zero swine discharge" scenario will be compared against the updated modeling estimates completed for the 2002 base-case scenario.

3.1.2.2 ASSETS EI Assessment

The previous work completed using the ASSETS EI on the Neuse River Estuary was done as part of the NEEA. The latest available data was provided in the NEEA Update (Bricker et al., 2007a). The input load of nitrogen used as input to the ASSETS EI for that assessment was 9,600,000 kg/yr. The exact source of this 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 within the period of 2000–2002 (S. Bricker, personal communication, 2008). As shown in **Figure 3.1-5**, the current assessment of the Neuse Estuary reveals a *Highly/Moderately Influenced* or *High* score for influencing factors where the nitrogen load is ranked as *Moderate to High* and a *Bad* overall ASSETS score for the estuary. In the 2002 base-case scenario, we will examine whether or not these scores vary from this previous analysis.

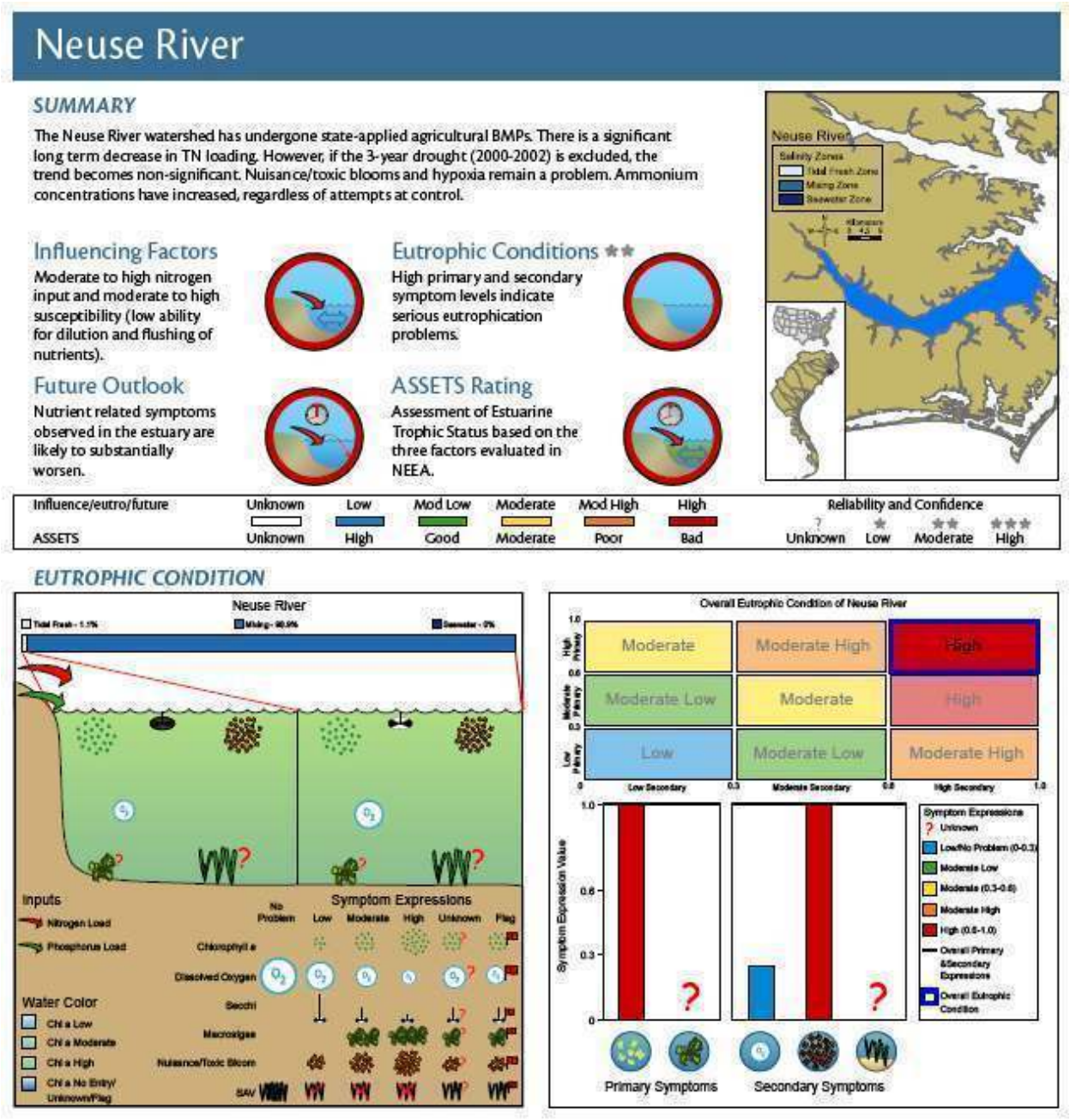

Figure 3.1-5. The ASSETS assessment summary for the Neuse River Estuary from the 2007 NEEA Update (Bricker et al., 2007a).

3.2 FUTURE CASE STUDY ASSESSMENTS

The case studies presented in the Results section of this report summarized work that had already been completed using the methods we seek to use for analyzing future reduction scenarios in NO_x and SO_x deposition. The next draft of this report will present base-case scenarios for the case study assessments using the 2002 CMAQ atmospheric deposition data

provided by EPA Clean Air Markets Division. The base-case scenario will provide a comparison point for the future reduction scenarios. Below we detail some of the differences we expect to see in the results and the additional data required to complete the 2002 base-case scenario as compared to the current summarized work. For any future comparisons between previous modeling efforts and the modeling efforts conducted under this risk and exposure assessment, we will examine the differences in atmospheric deposition inputs and the effects these differences may have on the modeling outcomes.

3.2.1 Potomac River Watershed

Within the Potomac River watershed, the atmospheric deposition of total nitrogen modeled using CMAQ for 2002 (**Figure 3.2-1**) can be compared to the atmospheric deposition inputs from NADP used in the Version 3 Chesapeake Bay SPARROW application, where interpolated values of wet deposition of nitrate were used (Figure 3.2-1). Comparisons between these two figures reveal that not only do the magnitudes of deposition values vary greatly, but the spatial aspects of deposition are almost completely reversed. Modeled total nitrogen deposition loads (normalized by area) are lowest in the more mountainous western side of the watershed and higher in the lowlands near the mouth of the Potomac River. Wet nitrate loads (normalized by area) were highest in the western, mountainous region of the watershed and loads in the southeastern portion of the watershed around the mouth of the Potomac River and the estuary.

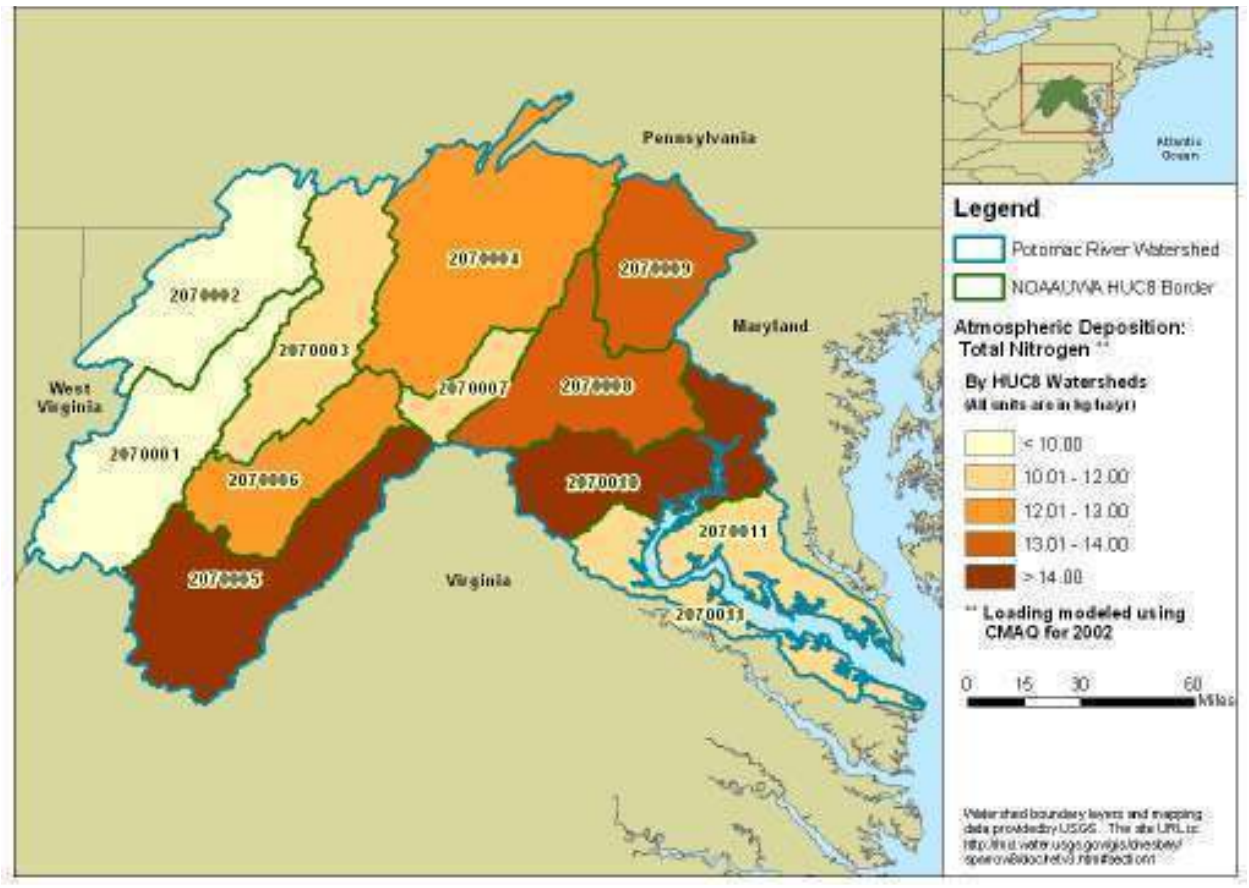

Figure 3.2-1. Atmospheric deposition inputs based on CMAQ simulations for 2002 for the Potomac River watershed and estuary. These inputs can be compared to Figure 3.1-1.

Greater spatial variability can also be seen when allocating the atmospheric deposition input loads to the segmented watershed units used within the Version 3 Chesapeake Bay SPARROW application. We suggest that the modeled CMAQ data be allocated to a smaller unit, such as the HUC14 level or the segmented watershed units from the Version 3 Chesapeake Bay SPARROW application or the updated NHD system. This will also allow for direct comparisons between the nitrate deposition from NADP used within the Version 3 Chesapeake Bay SPARROW application and the modeled nitrate deposition from CMAQ.

The components of the ASSETS EI were completed for 2002 during an analysis by NOAA (Bricker et al., 2006). The nitrogen load used to calculate the influencing factor portion of the ASSETS EI relied on an estimate of nitrogen inputs from the lower Potomac watershed to the estuary from Version 4.3 of the Chesapeake Bay Watershed Model (Bricker et al., 2006; MD DNR, 2005) for 2002. Therefore, when updating the base-case scenario in the next draft of this report, we will incorporate the CMAQ deposition data into a new SPARROW application, and

therefore provide an updated nitrogen load for use in calculating the influencing factors portion of the ASSETS EI. The 2002 score for the influencing factors portion of the ASSETS EI was evaluated as *Highly Influenced* (Figure 2.2-5). We expect the updated 2002 ASSETS EI score to remain the same. The remaining indices were evaluated at scores of High for the overall eutrophic condition (Figure 2.2-6), based on chlorophyll *a* and HAB symptoms, and Improve Low for the future outlook (Figure 2.2-8). The future outlook score will not be adjusted in the future policy scenarios because it relies on project population increases and slight reductions in nutrient loads. The overall eutrophic condition score will be assessed as discussed in Section 2.2.3. The chlorophyll *a* measures, which lead to a primary symptom score of *High*, could be considered in the borderline range (a *Medium* concentration at 16.4 ug/L at a *High* spatial coverage of 59% where the ranges for a *Medium* concentration is 5 ug/L–20 ug/L and a *High* spatial coverage is >50%). With improvements in nutrient loadings, it may be possible to predict a lower spatial coverage, which would improve the overall score. This score is an example of what will be examined through data mining, trend analysis, and expert judgment for the future policy scenarios.

3.2.2 Neuse River Watershed

The Neuse River watershed was the subject of a detailed modeling effort by RTI in a previous project, where the influences of the swine industry in North Carolina on the surface and groundwater were analyzed. This effort resulted in modeled deposition of ammonia due to swine operations in the state. Background deposition rates of reactive, oxidized, and organic nitrogen were also calculated based interpolated data from NADP, CASTNET, and some modeled estimates. These previous deposition estimates are compared to the 2002 CMAQ-modeled atmospheric data for the Neuse River watershed (**Figure 3.2-2),** which will be used in the future base-case scenario.

