



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



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**Policy Assessment for the Review of the Secondary
National Ambient Air Quality Standards for Oxides of
Nitrogen and Oxides of Sulfur**

**U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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This document has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication. This final document has been prepared by staff from the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency. Any opinions, findings, conclusions, or recommendations are those of the authors and do not necessarily reflect the views of the U.S. Environmental Protection Agency. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Any questions or comments concerning this document should be addressed to Richard Scheffe, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, C304-02, Research Triangle Park, North Carolina 27711 (email: scheffe.richard@epa.gov).

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EXECUTIVE SUMMARY

Introduction

This Policy Assessment has been prepared by staff in the Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards (OAQPS) in conjunction with the Agency's ongoing joint review of the secondary (welfare-based) national ambient air quality standards (NAAQS) for oxides of nitrogen and sulfur. This Policy Assessment evaluates the policy implications of the key scientific information contained in the Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur-Ecological Criteria, prepared by EPA's National Center for Environmental Assessment (NCEA), results from the analyses contained in the Risk and Exposure Assessment (REA) for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur, as well as additional staff analyses conducted for and presented in this document. It presents staff conclusions regarding the adequacy of the current NO₂ and SO₂ secondary standards as well as alternative standards for consideration in this review.

This Policy Assessment is intended to help "bridge the gap" between the relevant scientific and technical information and the judgments required of the EPA Administrator in determining whether, and if so, how, it is appropriate to revise the secondary NAAQS for oxides of nitrogen and sulfur. This Policy Assessment considers the available scientific evidence and quantitative risk-based analyses, together with related limitations and uncertainties, and focuses on the basic elements of air quality standards: indicator, averaging time, form, and level. These elements, which serve to define each standard, must be considered collectively in evaluating the public welfare protection afforded by the standards.

Scope

In conducting this periodic review of the secondary NAAQS for oxides of nitrogen and sulfur, EPA has decided to jointly assess the scientific information, associated risks, and standards because oxides of nitrogen and sulfur in the ambient air, and their associated transformation products, such as deposited nitrogen and sulfur, are linked from an atmospheric chemistry perspective, as well as jointly contributing to ecological effects.

For this Policy Assessment, we have chosen to focus much of our attention on effects in sensitive aquatic ecosystems caused by acidifying deposition of nitrogen and sulfur, which is a transformation product of oxides of nitrogen and sulfur in the ambient air. We have a high degree of confidence in the linkages between atmospheric oxides of nitrogen and sulfur, associated deposition of nitrogen and sulfur, and deposition-related aquatic acidification effects. Our objective in this Policy Assessment is to develop a framework for a multi-pollutant, multimedia standard that is ecologically relevant and reflects the combined impacts of these two pollutants as they deposit to sensitive aquatic ecosystems.

In so doing, we recognize that a standard developed specifically to address aquatic acidification would not likely provide targeted protection against other deposition-related ecological effects, including effects related to terrestrial acidification and nutrient enrichment effects in sensitive terrestrial and aquatic ecosystems. Nonetheless, it is likely that some additional protection from

these other effects would result from reductions in atmospheric oxides of nitrogen and sulfur that would likely occur in response to an ecologically relevant aquatic acidification standard.

In this Policy Assessment we use the term *total reactive oxidized nitrogen*, NO_y, as used by the scientific community, to represent the complete set of oxidized nitrogen compounds. The major gaseous and particulate constituents of NO_y include nitric oxide (NO), nitrogen dioxide (NO₂), nitric acid (HNO₃), peroxyacetyl nitrate (PAN), nitrous acid (HONO), organic nitrates, and particulate nitrate (NO₃). In contrast, the term NO_x more narrowly refers to the sum of NO₂ and NO. *Total oxides of sulfur* include both gaseous substances [e.g., sulfur dioxide (SO₂), sulfur monoxide (SO), sulfur trioxide (SO₃), thiosulfate (S₂O₃), and heptoxide (S₂O₇)], as well as particulate species, such as ammonium sulfate [(NH₄)₂SO₄]. Throughout this document, we focus more narrowly on SO_x, defined as the sum of SO₂ and particulate sulfate (SO₄), which represent virtually all of the oxidized sulfur mass in the atmosphere.

Deposition-related Ecological Effects Associated with Oxides of Nitrogen and Sulfur

Deposition-related ecological effects are broadly categorized into those related to acidification and nutrient enrichment. Acidification occurs in both aquatic and terrestrial ecosystems, with most aquatic effects occurring in freshwater lakes and streams. Nutrient enrichment also occurs in both aquatic and terrestrial ecosystems; however, the types and prevalence of nutrient enrichment effects vary between freshwater and estuarine aquatic ecosystems.

In the acidification process, geochemical components of terrestrial and freshwater aquatic ecosystems are altered in a way that leads to effects on biological organisms. Because oxides of nitrogen and sulfur deposited to terrestrial ecosystems often move through the soil and eventually leach into adjacent water bodies, deposition to terrestrial ecosystems is also a cause of acidification in aquatic ecosystems.

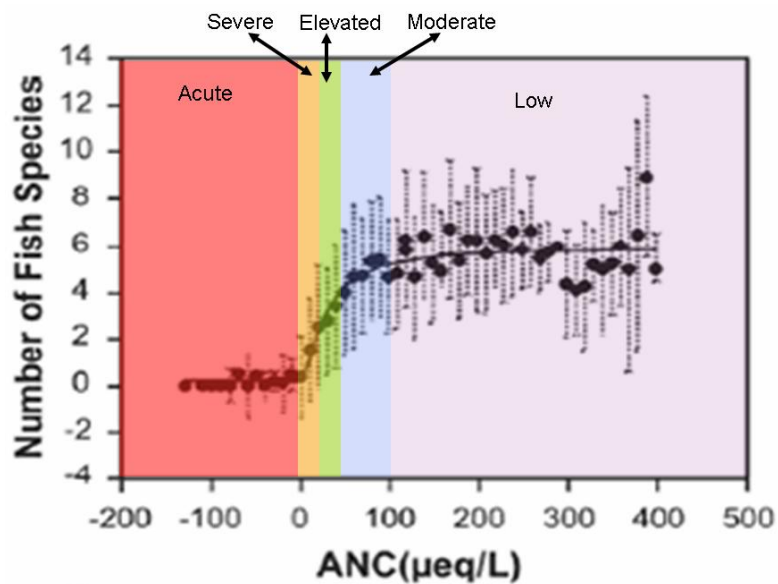
The scientific evidence is sufficient to infer a strong causal relationship between acidifying deposition and effects on biogeochemical processes and biota in aquatic ecosystems, and between acidifying deposition and changes in biogeochemistry in terrestrial ecosystems. Acidifying deposition is observed to alter sulfate and nitrate concentrations in surface waters, acid neutralizing capacity (ANC), inorganic aluminum, and surface water pH. These changes can result in the loss of acid-sensitive biological species such as salmonids and disrupt food web dynamics causing alteration to the diet, breeding distribution and reproduction of certain species of bird, such as goldeneye ducks and loons. Acidification in terrestrial ecosystems has been shown to cause decreased growth and increased susceptibility to disease and injury in sensitive tree species, including red spruce and sugar maple.

Principal factors governing the sensitivity of terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition include geology, plant uptake of nitrogen, soil depth, and elevation. Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Other factors that contribute to the sensitivity of soils and surface waters to acidifying deposition include topography, soil chemistry, land use, and hydrologic flowpath. Chronic as well as episodic acidification tends to occur primarily at relatively high elevations in areas that have base-poor bedrock, high relief, and shallow soils.

With regard to *aquatic acidification*, based on analyses of surface water data from freshwater ecosystem surveys and monitoring, the most sensitive lakes and streams are contained in New

England, the Adirondack Mountains, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), the mountainous West, and the Upper Midwest.

ANC is the most widely used indicator of acid sensitivity and has been found in various studies to be the best single indicator of the biological response and health of aquatic communities in acid sensitive systems. Annual or multi-year average ANC is a good overall indicator of sensitivity, capturing the ability of an ecosystem to withstand chronic acidification as well as episodic events such as spring melting that can lower ANC over shorter time spans. Biota are generally not harmed when annual average ANC levels are > 100 microequivalents per liter ($\mu\text{eq/L}$). At annual average ANC levels between 100 and $50 \mu\text{eq/L}$, the fitness of sensitive species (e.g., brook trout, zooplankton) begins to decline. When annual average ANC is $< 50 \mu\text{eq/L}$, negative effects on aquatic biota are observed, including large reductions in diversity of fish species, and declines in health of fish populations, affecting reproductive ability and fitness. Annual average ANC levels below $0 \mu\text{eq/L}$ are generally associated with complete loss of fish species and other biota that are sensitive to acidification. An example of the relationship between ANC level and aquatic effects based on lakes in the Adirondacks is illustrated in the following figure.



Recent studies indicate that acidification of lakes and streams can result in significant loss in economic value, which is one indicator of adversity associated with loss of ecosystem services. A 2006 study of New York residents found that they are willing to pay between \$300 and \$800 million annually for the equivalent of improving lakes in the Adirondacks region to an ANC level of $50 \mu\text{eq/L}$. Several states have set goals for improving the acid status of lakes and streams, generally targeting ANC in the range of 50 to $60 \mu\text{eq/L}$, and have engaged in costly activities to decrease acidification.

With regard to *terrestrial acidification*, forests of 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 and mountainous regions in the West are the regions most sensitive to acidifying deposition. The

health of at least a portion of the sugar maple and red spruce growing in the United States may have been compromised by acidifying total nitrogen and sulfur deposition in recent years. A commonly used indicator of terrestrial acidification is the base cation-to-aluminum ratio, Bc/Al. Many locations in sensitive areas of the U.S. have Bc/Al levels below benchmark levels we have classified as providing low to intermediate levels of protection to tree health. At a Bc/Al ratio of 1.2 (intermediate level of protection), red spruce growth can be reduced by 20 percent. At a Bc/Al ratio of 0.6 (low level of protection), sugar maple growth can be reduced by 20 percent. While not defining whether a 20 percent reduction in growth can be considered significant, existing economic studies suggest that avoiding significant declines in the health of spruce and sugar maple forests may be worth billions of dollars to residents of the Eastern U.S.

With regard to *nutrient enrichment*, the numerous ecosystem types that occur across the U.S. have a broad range of sensitivity to nitrogen deposition. Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability. Change in the availability of one important nutrient, such as nitrogen, may result in imbalances in ecosystems, with effects on ecosystem processes, structure and function. In certain nitrogen-limited ecosystems, including many ecosystems managed for commercial production, nitrogen deposition can result in beneficial increases in productivity. Nutrient enrichment effects from deposition of oxides of nitrogen are difficult to disentangle from overall effects of nitrogen enrichment. This is caused by two factors: the inputs of reduced nitrogen from deposition and, in estuarine ecosystems, a large fraction of nitrogen inputs from non-atmospheric sources.

Adequacy of the Existing NO₂ and SO₂ Standards

Current NO₂ and SO₂ secondary standards are designed to protect against direct exposure of vegetation to ambient concentrations of oxides of nitrogen and sulfur. All areas of the U.S. currently meet the existing NO₂ and SO₂ secondary standards. The NO₂ secondary standard is 0.053 parts per million (ppm), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO₂ concentrations. The SO₂ secondary standard is a 3-hour average of 0.5 ppm, not to be exceeded more than once per year. Based on currently available information, staff concludes that the current secondary standards serve to protect vegetation from direct damage associated with exposures to gaseous SO₂ and NO₂ and thus consideration should be given to retaining the current standards for that purpose.

With regard to *aquatic acidification*, recent data indicate that in the Adirondacks and Shenandoah areas, rates of acidifying deposition of oxides of nitrogen and sulfur are still well above pre-acidification (1860) conditions. Forty-four percent of Adirondack lakes evaluated exceed the critical load for an ANC of 50 µeq/L, and in these lakes recreationally important fish species such as trout are missing due to acidification. In the Shenandoah area, 85 percent of streams evaluated exceed the critical load for an ANC of 50 µeq/L, resulting in losses in fitness in species such as the Blacknose Dace.

With regard to *terrestrial acidification*, the REA evaluated a small number of sensitive areas as case studies. In the sugar maple case study area (Kane Experimental Forest, Pennsylvania), recent (2002) deposition levels are associated with a Bc/Al ratio below 1.2, indicating the potential for a greater than 20 percent reduction in growth. In the red spruce case study area (Hubbard Brook Experimental Forest, New Hampshire), recent deposition levels are associated with a Bc/Al ratio slightly above 1.2, indicating slightly less potential for significant reductions in growth. When the methodology was extended to a 27-state region, the calculated Bc/Al ratio

fell below 1.2 in 12% of the sugar maple plots and 5% of the red spruce plots; however, results from individual states ranged from 0 to 67% of the plots for sugar maple and 0 to 100% of the plots for red spruce fell below the Bc/Al ratio of 1.2.

Available ecological indicators for *estuarine nutrient enrichment* are not sufficiently sensitive to changes in atmospheric nitrogen oxides to be of use in assessing the adequacy of the current NO₂ secondary standard. Atmospheric nitrogen oxides can be an important contributor of nitrogen to estuarine nutrient enrichment, but additional analysis would be required to develop an appropriate indicator for assessing levels of protection from nutrient enrichment effects in estuaries related to deposition of nitrogen oxides.

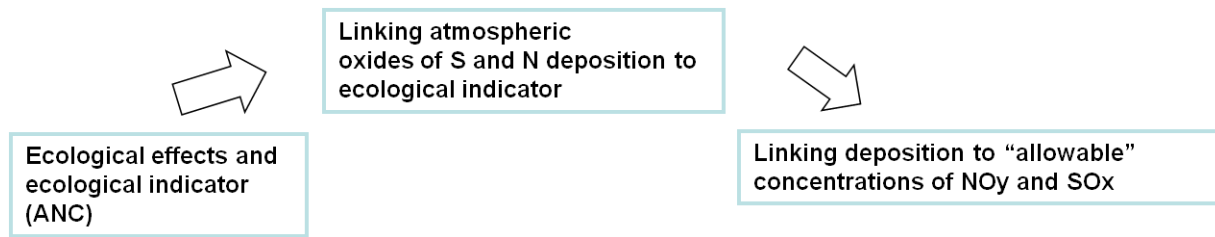
Nitrogen deposition can alter species composition and cause *eutrophication in freshwater systems*. In the Rocky Mountains, for example, deposition loads of 1.5 to 2 kg/ha/yr, which are within the range associated with ambient nitrogen oxide levels meeting the current standard, are known to cause changes in species composition in diatom communities indicating impaired water quality.

With regard to *terrestrial nutrient enrichment*, most terrestrial ecosystems in the U.S. are nitrogen-limited, and therefore they are sensitive to perturbation caused by nitrogen additions. Under recent conditions, nearly all of the known sensitive mixed conifer forest ecosystems receive total nitrogen deposition levels above 3.1 N kg/ha/yr, which is the ecological benchmark for changes in lichen species. Lichens are sentinels for broader ecosystem change in terrestrial systems. Some portions of the Sierra Nevadas receive total nitrogen deposition levels above 5.2 N kg/ha/yr, which is the ecological benchmark for shifts in the dominant species of lichen from acidophytic to tolerant species. In addition, in Coastal Sage Scrub ecosystems in California, nitrogen deposition exceeds the 3.3 N kg/ha/yr benchmark above which nitrogen is no longer a limiting nutrient, leading to potential alterations in ecosystem composition.

Based on the above considerations, staff concludes that currently available scientific evidence and assessments clearly call into question the adequacy of the current standards with regard to deposition-related effects on sensitive aquatic and terrestrial ecosystems, including acidification and nutrient enrichment. Further, staff recognizes that the elements of the current standards -- indicator, averaging time, level and form -- are not ecologically relevant, and are thus not appropriate for standards designed to provide such protection. Thus, staff concludes that consideration should be given to establishing a new ecologically relevant multi-pollutant, multimedia standard to provide appropriate protection from deposition-related ecological effects of oxides of nitrogen and sulfur on sensitive ecosystems, with a focus on protecting against adverse effects associated with acidifying deposition in sensitive aquatic ecosystems.

Design of an Ecologically Relevant Standard for Aquatic Acidification

The graphic below depicts the framework within which we are considering the structure of an ecologically relevant secondary standard for aquatic acidification. This conceptual diagram illustrates how an ecological indicator is linked to concentrations of ambient air indicators of oxides of nitrogen and sulfur through deposition.



This Policy Assessment is organized around this conceptual framework. It presents our current understanding of the ecological and atmospheric factors that modify the impacts of deposited oxides of nitrogen and sulfur on sensitive ecosystems. Applying this framework has resulted in the development of a new ecologically relevant standard that incorporates multi-pollutant and multimedia attributes in linking ambient air indicators of oxides of nitrogen and sulfur to an ecological indicator through atmospheric deposition. There are three main components of the conceptual design of the standard: (1) linkage between ecological indicators and ecological effects, (2) linkage between an ecological indicator and atmospheric deposition, and (3) linkage between deposition and ambient air indicators.

In this Policy Assessment, the focus is on developing a standard that protects against ecological effects associated with acidifying deposition of oxides of nitrogen and sulfur in aquatic ecosystems, recognizing that both oxides of nitrogen and sulfur are major contributors to aquatic acidification and that acidification of aquatic ecosystems is best characterized and understood in terms of the combined rather than individual effects of oxides of nitrogen and sulfur. In addition, there is a well developed body of scientific evidence linking the deposition of ambient oxides of nitrogen and sulfur to acidification in sensitive aquatic ecosystems. While we conclude that the available information and assessments are only sufficient to support the development of a national standard specifically to address aquatic acidification at this time, we recognize that this general conceptual framework could likely be applied to a broader set of deposition-related effects in the future.

In focusing on the effects of acidifying deposition on aquatic ecosystems, with respect to *linking ecological indicators to adverse effects* of fish mortality and decreased species diversity, staff concludes that ANC is the most appropriate ecological indicator to consider. ANC is the most widely used chemical indicator of acid sensitivity in aquatic ecosystems and has been found through numerous studies to be the best single indicator of the biological response and health of aquatic communities in acid sensitive ecosystems. Furthermore, ANC can be directly linked to both underlying water chemistry, e.g. pH and aluminum, and to biological impairment, specifically fish mortality and the number of fish species in a water body.

With respect to *linking atmospheric deposition to the ecological indicator*, staff concludes that steady state ecosystem acidification modeling that calculates critical loads is the appropriate methodology to link atmospheric deposition with ANC. A critical load for acidity is the amount of acidifying deposition beyond which a water body cannot achieve and sustain a target ANC level. Critical loads reflect the relative sensitivity to acidification of a water body within a distribution of water bodies.

With respect to *linking deposition to ambient air concentrations*, staff has developed the concept of transference ratios, which are the ratio of deposition to ambient air concentration, as an

appropriate approach to use in linking deposition to ambient air concentrations. Representative transference ratios that are averaged annually and over a specified spatial area have been developed for oxides of nitrogen and oxides of sulfur based on simulations using EPA's Community Multiscale Air Quality (CMAQ) model.

Staff Consideration of Alternative Standards for Aquatic Acidification

In applying the framework that reflects these three fundamental linkages, staff has developed an ecologically relevant standard for aquatic acidification in terms of the basic elements that together define a NAAQS: ambient air indicator, form, averaging time, and level.

With regard to *ambient air indicators*, staff concludes that consideration should be given to using total reactive oxidized nitrogen, NO_y , as the ambient air indicator for oxides of nitrogen and the sum of gaseous sulfur dioxide (SO_2) and particulate sulfate (SO_4), referred to in this assessment as SO_x , as the ambient air indicator for oxides of sulfur,

With regard to the *form* of such a multi-pollutant, deposition-related standard, staff concludes that consideration should be given to an ecologically relevant form that characterizes the relationships between the ambient air indicators for oxides of nitrogen and sulfur, the related deposition of nitrogen and sulfur, and the associated aquatic acidification effects in terms of the ecological indicator ANC.

Staff has developed such a form, termed an aquatic acidification index (AAI), using a simple equation to calculate an AAI value in terms of the ambient air indicators NO_y and SO_x and the relevant ecological and atmospheric factors that modify the relationships between the ambient air indicators and ANC. This AAI reflects the difference between the natural acid neutralizing capability of a region and acidifying deposition inputs from NO_y and SO_x in the ambient air. Recognizing the spatial variability of such factors across the U.S., we conclude it is appropriate to divide the country into ecologically relevant regions, characterized as acid sensitive or relatively non-acid sensitive, and specify the value of each of the factors in the AAI equation for each such region.

With regard to approaches to defining such ecologically relevant regions, staff concludes that consideration should be given to using Omernik Ecoregions, level III, as the appropriate set of regions over which to define the AAI. There are 84 such level III ecoregions that cover the continental U.S. This set of ecoregions is based on grouping a variety of vegetation, geological, and hydrological attributes that are directly relevant to aquatic acidification assessments and that allow for a practical application of an aquatic acidification standard on a national scale. The figure below illustrates the Omernik ecoregions with the level III delineations defined by the different colored areas within each level II group.

- (a) F1 reflects a relative measure of an ecosystem's ability to neutralize acidifying deposition. The value of F1 for each ecoregion would be based on a representative critical load for the ecoregion associated with a single national target ANC level, as well as a representative runoff rate. The representative runoff rate, which is also used in specifying values for the other factors, would be the median value of the distributions of runoff rates within the ecoregion. The representative critical load would be derived from a distribution of critical loads calculated for each water body in the ecoregion for which sufficient water quality and hydrology data are available. The representative critical load would be defined by selecting a specific percentile of the distribution.

In identifying a range of percentiles that are appropriate to consider for this purpose, we have considered regions characterized as acid sensitive separately from regions characterized as relatively non-acid sensitive. For acid sensitive regions, we conclude that consideration should be given to selecting a percentile value from within the range of the 70th to the 90th percentile. The lower end of this range was selected to be appreciably above the median value so as to ensure that the critical load would be representative of the population of relatively more acid sensitive water bodies within the region, while the upper end was selected to avoid the use of a critical load from the extreme tail of the distribution which is subject to a high degree of variability and potential outliers. For relatively non-acid sensitive regions, we conclude that consideration should be given to selecting the 50th percentile to best represent the distribution of water bodies within such a region, or alternatively to using the median critical load of all relatively non-acid sensitive areas, recognizing that such areas are far less frequently evaluated than acid sensitive areas. Using either of these approaches would avoid characterizing a generally non-acid sensitive region with a critical load that is representative of relatively acid sensitive water bodies that may exist within a generally non-acid sensitive region.

- (b) F2 reflects the deposition of reduced nitrogen. Consideration should be given to specifying the value of F2 for each region based on the averaged modeled value across the region, using national CMAQ modeling that has been conducted by EPA. Consideration could also be given to alternative approaches to specifying this value, such as allowance for the use of air quality modeling conducted by States using more refined model inputs.
- (c) F3 and F4 reflect transference ratios that convert ambient air concentrations of NO_y and SO_x, respectively, into related deposition of nitrogen and sulfur. Consideration should be given to specifying the values for F3 and F4 for each region based on CMAQ modeling results averaged across the region. We conclude that specifying the values for the transference ratios based on CMAQ modeling results alone is preferred to an alternative approach that combines CMAQ model estimates with observational data.
- (d) The terms [NO_y] and [SO_x] reflect ambient air concentrations measured at monitoring sites within each region.

With regard to *averaging time*, staff concludes that consideration should be given to averaging calculated annual AAI values over 3 to 5 years to provide reasonable stability in the resulting index value, in light of the relatively high degree of interannual variability expected in an index that is strongly related to the amount and pattern of precipitation that occurs within a region from year to year.

With regard to the *level* of a standard based on the above indicators, alternative forms, and averaging times, staff concludes that consideration should be given to a level within the range of 20 to 75 $\mu\text{eq/L}$. In reaching this conclusion, staff has considered the available information that links specific ANC levels to various types of acidification-related effects, and the uncertainties inherent in such linkages, and the severity of such effects, in sensitive ecosystems, as well as the extent to which such effects could reasonably be judged to be important from a public welfare perspective. This range also reflects consideration of the extent to which such a standard would protect against not only long-term but also episodic acidification, as well as the time lag in ecosystem response to changes in deposition that may result from such a standard. Relatively more protection from both long-term and episodic acidification would be provided by a standard in the mid- to upper part of this range, which would also accelerate the time frame in which the target ANC level would likely be reached in some sensitive ecosystems. This range also encompasses target ANC values that have been established by various States and regional and international organizations to protect against acidification of aquatic ecosystems.

Based on the evidence and assessments in the ISA and REA, we conclude that a target ANC value of 20 $\mu\text{eq/L}$ is a reasonable lower end of this range, so as to protect against chronic acidification-related adverse impacts on fish populations which have been characterized as severe at ANC values below this level. Further, we conclude that a target ANC value of 75 $\mu\text{eq/L}$ is a reasonable upper end of this range in recognition that the potential for additional protection at higher ANC values is substantially more uncertain in light of evidence that acidification-related effects are far less sensitive to increases in ANC above this value.

As defined above, an aquatic acidification standard would be interpreted as follows: the standard would be met at a monitoring site when the measured annual-average concentrations of NO_y and SO_x are such that the value of the annual AAI, averaged over 3 to 5 years, is equal to or greater than the level of the standard, when using the region-specific values of factors F1 through F4 for the ecoregion in which the monitor is located.

TABLE OF CONTENTS

List of Tables	v
List of Figures	vi
List of Acronyms/Abbreviations	xi
List of Key Terms	xiv
1 INTRODUCTION	1-1
1.1 Purpose.....	1-1
1.2 Background.....	1-2
1.2.1 Legislative Requirements.....	1-2
1.2.2 History of Reviews of NAAQS for Nitrogen Oxides and Sulfur Oxides ..	1-3
1.2.3 History of Related Assessments and Agency Actions	1-6
1.3 Scope of Current Review	1-9
1.4 Conceptual Framework for Deposition-Related Standards	1-11
1.5 Organization of This Document.....	1-15
1.6 References.....	1-17
2 CHARACTERIZING EMISSIONS, AIR QUALITY, DEPOSITION AND WATER QUALITY	2-1
2.1 Sources of Nitrogen and Sulfur.....	2-6
2.1.1 NO _x Emissions	2-6
2.1.2 NH ₃ Emissions	2-9
2.1.3 SO _x Emissions.....	2-10
2.2 Ambient Air Characterization.....	4-14
2.2.1 Air monitoring networks.....	2-16
2.2.2 Overview of CMAQ	2-24
2.2.3 Overview of air quality using modeled and observed data.....	2-27
2.3 Characterizing Deposition Through Monitoring and Models.....	2-34
2.3.1 Current patterns of dry and wet deposition.....	2-36
2.3.2 Characterizing deposition through CMAQ.....	2-37
2.3.3 Relationships between patterns of ambient concentrations and deposition	2-40
2.3.4 Monitoring considerations	2-41
2.4 Characterizing Freshwater Aquatic System Chemistry Using Models and Measurements	2-56
2.4.1 Water chemistry basics	2-56
2.4.2 Bedrock, soil and vegetation processes relevant aquatic acidification	2-65
2.4.3 Biogeochemical ecosystem models used to estimate water quality.....	2-69
2.4.4 Water quality network.....	2-77
2.5 Trends	2-82
2.5.1 Emissions	2-83
2.5.2 Air quality and deposition.....	2-85
2.5.3 Water quality.....	2-90
2.6 References.....	2-96

3	KNOWN OR ANTICIPATED ECOLOGICAL EFFECTS	3-1
3.1	Acidification: Evidence Of Effects on Structure and Function of Terrestrial and Freshwater Ecosystems	3-2
	3.1.1 Nature of acidification-related ecosystem responses	3-3
	3.1.2 Ecosystem sensitivity to acidification.....	3-12
	3.1.3 Magnitude of ecosystem responses to acidifying deposition.....	3-12
	3.1.4 Key uncertainties associated with acidification.....	3-17
3.2	Nitrogen Enrichment: Evidence of Effects on Structure and Function of Terrestrial and Freshwater Ecosystems	3-19
	3.2.1 Nature of nutrient enrichment-related ecosystem responses	3-20
	3.2.2 Ecosystem sensitivity to nutrient enrichment	3-22
	3.2.3 Magnitude of ecosystem responses.....	3-24
	3.2.4 Key uncertainties associated with nutrient enrichment	3-31
3.3	Ecological Effects Associated With Gas-Phase Oxides of Nitrogen and Sulfur.....	3-32
	3.3.1 Nature of ecosystem responses to gas-phase nitrogen and sulfur.....	3-32
	3.3.2 Ecosystem sensitivity.....	3-33
	3.3.3 Magnitude of ecosystem responses to gas-phase effects of oxides of nitrogen and sulfur	3-34
3.4	Summary	3-34
3.5	References.....	3-36
4	CONSIDERATIONS OF ADVERSITY TO PUBLIC WELFARE	4-1
4.1	Introduction.....	4-1
	4.1.1 Benchmarks from Other EPA Programs.....	4-2
	4.1.2 Other Federal Agencies and the European Union.....	4-7
4.2	Ecosystem Services and Adversity to Public Welfare.....	4-10
4.3	Applying Economic Valuation to Ecosystem Services	4-18
	4.3.1 Economics as a Framework to Illustrate Changes in Public Welfare.....	4-18
	4.3.2 The Role of Economics in Defining Adversity.....	4-20
	4.3.3 Collective Action as an Indicator of Adversity.....	4-21
4.4	Effects of Acidification and Nutrient Enrichment on Ecosystem Services	4-25
	4.4.1 Aquatic Acidification.....	4-26
	4.4.2 Value of Current Ecosystem Service Impairments Due to Aquatic Acidification.....	4-28
	4.4.3 Terrestrial Acidification.....	4-34
	4.4.4 Value of Current Ecosystem Service Impairments Due to Terrestrial Acidification.....	4-39
	4.4.5 Aquatic Nutrient Enrichment.....	4-40
	4.4.6 Value of Current Ecosystem Service Impairments Due to Aquatic Nutrient Enrichment.....	4-43
	4.4.7 Terrestrial Nutrient Enrichment.....	4-44
4.5	References.....	4-48

5	CO-PROTECTION FOR OTHER EFFECTS POTENTIALLY AFFORDED BY AN AQUATIC ACIDIFICATION STANDARD	5-1
5.1	Potential Co-Protection For Terrestrial Acidification.....	5-1
5.2	Potential Co-Protection For Terrestrial Nutrient Enrichment.....	5-4
5.3	Potential Co-Protection For Aquatic Nutrient Enrichment.....	5-6
5.3	References.....	5-7
6	ADDRESSING THE ADEQUACY OF THE CURRENT STANDARDS	6-1
6.1	Appropriateness of the Current Standard.....	6-1
6.2	Structures of the Current Oxides Of Nitrogen And Sulfur Secondary Standards and Relevant Ecological Indicators of Public Welfare Effects.....	6-3
6.3	Adverse Effects on the Public Welfare Occurring under Current Air Quality Conditions for NO ₂ and SO ₂	6-9
	6.3.1 Acidification in sensitive aquatic and terrestrial ecosystems	6-11
	6.3.2 Nutrient enrichment effects in sensitive aquatic and terrestrial ecosystems.....	6-16
	6.3.3 Other Ecological Effects Associated with the Deposition of Atmospheric Oxides Of Nitrogen and/or Sulfur	6-20
6.4	References.....	6-22
7	CONSIDERATION OF ALTERNATIVE STANDARDS FOR AQUATIC ACIDIFICATION	7-1
7.1	Indicators.....	7-3
	7.1.1 Ambient air indicators for oxides of sulfur.....	7-4
	7.1.2 Ambient air indicators for oxides of nitrogen.....	7-4
	7.1.3 Monitoring Considerations	7-7
7.2	Form.....	7-8
	7.2.1 Ecological indicator	7-10
	7.2.2 Linking ANC to deposition.....	7-17
	7.2.3 Linking deposition to allowable concentrations	7-21
	7.2.4 Completing the link from ecological indicator to ambient air indicators	7-26
	7.2.5 Spatial Aggregation	7-29
7.3	Averaging Time	7-42
7.4	Level	7-44
7.5	Considerations associated with alternative standards.....	7-53
7.6	Summary of System Uncertainties.....	7-64
	7.6.1 Overview.....	7-64
	7.6.2 Summary of results and conclusions.....	7-66
7.7	Summary of Staff Conclusions on Secondary Standards for Oxides of Nitrogen and Sulfur.....	7-75
7.8	References.....	7-80

APPENDICES

Appendix A	Analysis of Critical Loads, Comparing Aquatic and Terrestrial Acidification
Appendix B	Methodologies and Assumptions Used In Steady State Ecosystem Modeling
Appendix C	Ecoregions, Level III: Description and Summary of Environmental Conditions
Appendix D	Maps and Calculation Procedures for Alternative Standards
Appendix E	Derivation To Use Measured Total Nitrate As A Surrogate for NO _y
Appendix F	Evaluation of Variability, Sensitivity And Uncertainty In The Acidification Index
Appendix G	Cumulative Uncertainty Analysis

List of Tables

Table 2 -1	Description of parameters, units and conventions	2-4
Table 2-2	Annual National NO _x Emissions across Major Source Categories in 2002	2-7
Table 2-3a	Annual NO _x Emissions across Major Source Categories in 2002 for the Eastern United States	2-7
Table 2-3b	Annual NO _x Emissions across Major Source Categories in 2002 for the Western United States.....	2-8
Table 2-4	Annual National SO ₂ Emissions across Major Source Categories in 2002.....	2-12
Table 2-5a	Annual SO ₂ Emissions across Major Source Categories in 2002 for the Eastern United States	2-12
Table 2-5b	Annual SO ₂ Emissions across Major Source Categories in 2002 for the Western United States.....	2-13
Table 2-6	Summary of Monitoring Networks.....	2-17
Table 2-7	Geographic elements of domains used in RFS2 modeling.....	2-26
Table 2-8	Summary several commonly used acidification models.....	2-71
Table 2-9	Summary of data sources considered for the evaluation of national ANC.....	2-78
Table 2-10	Characteristics of TIME/LTM Sites	2-80
Table 2-11	Period 1 Emissions Density and Period 1-to-Period 3 Relative Changes (%) in Oxidized Sulfur and Nitrogen Emissions, Atmospheric Concentration, and Dry, Wet, and Total Deposition	2-85
Table 3-1	Summary of Fish Mortality Response to pH	3-8
Table 3-2	General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.	3-9
Table 3-3	Ecological effects associated with alternative levels of acid neutralizing capacity (ANC).....	3-15
Table 4-1	Crosswalk between Ecosystem Services and Public Welfare Effects ...	4-11
Table 4-2	Count of Impacted Lakes.....	4-29
Table 4-3	Present Value and Annualized Benefits of Recreational Fishing to NY Residents, Adirondack Region.....	4-30
Table 4-4	Aggregate Annual Benefit Estimates of Recreational Fishing to NY Residents for the Zero-Out Scenario.....	4-33
Table 4-5	Annual participation and value of outdoor (forest related) activity in the northeast.....	4-35
Table 4-6	Summary of Studies of Fall Color Viewing	4-36
Table 4.7	Value Components for WTP for Extensive Protection Program for Southern Appalachian Spruce-Fir Forests	4-37
Table 4-8	Summary of WTP Studies for Protection of Spruce Forests in the Southern Appalachians.....	4-38
Table 4-9	Summary of Values for Current Levels of Services and Changes in Service Levels in \$2007.....	4-42

Table 4-10	Summary of Annual Damages to Services due to Atmospheric Loading	4-43
Table 4-11	Summary of Current Levels of Ecosystem Services.....	4-46
Table 5.1	Results of the comparison of lake and stream aquatic critical loads (ANC of 50 $\mu\text{eq/L}$) to terrestrial critical loads (Bc:Al molar ratios of 10.0 in soil solution)	5-3
Table 5.2	Results of the comparison of lake and stream aquatic critical loads (ANC of 50 $\mu\text{eq/L}$) to terrestrial critical loads (Bc:Al molar ratios of 1.2 in soil solution)	5-3
Table 7-5.1a.	Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of 20 $\mu\text{eq/L}$	7-55
Table 7-5.1b	Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of 35 $\mu\text{eq/L}$	7-56
Table 7-5.1c	Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of 50 $\mu\text{eq/L}$	7-57
Table 7-5.1d	Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of 75 $\mu\text{eq/L}$	7-58
Table 7-5.2	Summary of the number of acid sensitive ecoregions (out of 29) not likely to meet alternative standards based on a 2005 CMAQ simulation	7-59
Table 7-6-1	Summary of Qualitative Uncertainty Analysis of Key Components of the AAI	7-70

List of Figures

Figure 1-1	Framework of an ecologically relevant secondary standard to address deposition-related effects on sensitive ecosystems.	1-12
Figure 1-2	Simplified conceptual design of the form of an aquatic acidification standard for oxides of nitrogen and sulfur	1-13
Figure 2-1	Overview of atmospheric, soil and aquatic processes relevant to acidification	2-1
Figure 2-2	Diagram illustrating the multiple pollutant, multiple media linkages that are incorporated in air quality models like CMAQ.....	2-2
Figure 2-3	Spatial distribution of annual total NO_x emissions (tons/yr) for 2002	2-9
Figure 2-4	Spatial distribution of annual total NH_3 emissions (tons/yr) for 2002	2-10
Figure 2-5	Spatial distribution of annual total SO_2 emissions (tons/yr) for 2002.....	2-14
Figure 2-6	Routinely operating surface monitoring stations measuring forms of atmospheric nitrogen.	2-18
Figure 2-7	Routinely operating surface monitoring stations measuring forms of atmospheric sulfur	2-19
Figure 2-8	Anticipated network of surface based NO_Y stations based on 2009 network design plans	2-21

Figure 2-9	Location of NADP passive ammonia sampling locations for the AMON network.....	2-23
Figure 2-10	Map of the CMAQ modeling domain.....	2-26
Figure 2-11	2005 CMAQ modeled annual average NO_y	2-29
Figure 2-12	2005 CMAQ modeled annual average total reduced nitrogen (NH_x) ...	2-29
Figure 2-13	2005 CMAQ modeled annual average total reduced nitrogen (NH_3) ...	2-30
Figure 2-14	2005 CMAQ modeled annual average ammonium, NH_4	2-30
Figure 2-15	2005 CMAQ modeled annual average SO_x ,	2-31
Figure 2-16	2005 CMAQ modeled annual average SO_2	2-31
Figure 2-17	2005 CMAQ modeled annual average SO_4	2-32
Figure 2-18	2005 annual average sulfur dioxide concentrations (total mass) based on CASTNET.....	2-32
Figure 2-19	2005 annual average sulfate concentrations (total mass) based on CASTNET.....	2-33
Figure 2-20	Annual average 2005 NO_y concentrations from reporting stations in the Air Quality System (AQS).....	2-33
Figure 2-21	Location of approximately 250 National Atmospheric Deposition Monitoring (NADP) National Trends Network (NTN) sites	2-37
Figure 2-22	2005 CMAQ modeled oxidized nitrogen deposition	2-38
Figure 2-23	2005 CMAQ modeled reduced nitrogen deposition	2-38
Figure 2-24	2005 CMAQ modeled ratio of reduced to total nitrogen deposition	2-39
Figure 2-25	2005 CMAQ modeled oxidized sulfur deposition	2-39
Figure 2-26	Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations and dry deposition of individual NO_y species.	2-49
Figure 2-27	Examples of the Relative Abundance of Several NO_y Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured NO_y Concentration.	2-50
Figure 2-28	Annual average fraction of NO_y ambient air contributed by NO_2 based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.....	2-51
Figure 2-29	Annual average fraction of NO_y ambient air contributed by HNO_3 based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.	2-52
Figure 2-30	Annual average fraction of NO_y ambient air contributed by PAN based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.....	2-53
Figure 2-31	Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations and dry deposition of individual SO_x species	2-54
Figure 2-32	Relationship of the change in total oxidized nitrogen deposition to changes in ambient nitric acid and ambient NO_y	2-55
Figure 2-33	Equilibrium diagram illustrating distribution of carbonate species as a function of pH which is closed to atmospheric CO_2 exchange.....	2-60
Figure 2-34	The same system open to atmospheric CO_2 exchange where the amount of dissolved carbon is determined by the partial pressure of atmospheric CO_2 and Ph.....	2-60
Figure 2-35	Equilibrium diagram of the log of aluminum species concentrations	

	as a function of pH.	2-65
Figure 2-36	Critical loads of acidifying deposition based on MAGIC modeling that each surface water location can receive in the Adirondack and Shenandoah Case Study Areas.....	2-73
Figure 2-37	Illustration of a generalized N + S deposition tradeoff curve that is calculated by using the FAB approach.	2-76
Figure 2-38	Active TIME/LTM sampling locations	2-79
Figure 2-39	Surface water alkalinity in the conterminous U.S	2-81
Figure 2-40	National map of ANC data ($\mu\text{eq/L}$) based on historical and contemporary data sorted by ANC classes.	2-81
Figure 2-41	Conceptual source to effects pipeline diagram illustrating basic accountability concepts as one proceeds from source emissions through the air and eventually to effects.	2-82
Figure 2-42	Time series trends of all anthropogenic NO _x and SO _x emissions based on EPA's National Emissions Inventory (NEI).	2-84
Figure 2-43	Trends of NO _x and SO _x reductions associated with EPA's Acid Rain Program.	2-84
Figure 2-44	Eastern U.S. annual average spatial distribution of SO ₂ and total nitrate concentrations averaged over 1989 -1991 and 2007 – 2009.....	2-87
Figure 2-45	Eastern U.S. annual average spatial distribution of SO ₄ concentrations averaged over 1989 -1991 and 2007 – 2009.....	2-88
Figure 2-46	U.S. annual average spatial distribution of wet sulfate and nitrate deposition averaged over 1989 -1991 and 2007 – 2009 based on the NADP.....	2-88
Figure 2-47	U.S. annual average spatial distribution of wet ammonium sulfate deposition and ambient air ammonium concentrations averaged over 1989 –1991 and 2007 – 2009 based on CASTNET and NADP.....	2-89
Figure 2-48	Superimposed Eastern U.S. emission and combined GOME and SCIAMACHY NO ₂ 1997-2002 trends.....	2-89
Figure 2-49	U.S. annual average spatial distribution of hydrogen ion concentration in rain water as pH averaged over 1989 -1991 and 2007 – 2009	2-90
Figure 2-50	Generalized trends in water quality variables ANC and sulfate ion	2-92
Figure 2-51	Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000.	2-93
Figure 2-52	Summary of regional trends in surface water chemistry from 1990 to 2000	2-93
Figure 2-53	Average NO ₃ ⁻ concentrations, SO ₄ ²⁻ concentrations, and ANC across the 44 lakes in the Adirondack Case Study Area.....	2-94
Figure 2-54	ANC concentrations of preacidification (1860) and 2006 conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC.....	2-94
Figure 2-55	Average NO ₃ ⁻ concentrations, SO ₄ ²⁻ concentrations, and ANC levels for the 60 streams in the Shenandoah Case Study Area modeled using MAGIC.	2-95

Figure 2-56	ANC levels of 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 60 streams in the Shenandoah Case Study Area modeled using MAGIC.....	2-95
Figure 3-1	Conceptual model of direct and indirect acidification effects on aquatic biota. Acidic pollutants (NO ₃ ⁻ and SO ₄ ⁻²) lower ANC, resulting in lower pH with direct toxic effects on fish.....	3-4
Figure 3-2	Equilibrium diagram of the log of aluminum species concentrations as a function of pH.	3-5
Figure 3-3	Mean residual number of species per lake for lakes in Ontario, by pH interval.....	3-10
Figure 3-4	Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators (REA 5.3.1.2) MCF-Mixed Conifer Forest, CSS-Coastal Sage Scrub.....	3-26
Figure 3-5	Observed effects from ambient and experimental atmospheric nitrogen deposition loads in relation to using CMAQ 2002 modeling results and NADP monitoring data.....	3-27
Figure 4-1	Common anthropogenic stressors and the essential ecological attributes they affect.	4-4
Figure 4-2	European maps of eutrophication (left) and acidification (right) which protect 95% of natural areas in 50x50 km ² European Monitoring and Evaluation Programme grid.....	4-10
Figure 4-3	Representation of the benefits assessment process indicating where some ecological benefits may remain unrecognized, unquantified, or unmonetized.....	4-13
Figure 4-4	Conceptual model showing the relationships among ambient air quality indicators and exposure pathways and the resulting impacts on ecosystems, ecological responses, effects and benefits to characterize known or anticipated adverse effects to public welfare.	4-15
Figure 4-5.	Locations of Eastern U.S. Public Lands relative to deposition of nitrogen and sulfur in sensitive aquatic areas.....	4-16
Figure 4-6.	Location of Western U.S. Public Lands relative to deposition of nitrogen and sulfur.	4-17
Figure 4-7.	Conceptual model linking ecological indicator (ANC) to affected ecosystem services.....	4-26
Figure 5.1	Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators.....	5-5
Figure 6-1.	Three hour average maximum 2005 SO ₂ concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base.....	6-7
Figure 6-2	Annual average 2005 NO ₂ concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base.....	6-8
Figure 6-3	National map highlighting the nine case study areas evaluated in the REA.....	6-12

Figure 7-1. Conceptual design of the form of an aquatic acidification standard for oxides of nitrogen and sulfur	7-9
Figure 7-2. The relationship between pH and ANC under equilibrium conditions with mineral phase gibbsite. Triangles indicate calculated values while circles indicate measurements (Bi and Liu 2001)	7-14
Figure 7-3 and 7-4. (Left) Relationship between ANC and number of fish species present in aquatic freshwater ecosystems in Shenandoah National Park (Source: Arthur Bulger, University of Virginia, reproduced from NAPAP, 2005.). (Right) Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes.....	7-15
Figure 7-5. Omernik Ecoregion II areas with ecoregion III subdivisions	7-33
Figure 7-6. The top panel captures some of the data details used in delineating acid sensitive and relatively non-acid sensitive regions, which are shown in the bottom panel.....	7-36

List of Acronyms and Abbreviations

AAPI	Atmospheric Acidification Potential Index
ADR	Adirondack Mountains of New York
Al ³⁺	free trivalent aluminum ion
ANC	acid neutralizing capacity
AQCD	Air Quality Criteria Document
AQRV	air quality related values
ASSETS EI	Assessment of Estuarine Trophic Status eutrophication index
Bc/Al	Base cation to aluminum ratio, also Bc:Al
C	carbon
Ca/Al	calcium to aluminum ratio
Ca ²⁺	calcium ion
CAA	Clean Air Act
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network
CCS	coastal sage scrub
Chl <i>a</i>	chlorophyll <i>a</i>
CLE	critical load exceedance
CMAQ	Community Multiscale Air Quality model
CSS	coastal sage scrub
CWA	Clean Water Act
DIN	dissolved inorganic nitrogen
DO	dissolved oxygen
DOI	U.S. Department of Interior
EMAP	Environmental Monitoring and Assessment Program
EPA	U.S. Environmental Protection Agency
FHWAR	fishing, hunting and wildlife associated recreation survey
FIA	Forest Inventory and Analysis National Program
FWS	Fish and Wildlife Service
GIS	geographic information systems
GPP	gross primary productivity
H ⁺	hydrogen ion
H ₂ O	water vapor
H ₂ SO ₄	sulfuric acid
ha	hectare
HAB	harmful algal bloom
HFC	hydrofluorocarbon
Hg ⁺²	reactive mercury
Hg ⁰	elemental mercury
HNO ₃	nitric acid
HONO	nitrous acid
HUC	hydrologic unit code
IMPROVE	Interagency Monitoring of Protected Visual Environments
ISA	Integrated Science Assessment
K ⁺	potassium ion

kg/ha-yr	kilograms per hectare per year
km	kilometer
LRMP	Land and Resource Management Plan
LTER	Long Term Ecological Monitoring and Research
LTM	Long-Term Monitoring
MAGIC	Model of Acidification of Groundwater in Catchments
MCF	Mixed Conifer Forest
MEA	Millennium Ecosystem Assessment
meq/m ² -yr	annual deposition rate in terms of milliequivalents per square meter
Mg ²⁺	magnesium
N	nitrogen
N ₂	gaseous nitrogen
N ₂ O	nitrous oxide
N ₂ O ₃	nitrogen trioxide
N ₂ O ₄	nitrogen tetroxide
N ₂ O ₅	dinitrogen pentoxide
Na ⁺	sodium
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NAWQA	National Water Quality Assessment
NEEA	National Estuarine Eutrophication Assessment
NEP	net ecosystem productivity
NH ₃	ammonia gas
NH ₄ ⁺	ammonium ion
(NH ₄) ₂ SO ₄	ammonium sulfate
NH _x	category label for NH ₃ plus NH ₄ ⁺
NO	nitric oxide
NO ₂	nitrogen dioxide
NO ₂ ⁻	nitrite ion
NO ₃ ⁻	nitrate ion
NOAA	National Oceanic and Atmospheric Administration
NO _x	nitrogen oxides
NO _y	total reactive oxidized nitrogen
NPP	net primary productivity
NPS	National Park Service
NRC	National Research Council
NSWS	National Surface Water Survey
NTN	National Trends Network
NTR	organic nitrate
O ₃	ozone
OAQPS	Office of Air Quality Planning and Standards
OW	Office of Water
PAN	peroxyacyl nitrates
PFC	perfluorocarbons
pH	negative base 10 logarithmic value of hydrogen ion concentration

ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PSD	prevention of significant deterioration
REA	Risk and Exposure Assessment
REMAP	Regional Environmental Monitoring and Assessment Program
S	sulfur
S ₂ O ₃	thiosulfate
S ₂ O ₇	heptoxide
SAV	submerged aquatic vegetation
SF ₆	sulfur hexafluoride
SMP	Simple Mass Balance
SO	sulfur monoxide
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
SO ₃ ²⁻	sulfite ion
SO ₄	wet sulfate
SO ₄ ²⁻	sulfate ion
SOM	soil organic matter
SO _x	sulfur oxides
SPARROW	SPATIally Referenced Regressions on Watershed Attributes
SRB	sulfate-reducing bacteria
STORET	STORage and RETrieval
TIME	Temporally Integrated Monitoring of Ecosystems
TMDL	total maximum daily load
TP	total phosphorus
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
µeq/L	microequivalents per liter
µg/m ³	micrograms per cubic meter

List of 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.
- Air Quality Indicator:** The substance or set of substances (e.g., PM_{2.5}, NO₂, SO₂) 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.
- Base Cation Saturation:** The degree to which soil cation exchange sites are occupied with base cations (e.g., Ca²⁺, Mg²⁺, K⁺) as opposed to Al³⁺ 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.
- Ecologically 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 ecological risk.
- Critical Load:** A quantitative estimate of an exposure to one or more pollutants, below which significant (as defined by the analyst or decision maker) harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge.
- Denitrification:** The anaerobic reduction of oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N₂O or N₂) by denitrifying bacteria.
- Dry Deposition:** The removal of gases and particles from the atmosphere to surfaces in the absence of precipitation (e.g., rain, snow) or occult deposition (e.g., fog).
- 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.

Equivalents. Concentrations in terms of the electrical charge units associated with ionic charge in water or the potential of atmospheric deposition of N or S to produce ions. Commonly reported as $\mu\text{eq/l}$ (water concentration) and $\text{meq/m}^2\text{-yr}$ (deposition)

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

Nitrification: The oxidation through plant, soil and microbiological processes of reduced nitrogen (ammonia gas and ammonium ion) into nitrite and eventually nitrate.

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 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).

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 PURPOSE

The U.S. Environmental Protection Agency (EPA) is presently conducting a joint review of the secondary (welfare-based) national ambient air quality standards (NAAQS) for oxides of nitrogen and oxides of sulfur. The EPA's overall plan and schedule for this review were presented in the *Integrated Review Plan for the Secondary National Ambient Air Quality Standards for Nitrogen Dioxide and Sulfur Dioxide* (U.S. EPA, 2007). The IRP identified key policy-relevant issues to be addressed in this review as a series of questions that frame our consideration of whether the current secondary NAAQS for oxides of nitrogen and sulfur should be retained or revised.

This Policy Assessment (PA), prepared by staff in the EPA's Office of Air Quality Planning and Standards (OAQPS) is intended to help "bridge the gap" between the relevant scientific information and assessments and the judgments required of the EPA Administrator in determining whether, and if so how, it is appropriate to revise the secondary NAAQS for oxides of nitrogen and sulfur.¹ This PA presents factors relevant to EPA's review of the secondary NAAQS for oxides of nitrogen and oxides of sulfur. It focuses on both evidence- and risk-based information, together with related limitations and uncertainties, in evaluating the adequacy of the current NAAQS and in identifying potential alternative standards for consideration.

In this PA, we consider the policy implications of the scientific information available in this review as assessed in the *Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria* (U.S. EPA, 2008), prepared by EPA's National Center for Environmental Assessment (NCEA), and the results from the analyses contained in the *Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur* (U.S. EPA, 2009).² In so doing, we focus on information that is most pertinent to evaluating the basic elements of NAAQS: indicator³, averaging time, form,⁴

¹ Preparation of a PA by OAQPS staff reflects Administrator Jackson's decision to modify the NAAQS review process that was presented in the IRP. See <http://www.epa.gov/ttn/naaqs/review.html> for more information on the current NAAQS review process.

² These documents are available at <http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html>.

³ The "indicator" of a standard defines the chemical species or mixture that is to be measured in determining whether an area attains the standard.

and level. These elements, which together serve to define each standard, must be considered collectively in evaluating the public welfare protection afforded by these standards.

Although this PA should be of use to all parties interested in this review of the secondary NAAQS for oxides of nitrogen and sulfur, it is written with an expectation that the reader has some familiarity with the technical discussions contained in the ISA and REA.

1.2 BACKGROUND

1.2.1 Legislative Requirements

Two sections of the Clean Air Act (CAA) govern the establishment and revision of the NAAQS. Section 108 (42 U.S.C. section 7408) directs the Administrator to identify and list certain air pollutants and then to issue air quality criteria for those pollutants. The Administrator is to list those “air pollutant[s]... [that] in his judgment, cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare; the presence of which in the ambient air results from numerous or diverse mobile or stationary sources; [and] for which air quality criteria had not been listed prior to December 31, 1970, but for which [the Administrator] plans to issue air quality criteria...”. Air quality criteria are intended to “accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of [a] pollutant in the ambient air” The air quality criteria include “(A) those variable factors (including atmospheric conditions) which of themselves or in combination with other factors may alter the effects on public health or welfare of such air pollutant; (B) the types of air pollutants which, when present in the atmosphere, may interact with such pollutant to produce an adverse effect on public health or welfare; and (C) any known or anticipated adverse effects on welfare.” 42 U.S.C. § 7408(b).

Section 109 (42 U.S.C. section 7409) directs the Administrator to propose and promulgate “primary” and “secondary” NAAQS for pollutants for which air quality criteria are issued. Section 109(b)(1) defines a primary standard as one “the attainment and maintenance of which in the judgment of the Administrator, based on [air quality] criteria and allowing an adequate margin of safety, are requisite to protect the public health.” A secondary standard, as

⁴ The “form” of a standard defines the metric that is to be compared to the level of the standard in determining whether an area attains the standard.

defined in section 109(b)(2), must “specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator, based on such criteria, is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air.”⁵

In setting standards that are “requisite” to protect public health and welfare, as provided in section 109(b), EPA’s task is to establish standards that are neither more nor less stringent than necessary for these purposes. *Whitman v. American Trucking Associations*, 531 U.S. 457, 473. In establishing “requisite” EPA may not consider the costs of implementing the standards. *Id.* at 471. Likewise, “[a]ttainability and technological feasibility are not relevant considerations in the promulgation of national ambient air quality standards.” *American Petroleum Institute v. Costle*, 665 F. 2d at 1185.

Section 109(d) (1) of the CAA requires that “[n]ot later than December 31, 1980, and at 5-year intervals thereafter, the Administrator shall complete a thorough review of the criteria published under section 108 and the national ambient air quality standards . . . and shall make such revisions in such criteria and standards and promulgate such new standards as may be appropriate ...” 42 U.S.C. § 7409(d)(1). Section 109(d)(2) requires that an independent scientific review committee “shall complete a review of the criteria ... and the national primary and secondary ambient air quality standards ... and shall recommend to the Administrator any new ... standards and revisions of existing criteria and standards as may be appropriate” 42 U.S.C. § 7409(d)(2). This independent review function is performed by the Clean Air Scientific Advisory Committee (CASAC) of EPA’s Science Advisory Board.

1.2.2 History of Reviews of NAAQS for Nitrogen Oxides and Sulfur Oxides

NAAQS for Oxides of Nitrogen

After reviewing the relevant science on the public health and welfare effects associated with oxides of nitrogen, EPA promulgated identical primary and secondary NAAQS for NO₂ in April 1971. These standards were set at a level of 0.053 parts per million (ppm) as an annual average (36 FR 8186). In 1982, EPA published *Air Quality Criteria for Oxides of Nitrogen* (U.S.

⁵ Welfare effects as defined in section 302(h) (42 U.S.C. section 7602(h)) include, but are not limited to, “effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being.”

EPA, 1982), which updated the scientific criteria upon which the initial standards were based. In February 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 in June 1985 (50 FR 25532).

The EPA began the most recent previous review of the oxides of nitrogen secondary standards in 1987. In November 1991 EPA released an updated draft AQCD for CASAC and public review and comment (56 FR 59285), which provided a comprehensive assessment of the available scientific and technical information on health and welfare effects associated with NO₂ and other oxides of nitrogen. The 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 NO₂” (Wolff, 1993). The *Air Quality Criteria for Oxides of Nitrogen* was then finalized (U.S. EPA, 1993). EPA’s OAQPS also prepared a Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised AQCD for oxides of nitrogen and identified the critical elements to be considered in the review of the NO₂ 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 October 1995 the Administrator announced her proposed decision not to revise either the primary or secondary NAAQS for NO₂ (60 FR 52874; October 11, 1995). A year later, the Administrator made a final determination not to revise the NAAQS for NO₂ after careful evaluation of the comments received on the proposal (61 FR 52852; October 8, 1996). While the primary NO₂ standard was revised in January 2010 by supplementing the existing annual standard with the establishment of a new 1-hour standard (75 FR 6474), the secondary NAAQS for NO₂ remains 0.053 ppm (100 micrograms per cubic meter [$\mu\text{g}/\text{m}^3$] of air), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO₂ concentrations.

NAAQS for Oxides of Sulfur

EPA promulgated primary and secondary NAAQS for SO₂ in April 1971 (36 FR 8186). The secondary standards included a standard set at 0.02 ppm, annual arithmetic mean, and a 3-hour average standard set at 0.5 ppm, not to be exceeded more than once per year. These

secondary standards were established solely on the basis of evidence of adverse effects on vegetation. 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 SO₂ 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 then-current concentrations of oxides of sulfur in the ambient air had 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 ambient concentrations of oxides of sulfur and such public welfare effects (38 FR 25679).

In 1979, EPA announced that it was revising the AQCD for oxides of sulfur concurrently with that for particulate matter (PM) and would produce a combined PM and oxides of sulfur 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., SO₂ 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 a substantial portion 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 oxides of nitrogen and PM and oxides of sulfur. Following CASAC closure on the AQCD for oxides of sulfur in December 1981, EPA’s OAQPS published a Staff Paper in November 1982, although the paper did not directly assess the issue of acid deposition. Instead, EPA subsequently prepared the following documents to address acid deposition: *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 scientific information relevant to acid deposition completed by EPA at that point.

In April 1988 (53 FR 14926), EPA proposed not to revise the existing primary and secondary standards for SO₂. This proposed decision with regard to the secondary SO₂ 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 decreased through ongoing research efforts, EPA would draft and support an appropriate set of control measures. Although EPA revised the primary SO₂ standard in June 2010 by establishing a new 1-hour standard and revoking the existing 24-hour and annual standards (75 FR 35520), no further decisions on the secondary SO₂ standard have been published.

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 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 Clean Air Act Amendments of 1990 included numerous separate provisions related to the acid deposition problem. The primary and most important of the provisions, the amendments to Title IV of the Act, established the Acid Rain Program to reduce emissions of SO₂ by 10 million tons and emissions of nitrogen oxides 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 considered 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. That 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 “effects on welfare” in Section 302(h) was expanded to state that the welfare effects include effects “...whether caused by transformation, conversion, or combination with other air pollutants.”