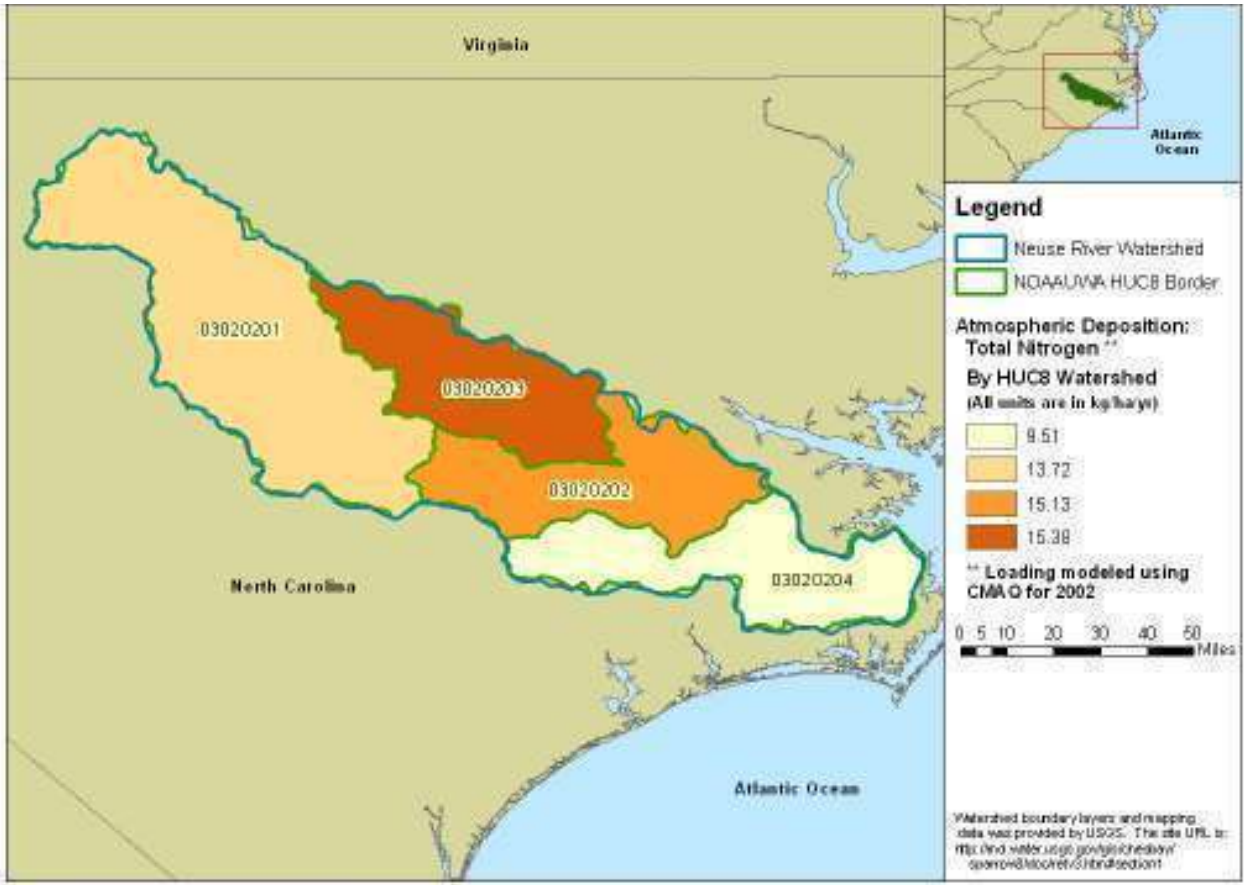

Figure 3.2-2. Atmospheric deposition inputs based on CMAQ simulations for 2002 for the Neuse River watershed and estuary. These inputs can be compared to Figure 3.1-4.

The spatial variance and magnitude of atmospheric deposition of total nitrogen (i.e., speciated nitrogen will be compared in future drafts) differ greatly between the interpolated NADP/CASTNET/modeled data from 1996–2000 used in the current work and the CMAQ modeled results. The CMAQ results appear to follow the modeled ammonia deposition from swine operations with the Neuse watershed more than the background interpolated concentrations. Although the current work took both the ammonia deposition from local, land use-based sources and the total nitrogen background deposition into account as separate atmospheric sources to the model, we expect that the future base-case nitrogen loading to the estuary from an updated SPARROW application using CMAQ data will vary, at least on the HUC14 level, from the current work. It is possible that the variations of surface water total nitrogen loads on a HUC14 level will average out to produce a similar total nitrogen load to the estuary, but this will be unknown until completion of an updated SPARROW application using the CMAQ data. We suggest that the CMAQ data be partitioned on the HUC14 or even 12-km

grid level rather than the HUC8 level. This will allow a more complete comparison between the modeled ammonia deposition because of local sources, and thus, a more complete analysis of deposition of N_r, including NO_x, and its effects on nitrogen loadings to the estuary.

The ASSETS EI reported for the Neuse River and estuary in the 2007 NEEA Update (Bricker et al., 2007a) represented conditions in the estuary for the 2000–2002 timeframe (Bricker, personal communication, 2008). We will seek to confirm the input data used in that assessment, but at this time, we expect to work under the same conditions as in the Potomac assessment, where the influencing factor portion of the score will change, but the overall eutrophic condition (i.e., rating of *High*) and future outlook (i.e., rating of *Worsen High*) portions will remain the same.

3.2.3 Discussion on Analysis of Changing Nitrogen Loads

As discussed in the previous section, the updated base-case scenario, as well as the future policy scenarios that examine reductions in NO_x and SO_x deposition, will rely on changes in the influencing factor score of the ASSETS EI because of changes in the predicted nitrogen load to the estuary. We must also consider that if there are considerable changes in the nitrogen loadings to the estuary, there may be changes in the indicators of the overall eutrophication condition as well. Without a comprehensive model that can calculate all five indicators as a function of nitrogen loads, we do not have a conclusive method to predict changes in these indicators for each policy scenario.

As we move forward in the policy scenarios, we will seek to use historical data to relate past nitrogen loads to each estuary to temporally corresponding indicators within the estuaries as an effort to create a response curve that can be used to predict whether or not the overall eutrophic condition score should be changed with each new calculated nitrogen load. This method will rely greatly on best professional judgment because it is not expected that large amounts of data will be available to create this curve (especially for the less studied systems discussed in the following section). Although this method will be highly speculative, it does make an attempt to account for changes in eutrophication, which would be otherwise overlooked in the analysis.

4. IMPLICATIONS FOR OTHER SYSTEMS

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 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, 2007a). 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 under suspicion of eutrophication. Data requirements and model formulations have been described and detailed throughout this report.

The method breaks down when attempting to assess eutrophication impacts on inland waters. SPARROW modeling can still 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. It is beyond the scope of this case study to further assess these inland waters. An additional case study in this project examines the effects of aquatic acidification on inland waters using dynamic modeling.

5. UNCERTAINTY

There are several areas of uncertainty with this method of assessment for aquatic nutrient enrichment, which are summarized below.

- **Data Inputs to SPARROW.** Two prominent choices of stream networks currently exist on which to build the updated SPARROW model for the Potomac watershed. The network used as part of the previous Chesapeake Bay SPARROW applications is

available with data inputs from the 1997 Version 3 application. The stream network set up for the Phase 5 version of the Chesapeake Bay Model, which utilizes 2002 data, is very similar to the aforementioned 1997 version in streamlines, but differs in watershed segments. These watershed segments have been divided not only based on streamlines, but also on geographic considerations. This allows for better defined data inputs, but provides a source of uncertainty in modeling with SPARROW's design of linked watershed segments based on streamlines. Upcoming work will combine the applicable data from these models to arrive at the best input dataset for the desired base-case scenario with the least amount of uncertainty possible.

- **Modeling Uncertainty in SPARROW Estimates.** With any measured or modeled results, there is a certain amount of uncertainty that should be quantified. Because SPARROW relies on a nonlinear regression basis, a number of parameters can be used to assess the uncertainty within the model and provide confidence intervals around the estimates.
- **Sensitivity of SPARROW Formulation Due to Atmospheric Inputs.** Differences in the final parameterization of the SPARROW model resulting from the use of the combination of CMAQ and NADP data as input to the model, in place of only NADP data as in previous applications, will allow for examination of the sensitivity of model parameters, evaluation statistics, and output to this more detailed data source.
- **Calibration Data for SPARROW Estimates.** Monitoring data will be used to calibrate the SPARROW model. By relying on data from federally recognized data systems, we aim to use data that has undergone quality assurance/quality control (QA/QC) procedures. Additionally, we will collaborate with the researchers who have conducted the previous SPARROW applications in each case study region to provide a rigorous check on the data used.
- **Data Inputs to the ASSETS EI.** As with the monitoring data used in calibrating SPARROW, the data inputs used to calculate the ASSETS EI must be confirmed from the previous analyses that we will be relying on as having undergone QA/QC procedures.
- **Heuristic Estimates of Future Outlook:** The estimation of the future outlook score in the ASSETS EI currently relies on heuristic estimates from systems experts. Future

NOAA efforts will seek to provide more scientifically structured estimates for this parameter, but at this time, we must rely on expert judgment on whether there will be increased or decreased pressures because of nutrient loads, population growth, and land use change.

- **Steady State Estimates/Mean Annual Estimates.** Both SPARROW and the ASSETS EI currently provide only longer-term estimates of the system conditions. There is the possibility of conducting the analyses on a seasonal basis, which may be appropriate because the trends in eutrophication indicators are likely to vary seasonally. For the current risk assessment, the analyses will be carried out for the entire 2002 base case.
- **Future Dynamic Model Applications, Including Eutrophication Indicators.** As highlighted in the introductory sections, higher level modeling approaches could potentially be used to evaluate the eutrophication effects of interest if significant data resources, time, and expertise were available for a specific site. An approach of this kind would not be scalable or applicable to wider regions, but would provide estimates with less uncertainty for a studied system.
- **Use of a Screening Method.** The methods used in this study are only of the screening level. As identified in the previous bullet, the screening level was more appropriate for a scalable, widely applicable set of case studies than for a highly detailed modeling effort. Undoubtedly, details, such as the degree to which the soil-groundwater system affects atmospherically deposited nitrogen, will be less quantified than detailed processes using this method. However, for an initial approach to determining the aquatic nutrient enrichment effects on a system, the screening method provides a response curve that can be used in the evaluation of ecosystem services.

6. CONCLUSIONS

The following are to be developed more fully in later drafts after comment period:

- Screening level method appropriate due to lack of link development
- Summary of current states of development
- Response curve developments and discussion provide implications for standards
- Summary of policy scenarios for case studies when available

- Future developments could supply higher level modeling efforts.

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ATTACHMENT 6

TERRESTRIAL NUTRIENT ENRICHMENT CASE STUDY

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August 14, 2008

Terrestrial Nutrient Enrichment Case Study

Draft

EPA Contract Number EP-D-06-003
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Prepared for

U.S. Environmental Protection Agency
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ACRONYMS AND ABBREVIATIONS

AM	*arbuscular mycorrhizae*
CASTNet	Clean Air Status and Trends Network
cm	centimeter
CMAQ	Community Multiscale Air Quality model
CO_2	carbon dioxide
CSS	coastal scrub sage
EMAP	Environmental Monitoring and Assessment Program
FIA	Forest Inventory and Analysis National Program
FRAP	Fire and Resource Assessment Program
FWS	U.S. Fish and Wildlife
GIS	geographic information systems
ISA	Integrated Science Assessment
kg	kilogram
km	kilometer
LTER	Long-Term Ecological Research
m	meter
m^2	square meter
MEA	Millennium Ecosystem Assessment
mm	millimeter
mo	month
NADP	National Atmospheric Deposition Program
NO_3^-	nitrate
NO_x	nitrogen oxides
NTN	National Trends Network
PNV	Potential Natural Vegetation
SMB	Simple Mass Balance
UNECE	United Nations Economic Commission for Europe
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service

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INTRODUCTION

This case study will demonstrate the influence of elevated levels of atmospheric nitrogen on selected ecosystems in California. The case study provides examples of habitats that may benefit from the management of atmospheric deposition, loading benchmarks, and ecosystem effects of nitrogen saturation. The investigations and approaches provided in this case study may be used to foster the research and management of elevated ambient air nitrogen and subsequent deposition on other terrestrial habitats across the United States.

In this case study, we identified sites in California that are of particular public interest and where nitrogen appears to be modifying habitats. Many acres of the coastal sage scrub (CSS) community have been set aside in reserves to protect the habitats and the species of concern that reside within the habitats. The mixed conifer forests on the slopes of the San Bernardino and Sierra Nevada Mountains have important recreational value, protect water resources, and provide habitats for many other species. In the mixed conifer forest, we investigated lichen communities associated with the forest stands and nitrogen saturation to identify the effects of nitrogen loadings. These habitats provide a number of ecological services, including regulation (e.g., water), cultural and aesthetic value (e.g., recreation, natural landscape, and sense of place), and provisioning (e.g., timber) (MEA, 2005). In addition, these locations have the following characteristics that make them good candidates for case studies:

- There is public interest
- An adequate amount of data (especially geographic information systems [GIS]) is available
- There are implications for other systems and ecosystem services
- Critical loading benchmarks may be developed
- The observed effects within the communities can be linked to atmospheric deposition of nitrogen.

A literature review was conducted to describe the habitats and species of concern, identify trends in habitats and their effects, and discuss research efforts that have investigated the variables and driving forces that may affect the communities. GIS data were obtained to explore

the spatial extent of the habitat and changes in that extent, the location of fire threat (an important variable in both CSS and mixed conifer forest habitats), and the location of species of concern. Additionally, the Community Multiscale Air Quality (CMAQ) 2002 modeling results were used to gain an understanding of how atmospheric deposition of nitrogen is spatially distributed. Spatial information and experimental results were acquired to help identify the driving forces in these ecosystems, describe the past and current extent of the habitats, and investigate the possibility of establishing benchmark loads.

1. BACKGROUND

The case study considered two ecosystems in California. For CSS, a conceptual model was developed that illustrates how nitrogen oxides (NO_x) is intertwined as a driving variable in changing CSS communities and how CSS can be used as a model for the other sensitive and critical habitats and/or species of concern. For mixed conifer forests, we examined the effects of atmospheric nitrogen in the context of other variables (i.e., ozone and fire), the effects of nitrogen saturation on forest communities, and loading benchmarks.

1.1 INDICATORS, ENDPOINTS, AND ECOSYSTEM SERVICES

Major indicators for nutrient enrichment to terrestrial systems from air deposition of reactive nitrogen involve measurements based on available monitoring stations for wet deposition (National Atmospheric Deposition Program [NADP]/National Trends Network [NTN]) and limited networks for dry deposition (Clean Air Status and Trends Network [CASTNet]). Wet deposition monitoring stations can provide more information on an extensive range of nitrogen species than can dry deposition monitoring stations. This creates complications when developing estimates for total nitrogen deposition levels because dry deposition data sources will likely be underestimated. In the Mediterranean systems of Southern California, dry deposition is particularly important. Individual studies measuring nitrogen deposition to terrestrial ecosystems that involve throughfall estimates for forested ecosystems can provide better approximations for total nitrogen deposition levels; however, such estimates and related bioassessment data are not available for the entire country. For terrestrial ecosystems, low calcium:nitrogen ratios in soils are commonly related to increased nitrification, potential

increases in soil acidity, and releases in nitrate to receiving waters; however, these measurements are not always widely available.

The indicators for nutrient enrichment effects on ecosystems reflect a combination of inputs from various media (e.g., air, discharges, diffuse runoff, groundwater inputs). Given the nature of major indicators for atmospheric deposition on ecological systems, a data-fusion approach that combines monitoring indicators with modeling inputs and outputs is often used (Howarth, 2007), and such an approach was used in this case study.

Ecosystem services are generally defined as the benefits individuals and organizations obtain from ecosystems. In the 2005 Millennium Ecosystem Assessment (MEA), ecosystem services are classified into four main categories:

- **Provisioning.** Includes products obtained from ecosystems.
- **Regulating.** Includes benefits obtained from the regulation of ecosystem processes.
- **Cultural.** Includes the nonmaterial benefits 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 (MEA, 2005).

A number of impacts on the endpoints of terrestrial ecosystems exist, including the following:

- CSS
  - Decline in CSS habitat, shrub abundance, species of concern – cultural and regulating
  - Increase abundance of non-natives – cultural and regulating
  - Increase in wildfires – cultural and regulating
- Mixed Conifer Forest
  - Change in habitat suitability and increased tree mortality – cultural and regulating
  - Decline in mixed conifer forest aesthetics – cultural
  - Increase in fire intensity, change in forest's nutrient cycling, other nutrients become limiting – regulating

– Decline in surface water quality – regulating

The terrestrial nutrient enrichment case study approach for CSS will focus on ecosystem services such as biodiversity; threatened and endangered species and rare species (both national and state); landscape view; water quality; and fire hazard mitigation. Linkage methods from endpoint to services could include measurement of changes in biodiversity and abundance and distribution of threatened and endangered species, comparison of past and present photography, and measurement of the distribution of soil moisture with depth and possible nitrate leakage.

The case study approach for mixed conifer forests will focus on ecosystem services, such as visual and recreational aesthetics provided by the community and water quality. Linkage methods from endpoint to services could include measurement of the densification of stands, shifts in tree dominance, shifts in lichen communities, foliar nitrogen increases, and increased NO_3^- in streams.

1.2 CASE STUDY SITE SELECTION

As described in the introduction of this report, the selection of case study areas specific to terrestrial nutrient enrichment began with GIS mapping. We used GIS datasets of physical, chemical, and biological properties that were indicative of potential terrestrial nutrient enrichment to identify sensitive areas in the United States (**Table 1.2-1**).

Table 1.2-1. Summary of Indicators and Mapping Layers for Targeted Ecosystems

Targeted Ecosystem Effect	**Indicator(s)**	**Mapping Layers**
Terrestrial Nitrogen Enrichment	▪ CEC ▪ C:N ratios ▪ Ca:Al ratios ▪ Air wet/dry deposition (corrected for throughfall using available data)	▪ Forest soils from USFS ▪ Forest type from USFS ▪ STATSGO soils ▪ NLCD ▪ CMAQ (N) by HUC

Note: CEC = cation exchange capacity, C:N = carbon:nitrogen, Ca:Al = calcium:aluminum, HUC = hydrologic unit code, N = nitrogen, NLCD = National Land Cover Data, STATSGO = State Soil Geographic database, USFS = U.S. Forest Service

We also considered the potential case study areas identified in the Integrated Science Assessment (ISA) (U.S. EPA, 2007). **Table 1.2-2** contains the relevant nutrient enrichment areas.

For purposes of the risk assessment, California's CSS and mixed conifer forest communities were selected for an initial case study analysis. We considered the following factors in choosing these case study areas:

- 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 from the case study area
- Representation of western United States ecosystems potentially impacted by nitrogen deposition
- Scalability and generalization opportunities for risk analysis results from the case studies.

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 nitrogen deposition in terrestrial ecosystems. California mixed conifer forests have 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.

Table 1.2-2. Potential Assessment Areas for Terrestrial Nutrient Enrichment Identified in the Draft ISA (U.S. EPA, 2007)

Area	Indicator	Detailed Indicator	Area Studies	Models	References in EPA, 2007	Source
Adirondacks	Terrestrial acidification		Paleoecological Investigation of Recent Lake Acidification (PIRLA) I and II; Episodic Response Project; Environmental Monitoring and Assessment Program (EMAP)	MAGIC; PnET-BGC	Baker and Laflen, 1983; Baker et al., 1990b; Baker et al., 1990c; Baker et al., 1996; Benoit et al., 2003; Chen and Driscoll, 2004; Confer et al., 1983; Cumming et al., 1992; Driscoll et al., 1987a; Driscoll et al., 1991; Driscoll et al., 1998; Driscoll et al., 2001a; Driscoll et al., 2001b; Driscoll et al., 2003b; Driscoll et al., 2003c; Driscoll et al., 2007a; Driscoll et al., 2007b; Evers et al., 2007; GAO, 2000; Havens et al., 1993; Ito et al., 2002; Johnson et al., 1994b; Landers et al., 1988; Lawrence et al., 2007; NAPAP, 1998; Siegfried et al., 1989; U.S. EPA, 2003; Sullivan et al., 1990; Sullivan et al., 2006a; Sullivan et al., 2006b; U.S. EPA, 1995b; Van Sickle et al., 1996; Whittier et al., 2002; Wigington et al., 1996; Zhai et al., 2007	ISA

Area	Indicator	Detailed Indicator	Area Studies	Models	References in EPA, 2007	Source
Shenandoah National Park	Terrestrial acidification		Shenandoah Watershed Study	MAGIC	Baker and Christensen, 1991; Baker et al., 1990b; Bulger et al., 1999; Bulger et al., 2000; Cosby et al., 2006; Dennis and Bulger, 1995; Dennis et al., 1995; Deviney et al., 2006; Eshleman and Hyer, 2000; Eshleman et al., 1995; Eshleman et al., 1998; Galloway et al., 1983; Hyer et al., 1995; MacAvoy and Bulger, 1995; Molot et al., 1989; Schofield and Driscoll, 1987; Sullivan et al., 2003; Sullivan et al., 2007a; Webb et al., 1995	ISA
Alpine and sub-alpine communities of the eastern slope of the Rocky Mountains in Colorado	Terrestrial nutrient enrichment	Biomass production; NO_3 leaching; species richness			Baron et al., 1994; Baron et al., 2000; Baron, 2006; Bowman, 2000; Bowman and Steltzer, 1998; Bowman et al., 1993; Bowman et al., 1995; Bowman et al., 2006; Burns, 2004; Fenn et al., 2003a; Fisk et al., 1998; Korb and Ranker, 2001; Rueth et al., 2003; Seastedt and Vaccaro, 2001; Sherrod and Seastedt, 2001; Steltzer and Bowman, 1998; Suding et al., 2006; Williams and Tonnessen, 2000; Williams et al.,1996a; Wolfe et al., 2001	ISA
Fernow Experimental Forest near Parsons, WV	Terrestrial nutrient enrichment	Forest growth			Adams et al., 1997, 2000; DeWalle et al., 2006; Edwards and Helvey, 1991; Gilliam et al., 2006; Peterjohn, 1996	ISA
Bear Brook, ME	Terrestrial acidification	Sugar maple; red spruce			Elvir et al., 2003	ISA

Area	Indicator	Detailed Indicator	Area Studies	Models	References in EPA, 2007	Source
Harvard Forest	Terrestrial nutrient enrichment	Forest growth—species			Magill et al., 2004; Magill, 2004	ISA
Southern California	Terrestrial nutrient enrichment	Forest growth—species; coastal sage scrub			Bytnerowicz and Fenn, 1996, 2003a; Takemoto et al., 2001	ISA
Jasper Ridge Biological Preserve in California	Terrestrial nutrient enrichment	Grasslands			Zavaleta et al., 2003	ISA
Loch Vale, CO	Terrestrial nutrient enrichment	Old-spruce growth			Rueth et al., 2003	ISA
Rocky Mountain National Park, CO	Terrestrial nutrient enrichment	Tundra composition switch			Interlandi and Kilham, 1998	ISA

Source: U.S. EPA, 2007a.

1

1.3 ECOSYSTEM OVERVIEW

1.3.1 Coastal Sage Scrub

CSS consists of more than 50 aromatic shrub and sub-shrub species, which range from approximately 0.5 meters (m) to 2 m in height (Burger et al., 2003; Westman, 1981a). The range of CSS extends from north of San Francisco down to Baja California in the lower elevation coastal range of California (see **Figure 1.3-1**); however, the species composition may vary with location (Westman, 1981b). According to the California Natural Diversity Database, there are 22 floristic alliances of CSS (i.e., Riversidian Sage Scrub, Venturan Sage Scrub, and Diegan Sage Scrub). These alliances consist of similar species that help determine the significance, rarity, and growth patterns of California vegetation types.

Figure 1.3-1. Range of coastal sage scrub communities.

CSS grows in a warm Mediterranean climate and is characterized by approximately 300 millimeters (mm) of annual rainfall falling from December through March and little or no rainfall from April through November (Egerton-Warburton and Allen, 2000; Westman, 1981b). Underlying substrate types of CSS communities vary greatly across the CSS stands, although many CSS floristic alliances are found on unconsolidated sand, sandstone, conglomerate, and shale (Westman, 1981b).

CSS is also known as "soft chaparral" because of its semi-deciduousness, drought-tolerant nature and its less-rigid leaves, respective to chaparral species (Westman, 1981b). CSS is considered a fire-adapted community, meaning that although vegetation layers may be destroyed in fires, CSS soil seed banks can withstand fire, and in some species, require fire to open the seed cases. However, many CSS species can flourish and propagate in the absence of any fire (Keeler-Wolf, 1995). CSS has been observed to maintain a permanent cover without fire or other disturbance regimes (e.g., land conversion, grazing) for at least a century (Westman, 1981a).

The resprouting and competition of species post-fire is generally dependent upon fire intensity, fire frequency, and seasonal timing (Keeler-Wolf, 1995). CSS species are generally poor colonizers after a fire (Minnich and Dezzani, 1998). Annual forbs and any grass seedlings present in the post-fire soils are usually dominant in the first few growth cycles. Significant shrub growth is most likely to occur in later cycles, further disturbance not withstanding (Keeler-Wolf, 1995).

The CSS community also supports the growth of more than 550 herbaceous annual and perennial species between and beneath the shrub canopy. Of these herbs, nearly half are endangered, sensitive, or of special status (Burger et al., 2003). Additionally, several avian, arthropod, herpetofauna, and mammalian species depend on the CSS community for foraging, breeding, and/or residence. These include several threatened and endangered species, such as the coastal California gnatcatcher (*Polioptila californica californica*), the Stephens' kangaroo rat (*Dipodomys stephensi*), and the Quino checkerspot butterfly (*Euphydryas editha quino*). **Figure 1.3-2** presents the range of these three species. **Table 1.3-1** presents a selected list of flora and fauna species that are associated with the CSS habitat.

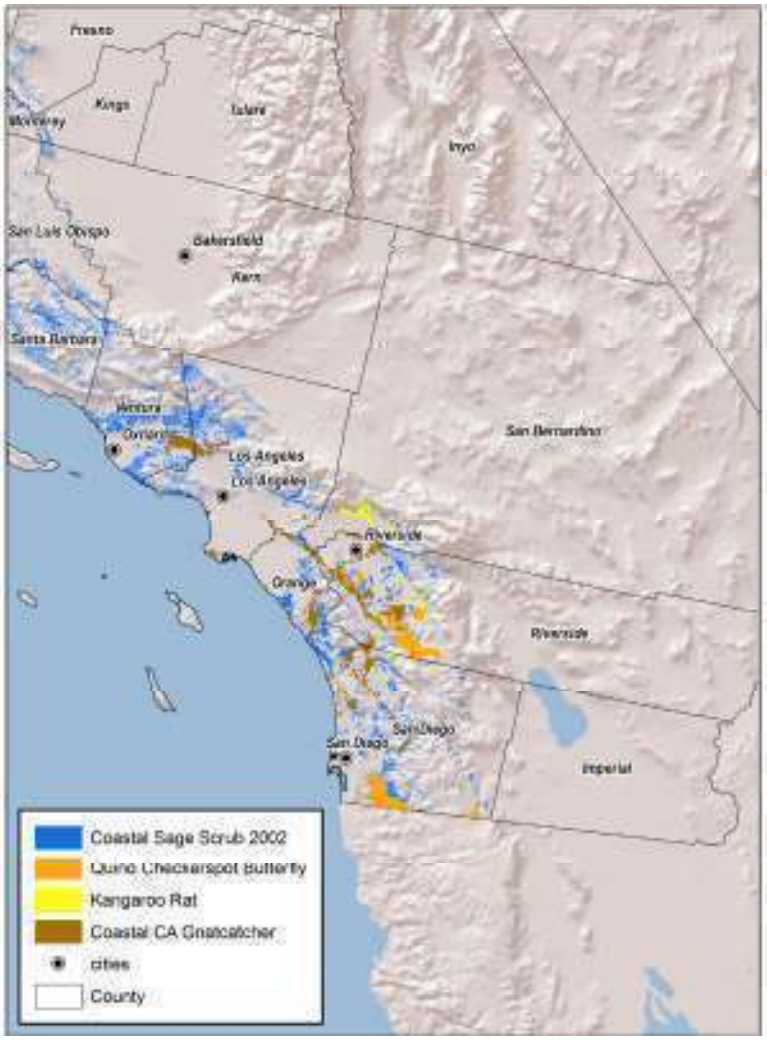

Figure 1.3-2. Presence of three threatened and endangered species in California's coastal sage scrub ecosystem.