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 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” (NSTC, 2010).

Given the state of the science as described in the ISA and in other recent reports, such as the NAPAP reports noted above, EPA has decided, in the context of evaluating the adequacy of the current NO₂ and SO₂ secondary standards in this review, to revisit the question of the appropriateness of setting secondary NAAQS to address remaining known or anticipated adverse public welfare effects resulting from the acidic and nutrient deposition of these criteria pollutants.

1.3 SCOPE OF CURRENT REVIEW

In conducting this periodic review of the secondary NAAQS for oxides of nitrogen and oxides of sulfur, as discussed in the IRP, EPA decided to assess the scientific information, associated risks, and standards relevant to protecting the public welfare from adverse effects associated jointly with oxides of nitrogen and sulfur. Although EPA has historically adopted separate secondary standards for oxides of nitrogen and oxides of sulfur, EPA is conducting a joint review of these standards because oxides of nitrogen and sulfur, and their associated transformation products are linked from an atmospheric chemistry perspective, as well as from an environmental effects perspective. The National Research Council (NRC) has recommended that EPA consider multiple pollutants, as appropriate, in forming the scientific basis for the NAAQS (NRC, 2004). As discussed in the ISA and REA, there is a strong basis for considering these pollutants together, building upon EPA'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.

In defining the scope of this review, we recognize that EPA has set secondary standards for two other criteria pollutants related to oxides of nitrogen and sulfur: ozone and particulate matter (PM). Oxides of nitrogen are precursors to the formation of ozone in the atmosphere, and under certain conditions, can combine with atmospheric ammonia to form ammonium nitrate, a component of fine PM. Oxides of sulfur are precursors to the formation of particulate sulfate, which is a significant component of fine PM in many parts of the U.S. There are a number of welfare effects directly associated with ozone and fine PM, including ozone-related damage to vegetation and PM-related visibility impairment. Protection against those effects is provided by the ozone and fine PM secondary standards. This review focuses on evaluation of the protection provided by secondary standards for oxides of nitrogen and sulfur for two general types of effects: (1) direct effects on vegetation associated with exposure to gaseous oxides of nitrogen and sulfur in the ambient air, which are the effects that the current NO₂ and SO₂ secondary standards protect against and (2) effects associated with the deposition of oxides of nitrogen and sulfur to sensitive aquatic and terrestrial ecosystems, including deposition in the form of particulate nitrate and particulate sulfate.

The ISA focuses on the ecological effects associated with deposition of ambient oxides of nitrogen and sulfur to natural sensitive ecosystems, as distinguished from commercially managed

forests and agricultural lands. This focus reflects the fact that the majority of the scientific evidence regarding acidification and nutrient enrichment is based on studies in unmanaged ecosystems. Non-managed terrestrial ecosystems tend to have a higher fraction of N deposition resulting from atmospheric nitrogen (ISA, section 3.3.2.5). In addition, the ISA notes that agricultural and commercial forest lands are routinely fertilized with amounts of nitrogen that exceed air pollutant inputs even in the most polluted areas (ISA, section 3.3.9). This review recognizes that the effects of nitrogen deposition in managed areas are viewed differently from a public welfare perspective than are the effects of nitrogen deposition in natural, unmanaged ecosystems, largely due to the more homogeneous, controlled nature of species composition and development in managed ecosystems and the potential for benefits of increased productivity in those ecosystems.

In focusing on natural sensitive ecosystems, this PA primarily considers the effects of ambient oxides of nitrogen and sulfur via deposition on multiple ecological receptors. The ISA highlighted effects including those associated with acidification and nitrogen nutrient enrichment. With a focus on these deposition-related effects, EPA's objective is to develop a framework for oxides of nitrogen and sulfur standards that incorporates ecologically relevant factors and that recognizes the interactions between the two pollutants as they deposit to sensitive ecosystems. The overarching policy objective is to develop a secondary standard(s) that is based on the ecological criteria described in the ISA and the results of the assessments in the REA, and is consistent with the requirement of the CAA to set secondary standards that are requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of these air pollutants in the ambient air. Also consistent with the CAA, as discussed above in section 1.2.1, this policy objective necessarily includes consideration of "variable factors . . . which of themselves or in combination with other factors may alter the effects on public welfare" of the criteria air pollutants included in this review.

In addition, we have chosen to focus on the effects of ambient oxides of nitrogen and sulfur on ecological impacts on sensitive aquatic ecosystems associated with acidifying deposition of nitrogen and sulfur, which is a transformation product of ambient oxides of nitrogen and sulfur. Based on the information in the ISA, the assessments presented in the REA, and advice from CASAC on earlier drafts of this PA (Russell and Samet, 2010a, 2010b), and as discussed below in chapter 2, we have the greatest confidence in the causal linkages between

oxides of nitrogen and sulfur and aquatic acidification effects relative to other deposition-related effects, including terrestrial acidification and aquatic and terrestrial nutrient enrichment.

In developing policy options for the Administrator's consideration, we note that decisions on retaining or revising the current secondary standards for oxides of nitrogen and sulfur are largely public welfare policy judgments based on the Administrator's informed assessment of what constitutes requisite protection against adverse effects to public welfare. A public welfare policy decision should draw upon scientific information and analyses about welfare effects, exposure and risks, as well as judgments about the appropriate response to the range of uncertainties that are inherent in the scientific evidence and analyses. The ultimate determination as to what level of damage to ecosystems and the services provided by those ecosystems is adverse to public welfare is not wholly a scientific question, although it is informed by scientific studies linking ecosystem damage to losses in ecosystem services, and information on the value of those losses of ecosystem services. In reaching such decisions, the Administrator seeks to establish standards that are neither more nor less stringent than necessary for this purpose.

1.4 CONCEPTUAL FRAMEWORK FOR DEPOSITON-RELATED STANDARDS

As noted above, there is a strong basis for considering deposition-related standards for oxides of nitrogen and sulfur together at this time, building upon EPA's and CASAC's 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. The REA introduced a conceptual framework for ecologically meaningful secondary standards that recognized the complex processes by which ecosystems are exposed through deposition to ambient oxides of nitrogen and sulfur. That framework provided a flow from ambient concentrations to exposures via deposition to ecological indicators and effects (Figure ES-2 in the REA Executive Summary). Figure 1-1 below is an adaptation of the REA framework, which represents the process by which we can determine the deposition-related risks to sensitive aquatic and terrestrial ecosystems associated with ambient concentrations of oxides of nitrogen and sulfur. This framework illustrates how a level of protection related to an indicator of ecological effect(s) can be linked to atmospheric concentrations of indicators of oxides of nitrogen and sulfur. It illustrates the linkages between ambient air concentrations and resulting deposition metrics, and between the deposition metric and the ecological indicator of concern.

What is referred to as an atmospheric deposition transformation function translates ambient atmospheric concentrations of oxides of nitrogen and sulfur to nitrogen and sulfur deposition metrics, while an ecological effect function transforms the deposition metric into an ecological indicator.

Structure of an Ecologically-based Standard

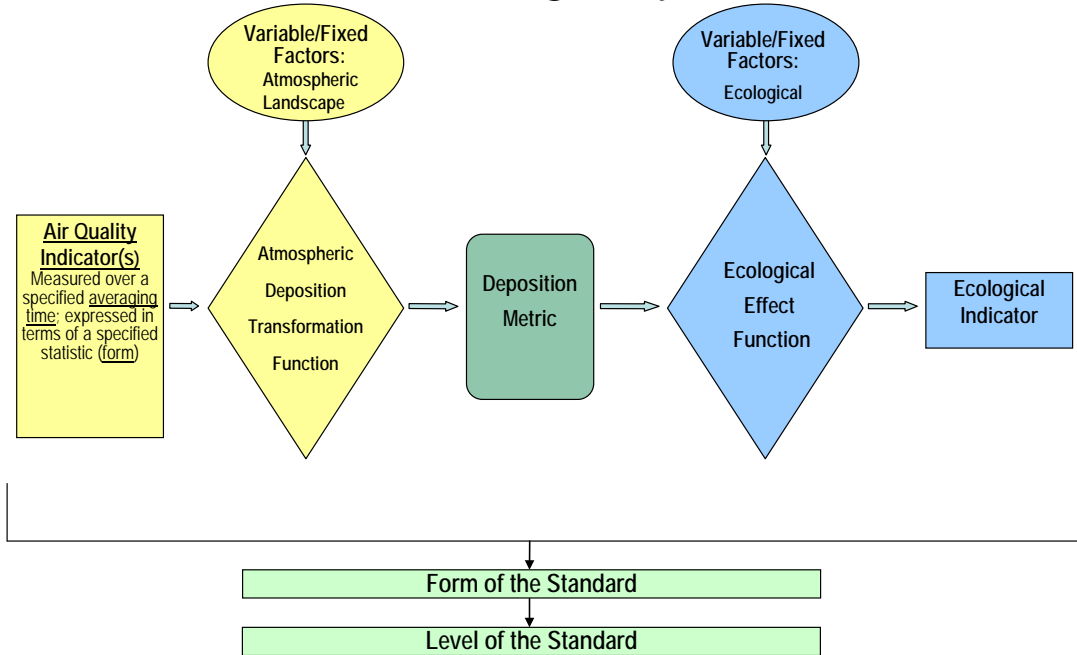


Figure 1-1. Framework of an ecologically relevant secondary standard to address deposition-related effects on sensitive ecosystems (adapted from the REA, Figure ES-2) .

Development of a form for an ecologically relevant standard that reflects this structure is a critical step in the overall standard setting process. The atmospheric levels of oxides of nitrogen and sulfur that afford a particular level of ecosystem protection are those levels that result in an amount of deposition that is less than the amount of deposition that a given ecosystem can accept without defined levels of degradation of the ecological indicator for a targeted effect.

Drawing from the framework developed in the REA, the framework we are using to structure an ecologically meaningful secondary standard in this PA is depicted below in a more

simple graphic, Figure 1-2, that highlights the three key linkages that need to be considered in developing an ecologically relevant standard.

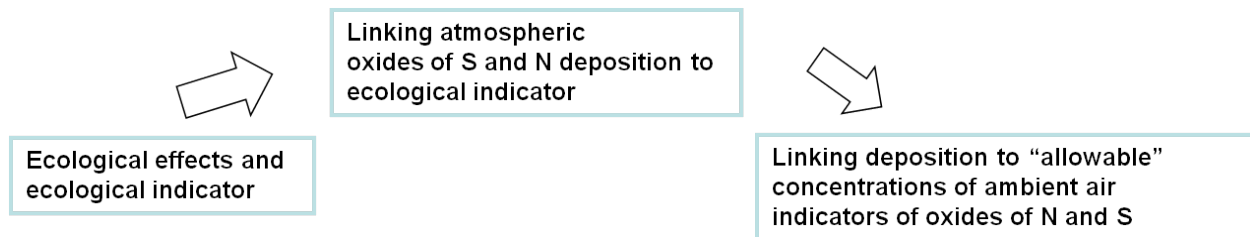


Figure 1-2. Simplified conceptual design of the form of an aquatic acidification standard for oxides of nitrogen and sulfur.

The details of this simplified conceptual framework are discussed in chapter 7, including discussions of modifying factors that alter the relationship between ambient atmospheric concentrations of oxides of nitrogen and sulfur and depositional loads of nitrogen and sulfur, and those that modify the relationship between deposition loads and the ecological indicator.

In setting NAAQS to protect public health and welfare, EPA has historically established standards which require the comparison of monitored concentrations of an air pollutant against a numerical metric of atmospheric concentration that does not vary geographically. This approach has appropriately protected public health, as at-risk populations are widely distributed throughout the nation. As more is learned about the effects of pollutants such as oxides of nitrogen and sulfur and the environment, however, such an approach cannot effectively or consistently provide the requisite level of protection to public welfare from effects on sensitive ecosystems. In this review, we are considering a standard that takes into account variable factors, such as atmospheric variables and location-specific characteristics of ecosystems, as the appropriate approach to protect the public welfare from the effects associated with the presence of these pollutants in the ambient air.

While EPA has most often considered the results of direct exposure to an air pollutant in the ambient air in assessing effects on public health and welfare, such as the health effects on humans when breathing in an air pollutant or the effects on vegetation through the uptake of air pollutants from the ambient air through leaves, EPA has also considered, where appropriate, the

effects of exposure to air pollutants through more indirect mechanisms. For example, both in 1978 and in 2008, EPA established a NAAQS for lead that addressed the health effects of ambient lead whether the lead particles were inhaled or were ingested after deposition on the ground or other surfaces. 73 FR 66964 (November 12, 2008), *Lead Industries v. EPA*, 647 F.2d 1130 (DC Cir. 1980) (1978 NAAQS). The deposition of ambient oxides of nitrogen and sulfur to terrestrial and aquatic environments can impact ecosystems through both direct and indirect mechanisms, as discussed in the REA and below in chapter 2. Given Congress' instruction to set a standard that "is requisite to protect the public welfare from "any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air," 42 U.S.C. § 109 (b)(2), this review appropriately considers widely acknowledged effects, such as acidification and nutrient enrichment, which are associated with the presence of oxides of nitrogen and sulfur in the ambient air through the deposition of nitrogen and sulfur that results from oxides of nitrogen and sulfur in the ambient air.

In this review, we are considering the development of a standard that takes into account the variability in deposition-related effects associated with levels of oxides of nitrogen and sulfur in the ambient air. The CAA requires EPA to establish "national" standards, based on the air quality criteria that provide the requisite degree of protection, but does not clearly address how to do so under the circumstances present here. In this PA we develop an approach that is designed to provide a generally uniform degree of protection throughout the country by allowing for varying concentrations of allowable ambient oxides of nitrogen and sulfur, depending on atmospheric conditions and other ecological variables, to achieve that degree of protection. Such a standard would protect sensitive ecosystems wherever such ecosystems are found. This approach recognizes that setting a standard that is sufficient to protect the public welfare, but not more than is necessary, calls for consideration of a standard such as the one discussed in this document.

1.5 ORGANIZATION OF THIS DOCUMENT

This PA includes staff's evaluation of the policy implications of the scientific assessment of the evidence presented and assessed in the ISA and the results of quantitative assessments based on that information presented and assessed in the REA. Taken together, this information informs staff conclusions and the identification of policy options for consideration in addressing

public and welfare effects associated with the presence of oxides of nitrogen and oxides of sulfur in the ambient air.

Following this introductory chapter, this document presents policy relevant information drawn from the ISA and REA as well as assessments that translate this information into a basis for staff conclusions as to policy options that are appropriate to consider in this review. The discussions are generally framed by addressing policy-relevant questions that have been adapted from those initially presented in the IRP.

Chapter 2 presents information that characterizes emissions, air quality, deposition and water quality. It includes discussions of the sources of nitrogen and sulfur in the atmosphere as well as current ambient air quality monitoring networks and models. Additional information in this section includes ecological modeling and water quality data sources.

Chapter 3 discusses the known or anticipated ecological effects associated with oxides of nitrogen and sulfur, including both deposition-related effects and well as direct effects. In so doing, we address questions about the nature and magnitude of ecosystem responses to reactive nitrogen and sulfur deposition, including responses related to acidification, nutrient enrichment, and the mobilization of toxic metals in sensitive aquatic and terrestrial ecosystems, and the uncertainties and limitations associated with the evidence of such effects. Consideration is given to how these responses are affected by landscape factors, and what types of ecosystems are sensitive to such responses. We also consider the extent to which ecosystem responses to nitrogen deposition can be separated into responses related to oxidized and reduced forms of reactive nitrogen compounds.

In chapter 4, we address questions related to linking ecological effects to measures that can be used to characterize the extent to which such effects are reasonably considered to be adverse to public welfare. This involves consideration of how to characterize adversity from a public welfare perspective. In so doing, consideration is given to the concept of ecosystem services, the evidence of effects on ecosystem services, and how ecosystem services can be linked to ecological indicators.

Having focused more heavily on deposition-related effects on aquatic acidification in chapters 3 and 4, chapter 5 considers the potential co-benefits that could be expected to result from a standard that is designed to provide protection from aquatic acidification. Consideration

is given to potential co-benefits related to terrestrial acidification as well as aquatic and terrestrial nutrient enrichment.

Chapter 6 presents an assessment of the adequacy of the current NO_2 and SO_2 secondary standards. Consideration is given both to the adequacy of protection afforded by the current standards for both direct and deposition-related effects, as well as to the appropriateness of the fundamental structure and the basic elements of the current standards for providing protection from deposition-related effects. In so doing, we address questions related to considering the extent to which deposition-related effects that could reasonably be judged to be adverse to public welfare are occurring under current conditions which are allowed by the current standards. We also consider the ways in which the structures and basic elements of the current NO_2 and SO_2 secondary standards are inadequate to protect against such effects.

Potential alternative standards for oxides of nitrogen and sulfur are considered in chapter 7, drawing on the information in the previous chapters. More specifically, chapter 7 discusses alternative approaches to defining the four elements of a NAAQS – indicator, form, averaging time, and level – for a standard intended to protect against effects on sensitive ecosystems associated with deposition-related aquatic acidification. This chapter considers the implications of alternative standards, including specific combinations of alternative forms and levels, in terms of identifying the sensitive ecosystems across the U.S. that would receive additional protection from such alternative standards. Staff conclusions as to alternative standards that are appropriate to consider in this review are presented, together with the rationales for such conclusions.

This document also includes a number of appendices providing additional information to support the document. Appendix A provides an analysis conducted to compare aquatic acidification to terrestrial acidification. Appendix B discusses critical loads derivations and modeling. Appendices C and D provide additional information regarding spatial aggregation and critical loads. An overview of alternative indicators for oxides of nitrogen is located in Appendix E and discussions of uncertainty analyses are included as Appendices F and G.

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2 CHARACTERIZING EMISSIONS, AIR QUALITY, DEPOSITION AND WATER QUALITY

This chapter provides an overview of air emissions, air quality, deposition, and water quality relevant to oxides of nitrogen and sulfur, with specific focus on information related to aquatic acidification processes (Figure 2-1). Atmospheric, terrestrial and aquatic systems are discussed, consistent with consideration of a multi-pollutant, multi-media standard, which makes the scope of this chapter much broader than to most NAAQS policy assessments that traditionally focus on atmospheric media only. While serving as a general resource for data availability and system descriptions (monitoring networks, models, emission inventories), the information presented here provides background and context for more focused policy-relevant discussions in the subsequent chapters. A source-to-effects continuum is adhered to in covering the suite of topics, starting with emissions (section 2.1) and proceeding through air quality (section 2.2), deposition (section 2.3), soils and surface waters (2.4), and followed by a summary of trends for these four topics (section 2.5).

Most of the atmospheric and water quality based data presented here are intended to reflect contemporary environmental conditions. A 2005 base year is the most contemporary atmospheric modeling available and is used frequently in this assessment to characterize air quality and deposition. While effort was made to present recent water quality data, we note that some of the most relevant water quality data is of late 1980s vintage.

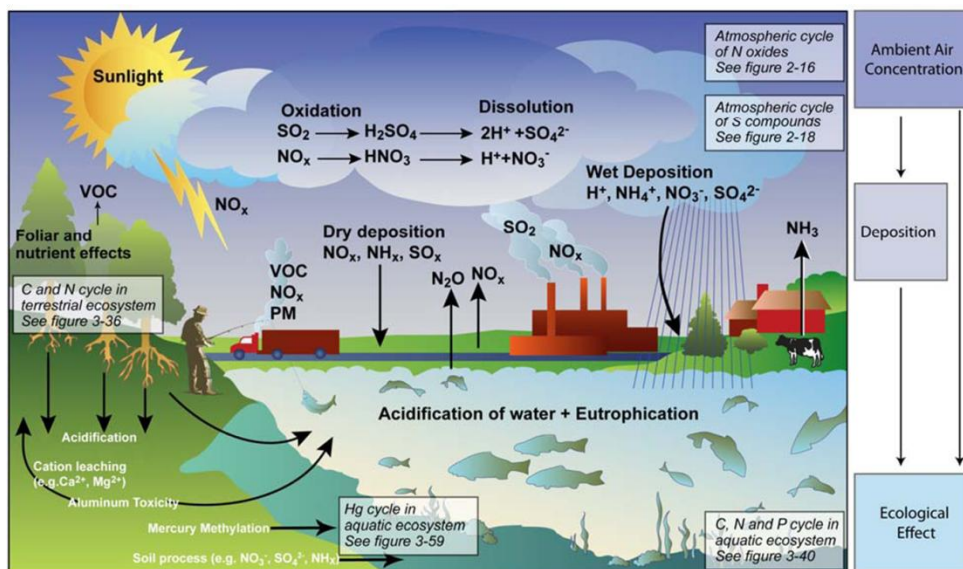


Figure 2-1. Overview of atmospheric, soil and aquatic processes relevant to acidification.

The multiple pollutant, multiple media technical systems framework

The multiple pollutant, multiple media context of this assessment (Figure 2-2; Scheffe et al., 2007, NARSTO, 2011) is based on the fact that air emissions move through the atmosphere and are modified by chemical and physical reactions, advected and dispersed and ultimately removed in the form of chemical deposition. The multiple pollutant context not only is related to the similarity of contributions to acidification from nitrogen and sulfur, but also to integration of so many atmospheric species that influence nitrogen and sulfur patterns and, conversely, the influences of nitrogen and sulfur on other air pollutant species of interest. Consequently, there are important linkages with other air pollutants and therefore other air management programs and rules. Because pollutants such as ozone and particulate matter are influenced by many of the same emission sources and atmospheric processes, those programs are of direct relevance, from a chemical systems perspective, to assessments of oxides of nitrogen and sulfur.

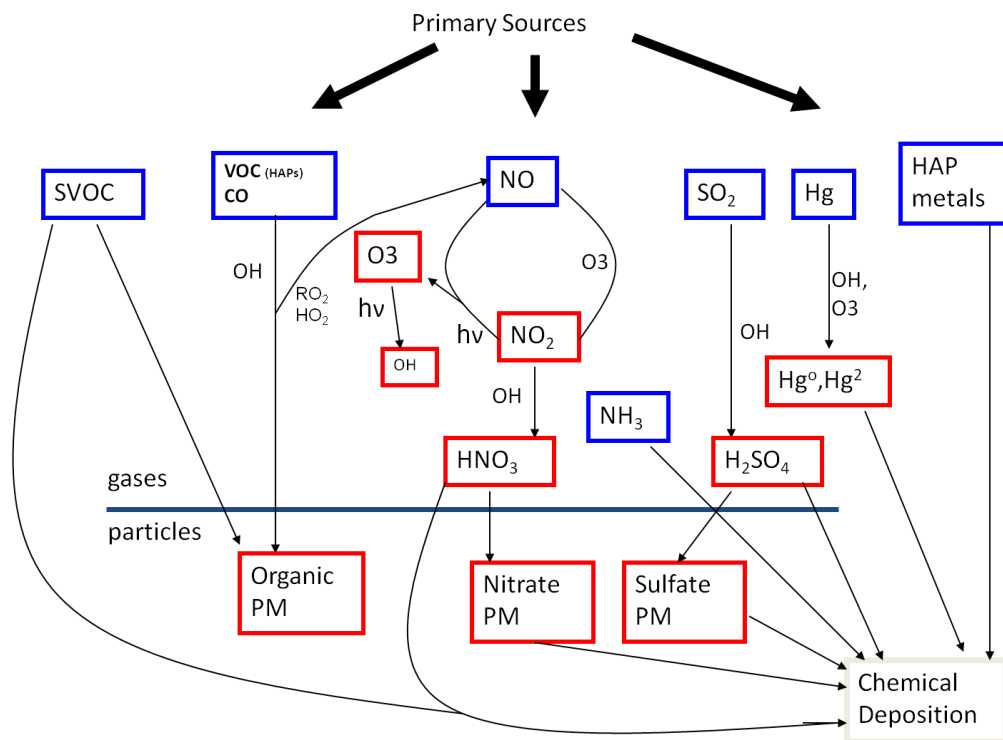


Figure 2-2 Diagram illustrating the multiple pollutant, multiple media linkages that are incorporated in air quality models like CMAQ. While this assessment focuses on the combined effects of oxides of nitrogen and sulfur, the technical basis for characterizing spatial and temporal patterns of N and S is dependent on several other atmospheric species.

Terminology, definitions and units.

Throughout this document numerous terms are used that address a variety of atmospheric and ecosystem processes and variables. We establish the terminology here, early in the document, as a reference source for the entire report.

As discussed in detail in the REA (REA 1.3.1), in the atmospheric science community NO_x is typically referred to as the sum of nitrogen dioxide (NO₂), and nitric oxide (NO). The term used by the scientific community to represent the complete set of reactive oxidized nitrogen compounds is total oxidized nitrogen (NO_y), commonly defined as NO, NO₂ and the all of the oxidation products of NO and NO₂. Reactive oxidized nitrogen is defined as NO_y = NO₂ + NO + HNO₃ + PAN + 2N₂O₅ + HONO + NO₃ + organic nitrates + particulate NO₃ (Finlayson-Pitts and Pitts, 2000). In this document, unless otherwise indicated, we use the term NO_y as the atmospheric indicators associated with the NO_x component of the proposed NO_x/SO_x standard.

For this assessment, SO_x is defined to include all oxides of sulfur, including multiple gaseous substances (e.g., SO₂, sulfur monoxide [SO], sulfur trioxide [SO₃], thiosulfate [S₂O₃], and heptoxide [S₂O₇], as well as particulate species, such as ammonium sulfate [(NH₄)₂SO₄]. Throughout this text we refer to sulfate as SO₄ and nitrate as NO₃, recognizing that they have charges of -2 for sulfate and -1 for nitrate. The sum of sulfur dioxide gas (SO₂) and particulate sulfate (SO₄), referred herein as (SO₂ + SO₄) is used throughout this document as the atmospheric indicator for the SO_x component of the proposed NO_x/SO_x standard. From a measurement and modeling perspective we only consider the sum of SO₂ and particulate SO₄ as the indicator for sulfur. The sum of SO₂ and SO₄ constitute virtually all of the ambient air sulfur budget and are measured routinely in monitoring networks.

Table 2-1 provides further explanation of these indicators, some of which is repeated in Section 7. Table 2-1 also provides details on the units used throughout the equations and examples in the PA. Again, because of difference in unit conventions between atmospheric and ecosystem sciences, there are detailed explanations of units as well as procedures for translating between different unit conventions. To facilitate the linkage between atmospheric and ecosystem processes, only the mass (or equivalent charge) associated with sulfur or nitrogen is considered in mass, mixing ratio, and deposition unit conventions.

Table 2 -1. Description of parameters, units and conventions.

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
Atmospheric species			
CMAQ defined NO _y species: NO (nitrogen oxide), NO ₂ (nitrogen dioxide), HNO ₃ (nitric acid), p-NO ₃ (particulate bound nitrate), NO ₃ (sum of HNO ₃ and p-NO ₃), PAN (peroxy acetyl nitrate), N ₂ O ₅ (dinitrogen pentoxide), PANX (higher order PANs), NTR (organic nitrates), PNA (HNO ₄); sulfur dioxide (SO ₂), particulate sulfate (SO ₄); NH _x species: NH ₃ (ammonia), ammonium ion (NH ₄)			
Lumped Atmospheric Species			
NO _y	The sum of all reactive oxidized nitrogen compounds derived through summing all nitrogen contributions (i.e., 1·HNO ₃ + 2·N ₂ O ₅ + ...) from the modeled species (HNO ₃ , p-NO ₃ , NO ₂ , NO, PAN ...) or through direct measurement which reduces all oxidized nitrogen species to NO and reports as ppb NO. All references to the quantity NO_y refer to the mass, molar or equivalent charge contribution of nitrogen only. All mass contributions of oxygen, hydrogen and carbon are not included.		
(SO ₂ + SO ₄)	Oxidized forms of sulfur defined as sulfate (SO ₄ + SO ₂); mass units maintained for consistency with deposition calculations Note that only mass as sulfur is counted in state variables; in practice, individual SO₂ and SO₄ are measured/modeled and converted to mass of sulfur atoms or equivalent charge units. Mass contribution of oxygen is not included.		
NH _x	Reduced nitrogen calculated as the sum of NH ₃ and NH ₄ . All references to the quantity NH_x used as state variables refer to the mass, molar or equivalent charge contribution of nitrogen only. Mass contribution of oxygen is not included.		
Atmospheric State Variables used in equations and derivations			
NO _y concentration SO _x NH _x Used in various conventions of: C _i ;	μg/m ³ as N or S	ppb = (MA/M _i) · ρ _{air} · μg/m ³ where ρ _{air} is the air density in units of (kg/m ³); ρ _{air} = 28.97(10) ⁻³ ·P/(R·T) R = 8.206(10) ⁻⁵ m ³ atm/(mol·K) P = atm T = degrees K MA = molecular weight of air (28.97) M _i = Atomic weight of nitrogen (14) or sulfur (32) meq/m³ = (1/M_i) · μg/m³	
NO _y deposition (SO ₂ + SO ₄) NH _x Used in various conventions of: Dep _i	meq/m ² -yr as N or S	kg/ha-yr = (M _i /q)(10) ⁻² · meq/m ² -yr where q = charge (1 for N, 2 for S)	
Ndep NO _y dep NH _x Sdep	meq/m ² -yr		Total (wet and dry) deposition; Ndep = NH _x + NO _y dep Sdep = SO _x =SO ₂ +SO ₄
Wet v _i	m/yr		wet deposition velocities
Dry Dep _i	meq/m ² -yr		dry deposition fluxes

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
Dep_i^{Wet}	$meq/m^2\text{-yr}$		wet deposition fluxes
Dep_i^{Total}	$meq/m^2\text{-yr}$		total (wet+dry) deposition
NO_y deposition ($SO_2 + SO_4$) NH_x Used in various conventions of: Dep_i	$meq/m^2\text{-yr as N or S}$	$kg/ha\text{-yr} = (M_i/q)(10)^{-2} \cdot meq/m^2\text{-yr}$ where q = charge (1 for N, 2 for S)	
Ndep NOydep NHx Sdep	$meq/m^2\text{-yr}$		Total (wet and dry) deposition; Ndep = NHx + NOydep Sdep = SOx=SO2 +SO4
v_i^{dry}	m/yr		dry deposition velocities
v_i^{wet}	m/yr		wet deposition velocities
Dep_i^{dry}	$meq/m^2\text{-yr}$		dry deposition fluxes
Dep_i^{Wet}	$meq/m^2\text{-yr}$		wet deposition fluxes
Dep_i^{total}	$meq/m^2\text{-yr}$		total (wet+dry) deposition
T_{SOx} T_{NOy}	m/yr	Calculated by dividing total ($SO_2 + SO_4$) or NOy deposition (wet and dry) by the annual average ($SO_2 + SO_4$) or NOy concentration.	the transfer ratio, which can be considered an aggregated, "effective" deposition velocity that relates total deposition of ($SO_2 + SO_4$) or NOy to the total ambient concentration, and represents an average of the chemical species specific v_i^{Tot} (= $v_i^{Dry} + v_i^{Wet}$) values
Ecosystem variables			
ANC	$\mu eq/L$		measured ANC in surface water
ANC _{limit}	$\mu eq/L$		a "target" ANC level
CL _{anclim(i)} CL(N+S) CL(S)	$meq/m^2\text{-yr}$		Critical load that does not cause the catchment to exceed a given ANC _{lim} , where i indicates the pollutant of interest
Q	m/yr		Average surface water runoff rate for a water body
Qr	m/yr		Median of the average runoff rates for water bodies in an ecoregion
N _{ECO}	$meq/m^2\text{-yr}$		Nitrogen uptake, retention and denitrification by terrestrial catchment
N _{leach}	$meq/m^2\text{-yr}$		N leaching based on observed surface water NO3
CLr	$meq/m^2\text{-yr}$		Ecoregion representative critical load

2.1 SOURCES OF NITROGEN AND SULFUR

This section recasts much of the information provided in EPA's Risk and Exposure Assessment (EPA, 2009). The emission summaries are based on the 2002 calendar year and are intended to convey the basic patterns and major contributors of NO_x, SO_x and NH₃ emissions. The air quality modeling simulations used in chapter 7, as well as some of the air quality and deposition illustrations in this chapter are based on a more modern 2005 calendar year simulation. For the purposes of presenting general patterns of emissions, the 2002 emissions presented here are not significantly different than the 2005 year data.

The National Emissions Inventory (NEI) annual total emissions data for 2002 (U.S. EPA, 2006) are used to characterize the magnitude and spatial patterns in emissions of NO_x, NH₃, and SO₂ nationwide¹. The spatial resolution of these data varies by source type. Emissions from most large stationary sources are represented by individual point sources (e.g., electric generating units, industrial boilers). Sources that emit over broad areas are reported as county total emissions. The national annual 2002 emissions of NO_x, NH₃, and SO₂ by major source category are presented in Table 2-1 of the ISA (U.S. EPA, 2008).

2.1.1 NO_x Emissions

The distribution of national total NO_x emissions across major source categories is provided in Table 2-2. Emissions summaries are also provided for the East² and West in Tables 2-3 a and b, respectively, to reveal regional differences in source emissions profiles. In addition to anthropogenic sources, there are also natural sources of NO_x, including lightning, wildfires, and microbial activity in soils. Nationally, transportation-related sources (i.e., on-road, nonroad, and aircraft/locomotive/marine) account for ~60% of total anthropogenic emissions of NO_x, while stationary sources (e.g., electrical utilities and industrial boilers) account for most of the remainder (U.S. EPA, 2008, AX2, Table 2-1). Emissions from on-road vehicles represent the major component of mobile source NO_x emissions. Approximately half the mobile source emissions are contributed by diesel engines, and half are emitted by gasoline-fueled vehicles and other sources (U.S. EPA, 2008, AX2, Section 2.1.1 and Table 2-1-1). Nationwide, the nonroad,

¹ For the purposes of this analysis, nationwide emissions do not include emissions from Alaska or Hawaii.

² In this analysis, the East is defined as all states from Texas northward to North Dakota and eastward to the East Coast of the United States. States from New Mexico northward to Montana and westward to the West Coast are considered to be part of the West.

aircraft/locomotive/marine, and non-electric generating unit point emissions sectors each contribute generally similar amounts to the overall NO_x inventory. Overall, NO_x emissions are broadly split between NO and NO₂ in a ratio of 90% NO and 10% directly emitted NO₂. However, this split can vary by source category, as described in Chapter 2.2.1 of the ISA (U.S. EPA, 2008).

Table 2-2. Annual National NO_x Emissions across Major Source Categories in 2002.

National Totals	NO _x	
	Emissions (million tons)	Percent of Total
Electric Generation Units	4.619	22%
Industrial Point Sources	2.362	11%
Stationary Area	1.529	7%
On-road	7.839	37%
Nonroad	2.219	10%
Aircraft/Locomotive/Marine	2.611	12%
Fires	0.080	< 1%
Total	21.259	

Table 2-3a. Annual NO_x Emissions across Major Source Categories in 2002 for the Eastern United States.

Eastern U.S.	NO _x	
	Emissions (million tons)	Percent of Total
Electric Generation Units	4.094	23%
Industrial Point Sources	2.031	12%
Stationary Area	1.295	7%
On-road	6.250	36%
Nonroad	1.709	10%
Aircraft/Locomotive/Marine	2.038	12%
Fires	0.028	< 1%
Total	17.445	

Table 2-3b. Annual NO_x Emissions across Major Source Categories in 2002 for the Western United States.

Western U.S.	NO _x	
	Emissions (million tons)	Percent of Total
Electric Generation Units	0.525	14%
Industrial Point Sources	0.331	9%
Stationary Area	0.234	6%
Onroad	1.589	42%
Nonroad	0.510	13%
Aircraft/Locomotive/Marine	0.573	15%
Fires	0.055	1%
Total	3.817	

In general, NO_x emissions in the East are nearly 5 times greater than NO_x emissions in the West. In both the eastern and western United States, the on-road sector is the largest contributor. Emissions from electric generation units are the second-largest contributor to NO_x emissions in the East with 23% of the total. Emissions in the East from industrial point sources, nonroad engines, and aircraft-locomotives-marine engines each contribute in the range of 10 to 12%. In the West, the contribution to NO_x emissions from electric generation units (14%) is in the same range as the contributions from nonroad engines (13%) and aircraft-locomotives-marine engines (15%).

The spatial patterns of 2002 annual NO_x emissions across the United States are shown in Figure 2-3³. Emissions of NO_x are concentrated in and near urban and suburban areas and along major highways. Moderate or higher levels of NO_x emissions (>100,000 tons/yr)⁴ are also evident in some rural areas at locations (i.e., grid cells) containing major point sources. The amount of NO_x emissions in and near each of the case study areas can be seen from this map. All of the case study areas contain or are near locations with NO_x emissions in excess of 100,000 tons/yr.

³ To create this map, NO_x emissions were allocated to a 36 x 36– km grid covering the United States in order to normalize for the differences in the geographic aggregation of point- and county-based emissions. The emissions are in tons per year per 36 x 36 km (1,296 km²).

⁴ Emissions are in tons per year per 36 x 36 km (1,296 km²).

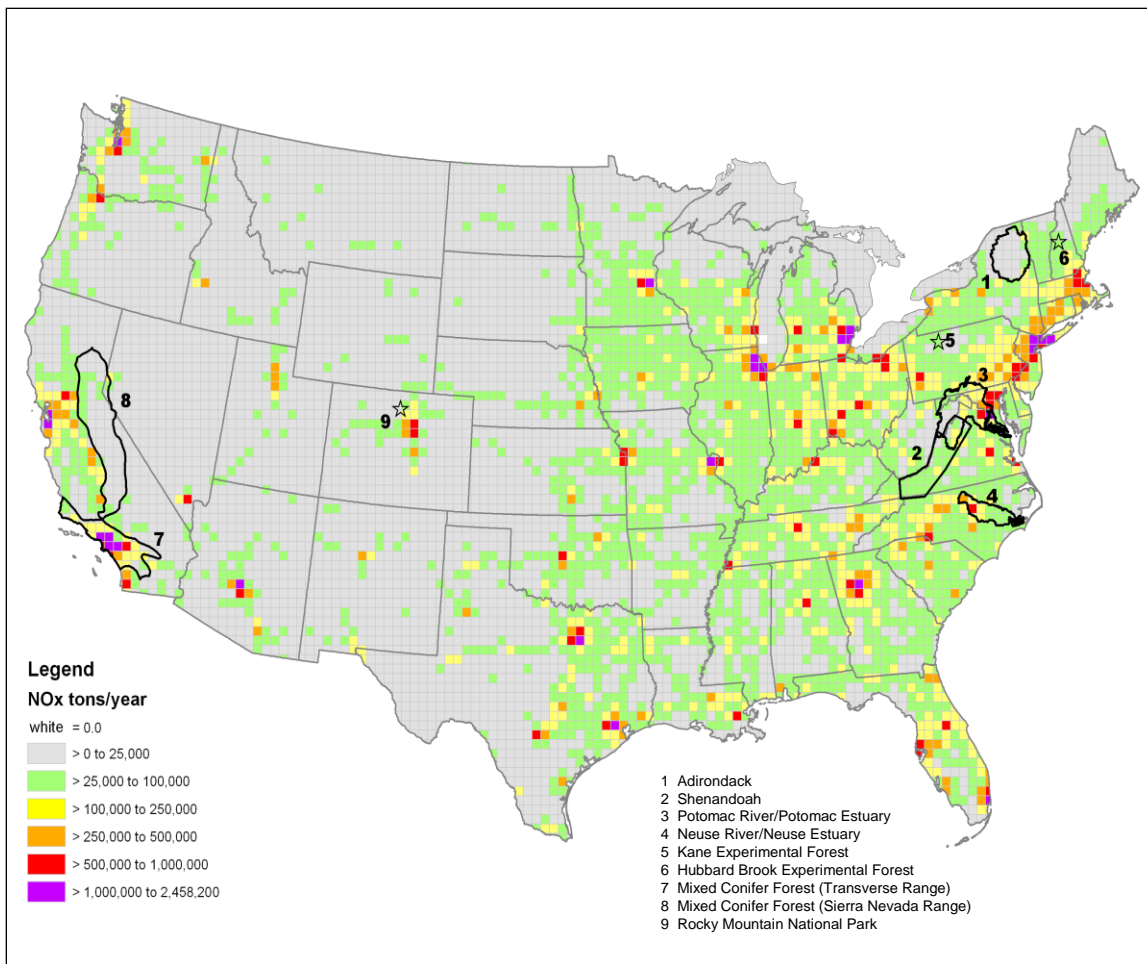


Figure 2-3. Spatial distribution of annual total NO_x emissions (tons/yr) for 2002.

2.1.2 NH₃ Emissions

The primary anthropogenic sources of NH₃ emissions are fertilized soils and livestock. Motor vehicles and stationary combustion are small emitters of NH₃. Some NH₃ is emitted as a byproduct of NO_x reduction in motor vehicle catalysts. The spatial patterns of 2002 annual NH₃ emissions are shown in Figure 2-4⁵. The highest emissions of NH₃ are generally found in areas of major livestock feeding and production facilities, many of which are in rural areas. In addition, NH₃ emissions exceeding 1,000 tons/yr are evident across broad areas that are likely associated with the application of fertilizer to crops. The patterns in NH₃ emissions are in

⁵ Note that, because overall emissions of NH₃ are much lower than emissions of NO_x, we used a more refined set of ranges to display emissions of NH₃ compared to what was used to display emissions of NO_x.

contrast to the more urban-focused emissions of NO_x . The Potomac River/Potomac Estuary, Neuse River/Neuse River Estuary, Shenandoah, and Mixed Conifer Forest (in the Sierra Nevada Range and the Transverse Range) case study areas all have sources with NH_3 emissions exceeding 5,000 tons/yr. Rocky Mountain National Park is adjacent to an area with relatively high NH_3 emissions exceeding 2,500 tons/yr. The Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas are more distant from sources of NH_3 of this magnitude.

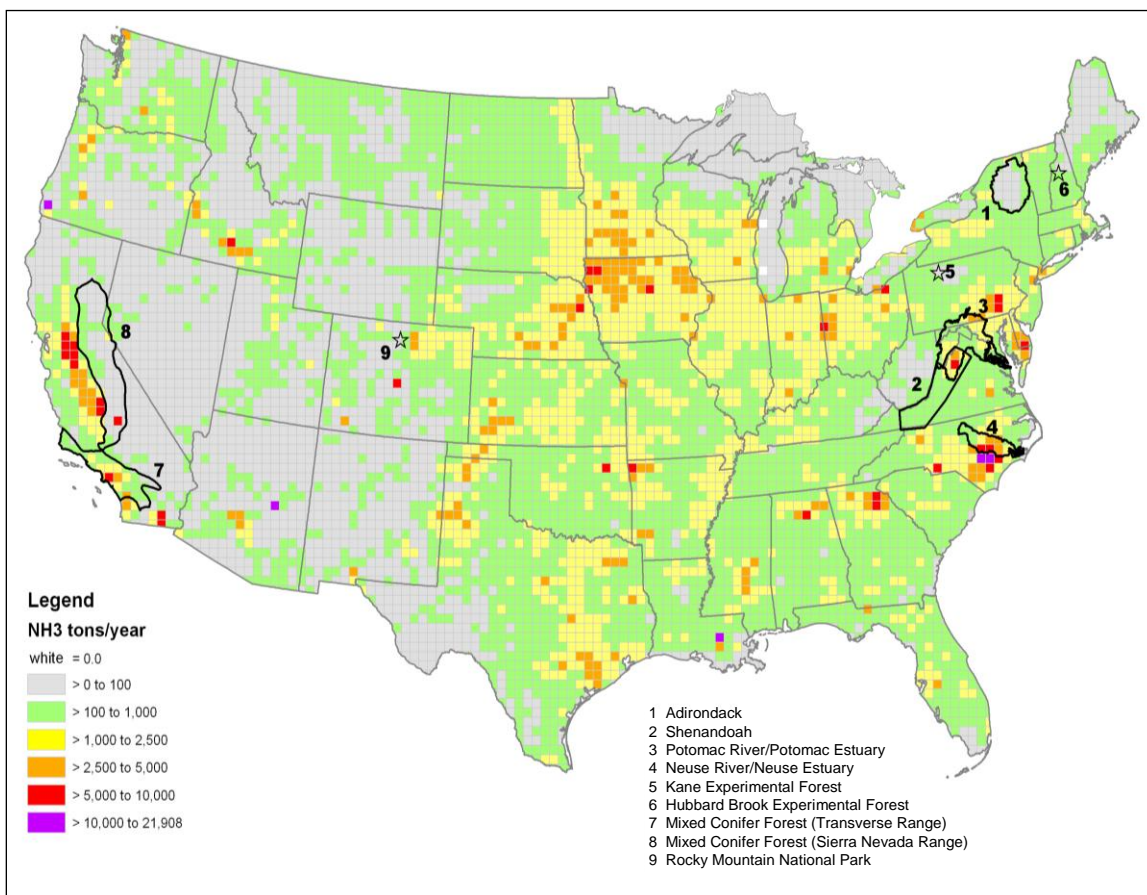


Figure 2-4. Spatial distribution of annual total NH_3 emissions (tons/yr) for 2002.

2.1.3 SO_x Emissions

The distributions of SO_2 emissions for major source categories nationally are provided in Table 2-4. Emissions of SO_2 for the East and West are presented in Tables 2-5 a and b, respectively. Anthropogenic emissions of SO_2 in the United States are mainly due to combustion

of fossil fuels by electrical generation units (70%) and industrial point sources (15%); transportation-related sources contribute minimally (7%). Thus, most SO₂ emissions originate from point sources. Almost all the sulfur in fuel is released as volatile components (SO₂ or SO₃) during combustion. The higher sulfur content of coal compared to other types of fossil fuels results in higher SO₂ emissions from electrical utilities using coal as fuel.

Emissions of SO₂ are more than 10 times greater in the East than in the West. Emissions from electric generation units are the largest contributor to SO₂ emissions in both the East and West, but are a much greater fraction of the inventory in the East (71%) compared to the West (44%). Stationary area sources and the aircraft-locomotive-marine engine sector have a greater relative contribution to SO₂ in the West compared to the East⁶.

The largest natural sources of SO₂ are volcanoes and wildfires. Although SO₂ constitutes a relatively minor fraction (0.005% by volume) of total volcanic emissions (Holland, 1978), concentrations in volcanic plumes can be range up to tens of parts per million (ppm). Sulfur is a component of amino acids in vegetation and is released during combustion. Emissions of SO₂ from burning vegetation are generally in the range of 1% to 2% of the biomass burned (Levine et al., 1999).

⁶ Note that SO₂ emissions from fires are understated in the NEI because of an error in the emissions calculations.

Table 2-4. Annual National SO₂ Emissions across Major Source Categories in 2002.

National Totals	SO₂	
	Emissions (million tons)	Percent of Total
Electric Generation Units	10.359	70%
Industrial Point Sources	2.249	15%
Stationary Area	1.250	8%
On-road	0.242	2%
Nonroad	0.188	1%
Aircraft/Locomotive/Marine	0.533	4%
Fires	0.050	< 1%
Total	14.871	

Table 2-5a. Annual SO₂ Emissions across Major Source Categories in 2002 for the Eastern United States.

Eastern U.S.	SO₂	
	Emissions (million tons)	Percent of Total
Electric Generation Units	9.923	71%
Industrial Point Sources	2.057	15%
Stationary Area	1.116	8%
On-road	0.214	2%
Nonroad	0.162	1%
Aircraft/Locomotive/Marine	0.398	3%
Fires	0.011	< 1%
Total	13.881	

Table 2-5b. Annual SO₂ Emissions across Major Source Categories in 2002 for the Western United States.

Western U.S.	SO ₂	
	Emissions (million tons)	Percent of Total
Electric Generation Units	0.436	44%
Industrial Point Sources	0.192	19%
Stationary Area	0.134	14%
On-road	0.029	3%
Nonroad	0.026	3%
Aircraft/Locomotive/Marine	0.136	14%
Fires	0.035	4%
Total	0.988	

The spatial patterns of 2002 annual SO₂ emissions are shown in Figure 2-5. High SO₂ emissions are scattered across the East, and there are large sources in both urban and rural locations. The greatest geographic concentration of SO₂ sources is in the Midwest, particularly along the Ohio River, where numerous electric generating units are located. As noted above, SO₂ emissions in the West are much lower than in the East, with sources concentrated in urban locations along with localized emissions in more rural areas associated with industrial sources (e.g., smelters) and gas-field operations.

The Potomac River/Potomac Estuary, Neuse River/Neuse River Estuary, Shenandoah, and Mixed Conifer Forest (Transverse Range portion) case study areas each contain numerous locations of major SO₂ emitters. The Kane Experimental Forest Case Study Area and Rocky Mountain National Park are relatively close to SO_x emission locations exceeding 5,000 tons/yr. The Adirondack, Hubbard Brook Experimental Forest, and Mixed Conifer Forest (Sierra Nevada Range portion) case study areas are more distant from SO_x sources of this magnitude.

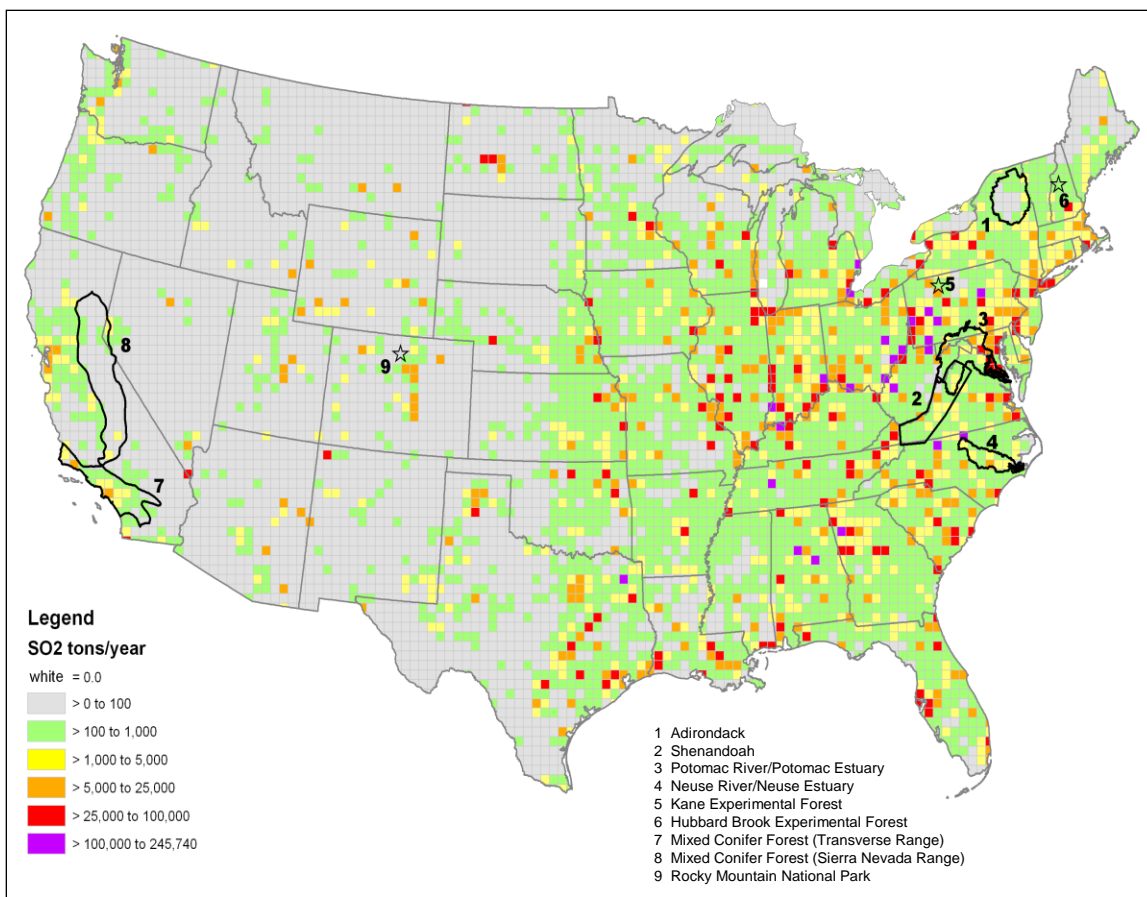


Figure 2-5. Spatial distribution of annual total SO₂ emissions (tons/yr) for 2002.

2.2 AMBIENT AIR CHARACTERIZATION

Characterizing air quality that is relevant to a secondary standard for oxides of nitrogen and sulfur in which effects are transmitted from the air to aquatic systems through deposition should include the species related to oxides of nitrogen and sulfur that have the potential to contribute to aquatic acidification. Because many of the atmospheric species that contribute to acidification are not measured routinely or the monitoring networks have relatively sparse spatial coverage, we take advantage of CMAQ to illustrate patterns of different atmospheric species. For the same reason, we also use CMAQ to characterize deposition, particularly dry deposition.

At certain points in this section, we describe certain basic concepts of air quality, deposition, soils and water chemistry processes to provide the background prior for developing the form of the standard in chapter 7. For example, we start here by defining the relevant species of NO_y and explain why NO_y is relevant to acidification by introducing explaining the

relationship of atmospheric species to equivalent charge, which is fundamental to linking atmospheric and aquatic systems. Also, we separate air quality and deposition in order to provide a more focused discussion on deposition processes and concepts which incorporated in engineering the form of the standard as described in chapter 7.

The key pollutants for this assessment are total oxidized nitrogen (NO_Y), total reduced nitrogen (NH_X), and total oxidized sulfur which is referenced herein as (SO_X) and defined as the sum of SO_2 (gas) and particulate sulfate, as described above. Total reactive oxidized atmospheric nitrogen, NO_Y , is defined as NO_X (NO and NO_2) and all oxidized NO_X products: $\text{NO}_Y = \text{NO}_2 + \text{NO} + \text{HNO}_3 + \text{PAN} + 2\text{N}_2\text{O}_5 + \text{HONO} + \text{NO}_3 + \text{organic nitrates} + \text{particulate NO}_3$ (Finlayson-Pitts and Pitts, 2000). This definition of NO_Y reflects the operational principles of standard measurement techniques in which all oxidized nitrogen species are converted to nitrogen oxide (NO) through catalytic reduction and the resulting NO is detected through luminescence. Thus, NO_Y is truly defined as total oxidized nitrogen as converted to NO , essentially representing all oxidized nitrogen atoms. NO_Y is not a strict representation of the all moles of oxidized nitrogen as the diatomic nitrogen species such as N_2O_5 yield 2 moles of NO . This definition is consistent with the relationship between atmospheric nitrogen and acidification processes as the reported NO_Y provides a direct estimate of the potential equivalents available for acidification. We emphasize NO_Y here as all of the individual NO_Y species are potential contributors to acidic deposition. All NO_Y species are derived directly from NO_X emissions or through atmospheric transformations, thus establishing a direct link to oxides of nitrogen as they are considered listed pollutants in the CAA.

Total reduced nitrogen (NH_X) includes ammonia, NH_3 , plus ammonium, NH_4 (EPA, 2008) is introduced because NH_X contributes potentially acidifying deposition, effectively behaving similarly to NO_Y . While NO_Y is not treated the same way as NO_Y in developing the form, it is incorporated because NH_X can contribute to acidifying deposition. Reduced nitrogen plus oxidized nitrogen is referred to as total reactive nitrogen. Total oxidized sulfur (SO_X) includes SO_2 gas and particulate sulfate, SO_4 . These species are converted to mass of sulfur which is used directly, or converted to charge equivalents, in deposition analyses linking atmospheric deposition and ecosystem models. Ammonium and sulfate are components of atmospheric particulate matter as well as directly measured and modeled in precipitation as direct deposition components.

The term charge equivalents refers to positively charged cations (e.g., Mg^{+2} , Ca^{+2} , H^+ , K^+ , Na^+) or negatively charged anions (NO_3^- , SO_4^{2-} , Cl^- , OH^-) in solution. Any nitrogen atom in the NO_y or NH_x species mix has the potential to provide one negative charge. Effectively, this means that regardless of the specific nitrogen compound structure, the nitrogen atom eventually can be transformed into nitrate, NO_3^- that enters an aquatic system. Similarly, for sulfur any atmospheric sulfur atom has the potential to be transformed into a sulfate ion, SO_4^{2-} , which has an equivalent charge of -2. For convenience, we use NO_3 and SO_4 to represent nitrate and sulfate ion, respectively. One can consider that each atom of sulfur offers twice the acidifying potential of any nitrogen atom. In this sense of recognizing the unique importance of nitrogen and sulfur atoms, there is a direct connection with emissions of oxides of nitrogen or sulfur as described by the CAA. In other words, every atom of emitted nitrogen in NO_x emissions remains in the atmosphere as a component of NO_y , irrespective of whether the species attached to a nitrogen atom is the same as emitted originally, or transformed to another form in the atmosphere.

Further discussion of the processes in the atmosphere and terrestrial and aquatic systems responsible for the transformations of nitrogen and sulfur species to NO_3 and SO_4 are briefly discussed in this section and in appendices where noted.

2.2.1 Air monitoring networks

There are over 1000 ground level monitoring platforms (Figures 2-6 and 2-7 and Table 2-6) that provide measurements of some form of atmospheric nitrogen or sulfur.

Table 2-6. Summary of Monitoring Networks.

Network	Number of Sites	Species Measured	Sampling Frequency	Comments
All Sulfur Sites				
NCore	82	SO ₂	Hourly	Includes 20 rural sites
SEARCH	8	SO ₂	Hourly	Includes 3 rural sites
SO ₂	751	SO ₂	Hourly	NAMS/SLAMS/PAMS for 2008
PM Speciation	242	Sulfates	24-hour	Measurements of Sulfates (88403) identified in AQS for Trends and Supplemental Speciation monitoring type for 2008
IMPROVE	215	Sulfates	24-hour	IMPROVE Monitoring Sites with Measurements of Sulfates (88403) identified in AQS
CASTNET	88	Sulfates	Weekly Ave.	EPA & NPS
All Nitrogen Sites				
NCore	82	NO/NO _y	Hourly	Includes 20 rural sites
SEARCH	8	NO/NO ₂ /NO _y /HNO ₃	Hourly	Includes 3 rural sites
PAMS	119	NO ₂ /NO _x	Hourly	Official sites as of 12/09
SLAMS	643	NO/NO ₂ /NO _x /NO _y	Hourly	All SLAMS Monitoring Sites with Measurements of NO, NO ₂ , NO _x or NO _y in 2009 identified in AQS
NO _y	59	NO _y	Hourly	All Monitoring Sites with Measurements of NO _y in 2009 identified in AQS, regardless of Monitoring Type
IMPROVE	214	Nitrates	24-hour	IMPROVE Monitoring Sites with Measurements of Nitrates (88306) identified in AQS
CASTNET	88	Nitrates	Weekly average	EPA & NPS
AMON	~20	NH ₃	Monthly average	New program component of NADP; passive sampling technique

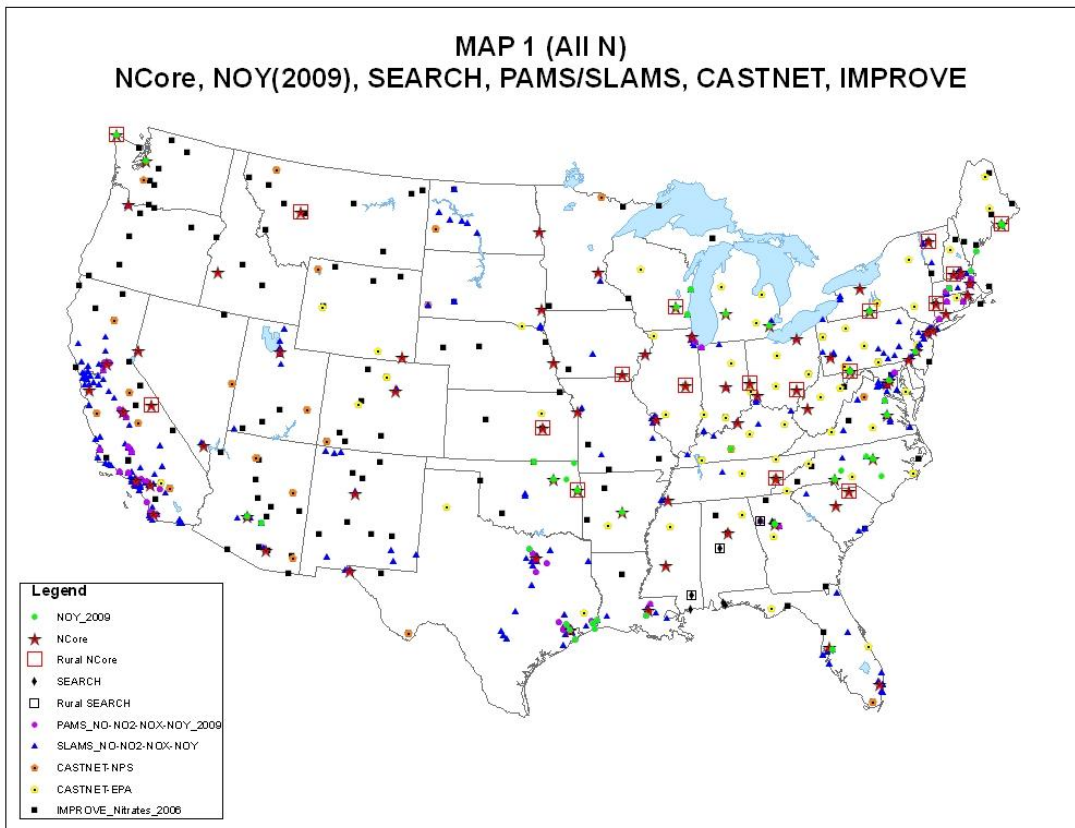


Figure 2-6. Routinely operating surface monitoring stations measuring forms of atmospheric nitrogen.