Table 1.3-1. Selected Flora and Fauna Associated with the Coastal Sage Scrub Community

Scientific Name	**Common Name**	**Life Form**	**Federal Listing***	**State Listing***
Buteo swainsoni	Swainson's Hawk	Bird		Threatened
Polioptila californica californica	Coastal California Gnatcatcher	Bird	Threatened	
Dipodomys merriami parvus	San Bernardino Kangaroo Rat	Mammal	Endangered	
Dipodomys stephensi	Stephens' Kangaroo Rat	Mammal	Endangered	Threatened
Bufo microscaphus californicus	Arroyo Toad	Amphibian	Endangered	
Euphydryas editha quino	Quino Checkerspot Butterfly	Insect	Endangered	
Rhaphiomidas terminatus abdominalis	Delhi Sands Flower-Loving Fly	Insect	Endangered	
Allium munzii	Munz's Onion	Perennial forb	Endangered	Threatened
Rosa minutifolia	Small-Leaved Rose	Shrub		Endangered
Deinandra conjugens	Otay Tarplant	Annual forb	Threatened	Endangered
Cordylanthus orcuttianus	Orcutt's Bird's Beak	Annual forb		
Ambrosia pumila	San Diego Ambrosia	Perennial forb	Proposed Endangered	
Acanthomintha ilicifolia	San Diego Thorn-Mint	Annual forb	Threatened	Endangered
Campylorhynchus brunneicapillus couesi	Coastal Cactus Wren	Bird		
Athene cunicularia	Burrowing Owl	Bird		
Cnemidophorus hyperythrus	Orange-Throated Whiptail	Reptile		
Phrynosoma coronatum blainvillei	San Diego Horned Lizard	Reptile		
Masticophis lateralis euryxanthus	Alameda Whipsnake	Reptile	Threatened	Threatened

* Status listed for threatened and endangered species only. Others may be species of concern, on federal watch lists, or state special status.

The principal source of nitrogen to the CSS community is atmospheric nitrogen species (e.g., NO_x, NH_x), primarily originating from urban area automobile emissions and other emissions related to fossil fuels. These nitrogen species are transported and deposited onto the historically nitrogen-limited CSS soil in the form of nitrates and nitric acid. In the soil, these nitrogen species are potentially available for plant uptake and nutrient cycles. The effects of increased availability of nitrogen species in the CSS ecosystem are the focus of this case study.

1.3.2 Mixed Conifer Forest

The mixed conifer forest ecosystems stand approximately 30–50 m tall and consist of conifer species that dominate mid-range elevations (1300–2800 m) of the California San Bernardino and Sierra Nevada mountain ranges. The San Bernardino Mountains lie east of the Los Angeles Air Basin, and the Sierra Nevada Mountains span the majority of the state longitudinally. **Figure 1.3-3** illustrates the range of mixed conifer forest in California. Mixed conifer forests have historically adapted to withstand fire at low, medium, and even high intensities. As in CSS communities, the climate is Mediterranean, where 80% of rainfall occurs from October through March (Takemoto et al., 2001).

Figure 1.3-3. Range of California's mixed conifer forest ecosystem.

Dominant tree species shift along a precipitation gradient. Ponderosa pine (*Pinus ponderosa*), white fir (*Abies concolor*), sugar pine (*P. lambertiana*), and incense cedar (*Calocedrus decurrens*) are the predominant species on moist windward slopes, whereas Jeffrey pine (*P. jeffreyi*) and white fir are commonly found on leeward slopes, as well as at higher elevations in the mixed conifer elevation range. Important deciduous components of the mixed conifer forests are canyon live oak ((*Quercus chrysolepis*), black oak (*Quercus kelloggi*), and quaking aspen (*Popus tremuloides*). These stands support a number of shrubs, sub-shrubs, and annual and perennial forbs, as well as mountain meadows Minnich, 2007). A federal-listed species, the Mountain yellow-legged frog (*Rana sierrae and Rana muscosa*), and a number of state-listed species, such as the California Spotted Owl (*S. occidentalis occidentalis*), are

dependant on a mixed conifer ecosystem. The range of two of these selected species is illustrated in **Figure 1.3-4. Table 1.3-2** shows selected flora and fauna associated with mixed conifer ecosystems.

Figure 1.3-4. Presence of two threatened and endangered species.

Table 1.3-2. Selected Flora and Fauna Associated with the Mixed Conifer Ecosystems

Scientific Name	**Common Name**	**Life Form**	**Federal Listing***	**State Listing***
Abies concolor	White fir	Tree		
Pinus ponderosa	Ponderosa pine	Tree		
Pinus lambertiana	Sugar pine	Tree		
Calocedrus decurrens	Incense cedar	Tree		
Rana sierrae	Sierra Madre yellow-legged frog	Amphibian	Endangered	
Spea hammondii	Western spadefoot	Amphibian		
Rana muscosa	Sierra Madre yellow-legged frog	Amphibian	Endangered	
Glaucomys sabrinus	Northern flying squirrel	Mammal		
Glaucomys sabrinus californicus	San Bernardino flying squirrel	Mammal		
Ovis canadensis nelsoni	Peninsular bighorn sheep	Mammal	Endangered	**Threatened**
Odocoileus hemionus	Black-tailed deer	Mammal		
Charina umbratica	Southern rubber boa	Reptile		**Threatened**
Packera bernardina	San Bernardino ragwort	Perennial forb		
Sidalcea pedata	Bird-foot checkerbloom	Perennial forb	Endangered	**Endangered**
Perideridia parishii ssp. parishii	Parish's yampah	Perennial forb		
Taraxacum californicum	California dandelion	Perennial forb	Endangered	
Gilia leptantha ssp. leptantha	San Bernardino gilia	Shrub		
Piranga rubra	Summer tanager	Bird		
Haliaeetus leucocephalus	Bald eagle	Bird	Delisted	**Endangered**
Strix occidentalis occidentalis	California spotted owl	Bird		
Strix nebulosa	Great gray owl	Bird		**Endangered**

* Status listed for Threatened and Endangered species only. Others may be species of concern, on federal watch lists, or state special status

Additionally, several lichen species are associated with the mixed conifer stands. Lichens are formed by a symbiotic relationship between fungus and algae or cyanobacterium. In the mixed conifer ecosystem, lichens are generally epiphytic, living on conifers and obtaining nutrients from the atmosphere. Epiphytic lichen serve as food, habitat, and nesting material for various species in the pine stands (Fenn et al., 2008). The presence of individual species is determined by the amount of nitrogen present and the pH of the vegetation on which it grows; however, general categories for lichens have been developed according to species' sensitivity to nitrogen. The categories include nitrophytes, neutrophytes, and acidophytes. (Jovan, 2008). Nitrophytes are generally associated with ammonia and high pH environments. Neutrophytes tolerate increased pH and ammonia, but exhibit slower growth patterns than nitrophytes. Acidophytes are sensitive to nitrogen species and deteriorate or die after relatively small increments of exposure to nitrogen species (Fenn et al., 2008). **Table 1.3-3** presents a list of lichen species, classified by nitrogen sensitivity, that have been observed in the San Bernardino and Sierra Nevada mountain ranges

Table 1.3-3. List of Lichen Species Present in the Sierra Nevada and San Bernardino Mountain Ranges (Jovan, 2008; Sigal and Nash, 1983)

Nitrophytes	**Potential acidophytes**	**Potential neutrophytes**	**Unknown**
Candelaria concolor	*Bryoria fremontii*	*Melanelia elegantula*	*Ahtiana sphaerosporella*
Flavopunctelia flaventiorb	*Cetraria canadensis*	*Melanelia exasperatula*	*Alectoria sarmentosa*
Phaeophyscia orbicularis	*Cetraria chlorophylla*	*Melanelia glabra*	*Collema furfuraceum*
Physcia adscendens	*Cetraria merrillii*	*Melanelia subargentifera*	*Esslingeriana idahoensis*
Physcia aipolia	*Cetraria orbata*	*Melanelia subelegantula*	*Leptogium lichenoides*
Physcia dimidiate	*Cetraria pallidula*	*Melanelia subolivacea*	*Letharia columbiana*
Physcia stellaris	*Cetraria platyphylla*	*Parmelia hygrophilab*	*Letharia vulpina*
Physcia tenella	*Evernia prunastri*	*Parmelia sulcata*	*Nodobryoria abbreviata*
Physconia enteroxantha	*Hypogymnia enteromorpha*	*Ramalina subleptocarphab*	*Nodobryoria oregana*
Physconia perisidiosa	*Hypogymnia imshaugii*		*Parmelina quercina*
Xanthomendoza fallax	*Hypogymnia occidentalis*		*Parmelina elegantula*
Xanthomendoza fulva	*Parmeliopsis ambigua*		*Physcia biziana*
Xanthomendoza hasseana	*Platismatia glauca*		*Physconia americana*
Xanthomendoza oregano	*Usnea filipendula*		*Physconia isidiigera*
Xanthoria candelaria			
Xanthoria polycarpa			

1.4 HISTORICAL TRENDS

1.4.1 Coastal Sage Scrub

The CSS habitat is a unique system that has experienced a significant decline in coverage since vegetation types in Southern California were inventoried in 1929. Subsequently, this community has been designated for special status in California (CA DFG, 1993). This decline is due to urban encroachment and sprawl, increased fire frequencies, and pollution (Minnich and Dezzani, 1998). CSS is decreasing at a higher rate than habitat destruction alone would indicate (Allen et al., 1998; Fenn et al., 2003; Minnich and Dezzani, 1998)

Non-native grasses were introduced to California by explorer expeditions and Franciscan missionaries arriving in the region prior to documentation of indigenous vegetation. However, accounts of herbaceous vegetation in the coastal range exist from the late 1700s and throughout the 1800s (Minnich and Dezzani, 1998). CSS was first scientifically inventoried during the California Forest and Range Experiment Station Vegetation Type Map (VTM) Survey, beginning in 1929. Through subsequent mapping surveys, fieldwork, and aerial photography comparisons, significant reductions in CSS were observed. **Figure 1.4-1** illustrates the decline in CSS from 1977–2002.

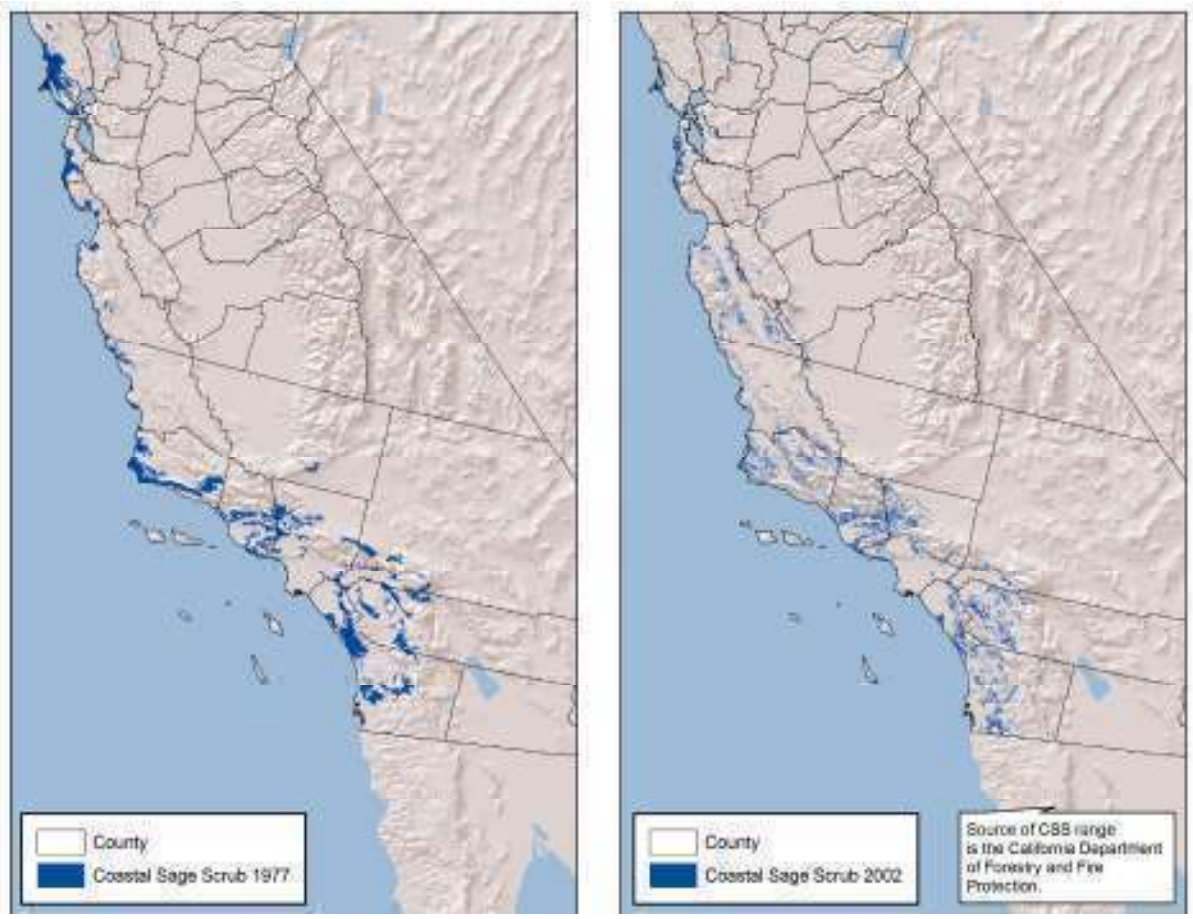

Figure 1.4-1. Decline of coastal sage scrub from 1977–2002.

Based on changes in CSS cover in VTM maps from the early 1930s–1990, it is estimated that approximately 18% of Riverside County CSS had been completely converted to non-native grasses, and an additional 42% of the cover had non-native grasses intermixed with CSS. Therefore, only 40% of the original CSS community in Riverside County remained intact and contiguous. Across the entire CSS range, Westman (1981a) estimated that only 10%–15% of the historical CSS extent remained in the late 1970s. This estimate is based upon the fraction of potential CSS land cover (in the absence of pressures) in which CSS vegetation was actually observed at the time of the study. The potential CSS land cover estimates may also be supported by the broad range in which specimens of the Quino checkerspot butterfly have historically been observed and collected (Mattoni et al., 1997). Therefore, the remaining extent of CSS is most likely between 10%–82% of the historical CSS coverage, depending on the development pressures and the spread of non-native grasses in each stand. Additionally, these non-native

grasses are less diverse and are not likely to support the majority of the sensitive, threatened, and endangered species that currently rely on CSS (Allen et al., 2005).

1.4.2 Mixed Conifer Forest

The major trends observed in mixed conifer forests are "densification" and increased litter accumulation. Densification occurs when aboveground biomass is stimulated, resulting in increased numbers of needles, decreased average tree age, decreased overall trunk size, and increased branches (Grulke et al 2008; Minnich et al., 1995; Takemoto et al., 2001). In a retrospective comparison of conifer stands in the San Bernardino Mountains from 1932–1992, Minnich and colleagues (1995) noted significant shifts in age distribution, stand density, and branch density. Tree density increased approximately 77% according to the VTM surveys, and there were 3–10 times the number of trees in the younger age brackets when compared to 60 years earlier. Additionally, a 79% increase in the average number of tree branches was reported in the San Bernardino conifer forests. Studies have indicated that increasing stand densities are also occurring within the Sierra Nevada Mountains (Minnich et al., 1995).

Increased litter on the forest floor has also been observed across the ecosystems, particularly in the mixed conifer forest stands in the San Bernardino mountain range. These forest stands have been observed to shed needles approximately six times faster than more remote northern Sierra Nevada conifer stands (Takemoto et al., 2001). Additionally, litterfall depths up to 15 centimeters (cm) have been noted in mixed conifer stands near Camp Paivika in the eastern San Bernadino range (Grulke et al., 2008).

Across the San Bernardino mountain range, a community composition shift was also noted. In mixed conifer stands where ponderosa pine has been historically dominant, trees in the youngest age bracket are now predominantly white fir and incense cedar. Additional research is needed to determine if a shift in community composition is also occurring in the Sierra Nevada mountain range (Minnich et al., 1995).

Lichen communities associated with the mixed conifer ecosystems have also been dramatically altered (Fenn et al., 2003: Sigal and Nash, 1983). Of 16 lichen species reported to be associated with the San Bernardino mixed conifer forests in the early part of the 20th century, only 8 species were found 60 years later. Additionally, deterioration was observed on some of

the lichen, particularly in the areas with the highest levels of air pollution (Sigal and Nash, 1983).

2. APPROACH AND METHODOLOGY

2.1 UNDERSTANDING THE TRENDS THROUGH LITERATURE REVIEW

2.1.1 Coastal Sage Scrub

A literature search was conducted during this case study to obtain all relevant peer-reviewed literature on the correlation between nitrogen enrichment and the decline in CSS communities in the northern and southern regions of California. Three major publication collection databases (i.e., ScienceDirect, Elsevier, and JSTOR) were searched for peer-reviewed journal articles that contained a combination of "nitrogen," "nitrate," or "nutrient," and "coastal sage scrub" in the title, keywords, or abstract. When the literature research was summarized, it was observed that increasing nitrogen and decreasing CSS stands may be linked through iterative changes in soil nitrogen stores, increased fire frequency, and changes in water infiltration and retention zones in soil. Additional research was conducted to determine the plausibility of the iterative and magnifying effects of increased nitrogen on declining CSS stands.

2.1.2 Mixed Conifer Forest

Research involving nitrogen enrichment and the lichen communities was obtained using an approach similar to that conducted for the CSS literature search. A combination of "nitrogen," "nitrate" or "nutrient," and "mixed conifer," "Ponderosa pine," "Jeffrey pine," or "lichen" were queried to obtain all relevant peer-reviewed articles in the San Bernardino and Sierra Nevada mountain ranges of California. The literature suggested that changes in the forest are complex and driven by atmospheric ozone, nitrogen, and fire. Lichen sensitivity to nitrogen was cited as a potential method to determine critical loading benchmarks for the habitat. Furthermore, it appeared that many parts of the mixed conifer forest ecosystem were experiencing signs of nitrogen saturation, providing an opportunity to consider community effects.

2.2 GIS METHODOLOGY

2.2.1 Overview

It is possible to delineate the areas in the Southern California case study area at risk for extirpation. Some of the factors that have been cited in the literature are available as either state-level or national-level datasets. It is important to use spatial data that are temporally and spatially compatible, as well as to have well-documented metadata and the ability for data to be scaled-up for a national characterization.

2.2.2 Available Data Inputs

- **Nitrogen deposition**. Wet nitrogen deposition in the forms of NO_3^- and NH_4^+ are available nationally from the NADP. This national network of 321 sampling stations is not very dense and is more concentrated in the east and upper midwest areas of the United States. There are only four stations in the Southern California case study area, making interpolation between stations tenuous; therefore, NADP was not used in this assessment. Dry nitrogen deposition can be estimated using the output from the CMAQ 2002 modeling system. This model produced estimates of many nitrogen species aggregated to 12-kilometer (km) squares. Although these data are fairly sparse, they are the best that are currently available.
- **Range of CSS communities.** There are two sources for the range of CSS communities. One is the Kuchler Potential Natural Vegetation (PNV) Groups data layer that was created to show "climax" vegetation that will occupy a site without disturbance or climate change. PNV is an expression of environmental factors, such as topography, soils, and climate across an area. Although this reveals where CSS communities might exist, a better source for the community range was the Fire and Resource Assessment Program (FRAP) data housed by the California Department of Forestry and Fire Protection. This agency classified California's vegetation into 59 different categories, including coastal scrub, at a spatial resolution of 100 m.
- **Fire threat.** The California Department of Forestry and Fire Protection's FRAP also compiles data about fire threat. These data consider fire rotation (i.e., how frequently fire occurs) and potential fire behavior, which take into account topography and potential

vegetative fuels. Fire threat is classified into four unique categories that range from moderate to extreme.

- **Changes to CSS communities.** In addition to the range of CSS communities in 2002, the California Department of Forestry and Fire Protection's FRAP also publishes data compiled in 1977. Both datasets contained CSS community boundaries and were compiled using similar data sources and techniques. A GIS was used to overlay the two datasets, creating three types of change. CSS loss was ascribed to areas where CSS existed in 1977, but did not exist in 2002. No change was ascribed to areas where CSS existed in both 1977 and 2002. CSS growth was ascribed to areas where CSS did not exist in 1977, but did exist in 2002.
- **Distribution of invasive species.** Two data sources for invasive species were found for California. The first is the PLANTS program, which is part of the U.S. Department of Agriculture (USDA) (http://plants.usda.gov/index.html). This resource posts maps that indicate whether a species is present or not in a given county, but not the distribution of that species within the county. The second is the California Invasive Plant Council (http://www.cal-ipc.org/ip/mapping/statewide_maps/index.php), which lists the relative abundance by county of a select number of species.
- **Threatened and endangered species habitat.** The U.S. Fish and Wildlife Service (FWS) publishes critical habitat information for threatened and endangered species by state, county, and species through the Critical Habitat Portal (http://crithab.fws.gov/). For example, the Critical Habitat Portal locates 16 species for Riverside County, 5 of which are associated with the CSS community.
- **Range of mixed conifer forest.** The most recent (2002) land cover dataset from the California Department of Forestry and Fire Protection's FRAP site was also used to extract the range of mixed conifer forest.
- **Distribution of acid sensitive lichens.** The U.S Forest Service's (USFS's) Forest Inventory and Analysis National Program (FIA) datasets were the source of lichen distributions.
- **Fenn field sites.** The locations of the field sites used by Fenn and colleagues (2008) for measuring nitrogen deposition were published in *Empirical and Simulated Critical Loads*

for Nitrogen Deposition in California Mixed Conifer Forests. These locations were listed as latitude and longitude coordinates, which were converted into a GIS layer with nitrogen deposition as an attribute.

2.2.3 Approach to Mapping

To scale the mapping approach used in this case study to a national level, datasets must be available nationally or be sufficient to provide a national picture. The terrestrial enrichment case study looked at the effects of atmospheric nitrogen on two ecosystems in California. The goal of mapping was to help illustrate CSS declines, areas of mixed conifer forest, species distributions, the distribution of atmospheric nitrogen deposition, and fire threat.

In our mapping approach, we identified the following inputs:

- The current range of CSS and mixed conifer forest communities
- The areas with a high threat of fire
- The areas with the highest nitrogen deposition.

3. RESULTS

Effects of elevated nitrogen deposition on the CSS and mixed conifer ecosystem are the result of long-term elevations in nitrogen rather than pulses. Additionally, it is difficult to quantify effects in both ecosystems because of confounding stressors, such as fire and ozone. Therefore, the literature available on long-term research and application of robust models on these ecosystems is extremely limited.

The CSS case study relies upon peer-reviewed literature and spatial analyses to derive major conclusions regarding the effects of nitrogen. Spatial analyses was used to determine the changes in the extent of CSS community and associated habitat, as well as to investigate the effects of nitrogen and fire, another driving component in alteration of the CSS ecosystem. The reviewed literature includes greenhouse experiments, field observations, and field manipulation experiments that document the observed and measured effects of nitrogen.

The mixed conifer case study also contains a peer-review literature summary; however, this case study focuses on the empirical loading benchmarks derived from an analysis by Fenn and colleagues (Fenn et al., 2008). The authors employ the Simple Mass Balance (SMB) model

and the DayCent simulation model to estimate critical loads. This case study focused on the results of the SMB model because of the simplicity and the incorporation of long-term values for soil nitrogen.

3.1 LITERATURE REVIEW FINDINGS

3.1.1 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 uses) will simply eliminate acres of habitat. Other pressures will come into play in modifying the remaining habitat. Research suggests that both fire and increased nitrogen can enhance the growth of non-native 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** contains a summary of selected experimental variables across multiple CSS study locations.

Table 3.1-1. Summary of Selected Experimental Variables across Multiple CSS Study Locations

Study Locations	**Soil Nitrogen**	**Atmospheric Nitrogen**	**Vegetation Change**	**Mycorrhizae Change**	**Fire Cycle**	**Author**
Riverside-Perris Plain*	x	x	x			Allen et al., 1998
Santa Margarita Ecological Reserve			x			Burger et al., 2003
Santa Monica Mountains	x		x			Carrington and Keeley, 1999
Orange County*			x			Diffendorfer et al., 2007
Rancho Jamul Ecological Reserve			x			
Voorhis Ecological Reserve			x			Drus, 2004
Riverside-Perris Plain*	x			x		Egerton-Warburton and Allen, 2000
Sedgwick Ranch Natural Reserve	x		x			Fierer and Gabet, 2002
Southern California fuel breaks*			x		x	Merriam et al., 2006
Critical review*			x		x	Keeley, 2001
Southern California burn sites*			x		x	Keeley et al., 2005
Riverside-Perris Plain*			x		x	Minnich and Dezanni, 1998
Greenhouse experiment	x					Padgett et al., 1999
Riverside-Perris Plain*	x	x				Padgett and Allen, 1999

Study Locations	Soil Nitrogen	Atmospheric Nitrogen	Vegetation Change	Mycorrhizae Change	Fire Cycle	Author
University of California–Riverside Agricultural Research Station			x			Padgett et al., 2000
Riverside-Perris Plain*	x			x		Siguenza et al., 2006
Riverside-Perris Plain*	x			x		Sirulnik et al., 2007a
Lake Skinner	x					Sirulnik et al., 2007b
Riverside-Perris Plain*	x					Vourlitis et al., 2007
67 sites across CSS range*			x			Westman, 1979, 1981a,b
Riverside-Perris Plain*	x					Wood et al., 2006
Lake Skinner Western Riverside County Multi-Species Reserve			x	x		Yoshida and Allen, 2001
Greenhouse experiment			x	x		

*Multiple data sites within the study location.

Increased nitrogen deposition has been observed to alter vegetation type 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). In the case of CSS, it is hypothesized that many stands are no longer limited by nitrogen and have instead become nitrogen saturated due to atmospheric nitrogen deposition (Allen et al., 1998; Westman, 1981a). 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., 2007a; Vourlitis et al., 2007). **Figure 3.1-1** illustrates the levels of atmospheric nitrogen deposition on CSS communities using CMAQ 2002 modeling results.

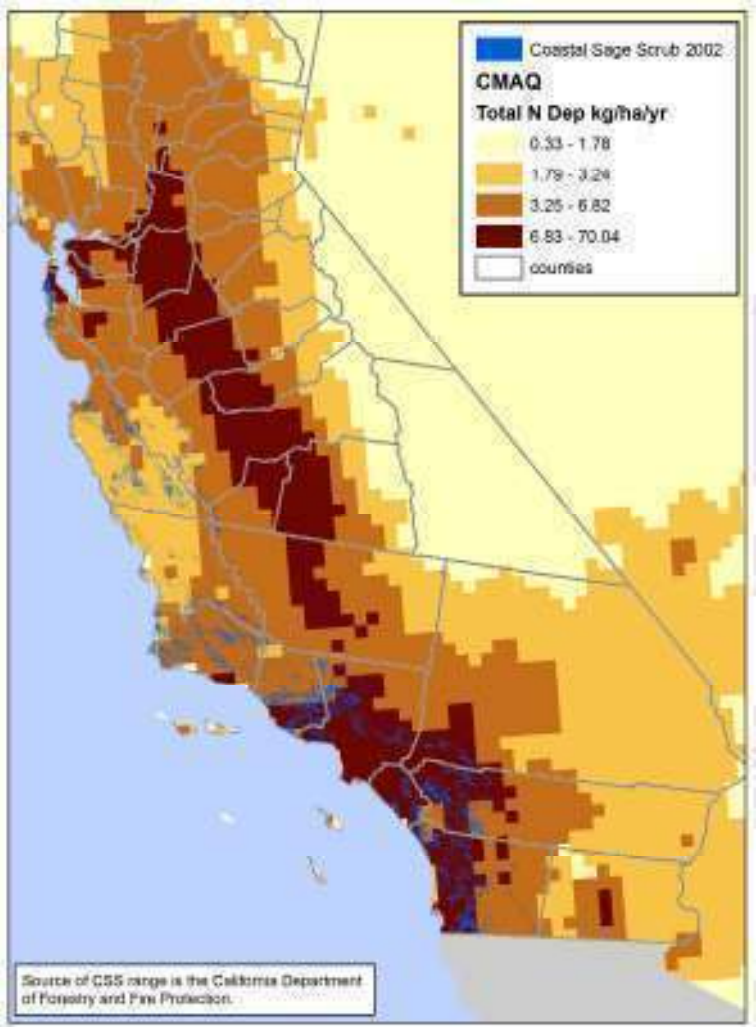

Figure 3.1-1. Coastal sage scrub range and total nitrogen deposition using CMAQ 2002 modeling results.