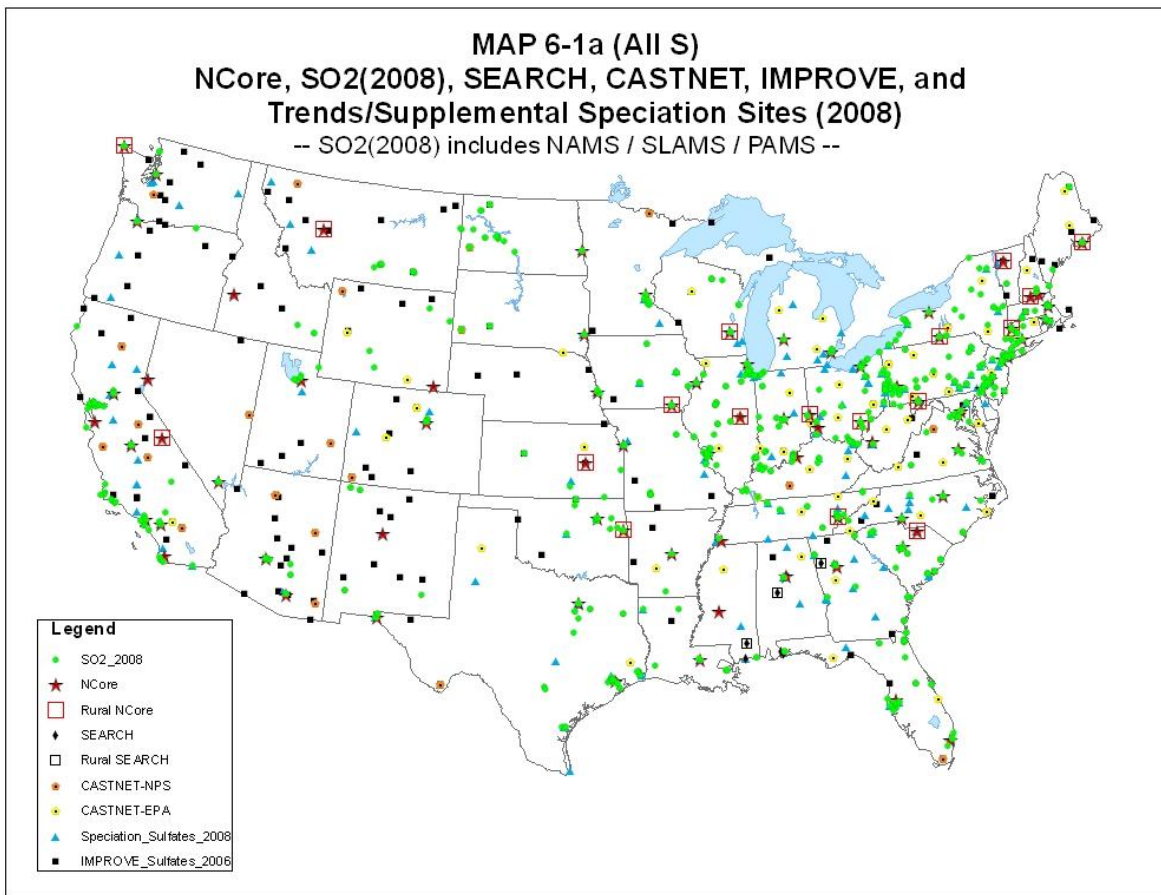


Figure 2-7. Routinely operating surface monitoring stations measuring forms of atmospheric sulfur. All site locations measure both SO₂ and sulfate except for the green SO₂ only sites.

As discussed in this section, there are only very limited routine measurements of total oxidized and reduced nitrogen. In addition, existing monitoring networks do not provide adequate geographic coverage to fully assess concentrations and deposition of reactive nitrogen and sulfur in and near sensitive ecosystems.

The principal monitoring networks include the regulatory based State and Local Air Monitoring Stations (SLAMS) providing mostly urban-based SO₂, NO and NO_x, the PM_{2.5} chemical speciation networks Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA's Chemical Speciation Network (CSN) providing particle bound sulfate and nitrate, and the Clean Air Status and Trends Network (CASTNET) providing weekly averaged values of SO₂, nitric acid, and particle bound sulfate, nitrate and ammonium. The private sector supported South Eastern Aerosol Research and Characterization (SEARCH) Study network of 4-8 sites in the Southeast provides the only routinely operating source of true continuous NO₂, ammonia, and nitric acid measurements. SEARCH also provides PM_{2.5} size fractions of nitrate and sulfate. Collectively, the SLAMS, Photochemical Assessment Measurement Stations (PAMS), SEARCH and NCore networks will provide over 100 sites measuring NO_y (Figure 2-8). The NCore network (Scheffe et al., 2009) is a multiple pollutant network with co-located measurements of key trace gases (CO, SO₂, O₃, NO and NO_y), PM_{2.5} and PM_(10-2.5) mass and PM_{2.5} chemical speciation. Additional air pollutants, particularly volatile organic compounds (VOCs), will be measured at those sites that are part of the existing PAMS and National Air Toxics Trends (NATTS) platforms. The NATTS (EPA, 2008) include 27 stations across the U.S. that monitor for a variety of hazardous air pollutants and are intended to remain in place to provide a long-term record. Additional measurements of ammonia and possibly true NO₂ are under consideration. True NO₂ is noted to differentiate from the NO₂ determined through routine regulatory networks that have known variable positive bias for NO₂.

The network currently is being deployed and expected to be operational with nearly 75 sites by January 2011. The sites are intended to serve as central site monitors capturing broadly representative (e.g., not strongly influenced by nearby sources) air quality in a suite of major and mid size cities and approximately 20 sites are located in rural locations.

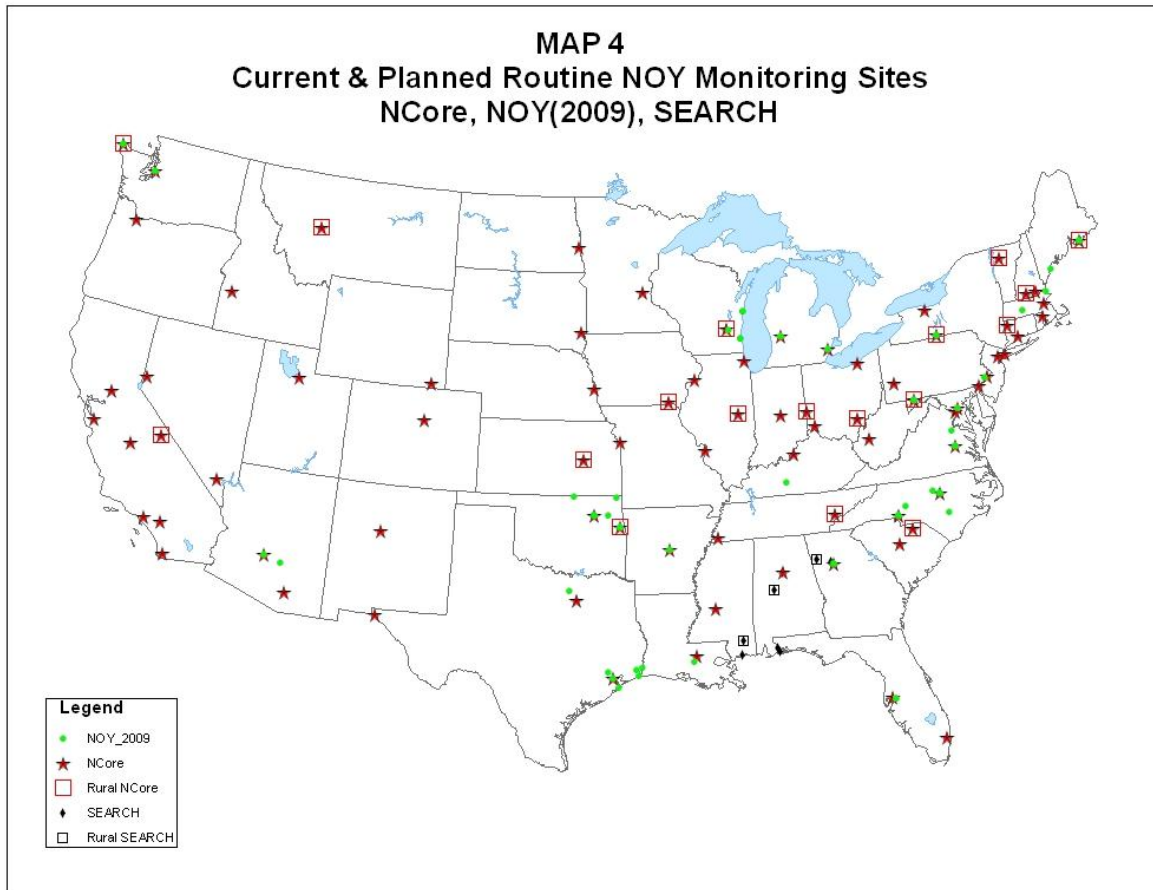


Figure 2-8. Anticipated network of surface based NO_Y stations based on 2009 network design plans. The NCore stations are scheduled to be operating by January, 2011.

There are significant measurement gaps for characterizing NO_Y, NH_X and SO₂ in the nations ambient air observation networks (EPA, 2008) that lead to greater reliance on air quality modeling simulations to describe current conditions. National design of routinely operating ambient air monitoring networks is driven mostly by data uses associated with implementing primary NAAQS, with noted exceptions of the CASTNET and IMPROVE networks. In addition to significant spatial gaps in sensitive ecosystem areas that arise from a population oriented network design, the current measurements for primary and secondary nitrogen are markedly different and in some instances of negligible value for secondary NO_X and SO_X standards. For example, a true NO_X (NO plus NO₂) measurement typically would capture less than 50% (see discussion below) of the total regional NO_Y mass in rural locations as the more aged air masses contain significant oxidized nitrogen products in addition to NO_X. With the

exception of the SEARCH network in the Southeast, there have been virtually no routine networks that measure ammonia until the recent addition of the AMON passive ammonia sampling network (Figure 2-9) as part of the NADP. EPA is considering adopting the AMON passive sampling techniques and other ammonia sampling options in the NCORE network. Ammonium is reported in EPA chemical speciation networks, although the values are believed to be biased low due to ammonia volatilization.

CASTNET provides mostly rural measurements of SO₂, total nitrate, and ammonium, and affords an existing infrastructure useful for future monitoring in support of a potential NO_x and SO_x secondary standard. However, the lack of NO_y, SO_x and NH_x measurements in sensitive ecosystems will require attention in conjunction with any rulemaking for a secondary standard for oxides of nitrogen and sulfur.

As a result of the limited monitoring networks for NO_y and SO_x in sensitive ecosystems, we are unable to use current ambient monitoring data to adequately link measured current atmospheric concentrations to ecological effects transmitted through deposition. At this time for the purpose of illustrating current atmospheric conditions, we supplement the available monitoring data with the use of sophisticated atmospheric modeling conducted using EPA's CMAQ model (as discussed in chapter 7).

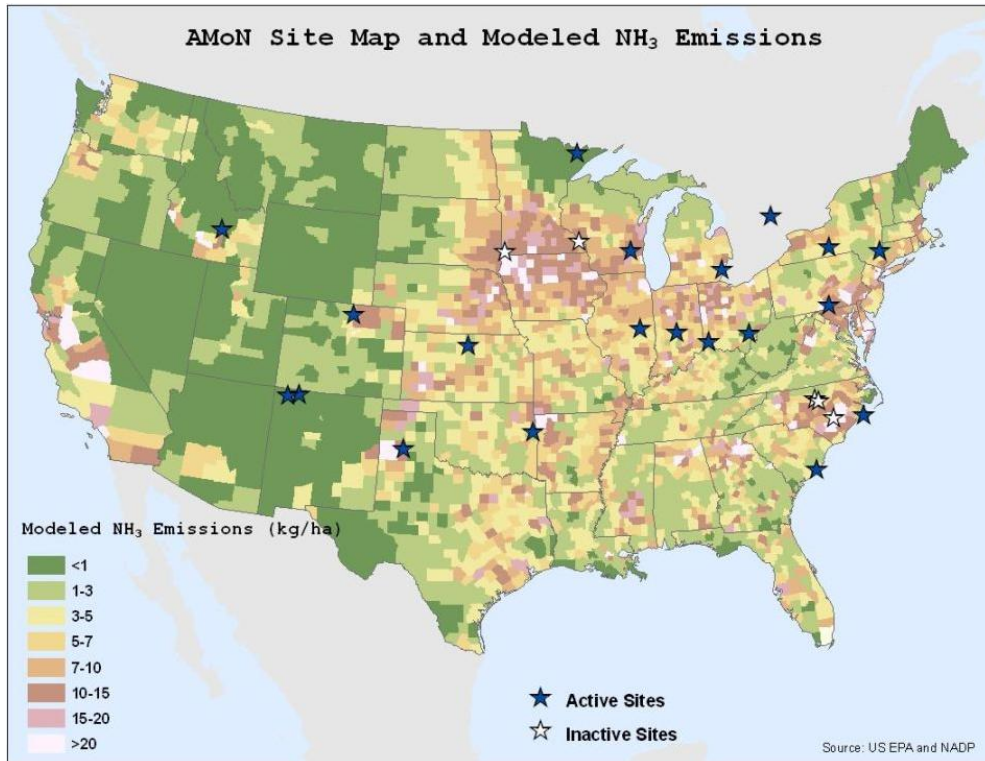


Figure 2-9. Location of NADP passive ammonia sampling locations for the AMON network (<http://nadp.sws.uiuc.edu/nh3net/>).

Of the currently operating monitoring networks, precipitation based sulfate, ammonium and nitrate measurements provided by the NADP are the most relevant measurements that would support the secondary standard as they provide atmospheric deposition inputs that drive ecosystem models, and NADP site locations generally include acid sensitive areas. However, there are significant gaps in ambient air (aerosols and gases) monitoring networks for the measurement of the likely ambient indicators of NO_Y , SO_2 , and SO_4 . CASTNET filter packs provide the most relevant source of ambient sulfate (SO_4) measurements as the open inlet of the filter packs incorporates the full range of particle sizes that contribute to deposition. The SO_2 measurements from CASTNET represent about 10% of all SO_2 sites nationally, but are especially relevant based on their locations in rural and regional settings, although CASTNET is not as spatially extensive (breadth and resolution) as the NADP network of precipitation sites. Although CASTNET does provide measurements of total ambient nitrate, other oxidized nitrogen species constituting a more complete NO_Y budget are not captured. In their current configuration, the State and local monitoring networks offer virtually no support for a secondary

standard for oxides of nitrogen and sulfur due to their urban-based site orientation and exclusion of important oxidized nitrogen species (e.g., nitrates and PAN). The chemical speciation networks, including rural based IMPROVE, all provide ambient sulfate measurements based on a 2.5 μ size cut. While the sulfate mass within that size fraction may constitute 80% or greater of the ambient sulfate budget, the missing larger size particles can contribute significantly to sulfate deposition due to their relatively high gravitationally driven deposition velocities. Finally, there are virtually no ambient ammonia measurements routinely collected in acid sensitive areas. CASTNET does provide ammonium measurements, but the routine speciation networks that report ammonium have expected artifacts due to ammonia off-gassing from nylon filters.

Although this summary of existing networks suggests significant challenges in meeting the monitoring needs of a new standard for oxides of nitrogen and sulfur, the networks do serve as a useful building block for moving forward. The site locations of NADP and CASTNET offer an infrastructure to accommodate additional instruments. The NCORE network has introduced nearly 75 NO_y trace level SO₂ monitors that are establishing operational familiarity and a basis for instrument performance characterization. In many cases, acid sensitive areas will be strongly influenced by regional transport of pollutants which typically is associated with relatively homogeneous spatial concentration patterns which allows for a correspondingly greater range of spatial representativeness of monitoring sites. Consequently, the expected burden on monitoring resources may be realistically dampened by the available infrastructure and expected homogeneity of air concentration patterns. A more thorough assessment of the adequacy of existing networks is predicated on identification of the area wide boundaries of the acid sensitive areas of concern which will initially be developed in the second PAD.

2.2.2 Overview of CMAQ

The Community Multiscale Air Quality (CMAQ) model was used to characterize air quality and deposition. CMAQ simulates the numerous physical and chemical processes involved in the formation, transport, and destruction of ozone, particulate matter and air toxics. In addition to the CMAQ model, the modeling platform includes the emissions, meteorology, and initial and boundary condition data which are inputs to this model.

The 2005-based CMAQ modeling platform was used as the basis for national maps of air quality and deposition reflect 2005 year meteorology and emissions. An emissions sensitivity

simulation with domain reductions of 48 and 42 % for NO_x and SO_x, respectively, was used to explore the behavior of the form of the standard to potential future changes in air quality associated with potential changes in emissions, and those results are discussed in chapter 7 and Appendix E. This platform represents a structured system of connected modeling-related tools and data that provide a consistent and transparent basis for assessing the air quality response to projected changes in emissions. The platform was developed by the EPA's Office of Air Quality Planning and Standards in collaboration with the Office of Research and Development and is intended to support a variety of regulatory and research model applications and analyses.

The CMAQ model is a comprehensive, peer-reviewed, three-dimensional grid-based Eulerian air quality model designed to simulate the formation and fate of gaseous and particle (i.e., particulate matter or PM) species, including ozone, oxidant precursors, and primary and secondary PM concentrations and sulfur and nitrogen deposition over urban, regional, and larger spatial scales (Byun and Schere, 2006). CMAQ is run for user-defined input sets of meteorological conditions and emissions.

Additional details of the modeling domain, emissions and meteorological inputs are provided in EPA (2009; REA Appendices).

Model domain and grid resolution.

CMAQ modeling analyses were performed for a domain covering the continental United States, as shown in Figure 2-10 and Table 2-7. This domain has a parent horizontal grid of 36 km with two finer-scale 12 km grids over portions of the eastern and western U.S. The model extends vertically from the surface to 100 millibars (approximately 15 km) using a sigma-pressure coordinate system. Air quality conditions at the outer boundary of the 36 km domain were taken from a global model and did not change over the simulations. In turn, the 36 km grid was only used to establish the incoming air quality concentrations along the boundaries of the 12 km grids. Table 2-7 provides some basic geographic information regarding the CMAQ domains.

Table 2-7. Geographic elements of domains used in RFS2 modeling.

	CMAQ Modeling Configuration		
	National Grid	Western U.S. Fine Grid	Eastern U.S. Fine Grid
Map Projection	Lambert Conformal Projection		
Grid Resolution	36 km	12 km	12 km
Coordinate Center	97 deg W, 40 deg N		
True Latitudes	33 deg N and 45 deg N		
Dimensions	148 x 112 x 14	213 x 192 x 14	279 x 240 x 14
Vertical extent	14 Layers: Surface to 100 millibar level (see Table II-3)		

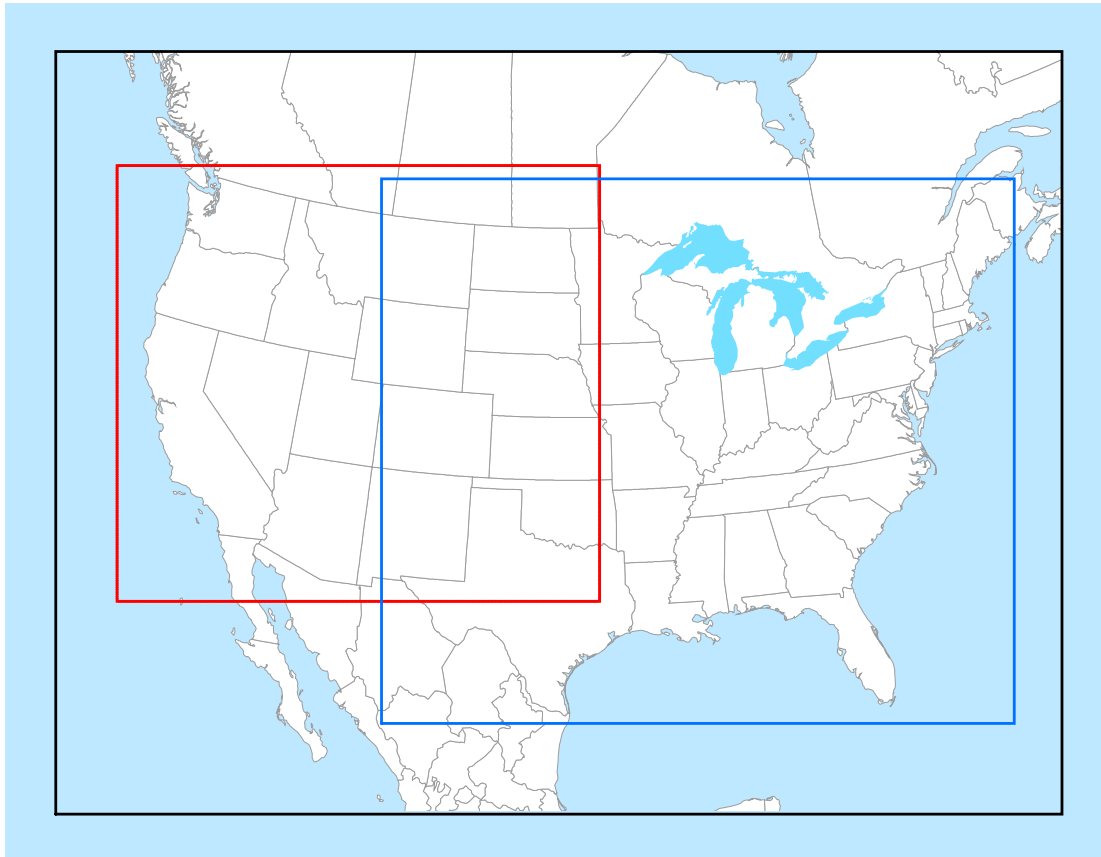


Figure 2-10. Map of the CMAQ modeling domain. The black outer box denotes the 36 km national modeling domain; the red inner box is the 12 km western U.S. fine grid; and the blue inner box is the 12 km eastern U.S. fine grid.

2.2.3 Overview of air quality using modeled and observed data

To provide information for use in characterizing the adequacy of the current standards, we assess the best available data for estimating the ambient concentrations of atmospheric nitrogen and sulfur across the U.S. Acidification and nutrient enrichment processes are largely dependent on the cycling of total nitrogen and sulfur species. From an atmospheric perspective, it is convenient and consistent with current measurement and modeling frameworks to consider the reduced and oxidized forms of atmospheric nitrogen. Virtually all atmospheric sulfur is considered oxidized sulfur in the forms of particulate bound sulfate and gaseous sulfur dioxide. In order to assess current concentrations of reactive nitrogen and sulfur, we evaluated data available from the existing monitoring networks as well as from the CMAQ model. Regarding the monitoring data, there are a number of important issues in understanding the measurements of NO_Y provided by different monitoring networks. In principle, measured NO_Y is based on catalytic conversion of all oxidized species to NO followed by chemiluminescence NO detection. We recognize the caveats associated with instrument conversion efficiency and possible inlet losses. The CMAQ treats the dominant NO_Y species as explicit species while the minor contributing non-PAN organic nitrogen compounds are aggregated. Atmospheric nitrogen and sulfur largely are viewed as regional air quality issues due to the importance of chemical conversion of primary emissions into secondarily formed species, a combination of ubiquitous sources, particularly mobile source emissions of NO_X , and elevated emissions of NO_X and SO_2 that aid pollutant mass dispersal and broader physical transport over large distances. In effect, the regional nature is due to both transport processes as well as the relatively ubiquitous nature of sources combined with chemical processes that tend to form more stable species with extended atmospheric lifetimes. This regionalized effect, particularly throughout the eastern United States, dominates the overall patterns discussed below of secondarily formed species such as sulfate or NO_Y , which is an aggregate of species with the more aged air masses consisting largely of chemically processed air dominated by secondarily formed peroxyacetyl nitrate (PAN), particulate nitrate and nitric acid.

Nationwide maps of CMAQ-predicted 2005 annual average NO_Y , NH_X (NH_3 and NH_4), NH_3 , NH_4 , SO_X , SO_4 , and SO_2 are provided in Figures 2-11 through 2-17 respectively. Given the considerable gaps in air quality observation networks as discussed in the REA and ISA (EPA, 2008), modeled concentration patterns are used here to illustrate national representations of

current air quality conditions for nitrogen and sulfur. The 2005 model year reflects the most recent available simulation for inclusion in this policy assessment. In addition, Figures 2-18 and 2-19 provide maps of 2005 annual average SO_2 and SO_4 , respectively based on CASTNET observations. Site specific annual average 2005 NO_Y measured concentrations at SLAMS (Figure 2-20) are typically are less than 40 ppb. The spatial patterns for the 2005 modeled and observed NO_Y , NH_x , and SO_2 concentrations are similar to the 2002 CMAQ-based maps provided in the REA, largely capturing the influence of major emissions patterns (Figures 2-2 – 2-4) throughout the nation. The NO_Y patterns (Figure 2-11) reflect the distribution of NO_x emissions power generation and widely dispersed transportation sources with a spreading into more rural locations associated with transformation of NO_x to more aged NO_Y species such as PAN and nitric acid, discussed in more detail in section 2-3. Ammonia and ammonium concentration patterns (Figures 2-13 – 2-14) are influenced strongly by the ammonia emissions distribution, with marginal spreading associated with the formation of NH_4 . The NH_x fields are more strongly influenced by source location, relative to sulfur, based on the fast removal of atmospheric ammonia through deposition. However, recent incorporation of ammonia bi-directional flux treatment (Appendix F) does reduce NH_3 spatial gradients. A spreading of the oxidized sulfur fields (Figures 2-15 to 2-17), relative to SO_2 , is consistent with sulfate transformation and associated air mass aging and transport. Note that SO_2 is the dominant contributing species in the mix of SO_2 and particulate SO_4 with the most elevated levels in proximity to the Ohio River valley.

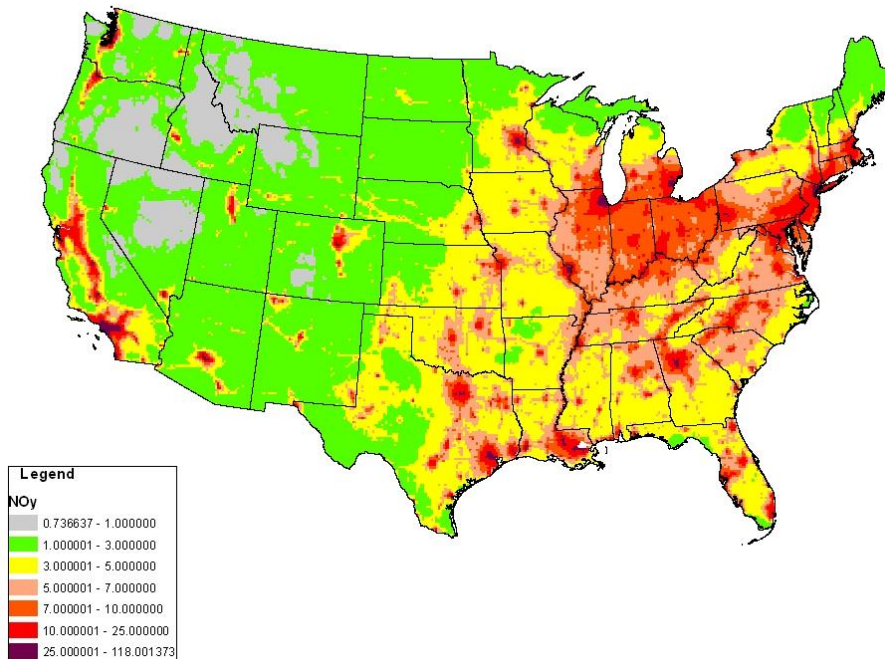


Figure 2-11. 2005 CMAQ modeled annual average NO_y (ppb; see Table 2-1 for unit conversions).

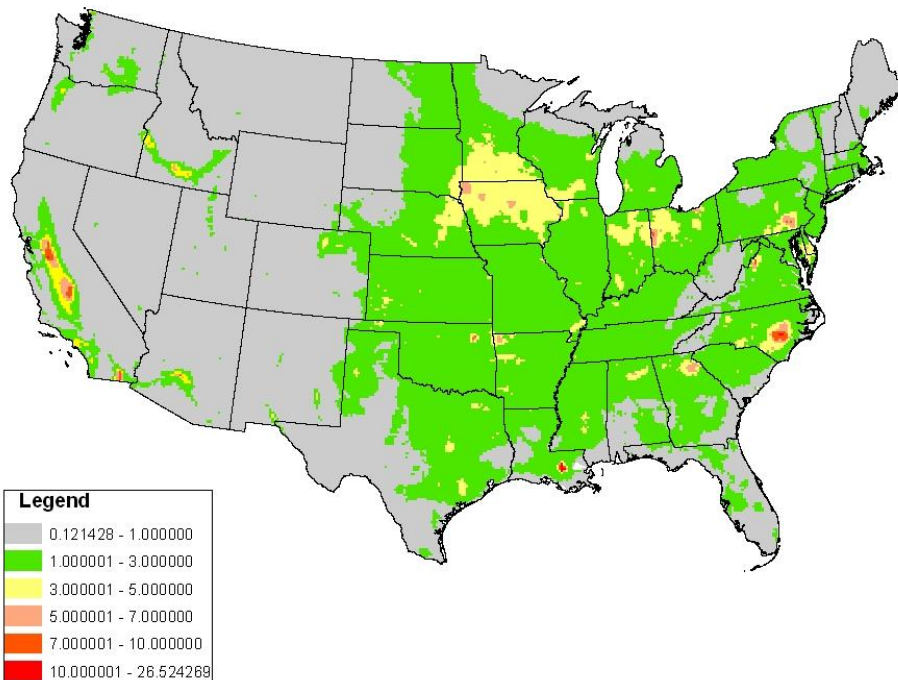


Figure 2-12. 2005 CMAQ modeled annual average total reduced nitrogen (NH_x) (as ug/m³ nitrogen – see Table 2-1 for unit conversions).

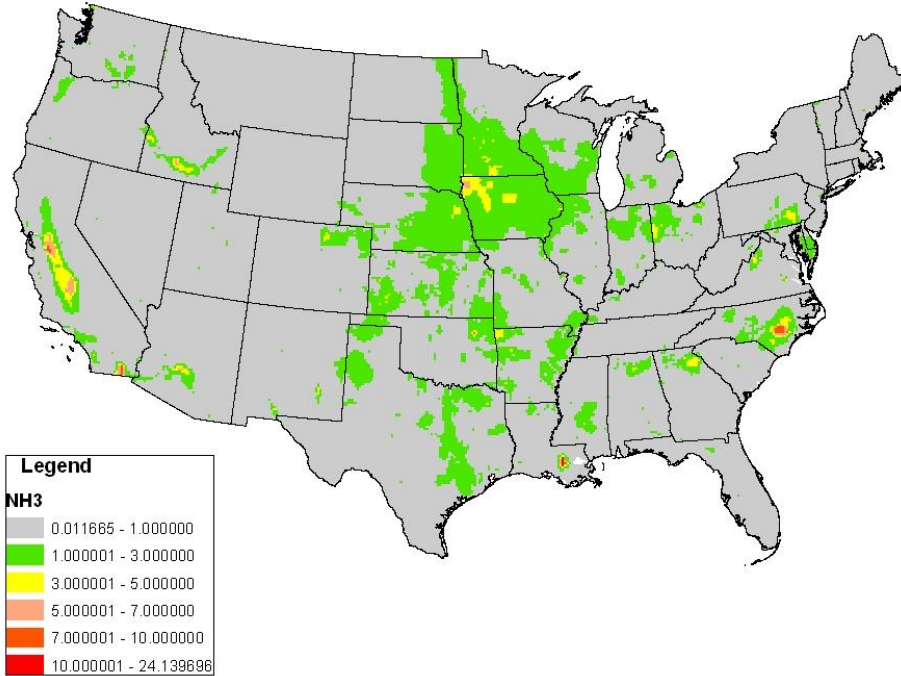


Figure 2-13. 2005 CMAQ modeled annual average total reduced nitrogen (NH₃) (as ug/m³ nitrogen – see Table 2-1 for unit conversions).

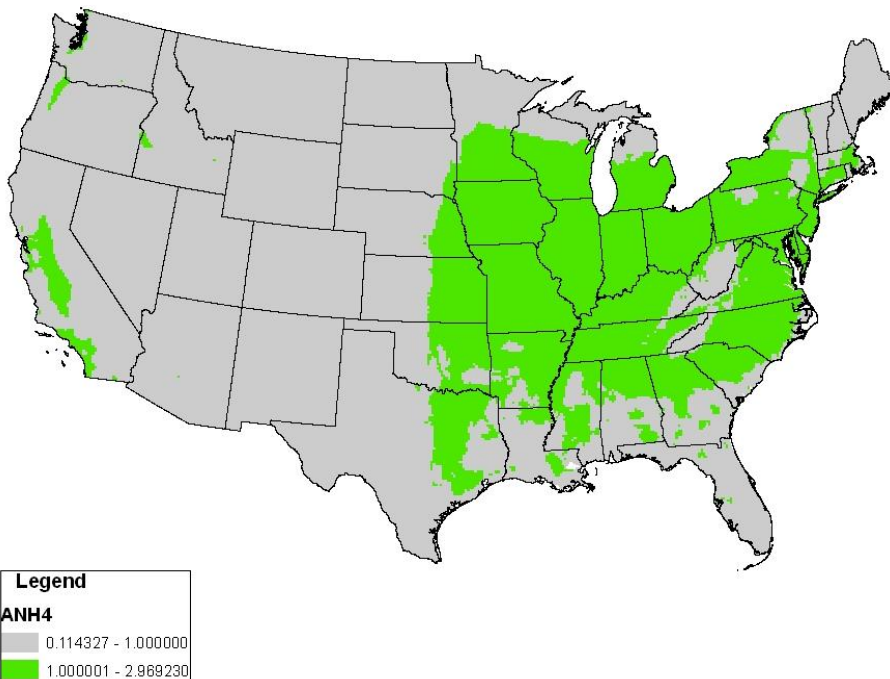


Figure 2-14. 2005 CMAQ modeled annual average ammonium, NH₄, (as ug/m³ N; see Table 2-1 for unit conversions).

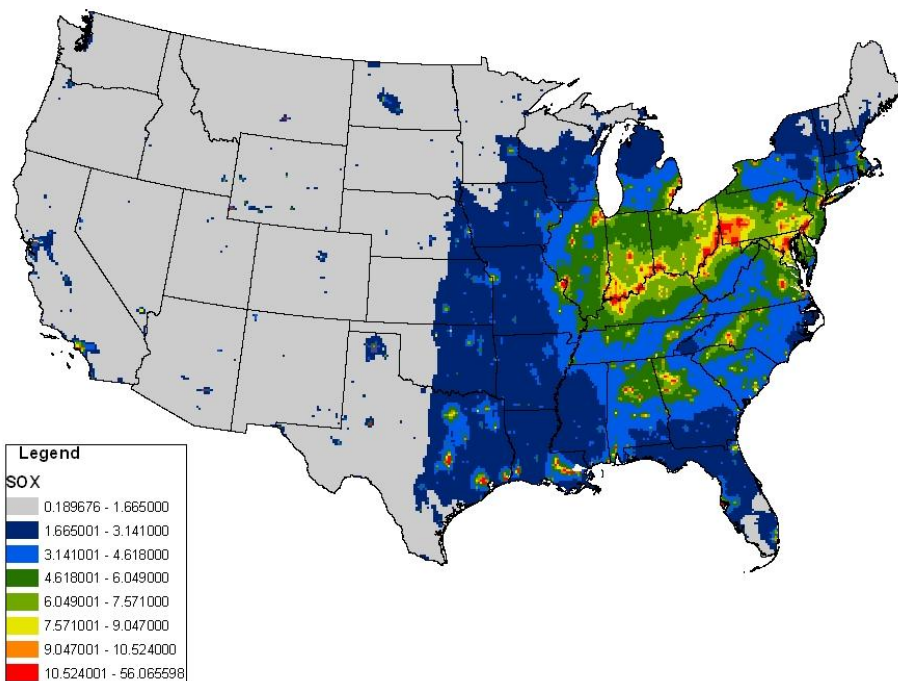


Figure 2-15. 2005 CMAQ modeled annual average SO_x, (as ug/m³ S from SO₂ and SO₄; see Table 2-1 for unit conversions).

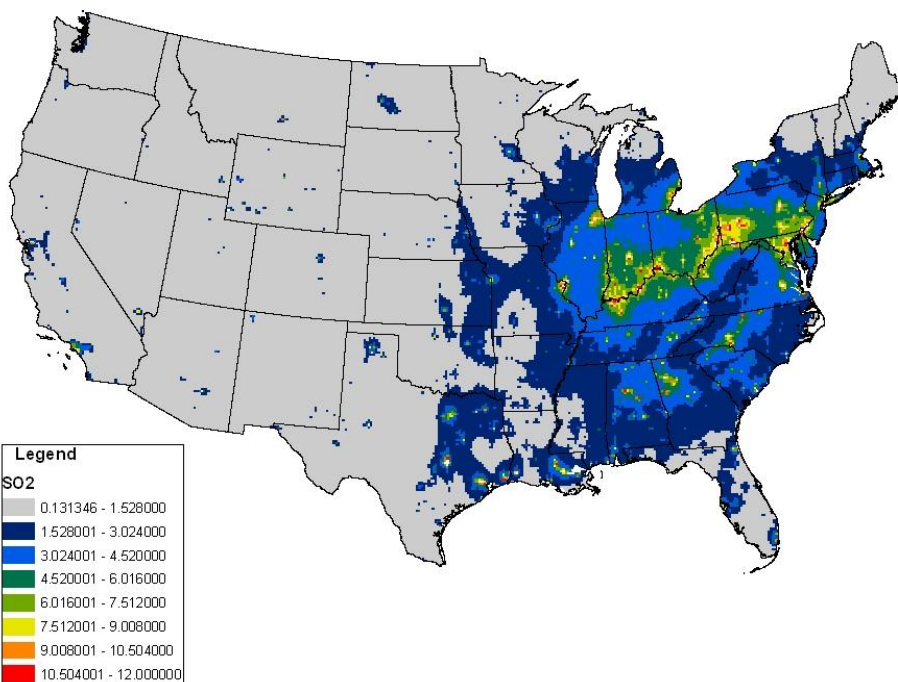


Figure 2-16. 2005 CMAQ modeled annual average SO₂ (as ug/m³ S; see Table 2-1 for unit conversions).

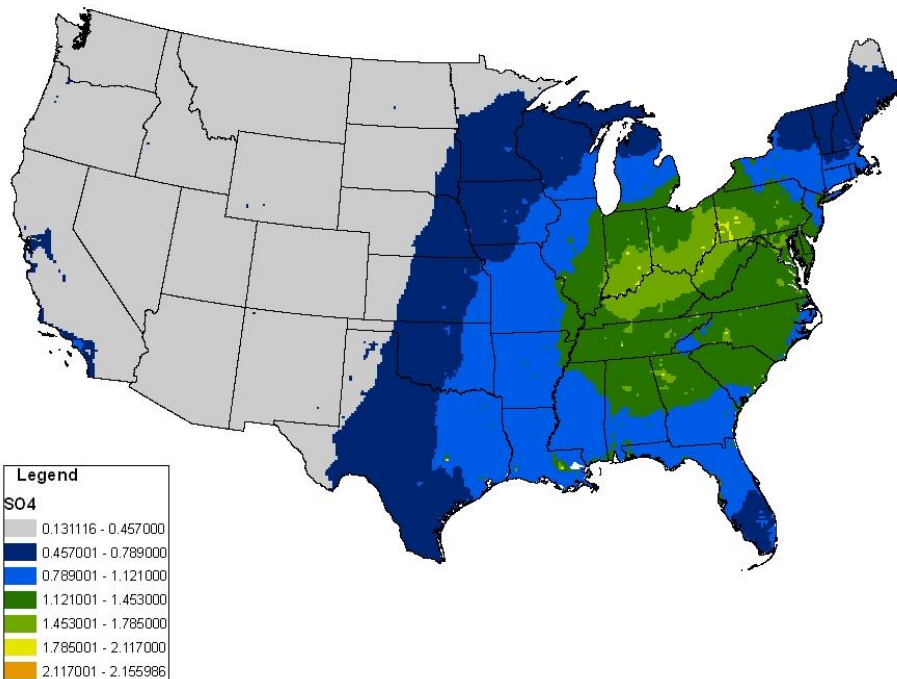


Figure 2-17. 2005 CMAQ modeled annual average SO₄ (as ug/m³ S; see Table 2-1 for unit conversions).

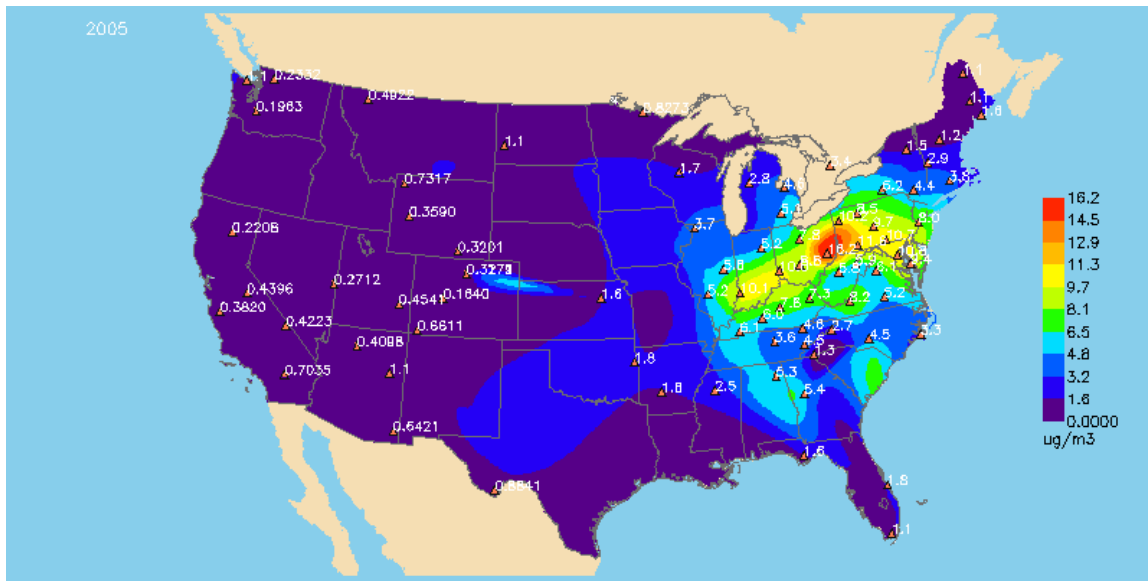


Figure 2-18. 2005 annual average sulfur dioxide concentrations (total mass) based on CASTNET generated by the Visibility Information Exchange Web System (VIEWS) (see Table 2-1 for unit conversions).

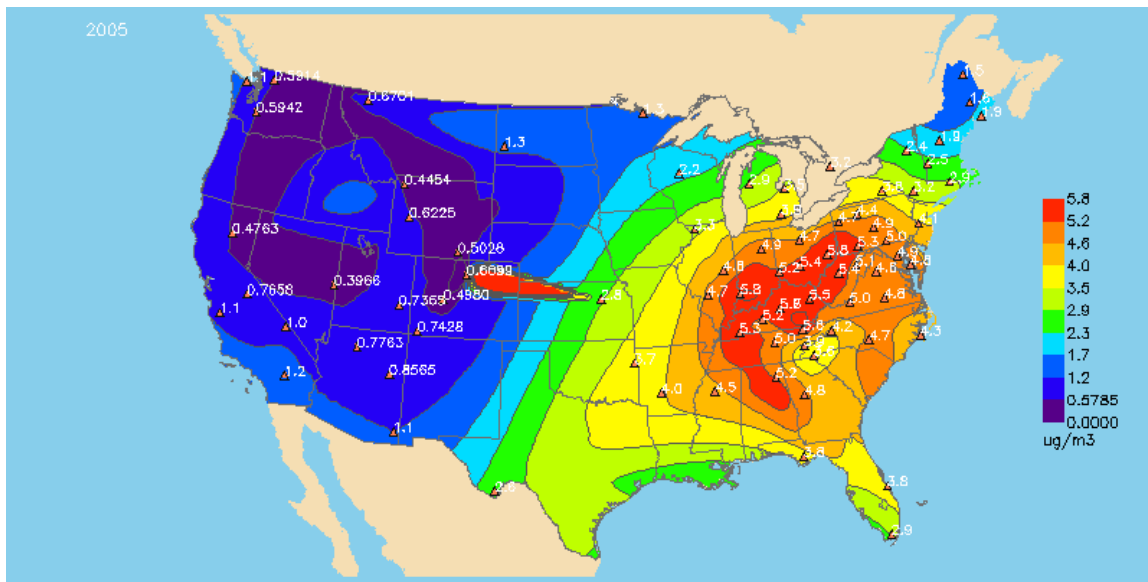


Figure 2-19. 2005 annual average sulfate concentrations (total mass) based on CASTNET generated by the Visibility Information Exchange Web System (VIEWS). [interpolating relative sparse data can produce unrealistic concentration plumes as demonstrated in the central U.S.] (see Table 2-1 for unit conversions).

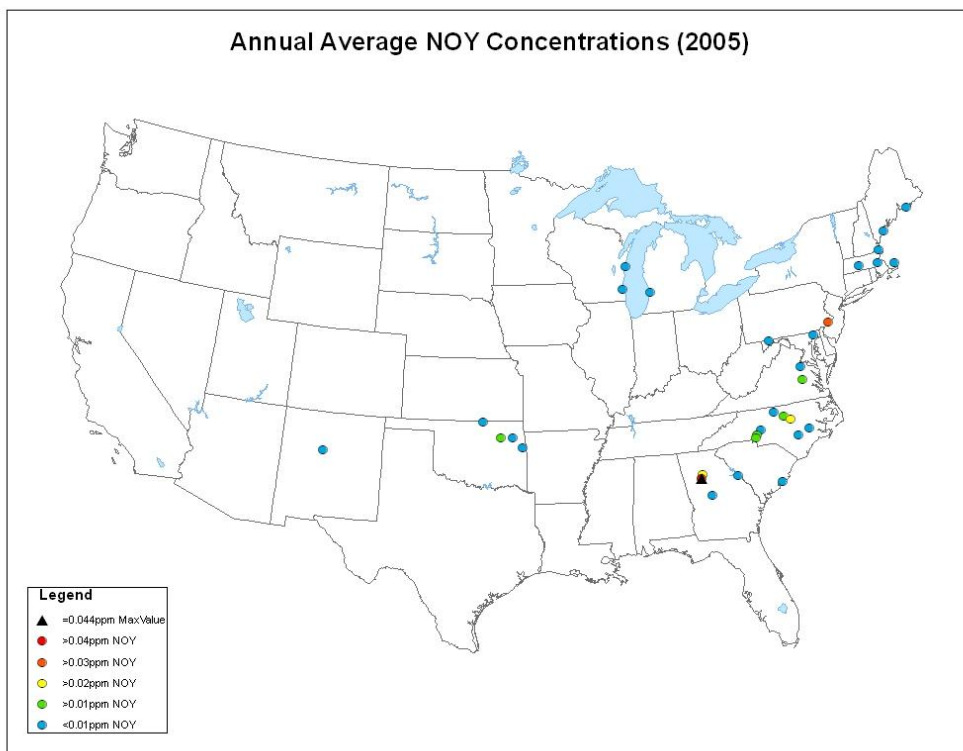


Figure 2-20. Annual average 2005 NO_Y concentrations from reporting stations in the Air Quality System (AQS). (see Table 2-1 for unit conversions).

2.3 CHARACTERIZING DEPOSITION THROUGH MONITORING AND MODELS

The removal of sulfur and nitrogen from the ambient air environments occurs through wet and dry deposition processes. Wet deposition results from the transfer of gaseous and particulate species into cloud droplets and their subsequent deposition as well direct scavenging by rain and snow. There also is deposition associated with direct contact between clouds, fog and surfaces, referred to as occult deposition. Occult deposition is not treated explicitly in air quality models like CMAQ and generally is assumed to be negligible with respect to contributions to annual average total deposition, although occult deposition can provide relatively greater contribution over shorter, episodic time frames. Dry deposition is the removal of gases and particles from the air to surfaces, vegetation and water. The collection of rainwater followed by chemical analysis enables direct observation of wet deposition. Dry deposition is not a directly measured variable in routine monitoring efforts. It is important to pursue the development of direct dry deposition measurements to improve model parameterizations of deposition processes and possibly evolve into routine operations. Estimates of dry deposition based on observations are provided through the CASTNET program. However, dry deposition is a calculated value represented as the product of ambient concentration (either observed or estimated through air quality modeling) and deposition velocity, $Dep_i^{Dry} = v_i^{Dry} \cdot C_i^{Amb}$

Deposition velocity is modeled as a mass transfer process through resistance layers associated with the canopy, uptake by vegetation, water and soil which collectively are influenced by micrometeorology, land surface and vegetation types and species specific solubility and reactivity. Dry deposition is calculated through deposition velocity models capturing these features and using species specific ambient air concentrations. This approach conceptually is similar using either observed or modeled air concentrations. Dry deposition estimates from the Community Multi-scale Air Quality (CMAQ) model have been used in this assessment to provide spatially more resolved and extensive estimates of dry deposition for sulfur and all reactive nitrogen (oxidized and reduced) species (CASTNET does not capture important gases such as nitrogen dioxide, ammonia and peroxyacetyl nitrate (PAN). All of the relevant meteorological, land use, vegetation and elevation data required to estimate deposition velocities are generated or accessible in the CMAQ and/or meteorological pre-processors.

CMAQ provides a platform that allows for a consistent mass accounting approach across ambient concentrations and dry and wet deposition values. Recognizing the limitations of ambient air networks, CMAQ was used to estimate dry deposition to complement NADP wet deposition for MAGIC modeling and for the first-order acidity balance (FAB) critical load modeling. CMAQ promotes analytical consistency and efficiency across analyses of multiple pollutants. EPA's Office of Research and Development continues to enhance the underlying deposition science in CMAQ. For the purposes of this policy assessment, CMAQ provides a consistent platform incorporating the atmospheric and deposition species of interest over the entire United States. The caveats and limitations of the use of model predictions are largely associated with the general reliance on calculated values, rather than on measurements. Model evaluation addressing the comparison of predictions with observed values is addressed in the REA and summarized in Appendix F as well as a summary of ongoing and planned model improvements.

CMAQ provides both concentrations and depositions for a large suite of pollutant species on an hourly basis for 12 km grids across the continental U.S. Deposition velocities are treated by:

1) v^{dry} values of gaseous pollutants are calculated in the CMAQ weather module called the Meteorology-Chemistry Interface Processor (MCIP) through a complex function of meteorological parameters (e.g. temperature, relative humidity) and properties of the geographic surface (e.g. leaf area index, surface wetness)

2) v^{dry} values for particulate pollutants are calculated in the aerosol module of CMAQ, which, in addition to the parameters needed for the gaseous calculations, also accounts for properties of the aerosol size distribution

3) v^{wet} values are not explicitly calculated. Wet deposition is derived from the cloud processing module of CMAQ, which performs simulations of mass transfer into cloud droplets and aqueous chemistry to incorporate pollutants into rainwater.

Due to lack of direct measurements, no performance evaluations of CMAQ's dry deposition calculations can be found; however, the current state of MCIP is the product of research that has been based on peer-reviewed literature from the past two decades (EPA, 1999) and is considered to be EPA's best estimate of dry deposition velocities. Although the model is continually undergoing improvement, CMAQ is EPA's state-of-the-science computational

framework for calculating deposition. The CMAQ was used in this assessment because it is the state of science model for simulating sources, formation, and fate of nitrogen and sulfur species. In addition to undergoing periodic independent scientific peer review, CMAQ bridges the scientific and regulatory communities as it is used extensively by EPA for regulatory air quality assessments and rules. CMAQ provides hourly estimates of the important precursor, intermediate and secondarily formed species associated with atmospheric chemistry and deposition processes influencing ozone, particulate matter concentrations and sulfur and nitrogen deposition. Simulations based on horizontal spatial scale resolutions of 12 km and 36 km were used in this policy assessment for 2002 – 2005.

2.3.1 Current patterns of dry and wet deposition

The National Atmospheric Deposition Program (NADP) includes approximately 250 sites (Figure 2-21) across the U.S. providing annual total wet deposition based on weekly averaged measures of wet deposition of nitrate, ammonium, sulfate and other ions based on the concentrations of these ions in precipitation samples. Meteorological models have difficulty in capturing the correct spatial and temporal features of precipitation events, raising the importance of the NADP as a principal source of precipitation chemistry. The NADP has enabled several organizations to participate in a measurement program with a centralized laboratory affording measurement and analysis protocol consistency nationwide. Virtually every CASTNET site is located at an NADP site and the combined NADP/CASTNET infrastructure is a starting point for discussions addressing future NO_x and SO_x monitoring needs. Analysis of organic bound nitrogen recently has been added to the NADP suite of parameters. Consideration might be given to adding NADP sites in locations where ambient air monitoring is conducted to assess compliance with a secondary NO_x / SO_x standard. For consistency, we use CMAQ developed national maps of total deposition. Additional NADP maps of wet deposition are available at <http://nadp.sws.uiuc.edu/>.

Ammonium ion wet deposition, 2005

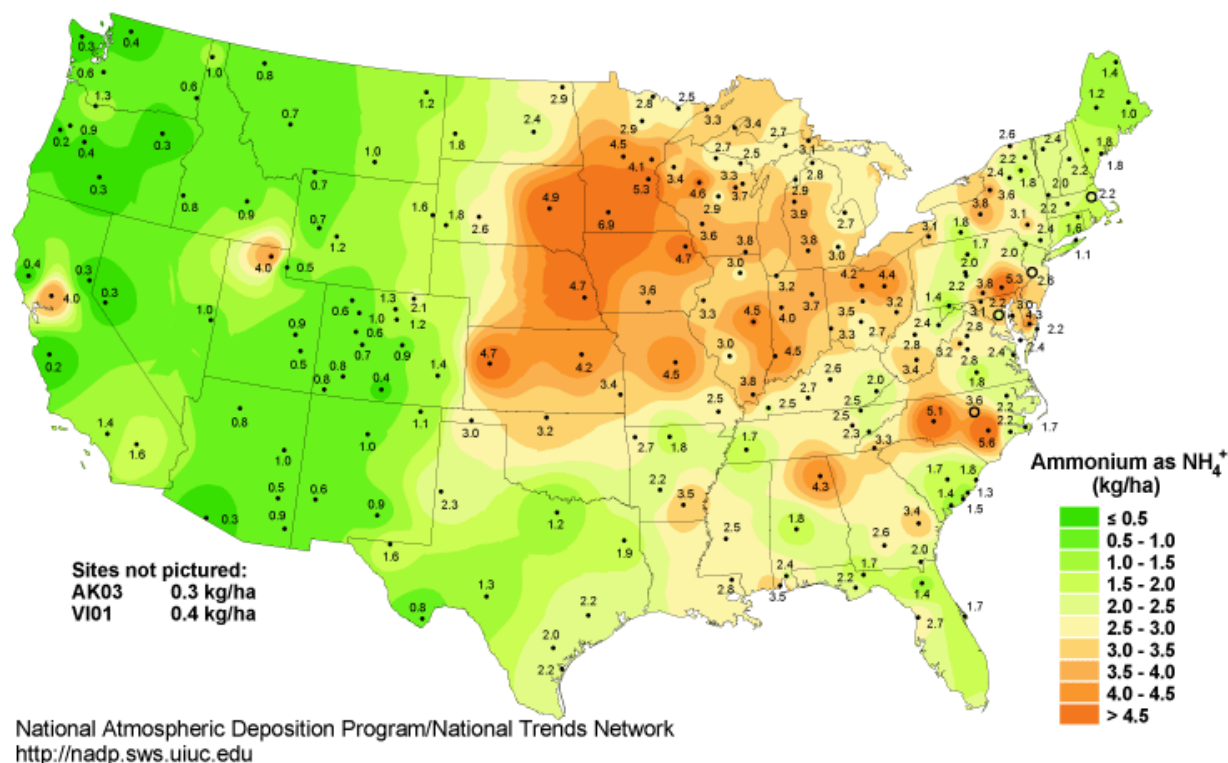


Figure 2-21. Location of approximately 250 National Atmospheric Deposition Monitoring (NADP) National Trends Network (NTN) sites illustrating annual ammonium deposition for 2005. Weekly values of precipitation based nitrate, sulfate and ammonium are provided by NADP.

2.3.2 Characterizing deposition through CMAQ

Total deposition for nitrogen, reduced nitrogen, the ratio of reduced to total nitrogen and sulfur (Figures 2-22 and 2-25) basically follow the patterns of ambient air concentrations described earlier. The contribution of reduced nitrogen to total nitrogen deposition (Figure 2-24) illustrates the strong influence of agricultural based ammonia emissions, particularly in upper midwest and eastern North Carolina. These maps represent the deposition values used in the calculations of areas likely not meeting alternative standards as described in in section 7.5.

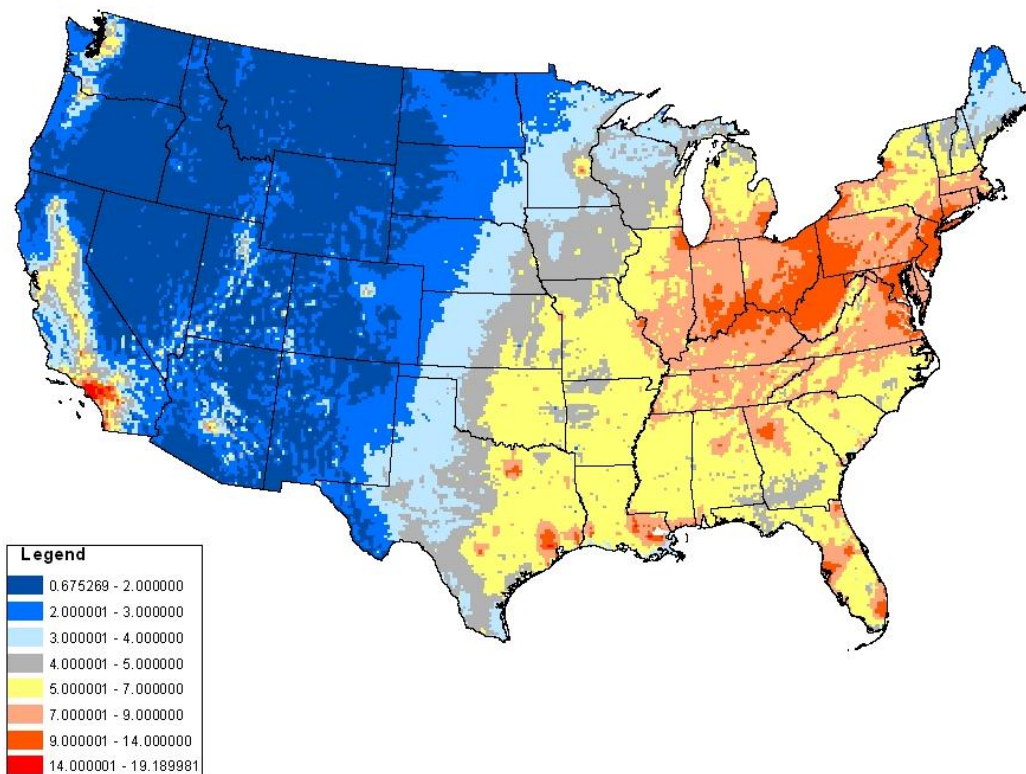


Figure 2-22. 2005 CMAQ modeled oxidized nitrogen deposition (kgN/ha-yr). (see Table 2-1 for unit conversions).

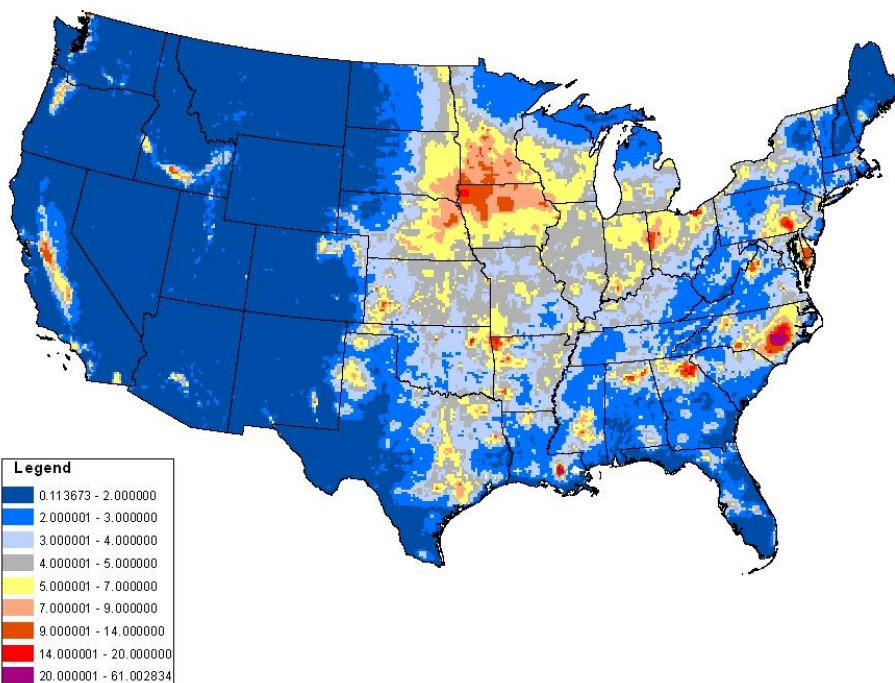


Figure 2-23. 2005 CMAQ modeled reduced nitrogen deposition (kgN/ha-yr). (see Table 2-1 for unit conversions).

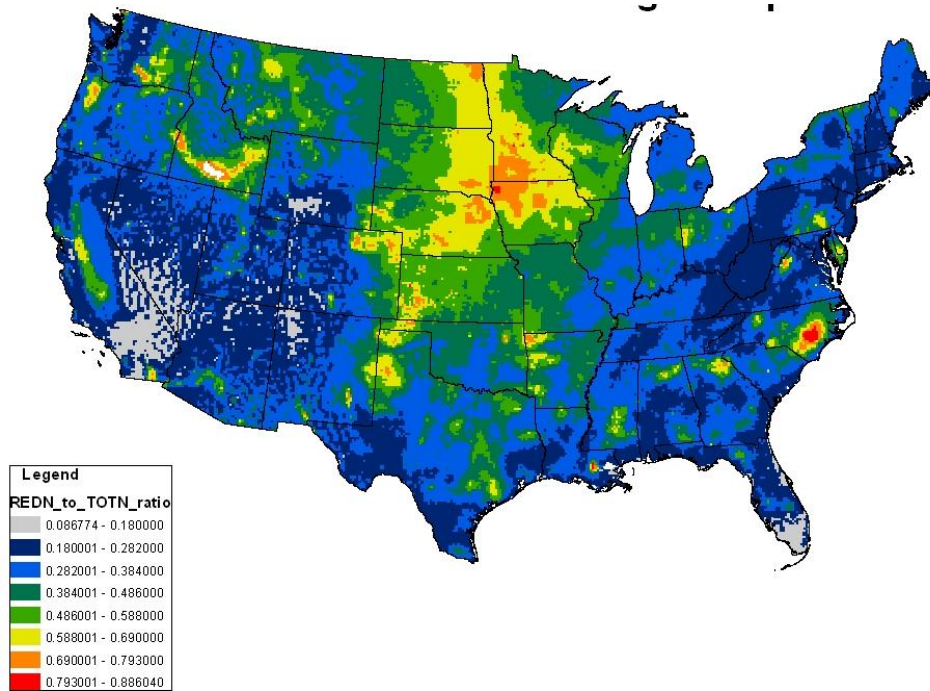


Figure 2-24. 2005 CMAQ modeled ratio of reduced to total nitrogen deposition.

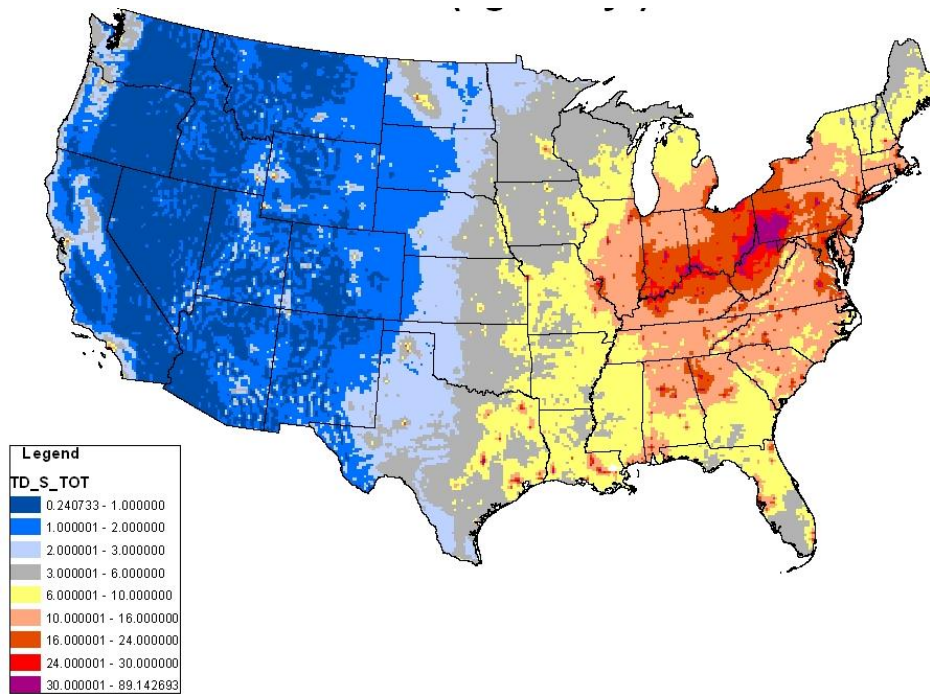


Figure 2-25. 2005 CMAQ modeled oxidized sulfur deposition (kgS/ha-yr). (see Table 2-1 for unit conversions).

2.3.3 Relationships between patterns of ambient concentrations and deposition

The development of an aquatic acidification standard relies on relationships between air concentrations and deposition. Consequently, it is informative to understand some of the basic patterns and relationships between concentrations and deposition of SO_x and NO_y species. While there are the obvious first order associations that we see between concentration patterns (Figures 2-11 to 2-17) and deposition (Figures 2-22 to 2-25), as well between emissions and concentrations, there exist marked differences between concentration and deposition at the individual species level. While the differences between emissions and air concentrations can generally be attributed to a plethora of atmospheric chemistry and transport mechanisms that change the nature and location of emitted species, the differences between concentration and deposition are all about the inherent characteristics of each species and how various meteorological and surface attributes (meaning landtypes, water systems, vegetation, suspended cloud and rain droplets) influence the transfer of a species to a (or through and within) a surface. This section describes these relationships and provides background for the discussion on the selection of ambient air indicators (section 7.1).

NO_y species

Air quality models and deposition models that use direct observations calculate deposition on a species by species basis to account for differences in deposition velocities. Consequently, the relative fractional contributions of individual NO_y or SO_x species to deposition or concentration is influenced by the differences in species deposition velocities. For example, nitric acid with a high deposition velocity would exhibit a larger relative contribution to overall deposition compared to ambient concentrations in a particular area (Figures 2-26 and 2-27). The dominant ambient air NO_y species are NO, NO₂, HNO₃, P-NO₃ and PAN. Near source urban environments typically have a relatively higher fraction of NO_x (NO and NO₂) compared to the products of NO_x reactions, nitrates and PAN, which are relatively more dominant in rural locations (Figures 2-27 – 2-30).

Sulfur Species

The use of SO₂ and SO₄ does reflect the use of individual where it is practical to measure each species independently. Although sulfur dioxide and particulate sulfate contribute approximately 60 and 40 %, respectively, to ambient SO_x concentrations, sulfur dioxide is the

dominant contributor to SO_x deposition (Figure 2-31), which is consistent with CASTNET observational studies (Sickles and Shadwick, 2007). With minor exceptions, the PM_{2.5} fraction generally accounts for over 80% of the ambient sulfate mass. However, as particle size diameters increase beyond 2.5 μ, gravitational settling imparts greater influence resulting in substantially enhanced deposition velocities. Consequently, the sulfate mass in size fractions greater than 2.5 μ potentially provides correspondingly greater contribution (to as much as 50% of dry sulfate deposition in certain locations (EPA , 2008; Grantz et al., 2003), which has implications for monitoring that are discussed below.

2.3.4 Monitoring Considerations

The differences in the relative patterns between ambient air and deposition on a species-by-species basis illustrate a number of challenges and considerations in developing a monitoring strategy. It is clear in the Adirondacks and Shenandoah areas, for example, that nitric acid is the most dominant contributing species from a deposition perspective (Figure 2-26), with significant contributions from particulate nitrate, PAN and NO₂. The original source of emissions (NO accounts for 90-95% of all emitted NO_x) ultimately is transformed in the atmosphere and provides very small fraction of oxidized nitrogen in ambient air and deposition in rural environments. The combination of nitric acid and particulate nitrate consistently contribute greater than 50% of the oxidized nitrogen dry deposition load, whereas PAN and NO₂ contribute roughly 15-25% of the deposition load.

Dry deposition of NO_y is treated as the sum of the deposition of each individual species in advanced process based air quality models like CMAQ. This raises the question of the relative importance of acquiring individual species measurements to a single aggregated measure, NO_y. For example, individual measurements of the dominant NO_y species (HNO₃, particulate nitrate, NO₂, NO, and PAN) could be coupled to their distinct deposition velocities to estimate dry deposition and provide useful diagnostic information to improve characterization of deposition processes. Currently, technology for measuring NO₂ in rural locations, HNO₃, and PAN generally is not available for routine network applications. If certain species provide negligible contributions to total NO_y deposition, then perhaps they could be excluded for the purpose of deposition assessments. All of the nitrogen species that constitute NO_y have species specific dry deposition velocities. Species with especially low relative deposition velocities, such as nitrogen dioxide, may contribute insignificant amounts of deposition relative to species

with high deposition velocities such as nitric acid. Based on the reasoning that a larger fraction of the deposited NO_Y is accounted for by total nitrate combined with the availability of reliable total nitrate measurements (the sum of nitric acid and particulate nitrate) through CASTNET, a total nitrate measurement may be adequate for deposition based assessments.

These patterns suggest the possibility of using total nitrate as a key indicator for acidifying deposition contributions associated with oxides of nitrogen. However, a nitrate observation alone would miss a considerable fraction of the ambient NO_Y burden reflected in significant levels of NO_2 and PAN. Characterization of NO_2 deposition is an area requiring further refinement especially considering that NO_2 is a significant component of total oxidized nitrogen. Zhang et al. (2005) suggest that NO_2 contributes up to 36% of dry NO_Y deposition in rural Eastern Canadian locations, and suggest, based on observational evidence (Figure 2-27), that in some locations NO_2 deposition may be similar to nitric acid contributions.

Another way of addressing the relative benefit of using part of the NO_Y mix relative to total NO_Y in regard to deposition is to probe the dynamic response of changes in oxidized nitrogen deposition to changes in ambient concentrations NO_Y and nitric acid. Dynamic response refers to sensitivity of the ambient to deposition response with respect to changes in NO_x emissions, which is relevant to air quality management as ambient indicators are used to assess if an area meets or exceeds a target value in current and future time frames. While such a response to emission changes may be linear or non-linear, the details of which are encoded in chemical transport air quality models like CMAQ, typically there is a directional relationship between the change in the precursor emissions and the target species of interest. By extension, one would expect that a significant change in emissions of NO_x would lead to a change both in the ambient and deposition fields of NO_Y species, recognizing that NO_Y species all evolve from NO_x emissions, which is dominated by nitrogen oxide, NO . We can apply this reasoning to the consideration of using HNO_3 as a more narrowly defined indicator, relative to NO_Y . A 2005 base case and projected 2030 CMAQ simulation, with roughly 50% NO_x and SO_x reductions, respectively, are used to illustrate the relationship of HNO_3 and NO_Y concentration changes to changes in NO_Y deposition (wet and dry) which address the question: Does the indicator respond in a manner directionally similar to deposition over periods of significant emissions reductions? Based on this paired set of current and future projection scenarios, the absolute change in ambient NO_Y is greater than the absolute change in nitric acid concentrations and both

NO_y and nitric acid respond in a similar relative directional manner (Figure 2-32). The higher magnitude of absolute change is a desired attribute from an indicators perspective as signal changes over time are more likely to be detectable.

These examples suggest that the acidifying contributions of all NO_y species should be accounted for in linking ambient air to deposition. Ideally, observations of individual NO_y species are preferable as they allow for a more refined understanding of the contribution of individual species to deposition, and afford data to diagnose air quality model behavior that can lead to improved parameterization of deposition processes. However, limitations of available technology suggest that measurements for aggregated NO_y are available for routine application. An aggregate NO_y measure does, in concept, capture the potential for acidifying contributions of all oxidized nitrogen species. Nevertheless, complementary measurements of NO₂, HNO₃, p-NO₃ and PAN to allow for diagnostic evaluations of both air quality models and the NO_y measurement itself should be strategically placed in two to five areas, in different air quality mixes and ecologically relevant locations.

Measurement technology issues generally are not as complex for SO_x as they are for NO_y and individual NO_y species, partly because just two sulfur species, sulfur dioxide and particulate sulfate, dominate oxidized sulfur composition in the atmosphere. However, as noted earlier there are concerns related to capturing the full range of sulfate particle size fractions.

Ammonia and ammonium ion both provide the potential to contribute acidifying deposition and, therefore, should be accounted for in assessments addressing acid deposition. Characterization of reduced nitrogen deposition processes is an active developmental area which would benefit markedly from NH_x measurements in order to assess modeled predictions of ambient patterns of ammonia and ammonium. This need for monitoring ammonia in rural environments is further supported by emerging evidence that ammonia acts as a regionally dispersed species based on the inclusion of ammonia bi-directional flux in CMAQ simulations as discussed in Appendix F and Dennis et al., 2010. Monitoring method approaches under consideration for routine application typically are limited to time averaged filter and denuder technologies, including passive sampling approaches which are utilized in the new NADP AMON network.

As discussed earlier, two - five locations nationally, in airsheds with different atmospheric chemistries, that sample not only for the NAAQS indicator NO_y but for the suite of

major NO_Y species as well; HNO_3 , $p\text{-NO}_3$, PAN, NO_2 , and NO as discussed earlier. Not only is this important from a modeling and process diagnosis perspective, but it is especially useful in the introduction of new measurements that have a limited track record to provide insight into instrument performance. In the case of NO_Y , it is even more relevant since there effectively are no standards that explicitly challenge instrument accuracy given the highly variable nature of NO_Y species distribution and the instability associated with mixing NO_Y gases. This quality assurance issue is analogous to $\text{PM}_{2.5}$ where aerosol standards are not available and measurement accuracy is judged against periodic challenges relative to a “gold standard” instrument. Reduced nitrogen measurements of ammonia and ammonium ion are recommended at all locations with FRM/FEM instruments based on the need to support the AAPI as discussed above.

Sampling frequencies

The averaging time for the standard is likely to be an annual average, perhaps based on 3-5 years of data collection to minimize the influence of interannual variability in meteorology, especially precipitation. Conceptually, extended sampling periods no longer than one year would be adequate for the specific purposes of comparison to a standard. However, there are significant peripheral benefits relevant to improving the scientific foundation for subsequent reviews and a variety of related air quality and deposition assessments to be gleaned from more highly time resolved data. In particular, the critical role of air quality models in deposition assessments implies value to be derived from measurements that support model evaluation and improvement. Many of the monitoring approaches that are used throughout the nation sample (or at least report out) on daily ($\text{PM}_{2.5}$ chemical speciation), weekly (CASTNET) and hourly (all inorganic gases) periods. There is a tradeoff to consider in sampling period design. For example, the weekly CASTNET collection scheme covers all time periods throughout a year, but only provides weekly resolution that misses key temporal and episodic features valuable for diagnosing model behavior. The every third day, 24-hour sampling scheme used in IMPROVE and EPA speciation monitoring does provide more information for a specific day of interest yet misses 2/3 of all sampling periods. The missing sampling period generally is not a concern when aggregating upward to a longer term average value as the sample number adequately represents an aggregated mean value. Additionally, there is a benefit to leveraging existing networks which should be considered in sampling frequency recommendations. A possible starting point would be to assume gaseous oxidized species, NO_Y and SO_2 , are run continually all year reporting

values every hour, consistent with current routine network operations. Sulfate sampling periods should coincide with either the chemical speciation network schedules or with CASTNET. There are advantages to coordinating with either network. Ammonia gas and ammonium ion present challenges in that they are not routinely sampled and analyzed for, and the combined quantity, NH_x is of interest. Because NH_x is of interest, some of the problems of volatile ammonia loss from filters may be mitigated. However, for model diagnostic purposes, delineation of both species at the highest temporal resolution is preferred.

Sample collection period is not an issue for gaseous measurements of NO_Y and SO_2 that operate continuously. However, consideration should be given to using the CASTNET filter pack (FP) for SO_2 measurements to maximize leveraging of monitoring assets, assuming the FPs will be used for particulate sulfate. However, the availability of highly time resolved data will support the continual evaluation of SO_2 and sulfate balance in air quality modeling systems which is a critical underpinning for both human and ecosystem health assessments.

Spatial scales

The current observation network for NO_Y , NH_x and SO_x is very modest and includes a monitoring network infrastructure that is largely population oriented with the exception of CASTNET and IMPROVE. While there is platform and access infrastructure support provided by CASTNET, NADP and IMPROVE, those locations by themselves are not likely to provide the needed spatial coverage to address acid sensitive watersheds across the United States. Ambient monitoring at every watershed will not be required given the reality of resource constraints and the relative spatial homogeneity of air concentrations that are averaged over annual time periods and within ‘acid sensitive’ areas. The spatial monitoring requirements will be associated with the determination of acid sensitive areas, which is discussed in chapter 7. The number of sites per area will be addressed in rule development and general guidance based on an understanding of the spatial variability of NO_Y , NH_x , sulfate and SO_2 combined with resource allocations will help inform those decisions.

Critical load models applied for the purposes of this standard would be based on annual averages, which would effectively serve to dampen much of the spatial variability. Furthermore, the development of an area-wide depositional load tradeoff curve implies focus on region wide characterization. Toward that end, CMAQ concentration fields will provide insight into the likely spatial representativeness of monitors leading to efficient application of monitoring

resources. For example, the CMAQ based spatial coefficient of variation (standard deviation/mean) of oxidized nitrogen in the Adirondacks was 1.46%. Improved dry deposition estimates will result from enhancements of ambient monitoring addressing the N/S secondary standards as each additional location could serve a similar role that existing CASTNET sites provide in estimating dry deposition.

Candidate monitoring methods

Ambient NO_y , SO_2 and particulate sulfate (SO_4) concentrations are likely candidates for ambient air indicators (section 7.1). All of these indicators are measured in different places within the current routine monitoring networks. Traditionally, Federal Reference or Equivalency Method (FRM/FEM) status of measurement techniques is used for estimating air concentrations for NAAQS comparisons. A FRM for SO_2 exists, but not for NO_y or SO_4 . Only recently have NO_y measurements, which historically were viewed as research venue measurements, been incorporated as “routine” observations, partly as a result of the NCore program. Particulate SO_4 is measured at over 500 sites nationally, and there is a general consensus that methods available are reliable and provide consistent data.

Particulate- SO_4 . Particulate sulfate (p- SO_4) has been measured for several years in the IMPROVE, CASTNET and EPA CSN networks. The nation has over 500 24-hour average, every third day sulfate measurements produced by the $\text{PM}_{2.5}$ speciation networks (IMPROVE and EPA CSN) and nearly 80 CASTNET sites that provide continuous weekly average samples of sulfate with an open inlet accommodating all particle sizes. As discussed above, particle size diameters increase beyond 2.5μ should be accounted for in deposition based assessments, perhaps ruling out the use of $\text{PM}_{2.5}$ data serving as indicators for a NO_x/SO_x secondary standard.

The routinely operating methodology for p- SO_4 is based on an integrated (i.e., time averaged over several hours or days) sample collection on a Teflon filter followed by ion chromatography (IC) detection in the laboratory. Two major variations of this approach are applied in the $\text{PM}_{2.5}$ speciation (exclusion of particles larger than 2.5μ and 24-hour collection typically every third day) and CASTNET (weekly average integrated sampling all year with an open inlet to include all size fractions). There are additional variations related to inlet design and flow characteristics of $\text{PM}_{2.5}$ speciation samplers in which two designs are prevalent in the networks: (IMPROVE and EPA CSN SASS samplers). These variations are considered minor as

sulfate species (dominated by ammonium sulfate) typically are not subject to major sampling artifacts associated with volatilization or condensation. The difference in inlets (open vs. 2.5 μ) is perceived by some as not an issue of concern as 80 - 90 % of the PM sulfate mass is distributed in size fractions less than 2.5 μ . However, the higher deposition velocities associated with larger diameter particles argue for including all size fractions as discussed above. Continuously operating in-situ sulfate instruments that allow for hourly, or less, data reporting are available. However, the limited deployment (less than 20 sites nationally) of these instruments combined with the 2.5 μ inlet cutoff configuration preclude consideration at this time.

The CASTNET FP offers three important attributes: a history of high quality data, existing infrastructure and network to build on and an open inlet to capture the full range of particle diameters. EPA intends to develop FRM status for this method. A significant additional advantage of using the FP method will be the availability of important co-measured species (e.g., SO₂, total nitrate, and ammonium). While EPA plans to expedite the certification process for the CASTNET FP, in the future consideration should be given to other available methods to more efficiently leverage network assets. For example, the SASS sampler potentially would accommodate ammonia gas and ammonium ion measurements, as well as other standard chemical speciation parameters depending on the configuration of this multi channel system. Continuous sulfate measurements would be extremely useful for model evaluation, especially considering the availability of continuous SO₂ data that would be required as part of the NAAQS indicators. A performance based approach to meet equivalency requirements, given the variety of sulfate measurement approaches and well vetted and accurate analytical procedures.

SO₂. A FRM is available for SO₂. See 75 FR at 35554-56 and 35593-95 (June 22, 2010) (adopting a second FRM for SO₂). As part of the NCore network development effort, trace gas SO₂ analyzers capable of sub ppb resolution became commercially available and are the preferred instruments for implementation in rural locations. As discussed above, the near continuous data output of gaseous analyzers is desired for peripheral support of model evaluation. Nevertheless, the convenience and resource savings associated with the CASTNET FP suggest that Federal Equivalency Method (FEM) status should be incorporated in concert with the sulfate certification process.

NO_y. In principle, measured NO_y is based on catalytic conversion of all oxidized species to NO followed by chemiluminescence NO detection. While there are caveats associated with

instrument conversion efficiency and possible inlet losses, the technique is considered adequate and routinely operational. Approximately 25 sites (out of a planned 75) in EPA's NCORE network are operating NO_Y instruments, and additional sites are operated in SEARCH, CASTNET and other programs. NO_Y measurements are nearly continuous, reporting at hourly intervals providing far greater temporal information compared to filter or denuder based methods.

FRM certification for NO_Y presents challenges given the limited history of routinely operating instruments. NO_Y measurements are in a transition period from largely being viewed as a research level measurement to now being deployed as a routine measurement in EPA's national 75 site NCORE network. The general consensus on NO_Y measurement is that the methodology is sound and applicable for routine/regulatory use, but there does not exist a well defined understanding of the quality of NO_Y data. Inorganic dry nitrate (nitric acid and particulate nitrate) is measured routinely in the CASTNET network with filter packs (FP). Acquiring FRM status for NO_Y instruments may require better characterization of the conversion efficiencies, mass loss and updated guidance on operating and siting procedures.

One of the challenges associated with specifying performance attributes for p-SO₄ and NO_Y is the lack of specific challenge standards. For example, instruments measuring discrete gases such as ozone or nitrogen oxide can be challenged by comparing an instrument's reading when measuring known concentrations of gases which are readily provided for single gas concentrations. Particle standards are not available. NO_Y performance typically is challenged by known mixtures of NO₂, and occasionally with N-propyl nitrate, which only addresses part of the spectrum of nitrogen species in an NO_Y mix. Consequently, instrument performance in EPA's national networks for aerosol mass is quantified in terms of bias and precision relative to a co-located "performance evaluation" instrument. There is no comparable program in place for p-SO₄ or NO_Y.

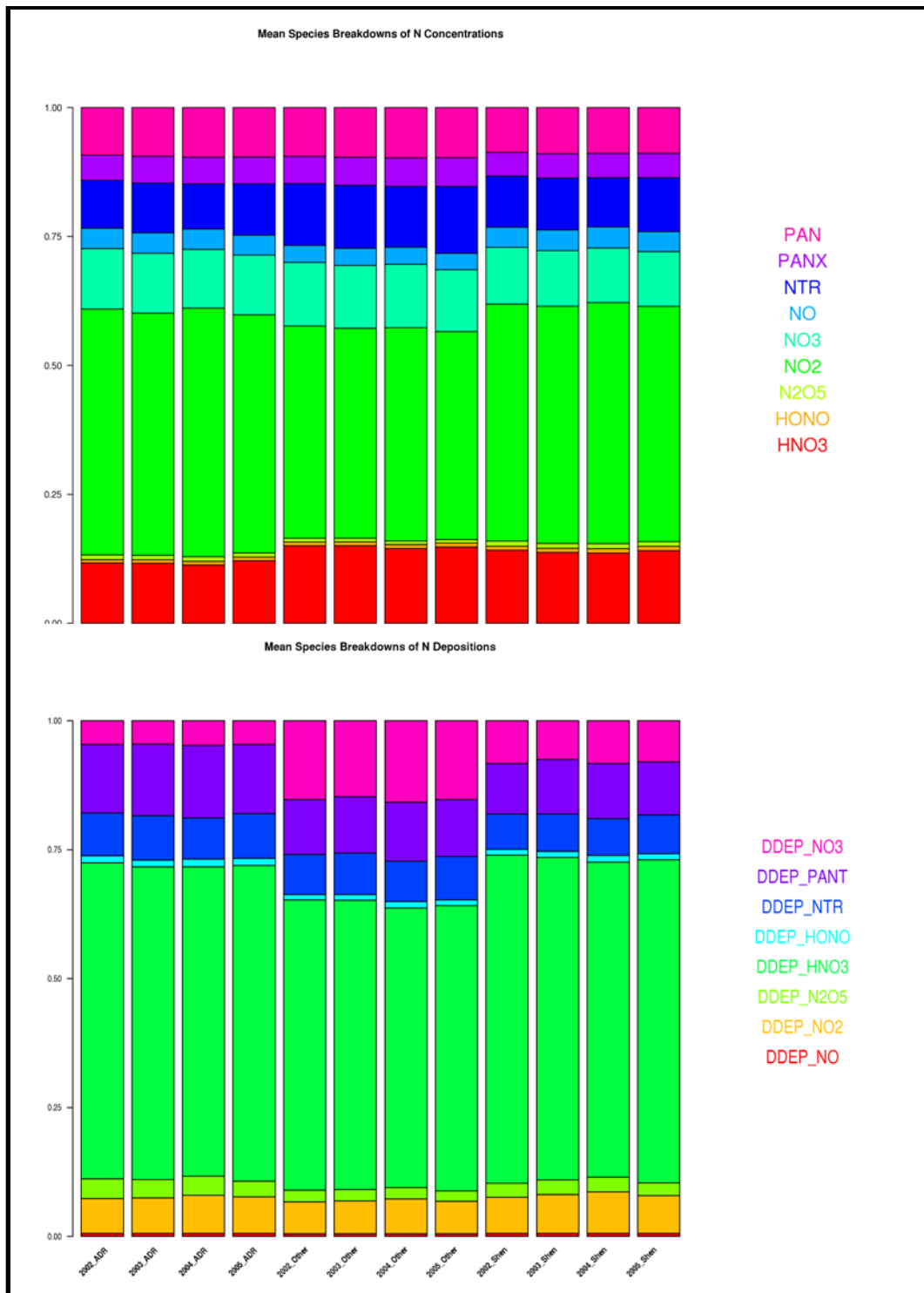


Figure 2-26. Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and dry deposition (below) of individual NO_y species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain. NTR refers to non-PAN organic nitrates. PANX refers to aggregation of PAN type compounds, other than PAN, specifically.

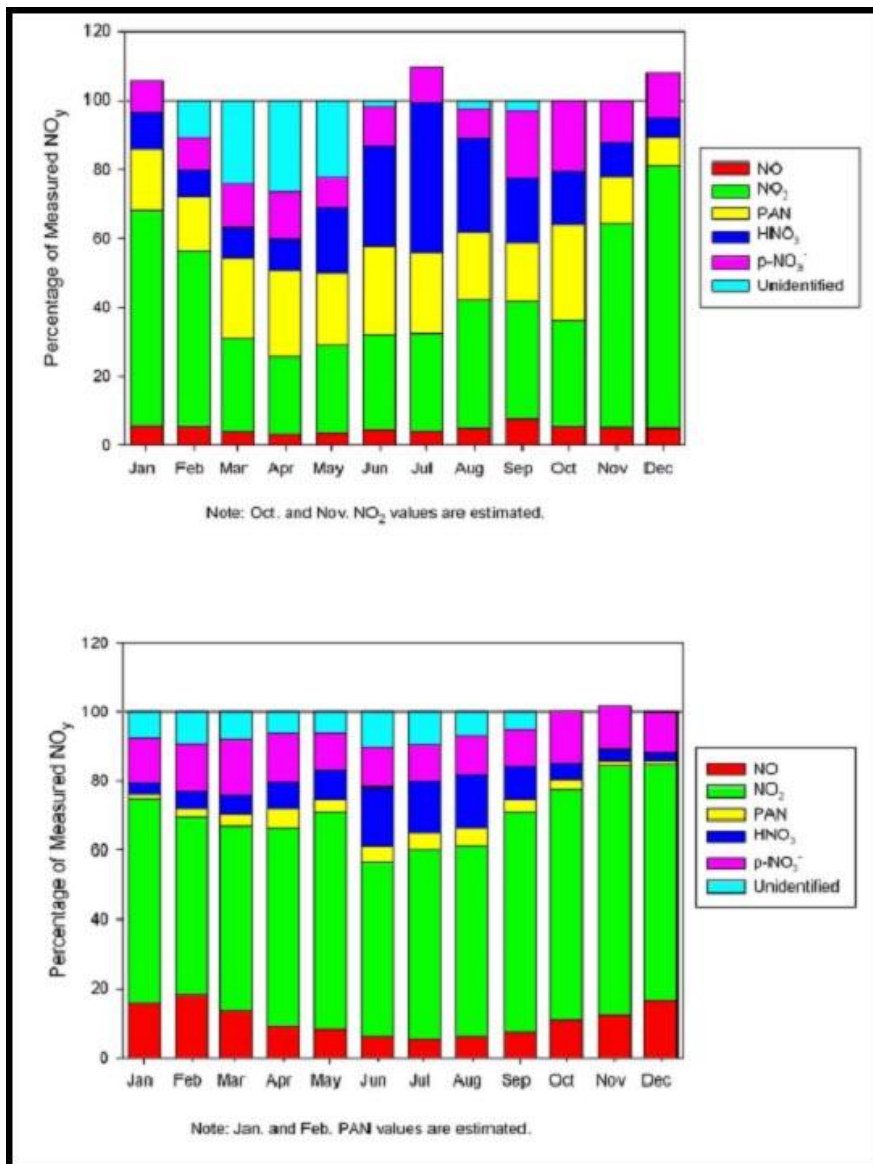


Figure 2-27. Examples of the Relative Abundance of Several NO_y Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured NO_y Concentration -- Kejimikujik, NS, (top) and Egbert, ON, (bottom) during 2003. Although both sites are in rural locations, the Kejimikujik, NS site represents more aged air masses as it lies considerably further downwind from major sources of NO_x relative to the Egbert site. (Source: NARSTO, 2011).

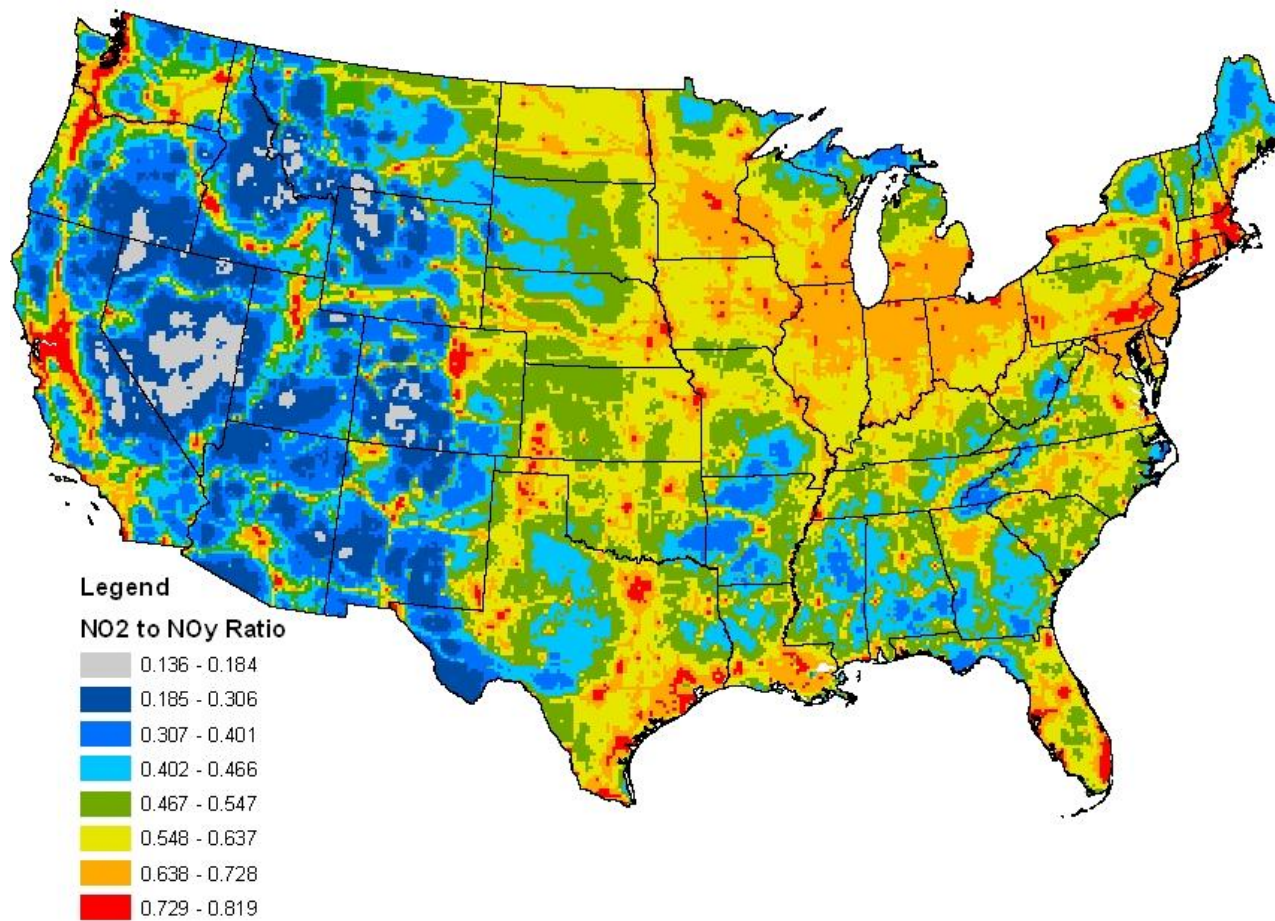


Figure 2-28. Annual average fraction of NO_y ambient air contributed by NO₂ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

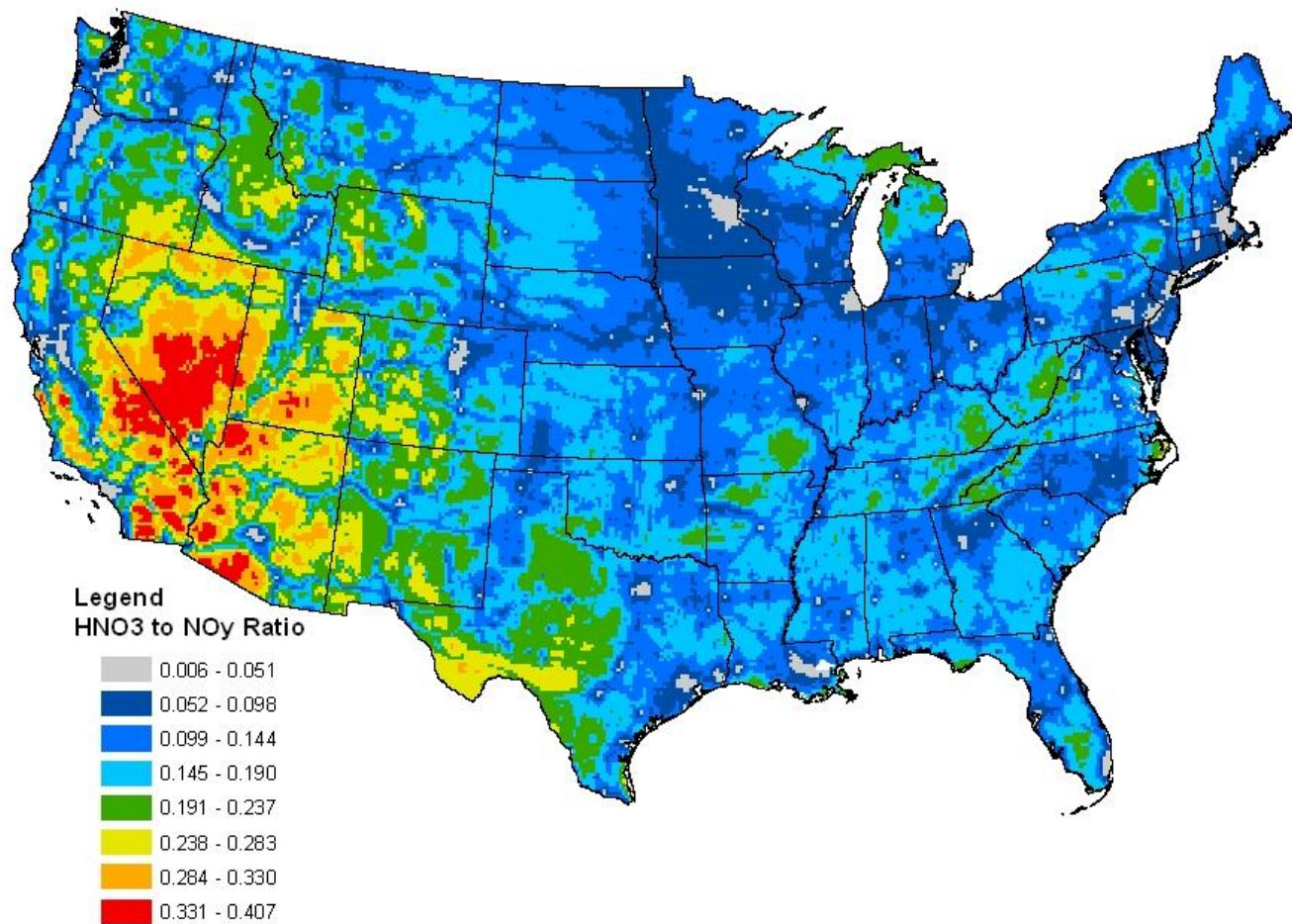


Figure 2-29. Annual average fraction of NO_y ambient air contributed by HNO₃ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

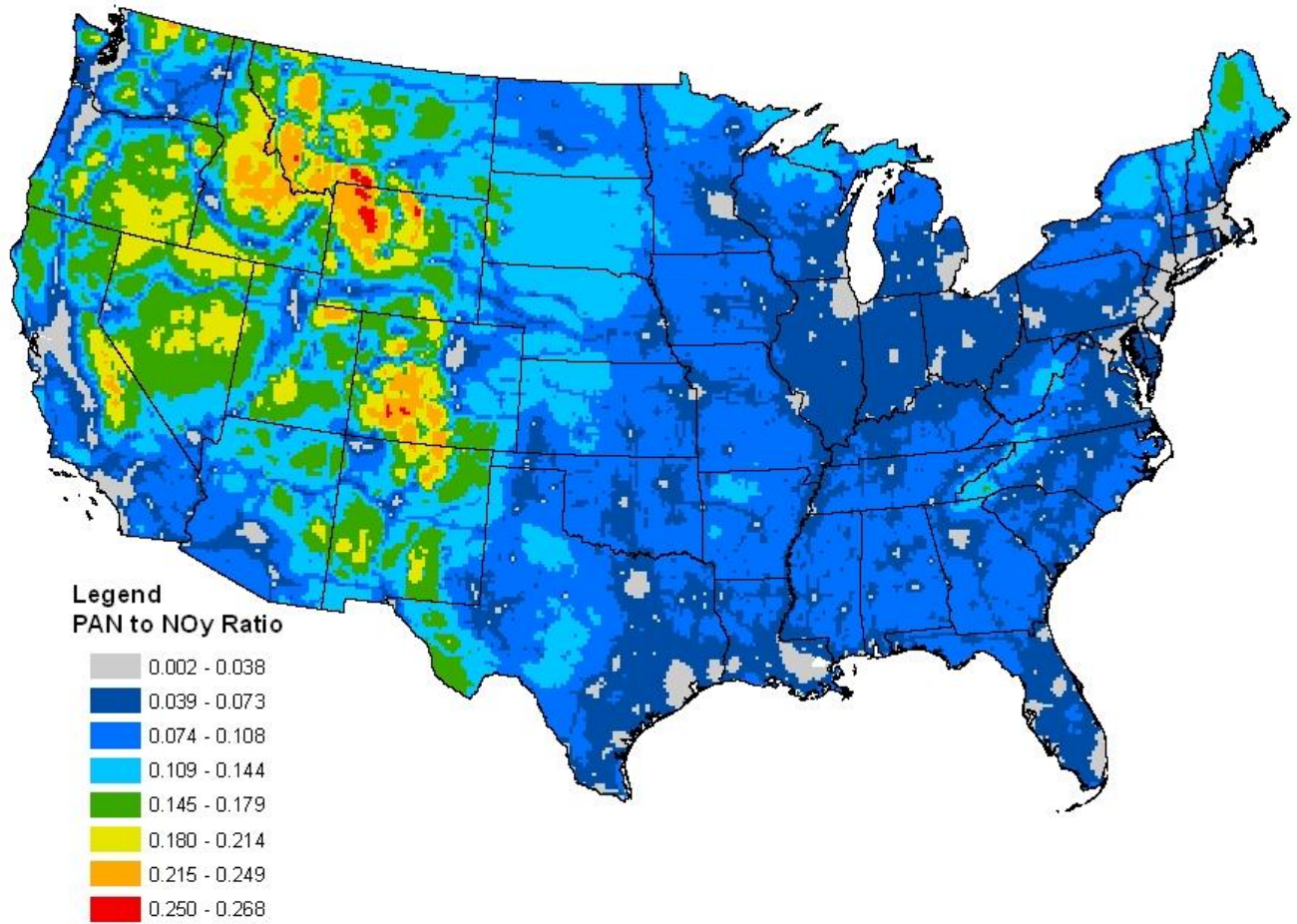


Figure 2-30. Annual average fraction of NO_y ambient air contributed by PAN based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

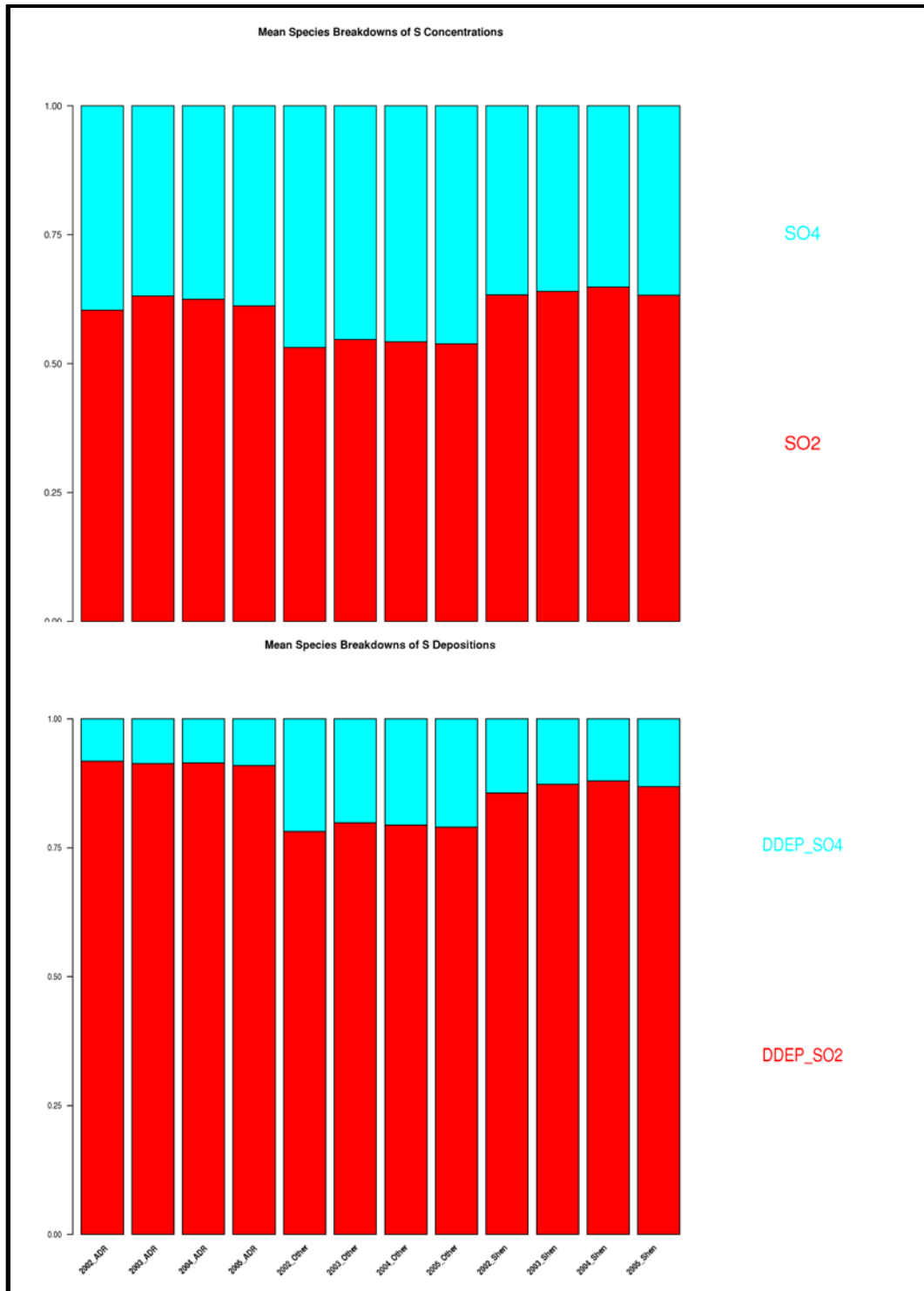


Figure 2-31. Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and dry deposition (below) of individual SO_x species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.

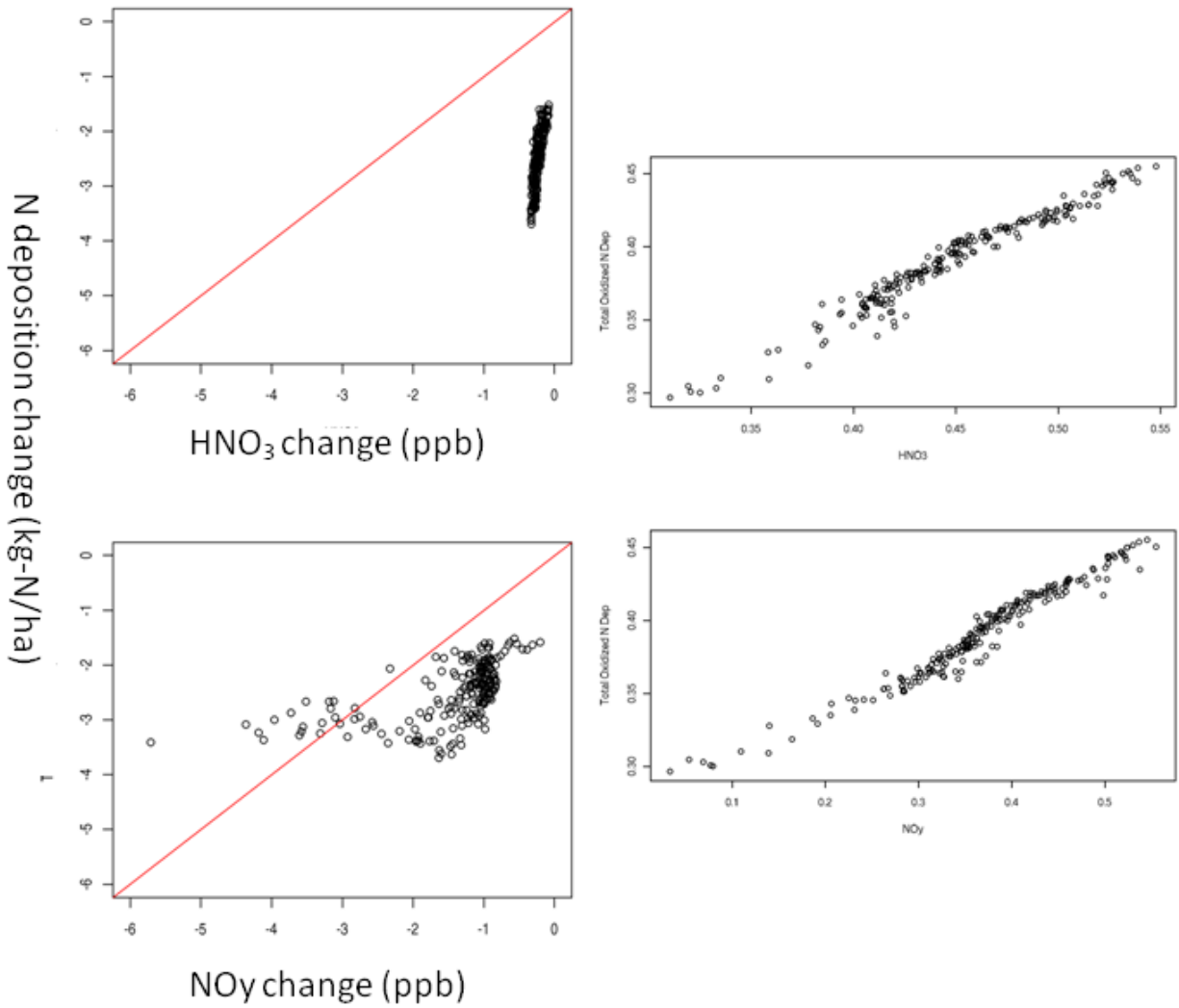


Figure 2-32. Relationship of the change in total oxidized nitrogen deposition to change in ambient nitric acid (top) and ambient NO_y (bottom) based on changes in concentration and deposition fields associated with current (2005) and reduced emission CMAQ simulations. The values are based on the changes imparted for each 12 km grid cell within the Adirondack region. The NO_x and SO_x emissions reflect reductions of 48% and 42%, respectively, across the entire Eastern U.S. The left side panels reflect absolute differences (reduced – 2005) and the right hand side reflects relative changes (2005 – reduced)/2005.

2.4 CHARACTERIZING FRESHWATER AQUATIC SYSTEM CHEMISTRY USING MODELS AND MEASUREMENTS

This section introduces basic water chemistry concepts and soil and watershed processes incorporated in biogeochemical models used to estimate changes in water quality driven by atmospheric deposition of nitrogen and sulfur. A summary of the of those models, with an emphasis on those used in this assessment, as well as the major monitoring networks providing water quality data relevant to acidification of freshwater systems are included as a reference source to allow for a more focused policy relevant discussion of the standard in chapter 7.

2.4.1 Water chemistry basics

Throughout this document basic water chemistry parameters and concepts such as pH, acid neutralizing capacity (ANC), dissolved aluminum and charge balance are incorporated in much of the rationale applied in developing the form of the standard. A brief discussion of *chemical equilibrium and electroneutrality* and *acid-base chemistry* provide a basis for understanding much of the terminology and rationale relevant to aquatic acidification. Much of the basic descriptions here are based on Stumm and Morgan (1981), which more or less has served as the guide to aquatic chemistry of natural systems.

First, neutrality is always adhered to, meaning that the sum of positively charged cations equals the sum of positively charged anions. Natural water systems are dominated by substances which dissociate into ions (cations and anions) that are held to two conditions. First, the degree of dissociation is governed by the equilibrium relationship of the dissociated ions and its “parent” compound. In a solution of pure water, water dissociates into hydrogen ion, H⁺, and hydroxide ion, OH⁻. The dissociation constant of water, $K_w = 1 \times 10^{-14}$, at standard temperature and pressure conditions, which is expressed as:

$$[\text{OH}][\text{H}] = K_w = 1 \times 10^{-14} \quad (2-1)$$

Equation 2-1 describes the equilibrium condition. The second condition to be adhered to is electroneutrality. The only species in solution is pure water, H₂O, and its ions, H⁺ and OH⁻. Consequently, the concentration of OH⁻ must equal the concentration of H⁺ to maintain a neutral solution. Therefore, the concentration of OH is the as H = 1*(10)⁻⁷ for a solution of pure water.

The variable, pH, refers to the negative logarithmic value of hydrogen ion concentration. This explains why solution of pure water has a pH value of 7. So, two fundamental principles of

water chemistry, equilibrium and charge neutrality essentially determine the chemical characterization of natural water systems.

Principles of acid–base chemistry, which builds on electroneutrality and equilibrium concepts, helps explain the meaning of acidification and ANC. Although various definitions of acids and bases exist, the most relevant explanation builds off of the Bronsted concept that an acid is a substance that can donate a proton to another substance and a base can receive a proton. Hydrogen ion essentially can be thought of a proton, as indicated by the positive charge, although the H^+ symbol really reflects a hydronium ion, H_3O^+ , where water acts as an acid that donates a proton in the form of H_3O^+ which for convenience is symbolized as H^+ . Acids are substances that donate more protons than they receive relative to a reference substance, which for convenience is water. A strong acid such as hydrochloric acid HCl dissociates nearly completely into hydrogen and chlorine ions with an equilibrium relationship defined by:

$$K_a = [H^+][Cl^-]/[HCl] = 10^{+3} \text{ at } 25^\circ\text{C} \quad (2-2)$$

If a known amount of HCl, HCl_t is added to water, electroneutrality (also referred to as the proton condition) must be maintained, meaning that:

$$OH^- + Cl^- = H^+; \quad (2-3)$$

In addition, the dissociation of water as described above must be maintained:

$$[OH^-][H^+] = 10^{-14}; \quad (2-4)$$

And Cl mass also must be retained:

$$[HCl] + [Cl^-] = [HCl]_t \quad (2-5)$$

Consequently, for a known amount of HCl_t added to pure water, equations 2-1 to 2-4 are easily solved as there are four equations and four unknowns, $[HCl]$, $[OH^-]$, $[H^+]$ and $[Cl^-]$.

Because the addition of HCl, which is a strong acid, results in the addition of strong anions, Cl^- ,

the solution maintains neutral charge by the addition of hydrogen ions and consequently the pH is lowered when a strong acid is introduced.

A strong base added to water must adhere to the same equilibrium and charge neutrality conditions as described above. For example, the addition of a known amount of strong base, sodium hydroxide, NaOH, dissociates into Na⁺ and OH⁻ and adheres to the equilibrium condition:

$$K_b = [\text{Na}^+][\text{OH}^-]/[\text{NaOH}] \quad (2-6)$$

Electroneutrality is met by:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-], \quad (2-7)$$

resulting in a reduction of H⁺, and raising of pH, associated with the addition of a strong cation, Na⁺. These concepts that associate strong cations with bases and strong anions with acids explain much of the formulation of ecosystem water chemistry models that balance the acidifying atmospheric deposition of strong anions (NO₃⁻ and SO₄⁻²) with the natural supply of strong cations (Ca⁺², Mg⁺, K⁺, Na⁺). The term strong, broadly represents the near complete dissociation of the parent salts or acids/bases from which the ions are derived from.

Natural aquatic systems are more appropriately explained as a system of weak acids that do have large dissociation constants. The examples of strong acids and bases above illustrate basic acid base and water chemistry equilibrium concepts and establish some context for explaining titration and ANC a little later in this discussion. The most common acid in natural systems is a weak acid, carbonic acid, H₂CO₃, which originates is formed from the reaction with water of dissolved atmospheric CO₂. Carbonic acid exists in equilibrium with its dissociated ions, bicarbonate, HCO₃⁻, and carbonate, CO₃⁻². Therefore, to meet the electroneutrality condition, hydrogen ion must now balance additional weak anions in addition to hydroxide ion,

$$[\text{H}^+] = [\text{OH}^-] + 2[\text{CO}_3^{-2}] + [\text{HCO}_3^-]; \quad (2-8)$$

To the extent carbonic acid dissociates (Figures 2-33 and 2-34), it adds negatively charged anions that can only be balanced by hydrogen ion, consequently lowering the pH of a system of pure water exposed to atmospheric CO₂. This example explains why natural water often has a pH lower than 7 of approximately 5.7.