The ecological effects of increased nitrogen are most easily explained chronologically through the seasonal stages of a semi-arid Mediterranean ecosystem. In the rainy, winter season, deposited surface nitrogen is transported deeper into the soil and is rapidly mineralized by microbes, thus making it available for plants. Faster nitrogen availability may favor the germination and growth of nitrophylous colonizers, more specifically non-native grasses (e.g., *Bromus madritensis*, *Avena fatua,* and *Hirschfeldia incana*). This earlier 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 water storage capability of the soil and underlying bedrock (Wood et al., 2006). Establishment of CSS species, such as *Artemisia californica*, *Eriogonum fasciculatum*, and *Encelia farinose*, may be reduced because of decreased water and nitrogen availability at the deeper depths where more woody CSS tap roots are found (Keeler-Wolf, 1995; Wood et al., 2006). These findings are supported by the increased percentage of shrub species established during wet years (Keeley et al., 2005).

Elevated nitrogen may also play a role in altering the nutrient-uptake capabilities of CSS species by decreasing the species' richness and abundance of mutualistic fungal communities, such as *arbuscular mycorrhizae* (AM) (Egerton-Warburton and Allen, 2000; Siguenza et al., 2006). Although both CSS and non-native grass species have AM and other non-mycorrhizal fungal associations, which increase the surface area and capacity for nutrient uptake, CSS is predominantly colonized by a coarse AM species, and non-native grasses are more likely mutualistic with finer AM species. In the presence of elevated nitrogen, coarse AM colonizations were depressed in number and volume. At sites with the highest levels of soil nitrogen tested (e.g., 57 μg/g average annual soil nitrogen present in Jurupa Hills, Riverside County), a shift in the timing of AM growth was also observed. Therefore, it is suggested that these reduced mutualistic associations may contribute to a decline in the overall health of CSS via a loss in nutrient uptake capacity.

In a greenhouse fertilization experiment, soil nitrogen levels of 50 μg/g ammonium nitrate had a 100% mortality rate after 9 months of continuous growth. The plants began to senesce at approximately 6 months, whereas all lower exposure individuals were still healthy and remained healthy for more than 1 year (Allen et al., 1998). In the field, seasonal changes do not allow for 12 months of uninterrupted growth; therefore, the increased mortality shown in this study may be realized over much longer periods of time in situ. Additionally, studies have

suggested that soil nitrogen may now be increasing because of soil fertility in conjunction with atmospheric deposition so that the soil itself becomes an intrinsic source (Padgett et al., 1999). In combination with decreased establishment and the capacity for nutrient uptake, these responses to elevated nitrogen levels may represent a significant, detrimental, and long-term pressure on CSS at varying levels of nitrogen additions. **Table 3.1-2** summarizes the various ecosystem responses to nitrogen levels that affect CSS communities.

Table 3.1-2. Research Evidence of Ecosystem Responses to Nitrogen Relevant to Coastal Sage Scrub Communities

Environmental Impact	**Location**	**Reference**
Enhanced growth of non-native species	Southern California	Minnich and Dezanni, 1998; Allen et al., 1998; Weiss, 2006; Westman, 1981a,b
Nitrogen enrichment of soil and plants	Riverside-Perris Plain, San Diego County	Sirulnik et al., 2007a; Allen et al., 1998; Padgett et al., 1999; Vourlitis et al., 2007
Decreased growth regulation of shrubs	Greenhouse experiment	Padgett and Allen, 1999
Decreased diversity of mycorrhizal communities	Riverside-Perris Plain	Egerton-Warburton and Allen, 2000; Siguenza et al., 2006
Increased runoff and nutrient loss	Santa Barbara	Fierer and Gabet, 2002
Altered fire cycle	Riverside-Perris Plain	Wood et al., 2006
Increased dependent species vulnerability	All CSS; San Diego County	Weiss, 2006; Weaver, 1998
Increased erosion		Keeler-Wolf, 1995

Fire is also an inextricable and significant component in CSS losses. Although CSS communities are fire resilient, non-native grass seeds are quick to establish in burned lands, reducing 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 due by senescing earlier in the annual season and increasing the dry, ignitable fuel availability (Keeley et al., 2005). With increased fire frequencies and faster non-native colonizations, CSS seed banks are eventually eradicated from the soil, and the probability

of re-establishment decreases significantly (Keeley et al., 2005). **Figure 3.1-2** represents the fire threats to CSS communities.

Figure 3.1-2. Current fire threats to coastal sage scrub communities.

It appears that both atmospheric nitrogen deposition and fire are critical factors involved in the decline of CSS. **Figure 3.1-3** presents a preliminary conceptual model that provides an overview of system response to nitrogen and fire. Note that the model does not indicate that either fire or nitrogen deposition is playing a larger role than the other. Rather, current research indicates that both are playing critical roles. The model indicates some positive feedback loops and possible synergies between fire and nitrogen loadings and research questions that might be pursued.

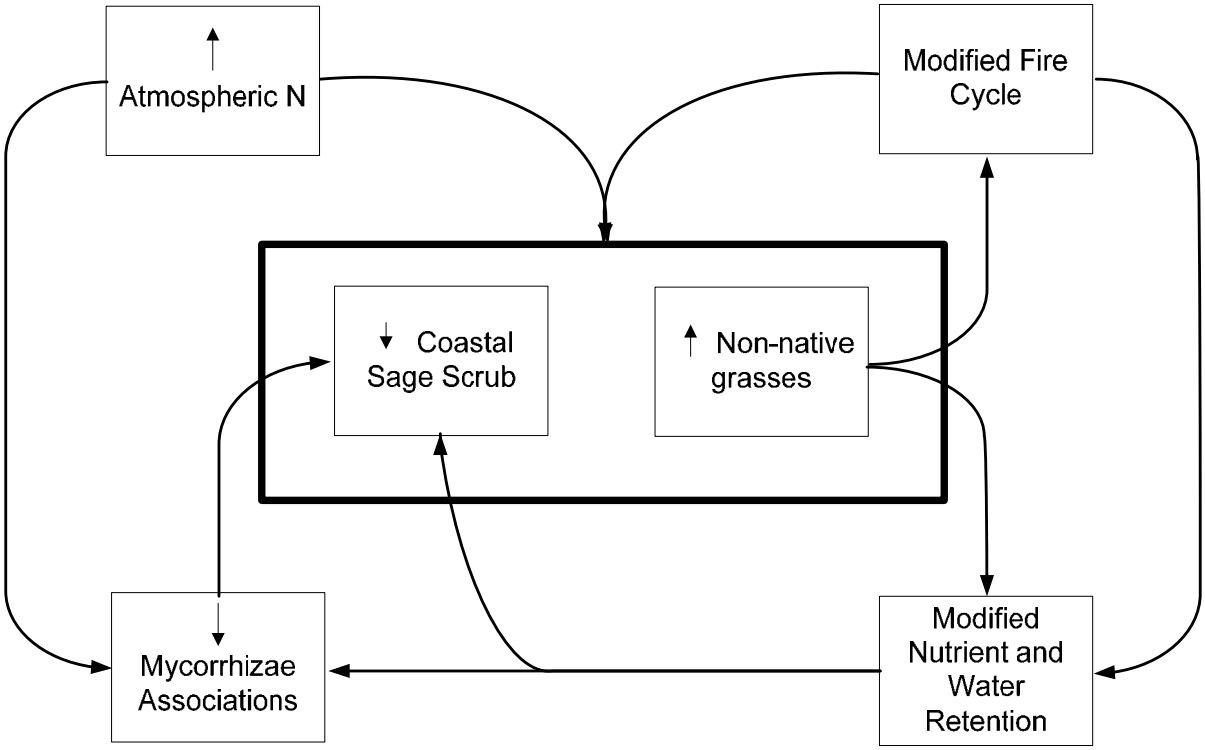

Figure 3.1-3. Conceptual model of coastal sage scrub community in relation to fire and nitrogen deposition.

3.1.2 Mixed Conifer Forest

The mixed conifer forest has been a subject of study for many years. There are a number of important stressors on the community, including atmospheric fire, ozone, and nitrogen. Although fire suppression in the 20th century is probably the most significant change that has led to alterations in the morphology and perhaps to shifts in forest composition (Minnich et al., 1995), stress from elevated levels of ambient nitrogen concentrations is the subject of increasing research.

3.1.2.1 Nitrogen and Ozone Effects on Conifers

Measurements documenting increases in nitrogen deposition have been recorded with some regularity since the 1980s (Bytnerowicz and Fenn, 1996); however, the Los Angeles area has seen elevated atmospheric nitrogen for the last 50 years (Bytnerowicz and Fenn, 1996). The pressures exerted on mixed conifer ecosystems in California form a gradient across the Sierra Nevada and San Bernardino mountain ranges. Nitrogen throughfall levels in the northern Sierra Nevada Mountains are as low as 1.4 kg nitrogen per hectare annually, whereas forests in the

western San Bernardino Mountains experience throughfall nitrogen levels up to 33–71 kg nitrogen per hectare per year. 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 mountains (Grulke et al., 2008). **Figure 3.1-4** illustrates the current total nitrogen deposition on mixed conifer forests in California.

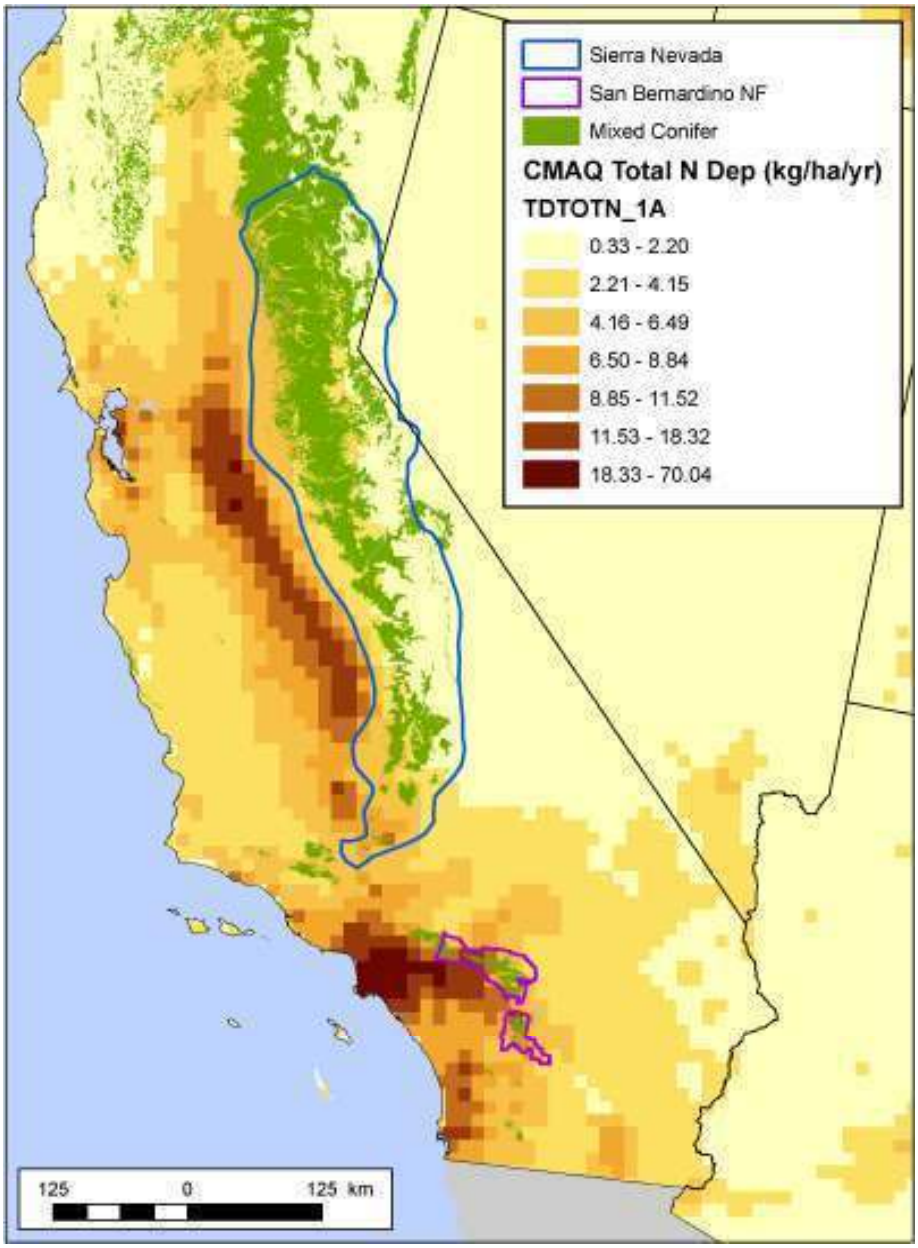

Figure 3.1-4. Mixed conifer forest range and total nitrogen deposition using CMAQ 2002 modeling results.