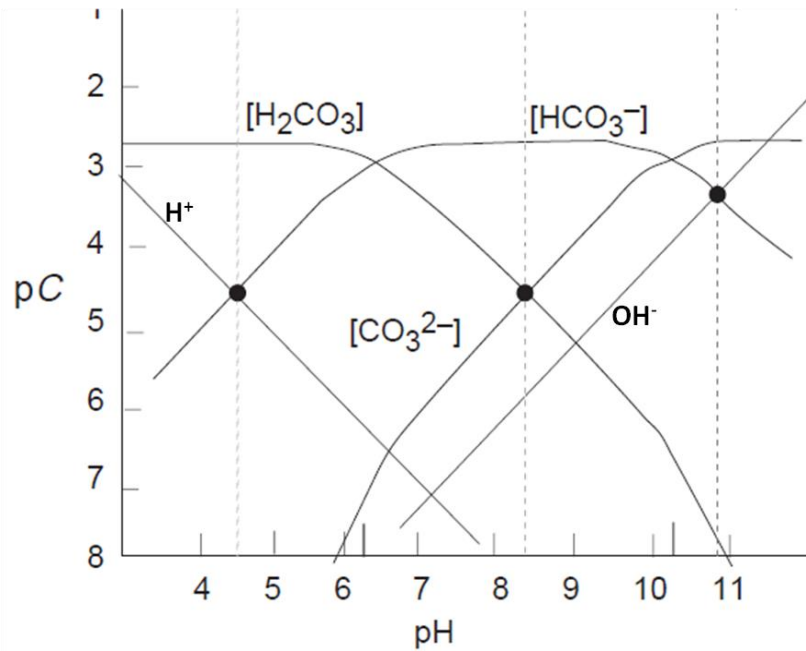


Figure 2-33. Equilibrium diagram illustrating distribution of carbonate species as a function of pH which is closed to atmospheric CO_2 exchange and therefore has a constant fixed amount of dissolved carbonate. The intersection where H^+ equals HCO_3^- is the common equivalence point, approximately a pH of 4.5, used when titrating a solution with strong acid to determine ANC. The amount of strong acid that it would take to reach that equivalent point is a measure of ANC or alkalinity. Adopted from Stumm and Morgan, 1981.

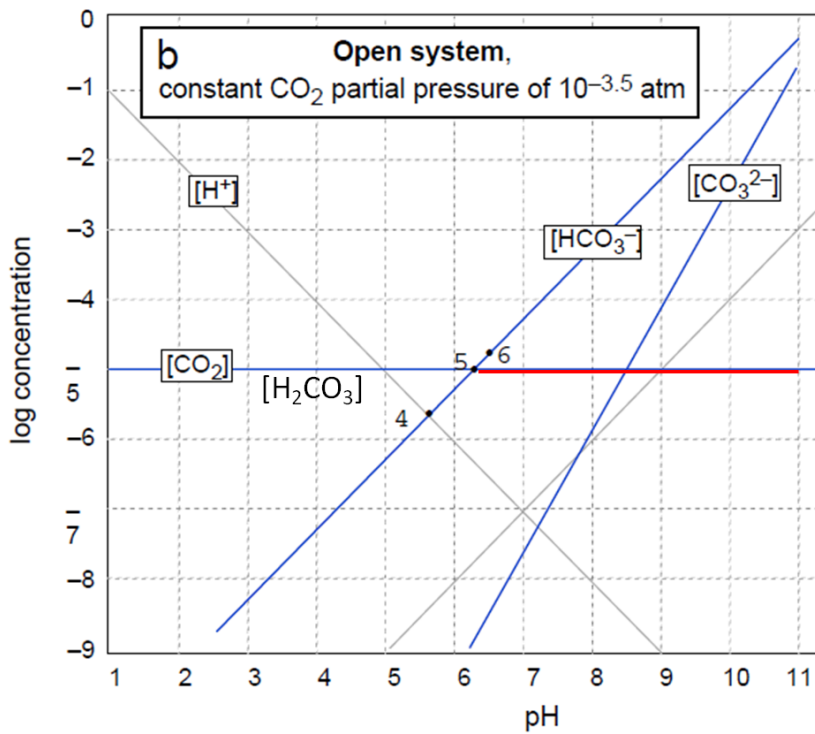


Figure 2-34. The same system open to atmospheric CO_2 exchange where the amount of dissolved carbon is determined by the partial pressure of atmospheric CO_2 and pH. Note that a pH of about 5.7 reflects a pH of pure water exposed just to atmospheric CO_2 .

Natural water systems are never as simple as just consisting of water and carbonic acid and carbonate ions, as typically there is a natural supply of strong base cations, C_B , due to weathering of rocks and soils, atmospheric deposition, and decomposing biomass. There also is a supply of strong anions, C_A (NO_3^- and SO_4^{2-}), derived mostly with atmospheric deposition and nitrification processes in vegetation and soils. For a natural carbonate system in the presence of strong cations and anions, electroneutrality is given by;

$$C_B + [H^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + C_A; \quad (2-9)$$

Therefore:

$$C_B - C_A = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] - [H^+]. \quad (2-10)$$

Defining ANC. The right side of equation represents the capacity of the system to neutralize available excess protons, H^+ , and conceptually represents acid neutralizing capacity, ANC. The actual definition of ANC is more specific and is based on how much strong acid it takes to titrate a solution to a defined reference or equivalence point. In effect, the equivalence point is synonymous with the point where there no longer is a deficit of protons. This definition of ANC reflecting the difference between major cations and anions ($C_B - C_A$) is operationally defined by equation 2-10 and is incorporated in many ecosystem models and this policy assessment:

$$ANC = 2([Ca^{2+}] + [Mg^{2+}]) + [K^+] + [NH_4^+] - (2[SO_4^{2-}] + [NO_3^-] + [Cl^-]) \quad (2-11)$$

Two other related terms used in water quality are acidity (ACY) and alkalinity (ALK). Acidity can thought of as the opposite of ANC (e.g., $ACY = C_A - C_B$), and reflects the excess of protons. From a titration perspective, ACY is defined as how much strong base it takes so that no protonation exists. Alkalinity is very similar to ANC and some of the differences in definitions regarding both ANC and ALK are operationally defined as explained in Hemond, 1990. To some extent, alkalinity reflects just the carbonate component of ANC, whereas ANC accounts

more fully for other weak organic acids. In this assessment, we emphasize ANC and the occasional use ALK is intended to reflect ANC conditions and meaning.

pH and ANC relationships. ANC is a conserved property. This means that ANC can be tracked in a mass balance sense as the level of ANC in a system (e.g., a lake or stream) is calculated by adding how much ANC initially exists with how much flows in and is deposited, balanced how much flows out. The term “mass balance” underlies the basic formulation of any physical modeling construct, and refers to the accounting of the flow of mass into a system, the transformation to other forms, and the loss due to flow out of a system and other removal processes. Hydrogen ion is not a conserved property as its concentration in a system is not related to the inflow and outflow of hydrogen ion, but influenced by several factors such as temperature, atmospheric pressure, mixing conditions of a water body and the levels of several chemical species in the system which all exist, or at least move towards, a state of equilibrium. The conservative nature of ANC also can be explained by Equation 2-11 in which the quantities of strong cations and anions are directly attributable to inputs to and outputs from a system. Strong cations (Mg^+ , Ca^{+2} , K^+ , Na^+) and strong anions (NO_3 , SO_4 , Cl) are always completely dissociated in surface waters, that is why they are referred to as strong ions. Consequently, they can be accounted for in basic modeling approaches. Hydrogen ion, on the other hand, is dependent on the balance of all ions in meeting electroneutrality conditions, as are other “weak” ions associated with dissolved inorganic (DIC) and organic (DOC) carbon.

The only condition that is always held constant for hydrogen ion is its relationship with hydroxide ion, OH^- , where the product of hydrogen ion and hydroxide ion concentrations always $= 1 \times 10^{-14}$ eq/L at standard conditions, which reflects the equilibrium relationship between water and its hydrolysis products, OH^- and H^+ . The addition of acids (strong anions) or bases (strong cations) changes the concentrations of hydrogen ion. Also, changes in temperature effect hydrogen ion concentration. Because of the influence on hydrogen ion of equilibrium constraints and other factors constraints, the concentration can be highly variant and not modeled as direct function of accounting for hydrogen ion supply and removal. That does not mean that hydrogen ion cannot be modeled, as water chemistry models calculate pH by solving for the total charge balance in the system while accounting for the equilibrium relationships of weak acids and adjusting for temperature. The amount of dissolved inorganic carbon and ANC basically determine pH. Because of these dependencies, the response of hydrogen ion to acidification

inputs is inherently nonlinear. pH measurements themselves are relatively unstable due to the influence of temperature changes and mixing effects. Modeling a relatively conservative reactive atmospheric species like carbon monoxide has always been viewed as less complex than modeling a reactive species. This is analogous to pH and ANC, where ANC is a conserved species and pH is not.

To further explain why ANC is emphasized in water quality models is perhaps best understood by realizing that acidifying atmospheric deposition of nitrogen and sulfur can be thought as direct inputs of potential acidity (ACY), or stated as negative ANC. Consequently, there is well defined linear relationship between potential acidifying deposition and ANC. This ANC and deposition relationship facilitates the linkage between ecosystem models that calculate an ecological indicator and the atmospheric deposition of NO_x and SO_x. On the other hand, there is no direct linear relationship between deposition and pH. There certainly is a relationship, as acid inputs from deposition lower pH, but the relationship can be extremely nonlinear and there is no direct connection from a modeling or mass balance perspective between the amount of deposition entering a system and pH.

Finally, to illustrate the transient, non-conservative nature of pH, consider two beakers of pure distilled water, one closed to the atmosphere and the other open. The pH of the closed beaker would be 7, representing neutrality where the concentration of hydrogen ion = the concentration of hydroxyl ion and their product is 10^{-14} , hence a pH of 7. The beaker open to the atmosphere receive no inputs of hydrogen ions, but is open to carbon dioxide exchange with the atmosphere. Dissolved carbon dioxide turns into carbonic acid, H₂CO₃, and its dissolution ions, bicarbonate, HCO₃⁻, and carbonate, CO₃⁻². The consequence is that an acid is introduced which lowers the pH to a value of about 5.7, illustrating the fluctuation of hydrogen ion without change in hydrogen ion input or export. This illustration also helps explain the condition of electroneutrality, as well as explaining why natural aquatic systems often have pH values less than 7 without anthropogenic inputs and why measuring pH is confounded by the amount of mixing. Relatedly, rising CO₂ levels are associated with increased acidification and impairment of oceanic coral reef ecosystems. For now, the effect of rising CO₂ on freshwater systems in the U.S. is insignificant relative to the strong acid inputs associated with NO_x and SO_x. Since carbonate and bicarbonate are negatively charged, the only available positively charged ions to

counter are hydrogen ion from a limitless supply of water. Essentially, that explains the definition of an acid which is the ability to affect the transfer of a proton, H^+ , from water.

Dissolved Organic Carbon (DOC). Many humic organic substances produced from decaying organic matter are considered as weak acids. Natural acidity is often associated with areas rich in humic substances and high levels of DOC. One of the positive attributes of defining ANC as the difference of strong cations and anions is that it is an unambiguous definition compared to the concept of titrating to an equivalence point where all weak anions become protonated. This is because there are so many different organic acids that would not be fully protonated at an arbitrary pH of 4.5. Consequently, the common use of DOC and ANC to define pH is not valid for systems with considerable DOC levels as the contributions of weak organic acid ions also must be balanced by hydrogen ion and therefore pH is lowered relative to a DOC free system. Many water quality models aggregate all organic acids into a simple monoprotic (i.e., only one ion representing all organic acid ions) term with an average equilibrium constant. Therefore, knowledge of any three variables of the pH, ANC, DIC, DOC) is needed to define the fourth.

Dissolved Aluminum. Aluminum species in natural systems is commonly based on the equilibrium relationships among solid Gibbsite and its dissolved ions (Figure 2-35). Dissolved aluminum affects the charge relationships in aquatic systems and the distribution of dissolved Al species is a function of pH. The prevalence of relatively toxic AL^{+3} at low pH levels is perhaps the most direct causative chemical species with regard to adverse biological effects. From a chemical characterization perspective, aluminum solubility is treated like other weak acid base systems, DIC and ANC, and therefore knowledge of 4 of the 5 variables among total dissolved aluminum, DIC, DOC, ANC and pH uniquely determine the fifth variable. Collectively, these principles of mass conservation, equilibrium and electroneutrality are adhered to in water chemistry models used to estimate key water quality variables as a system responds to acidification inputs.

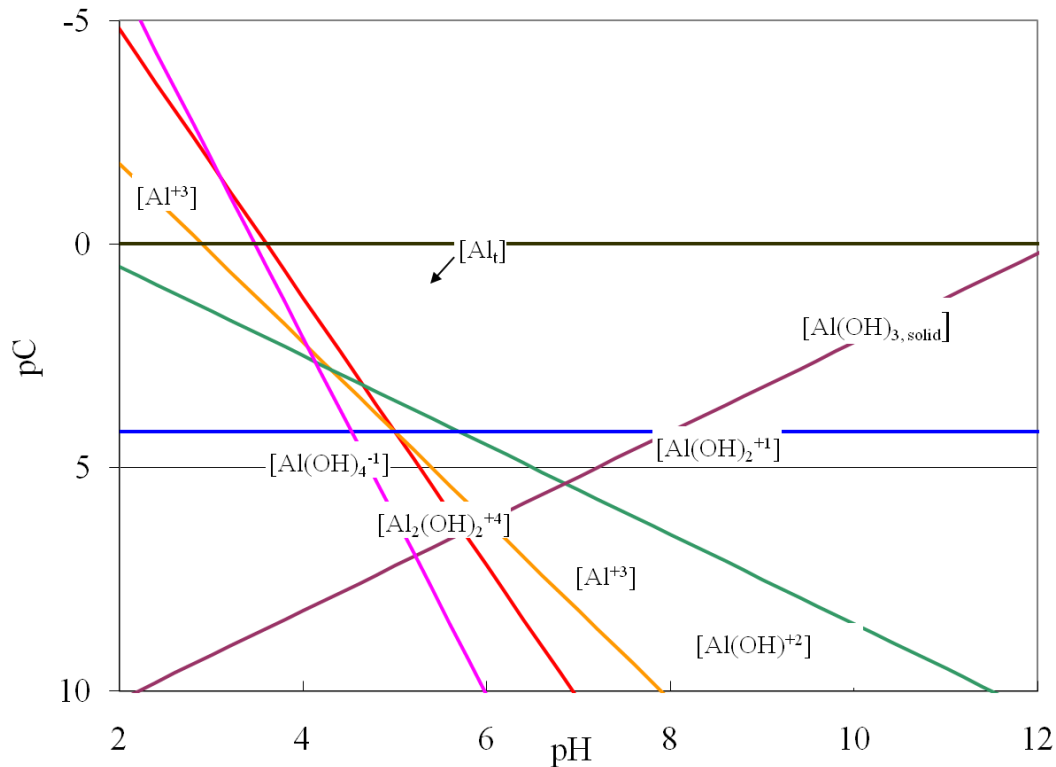


Figure 2-35. Equilibrium diagram of the log of aluminum species concentrations as a function of pH. At lower pH there is far greater proportion of dissolved Al species relative to solid gibbsite (solid aluminum hydroxide, $\text{Al}(\text{OH})_3$). The most toxic form of Al, free trivalent aluminum, Al^{+3} levels rapidly increase with lower pH values.

2.4.2 Bedrock, soil and vegetation processes relevant aquatic acidification.

The discussion in section 2.4.1 can be thought of as what happens in a lake or stream watershed relative to inputs from an inflow stream, slope runoff, transport through soils and direct atmospheric deposition. Biogeochemical acidification models, discussed below in section 2.4.4, basically attempt to define the chemical makeup of all inputs into a lake that along with natural chemical conditions and loss processes, determine the chemistry of a surface water. There are very important processes within a watershed that affect the supply of acids (or strong anions) and bases (or strong cations to a water body). These include weathering of parent rock material and soils, which provide a natural supply of base cations, soil cation exchange and adsorption processes, which influence the quantity, character (chemical species) and delivery of ions, and vegetation and microbiological processes that modify deposited nitrogen through

nitrification and uptake. Removal of atmospheric nitrogen, or neutralization, refers broadly to plant uptake of nitrogen as a nutrient and general immobilization through adsorption in soil and vegetation layers.

Soil physical/chemical processes and acidification

Soil chemical processes lie at the heart of the acidification process. The adsorption and desorption of anions and cations on soil surfaces, the dissolution of minerals, and the natural formation of alkalinity in soils control the process of acidification in association with the deposition and movement of strong anions (NO_3^+ , SO_4^{-2} , Cl^-) through the soil.

The adsorption and desorption of anions and cations on soil surfaces is an important factor that modifies the effects of acidic deposition to soils. Sulfate is the most important anion contributing by acidic deposition in most, but not all, parts of the United States. Depending on the soil characteristics, deposited SO_4^{-2} can move readily through soils into surface water. However, SO_4^{-2} is less mobile in some areas and is an important factor governing the degree to which SO_4^{-2} deposition contributes to soil and water acidification, base cation depletion, and aluminum (Al) mobilization, each of which can harm biological components of sensitive ecosystems.

Sulfur deposition can be adsorbed to soil particles, a process that removes SO_4^{-2} from soil solution, and therefore prevents leaching of cations and further acidification. The degree to which SO_4^{-2} adsorbs on soil is dependent on soil characteristics, in particular the content of clay minerals. 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 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} . The adsorbed SO_4^{-2} acts to delay the soil and surface water from acidifying. However, this potentially reversible process results in an accumulation of S in the soil, which can contribute to soil acidification if, and when, that SO_4^{-2} is eventually released back into solution.

In natural systems with minimal anthropogenic inputs, an increase in the concentration of strong-acid anions (NO_3^+ , SO_4^{-2} , Cl^-) in surface water will be balanced by an equivalent increase in the concentration of cations. Thus, neutralization of acidity is controlled by the soil and involves the release of base cations from the soil into soil water, through weathering, cation exchange, and mineralization. Loss of base cations from soil is a natural process, but the limited

mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching under conditions of low atmospheric deposition of S and N. Because inputs of sulfuric and nitric acid in acidic deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids (e.g., organic acids and carbonic acid) these mineral acid anions accelerate natural rates of base cation leaching.

Soils contain a pool of biological available base cations termed “exchangeable base cations,” which are adsorbed to negatively charged surfaces of soil particles. Base cations can be released from the soil and enter soil pore water solution by exchanging with other dissolved cations, such as H^+ or Al^{+3} . Under natural conditions, base cations in the exchangeable pool are gradually leached from the soil in drainage water, however, are constantly resupplied through the weathering of the bedrock and soil. Weathering slowly breaks down rocks and minerals, releasing base cations to the pool of adsorbed base cations in the soil. The balance between base cation supply and base cation loss determines whether the pool of available base cations is increasing or decreasing in size. Thus, the main source of cations for acid neutralization in most watersheds is the accumulated supply of exchangeable base cations in the soil that are mainly supplied by weathering. Moreover, the size of this supply, and thus the degree to which soil and surface water acidification occurs, is ultimately determined by the availability of base cations in watershed bedrock (Webb et al., 1989; Church et al., 1992; Herlihy et al., 1993).

It has long been known that leaching of base cations by acidic deposition might deplete the soil of exchangeable bases faster than they are resupplied, which is termed “base cation depletion.” Base cation depletion occurs in three-stage process in which buffering of acidity in the mineral soil is first accomplished by weathering of carbonates and other mineral forms that weather relatively rapidly. Once these mineral forms are depleted, buffering is accomplished largely by cation exchange on the soil, in which H^+ is substituted for base cations and concentrations of exchangeable base cations decreases. Once the buffering capacity provided by cation exchange is depleted, acid neutralization is accomplished by weathering of crystalline minerals that contain large amounts of silicon (Si) and Al and relatively small amounts of base cations. At this stage, Al is mobilized within the soil and exchangeable Al concentrations increase.

Therefore, neutralization of drainage water is accomplished at the expense of soil base cations. The ability of a soil to exchange base cations between drainage waters is known as the

cation exchange capacity (CEC) and is determined by many factors. Soils north of the maximum extent of glaciation, CEC is largely derived from organic matter, whereas in older southern soils the surface charge of highly weathered clay minerals is the primary source of CEC. The CEC derived from organic matter is pH-dependent. Decreases in pH result in a decrease in CEC as strong-acid anions (NO_3^- , SO_4^{2-} , Cl^-) are loaded into the soils. The percent base saturation tells what percent of the exchange sites are occupied by the basic cations. Soil acidification in the context of acidic deposition can refer to a decrease in soil pH, a decrease in soil percent base saturation, an increase in Al mobilization, or a combination of these changes.

Conceptualized Model of Acidification

Galloway et al. (1983) provided a conceptualized model on how terrestrial systems undergoing acidification and how base cation concentration in a stream and catchment respond to a period of elevated inputs of acidic compounds. This model can be broken down into 5 stages, starting from the preacidification condition to recovery. Stage I, the period before acidification, base cations release is equivalent to the rate of chemical weathering plus atmospheric inputs. Base cation supply is in steady state equilibrium with cation exchange surface and biomass. Stage II, as acid loading increases, the net desorption of cations increases, causing base cations to increase in surface waters in order to provide an equivalent countercharge to the increase in acid anions. Stage III, as acid loading continues soil base saturation is reduced to a new equilibrium state with respect to acid inputs and the supply of base cations is controlled only by chemical weathering, which is relatively unchanged. The reduced base saturation from acidification results in decreased export of base cations from desorption, while Al increases. Stage IV, as extra acid loading ceases, soils rapidly adsorb cations released by chemical weathering, thereby reducing the flux of cations to surface waters and slowing or potentially halting the recovery of ANC in surface waters associated with decline concentration of acid anions. Stage V, base cations increase as soils reach a new steady state with chemical weathering, atmospheric inputs, and biomass.

While the Galloway et al. (1983) model has been fully tested and varied using process-oriented numerical model (Cosby et al. 1985a,b,c), empirical evidence for the evolution of these acidification processes is rare because of the time scale of acidification. Acidification caused by acidic deposition takes tens of years or more and there are few time series of appropriate data, with enough resolution, and quality data to demonstrate all the processes. The Bear Brooks

Watershed Manipulation Maine (BBWM), Hubbard Brook Experimental Forest (HBEF) and other programs has provided empirical evidence of stages II and III and that base cation deposition in soils has occurred as a consequence of chronic acidification from atmospheric deposition (Norton et al. 1999). Moreover, many long-term monitoring programs, such as LTM and TIME with 20 years or more of data, show a slowing of the recovery of ANC in surface waters despite continued reductions acid anions from acid deposition (http://www.epa.gov/airmarkets/progress/ARPO9_3.html). While this pattern of slowing surface water recovery follows Galloway's model, it is uncertain what is driving the slowing recovery of ANC because of limited soil data. Currently, no study has shown an increase in soil base saturation as a result of decreasing in acid deposition. Most soil studies continue to show declining base saturations in areas impacted by acidic deposition (Warby et al 2009).

2.4.3 Biogeochemical ecosystem models used to estimate water quality

Biogeochemical acidification ecosystem models which incorporate the basic chemical principles discussed above are important tools to evaluate how multiple environmental factors alter the relationship between ANC and atmospheric deposition. Acidification models are capable of estimating how much acidifying deposition a watershed can accommodate to maintain a desired ANC, referred to as a critical load (Figure 2-36). The most commonly used models of acidification are presented in Table 2-8. These models are designed to be applied at the spatial scale of the watershed, with the exception of the SMART model.

Basic approach of steady-state vs. dynamic acidification models

Acidification models are based on steady-state or dynamic formulations. The basic principle of the steady-state approach of aquatic acidification models relates the long term sustainable ANC to constant levels of acidifying atmospheric deposition. Because a system response to time is not required, several simplifying assumptions are invoked which reduces the model complexity and amount of input data required for execution. The steady-state models relate an aquatic ecosystem's critical load to the weathering rate of its drainage basin expressed in terms of the base cation flux. The weathering of bedrock and soil minerals is often a major source of base cation supply to an ecosystem and, therefore, one of the governing factors of ecosystem critical loads. Dynamic models include mathematical descriptions of processes that are important in controlling the chemical response of a catchment. One of the most well-known dynamic models of aquatic acidification is MAGIC (Cosby et al., 1985a; 1985b; 1985c). It is a lumped-parameter model of soil and surface water acidification in response to atmospheric deposition based on process-level information about acidification. "Lumped-parameter" refers to the extent that spatially distributed physical and chemical processes in the catchment are averaged or lumped together without affecting the model's reproduction of catchment response. Process-level information refers to how the model characterizes acidification into (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of aluminum, and dissolution-speciation of inorganic carbon; and (2) a mass balance section 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. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Table 2-8. Summary several commonly used acidification models (See ISA Annex A for a more comprehensive list and discussion of acidification models).

Model name	Dynamic or steady state	Model description
Steady-state mass balance models /Steady-state water Chemistry (SSWC)/	Steady-state	The basic principle is based on identifying the long-term average sources of acidity and alkalinity in order to determine the maximum acid input that will balance the system at a biogeochemical safe-limit. Several assumptions have been made in the steady state calculations. First, it is assumed that ion exchange is at steady state and there is no net change in base saturation or no net transfer of ANC from soil solution to the ion exchange matrix. It is assumed that for N there is no net denitrification, adsorption or desorption and the N cycle is at steady state. Sulfate is also assumed to be at steady state: no sulfide oxidation, sulfate uptake, sulfate permanent fixation or sulfate reduction are significant. Simple hydrology is assumed where there is straight infiltration through the soil profile.
First-order Acid Balance model (FAB)	Steady-state	The FAB model includes more explicit modeling of N processes including soil immobilization, denitrification, and wood removal, in-lake retention of N and S, as well as lake size.
Model of Acidification of Groundwater in Catchment (MAGIC)	Dynamic	MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long term effects of acidic deposition on surface water chemistry. 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: a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO ₄ ²⁻ adsorption, cation exchange, dissolution-precipitation- speciation of aluminum, and dissolution-speciation of inorganic carbon; and a mass balance section 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.
PnET-BGC	Dynamic	PnET/BGC simulates major biogeochemical processes, such as forest canopy element transformations, hydrology, soil organic matter dynamics, N cycling, geochemical weathering, and chemical equilibrium reactions in solid and solution phases, and allows for simulations of land disturbance. The model uses mass transfer relationships to describe weathering, canopy interactions and surface water processes. Chemical equilibrium relationships describe anion adsorption, cation exchange and soil solution and surface water speciation. The model can be set to operate on any time set, but is generally run on a monthly time-step. It is applied at the stand to small-watershed scale.
DayCent-Chem	Dynamic	DayCent-Chem links two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland,

Model name	Dynamic or steady state	Model description
		and savanna systems, DayCent (Parton et al., 1998), and the other of soil and water geochemical equilibrium, PHREEQC (Parkhurst and Appelo, 1999). The linked DayCent/PHREEQC model was created to capture the biogeochemical responses to atmospheric deposition and to explicitly consider those biogeochemical influences on soil and surface water chemistry. The linked model expands on DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions of many other chemical species in surface water.
Very Simple Dynamic (VSD) soil acidification model	Dynamic	This model is frequently used in Europe to simulate acidification effects in soils when observed data are sparse. The VSD model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It only includes weathering, cation exchange, N immobilization processes, and a mass balance for cations, sulfur and N. In the VSD model, the various ecosystem processes have been limited to a few key processes. Processes that are not taken into account include canopy interactions; nutrient cycling processes; N fixation and NH ₄ adsorption; SO ₄ ²⁻ transformations (adsorption, uptake, immobilization, and reduction); formation and protonation of organic anions; and complexation of Al.
Simulation Model for Acidification's Regional Trends (SMART)	Dynamic	The the SMART model consists of a set of mass balance equations, describing soil input/output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It includes most of the assumptions and simplifications given for the VSD model. SMART models the exchange of Al, H, and divalent base cations using Gaines Thomas equations. Additionally, SO ₄ ²⁻ adsorption is modeled using a Langmuir equation (as in MAGIC) and organic acids can be described as mono-, di-, or tri-protic. The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994).

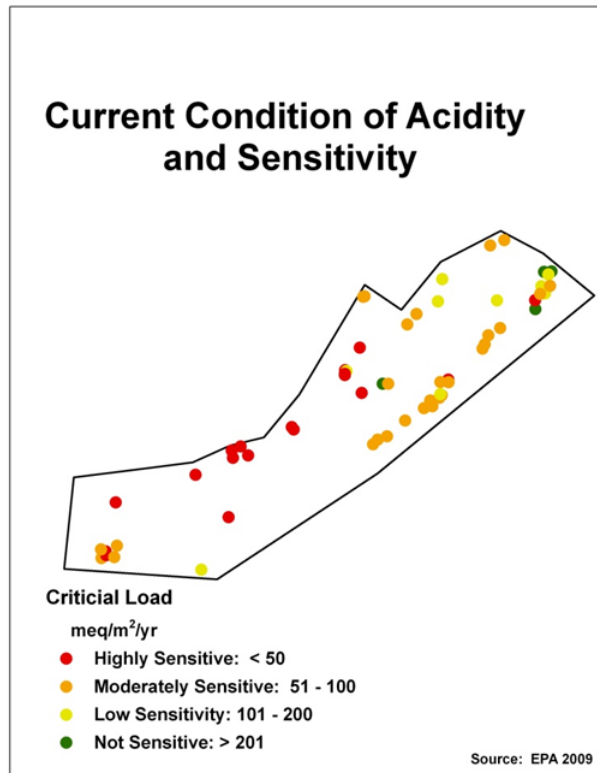
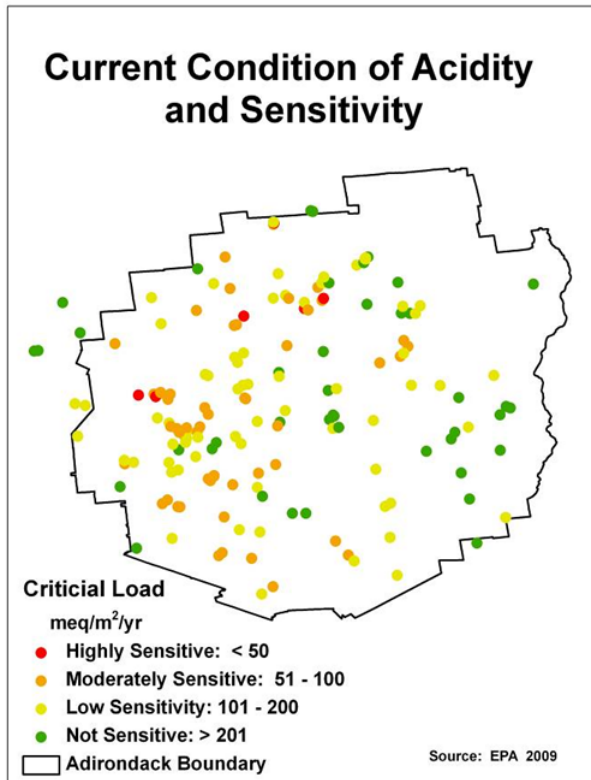


Figure 2-36. Critical loads of acidifying deposition based on MAGIC modeling that each surface water location can receive in the Adirondack and Shenandoah Case Study Areas while maintaining or exceeding an ANC concentration of 50 $\mu\text{eq/L}$ based on 2002 data. Watersheds with critical load values $<100 \text{ meq/m}^2/\text{yr}$ (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values $>100 \text{ meq/m}^2/\text{yr}$ (yellow and green circles) are less sensitive sites.

Trajectory of recovery for ecosystems from CL calculated by steady-state vs. dynamic acidification models

Steady-state models assume that the ecosystem is in equilibrium with the critical load of deposition; therefore the long-term sustainable deposition is indicated. This is the relevant information needed to provide protection from deposition in perpetuity as the system comes into equilibrium with the pollutant critical load (ISA Appendix D). In the U.S., few (if any) ecosystems qualify as steady-state systems. Therefore the assumption of equilibrium in the steady-state model is often false. This has implications for the temporal aspects of ecosystem recovery. The steady-state models give no information concerning the time to achieve the equilibrium or what may happen to the receptor along the path to equilibrium. The recovery of an ecosystem based on a critical load from a steady state model may take several hundred years. In other words the assumption that attainment of deposition values below the steady-state critical load will result in biological recovery within a specified time period may not be valid.

Dynamic models calculate time-dependent critical loads and therefore do not assume an ecosystem is in equilibrium. This is the relevant information needed to provide protection from damage by the pollutant within a specified time frame. As a general rule, the shorter the time frame selected, the lower the critical load.

The most comprehensive study done in the United States is Holdren et al. 1992 that compared critical loads calculated by the dynamic MAGIC model versus SSWC steady-state approach. A 50-yr simulation critical load was obtained from the MAGIC model. Holdren et al. 1992 found that both models yielded the same general trends. The critical load estimates projected using the dynamic versus steady-state models are consistently higher. Both models produced critical load values approximately equal for systems with critical loads of about zero. However, at higher critical load values the two model outputs diverge rapidly, implying that watersheds with larger inherent buffering capacities respond more slowly to a given level of acidic deposition. The apparent reason for this is that the watersheds represented by the dynamic model retain a larger fraction of their buffering capacity in the base cation exchange pool for the 50-year time scale of the simulation. In the steady-state models, the cation exchange pool is assumed to be in equilibrium and does not provide additional buffering.

Data Requirements of steady-state vs. dynamic acidification models

There are various factors that modify the ANC to deposition relationship, which are described by models that parameterize ecosystems to simulate the process of acidification. The steady-state models used for critical loads analysis in the REA required input data for between 17 and 20 variables, including water chemistry data from the TIME and LTM programs, which are part of the Environmental Monitoring and Assessment Program (EMAP). A summary of the variables for steady state models (and data sources for the calculations made in the REA) is given in Appendix A.

The data requirements required to run dynamic models, such as MAGIC, are greater. The equations that characterize the chemical composition of soil water in MAGIC contain 33 variables and 21 parameters (Cosby et al. 1985a). Data required to conduct dynamic modeling are not available for as many places as the data required to conduct steady-state modeling.

Comparison of two steady-state models: FAB and SSWC

The steady state models used in the REA were the Steady State Water Chemistry model (SSWC), and the First-order Acid Balance model (FAB). The SSWC and FAB models were used to calculate critical loads for specified ANC levels in the case study areas.

The SSWC and FAB make different assumptions of ecosystem function. Most notably, biogeochemical pathways of N deposition are considered differently in the two models. In the SSWC model, sulfate is assumed to be a mobile anion (i.e. S leaching = S deposition), while nitrogen is retained in the catchment by various processes. The assumption that all N is retained by the ecosystem and does not contribute to acidification is incorrect because in many ecosystems nitrate leaching is observed. If nitrate is leaching out of an ecosystem, it cannot also be true that it has all been retained. Nitrate leaching is determined from the sum of the measured concentrations of nitrate in the runoff. The critical load for sulfur that is calculated by SSWC can be corrected for the amount of nitrogen that contributes to acidification. When an exceedance value for the critical load is calculated, the critical load is subtracted from S deposition plus the amount of nitrate leaching, as it represents the difference between N deposition and N retention by the ecosystem. N leaching data used in this calculation are considered robust.

In contrast to the SSWC approach, the FAB model includes more explicit modeling of N processes including soil immobilization, denitrification, and wood removal, in-lake retention of N and S, as well as lake size. Although N cycling is more detailed in the FAB model, there is greater uncertainty in the input data needed to characterize the components of the N cycle. The FAB model yields a deposition load function for a specified level of an endpoint. This function is characterized by three nodes that are illustrated on Figure 2-37, 1. the maximum of amount of N deposition when S deposition equals zero ($DL_{max}(N)$); 2. the amount of N deposition that will be captured by the ecosystem before it leaches ($DL_{min}(N)$); and 3. the maximum amount of S deposition considering the N captured by the ecosystem ($DL_{max}(S)$). The function represents many unique pairs of N and S deposition that will equal the critical load for acidifying deposition.

The three models, MAGIC, SSWC and FAB, discussed above were widely used in the REA and this PA. MAGIC enabled the construction of time series estimates of water quality change and provided a more scientifically rigorous model to conduct comparisons with certain parameterizations used in steady state models. As will be described in Section 7, attributes of SSWC and FAB modeling, several of which are illustrated in Figure 2-37, were incorporated in constructing the form of the standard.

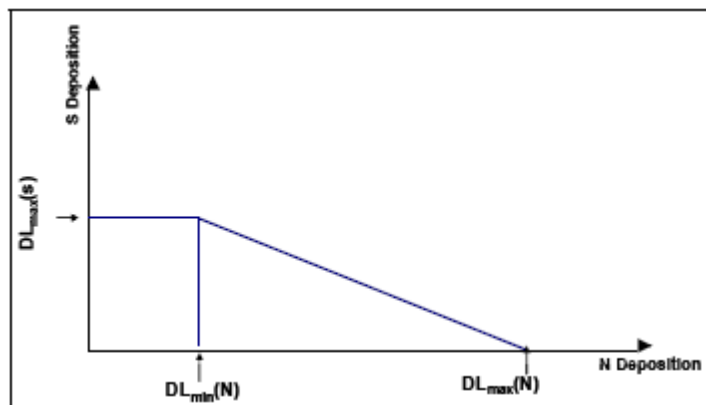


Figure 2-37. Illustration of a generalized N + S deposition tradeoff curve that is calculated by using the FAB approach.

2.4.4 Water Quality Networks

An overview of surface water chemistry monitoring programs is incorporated in EPA's ISA (EPA, 2008) and is the basis for much of this discussion. The TIME/LTM program is described immediately below. A summary of the water quality data bases used in the PA are provided in Table 2- 9. National alkalinity and ANC maps, which help support development of acid sensitive and less sensitive categories which are considered in developing the standard (see section 7.2.5), are included at the end of this sub-section (Figures 2-39 and 2-40). Appendix D provides data summaries of water chemistry variables (SO_4 , natural base cation supply, DOC, ANC) delineated by Omernik Ecoregion Level III categories.

TIME/LTM Program descriptions

The Temporally Integrated Monitoring of Ecosystems (TIME) and the long-Term Monitoring (LTM) programs (Table 2-10; Figure 2-38) are complementary EPA surface water monitoring networks that provide information on a variety of indicators necessary for tracking temporal and spatial trends in environmental response to changes in regional air quality and acid deposition in ecosystems sensitive to acid rain in the eastern United States. Some of these indicators include, but are not limited to: acid neutralizing capacity (ANC), sulfate (SO_4^{2-}), and nitrate (NO_3^-). Both programs are operated cooperatively with numerous collaborators in state agencies, academic institutions, and other federal agencies.

The TIME program was developed as a special study within EPA's Environmental Monitoring and Assessment program (EMAP) to track, in more detail, the trends in acid relevant chemistry of particular classes of acid sensitive lakes and streams in the eastern United States. TIME lakes, located in the Adirondacks and New England, have been sampled annually each summer since 1991, while TIME streams, located in the Ridge and Blue Ridge Provinces and the Northern Appalachian Plateau, have been sampled annually in spring since 1993. Based on the concept of a probability sample, TIME sites were statistically selected to be representative of a larger, target population, thus results from TIME samples can be extrapolated, with known confidence, to the target populations as a whole.

The LTM program focuses on detecting long-term trends in acid relevant chemistry in lakes and streams across a gradient of acidic deposition. LTM sites are a subset of sensitive lakes and streams in the eastern United States with long-term data that, in most cases, date back

to the early 1980s. Sites are sampled 3 to 15 times per year to provide information on how the most sensitive of aquatic systems in each region are responding to changing deposition, as well as give information on seasonal chemistry and episodic acidification. LTM lake sites are located in the Adirondacks and New England while LTM stream sites are located in the Catskills/Northern Appalachian Plateau and the Ridge and Blue Ridge Provinces.

Table 2-9. Summary of data sources considered for the evaluation of national ANC.

Program	Dates of observations	Reference
EPA Long Term Monitoring Vermont (LTM_VT)	1983-2007	EPA/903/R-00/015
EPA Eastern Lakes Survey (ELS)	1984	EPA/620/R-93/009
Adirondack Lake Survey (ALS)	1984-1987	Stoddard.et.al.WRR.1996
EPA Western Lake Survey (WLS)	1985	EPA 620-R-05-005
EPA National Stream Survey (NSS)	1986	Stoddard.et.al.WRR.1996
VT SSS	1987 & 2000	EPA 841-B-06-002
EPA Long Term Monitoring_Colorado sites (LTM_CO)	1990-1994	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Midwest Sites (LTM_MW)	1990-2000	Stoddard.et.al.WRR.1996
VT SSS LTM	1990-2007	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Pennsylvania sites(LTM_PA)	1990-2007	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Catskill sites (LTM_CAT)	1990-2007	EPA 905-R-92-001
EPA Long Term Monitoring: Annual average from 1992-2007	1990-2007	EPA/600/4-88/032
EPA EMAP Northeast Lake Survey	1991-1994	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Maine sites (LTM_ME)	1992-2007	reg1_qa.pdf
Regional Environmental Monitoring Program_Maine sites (REMAP_ME)	1993	Stoddard.et.al.WRR.1996
EPA EMAP_Mid Atlantic streams (EPA EMAP_MAIA)	1993-1996	EPA/R-06/XX
EPA EMAP_Mid Atlantic streams (EPA EMAP_MAIA)	1997-1998	EPA-600-388-021a
EPA EMAP Western Stream and River Survey (EMAP WEST)	2000-2004	EPA/600/3-86/054b
EPA National Lakes Survey (NLS)	2010	EPA 841-F-09-007.
USGS NAWQA Program		http://water.usgs.gov/nawqa/
EPA Storet Program		http://www.epa.gov/storet/

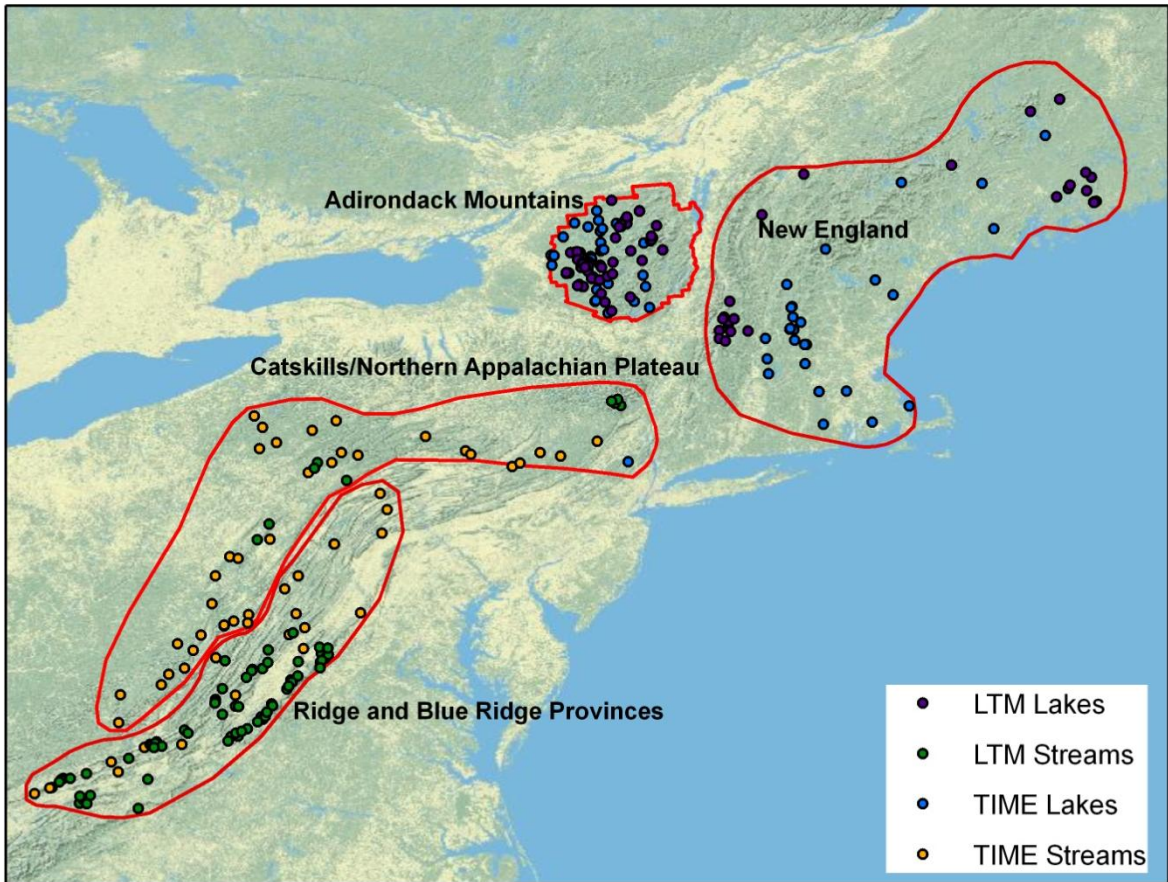


Figure 2-38. Active TIME/LTM sampling locations.

Table 2-9. Characteristics of TIME/LTM Sites

	Sites	Collection interval*	Major ions collected	Total AI Collected	AI Speciated	Limited AI Speciation
TIME Lakes**						
<i>Adirondacks (New York)</i>	43	Summer/Fall	X	X	X	--
<i>Maine</i>			X	X	X	--
- Massachusetts	8	Summer				
- Maine	5	Summer				
- New Hampshire	14	Summer				
- Rhode Island	1	Summer				
- Vermont	1	Summer				
Total TIME Lakes	72					
TIME Streams**						
<i>Northern Appalachians</i>			X	X	X	--
- Pennsylvania	21	Spring				
- West Virginia	14	Spring				
<i>Ridge / Blue Ridge</i>			X	X	X	--
- Maryland	1	Spring				
- Pennsylvania	3	Spring				
- Virginia	13	Spring				
- West Virginia	4	Spring				
Total TIME Streams	56					
Total TIME Lakes and Streams	128					
LTM Lakes						
<i>Adirondacks (New York)</i>	52	Monthly	X	X	X	--
<i>Maine</i>	16	Quarterly	X	X	--	X
<i>Vermont</i>	12	Quarterly	X	X	X	--
Total LTM Lakes	80					
LTM Streams						
<i>Appalachians</i>	5	Monthly	X	X	--	X
- Pennsylvania±						
<i>Catskills</i>		Monthly/Episodes	X	X	X	--
-New York ±	4					
<i>Virginia Intensive ±</i>	3	Weekly/Episodes	X	--	--	X
<i>Virginia Extensive (Trout Streams)</i>	64	Quarterly	X	--	--	X
Total LTM Streams	76					
Total LTM Lakes and Streams	156					
TOTAL TIME/LTM SITES	284					

* Samples are collected once per specified season/interval

** All TIME sites are monitored annually

± Stream flow data are collected from these sites

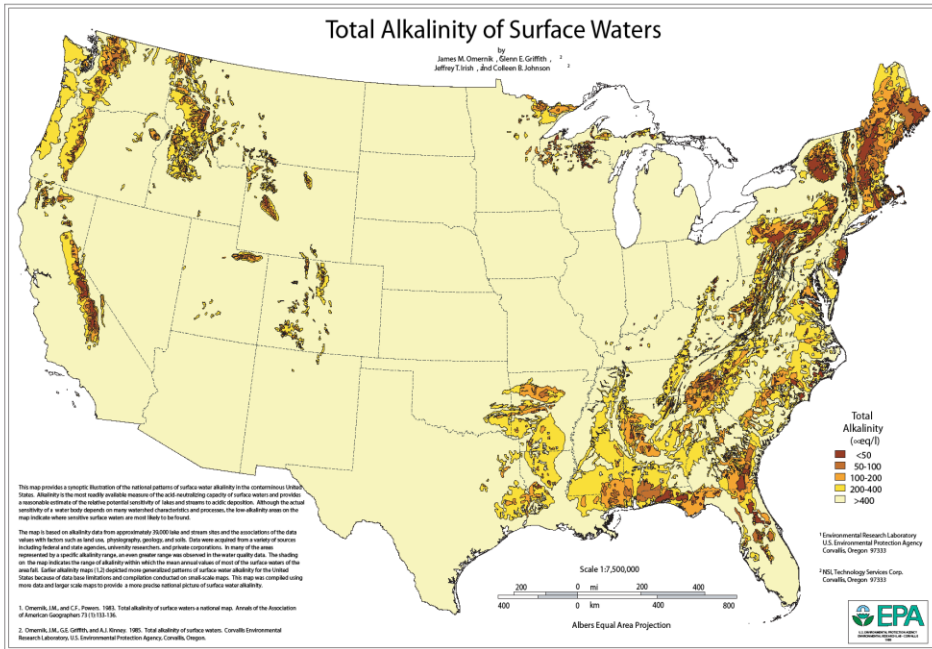


Figure 2-39. Surface water alkalinity in the conterminous U.S. Shading indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall (Omernik and Powers), 1983.

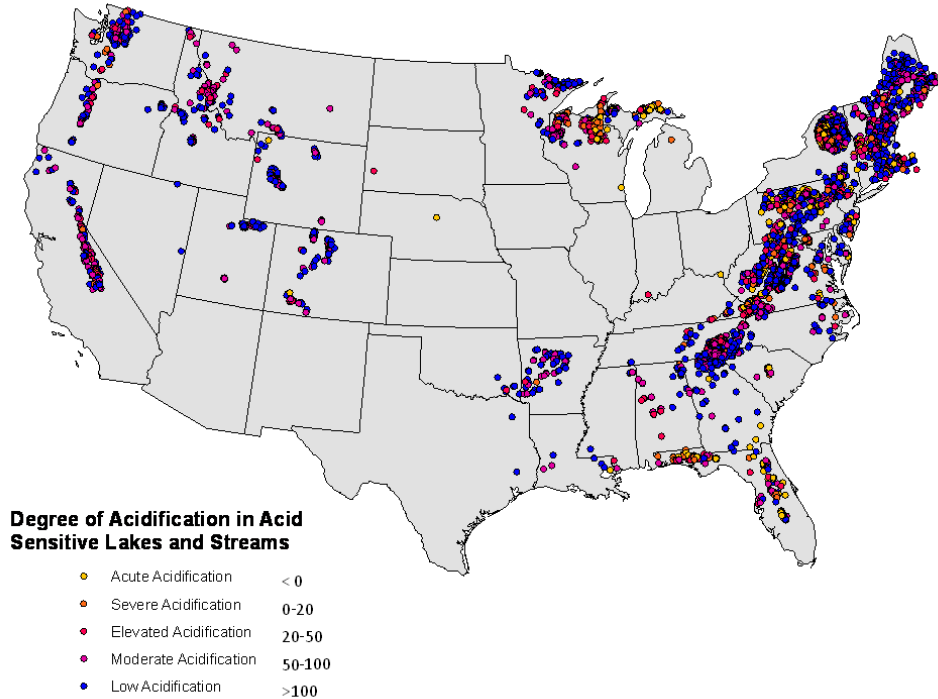


Figure 2-40. National map of ANC data (µeq/L) based on historical and contemporary data sorted by ANC classes.

2.5 TRENDS

This section provides summaries of time series trends of emissions, air quality, deposition and water quality relevant to oxides of nitrogen and sulfur and aquatic acidification. The value of this summary is in bringing the four components in the source-to-effects continuum (Figure 2-41) together in one place to provide general trends information but also to develop, at least conceptually, a retrospective view of how the basic components which underlie the form of the standard (section 7.2) respond together. Extensive use is made of EPA's own annual reports on progress associated with the Acid Rain Program (EPA, 2010). This information is a response to suggestions that the form of the standard be studied in a "hindcast" manner. Unfortunately, historical data and modeling results are not available to adequately support calculation of the standard as described in chapter 7. Consequently, these combined time series examples are used to demonstrate in an associative manner that the basic tenets of the conceptual model of the standard are valid for the standard being developed in this assessment, which relies on similar directional changes in the source to effects continuum. One could identify the acid rain emissions limits as part of Title IV as a marker to assess progress that is specific to the mission component at the beginning of the source-to-effects continuum. Similarly, the standard developed in this assessment might be thought of as providing an atmospheric marker upon which future progress can be judged.

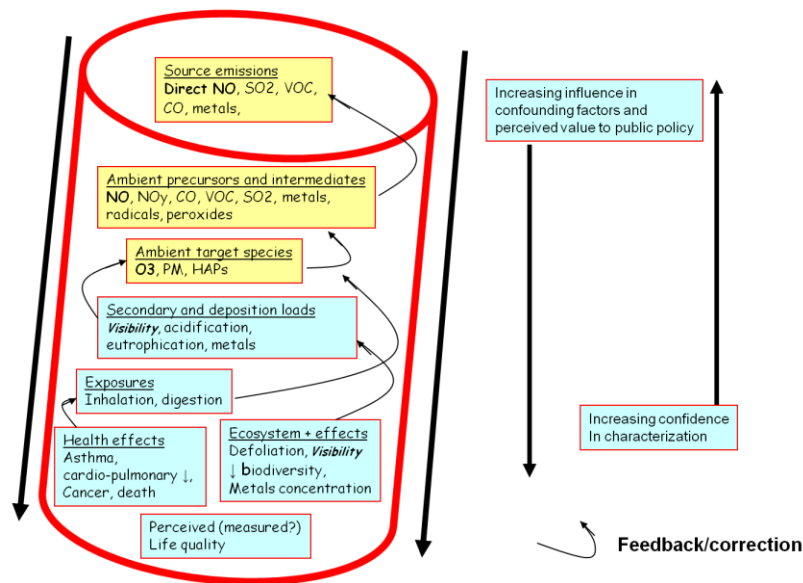


Figure 2-41. Conceptual source to effects pipeline diagram illustrating basic accountability concepts as one proceeds from source emissions through the air and eventually to effects.

2.5.1 Emissions

Sickles and Shadwick (2007) summarize NO_x and SO_x emission changes from 1990 – 2004. Title IV (Acid Rain provisions) of the Clean Air Act Amendments of 1990 (CAAA) established phased year-round controls for SO₂ and NO_x emissions from electrical generating units (EGUs) that became effective in 1995 for SO₂ and 1996 for NO_x (Phase I); while additional controls became effective under Phase II in 2000. Over half of the EGUs targeted by the CAAA are in six states located along the Ohio River (IL, IN, KY, OH, PA, and WV). Beginning in 1999, O₃ season (i.e., summer) NO_x controls focusing on EGUs became effective in selected eastern states under the Ozone Transport Commission (OTC) and were superseded in 2003 by the NO_x State Implementation Plan (SIP) Call. The affected states have chosen to meet their mandatory SIP Call NO_x reductions by participating in the NO_x Budget Trading Program, a market-based cap and trade program for EGUs and large industrial units. In addition, various mobile source NO_x emissions control programs began in the mid to late 1990s. These mobile source programs have a cumulative effect of reducing NO_x emissions over time as the mobile fleet is replaced.

The recent declines from 2005 to 2009 in NO_x and SO_x emissions (Figures 2-42 and 2-43) are attributed to continued implementation of NO_x SIP CALL and transportation sector rules, as well efforts to implement controls associated with the Clean Air Interstate Rule (CAIR). Annual reports explaining the rules and programs addressing EGUs and the relationships between emission reductions and air quality and deposition changes is provided by EPA's Clean Air Market Division at <http://www.epa.gov/airmarkets/progress/progress-reports.htm>. Major reductions in EGU SO_x and NO_x emissions are associated with market trading of emissions which was a tool in implementing emissions reduction targets in Title IV and other rules.

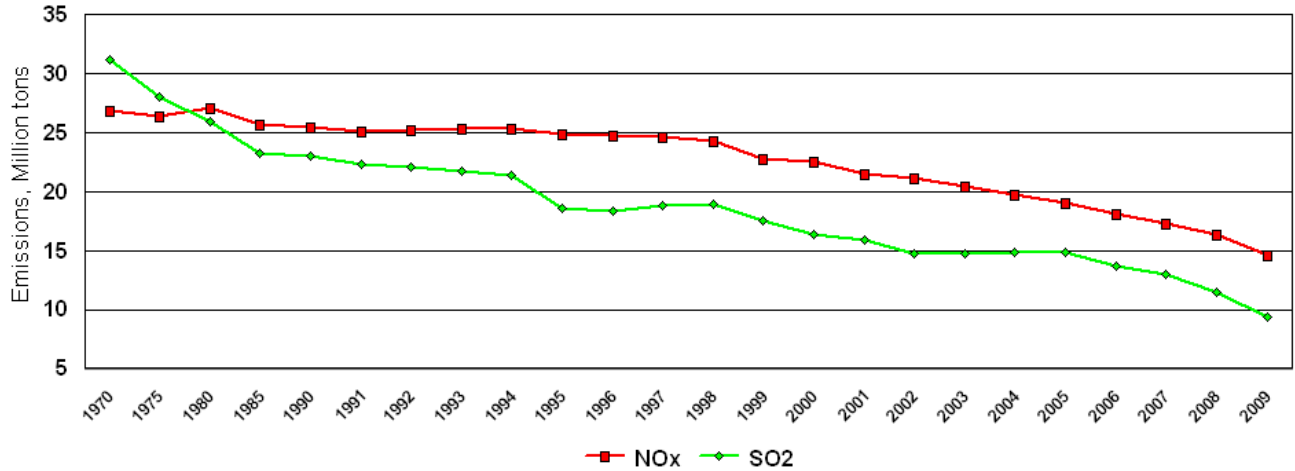


Figure 2-42 Time series trends of all anthropogenic NOx and SOx emissions based on EPA’s National Emissions Inventory (NEI).

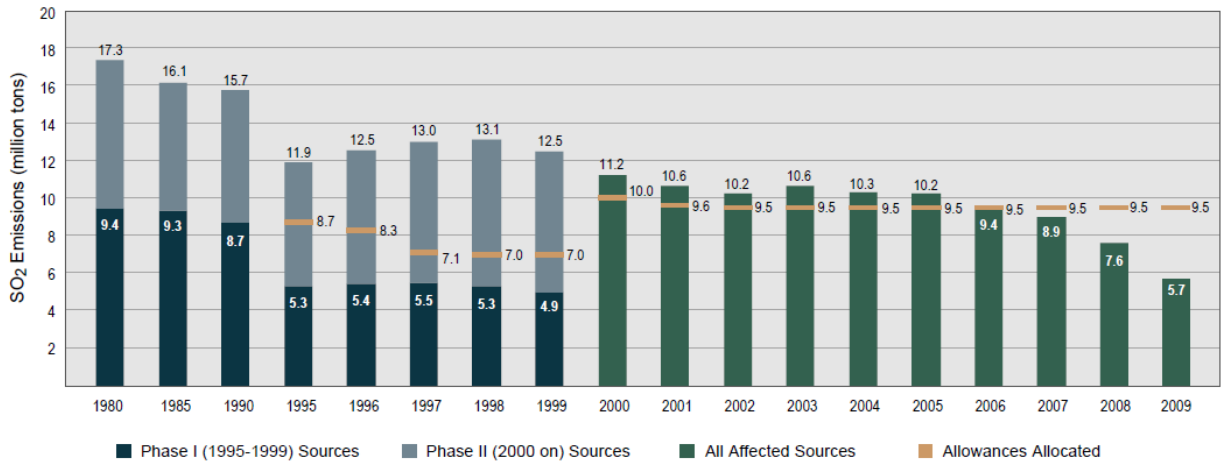
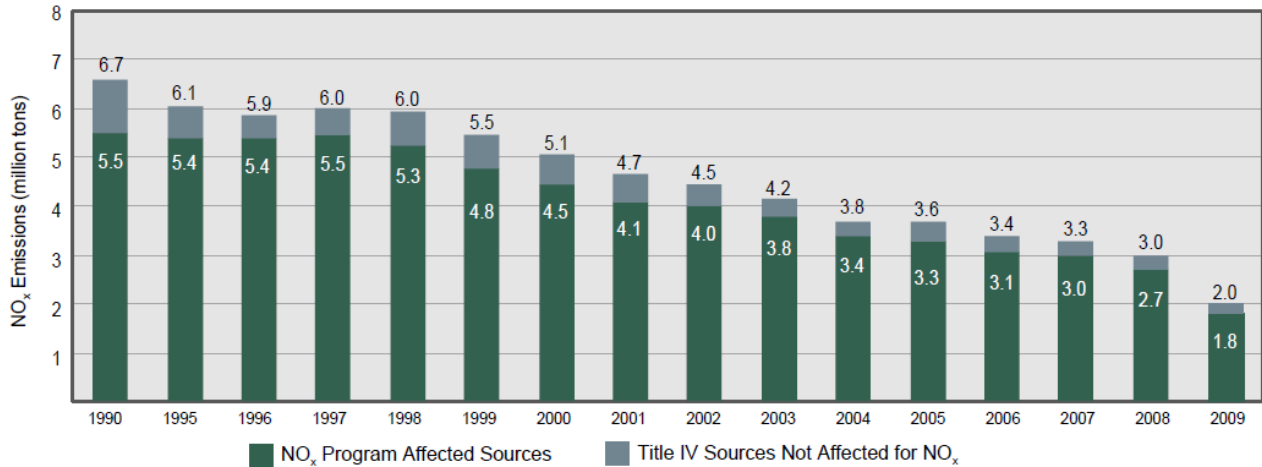


Figure 2-43. Trends of NOx (above) and SOx (below) reductions associated with EPA’s Acid Rain Program (ARP) which established market trade units for NOx and SOx emissions associated with EGUs (EPA, 2010). Trends of SO2 reductions associated with EPA’s Acid Rain Program (ARP) which established market trade units for NOx and SOx emissions associated with EGUs. ARP units have reduced annual SO2 emissions by 67 percent compared with 1980 levels and 64 percent compared with 1990 levels (EPA, 2010).