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 reducing the demand for belowground nutrient uptake (Fenn et al., 2000). Carbon allocation gradually shifts from root to shoot, and fine root biomass is reduced (Fenn and Bytnerowicz, 1997; U.S. EPA, 2007a). Grulke and colleagues (1998) observed a 6- to 14-fold increase in fine root mass in areas of low nitrogen deposition as compared to areas of high deposition. Medium roots also declined at high levels (Fenn et al., 2008).

At the stand level, elevated atmospheric nitrogen has been associated with increased stand density. Although other factors, such as fire suppression and ozone, contribute elevated nitrogen and can increase mortality rates (U.S. EPA, 2007a). 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 mountain range, where air pollution levels are among the highest found in the California conifer ranges studied (Minnich et al., 1995; Fenn et al., 2008).

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 health and physiology as being the result of both (i.e., 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 nitrogen deposition up to 15 times more than in areas with low deposition (Fenn et al., 2000; Grulke et al., 2008). The increased litter deposition may facilitate faster rates of microbial decomposition initially, but may decompose over the long term because

of changes in the carbon:nitrogen ratio and increasing lignin content over time (Grulke et al., 2008; U.S. EPA, 2007a). The increased litter depth may then affect subcanopy growth and stand regeneration over long periods of time.

In addition to these effects, as well as the changes in decreased fine root mass, increased needle turnover, and the associated chemostructural alterations that occur as a result, mixed conifer forests with 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. This complex model is displayed in **Figure 3.1-5** as a graphic developed by Grulke and colleagues (2008).

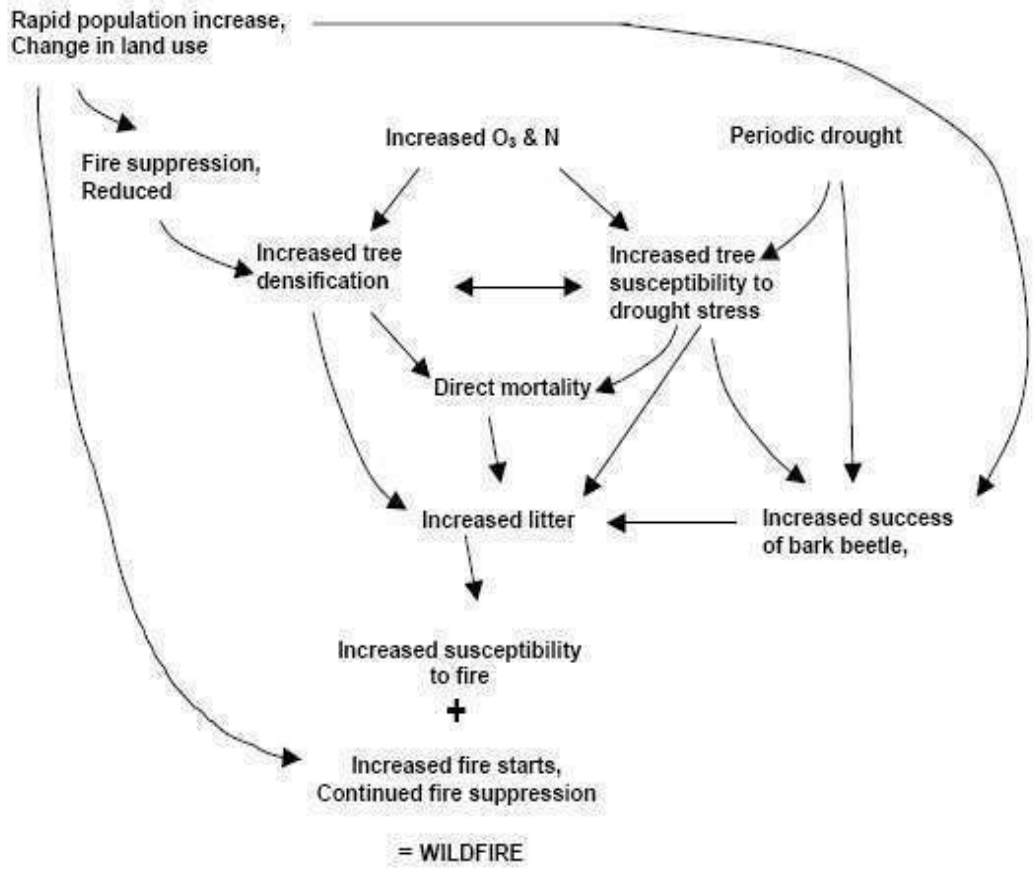

Figure 3.1-5. Conceptual model for increased susceptibility to wildfire in mixed conifer forests (Grulke et al., 2008).

3.1.2.2 Nitrogen Effects on Lichens

Lichens emerged as an indicator of nitrogen enrichment from the research on the effects of acid rain. Lichen species can be sensitive to air pollution; in particular, nitrogen deposition.

Since the 1980s, information about lichen communities has been gathered, and lichens have been used as indicators to detect changes in forest communities. Jovan (2008) depicts how lichens might be considered as sentinels in the mixed conifer forest community (**Figure 3.1-6**).

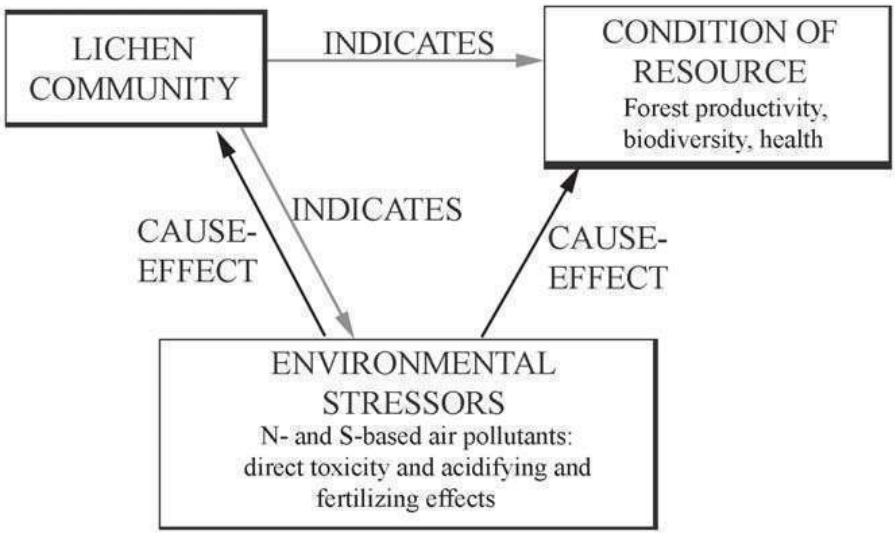

Figure 3.1-6. Importance of lichens as an indicator of ecosystem health (Jovan, 2008).

As 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 and colleagues (2008) were able to quantify the change in the lichen community, noting that for every 1 kg nitrogen per hectare per year increase, the abundance of acidophytic lichens declined by 5.6%. **Figure 3.1-7** illustrates the presence of acidophyte lichens and the total nitrogen deposition in the California ranges.

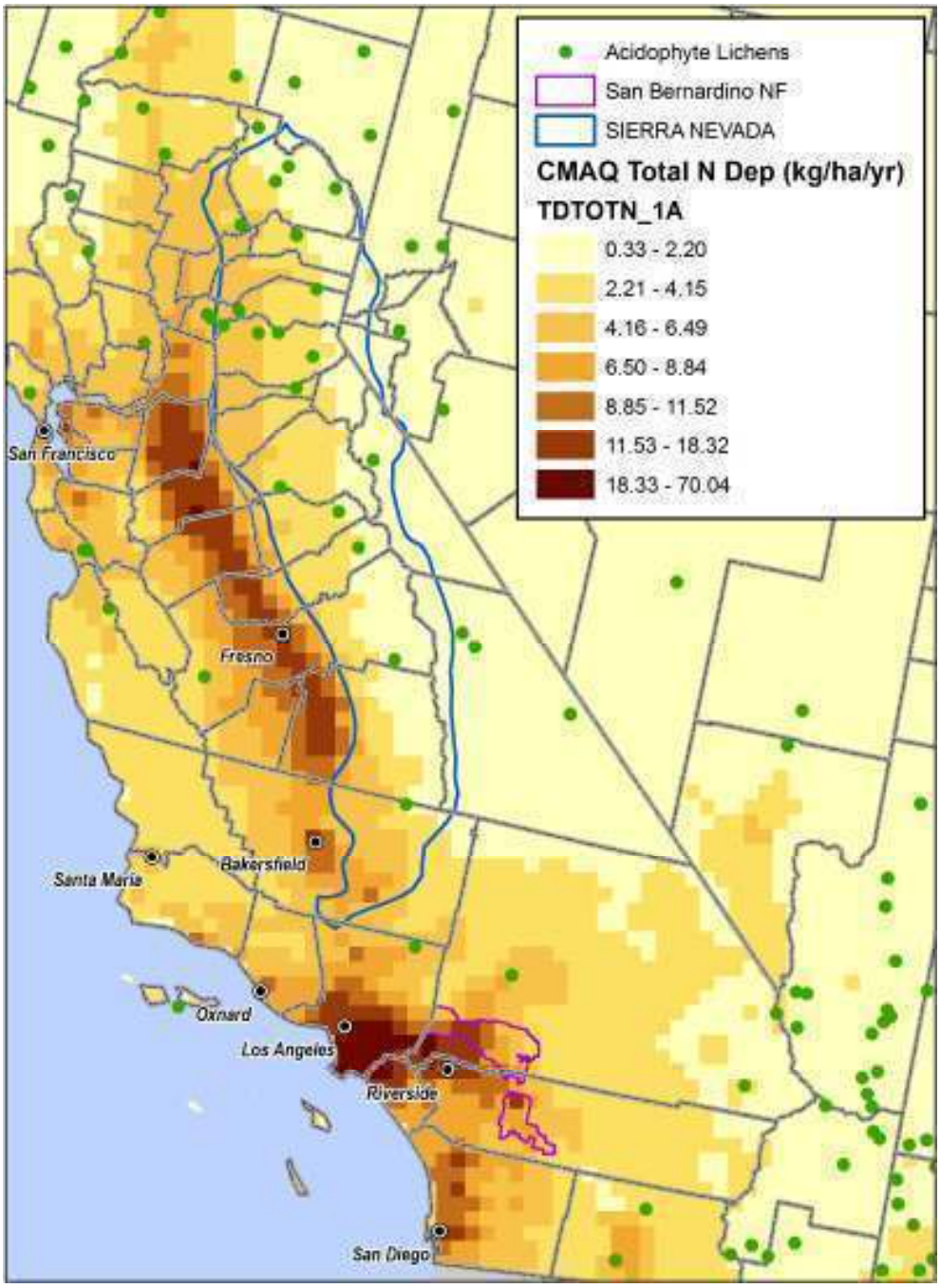

Figure 3.1-7. Presence of acidophyte lichens and the total nitrogen deposition in the California ranges.

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 mixed conifer forests, with the areas of

highest pollution levels exhibiting low species richness, decreased abundance and cover, and morphological deterioration of existing lichen (Sigal and Nash, 1983).

3.1.2.3 Nitrogen Saturation and Critical Loading Benchmarks

The established signs of nitrogen saturation have been shown within the mixed conifer ecosystem. These symptoms include the following:

- **Increased carbon and nitrogen cycling.** The foliar turnover rates and changes in microbial decomposition both suggest that carbon and nitrogen cycles have been altered as a result of elevated nitrogen. Additionally, nitrogen fluxes in San Bernardino soils are elevated when compared to conifer forests in the northern Sierra Nevada Mountains (Bytnerowicz and Fenn, 1996).
- **Decreased nitrogen uptake efficiency of plants.** Changes in root:shoot ratio demonstrate structural alterations in response to increasing available nitrogen.
- **Increased loss of forest nitrates to streamwater (NO_3 leachate).** Elevated NO_3 leachate levels are estimated to have begun in the late 1950s and have been observed from the western conifer forests in the San Bernardino mountain range since 1979 (Fenn et al., 2008). These losses are a result of high soil nitrogen driven by the combined litter, needle turnover, and throughfall nitrogen exerted in these areas (Bytnerowicz and Fenn, 1996).

Changes in root biomass and stream leachate, in addition to lichen species compositional shifts, have been used to develop benchmarks for nitrogen thresholds in the mixed conifer ecosystem. These critical loading benchmarks, or empirical loads, are designed to estimate the levels at which atmospheric nitrogen concentrations and subsequent deposition begin to affect selected components of the ecosystem, such as forest growth, health, and composition. Some benchmarks aim to estimate individual changes to an ecosystem, whereas others assess the levels at which the entire ecosystem will not be altered because of nitrogen deposition. The following sections discuss the possibility of using the mixed conifer forest as a model for benchmarking.

Fenn and colleagues (2008) established a critical loading benchmark of 17 kilograms (kg) throughfall nitrogen per hectare annually in the San Bernardino and Sierra Nevada mixed conifer ecosystems. This benchmark represents the level of nitrogen deposition at which elevated concentrations of streamwater NO_3 leachate or potential nitrogen saturation may occur. At this

deposition level, a 26% reduction 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 nitrogen deposition level. This benchmark is based on 30–60 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.

For the lichen community, Fenn and colleagues (2008) established a critical loading benchmark of 3.2 kg nitrogen per hectare per year and suggested that this level of atmospheric nitrogen deposition would result in little or no nitrogen-induced changes to the mixed conifer ecosystem. It should be noted that this level of nitrogen deposition is currently exceeded in the majority of the San Bernardino Mountains, as well as areas with urban influence in the southwestern Sierra Nevada Mountains mixed conifer stands (Fenn et al., 2008).

4. IMPLICATIONS FOR OTHER SYSTEMS

The terrestrial enrichment case study looked at the effects of atmospheric nitrogen on two ecosystem types in California. We attempted to identify places where data were available that might have implications for other systems and ecosystem services and where we might find a compelling case that shows 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 lichen 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 nitrogen deposition.** The established signs of nitrogen saturation are increased leaching of nitrates 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 efficiently use, retain, or recycle nitrogen species 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 of the California habitats discussed in this case study, a large portion of nitrogen is deposited in the dry form and remains on the foliage and soil surface until the beginning of the rainy season in the winter when nitrogen will be flushed into the soil.