2.5.2 Air quality and deposition

Significant reductions in ambient air concentrations in the Eastern U.S. of SO₂, NO₃ and SO₄ over the last two decades (Figures 2-44 and 2-45) are consistent with emission trends for NO_x and SO_x over the same period. Trends of observed wet deposition have been provided as a feature product by the NADP; sulfate and nitrate wet deposition patterns (Figure 2-46) generally exhibit the same features of the analogous air quality patterns. Dry deposition patterns can be assumed to exhibit identical patterns of air quality concentrations, given the direct dependence of dry deposition on concentration. Sickles and Chadwick (2007) provide quantitative estimates linking changes in emissions, concentrations and deposition patterns from 1990 to 2004. Their findings (Table 2-11) broken down by pollutant and three subregions across the Eastern U.S. demonstrate similar patterns of reductions through emission, concentrations and deposition. However, stronger correlations between emissions changes and total oxidized nitrogen and sulfur in concentration and deposition fields relative to relationships between emissions and a single species.

Table 2-11 Period 1 Emissions Density and Period 1-to-Period 3 Relative Changes (%) in Oxidized Sulfur and Nitrogen Emissions, Atmospheric Concentration, and Dry, Wet, and Total Deposition (from Sickles and Chadwick, 2007).

Region	Emissions		Atmospheric Concentration			Deposition		
	P1 Density ^a	SO ₂ , %	SO ₂ , %	SO ₄ ²⁻ , %	S, %	Dry S, %	Wet S, %	Total S, %
E	37	-39	-33	-21	-30	-31	-22	-26
MW	50	-49	-34	-22	-32	-29	-27	-28
NE	38	-38	-31	-21	-29	-30	-20	-25
SO	28	-30	-35	-20	-30	-33	-19	-25

Region	Emissions		Atmospheric Concentration			Deposition		
	P1 Density ^b	NO _x , %	HNO ₃ , %	NO ₃ ⁻ , %	OxN, %	Dry OxN, %	Wet OxN, %	Total OxN, %
E	19	-22	-13	11	-4	-8	-12	-11
MW	20	-21	-11	8	-1	-3	-12	-8
NE	25	-35	-18	19	-8	-13	-14	-14
SO	15	-14	-10	9	-5	-8	-10	-9

^aSO₂ emissions density in units of kgS/(ha y).

^bNO_x emissions density in units of kgN/(ha y).

Trends in reduced nitrogen are based only on ammonium ion observations, given the very limited availability of ammonia gas monitoring. Patterns of reduced nitrogen (Figure 2-47) based on ammonium ion are difficult to interpret with respect to trends of precursor ammonia emissions, which are not presented in this section. Ambient ammonium levels have decreased while wet deposition has increased over the same period. Because ammonium is associated atmospheric nitrate or sulfate, reductions in NO_x and SO_x emissions that lead to reductions in

atmospheric nitrate and sulfate also lead to reduced atmospheric ammonium. However, because ammonia gas is a precursor for ammonium, and ammonium is dependent on sulfate and nitrate, very little can be inferred regard from atmospheric ammonium levels in regard to total contribution to reduced nitrogen. One can infer that dry deposition of ammonium has been reduced, as has the contribution of ammonium to particulate matter mass. The sum of dry and wet ammonium deposition is a better indicator relative for associating atmospheric data with trends of ammonia emissions. While dry deposition trends are not presented here, wet ammonium levels have increased and it is reasonable that infer that total reduced nitrogen (NH_x), which is associated with ammonia emissions, probably has not changed in the same manner as NO_x and SO_x emissions.

Kim et al (2006) quantified changes in NO_x emission reductions and NO_2 concentrations for New York and Ohio, using satellite column NO_2 observations to capture region wide NO_2 patterns (Figure 2-48). The use of satellite data to capture region wide NO_2 patterns is indicative of the shortage of available NO_2 data in rural locations, as described earlier in section 2.2.

Before describing water quality trends, it is informative to note changes in pH over the last two decades. In this context, pH serves simply as an indicator and does reflect that concurrent reductions in emissions of acid generating gases, NO_x and SO_x , clearly have resulted in significant reductions in rain water hydrogen ion levels (Figure 2-49). The pH patterns continue to reflect a sulfur dominated air regime in the Eastern U.S., relative to the rest of the contiguous U.S.

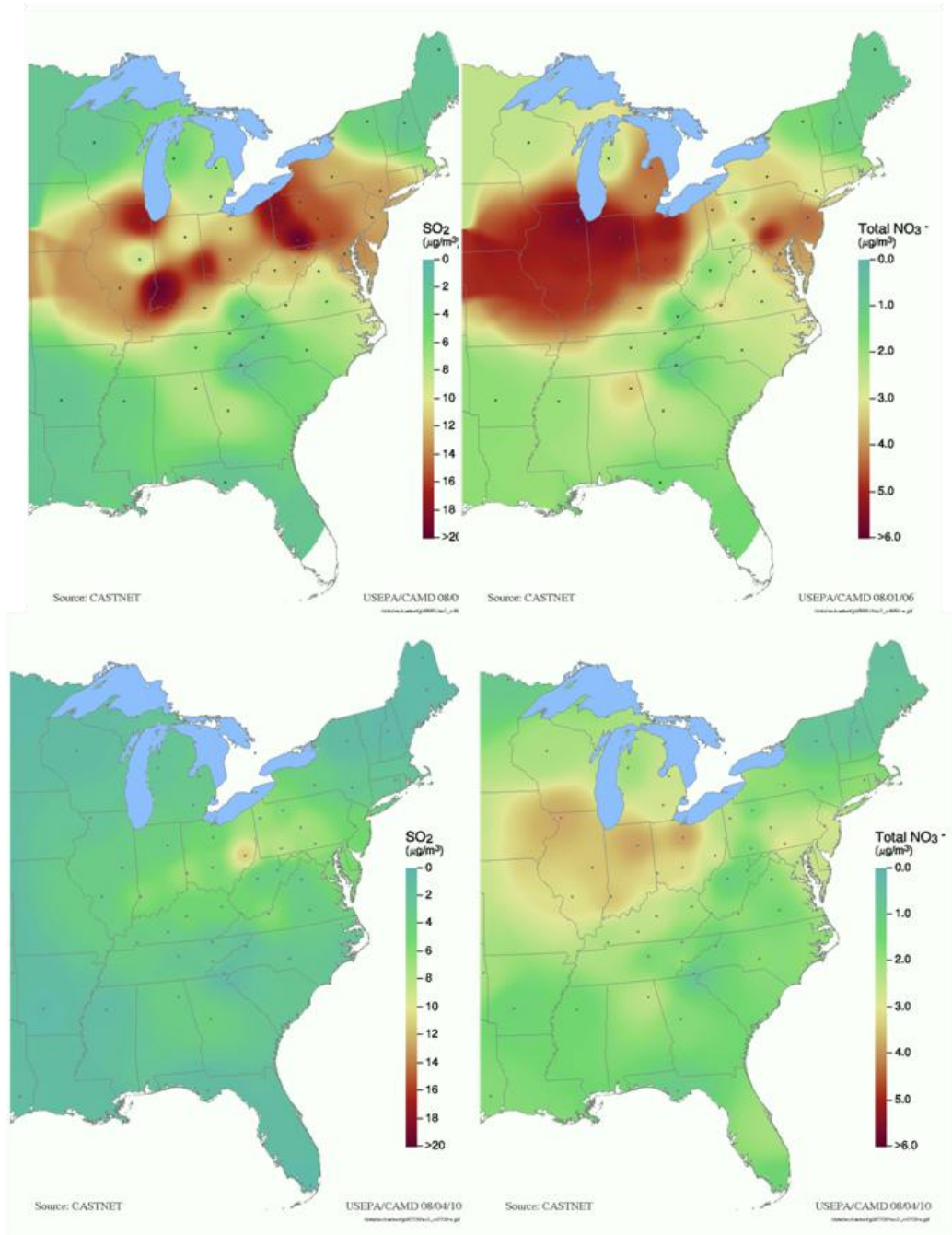


Figure 2-44. Eastern U.S. annual average spatial distribution of SO₂ (left) and total nitrate (right) concentrations averaged over 1989 -1991 (top) and 2007 – 2009 (bottom). Data are based on EPA’s CASTNET program.

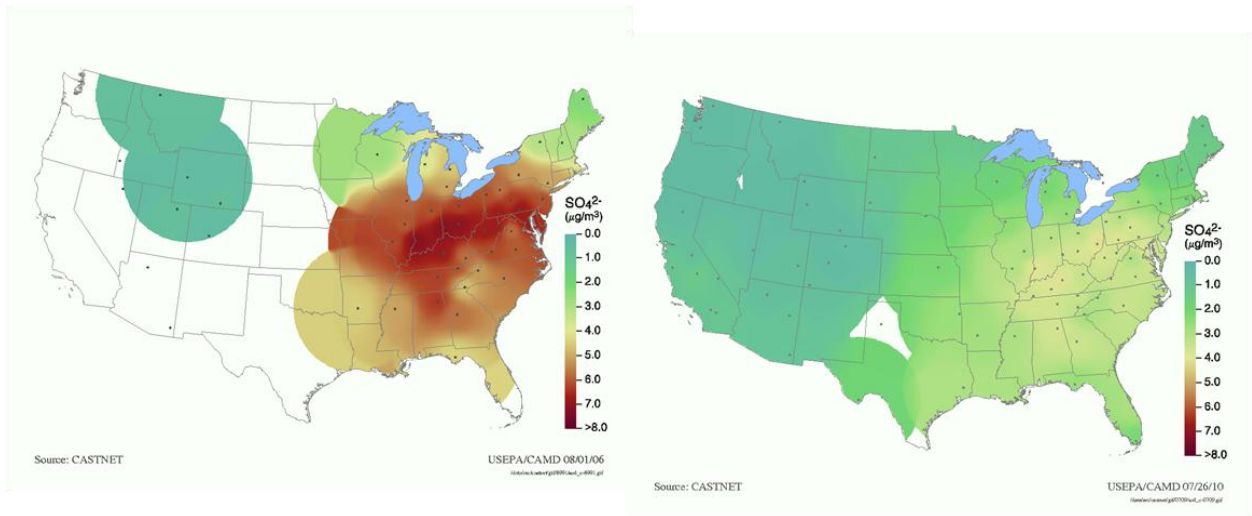


Figure 2-45. Eastern U.S. annual average spatial distribution of SO₄ (left) concentrations averaged over 1989 - 1991 (left) and 2007 - 2009 (right). Data are based on EPA's CASTNET program.

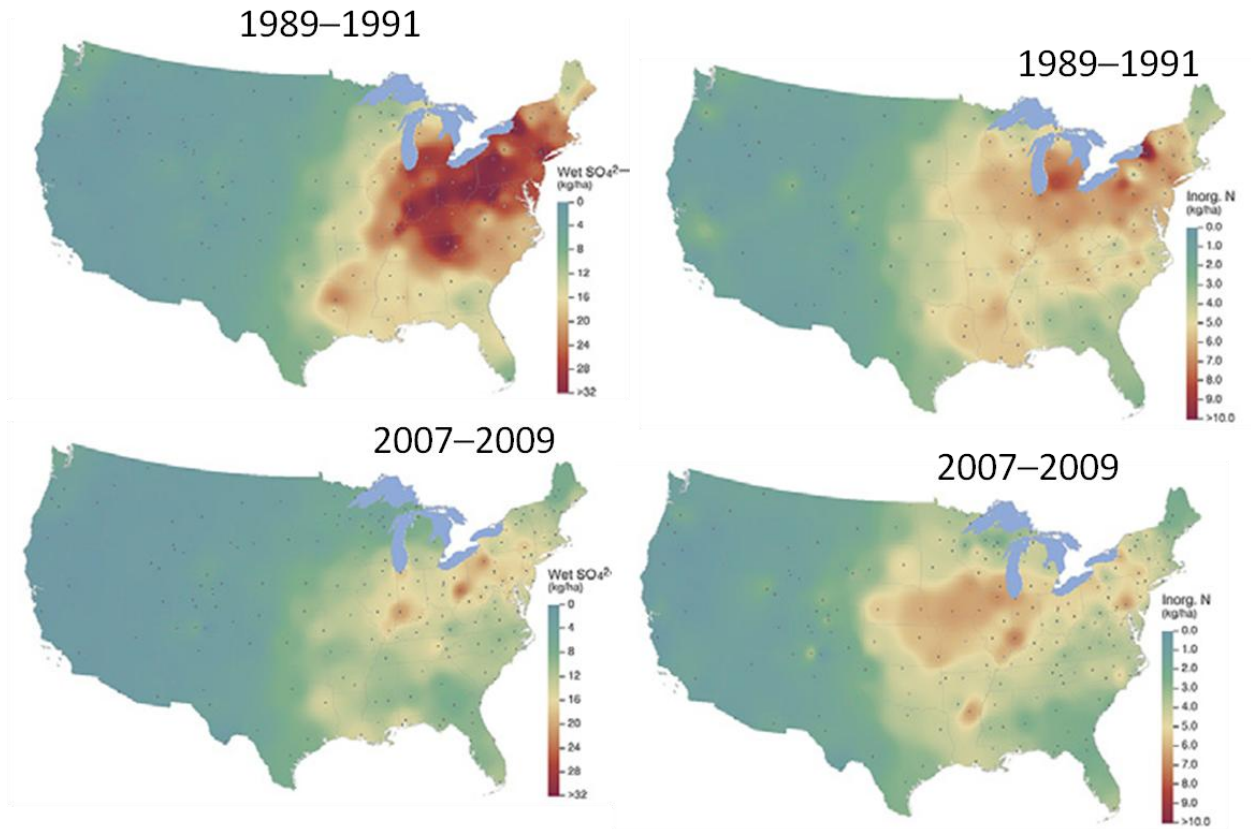


Figure 2-46. U.S. annual average spatial distribution of wet sulfate (left) and nitrate (right) deposition averaged over 1989 - 1991 (top) and 2007 - 2009 (bottom) based on the NADP.

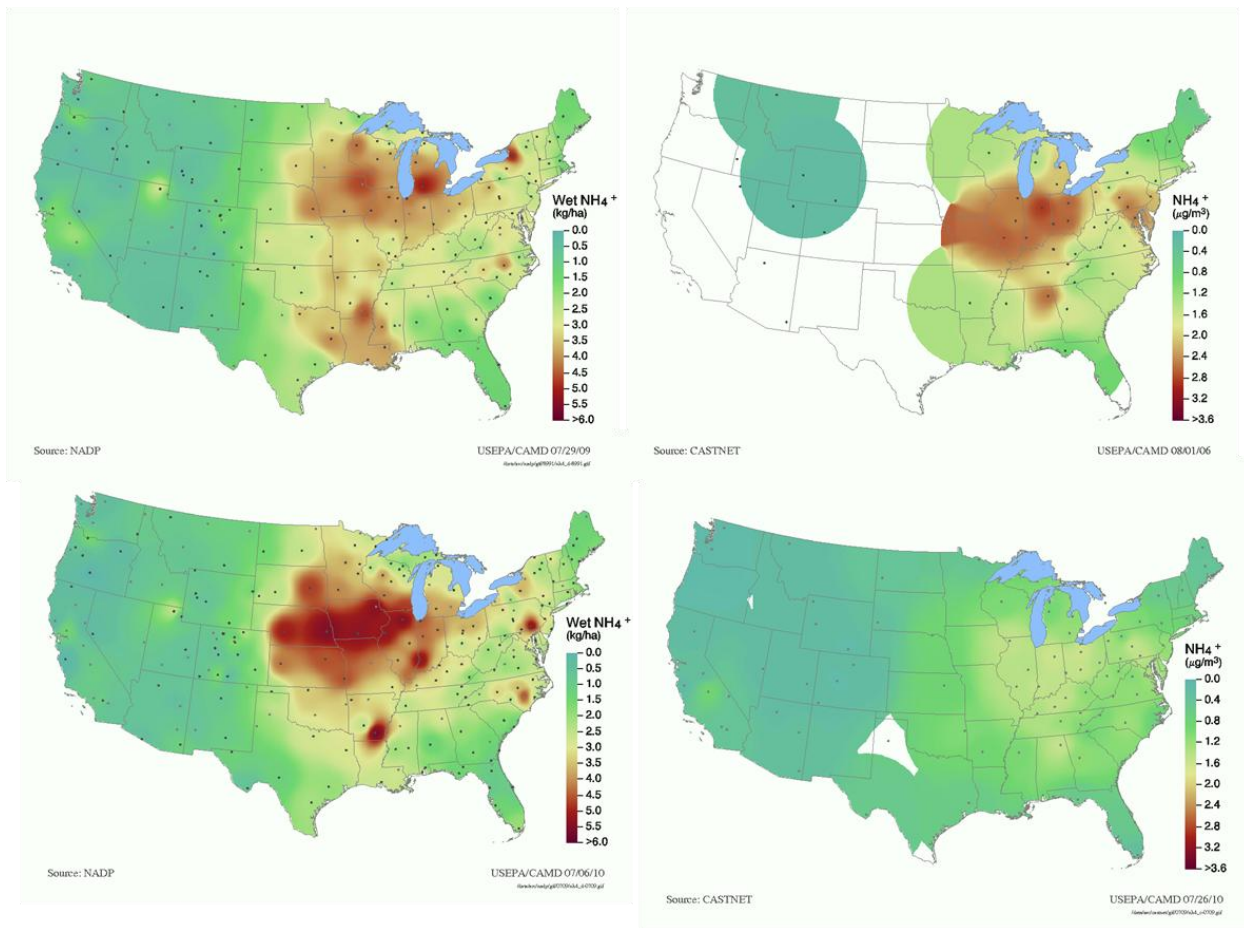


Figure 2-47. U.S. annual average spatial distribution of wet ammonium sulfate deposition (left) and ambient air ammonium concentrations (right) averaged over 1989 -1991 (top) and 2007 – 2009 (bottom) based on CASTNET and NADP.

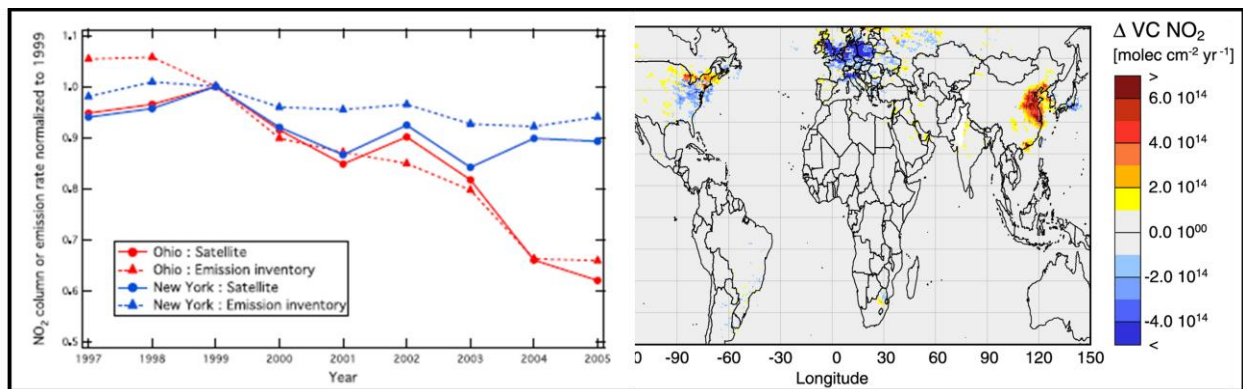


Figure 2-48. Left - superimposed Eastern U.S. emission and combined GOME and SCIAMACHY NO₂ 1997-2002 trends (Kim et al., 2006); right - GOME NO₂ trends from 1995 – 2002 (after Richter et al., 2005). Clear evidence of reductions in midwest U.S. and European NO_x emissions, and increased NO_x generated in Eastern Asia

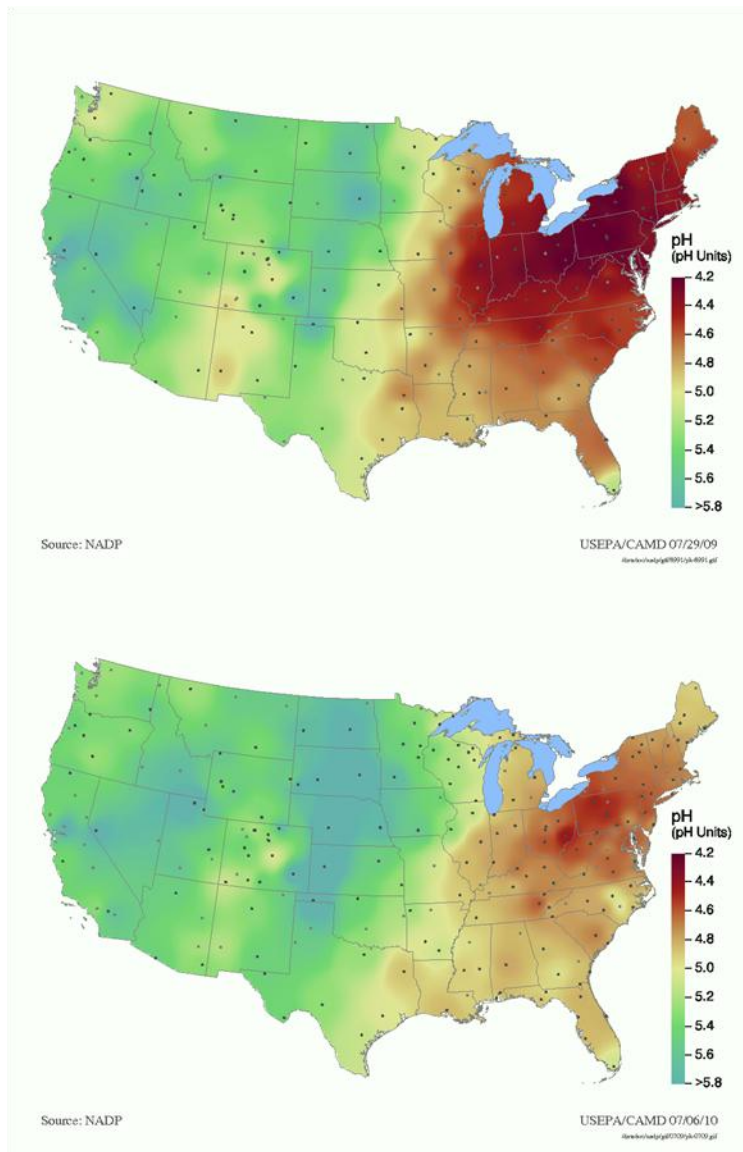


Figure 2-49. U.S. annual average spatial distribution of hydrogen ion concentration in rain water as pH averaged over 1989 -1991 (top) and 2007 – 2009 (bottom) based on the NADP.

2.5.3 Water quality

General patterns in the trends of major anions directionally track emission changes over the last two decades (EPA, 2010; Figures 2-50 to 2-52). Summaries of water quality trends prior to 2000 (Driscoll et al, 2003; Stoddard, 2003; Figures 2-51 to 2-52) illustrate the initial period of declining SO_x emissions with evidence of decreasing anions and increasing ANC. Several

studies have illustrated the general trend of decreasing water column levels of strong ions and increasing ANC with reductions in SO_x and NO_x deposition are synthesized in EPA's ISA.

However, as one proceeds through the source to effects continuum, strong direct relationships gradually diminish at each step as there are a myriad of confounding factors that start to affect each stage. This is particularly true in moving from deposition to water quality, where a variety of ecosystem processes moderate nitrogen and sulfur deposition both in terms of chemical transformations and delivery rates associated with soils and vegetation processes discussed above. For example, there are directionally different responses of water column sulfate (e.g., increase in southern Appalachians, decreases in Adirondacks) to declining levels of sulfate deposition (Figure 2-50). The inherent lag in recovering from acidification largely associated with soil adsorption and exchange processes implies that several decades of information may be required to sort out long term responses in water column chemistry relative to changes in emissions, air and deposition but the relative degree of responsiveness will be influenced strongly by watershed soil and vegetation characteristics. A recognition of the inherent lag in ecosystem response to changes in atmospheric variables is necessary to conceptualize the linking of air quality to water quality that rely on steady state models ecosystem models which provide the long term sustained response of water chemistry to atmospheric conditions. This understanding underlies the basic difference between the air quality water indices of acidification, both of which are incorporated in the form of the standard (section 7.2). An air quality acidification index reflects the eventual steady state conditions in aquatic systems that would be achieved assuming atmospheric a given atmospheric state of air quality conditions. The time lag in those conditions between aquatic and atmospheric media can range from near real time to decadal differences.

For example, the analyses of the Adirondack and Shenandoah Case Study Areas indicated that although wet deposition rates for SO₂ and NO_x have been reduced since the mid-1990s, current concentrations are still well above simulated pre-acidification (1860) conditions (Figures 2-53 to 2-56). Modeling predicts NO₃⁻ and SO₄²⁻ are 17- and 5-fold higher, respectively, in 2006 than under simulated pre-acidification conditions. Based on the 2006 Model of Acidification of Groundwater in Catchment (MAGIC) simulations, the estimated average ANC across the 44 lakes in the Adirondack Case Study Area is 62.1 µeq/L (± 15.7

$\mu\text{eq/L}$); 78 % of all monitored lakes in the Adirondack Case Study Area have a current risk of *Elevated, Severe, or Acute*. Of the 78%, 18% are chronically acidic (**REA 4.2.4.2**).

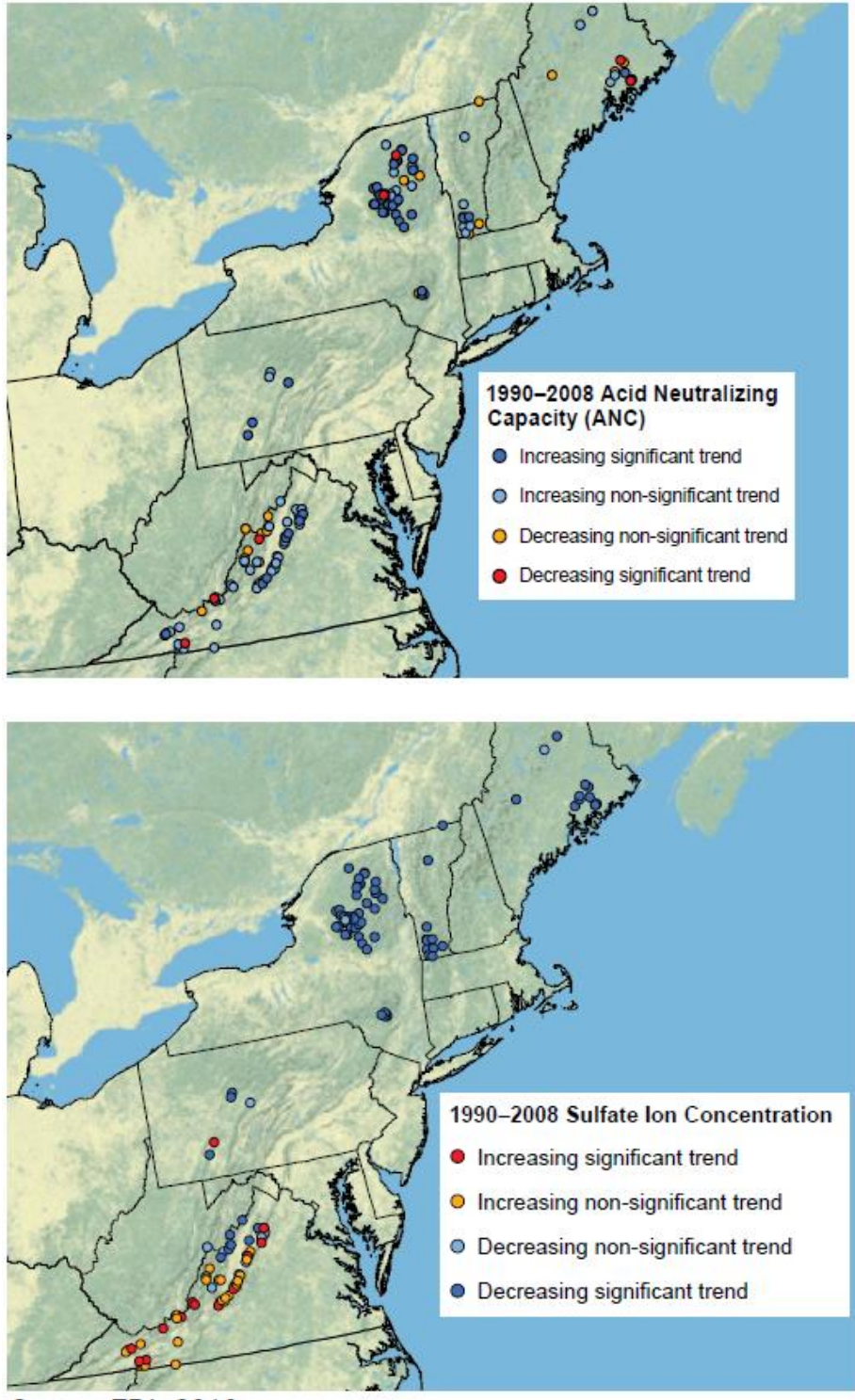
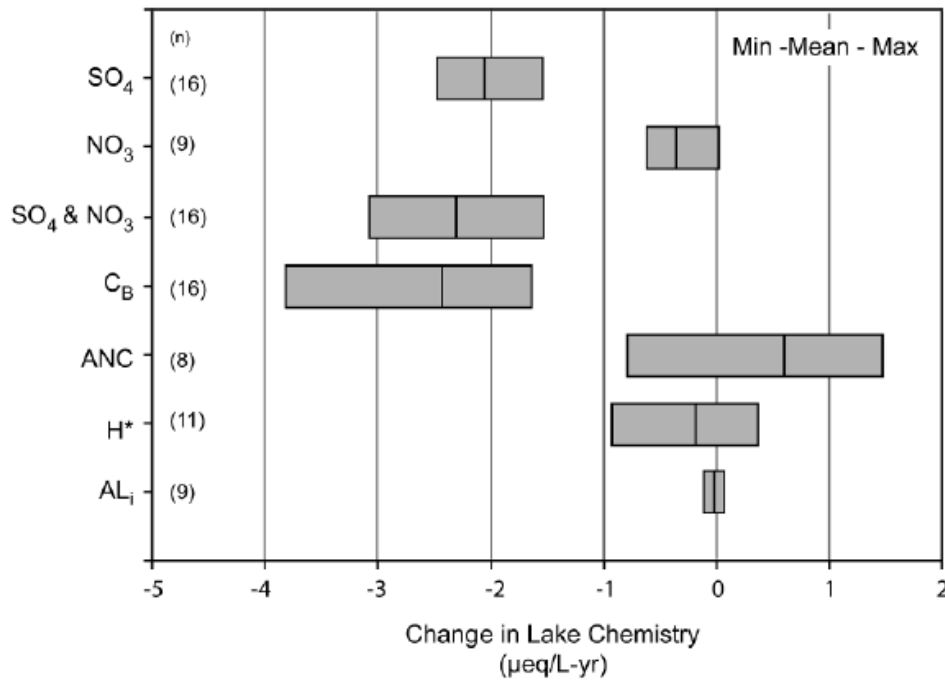


Figure 2-50. Generalized trends in water quality variables ANC (above) and sulfate ion (below) – EPA, 2010.



Source: Driscoll et al. (2003b)

Figure 2-51. Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in µeq/L/yr, except for concentrations of inorganic monomeric aluminum (Al_i), which are expressed in µM/yr.

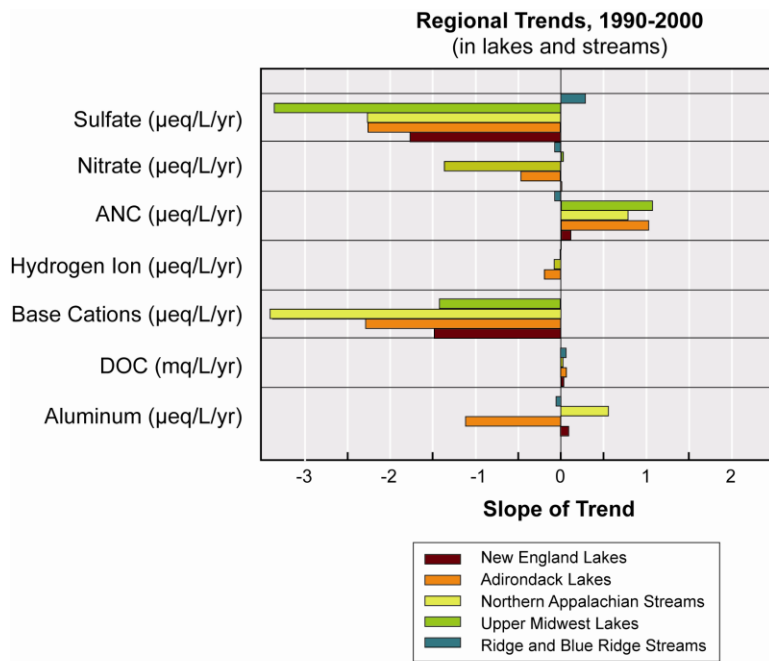


Figure 2-52 Summary of regional trends in surface water chemistry from 1990 to 2000, based on Stoddard et al. (2003).

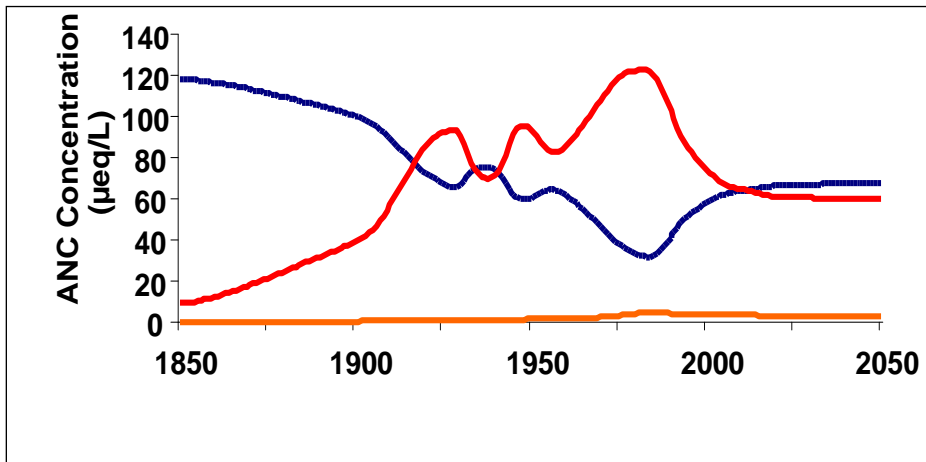


Figure 2-53. Average NO₃⁻ concentrations (orange), SO₄²⁻ concentrations (red), and ANC (blue) across the 44 lakes in the Adirondack Case Study Area modeled using MAGIC for the period 1850 to 2050.

ANC Preacidification (1860) and Current Condition (2006)

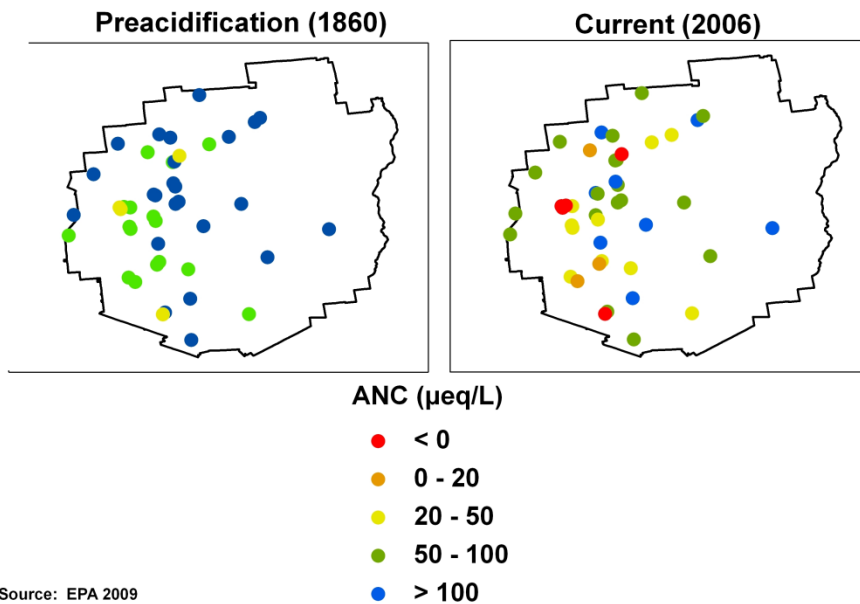


Figure 2-54. ANC concentrations of preacidification (1860) and 2006 conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC.

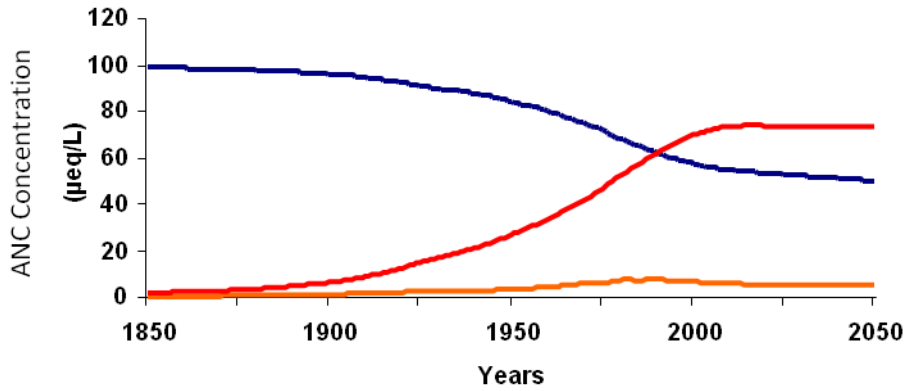


Figure 2-55. Average NO₃⁻ concentrations (orange), SO₄²⁻ concentrations (red), and ANC (blue) levels for the 60 streams in the Shenandoah Case Study Area modeled using MAGIC for the

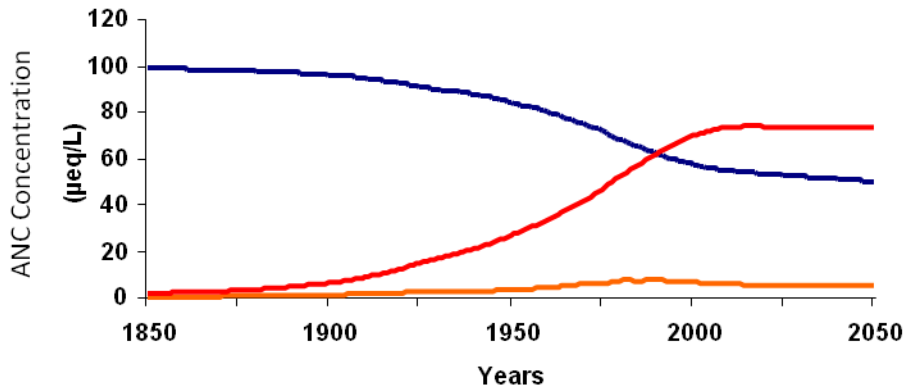


Figure 2-56. ANC levels of 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 60 streams in the Shenandoah Case Study Area modeled using MAGIC

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3 KNOWN OR ANTICIPATED ECOLOGICAL EFFECTS

In this chapter we address the evaluation of the effects of ambient oxides of nitrogen and sulfur on ecosystems, and the relationship between those effects and the measure of dose in the ecosystem, indicated by the depositional loadings of N and S. In section 302(h) of the Clean Air Act, welfare effects addressed by a secondary NAAQS include, but are not limited to, “effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being”. Of these welfare effects categories, the effects of oxides of nitrogen and sulfur on aquatic and terrestrial ecosystems, which encompass soils, water, vegetation, wildlife, and contribute to economic value and well-being, are of most concern at concentrations typically occurring in the U.S. Direct effects of oxides of nitrogen and sulfur on vegetation are also discussed in this chapter, and have been the focus of previous reviews. However, for this review, the focus of this chapter is on the known and anticipated effects to ecosystems caused by exposure to oxides of nitrogen and sulfur through deposition.

The information presented here is a concise summary of conclusions from the ISA and the REA. This chapter focuses on effects on specific ecosystems with a brief discussion on critical uncertainties associated with acidification and nutrient enrichment. Those effects are then evaluated in Chapter 4 within the context of alternative definitions of, including assessments of potential impacts on ecosystem services. Effects are broadly categorized into acidification and nutrient-enrichment in the proceeding sections. This is background information intended to support new approaches for the design of ecologically relevant secondary oxides of nitrogen and sulfur standards which are protective of U.S. ecosystems. More detailed information on the conceptual design and specific options for the standards is presented in Chapters 6 and 7 of this policy assessment document. While we provide a summary of effects for four of the primary effects categories (aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, and terrestrial nutrient enrichment), we reiterate that the focus of this second draft policy assessment is on effects related to aquatic acidification, without downplaying the potential importance of effects in other categories.

3.1 ACIDIFICATION: EVIDENCE OF EFFECTS ON STRUCTURE AND FUNCTION OF TERRESTRIAL AND FRESHWATER ECOSYSTEMS

Sulfur oxides (SO_x) and nitrogen oxides (NO_x) in the atmosphere undergo a complex mix of reactions in gaseous, liquid, and solid phases to form various acidic compounds. These acidic compounds are removed from the atmosphere through deposition: either wet (e.g., rain, snow), fog or cloud, or dry (e.g., gases, particles). Deposition of these acidic compounds to ecosystems can lead to effects on ecosystem structure and function. Following deposition, these compounds can, in some instances unless retained by soil or biota, leach out of the soils in the form of sulfate (SO_4^{2-}) and nitrate (NO_3^-), leading to the acidification of surface waters. The effects on ecosystems depend on the magnitude and rate of deposition, as well as a host of biogeochemical processes occurring in the soils and waterbodies (REA 2.1). The chemical forms of nitrogen that may contribute to acidifying deposition include both oxidized and reduced chemical species.

When sulfur or nitrogen leaches from soils to surface waters in the form of SO_4^{2-} or NO_3^- , an equivalent amount of positive cations, or countercharge, is also transported. This maintains electroneutrality. If the countercharge is provided by base cations, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), or potassium (K^+), rather than hydrogen (H^+) and dissolved inorganic aluminum, the acidity of the soil water is neutralized, but the base saturation of the soil decreases. Continued SO_4^{2-} or NO_3^- leaching can deplete the available base cation pool in soil. As the base cations are removed, continued deposition and leaching of SO_4^{2-} and/or NO_3^- (with H^+ and Al^{3+}) leads to acidification of soil water, and by connection, surface water. Introduction of strong acid anions such as sulfate and nitrate to an already acidic soil, whether naturally or due to anthropogenic activities, can lead to instantaneous acidification of waterbodies through direct runoff without any significant change in base cation saturation. The ability of a watershed to neutralize acidic deposition is determined by a variety of biogeophysical factors including weathering rates, bedrock composition, vegetation and microbial processes, physical and chemical characteristics of soils and hydrologic flowpaths. (REA 2.1) Some of these factors such as vegetation and soil depth are highly variable over small spatial scales such as meters, but can be aggregated to evaluate patterns over larger spatial scales. Acidifying deposition of oxides of nitrogen and sulfur and the chemical and biological responses associated with these inputs vary temporally. Chronic or long-term deposition processes in the time scale of years to decades result in increases in inputs of N and S to ecosystems and the associated ecological effects.

Episodic or short term (i.e., hours or days) deposition refers to events in which the level of the acid neutralizing capacity (ANC) of a lake or stream is temporarily lowered. In aquatic ecosystems, short-term (i.e., hours or days) episodic changes in water chemistry can have significant biological effects. Episodic acidification refers to conditions during precipitation or snowmelt events when proportionately more drainage water is routed through upper soil horizons that tend to provide less acid neutralizing than was passing through deeper soil horizons (REA 4.2). In addition, the accumulated sulfate and nitrate in snow packs can provide a surge of acidic inputs. Some streams and lakes may have chronic or base flow chemistry that is suitable for aquatic biota, but may be subject to occasional acidic episodes with deleterious consequences to sensitive biota.

The following summary is a concise overview of the known or anticipated effects caused by acidification to ecosystems within the United States. Acidification affects both terrestrial and freshwater aquatic ecosystems.

3.1.1 Nature of acidification-related ecosystem responses

The ISA concluded that deposition of SO_x , NO_x , and NH_x leads to the varying degrees of acidification of ecosystems (EPA 2008). In the process of acidification, biogeochemical components of terrestrial and freshwater aquatic ecosystems are altered in a way that leads to effects on biological organisms. Deposition to terrestrial ecosystems often moves through the soil and eventually leaches into adjacent water bodies.

Aquatic ecosystems

*The scientific evidence is sufficient to infer a **causal** relationship between acidifying deposition and effects on biogeochemistry and biota in aquatic ecosystems (ISA 4.2.2).* The strongest evidence comes from studies of surface water chemistry in which acidic deposition is observed to alter sulfate and nitrate concentrations in surface waters, the sum of base cations, ANC, dissolved inorganic aluminum and pH. (ISA 3.2.3.2). Consistent and coherent documentation from multiple studies on various species from all major trophic levels of aquatic systems shows that geochemical alteration caused by acidification can result in the loss of acid-sensitive biological species (ISA 3.2.3.3). For example, in the Adirondacks, of the 53 fish species recorded in Adirondack lakes about half (26 species) were absent from lakes with pH below 6.0 (Baker et al., 1990). Biological effects are linked to changes in water chemistry

including decreases in ANC and pH and increases in inorganic Al concentration. The direct biological effects are caused by lowered pH which leads to increased inorganic Al concentrations (Figure 3-1 and 3-2). While ANC level does not cause direct biological harm it is a good overall indicator of the risk of acidification (See further discussion in Section 3.1.3).

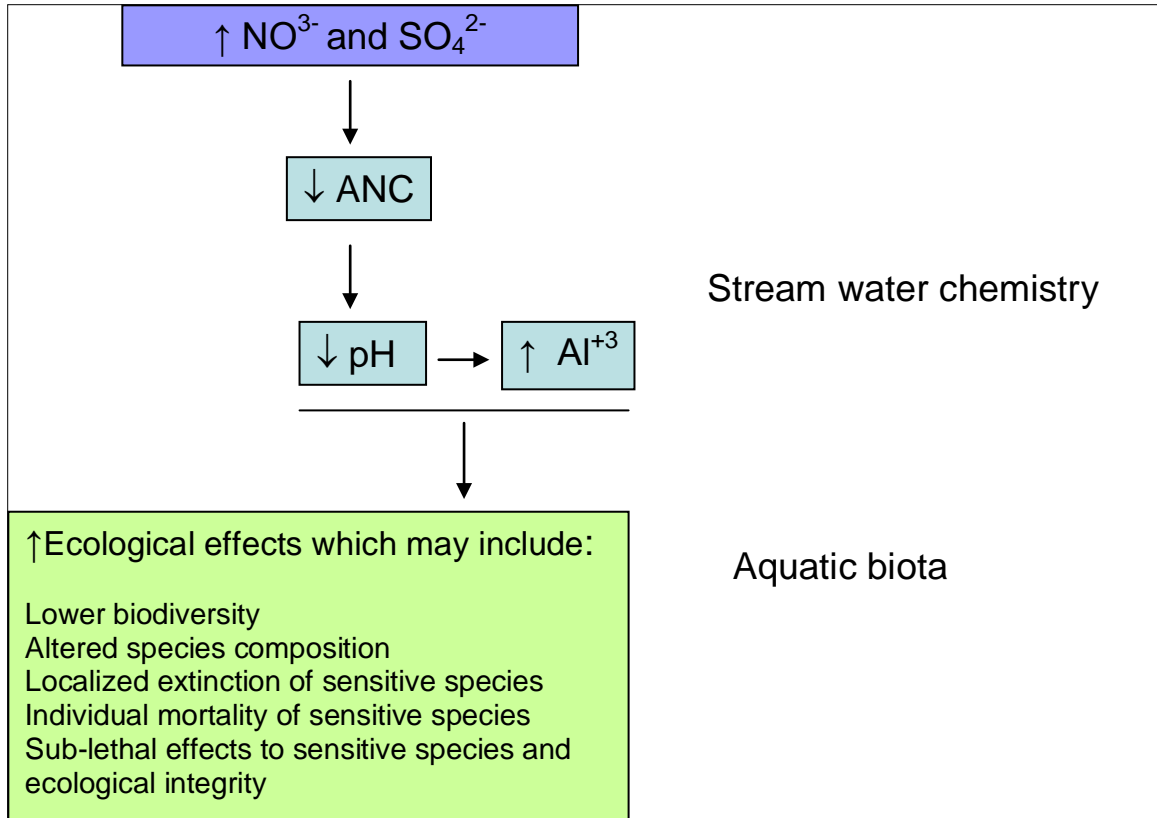


Figure 3-1. Conceptual model of direct and indirect acidification effects on aquatic biota. Acidic pollutants (NO_3^- and SO_4^{2-}) lower ANC, resulting in lower pH with direct toxic effects on fish. The lower pH mobilizes Al^{3+} from soils often resulting in higher concentration in stream water causing direct toxicity to fish.

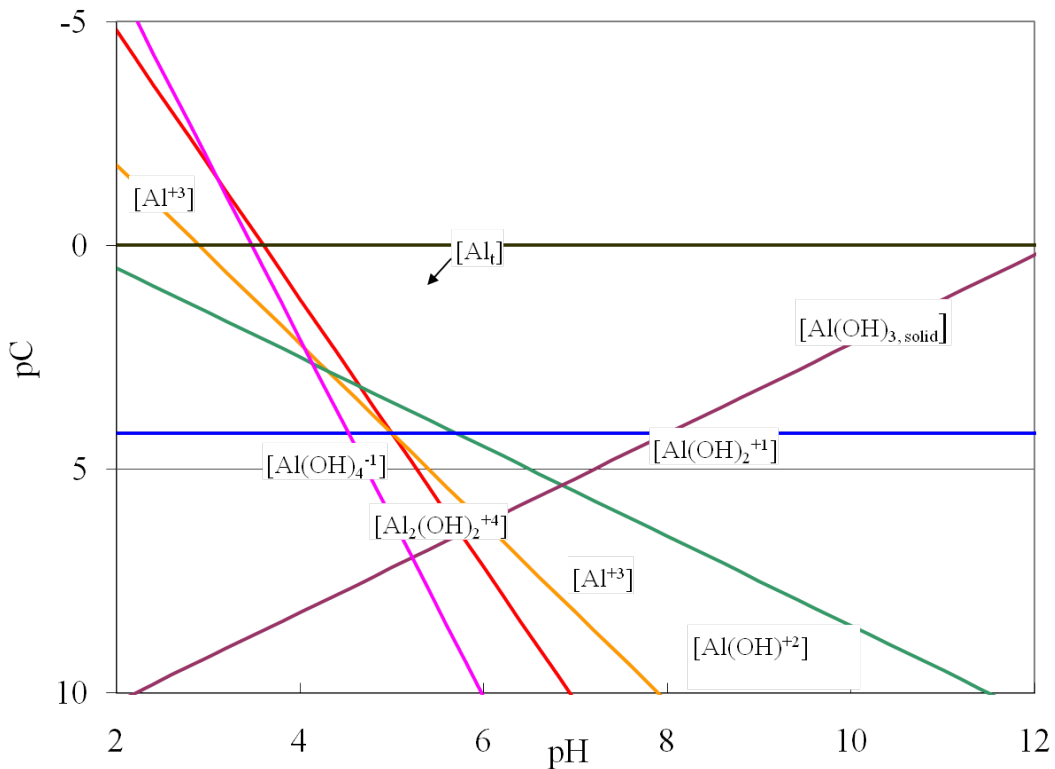


Figure 3-2. Equilibrium diagram of the log of aluminum species concentrations as a function of pH. At lower pH there is far greater proportion of dissolved Al species relative to solid gibbsite (solid aluminum hydroxide, $\text{Al}(\text{OH})_3$). The most toxic form of Al, free trivalent aluminum, (Al^{+3}) levels rapidly increase with lower pH values.

There are clear associations between pH and aquatic species mortality and health which are summarized in Tables 3-1 and 3-2 and illustrated in Figure 3-3. Significant harm to sensitive aquatic species has been observed at pH levels below 6. Normal stream pH levels with little to no toxicity ranges from 6 to 7 (MacAvoy et al, 1995). Baker et al (1990) observed that “lakes with pH less than approximately 6.0 contain significantly fewer species than lakes with pH levels above 6.0”. As noted in Chapter 3, typically at pH <4.5 and an ANC <0 $\mu\text{eq/L}$, complete to near-complete loss of many taxa of organisms occur, including fish and aquatic insect populations, whereas other taxa are reduced to only acidophilic species.

Additional evidence can help refine the understanding of effects occurring at pH levels between 4.5 and 6. When pH levels are below 5.6, relatively lower trout survival rates were observed in the Shenandoah National Park. In field observations, when pH levels dropped to 5, mortality rates went to 100 percent. (Bulger et al, 2000). At pH levels ranging from 5.4 to 5.8,

cumulative mortality continues to increase. Several studies have shown that trout exposed to water with varying pH levels and fish larvae showed increasing mortality as pH levels decrease. In one study almost 100 percent mortality was observed at a pH of 4.5 compared to almost 100 percent survival at a pH of 6.5. Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control (6.5), but not by statistically significant amounts (ISA 3.2.3.3).

One important indicator of acid stress is increased fish mortality. The response of fish to pH is not uniform across species. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH is lower, there is a greater likelihood that more fish species could be lost without replacement, resulting in decreased richness and diversity. In general, populations of salmonids are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than about 5.2 to 5.5. From Table 3-1, only one study showed significant mortality effects above a pH of 6, while a number of studies showed significant mortality when pH levels are at or below 5.5.

The highest pH level for any of the studies reported in Table 3-2 is 6.0, suggesting that pH above 6.0 is protective against mortality effects for most species. Most thresholds are in the range of pH of 5.0 to 6.0, which suggests that a target pH should be no lower than 5.0. Protection against mortality in some recreationally important species such as lake trout (pH threshold of 5.6) and crappie (pH threshold of 5.5), combined with the evidence of effects on larval and embryo survival suggests that pH levels greater than 5.5 should be targeted to provide protection against mortality effects throughout the life stages of fish.

Non-lethal effects have been observed at pH levels as high as 6. A study in the Shenandoah National Park found that the condition factor, a measure of fish health expressed as fish weight/length³ multiplied by a scaling constant, is positively correlated with stream pH levels, and that the condition factor is reduced in streams with a pH of 6.0 (ISA 3.2.3.3).

Biodiversity is another indicator of aquatic ecosystem health. As discussed in Chapter 2, a key study in the Adirondacks found that lakes with a pH of 6.0 had only half the potential species of fish (27 of 53 potential species). There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 to 100 µeq/L (Bulger et al., 1999; Sullivan et al., 2006). Such observed relationships are

complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases. Nevertheless, fish species richness is relatively easily determined and is one of the most useful indicators of biological effects of surface water acidification.

In a study of Ontario lakes, Matuszek and Beggs (1988) found that the number of fish species is positively correlated with pH, with a clear loss of species starting at pH levels less than or equal to 5.5. This relationship is displayed in Figure 3-3.

Table 3-1. Summary of Fish Mortality Response to pH; source: EPA, 2008 (ISA).

Mortality Endpoint	Authors	Species	pH Level	Notes
Increased Mortality	Johnson et al. (1987)	Blacknose dace, creek chub	5.9 - 6.0	In situ bioassay with early life stages in Adirondack surface waters
		Brook trout	4.8 - 5.1	
	Holtze and Hutchinson (1989)	Common shiner	5.4 - 6.0	Laboratory exposure of early life stages to pH and Al.
		Lake whitefish, white sucker, walleye	5.1 - 5.2	
		Smallmouth bass	4.8	
	Johansson et al. (1977)	Atlantic salmon	5.0	Laboratory tests with eggs exposed to low pH, no Al.
		Brown trout	4.5 - 5.0	
		Brook Trout	4.5	
	Swenson et al. (1989)	Black crappie	5.5	Laboratory tests with early life stages exposed to pH and Al.
		Rock bass	5.0	
		Yellow perch, largemouth bass	4.5	
	Mills et al. (1987)	Fathead minnow	5.9	Whole-lake treatment (fish population recruitment failure)
		Slimy sculpin	5.6 - 5.9	
		Lake Trout	5.6	
		Pearl dace	5.1	
White sucker		5.0 - 5.1		
>50% larval mortality	Buckler et al. (1987)	Striped bass	6.5	Lab bioassay
	Klauda et al. (1987)	Blueback herring	5.7	Lab bioassay
	Kane and Rabeni (1987)	Smallmouth bass	5.1	Lab bioassay
embryo survival				
Significant decrease	McCormick et al. (1989)	Fathead minnow	6.0	Lab bioassay
>50% embryo mortality	Holtze and Hutchinson (1989)	Common shiner	5.4	Lab bioassay
Substantial reduction	Baker and Schofield (1980)	White sucker	5.2	Lab bioassay

Table 3-2. General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.

pH Decrease	General Biological Effects
6.5 to 6.0	<p>Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.</p> <p>Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).</p>
6.0 to 5.5	<p>Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.</p> <p>Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.</p> <p>Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.</p> <p>Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.</p>
5.5 to 5.0	<p>Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.</p> <p>Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.</p> <p>Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.</p> <p>Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.</p> <p>Inhibition of nitrification.</p>
5.0 to 4.5	<p>Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass).</p> <p>Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.</p>

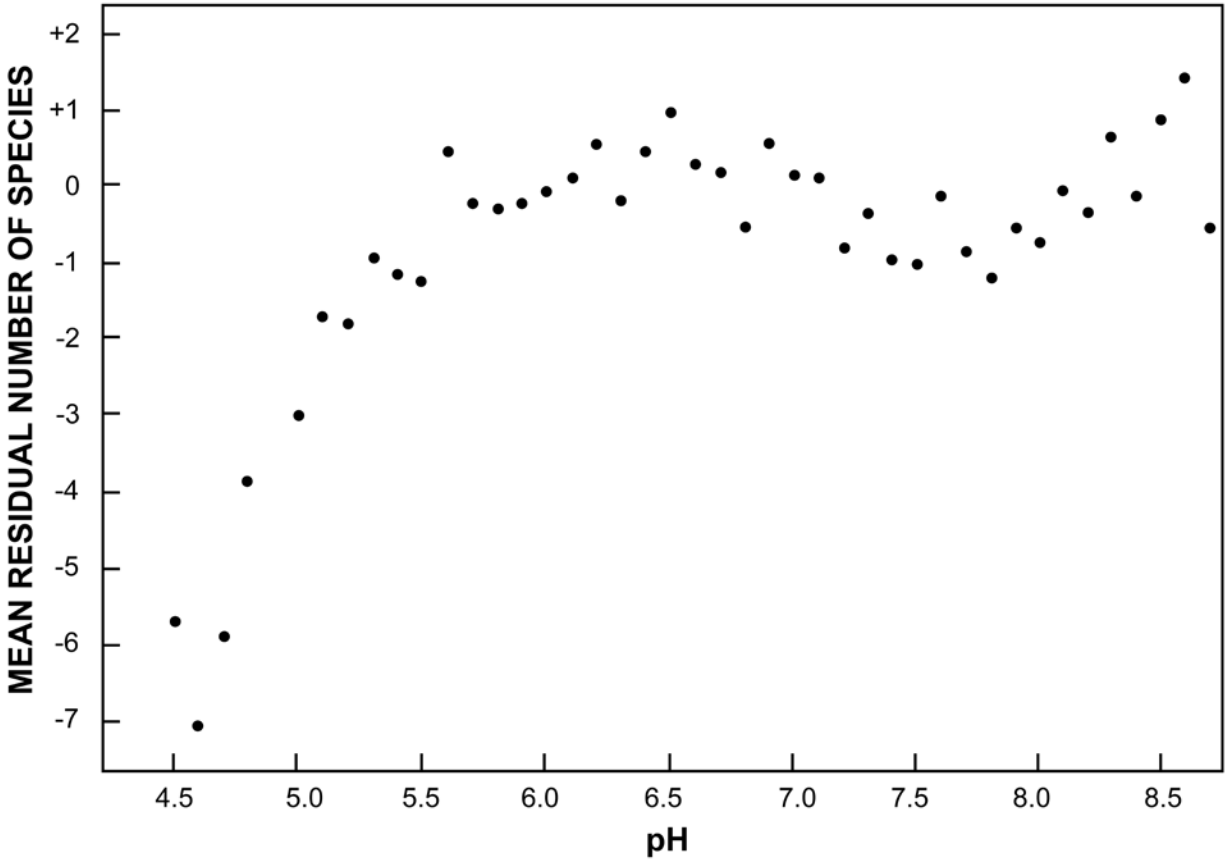


Figure 3-3. Mean residual number of species per lake for lakes in Ontario, by pH interval. The residual number of species for a lake is the deviation of the observed number from the number predicted by lake area (Matuszek and Beggs, 1988).