In addition to the classic signs of nitrogen saturation, it is interesting to note that both CSS and the mixed conifer ecosystems had responses in epiphytic associations, as well as increased susceptibility to wildfire and invasion. Water use was also modified in these systems. The implication and inferential magnitude of these results may warrant future investigations.

5. UNCERTAINTY

5.1 COASTAL SAGE SCRUB

There are several areas of uncertainty associated with this case study on CSS.

- Although current research indicates that both nitrogen deposition and fire have contributed to the decline of CSS, the interaction between the variables and the extent of their contributions requires further research. CSS declines have been observed in the absence of fire when elevated nitrogen levels are present, and they have also been observed in the absence of elevated nitrogen due to fire. Therefore, there is still a need for quantifiable and predictive results to indicate the pressure of each variable, as well as the pressure of the combined variables (if synergism is present). Additional studies are also required to test the proposed nitrogen-fire feedback loop and the associated biogeochemical elements (e.g., changes in water availability and mycorrhizal associations) that contribute to CSS decline.
- 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. Assessing the health of CSS stands may help to identify a response curve to the factors associated with CSS decline.

- 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 slower 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, we will have a better sense of the relationship between the current distribution of CSS and atmospheric nitrogen loads. If we attempt to assess the relationship between atmospheric nitrogen loads and CSS in areas where fire threat is low, will we be able to acquire information on the condition of the habitat and species of concern.
- The last area of uncertainty is the relationship between current CSS distribution and the changing climate.
- 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, 1981a).

Figures 5.1-1 and 5.1-2, respectively, show how the primary drivers overlap with the loss of CSS over the past 30 years and fire threat and the loss of CSS and CMAQ nitrogen deposition. The extent of this loss may be useful for calculating a loss in recreational value or sense of place for ecosystem valuation. Of interest are those places where fire threat is low and CSS still exists. These are the locations where it may be possible to get a first-order look at the differences found in the condition of the CSS habitat correlated to a gradient in atmospheric nitrogen deposition.

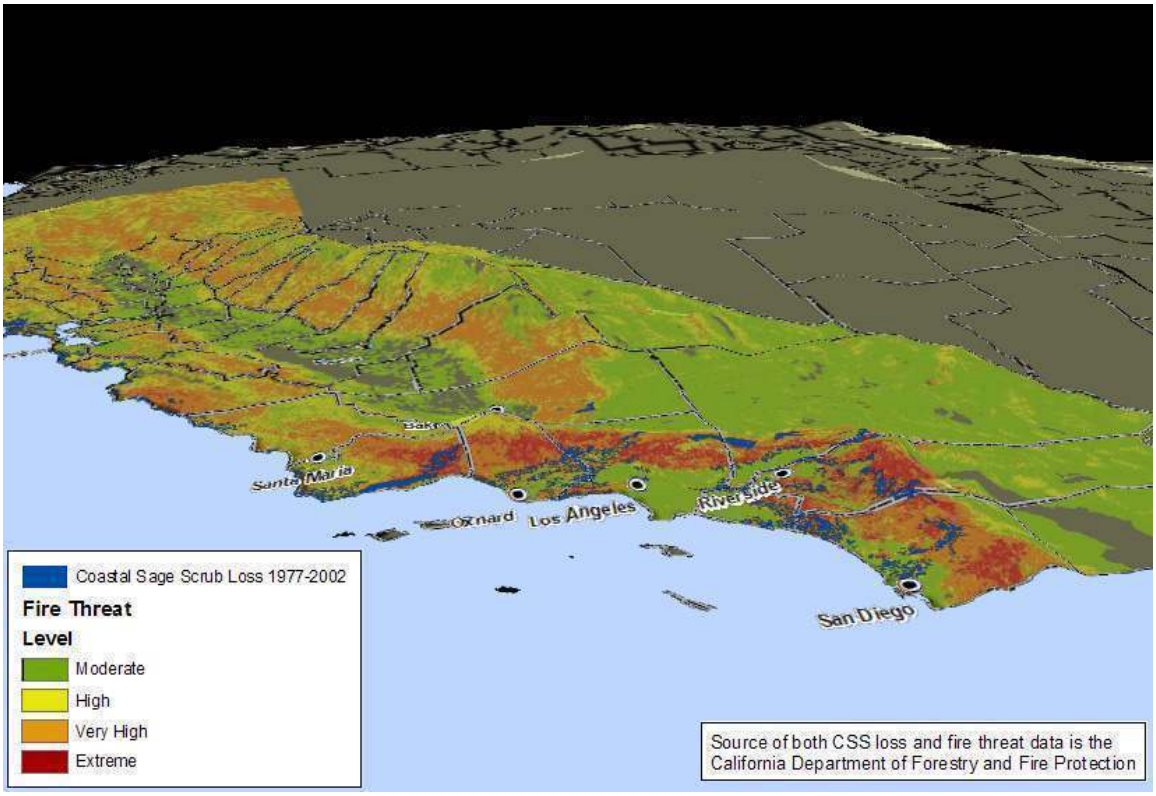

Figure 5.1-1. Relief map showing the loss of CSS over the past 30 years and fire threat.

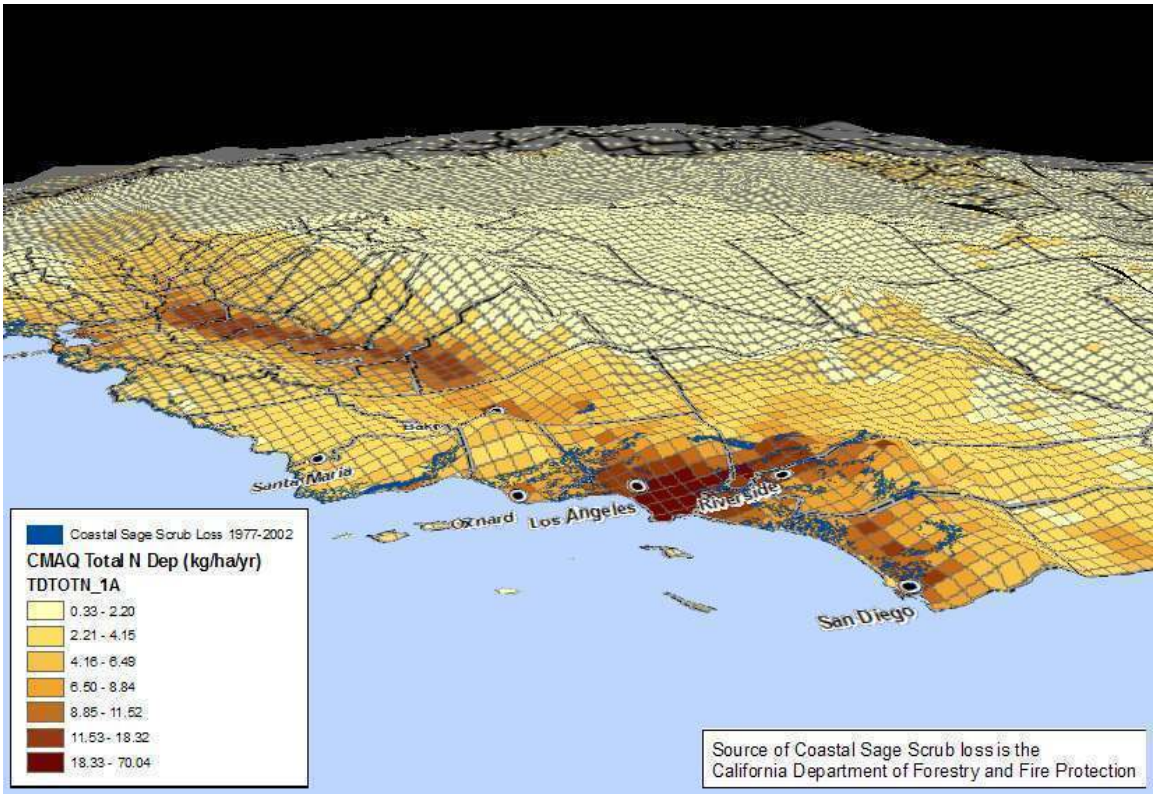

Figure 5.1-2. Relief map showing the loss of CSS and CMAQ nitrogen deposition.

An estimate of an appropriate secondary nitrogen standard or an empirical critical loading benchmark may be possible by investigating questions that may stem from the interpretation of CMAQ modeling data and the spatial extent of the CSS. Potential investigations include the following questions:

- Can we establish a longer trend using the VTM maps from the 1920s and 1930s that have recently been digitized? Can we look at such a trend on a map of development and atmospheric nitrogen deposition at certain points in time?
- When will the 4-km CMAQ data become available? With a habitat that is as fragmented as the CSS, the finer CMAQ resolution data will be more useful for spatial understanding.
- Is there information on CSS condition that can be obtained from managers of habitat reserves, especially on threatened and endangered species?
- Can we use the increased biomass production of non-native annual grasses, under certain levels of nitrogen addition, to estimate a standard or critical load (i.e., an amount of deposition that results in no decline or harm to a community) or an endpoint?
- Can we use the response of mycorrhizal species to nitrogen as a way to estimate a standard or an endpoint?
- Can we use the conceptual model to frame research questions that would lend themselves to revisiting existing research and analyzing it in a different way?

5.2 MIXED CONIFER FOREST

The currently known areas of uncertainty for mixed conifer forests are as follows:

- The long-term consequences of increased nitrogen on conifers are unclear. Although the results indicate an increased susceptibility to wildfire and disease, the long-term health of the stands and risk of cascading effects into the ecosystem require further investigation.
- The effects of ozone for both mixed conifer and lichen confound the effects of nitrogen.
- The intermingling of fire and nitrogen cycling require additional research.
- Research suggests that critical loading thresholds can decrease over time if the nitrogen threshold is exceeded for long periods of time because of decreasing nitrogen efficiencies within nitrogen-saturated ecosystems (Fenn et al., 2008). This may indicate that a sliding-

scale approach will be required when evaluating ecosystems of varying nitrogen responses.

- There remains considerable uncertainty in the potential response of soil carbon to increases in reactive nitrogen additions.

The mixed conifer forest community presents an opportunity to examine the influence of varying nitrogen deposition loads on habitat condition. Applying a common gradient of nitrogen deposition loads will allow us to investigate how lichen communities and nitrogen saturation symptoms change across the gradient. Among the questions we might ask are the following:

- Are trends data available for lichen communities over the nitrogen deposition gradient to investigate critical load benchmarks?
- Are trends data available for nitrogen saturation indicators over the nitrogen deposition gradient to establish where critical load benchmarks were exceeded?
- What is the benchmark in nitrogen deposition to preserve and maintain the health of lichen communities?
- What is the benchmark in nitrogen deposition to minimize foliar impacts on conifer stands?
- What is the benchmark in nitrogen deposition to avoid nitrate leaching out of forest floors and impacting water quality?
- Can we use the conceptual model to frame research questions that would lend themselves to revisiting existing research and analyzing it in a different way?
- What role does ozone play in conjunction with nitrogen deposition in fire hazard?
- What role does elevation play in conifer health across the nitrogen deposition gradient?
- What is the relationship of nitrogen deposition to conifer root production?
- Decomposition of litterfall is often facilitated by heterotrophic bacteria and mycorrhizae. At what rate does elevated nitrogen deposition result in increased microbial metabolism in soil?

6. CONCLUSIONS

California's CSS and mixed conifer forests on the slopes of the San Bernardino and Sierra Nevada mountains have important recreational value, protect water resources, and provide habitats for many other species. In the CSS community, there is compelling evidence that elevated nitrogen deposition is a driving force in the habitat degradation of CSS. A conceptual model was developed to help identify and parse the pressures and changes occurring within the ecosystem. In the mixed conifer forest, lichen communities and nitrogen saturation can provide a means to monitor and quantify the effects of nitrogen loadings. Both habitats provide a number of ecological services, including regulation (water), cultural and aesthetic values (recreation, natural landscape, and sense of place), and provisioning services (timber) (MEA, 2005).

6.1 COASTAL SAGE SCRUB

The CSS community represents a unique and threatened habitat that includes many threatened and endangered plants and animals; however, this community has experienced significant declines in extent and quality over the past several decades. The process by which nitrogen is driving CSS decline is still being researched, but the indication is that increased atmospheric nitrogen is an important contributor. Nitrogen deposition has been observed to affect the ecosystem through altered mycorrhizae associations, nitrogen cycling, and rates of senescence. These effects, in conjunction with other ecosystem processes and identified stressors, are the basis of the conceptual model presented in this case study. In subsequent analyses, the conceptual model will allow us to formulate some questions about the effects of nitrogen on the system and help isolate the potential mechanisms that could be used to investigate empirical critical loading in the CSS community.

6.2 MIXED CONIFER FOREST

Unlike CSS, the mixed conifer ecosystem has no critical habitat, and threatened and endangered species may currently be less common. However, the forest communities exhibit elevated NO_3^- leaching in streamwater, reduction in nitrogen-sensitive lichen species, and reduced fine-root biomass in ponderosa pine (*Pinus ponderosa).* Each of these conditions is a valuable indicator of nitrogen loading. More research, however, is required to understand the interplay of fire suppression, ozone, and nitrogen deposition, along with other variables that

result in changes to the community. There appears to be enough data from lichen study and from locations where nitrogen saturation has occurred to develop empirical critical loads for benchmarking.

The research reported in this case study shows that nitrogen deposition has altering effects that are modifying different types of valued ecosystems. With mixed conifer forests, the study shows that densification and changes in plant structure can help increase the forests' susceptibility to wildfires. Also, species such as nitrogen-sensitive lichen, species that depend on these lichen, and species that depend on older mixed conifers may be disrupted. With mixed conifer forests, the study shows that although subtle changes in complex systems are occurring due to nitrogen deposition, these changes can be measured using indicators such as nitrogen saturation and lichen to gauge the load beyond which nitrogen is no longer beneficial to a forest system and its surface waters.

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