Changes in stream water pH also contribute to declines in taxonomic richness of zooplankton, and macroinvertebrates which are often sources of food for fish, birds and other animal species in various ecosystems. These fish may also serve as a source of food and recreation for humans (see Chapter 4). Acidification of ecosystems has been shown to disrupt food web dynamics causing alteration to the diet, breeding distribution and reproduction of certain species of birds (ISA Section 4.2.2.2. and Table 3-9). For example, breeding distribution of the common goldeneye (*Bucephala clangula*) an insectivorous duck may be affected by changes in acidifying deposition (Longcore and Gill, 1993). Similarly, decreases in prey diversity and quantity have been observed to create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker 1988).

Terrestrial ecosystems

*In terrestrial ecosystems, the evidence is sufficient to infer a **causal** relationship between acidifying deposition and changes in biogeochemistry* (ISA 4.2.1.1). The strongest evidence comes from studies of forested ecosystems, with supportive information on other plant taxa, including shrubs and lichens (ISA 3.2.2.1.). Three useful indicators of chemical changes and acidification effects on terrestrial ecosystems, showing consistency and coherence among multiple studies are: soil base saturation, Al concentrations in soil water and soil C:N ratio (ISA 3.2.2.2).

In soils with base saturation less than about 15 to 20%, exchange chemistry is dominated by Al (Reuss, 1983). Under these conditions, responses to inputs of sulfuric acid and nitric acid largely involve the release and mobilization of dissolved inorganic Al. The effect can be neutralized by weathering from geologic parent material or base cation exchange. The Ca²⁺ and Al concentrations in soil water are strongly influenced by soil acidification and both have been shown to have quantitative links to tree health, including Al interference with Ca²⁺ uptake and Al toxicity to roots (Parker et al., 1989; U.S. EPA, 2009). Effects of nitrification and associated acidification and cation leaching have been consistently shown to occur only in soils with a C:N ratio below about 20 to 25 (Aber et al., 2003; Ross et al., 2004).

Soil acidification caused by acidic deposition has been shown to cause decreased growth and increased susceptibility to disease and injury in sensitive tree species. Red spruce (*Picea rubens*) dieback or decline has been observed across high elevation areas in the Adirondack, Green and White mountains (DeHayes et al., 1999). The frequency of freezing injury to red spruce needles has increased over the past 40 years, a period that coincided with increased emissions of S and N oxides and increased acidifying deposition (DeHayes et al., 1999). Acidifying deposition can contribute to dieback in sugar maple (*Acer saccharum*) through depletion of cations from soil with low levels of available Ca (Horsley et al., 2000; Bailey et al., 2004). Grasslands are likely less sensitive to acidification than forests due to grassland soils being generally rich in base cations (Fenn et al., 2003; Blake et al., 1999).

3.1.2 Ecosystem sensitivity to acidification

The intersection between current deposition loading, historic loading, and sensitivity defines the ecological vulnerability to the effects of acidification. Freshwater aquatic and some terrestrial ecosystems, notably forests, are the ecosystem types which are most sensitive to acidification. The ISA reports that the principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition is geology (particularly surficial geology). Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Other factors that contribute to the sensitivity of soils and surface waters to acidifying deposition include topography, soil chemistry, land use, and hydrologic flowpaths. Episodic and chronic acidification tends to occur in areas that have base-poor bedrock, high relief, and shallow soils (ISA 3.2.4.1).

3.1.3 Magnitude of ecosystem responses to acidifying deposition

Terrestrial and aquatic ecosystems differ in their response to acidifying deposition. Therefore the magnitude of ecosystem response is described separately for aquatic and terrestrial ecosystems in the following sections. The magnitude of response refers to both the severity of effects and the spatial extent of the U.S. which is affected.

Aquatic acidification

Freshwater ecosystem surveys and monitoring in the eastern United States have been conducted by many programs since the mid-1980s, including EPA's Environmental Monitoring and Assessment Program (EMAP), National Surface Water Survey (NSWS), Temporally Integrated Monitoring of Ecosystems (TIME) (Stoddard, 1990), and Long-term Monitoring (LTM) (Ford et al., 1993; Stoddard et al., 1996) programs. Based on analyses of surface water data from these programs, New England, the Adirondack Mountains, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), and the Upper Midwest contain the most sensitive lakes and streams (i.e., ANC less than about 50 $\mu\text{eq/L}$). Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidifying deposition in this region is less clear. The western U.S. contains many of the surface waters most sensitive to potential acidification effects, but with the exception of the Los Angeles Basin and surrounding areas, the levels of acidifying deposition are low in most areas. Therefore, acidification of surface waters by acidic deposition is not as prevalent in the western U.S., and the extent of chronic surface water acidification that has occurred in that region to date has likely been very limited relative to the Eastern U.S. (ISA 3.2.4.2 and REA 4.2.2).

There are a number of species including fish, aquatic insects, other invertebrates and algae that are sensitive to acidification and cannot survive, compete, or reproduce in acidic waters (ISA 3.2.3.3). Decreases in ANC and pH have been shown to contribute to declines in species richness and declines in abundance of zooplankton, macroinvertebrates, and fish (Keller and Gunn 1995; Schindler et al., 1985). Reduced growth rates have been attributed to acid stress in a number of fish species including Atlantic salmon (*Salmo salar*), Chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook trout (*Salvelinus Fontinalis*), and brown trout (*Salmo trutta*) (Baker et al., 1990). 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. The effects of acidification are continuous, with more species being affected at higher degrees of acidification. At a point, typically a pH <4.5 and an ANC <0 $\mu\text{eq/L}$, complete to near-complete loss of many taxa of organisms occur, including fish and aquatic insect populations, whereas other taxa are reduced to only acidophilic species. These changes in taxa composition are associated with the high energy cost in maintaining physiological homeostasis, growth, and

reproduction at low ANC levels (Schreck, 1981, 1982; Wedemeyer et al., 1990; REA appendix 2.3). Decreases in species richness related to acidification have been observed in the Adirondack Mountains and Catskill Mountains of New York (Baker et al., 1996), New England and Pennsylvania (Haines and Baker, 1986), and Virginia (Bulger et al., 2000). From the sensitive areas identified by the ISA, further “case study” analyses on aquatic ecosystems in the Adirondack Mountains and Shenandoah National Park were conducted to better characterize ecological risk associated with acidification (REA Chapter 4).

ANC is the most widely used indicator of acid sensitivity and has been found in various studies to be the best single indicator of the biological response and health of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006; EPA, 2008). In the REA, surface water trends in SO_4^{2-} and NO_3^- concentrations and ANC levels were analyzed to affirm the understanding that reductions in deposition could influence the risk of acidification. ANC values were categorized according to their effects on biota, as shown in Table 3-3. Monitoring data from TIME/LTM and EMAP programs were assessed for the years 1990 to 2006, and past, present, and future water quality levels were estimated by both steady-state and dynamic biogeochemical models.

Table 3-3. Ecological effects associated with alternative levels of acid neutralizing capacity (ANC). (source: USEPA, Acid Rain Program)

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

Studies on fish species richness in the Adirondacks Case Study Area demonstrated the effect of acidification. Of the 53 fish species recorded in Adirondack Case Study Area lakes, only 27 species were found in lakes with a pH <6.0. The 26 species missing from lakes with a pH <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), as well as ecologically important minnows that are commonly consumed by sport fish. A survey of 1,469 lakes in the late 1980s found 346 lakes to be 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 a pH <4.5 to about six species per lake for lakes having a pH >6.5 (Driscoll

et al., 2001; Kretser et al., 1989). In the Adirondacks, a positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes (ISA 3.2.3.4).

Since the mid-1990s, streams in the Shenandoah Case Study Area have shown slight declines in NO₃⁻ and SO₄²⁻ concentrations in surface waters. The 2006 concentrations are still above pre-acidification (1860) conditions. MAGIC modeling predicts surface water concentrations of NO₃⁻ and SO₄²⁻ are 10- and 32-fold higher, respectively, in 2006 than in 1860. The estimated average ANC across 60 streams in the Shenandoah Case Study Area is 57.9 µeq/L (± 4.5 µeq/L). 55% of all monitored streams in the Shenandoah Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 55%, 18% are chronically acidic today (REA 4.2.4.3).

Based on a deposition scenario for this study area that maintains current emission levels from 2020 to 2050, the simulation forecast indicates that a large number of streams still have *Elevated* to *Acute* problems with acidity. In fact, from 2006 to 2050, the percentage of streams with *Acute Concern* is predicted to increase by 5%, while the percentage of streams in *Moderate Concern* decreases by 5%.

Biological effects of increased acidification documented in the Shenandoah Case Study Area include a decrease in the condition factor in blacknose dace (Dennis and Bulgar 1999, Bulgar et al., 1999) and a decrease in fish biodiversity associated with decreasing stream ANC (Bulger et al., 1995; Dennis and Bulger, 1999; Dennis et al., 1995; MacAvoy and Bulger, 1995, Bulgar et al., 1999). On average, the fish species richness is lower by one fish species for every 21 µeq/L decrease in ANC in Shenandoah National Park streams (ISA 3.2.3.4).

Terrestrial acidification

The ISA identified a variety of indicators that can be used to measure the effects of acidification in soils. Most effects of terrestrial acidification are observed in sensitive forest ecosystem in the U.S. Tree health has been linked to the availability of base cations (Bc) in soil (such as Ca²⁺, Mg²⁺ and potassium), as well as soil Al content. Tree species show a range of sensitivities to Ca/Al and Bc/Al soil molar ratios, therefore these are good chemical indicators because they directly relate to the biological effects. Critical Bc/Al molar ratios for a large variety of tree species ranged from 0.2 to 0.8 (Sverdrup and Warfvinge, 1993, a meta-data analysis of laboratory and field studies). This range is similar to critical ratios of Ca/Al. Plant

toxicity or nutrient antagonism was reported to occur at Ca/Al molar ratios ranging from 0.2 to 2.5 (Cronan and Grigal, 1995; meta-data assessment) (REA pg 4-54, REA Appendix 5).

There has been no systematic national survey of terrestrial ecosystems to determine the extent and distribution of terrestrial ecosystem sensitivity to the effects of acidifying deposition. However, one preliminary national evaluation estimated that ~15% of forest ecosystems in the U.S. exceed the estimated critical load based on soil ANC leaching for S and N deposition by $>250 \text{ eq ha}^{-1} \text{ yr}^{-1}$ (McNulty et al., 2007). Forests of 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 are the regions most sensitive to terrestrial acidification effects from acidifying deposition (ISA 3.2.4.2). While studies show some recovery of surface waters, there are widespread measurements of ongoing depletion of exchangeable base cations in forest soils in the northeastern U.S. despite recent decreases in acidifying deposition, indicating a slow recovery time.

In the REA, a critical load analysis was performed for sugar maple and red spruce forests in the eastern United States by using Bc/Al ratio in acidified forest soils as an indicator to assess the impact of nitrogen and sulfur deposition on tree health. These are the two most commonly studied tree species in North America for effects of acidification. At a Bc/Al ratio of 1.2, red spruce growth can be decreased by 20%. Sugar maple growth can be decreased by 20% at a Bc/Al ratio of 0.6 (REA 4.4). The REA analysis determined the health of at least a portion of the sugar maple and red spruce growing in the United States may have been compromised with acidifying total nitrogen and sulfur deposition. Specifically, total nitrogen and sulfur deposition levels exceeded three selected critical loads for tree growth in 3% to 75% of all sugar maple plots across 24 states. For red spruce, total nitrogen and sulfur deposition levels exceeded three selected critical loads in 3% to 36% of all red spruce plots across eight states (REA 4.4).

3.1.4 Key uncertainties associated with acidification

There are different levels of uncertainty associated with relationships between deposition, ecological effects and ecological indicators. In Chapter 7 of the REA, the case study analyses associated with each targeted effect area were synthesized by identifying the strengths, limitations, and uncertainties associated with the available data, modeling approach, and relationship between the selected ecological indicator and atmospheric deposition as described by the ecological effect function (REA Figure 1-1). The key uncertainties were characterized as

follows to evaluate the strength of the scientific basis for setting a national standard to protect against a given effect (REA 7.0):

- **Data Availability: *high, medium or low quality.*** This criterion is based on the availability and robustness of data sets, monitoring networks, availability of data that allows for extrapolation to larger assessment areas, and input parameters for modeling and developing the ecological effect function. The scientific basis for the ecological indicator selected is also incorporated into this criterion.
- **Modeling Approach: *high, fairly high, intermediate, or low confidence.*** This value is based on the strengths and limitations of the models used in the analysis and how accepted they are by the scientific community for their application in this analysis.
- **Ecological Effect Function: *high, fairly high, intermediate, or low confidence.*** This ranking is based on how well the ecological effect function describes the relationship between atmospheric deposition and the ecological indicator of an effect.

Aquatic acidification

The REA concludes that the available data are robust and considered *high quality*. There is high confidence about the use of these data and their value for extrapolating to a larger regional population of lakes. The EPA TIME/LTM network represents a source of long-term, representative sampling. Data on sulfate concentrations, nitrate concentrations and ANC from 1990 to 2006 used for this analysis as well as EPA EMAP and REMAP surveys, provide considerable data on surface water trends.

There is *fairly high confidence* associated with modeling and input parameters. Uncertainties in water quality estimates (i.e., ANC) from MAGIC were derived from multiple site calibrations. The 95% confidence interval for pre-acidification of lakes was an average of 15 $\mu\text{eq/L}$ difference in ANC concentrations or 10% and 8 $\mu\text{eq/L}$ or 5% for streams (REA 7.1.2). The use of the critical load model used to estimate aquatic critical loads is limited by the uncertainties associated with runoff and surface water measurements and in estimating the catchment supply of base cations from the weathering of bedrock and soils (McNulty et al., 2007). To propagate uncertainty in the model parameters, Monte Carlo methods were employed to develop an inverse function of exceedences. There is *high confidence* associated with the ecological effect function developed for aquatic acidification. In calculating the ANC function,

the depositional load for N or S is fixed by the deposition of the other, so deposition for either will never be zero (REA Figure 7.1-6).

Terrestrial acidification

The available data used to quantify the targeted effect of terrestrial acidification are robust and considered *high quality*. The USFS-Kane Experimental Forest and significant amounts of research work in the Allegheny Plateau have produced extensive, peer-reviewed data sets. A meta-analysis of laboratory studies showed that tree growth was decreased by 20% relative to controls for BC/Al ratios (ISA 7.2.1 and Figure 7.2-1). Sugar maple and red spruce were the focus of the REA since they are demonstrated to be negatively affected by soil available Ca^{2+} depletion and high concentrations of available Al, and occur in areas that receive high acidifying deposition. There is high confidence about the use of the REA terrestrial acidification data and their value for extrapolating to a larger regional population of forests.

There is *high confidence* associated with the models, input parameters, and assessment of uncertainty used in the case study for terrestrial acidification. The Simple Mass Balance (SMB) model, a commonly used and widely applied approach for estimating critical loads, was used in the REA analysis (ISA 7.2.2). There is fairly high confidence associated with the ecological effect function developed for terrestrial acidification (REA 7.2.3).

3.2 NITROGEN ENRICHMENT: EVIDENCE OF EFFECTS ON STRUCTURE AND FUNCTION OF TERRESTRIAL AND FRESHWATER ECOSYSTEMS

The following summary is a concise overview of the known or anticipated effects caused by nitrogen nutrient enrichment to ecosystems within the United States. Nutrient-enrichment affects terrestrial, freshwater and estuarine ecosystems. Nitrogen deposition is a major source of anthropogenic nitrogen. For many terrestrial and freshwater ecosystems other sources of nitrogen including fertilizer and waste treatment are greater than deposition. Nitrogen deposition often contributes to nitrogen-enrichment effects in estuaries, but does not drive the effects since other sources of N greatly exceed N deposition. Both oxides of nitrogen and reduced forms of nitrogen (NH_x) contribute to nitrogen deposition. For the most part, nitrogen effects on ecosystems do not depend on whether the nitrogen is in oxidized or reduced form. Thus, this summary focuses on the effects of nitrogen deposition in total.

3.2.1 Nature of nutrient enrichment-related ecosystem responses

The ISA found that deposition of nitrogen, including NO_x and NH_x , leads to the nitrogen enrichment of ecosystems (EPA 2008). In the process of nitrogen enrichment, biogeochemical components of terrestrial and freshwater aquatic ecosystems are altered in a way that leads to effects on biological organisms.

*The evidence is sufficient to infer a **causal** relationship between N deposition and the alteration of biogeochemical cycling in terrestrial ecosystems* (ISA 4.3.1.1 and 3.3.2.1). This is supported by numerous observational, deposition gradient and field addition experiments in sensitive ecosystems. Stoddard (1994) identified the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water as two of the primary indicators of N enrichment. Several N-addition studies indicate that NO_3^- leaching is induced by chronic additions of N (Edwards et al., 2002; Kahl et al., 1999; Peterjohn et al., 1996; Norton et al., 1999). Aber et al. (2003) found that surface water NO_3^- concentrations exceeded $1 \mu\text{eq/L}$ in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition. N deposition disrupts the nutrient balance of ecosystems with numerous biogeochemical effects. The chemical indicators that are typically measured include NO_3^- leaching, soil C:N ratio, rates of N mineralization, nitrification, denitrification, foliar N concentration, and soil water NO_3^- and NH_4^+ concentrations. Note that N saturation (N leaching from ecosystems) does not need to occur to cause effects. Substantial leaching of NO_3^- from forest soils to stream water can acidify downstream waters, leading to effects described in the previous section on aquatic acidification. Due to the complexity of interactions between the N and C cycling, the effects of N on C budgets (quantified input and output of C to the ecosystem) are variable. Regional trends in net ecosystem productivity (NEP) of forests (not managed for silviculture) have been estimated through models based on gradient studies and meta-analysis. Atmospheric N deposition has been shown to cause increased litter accumulation and carbon storage in above-ground woody biomass (Thomas et al., 2010). In the West, this has led to increased susceptibility to more severe fires. Less is known regarding the effects of N deposition on C budgets of non-forest ecosystems.

*The evidence is sufficient to infer a **causal** relationship between N deposition on the alteration of species richness, species composition and biodiversity in terrestrial ecosystems* (ISA 4.3.1.2). Some organisms and ecosystems are more sensitive to N deposition and effects of N deposition are not observed in all habitats. The most sensitive terrestrial taxa to N deposition

are lichens. Empirical evidence indicates that lichens in the U.S. are affected by deposition levels as low as 3 kg N/ha/yr. Alpine ecosystems are also sensitive to N deposition, changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr and modeling indicates that deposition levels near 10 kg N/ha/yr alter plant community assemblages. In several grassland ecosystems, reduced species diversity and an increase in non-native, invasive species are associated with N deposition (Clark and Tillman, 2008; Schwinning et al., 2005).

*In freshwater ecosystems, the evidence is sufficient to infer a **causal** relationship between N deposition and the alteration of biogeochemical cycling in freshwater aquatic ecosystems (ISA 3.3.2.3).* N deposition is the main source of N enrichment to headwater streams, lower order streams and high elevation lakes. The most common chemical indicators that were studied included NO_3^- and dissolved inorganic nitrogen (DIN) concentration in surface waters as well as Chl a:total P ratio. Elevated surface water NO_3^- concentrations occur in both the eastern and western U.S. Bergstrom and Jansson (2006) report a significant correlation between N deposition and lake biogeochemistry by identifying a correlation between wet deposition and [DIN] and Chl a: Total P. Recent evidence provides examples of lakes and streams that are limited by N and show signs of eutrophication in response to N addition.

*The evidence is sufficient to infer a **causal** relationship between N deposition and the alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems (ISA 3.3.5.3).* Increased N deposition can cause a shift in community composition and reduce algal biodiversity, especially in sensitive oligotrophic lakes.

*In the ISA, the evidence is sufficient to infer a **causal** relationship between N deposition and the biogeochemical cycling of N and carbon (C) in estuaries (ISA 4.3.4.1 and 3.3.2.3).* In general, estuaries tend to be nitrogen-limited, and many currently receive high levels of nitrogen input from human activities (REA 5.1.1). It is unknown if atmospheric deposition alone is sufficient to cause eutrophication; however, the contribution of atmospheric nitrogen deposition to total nitrogen load is calculated for some estuaries and can be >40% (REA 5.1.1).

*The evidence is sufficient to infer a **causal** relationship between N deposition and the alteration of species richness, species composition and biodiversity in estuarine ecosystems (ISA 4.3.4.2 and 3.3.5.4).* Atmospheric and non-atmospheric sources of N contribute to increased phytoplankton and algal productivity, leading to eutrophication. Shifts in community

composition, reduced hypolimnetic DO, decreases in biodiversity, and mortality of submerged aquatic vegetation are associated with increased N deposition in estuarine systems.

3.2.2 Ecosystem sensitivity to nutrient enrichment

The numerous ecosystem types that occur across the U.S. have a broad range of sensitivity to N deposition (Clark and Tilman 2008; Aber et al., 2003; Fenn et al., 2003; Fenn et al., 2007; Rueth et al., 2003; Egerton-Warburton and Allen 2000; Williams et al., 1996; and additional studies summarized in ISA Table 4-4). Increased deposition to N-limited ecosystems can lead to production increases that may be either beneficial or adverse depending on the system and management goals.

Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability. Change in the availability of one important nutrient, such as N, may result in an imbalance in ecological stoichiometry, with effects on ecosystem processes, structure and function (Sterner and Elser, 2002). In general, N deposition to terrestrial ecosystems causes accelerated growth rates in some species deemed desirable in commercial forests but may lead to altered competitive interactions among species and nutrient imbalances, ultimately affecting biodiversity. The onset of these effects occurs with N deposition levels as low as 3 kg N/ha/yr in sensitive terrestrial ecosystems to N deposition. In aquatic ecosystems, N that is both leached from the soil and directly deposited to the water surface can pollute the surface water. This causes alteration of the diatom community at levels as low as 1.5 kg N/ha/yr in sensitive freshwater ecosystems.

The degree of ecosystem effects lies at the intersection of N loading and N-sensitivity. N-sensitivity is predominately driven by the degree to which growth is limited by nitrogen availability. Grasslands in the western United States are typically N-limited ecosystems dominated by a diverse mix of perennial forbs and grass species (Clark and Tilman, 2008; Suding et al., 2005). A meta-analysis by LeBauer and Treseder (2008) indicated that N fertilization increased aboveground growth in all non-forest ecosystems except for deserts. In other words, almost all terrestrial ecosystems are N-limited and will be altered by the addition of anthropogenic nitrogen (LeBauer and Treseder, 2008). Likewise, a freshwater lake or stream must be N-limited to be sensitive to N-mediated eutrophication. There are many examples of fresh waters that are N-limited or N and phosphorous (P) co-limited (ISA 3.3.3.2). In a meta-

analysis that included 653 datasets, Elser et al. (2007) found that N-limitation occurred as frequently as P-limitation in freshwater ecosystems. Additional factors that govern the sensitivity of ecosystems to nutrient enrichment from N deposition include rates and form of N deposition, elevation, climate, species composition, plant growth rate, length of growing season, and soil N retention capacity (ISA 4.3). Less is known about the extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to the effects of nutrient enrichment from atmospheric N deposition compared to acidification.

Because the productivity of estuarine and near shore marine ecosystems is generally limited by the availability of N, they are susceptible to the eutrophication effect of N deposition (ISA 4.3.4.1). A recent national assessment of eutrophic conditions in estuaries found the most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker et al., 2007). In the REA, the National Oceanic and Atmospheric Administration's (NOAA) National Estuarine Eutrophication Assessment (NEEA) assessment tool, Assessment of Estuarine Tropic Status (ASSETS) categorical Eutrophication Index (EI) (Bricker et al., 2007) was used to evaluate eutrophication due to atmospheric loading of nitrogen. ASSETS EI is an estimation of the likelihood that an estuary is experiencing eutrophication or will experience eutrophication based on five ecological indicators: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms and submerged aquatic vegetation (SAV) (Bricker et al., 2007).

In the REA, two regions were selected for case study analysis using ASSETS EI, the Chesapeake Bay and Pamlico Sound. Both regions received an ASSETS EI rating of *Bad* indicating that the estuary had moderate to high pressure due to overall human influence and a moderate high to high eutrophic condition (REA 5.2.4.1 and 5.2.4.2). These results were then considered with SPATIALLY Referenced Regression (SPARROW) modeling to develop a response curve to examine the role of atmospheric nitrogen deposition in achieving a desired decrease in load. To change the Neuse River Estuary's EI score from *Bad* to *Poor* not only must 100% of the total atmospheric nitrogen deposition be eliminated, but considerably more nitrogen from other sources as well must be controlled (REA section 5.2.7.2). In the Potomac River estuary, a 78% decrease of total nitrogen could move the EI score from *Bad* to *Poor* (REA 5.2.7.1). The results of this analysis indicated decreases in atmospheric deposition alone could not eliminate coastal eutrophication problems due to multiple non-atmospheric nitrogen inputs (REA 7.3.3).

However, by decreasing atmospheric contributions, it may help avoid the need for more costly controls on nitrogen from other sources. In addition, the somewhat arbitrary discreteness of the EI scale can mask the benefits of decreases in nitrogen between categories.

In general, estuaries tend to be N-limited (Elser et al., 2008), and many currently receive high levels of N input from human activities to cause eutrophication (Howarth et al., 1996; Vitousek and Howarth, 1991). Atmospheric N loads to estuaries in the U.S. are estimated to range from 2-8% for Guadalupe Bay, TX on the lowest end to as high as 72% for St Catherines-Sapelo estuary, GA (Castro et al., 2003). The Chesapeake Bay is an example of a large, well-studied and severely eutrophic estuary that is calculated to receive as much as 30% of its total N load from the atmosphere.

3.2.3 Magnitude of ecosystem responses

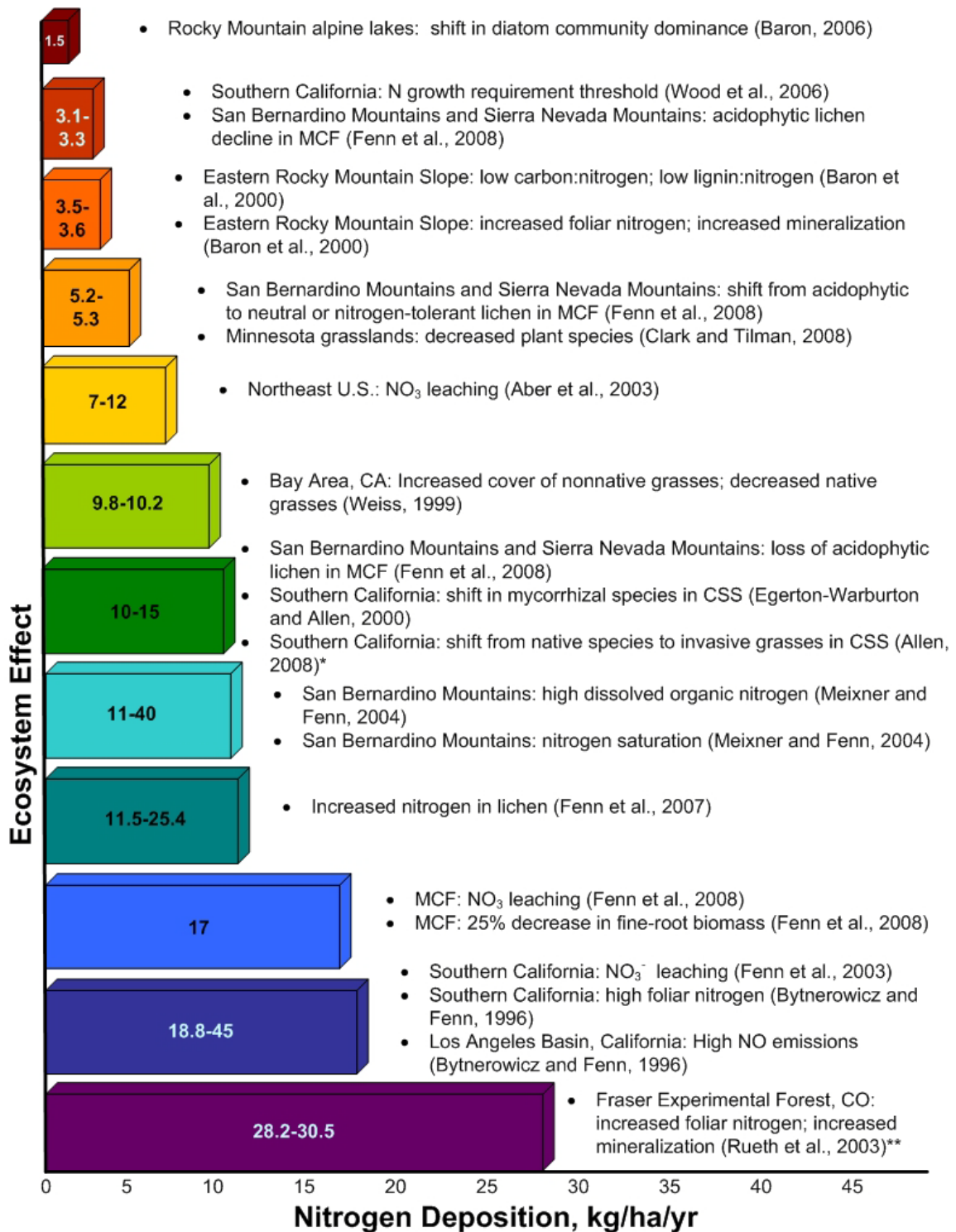
Terrestrial ecosystems

Little is known about the full extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to impacts caused by nutrient enrichment from atmospheric N deposition. As previously stated, most terrestrial ecosystems are N-limited, therefore they are sensitive to perturbation caused by N additions (LeBauer and Treseder, 2008). Effects are most likely to occur where areas of relatively high atmospheric N deposition intersect with N-limited plant communities. The alpine ecosystems of the Colorado Front Range, chaparral watersheds of the Sierra Nevada, lichen and vascular plant communities in the San Bernardino Mountains and the Pacific Northwest, and the southern California coastal sage scrub (CSS) community are among the most sensitive terrestrial ecosystems. There is growing evidence that existing grassland ecosystems in the western United States are being altered by elevated levels of N inputs, including inputs from atmospheric deposition (Clark and Tilman, 2008; Suding et al., 2005).

In the eastern U.S., the degree of N saturation of the terrestrial ecosystem is often assessed in terms of the degree of NO_3^- leaching from watershed soils into ground water or surface water. Stoddard (1994) estimated the number of surface waters at different stages of saturation across several regions in the eastern U.S. Of the 85 northeastern watersheds examined 60% were in Stage 1 or Stage 2 of N saturation on a scale of 0 (background or pretreatment) to 3 (visible decline). Of the northeastern sites for which adequate data were available for assessment,

those in Stage 1 or 2 were most prevalent in the Adirondack and Catskill Mountains. Effects on individual plant species have not been well studied in the U.S. More is known about the sensitivity of particular plant communities. Based largely on results obtained in more extensive studies conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems (ISA 3.8.2).

The REA used published research results (REA 5.3.1 and ISA Table 4.4) to identify meaningful ecological benchmarks associated with different levels of atmospheric nitrogen deposition. These are given by Figure 3-4. The sensitive areas and ecological indicators identified by the ISA were analyzed further in the REA to create a national map that illustrates effects observed from ambient and experimental atmospheric nitrogen deposition loads in relation to Community Multi-scale Air Quality (CMAQ) 2002 modeling results and NADP monitoring data. This map, reproduced in Figure 3-5, depicts the sites where empirical effects of terrestrial nutrient enrichment have been observed and site proximity to elevated atmospheric N deposition.



* Personal communication, 2008. Also referenced in Bobbink et al., 2010, Ecological Applications, 20(1):30-59 and USFS FS, 2010, http://www.nrs.fs.fed.us/clean_air_water/clean_water/critical_loads/local-resources/docs/Empirical_CLS_of_N_100414.pdf

**Nitrogen deposition levels include ambient and experimental additions.

Figure 3-4. Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators (REA 5.3.1.2) MCF-Mixed Conifer Forest, CSS-Coastal Sage Scrub.

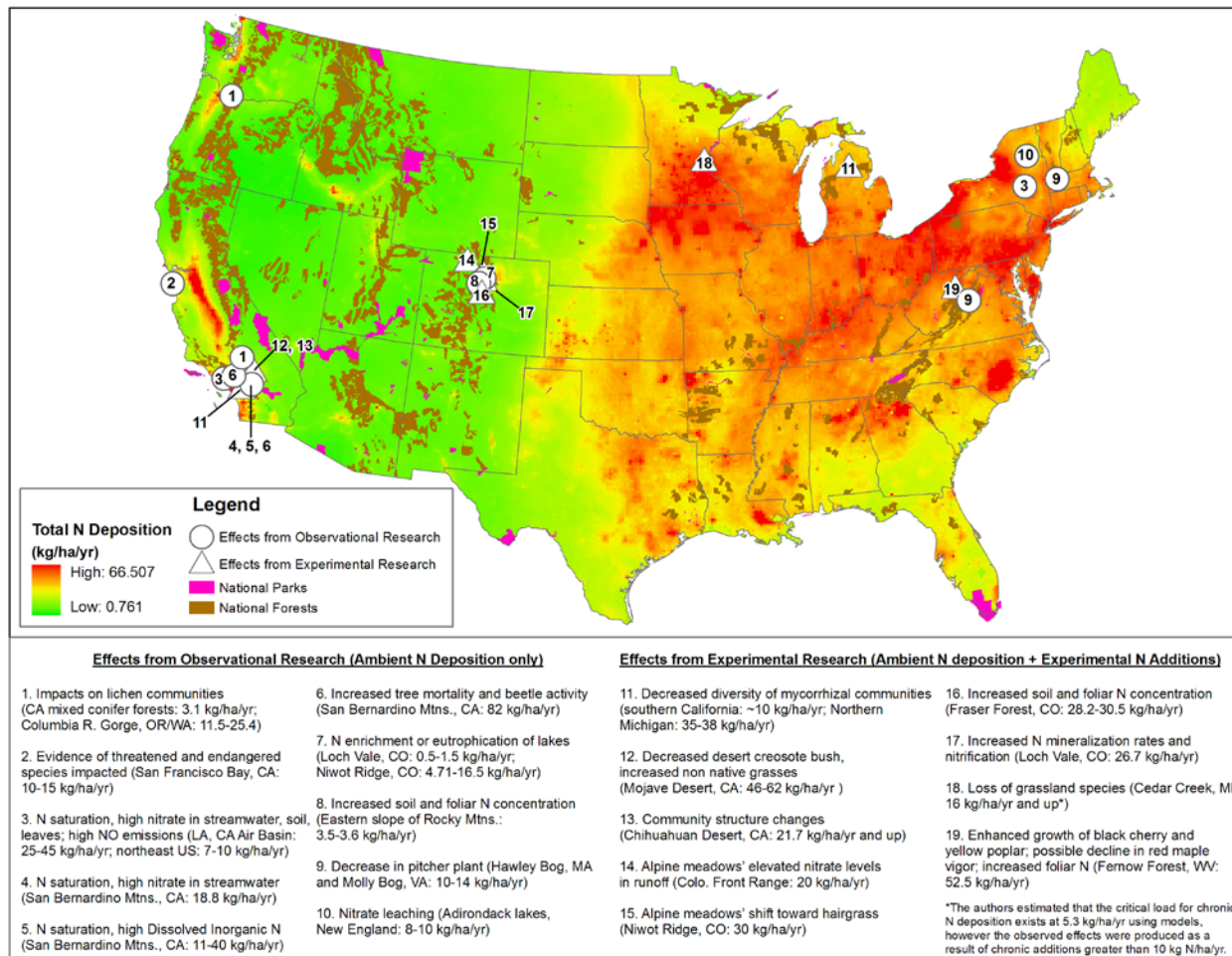


Figure 3-5. Observed effects from ambient and experimental atmospheric nitrogen deposition loads in relation to using CMAQ 2002 modeling results and NADP monitoring data.

Citations for effect results are from the ISA, Table 4.4 (U.S. EPA, 2008) 1=Fenn et al. (2008), 2=Weiss (1999), 3=Bytnerowicz and Fenn (1996), 4=Fenn et al. (2000), 5=Meixner and Fenn (2004), 6=Jones et al. 2004, 7=Baron (2006), 8=Baron et al. (2000), 9=Gotelli and Ellison (2002), 10=Stoddard et al. (1994), 11=Egerton Warburton and Allen (2000), 12=Brooks (2003), 13=Baez et al. (2007), 14=Bowman et al. (2006), 15=Bowman et al. (1995), 16=Rueth et al. (2003), 17=DeWalle et al. (2006), 18=Clark and Tillman (2008), 19=Rueth et al. 2003

Based on information in the ISA and initial analysis in the REA, further case study analyses on terrestrial nutrient enrichment of ecosystems were developed for the CCS community and Mixed Conifer Forest (MCF) (EPA, 2009). Geographic information systems (GIS) analysis supported a qualitative review of past field research to identify ecological benchmarks associated with CSS and mycorrhizal communities, as well as MCF's nutrient-sensitive acidophyte lichen communities, fine-root biomass in Ponderosa pine, and leached nitrate in receiving waters.

The ecological benchmarks that were identified for the CSS and the MCF are included in the suite of benchmarks identified in the ISA (ISA 3.3). There are sufficient data to confidently relate the ecological effect to a loading of atmospheric nitrogen. For the CSS community, the following ecological benchmarks were identified:

- 3.3 kg N/ha/yr – the amount of nitrogen uptake by a vigorous stand of CSS; above this level, nitrogen may no longer be limiting
- 10 kg N/ha/yr – mycorrhizal community changes

For the MCF community, the following ecological benchmarks were identified:

- 3.1 kg N/ha/yr – shift from sensitive to tolerant lichen species
- 5.2 kg N/ha/yr – dominance of the tolerant lichen species
- 10.2 kg N/ha/yr – loss of sensitive lichen species
- 17 kg N/ha/yr – leaching of nitrate into streams.

These benchmarks, ranging from 3.1 to 17 kg N/ha/yr, were compared to 2002 CMAQ/NADP data to discern any associations between atmospheric deposition and changing communities. Evidence supports the finding that nitrogen alters CSS and MCF. Key findings include the following: 2002 CMAQ/NADP nitrogen deposition data show that the 3.3 kg N/ha/yr benchmark has been exceeded in more than 93% of CSS areas (654,048 ha). These deposition levels are a driving force in the degradation of CSS communities. Although CSS decline has been observed in the absence of fire, the contributions of deposition and fire to the CSS decline require further research. CSS is fragmented into many small parcels, and the 2002 CMAQ/NADP 12-km grid data are not fine enough to fully validate the relationship between CSS distribution, nitrogen deposition, and fire. 2002 CMAQ/NADP nitrogen deposition data exceeds the 3.1 kg N/ha/yr benchmark in more than 38% (1,099,133 ha) of MCF areas, and nitrate leaching

has been observed in surface waters. Ozone effects confound nitrogen effects on MCF acidophyte lichen, and the interrelationship between fire and nitrogen cycling requires additional research.

Freshwater ecosystems

The magnitude of ecosystem response may be thought of on two time scales, current conditions and how ecosystems have been altered since the onset of anthropogenic N deposition. As noted previously, Elser et al. (2007) found that N-limitation occurs as frequently as P-limitation in freshwater ecosystems (ISA 3.3.3.2). Recently, a comprehensive study of available data from the northern hemisphere surveys of lakes along gradients of N deposition show increased inorganic N concentration and productivity to be correlated with atmospheric N deposition (Bergström and Jansson 2006). The results are unequivocal evidence of N limitation in lakes with low ambient inputs of N, and increased N concentrations in lakes receiving N solely from atmospheric N deposition (Bergström and Jansson, 2006). These authors suggested that most lakes in the northern hemisphere may have originally been N-limited, and that atmospheric N deposition has changed the balance of N and P in lakes.

Available data suggest that the increases in total N deposition do not have to be large to elicit an ecological effect. For example, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros et al., 2003). Pre-industrial inorganic N deposition is estimated to have been only 0.1 to 0.7 kg N/ha based on measurements from remote parts of the world (Galloway et al., 1995; Holland et al., 1999). In the western U.S., pre-industrial, or background, inorganic N deposition was estimated by (Holland et al., 1999) to range from 0.4 to 0.7 kg N/ha/yr.

Eutrophication effects from N deposition are most likely to be manifested in undisturbed, low nutrient surface waters such as those found in the higher elevation areas of the western U.S. The most severe eutrophication from N deposition effects is expected downwind of major urban and agricultural centers. High concentrations of lake or streamwater NO_3^- , indicative of ecosystem saturation, have been found at a variety of

locations throughout the U.S., including the San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the Front Range of Colorado (Baron et al., 1994; Williams et al., 1996), the Allegheny mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al., 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994) (ISA 3.3.8).

Estuaries

In contrast to terrestrial and freshwater systems, atmospheric N load to estuaries contributes to the total load but does not necessarily drive the effects since other combined sources of N often greatly exceed N deposition. In estuaries, N-loading from multiple anthropogenic and non-anthropogenic pathways leads to water quality deterioration, resulting in numerous effects including hypoxic zones, species mortality, changes in community composition and harmful algal blooms that are indicative of eutrophication. The following summary is a concise overview of the known or anticipated effects of nitrogen enrichment on estuaries within the United States.

There is a scientific consensus that nitrogen-driven eutrophication in shallow estuaries has increased over the past several decades and that the environmental degradation of coastal ecosystems due to nitrogen, phosphorus, and other inputs 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) and Pamlico estuaries in North Carolina (Paerl et al., 1998) and along the continental shelf adjacent to the Mississippi and Atchafalaya rivers' discharges to the Gulf of Mexico (Eadie et al., 1994).

A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions and generally received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al., 2007). Most eutrophic estuaries occurred in the mid-Atlantic region and the estuaries with the lowest degree of eutrophication were in the North Atlantic (Bricker et al., 2007). Other regions had mixtures of low, moderate, and high degrees of eutrophication (ISA 4.3.4.3).

The mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of submerged aquatic vegetation due to eutrophication (ISA 4.3.4.2). Submerged aquatic vegetation is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments (ISA 4.3.4.2). It is partly because many estuaries and near-coastal marine waters are degraded by nutrient enrichment that they are highly sensitive to potential negative impacts from nitrogen addition from atmospheric deposition.

3.2.4 Key uncertainties associated with nutrient enrichment

There are different levels of uncertainty associated with relationships between deposition, ecological effects and ecological indicators. The criteria used in the REA to evaluate the degree of confidence in the data, modeling and ecological effect function are detailed in Chapter 7 of the REA and summarized in section 3.1.4 of this chapter.

Aquatic ecosystems

The approach for assessing atmospheric contributions to total nitrogen loading in the REA, was to consider the main-stem river to an estuary (including the estuary) rather than an entire estuary system or bay. The biological indicators used in the NOAA ASSETS EI required the evaluation of many national databases including the US Geological Survey National Water Quality Assessment (NAWQA) files, EPA's STORAGE and RETRIEVAL (STORET) database, NOAA's Estuarine Drainage Areas data, and EPA's water quality standards nutrient criteria for rivers and lakes (REA Appendix 6, Table 1.2.-1). Both the SPARROW modeling for nitrogen loads and assessment of estuary conditions under NOAA ASSETS EI, have been applied on a national scale. The REA concludes that the available data are *medium quality with intermediate confidence* about the use of these data and their values for extrapolating to a larger regional area (REA 7.3.1). *Intermediate confidence* is associated with the modeling approach using ASSETS EI and SPARROW. The REA states there is low confidence with the ecological effect function due to the results of the analysis which indicated that reductions in atmospheric deposition alone could not solve coastal eutrophication problems due to multiple non-atmospheric nitrogen inputs (REA 7.3.3).

Terrestrial ecosystems

Ecological thresholds are identified for CSS and MCF and these data are considered to be of *high quality*, however, the ability to extrapolate these data to larger regional areas is limited (REA 7.4.1). No quantitative modeling was conducted or ecological effect function developed for terrestrial nutrient enrichment reflecting the uncertainties associated with these depositional effects.

3.3 ECOLOGICAL EFFECTS ASSOCIATED WITH GAS-PHASE OXIDES OF NITROGEN AND SULFUR

Acidifying deposition and nitrogen enrichment are the main focus of this policy assessment; however, there are other known ecological effects attributed to gas-phase oxides of nitrogen and sulfur. Acute and chronic exposures to gaseous pollutants such as sulfur dioxide (SO₂), nitrogen dioxide (NO₂), nitric oxide (NO), nitric acid (HNO₃) and peroxyacetyl nitrite (PAN) are associated with negative impacts to vegetation. The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase NO_x or SO_x, such as foliar injury, decreased photosynthesis, and decreased growth. The following summary is a concise overview of the known or anticipated effects to vegetation caused by gas phase N and S. Most phototoxic effects associated with gas phase oxides of nitrogen and sulfur occur at levels well above ambient concentrations observed in the U.S. (ISA 3.4.2.4).

3.3.1 Nature of ecosystem responses to gas-phase nitrogen and sulfur

The 2008 ISA found that gas phase N and S are associated with direct phytotoxic effects (ISA 4.4). *The evidence is sufficient to infer a **causal** relationship between exposure to SO₂ and injury to vegetation* (ISA 4.4.1 and 3.4.2.1). Acute foliar injury to vegetation from SO₂ may occur at levels above the current secondary standard (3-h average of 0.50 ppm). Effects on growth, reduced photosynthesis and decreased yield of vegetation are also associated with increased SO₂ exposure concentration and time of exposure.

*The evidence is sufficient to infer a **causal** relationship between exposure to NO, NO₂ and PAN and injury to vegetation* (ISA 4.4.2 and 3.4.2.2). At sufficient concentrations, NO, NO₂ and PAN can decrease photosynthesis and induce visible foliar

injury to plants. *Evidence is also sufficient to infer a **causal** relationship between exposure to HNO₃ and changes to vegetation (ISA 4.4.3 and 3.4.2.3).* Phytotoxic effects of this pollutant include damage to the leaf cuticle in vascular plants and disappearance of some sensitive lichen species.

3.3.2 Ecosystem sensitivity

Vegetation in ecosystems near sources of gaseous oxides of nitrogen and sulfur or where ambient concentrations of SO₂, NO, NO₂, PAN and HNO₃ are higher are more likely to be impacted by these pollutants. Uptake of these pollutants in a plant canopy is a complex process involving adsorption to surfaces (leaves, stems and soil) and absorption into leaves (ISA 3.4.2). The functional relationship between ambient concentrations of gas phase oxides of nitrogen and sulfur and specific plant response are impacted by internal factors such as rate of stomatal conductance and plant detoxification mechanisms, and external factors including plant water status, light, temperature, humidity, and pollutant exposure regime (ISA 3.4.2).

Entry of gases into a leaf is dependent upon physical and chemical processes of gas phase as well as to stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as water availability, humidity, temperature, and light intensity. When the stomata are closed, resistance to gas uptake is high and the plant has a very low degree of susceptibility to injury. Mosses and lichens do not have a protective cuticle barrier to gaseous pollutants or stomata and are generally more sensitive to gaseous sulfur and nitrogen than vascular plants (ISA 3.4.2).

The appearance of foliar injury can vary significantly across species and growth conditions affecting stomatal conductance in vascular plants (REA 6.4.1). For example, damage to lichens from SO₂ exposure include decreases in photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of nitrogen fixation, decreased K⁺ absorption, and structural changes (Belnap et al., 1993; Farmer et al., 1992, Hutchinson et al., 1996).

3.3.3 Magnitude of ecosystem responses to gas-phase effects of oxides of nitrogen and sulfur

The phytotoxic effects of gas phase oxides of nitrogen and sulfur are dependent on the exposure concentration and duration and species sensitivity to these pollutants. Effects to vegetation associated with oxides of nitrogen and sulfur, are therefore, variable across the U.S. and tend to be higher near sources of photochemical smog. For example, SO₂ is considered to be the primary factor contributing to the death of lichens in many urban and industrial areas, with fruticose lichens being more susceptible to SO₂ than many foliose and crustose species (Hutchinson et al., 1996).

The ISA states there is very limited new research on phytotoxic effects of NO, NO₂, PAN and HNO₃ at concentrations currently observed in the United States with the exception of some lichen species (ISA 4.4). Past and current HNO₃ concentrations may be contributing to the decline in lichen species in the Los Angeles basin (Boonpragob and Nash 1991; Nash and Sigal, 1999; Riddell et al., 2008). PAN is a very small component of nitrogen deposition in most areas of the United States (REA 6.4.2). Current deposition of HNO₃ is contributing to N saturation of some ecosystems close to sources of photochemical smog (Fenn et al., 1998) such as the MCF's of the Los Angeles basin mountain (Bytnerowicz et al., 1999). Most phototoxic effects associated with gas phase oxides of nitrogen and sulfur occur at levels well above ambient concentrations observed in the U.S. (ISA 3.4.2.4).

3.4 SUMMARY

In summary, oxides of nitrogen and sulfur in the atmosphere contribute to effects on individual species and ecosystems through direct contact with vegetation, and more significantly through deposition to sensitive ecosystems. The ISA concludes that the evidence is sufficient to conclude causal relationships between acidifying deposition of N and S and effects on freshwater aquatic ecosystems and terrestrial ecosystems, and between nitrogen nutrient enrichment and effects on sensitive terrestrial and freshwater aquatic ecosystems. The ISA also concludes that a causal relationship is supported between nitrogen nutrient enrichment and effects on estuarine ecosystems; however, the

contribution of atmospheric oxidized nitrogen relative to reduced nitrogen and non-atmospheric nitrogen is more difficult to determine.

The REA provides additional support that under recent conditions; deposition levels have exceeded benchmarks for ecological indicators of acidification and nutrient enrichment that indicate that effects are likely to be widespread in lakes and streams within sensitive ecosystems.

When considering all of the depositional effects together, it is clear that more research has been done on quantifying the relationship between atmospheric deposition and aquatic acidification than on terrestrial acidification or nitrogen enrichment of terrestrial or aquatic ecosystems. Therefore, staff concludes that it is appropriate to focus on the development of a secondary NAAQS to protect against the deposition-related effects of aquatic acidification in this review. Chapter 5 addresses the co-benefits that such a standard would afford with regard to protection against other deposition-related effects.

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4 CONSIDERATIONS OF ADVERSITY TO PUBLIC WELFARE

4.1 INTRODUCTION

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

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

While the text above lists a number of welfare effects, these effects do not define public welfare in and of themselves.

Although there is no specific definition of adversity to public welfare, the paradigm of adversity to public welfare as deriving from disruptions in ecosystem structure and function has been used broadly by EPA to categorize effects of pollutants from the cellular to the ecosystem level. An evaluation of adversity to public welfare might consider the likelihood, type, magnitude, and spatial scale of the effect as well as the potential for recovery and any uncertainties relating to these considerations.

Similar concepts were used in past reviews of secondary NAAQS for ozone, PM (relating to visibility), as well as in initial reviews of effects from lead deposition. Because oxides of nitrogen and sulfur are deposited from ambient sources into ecosystems where they affect changes to organisms, populations and ecosystems, the concept of adversity to public welfare as related to impacts on the public from alterations in structure and function of ecosystems is appropriate for this review. Other information that may be helpful to consider includes the role of critical loads and ecosystem service impacts as benchmarks or measures of impacts on ecosystems that may affect public welfare. Ecosystem services can be related directly to concepts of public welfare to inform discussions of societal adverse impacts.

Subsequent sections of Chapter 4 discuss benchmarks of adversity from other EPA programs, other federal agencies and the European Union. We will also define and discuss ecosystem services and the role of economics in defining adversity to public welfare. Finally we

will discuss the results of analyses relating adversity to public welfare to aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, and terrestrial nutrient enrichment.

4.1.1 Benchmarks from Other EPA Programs

Various federal laws and policies exist to protect ecosystem health. How other EPA programs and offices consider ecosystem effects in carrying out their programs can help inform the Administrator when she evaluates the adversity of ecosystem impacts on public welfare. From the 1996 National Acid Precipitation Assessment Program Report to Congress: “The 1990 Clean Air Act Amendments require that the National Acid Precipitation Assessment Program (NAPAP) prepare biennial reports to Congress, and that “every four years ... the report ... shall include the reduction in deposition rates that must be achieved in order to prevent adverse ecological effects” (Public Law 101-549, Title IX, Section 903 (j)(3)(F)(i), codified as amended at 42 USC §7403(j)(3)(F)(I)). Although the term *adverse ecological effects* is not specifically defined in the Clean Air Act Amendments, a working definition can be derived from relevant statements at various locations in the statute. Congress expresses its concern with ecological components (the scope is broad and inclusive, since ecology encompasses the interrelationships of organisms and their environment) in the preceding subsection (E) of the statute. That subsection requires reporting on “the status of ecosystems (including forest and surface waters) ... affected by acid deposition ... including changes in surface water quality and forest and soil conditions ... [and] high elevation watersheds” (42 USC §7403(j)(3)(E)(iii-v)). The adverse effects of concern to Congress, as evidenced in its findings and declaration of purpose, are the “dangers to the public health and welfare ... including injury ... damage ... and ... deterioration” (42 USC §7401(a)). Based on the intent of Congress, as expressed above and elsewhere in the Clean Air Act, and shaped by indications of intent expressed in other relevant environmental statutes and regulations, the following working definition of *adverse ecological effects* has been derived and is used in the preparation of the NAPAP report:

any injury (i.e., loss of chemical or physical quality or viability) to any ecological or ecosystem component, up to and including at the regional level, over both long and short terms. Similarly, adverse effects for other areas of concern addressed in this report—i.e., visibility, materials, and human health—consist of loss of quality up to and including at the

regional level, over both long and short terms.”

As another example, an effect may be considered adverse to *public welfare* if it contributes to the inability of areas to meet water quality objectives as defined by the Clean Water Act. The following federal statutes and policies may prove helpful to consider.

Ozone NAAQS Review

The evaluation of adversity from a public welfare perspective in the context of ozone and particulate matter (PM) are relevant to this current review. Both ozone and PM have documented effects on ecological receptors. These criteria pollutants are being reviewed on a schedule as part of the NAAQS process. The ozone secondary standard is currently under reconsideration from the 2008 ruling with a proposal was published January 6, 2010. The final Policy Assessment for PM is being developed and is expected to be finalized in the fall of 2010.

For the purposes of the reconsideration of the secondary standard for ozone, welfare effects of ozone are primarily limited to vegetation. These effects begin at the level of the individual cell and accumulate up to the level of whole leaves and plants. If effects occur on enough individual plants within the population, communities and ecosystems may be impacted. Prior to the 2008 ozone review, Ozone vegetation effects were classified as either “injury” or “damage” (FR 72 37889). “Injury” was defined as; encompassing all plant reactions, including reversible changes or changes in plant metabolism, quality or reduced growth that does not impair the intended use of the plant while “damage” includes those injury effects that reach sufficient magnitude as to decrease or impair the intended use of the plant (FR 72 37890). The “intended use” of the plant was imbedded with the concept of adversity to public welfare. Ozone-associated “damage” was considered adverse if the intended use of the plant was compromised (i.e. crops, ornamentals, plants located in Class I areas). Effects of ozone on single plants or species grown in monocultures such as agricultural crops and managed forests were evaluated without consideration of potential effects on natural forests or entire ecosystems.

In the 2008 rulemaking, EPA expanded the characterization of adversity beyond the individual plant level and this language is continued in the 2010 ozone reconsideration. The 2008 final rule and 2010 proposal conclude that a determination of what constitutes an “adverse” welfare effect in the context of secondary NAAQS review can appropriately occur by considering effects at higher ecological levels (populations, communities, ecosystems) as supported by recent literature. The ozone review uses the example of the construct presented in

Hogsett et al. (1997) as a model for assessing risks to forests. This study suggests that adverse effects could be classified into one or more of the following categories: (1) economic production, (2) ecological structure, (3) genetic resources, and (4) cultural values. Another recent publication, “A Framework for Assessing and Reporting on Ecological Condition: an SAB report” (Young and Sanzone, 2002) provides additional support for expanding the consideration of adversity beyond the species level and at higher levels by making explicit the linkages between stress-related effects at the species level and at higher levels within an ecosystem hierarchy (See Figure 4-1).

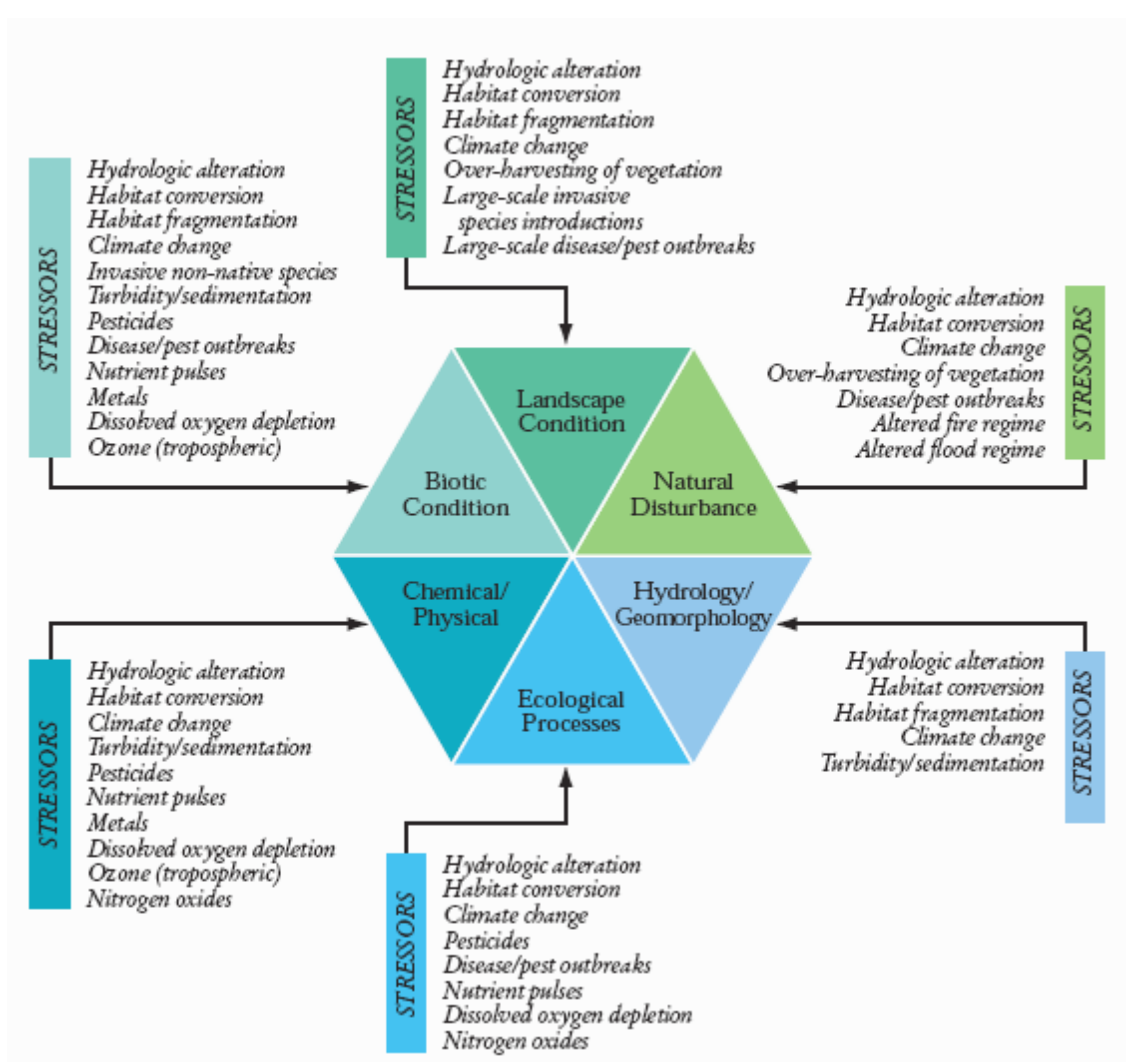


Figure 4-1. Common anthropogenic stressors and the essential ecological attributes they affect. Modified from Young and Sanzone (2002).

In the 2008 ozone NAAQS review and current ozone NAAQS proposal, the interpretation of what constitutes an adverse effect on public welfare can vary depending on the location and intended use of the plant. The degree to which O₃-related effects are considered adverse to public welfare depends on the intended use of the vegetation and its significance to public welfare (73 FR 16496). Therefore, effects on vegetation (e.g., biomass loss, foliar injury, impairment of intended use) may be judged to have a different degree of impact on public welfare depending, for example, on whether that effect occurs in a Class I area, a city park, commercial cropland or private land.

In the proposed ozone reconsideration in 2010 the Administrator has found that the types of information most useful in informing the selection of an appropriate range of protective levels is appropriately focused on information regarding exposures and responses of sensitive trees and other native species that occur in protected areas such as Class I areas or on lands set aside by States, Tribes and public interest groups to provide similar benefits to the public welfare. She further notes that while direct links between O₃ induced visible foliar injury symptoms and other adverse effects (e.g., biomass loss) are not always found, visible foliar injury in itself is considered by the National Park Service (NPS) to affect adversely air quality related values (AQRV) in Class I areas. While the Administrator recognizes that uncertainty remains as to what level of annual tree seedling biomass loss when compounded over multiple years should be judged adverse to the public welfare, she believes that the potential for such anticipated effects should be considered in judging to what degree a standard should be precautionary (73 FR 16496). The range of proposed levels from 7 – 15 ppb includes at the maximum level of 15 ppb protection of approximately 75% of seedlings from more than 10% biomass loss.

Prevention of Significant Deterioration Program

The Clean Air Act's Prevention of Significant Deterioration (PSD) program (42 U.S.C. 7470) purposes include to "preserve, protect and enhance the air quality in national parks, wilderness areas and other areas of natural, recreational, scenic or historic value" Also, the PSD program charges the Federal Land Managers, including the NPS, with ". . . an affirmative responsibility to protect the air quality related values . . . "within federal Class I lands. (42 U.S.C. 7475(d)(2)(B)).

EPA Office of Water

Section 101 of the Clean Water Act (CWA) (Declaration of Goals and Policy) states that the objective of the CWA is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters and to attain, where possible, water quality that protects fish, shellfish, wildlife and provides for water-based recreation.

The CWA also authorizes EPA to develop water quality criteria as a guide for the states to set water quality standards to protect aquatic life. In consideration of acidification effects, EPA's Redbook, *Quality Criteria for Water*, published originally in 1976, recommends that alkalinity be 20 mg/l\l or more as CaCO₃ for freshwater aquatic life except where natural concentrations are less.

Chesapeake Bay Total Maximum Daily Loads

Under section 303(d) of the Clean Water Act, states, territories, and authorized tribes are required to develop lists of impaired waters. These are waters that are too polluted or otherwise degraded to meet the water quality standards set by states, territories, or authorized tribes. The law requires that these jurisdictions establish priority rankings for waters on the lists and develop TMDLs for these waters. A Total Maximum Daily Load, or TMDL, is a calculation of the maximum amount of a pollutant that a waterbody can receive and still safely meet water quality standards. EPA is developing a TMDL for the Chesapeake Bay and its tributaries. The Chesapeake Bay Program has modeled the level of nitrogen that can reach the Bay and still meet the Bay's water quality standards. The TMDL, with full public participation, will set waste load allocations for point source discharges and load allocations for nonpoint sources of nitrogen. Air deposition to the Bay and its watershed, as a source category, will have a specific allocation.

According to an EPA draft report responding to Section 202a of Executive Order 13508 (EPA, 2009a), within the Chesapeake Bay watershed, inorganic forms of nitrogen deposition have been modeled and monitored. Organic forms have not been well quantified. Of the inorganic nitrogen deposited from the air to the Chesapeake Bay watershed in 2002, approximately 67 percent is oxidized nitrogen due to air emissions of NO_x. The remaining 33 percent is in the form of reduced nitrogen from emissions of ammonia. There still remains significant uncertainty in the ammonia emissions inventory, which will be improved with further emission and ambient measurements.

In 2002, about 87 million pounds (19 percent) of nitrogen load deposited on the watershed was delivered to the Bay. An additional 22 million pounds of nitrogen were atmospherically deposited directly onto the surface of the tidal Bay's waters.

Ammonia emissions, in 2002, were estimated to contribute approximately 147 of the 452 million pounds of nitrogen atmospheric deposition to the Bay watershed. About 80 percent of the deposited ammonia loads were estimated to originate from agricultural operations and 20 percent were from mobile and industrial sources, fires, and other sources.

The allocation can be used to calculate the level of ambient air concentrations of reactive nitrogen that are likely to meet the deposition allocation. To find the NO_x portion of the allocation one would subtract the reduced forms from the total allocation. If the total load to the Bay of nitrogen from all the allocated source categories remains below the allocations, then the Bay is expected to meet the water quality standards, which are set to protect the designated uses of the Bay. Since the designated uses are set by the states with public input, not meeting the designated uses can be seen as having an adverse effect to public welfare.

4.1.2 Other Federal Agencies and the European Union

National Park Service

The National Park Service (NPS) is responsible for the protection of all resources within the national park system. These resources include those that are related to and/or dependent upon good air quality, such as whole ecosystems and ecosystem components. The NPS, in its Organic Act (16 U.S.C. 1), is directed to conserve the scenery, natural and historic objects and wildlife and to provide for the enjoyment of these resources unimpaired for current and future generations.

The Wilderness Act of 1964 asserts wilderness areas will be administered in such a manner as to leave them unimpaired and preserve them for the enjoyment of future generations.

NPS Management Policies (2006) guide all NPS actions including natural resources management. In general, the NPS Management Policies reiterate the NPS Organic Act's mandate to manage the resources "unimpaired."

U.S. Fish and Wildlife Service

On endangered species, Title 16 USC Chapter 35 Section 1531 states "The Congress finds and declares that— these species of fish, wildlife , and plants are of esthetic , ecological,

educational, historical, recreational, and scientific value to the Nation and its people and that all Federal departments and agencies will use their authorities to conserve threatened and endangered species.

The United States Fish and Wildlife Service (FWS) manages the National Wildlife Refuge System lands to “...ensure that the biological integrity, diversity, and environmental health of the Systems are maintained for the benefit of present and future generations of Americans.” 16 U.S.C. Section 668dd(a)(4)(B)(1997).

U.S. Forest Service

The National Forest units are managed consistent with Land and Resource Management Plans (LRMPs) under the provisions of the National Forest Management Act (NFMA). 16 §U.S.C. 1604 (1997). LRMPs are, in part, specifically based on recognition that the National Forests are ecosystems and their management for goods and services requires an awareness and consideration of the interrelationships among plants, animals, soil, water, air, and other environmental factors within such ecosystems. 36 C.F.R. §219.1(b)(3)

Any measures addressing Air Quality Related Values (AQRV) on National Forest System lands will be implemented through, and be consistent with, the provisions of an applicable LRMP or its revision (16 U.S.C. §1604(i)). Additionally, the Secretary of Agriculture must prepare a Renewable Resource Program that recognizes the need to protect and, if necessary, improve the quality of air resources. 16 U.S.C. §1602(5)(C).

AQRVs in Wilderness areas may receive further protection by the previously mentioned 1964 Wilderness Act. For Wilderness Areas in the National Forest System, the Act's implementing regulations are found at 36 C.F.R. §293 requiring these Wilderness Areas be administered to preserve and protect [their] wilderness character.

United Nations Economic Commission for Europe (UNECE)

In many European countries a critical loads framework is used to determine a level of damages to ecosystem services from pollution that is legally allowed. The term critical load is used to describe the threshold of air pollution deposition that causes a specified level of harm to sensitive resources in an ecosystem. A critical load is technically defined as “the quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not expected to occur according to present knowledge” (Nilsson and Grennfelt, 1988). The determination of when a harmful effect becomes “significant” may be in the view of a researcher or through a policy development process. Critical loads have been modeled by individual countries and submitted to the UNECE (in cases where countries have not submitted their own critical loads those loads have been calculated for them) and are being used to support international emissions reduction agreements including the 1999 Gothenburg protocol and the National Emission Ceiling Directive of the European Commission. Figure 3-2 shows critical loads for eutrophication (nitrogen) and acidification (sulfur) that protect 95% of forests, seminatural vegetation or surface waters in Europe.

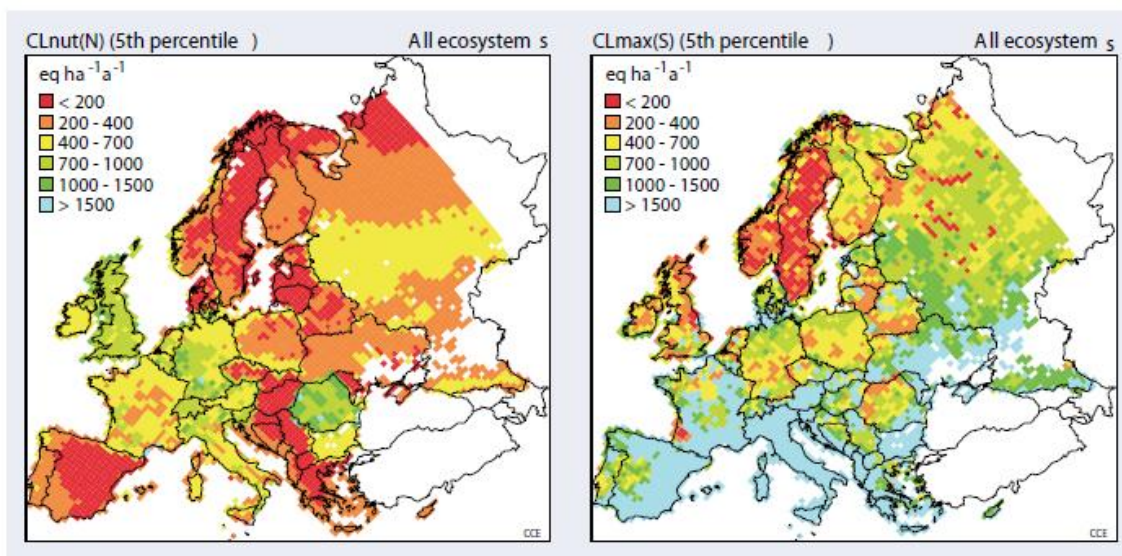


Figure 4-2 European maps of eutrophication (left) and acidification (right) which protect 95% of natural areas in 50x50 km² European Monitoring and Evaluation Programme grid. [Red shaded areas illustrate grid cells where deposition needs to be lower than 200 eq ha⁻¹ a⁻¹ to reach protection targets Specifically protection from eutrophication or an ANC lower than 20µeq/L for acidification. Source: Critical Load, Dynamic Modelling and Impact Assessment in Europe CCE Status Report 2008 available at <http://www.pbl.nl/en/publications/2009/Critical-load-dynamic-modelling-and-impact-assessment-in-Europe-CCE-Status-Report-2008.html><http://www.pbl.nl/en/publications/2009/Critical-load-dynamic-modelling-and-impact-assessment-in-Europe-CCE-Status-Report-2008.html>]

The Coordination Center for Effects, a working center for the Working Group on Effects of the Convention on Long Range Transboundary Pollution, in the 2008 status report shows calculated critical loads based on an ANC target of 20µeq/L for the protection of brown trout. Individual countries have also set ANC targets for other species for example Norway uses a critical load of 30µeq/L for Atlantic salmon (Jenkins et al, 2003).

4.2 ECOSYSTEM SERVICES AND ADVERSITY TO PUBLIC WELFARE

An additional concept that may be useful in considering the issue of adversity to public welfare is ecosystem services. In the next section the concept of ecosystem services, its relationship to adversity and public welfare within the context of this review are explained.

Ecosystem services can be generally defined as the benefits individuals and organizations obtain from ecosystems. Ecosystem services can be classified as provisioning (food and water), regulating (control of climate and disease), cultural (recreational, existence, spiritual, educational), and supporting (nutrient cycling) (MEA 2005). Conceptually, changes in ecosystem services may be used to aid in characterizing a known or anticipated adverse effect to

public welfare. In the context of this review, ecosystem services may also aid in assessing the magnitude and significance to the public of a resource and in assessing how oxides of nitrogen and sulfur concentrations and deposition may impact that resource. The relationship between ecosystem services and public welfare effects is illustrated in Table 4-1.

Table 4-1. Crosswalk between Ecosystem Services and Public Welfare Effects.

Public Welfare Effect	Ecosystem Service	Service Category
Soils	Nutrient Cycling, Water Filtration	Supporting, Provisioning
Water	Drinking water, Recreation, Aesthetic , Nonuse	Provisioning, Cultural
Crops	Food, Fuel Production, Forest Products	Provisioning
Vegetation	Food, Forest Products,, Recreation, Aesthetic, Nonuse**	Provisioning, Cultural
Wildlife	Recreation, Food, Nonuse**	Cultural, Provisioning
Climate	Climate Regulation including carbon sequestration, denitrification product emissions, effects on albedo, biogenic emissions, and microclimate effects	Regulating
*Personal Comfort and Wellbeing		

*All ecosystem services contribute to personal comfort and wellbeing.

** Nonuse values include existence, preservation, and bequest values.

EPA has defined ecological goods and services for the purposes of a Regulatory Impact Analysis as the “outputs of ecological functions or processes that directly or indirectly contribute to social welfare or have the potential to do so in the future. Some outputs may be

bought and sold, but most are not marketed” (US EPA 2006). Additionally Executive Order 12866 requires a regulatory Impact Analysis for any rule considered “economically significant” and defines significant as a rule having \$100 million or more in impacts. Though this is not a definition specifically for use in the NAAQS process it may be a useful one in considering the scope of ecosystem services and the effects of air pollutants upon those services. Especially important is the acknowledgement that it is difficult to measure and/or monetize the goods and services supplied by ecosystems. Valuing ecological benefits, or the contributions to social welfare derived from ecosystems, can be challenging as noted in EPA’s Ecological Benefits Assessment Strategic Plan (US EPA 2006) and the Science Advisory Board report “Valuing the Protection of Ecological Systems and Services” (US EPA, 2009). It can be informative in characterizing adversity to public welfare to attempt to place an economic valuation on the set of goods and services that have been identified with respect to a change in policy however it must be noted that this valuation will be incomplete and illustrative only. The stepwise concept leading to the valuation of ecosystem services is graphically depicted in Figure 4-3.

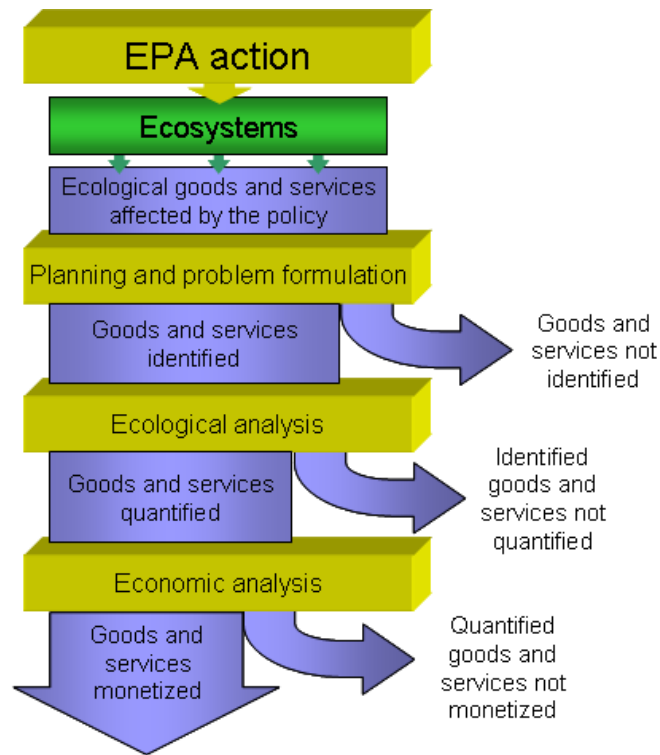


Figure 4-3. Representation of the benefits assessment process indicating where some ecological benefits may remain unrecognized, unquantified, or unmonetized. (Source: EBASP USEPA 2006).

A conceptual model integrating the role of ecosystem services in characterizing known or anticipated adverse effects to public welfare is shown in Figure 4-4. Under Section 109 of the CAA, the secondary standard is to specify a level of air quality that is requisite to protect public welfare. For this review, the relevant air quality indicator is interpreted as ambient oxides of nitrogen and sulfur concentrations that can be linked to levels of deposition for which there are ecological effects that are adverse to public welfare. The case study analyses (described in Chapters 4 and 5 of the REA) link deposition in sensitive ecosystems (e.g., the exposure pathway) to changes in a given ecological indicator (e.g., for aquatic acidification, changes in acid neutralizing capacity [ANC]) and then to changes in ecosystems and the services they provide (e.g., fish species richness and its influence on recreational fishing). To the extent possible for each targeted effect area, ambient concentrations of nitrogen and sulfur (i.e., ambient air quality indicators) were linked to deposition in sensitive ecosystems (i.e., exposure

pathways), and then deposition was linked to system response as measured by a given ecological indicator (e.g., lake and stream acidification as measured by ANC). The ecological effect (e.g., changes in fish species richness) was then, where possible, associated with changes in ecosystem services and their public welfare effects (e.g., recreational fishing). We recognize that there is a certain amount of natural change in ecosystems over time that can affect the level of acidity and the response of the ecosystem to additional acid and nutrient inputs. However, this review is focused on the impact of anthropogenic nitrogen and sulfur deposition given the existing state of non-anthropogenically determined ecosystem characteristics, and as such we essentially hold these other factors as “fixed” for the purposes of the review.

Knowledge about the relationships linking ambient concentrations and ecosystem services can be used to inform a policy judgment on a known or anticipated adverse public welfare effect. The conceptual model outlined for aquatic acidification in Figure 4-4 can be modified for any targeted effect area where sufficient data and models are available. For example, a change in an ecosystem structure and process, such as foliar injury, would be classified as an ecological effect, with the associated changes in ecosystem services, such as primary productivity, food availability, forest products, and aesthetics (e.g., scenic viewing), classified as public welfare effects. Additionally, changes in biodiversity would be classified as an ecological effect, and the associated changes in ecosystem services—productivity, existence (nonuse) value, recreational viewing and aesthetics—would be classified as public welfare effects. This information can then be used by the Administrator to determine whether or not the changes described are adverse to public welfare. In subsequent sections these concepts are applied to characterize the ecosystem services potentially affected by nitrogen and/or sulfur for each of the effect areas assessed in the REA.

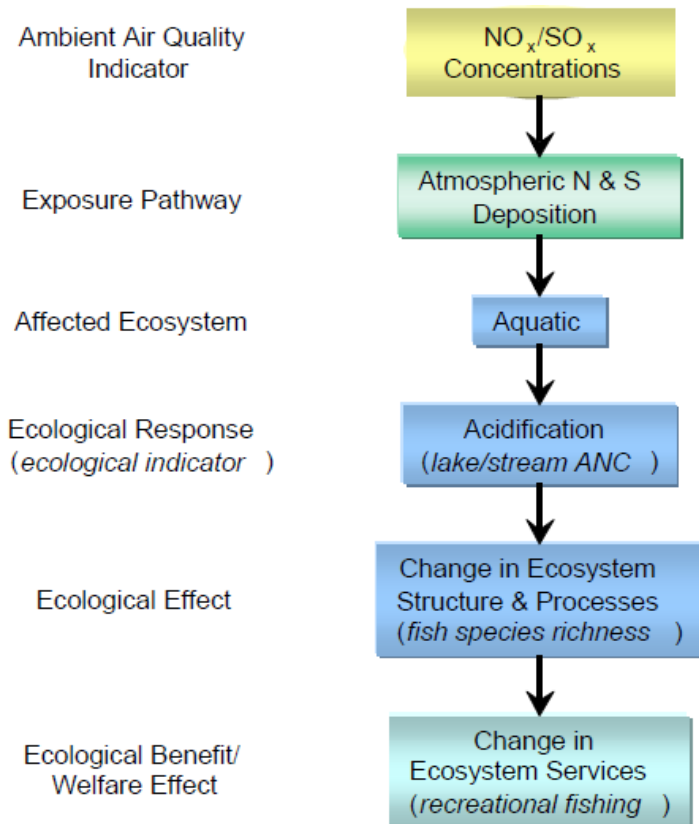


Figure 4-4. Conceptual model showing the relationships among ambient air quality indicators and exposure pathways and the resulting impacts on ecosystems, ecological responses, effects and benefits to characterize known or anticipated adverse effects to public welfare.

These concepts can also be applied to the programs described in section 4.1. National parks represent areas of nationally recognized ecological and public welfare significance, which are afforded a higher level of protection. Therefore, staff has also focused on air quality and deposition in the subset of national park sites and important natural areas. The spatial relationships between sensitive regions, Class 1 areas, federal and state public lands, and nitrogen deposition levels are illustrated in Figures 4-5 and 4-6. Please note that the scale of deposition levels is different for the two maps to allow greater differentiation of the deposition in

the western US.

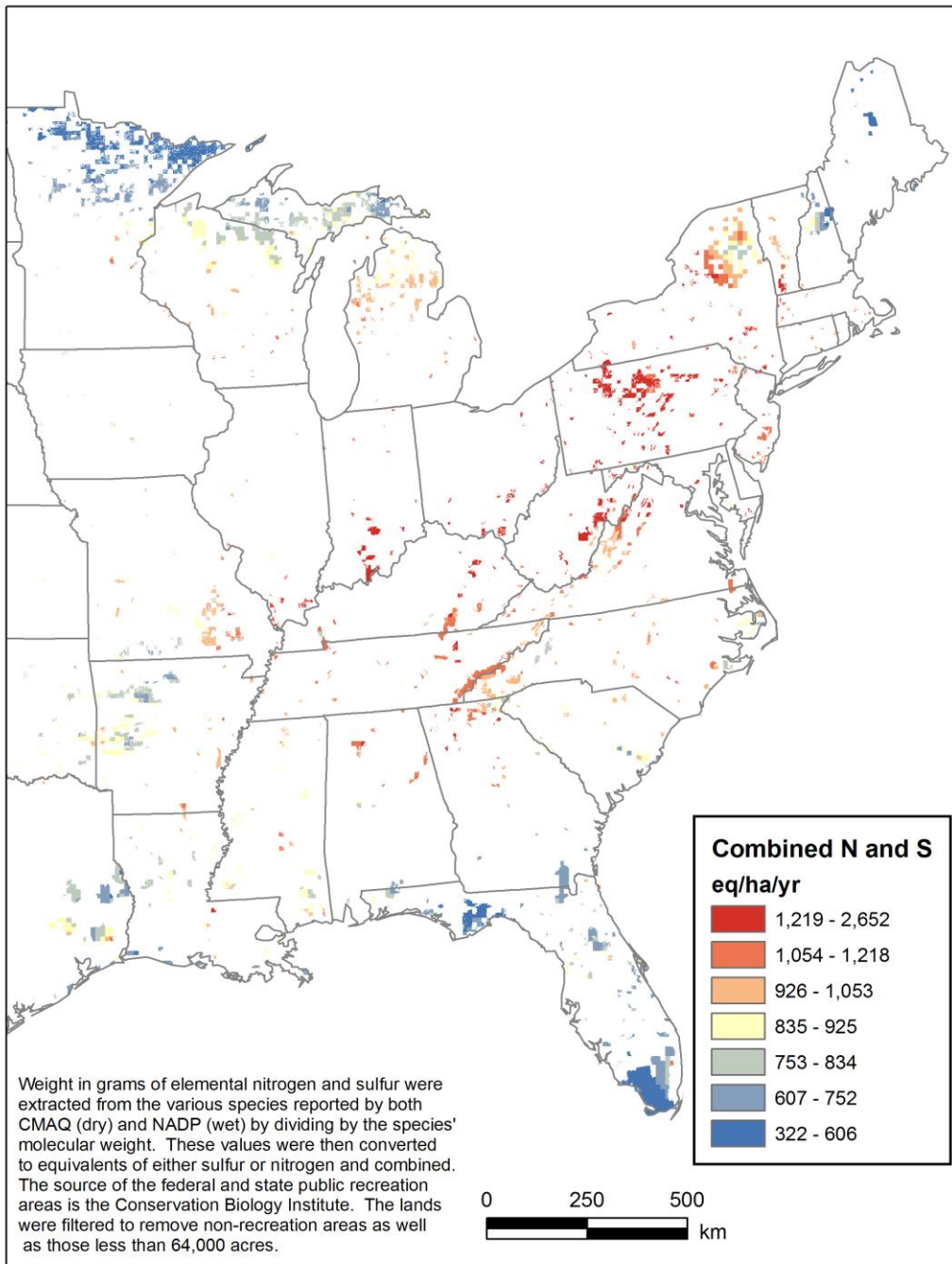


Figure 4-5. Locations of Eastern U.S. Public Lands relative to deposition of nitrogen and sulfur in sensitive aquatic areas. Source 2005 CMAQ and NADP. Note: Total N includes reduced nitrogen forms.

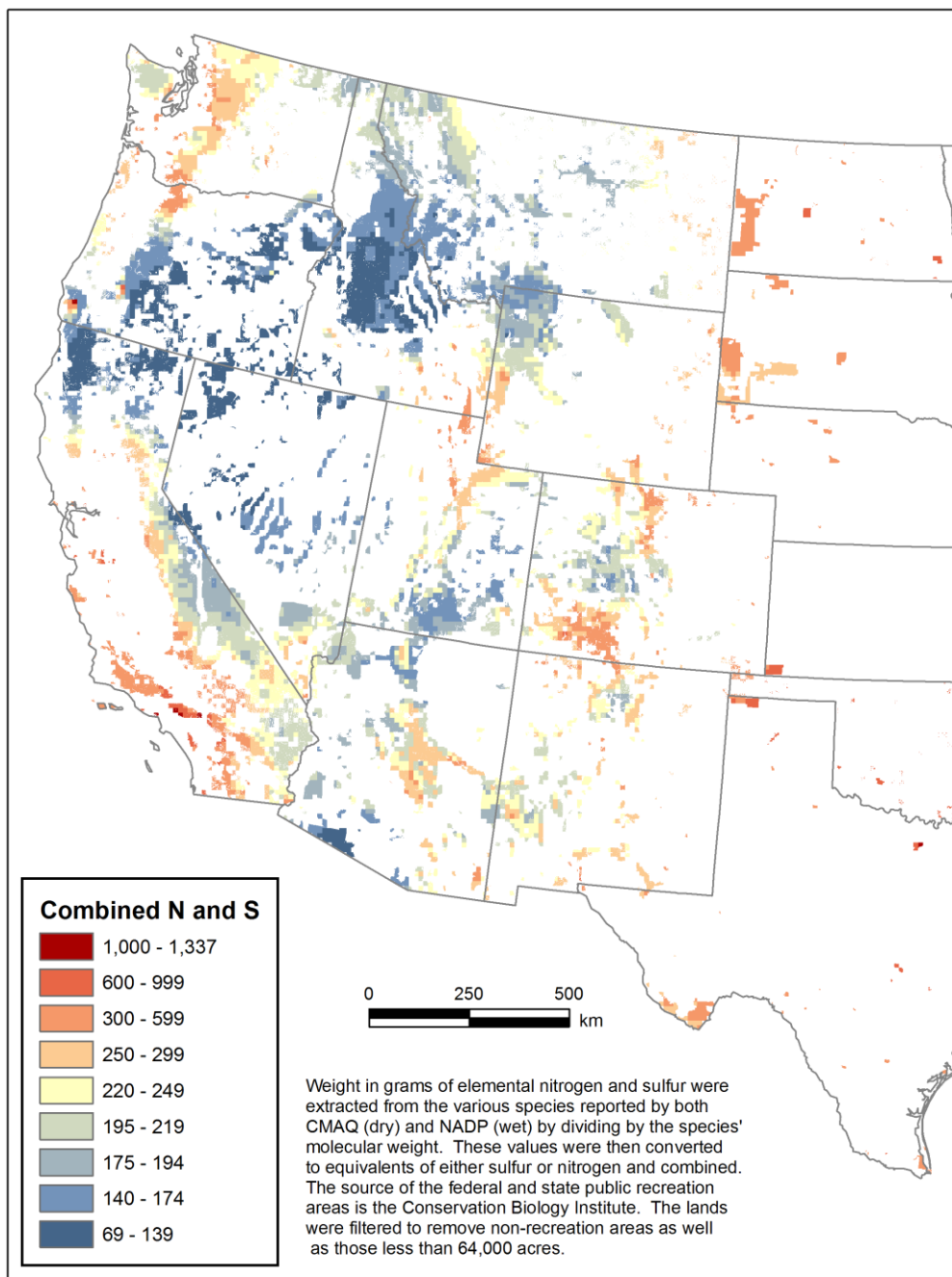


Figure 4-6. Location of Western U.S. Public Lands relative to deposition of nitrogen and sulfur. Source 2005 CMAQ and NADP. Note: Total N includes reduced nitrogen forms.

4.3 APPLYING ECONOMIC VALUATION TO ECOSYSTEM SERVICES

As discussed earlier in this document, a secondary NAAQS is required to be set at the “level(s) of air quality necessary to protect the public welfare from any known or anticipated adverse effects”. As part of the effort to determine the standard, EPA linked the changes in the ambient air concentrations of oxides of nitrogen and sulfur to the changes in ecosystem services and ultimately to changes in public welfare (U.S. EPA, 2009). The difficulty in the monetization for ecosystem services has been previously emphasized. This difficulty necessitates focusing on a subset of services for economic valuation. And although economics on its own cannot determine what level of impact on public welfare is “adverse,” economics can be helpful in the context of a secondary NAAQS for determining the degree to which improvements are beneficial to public welfare and illustrating and aggregating those impacts.¹

An ecosystem service framework provides a structure to measure changes in public welfare from changes in ecosystem functions affected by air pollution. EPA’s Risk Assessment for this rulemaking defines ecosystem services as “the ecological processes or functions having monetary or nonmonetary value to individuals or society at large” (EPA 2009). The discipline of economics provides a useful approach for summarizing how the public values changes in the services provided by the environment. An ecosystem services framework (with or without valuation) can characterize and describe how changes in ecosystem function affect public welfare and provide measures of changes in public welfare where those affects can be quantified.

4.3.1 Economics as a Framework to Illustrate Changes in Public Welfare

Economics can provide a framework to illustrate how public welfare changes in response to changes in environmental quality by quantitatively linking changes in ecosystem services to preferences. Economics assumes that the choices that individuals make reflect their preferences over certain outcomes and that, generally speaking, they will make choices that, in expectation, will make them as well off as possible given their resources. An individual’s preferred outcomes may include not just their own use and enjoyment of an ecosystem but also preservation and

¹ Section 109 of the Clean Air Act forbids consideration of the compliance costs of reducing pollution when setting a NAAQS. However, there is no prohibition regarding the consideration of the monetized impacts of welfare effects occurring due to levels of pollution above alternative standards in evaluating the adversity of the impacts to public welfare. Ecosystem services can be characterized as a method of monetizing the impacts of the air pollution. Although a separate regulatory document quantifying the costs and benefits of attaining a NAAQS is prepared simultaneously, this document is not considered when selecting a standard.

bequest value. In economics, revealed and stated preference methods are used to observe the choices individuals make to understand the outcomes individuals prefer. What individuals are willing to give up for an outcome is their willingness-to-pay (WTP) for that outcome. An example of an outcome is an improvement in an ecosystem service. Often, to provide comparability to other goods and services, in economics these tradeoffs are framed relative to dollars for convenience.

Economics could inform the Administrator by valuing and characterizing the changes in public welfare from changes in the quantity and quality of ecosystem services. Overall, this assessment intends to characterize changes in ecosystem services from a scientific perspective using effects on ecosystem structures and functions or ecosystem integrity. Economics then estimates the effect on public welfare of these changes in the quantity and quality of ecosystem services using willingness to pay as a measure of this effect. For example, a decrease in a particular bird species can be characterized by its effect on the ecosystem's structure and function, while from an economic perspective, the effects would be based on the impact on public welfare or the value the public places on that species. A simple example is a comparison between a decrease in a bird species that is relatively unknown compared to a decrease in a very prominent species (e.g. bald eagle). The public is likely to have a higher WTP to avoid the latter, and thus the decrease would affect the public welfare more, even if the changes in the two bird species generally have the same impact on an ecosystem's structure or function.

There are important complications with using preferences to understand the effect of pollution on public welfare. For example, while the field of economics generally assumes that public preferences are the paramount consideration; care must be taken that these preferences may change when the public receives new information. Evaluation of public preferences should take place under conditions of full information. If individuals do not understand how pollution will affect ecosystem services, or even how those ecosystem services affect their quality of life, then they will have a difficult time valuing changes in those services. Similarly, it may be very difficult and time-consuming for individuals to learn and understand how changes in particular ecosystem services may affect them, in part because typically there are significant interdependencies within an ecosystem. Because of this complexity, individuals may implicitly value a species, or habitat, or ecosystem function because it supports an ecosystem service that they do clearly value. Furthermore, the public also has limited understanding regarding

irreversibilities, tipping points, and other more complex aspects of ecosystems, which limits the ability to adequately value these ecosystems.² In addition, where and when a change in an ecosystem takes place is crucial for characterizing the associated change in an ecosystem service, and will also affect the value the public places on that change.

The fact that collective action activities are being undertaken by communities, Non-Governmental Organizations (NGO's) and States underscores the fact that there is a societal demand for further improvement to the quality of many water bodies which have been impaired by acidic deposition.³ However, as illustrated below they provide insufficient quantitative evidence as to what society willingness to pay to reduce lake and stream acidity because it is difficult to separately identify individual preferences from the actions of the group.

4.3.2 The Role of Economics in Defining Adversity

If economic valuation can establish a significant loss to public welfare, then this can provide strong support for a determination of an “adverse” effect. However, there is neither an economic definition of how much loss in public welfare is adverse nor an economic definition of adversity. While an economist might consider a particular scenario adverse because it might imply some harm or potential for improvement, there is no specific threshold level when a loss in welfare (e.g. loss in dollars) becomes adverse. An individual might be willing to give up some of their resources to avoid a threat or negative outcome (i.e., willing to pay to avoid a particular outcome). According to economic theory, if an individual is willing to give up something to avoid the outcome, then imposing the outcome on the individual must make them worse off, at which point an economist might describe the outcome as adverse. However, the amount an individual is willing to pay to avoid the outcome may or may not rise to the level of harm that the Administrator interprets as “adverse” to public welfare. At the same time, an economic valuation that shows that there are substantial damages from current levels of acidification or nutrient enrichment would provide strong evidence for finding that current impacts are adverse

² While the public may not fully appreciate the interdependencies within ecosystems, they can learn them, but again it may be costly to do so. It is possible for individuals to value outcomes that are irreversible or result in discrete changes (i.e., tipping points) in the quality and quantity of ecosystem services. Avoiding irreversible outcomes should be and are more valued by individuals than outcomes that are not irreversible (Arrow and Fischer, 1974).

³ However, one must recognize that often times reducing acidity is often part of a larger effort to generally improve the quality of a water body. Therefore, separating out the portion of people's desire to just to reduce acidity from the more general improvements is difficult.

to public welfare. In summary, economic analysis (particularly valuation) can provide useful information for the Administrator as to the interpretation of the word “adverse” in the context of public welfare, but it does not provide a complete set of information needed to make that determination.

4.3.3 Collective Action as an Indicator of Adversity

Typically, economics uses information on willingness to pay for improved environmental quality that is gathered from observing individuals’ market behavior (revealed preference) or that they provide through surveys (i.e., stated preference methods). The analyses in the following sections use revealed and stated-preference information to quantify a portion of the social costs of current levels of acidification and nutrient enrichment. However, the studies supporting these analyses evoke specific contexts and thus the findings may not be generalizable across all of those affected by acidification or nutrient enrichment.⁴ An alternative source of revealed information on the damages caused by acidification can be found in the behavior of groups. Often groups collectively make choices to engage in activities that improve the collective welfare of the group. For example, a community around an acidified lake might undertake activities designed to improve the quality of that lake, including purchasing lime, to use as a tool to reduce the acidity of the lake. These collective decisions can be used to gain insights into how people value improvements to ecosystem services. However, there are many obstacles to collective actions, including problems of organization, free ridership and others (Olson 1965) that make it difficult to use the actions of organizations to interpret individuals’ preferences.

In addition to communities, states may also take actions to increase the quality of their impaired lakes. Non-Governmental Organizations or advocacy groups, as well may organize support for, and/or directly undertake, activities to improve lake and stream quality on behalf of its members/donors. How individual’s preferences are expressed through these collective actions is discussed below. For brevity, this discussion will focus on collective efforts to reduce acidity of lakes and streams by Communities, Nongovernmental Organizations and States.

⁴ Even in the case where the existing studies provide a reliable characterization of the effects of acidification or nutrient enrichment on a limited number of individuals, it is advisable to make use of corroborating data and studies when such information is available.

Communities

In cases where property rights to a resource are well defined, collective action is more likely to take place, as individuals have greater ownership and control over the affected resource. Rights to use a lake, as well as, mandatory membership in a lake association is often written right into the deed of properties which abut or surround a lake, giving these property owners more control over the resource. This mechanism of granting rights and responsibilities to the lake encourages better management of the lake resource by remedying unrestricted access and free rider problems. This coupling of the costs of resource improvements with their benefits encourages individuals to maintain the quality of the resource.

There have been several documented instances where communities (particularly Homeowners Associations) have spent time and money to improve the quality of a lake. These include actions to combat acidity, eutrophication, invasive species (e.g. Zebra Mussels) and other problems. The Lake Wononscopomuc Association in Salisbury, Connecticut is a typical example (Mayland 2009.) They spend their own funds to hire scientific consultants to survey and test the lake water (for e.g. pH., dissolved oxygen, visibility, and many other factors related to the lake's condition) and recommend management strategies to improve the quality of the lake. Likewise, in Georgia, the Berkeley Lake Homeowners Association (BLHA) is a non-profit homeowner association dedicated to protecting Berkeley Lake. BLHA is typical of many other home owners associations with access to a lake, in that they are also concerned with and managing acidity, eutrophication, invasive species and a whole host of more mundane upkeep and maintenance issues (Hunkapiller 2006.) BLHA recognizes the relationship between lake acidity and resident's enjoyment of the lake's fishing swimming and aesthetics.

Nongovernmental Organizations

Nongovernmental Organizations (NGOs) or Advocacy Groups organize individuals and smaller groups thereby reducing the transaction costs associated with individual's desires to advance a specific goal. For example, Living Lakes, Inc. (LLI) is a not-for profit organization which sponsors an applied aquatic resources restoration demonstration program for acidified waters. In the late 1980's LLI began evaluation of seven different liming technologies on 22 lakes and 10 streams in 6 states. Lakes and streams have been treated in the states of Massachusetts, Rhode Island, New York, Pennsylvania, Maryland and West Virginia (Brocksen and Emler 1988.) Likewise, sportsman groups such as Trout Unlimited, as well as, smaller local

groups, have an interest in improving or maintaining the quality of lakes and streams. Trout Unlimited is well known for these activities and is discussed further later on. However, several smaller, localized groups also work to decrease aquatic acidification. One of these is the Mosquito Creek Sportsman's Association in Pennsylvania. Mosquito Creek and its main tributary Gifford Run were once famous for naturally reproducing wild brook and brown trout. However, since the early 1960's, the pH of the stream steadily declined due to acid rain. As a result, wild brook trout and brown trout have substantially declined in the watershed (Hoover and Rightnour, 2002.) Aerial liming was undertaken as part of an overall watershed restoration program that included constructed wetlands, forest liming, and in-stream liming to improve this fishery and provide increased opportunities for public recreation in the region. Fifty tons of lime were applied in the headwaters of Mosquito Creek Watershed. This liming project was part of the Mosquito Creek Sportsman's Association's efforts to improve the water quality of the 90 square mile watershed located in Clearfield and Elk counties. However, while the project first phase and the other ongoing phases of the overall restoration project have been initiated by the Mosquito Creek Sportsman Association, they received technical support from multiple public, private and other non-profit groups.⁵ "A benefit/cost analysis was prepared on the four implementation phases of this project. Costs were based on alkaline deficiencies and the additional costs determined for the technologies. Benefits were estimated as returns on direct recreational use losses and community willingness-to-pay. Full restoration of the watershed is estimated to cost approximately \$3.4 million over 15 years, for an annualized cost of \$229,000, or \$5,400 per mile per year for 42 miles of potential improvements. Expected returns range from \$1.2 million per year for recreational use to \$6.1 million per year for total community willingness-to-pay. It was concluded that restoration is technically feasible and economically beneficial for the Mosquito Creek watershed, and it is recommended that planned projects and the remainder of the progressive restoration plan be implemented." (Hoover and Rightnour, 2002)

⁵ These included: the Pennsylvania State University Environmental Resource Research Institute, Pennsylvania Game Commission, Pennsylvania DCNR Bureau of Forestry, Pennsylvania Fish and Boat Commission, Pennsylvania Department of Environmental Protection, Pennsylvania Department of Corrections Quehanna Boot Camp, Wood Duck Chapter Trout Unlimited, Canaan Valley Institute, Clearfield County Conservation District and Pennsylvania USDA Natural Resource Conservation Service.

States

Several states including Vermont, New Hampshire, New York and Tennessee have developed Total Maximum Daily Loads (TMDLs) for lakes impaired for acidification in their jurisdictions. As mentioned in the previous section regarding the TMDL for the Chesapeake Bay the applicable water quality standards and designated uses are set by the states with public participation. Although most states set their standard either by legislation or regulations, in at least one case, specifically New York, the designated uses and water quality standard are part of the state constitution. The Adirondack Forest Preserve is required to be “forever kept as wild forest lands.” New York has interpreted this to mean that the waters included in the preserve are required to be kept in natural conditions. To this end New York has chosen to set a tiered TMDL that allows interim water quality targets in order to address the reality that some lakes in the Adirondacks will naturally have a pH that does not meet the state’s water quality standards. For lakes that can meet the standards the state has chosen to set the water quality standard for pH values above 6.5. New Hampshire has chosen to set their water quality target at an ANC of 60µeq/L that, according to the TMDL document, corresponds to a pH of 6.5. Vermont, in a similar process has chosen a target ANC of 50µeq/L. In Tennessee the state faces a similar problem as New York in trying to set levels to protect streams Great Smoky Mountains National Park which include some naturally acidic streams. Accordingly they have set site specific ANC targets where data is available to do so and chosen to target an ANC of 50µeq/L as a default value where data is not available. The Tennessee TMDL is a partnership between the state and the National Park Service which is sharing the data collection and modeling activities with academic institutions.

In each case the implementation sections of these TMDLs cites the fact that the sources of pollution responsible for the degradation of water quality in the named lakes and streams are not located within the jurisdiction of the state. Each state has called on EPA to require regional or national decreases in acidifying deposition. Vermont goes so far as to say “In short, implementation of this TMDL is primarily the responsibility of EPA.... This TMDL sets out clear endpoints to guide EPA actions. However, in the absence of vigorous efforts by EPA to bring about reductions in acid emissions from out-of-state sources this TMDL will merely have been a paper exercise.”

Public-Private Collaborations

In some cases, industry, government and private efforts partner to reduce the acidity of a lake or stream. In one such instance in 2005, The U.S. Forest Service used helicopters to apply 200 tons of limestone sand into the St. Marys River and its tributaries to lower acid levels in one of Virginia's prime trout fisheries to mitigate the impacts of acidification until a long-term solution to acidification is found. The NGO, Trout Unlimited was one of the partners in the liming project, while Dominion Virginia Power provided \$10,000 for the liming project (Associated Press 2005.) In another partnership, Living Lakes participated in a project in the Woods Lake Watershed in the Adirondack region of the state of New York that was co-sponsored by the Electric Power Research Institute (EPRI), which sponsored the original research on lake liming in the Adirondacks (Scheffe et al., 1986). There are many such examples, where all three of these types of groups partner on the same project.

4.4 EFFECTS OF ACIDIFICATION AND NUTRIENT ENRICHMENT ON ECOSYSTEM SERVICES

The process used to link ecological indicators to ecosystem services is discussed extensively in Appendix 8 of the REA. In brief, for each case study area assessed the ecological indicators were linked to an ecological response that was subsequently linked, to the extent possible, to associated services. For example in the case study for aquatic acidification the chosen ecological indicator is ANC which can be linked to the ecosystem service of recreational fishing as illustrated in the conceptual model shown in Figure 4-7. Although recreational fishing losses are the only service effects that can be independently quantified or monetized at this time, there are numerous other ecosystem services that may be related to the ecological effects of acidification.

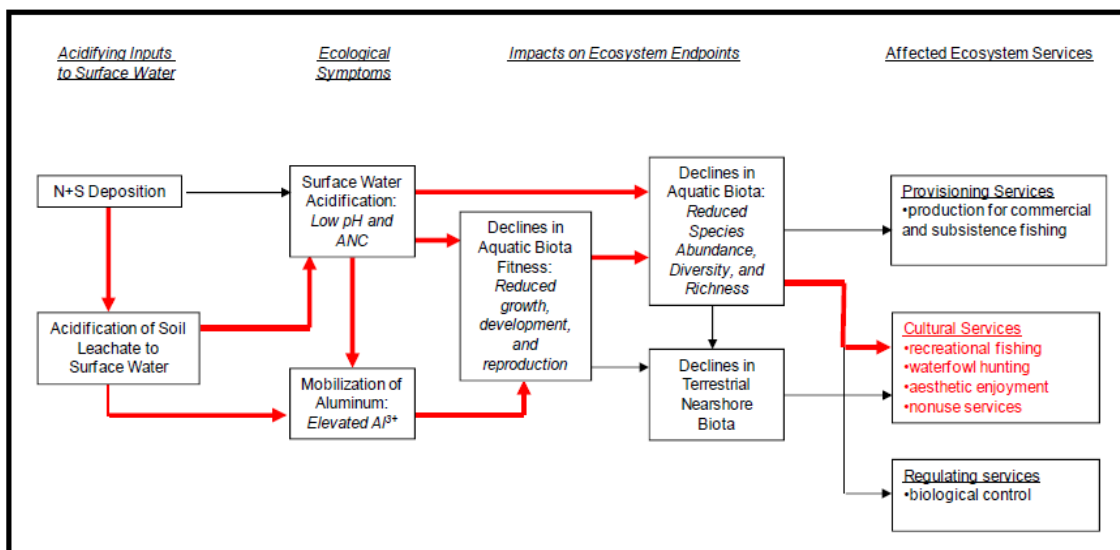


Figure 4-7. Conceptual model linking ecological indicator (ANC) to affected ecosystem services. The red arrows highlight the path to monetization of recreational fishing effects. Nonuse services include biodiversity, habitat preservation, existence, and bequest value.

While aquatic acidification is the focus of this policy assessment, the other effect areas analyzed in the REA still merit some discussion in view of the fact that these ecosystems are being harmed by nitrogen and sulfur deposition and will obtain some measure of protection with any decrease in that deposition regardless of the reason for the decrease. In next four sections we summarize the current levels of specific ecosystem services for aquatic and terrestrial acidification, and aquatic and terrestrial nutrient enrichment. We also present results of analyses that have attempted to quantify and monetize the harms to public welfare, as represented by ecosystem services, due to nitrogen and sulfur deposition.

4.4.1 Aquatic Acidification

Acidification primarily affects the ecosystem services that are derived from the fish and other aquatic life found in these surface waters (REA, Section 5.2.1.3). In the northeastern United States, the surface waters affected by acidification are not a major source of commercially raised or caught fish; however, they are a source of food for some recreational and subsistence fishers and for other consumers. Although data and models are available for examining the effects on recreational fishing, relatively little data are available for measuring the effects on subsistence and other consumers. For example, although there is evidence that certain

population subgroups in the northeastern United States, such as the Hmong and Chippewa ethnic groups, have particularly high rates of self-caught fish consumption (Hutchison and Kraft, 1994; Peterson et al., 1994), it is not known if and how their consumption patterns are affected by the reductions in available fish populations caused by surface water acidification.

Inland surface waters support several cultural services, such as recreational fishing, aesthetic and educational services; however, Banzhaf et al (2006) has shown that non-use services, which include existence (protection and preservation with no expectation of direct use) and bequest values, are arguably a significant source of benefits from reduced acidification. The areas of the country containing the most sensitive lakes and streams are New England, the Adirondack Mountains which are part of the Adirondack Forest Preserve – that have been set aside to be kept “forever wild” see PA Sec 4.3.4, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region) and the Upper Midwest. Within the Adirondack Mountains approximately 8% of the lakes were considered acidic and in the northern Appalachian Plateau and Ridge/Blue Ridge 6 – 8% of the streams (ISA 3.2.4.2 and REA 4.2.2). Recreational fishing in lakes and streams is among the most popular outdoor recreational activities in the northeastern United States. Data from the 2006 National Survey of Fishing, Hunting, and Wildlife Associated Recreation (FHWAR) indicate that more than 9% of adults in this part of the country participate annually in freshwater fishing with 140 million freshwater fishing days. Based on studies conducted in the northeastern United States, Kaval and Loomis (2003) estimated average consumer surplus values per day of \$35 for recreational fishing (in 2007 dollars). Therefore, the implied total annual value of freshwater fishing in the northeastern United States was \$5 billion in 2006. We recognize that embedded in these numbers is a degree of harm to recreational fishing services due to acidification that has occurred over time. These harms have not been quantified on a regional scale. However given the magnitude of the resource, the length of time nitrogen and sulfur have been affecting freshwaters in the northeast and the level of monetary damages calculated for the case study in the Adirondacks described in the next section we would expect these damages to be significant.

In general, inland surface waters such as lakes, rivers, and streams provide a number of regulating services, playing a role in hydrological regimes and climate regulation. There is little evidence that acidification of freshwaters in the northeastern United States has significantly

degraded these specific services; however, freshwater ecosystems also provide biological control services by providing environments that sustain delicate aquatic food chains.

The toxic effects of acidification on fish and other aquatic life impair these services by disrupting the trophic structure of surface waters (Driscoll et al., 2001). Although it is difficult to quantify these services and how they are affected by acidification, it is worth noting that some of these services may be captured through measures of provisioning and cultural services. For example, these biological control services may serve as “intermediate” inputs that support the production of “final” recreational fishing and other cultural services.

4.4.2 Value of Current Ecosystem Service Impairments Due to Aquatic Acidification

In the previous section we described the ecosystem services that are most likely to be affected by N and S deposition and summarized evidence regarding the current magnitude and values of recreational fishing services, the degree to which these services are impaired by existing NO_x/SO_x levels has not been quantified. To address this limitation, the REA (Appendix 8) provides insights into the magnitude of ecosystem service impairments. The REA provides quantitative estimates of selected ecosystem services impairments or enhancements for three main categories of ecosystem effects – aquatic acidification, terrestrial acidification, and aquatic nutrient enrichment⁶. Within these three categories, the selection of specific ecosystem services for more in-depth analysis depended primarily on the expected magnitude of impairments and on the availability of appropriate data and modeling tools.

The analysis of ecosystem service impairments due to aquatic acidification builds on the case study analysis of lakes in the New York Adirondacks. In this study estimates of changes in recreational fishing services are determined, as well as changes more broadly in “cultural” ecosystem services (including recreational, aesthetic, and nonuse services). First, the MAGIC model (REA, Appendix 8, Sec 2.2) was applied to 44 lakes to predict what ANC levels would be under both “business as usual” conditions (i.e., allowing for some decline in deposition due to existing regulations) and pre-emission (i.e., background) conditions. These model runs assumed a 2010 “zero-out” emissions scenario (where all N and S deposition is eliminated) with a projected lag time between the elimination of emissions to observed improvement in ANC of 10 years thus benefits results were calculated for the year 2020. These predictions were then

⁶ Estimates for terrestrial nutrient enrichments were not generated due to the limited availability of necessary data and models for this effect category.

extrapolated to the full universe of Adirondack lakes. Table 4-2 reports the number of “impacted” lakes in each year, where impact means that the lake is predicted to be below the ANC threshold under business-as-usual *and* above the threshold under pristine conditions.

Table 4-2. Count of Impacted Lakes.

ANC Threshold (in $\mu\text{eq/L}$)	Year	Lake Count
20	2020	107
20	2050	95
20	2100	74
50	2020	244
50	2050	222
50	2100	200
100	2020	430
100	2050	404
100	2100	354

Note: There are 1,076 lakes in the “Adirondack Region”.

Second, to estimate the recreational fishing impacts of aquatic acidification in these lakes, an existing model of recreational fishing demand and site choice was applied. This model predicts how recreational fishing patterns in the Adirondacks would differ and how much higher the average annual value of recreational fishing services would be for New York residents if lake ANC levels corresponded to background (rather than business as usual) conditions. Table 4-3 summarizes the results and the present value of benefits and annualized benefits at 3 and 7% discount rates.

Table 4-3. Present Value and Annualized Benefits of Recreational Fishing to NY Residents, Adirondack Region.

ANC Threshold (in $\mu\text{eq/L}$)	Present Value Benefits ^a (in million of 2007 dollars)		Annualized Benefits ^b (in million of 2007 dollars)	
	3% Discount Rate	7% Discount Rate	3% Discount Rate	7% Discount Rate
20	\$142.59	\$60.05	\$4.46	\$3.94
50	\$285.15	\$114.18	\$8.91	\$7.49
100	\$298.67	\$120.61	\$9.33	\$7.91

^a Annual benefits for 2010 to 2100 discounted to 2010.

^b Present value benefits annualized over 2009–2100.

Current annual impairments are most likely of a similar magnitude because, although current NO_x/SO_x levels are somewhat higher than those expected in 2020 (under business as usual – given expected emissions controls associated with Title IV regulations but no additional nitrogen or sulfur controls), and the affected NY population is also somewhat smaller (based on U.S. Census Bureau projections).

To estimate impacts on a broader category of cultural (and some provisioning) ecosystem services, results from the Banzhaf et al (2006) valuation survey of New York residents were adapted and applied to this context. The survey used a contingent valuation approach to estimate the average annual household WTP for future reductions (20% and 45%) in the percent of Adirondack lakes impaired by acidification. The focus of the survey was on impacts on aquatic resources. Pretesting of the survey indicated that respondents nonetheless tended to assume that benefits would occur in the condition of birds and forests as well as in recreational fishing. The survey that measured the benefits of 20% of the lakes improving indicated that terrestrial benefits were minor and econometric controls were used to adjust the willingness to pay estimate for those that suspected that terrestrial improvements were greater than described in the survey. The survey that measured the benefits of improving 45% of the total number of lakes also indicated that the benefits to forests and birds were significant.

The WTP estimates from the two versions of the survey were then (1) scaled to reflect predicted changes between business-as-usual and background conditions in 2020 (MAGIC lake modeling results indicate that impaired lakes would decrease from 22 to 31% using background conditions with ANC increasing from 20 to $50\mu\text{eq/L}$), and (2) aggregated across New York

households. The scaling entails converting the average household willingness-to-pay for the improvements described in the Adirondacks surveys to an average household willingness-to-pay per percentage point of the total population of lakes improved.⁷ The results are summarized in Table 4-4. The range of average household willingness to pay reflects the range in willingness to pay per percentage point of lakes improved described in the two versions of the survey. Estimates are provided at ANC 20, 50, and 100 to reflect the range of ANC discussed throughout the REA and this document and for consistency with the Random Utility Model analysis.

The “base” version of the survey asserts that, in the absence of any direct policy intervention, the condition of the 1,500 unhealthy lakes and 1,500 healthy lakes is expected to remain unchanged over the next 10 years. However, if a liming program is undertaken, it would improve 20% (600) of the lakes in the Park relative to their expected 2014 condition without the program. In contrast, the “scope” version describes a gradually worsening status quo without the liming program, in which 5% (150) of the healthy lakes are expected to gradually become unhealthy. In other words, without the program, 55% (1,650) of the lakes would be unhealthy in 2014. With the liming program, however, only 10% of the lakes would be unhealthy in 2014, so the program improves 45% (1,350) of the lakes relative to their expected 2014 condition without the program.

Although scientific evidence indicates that a liming policy would not significantly improve the condition of birds and forests, pretesting of the survey indicated that respondents nonetheless tended to assume that these other benefits would occur. Therefore, to make the scenarios more acceptable to respondents, other nonlake effects were added to the two survey versions. In the base case, the red spruce (covering 3% of the forests’ area) and two aquatic bird species (common loon and hooded merganser) are said to be affected. In this version, the health of birds and forests is described as unchanged in the absence of intervention, and minor improvements are said to result from the program. In the scope version, a broader range of damages is associated with acid rain—two additional species of trees (sugar maple and white ash, all together covering 10% of forest area) and two additional birds (wood thrush and tree swallow) are said to be affected. The scope version describes a gradually worsening status quo along with large improvements due to the program.

⁷ Scaling is required because neither of the surveys administered by Banzhaf et al. (2006) describe improvements that correspond exactly to the improvement scenario modeled here.

Each respondent was presented with one of these (base or scope) policy scenarios and then asked how they would vote in a referendum on the program, if it were financed by an increase in state taxes for 10 years. To estimate the distribution of WTP, the annual tax amounts were randomly varied across respondents. Based on a detailed analysis of the survey data, Banzhaf et al. (2006) defined a range of best WTP estimates, which were converted from 10-year annual payments to permanent annual payments using discount rates of 3% and 5%. For the base version, the best estimates ranged from \$48 to \$107 per year per household (in 2004 dollars), and for the scope version they ranged from \$54 to \$154.

To specify values for WTP_{Adr} , these estimates were converted to 2007 dollars using the CPI and each of them was divided by the corresponding change in the percentage of lakes that are unhealthy (20% for the base version and 45% for the scope version). For the base version, the WTP_{Adr} estimates range from \$2.63 to \$5.87 per percentage decrease in unhealthy lakes, and for the scope version they range from \$1.32 to \$3.76.

To estimate N_{NY} , the Census population projection for New York for 2010 was used, which is 19.26 million people, and this amount was divided by the ratio of population size to the number of households in New York (2.69) in the year 2000 (assuming that this ratio stays constant from 2000 to 2010).

Finally, to estimate $\Delta\%IL$ the MAGIC model results were used, and it was assumed that the distribution of ANC levels for these 44 lakes is representative of all 3,000 lakes in the Adirondacks Park. In 2020, the *reduction* in the percentage of lakes that are unhealthy in the zero-out condition compared to the reference condition is 22% for the 20 $\mu\text{eq/L}$ threshold. For the 50 $\mu\text{eq/L}$, and 100 $\mu\text{eq/L}$ thresholds, it is 31% and 26%, respectively. These 3% reduction values were used as the main estimates of $\Delta\%IL$.

To estimate aggregate benefits for the zero-out scenario using the RFF survey results, it is important to use the results from the survey version that most closely match this scenario. Although both RFF survey versions use 2004 as the “current” year instead of 2010, they both use a 10-year horizon, which corresponds to the zero-out scenario. Although no direct matches exist, the closest correspondence is between the zero-out scenario assuming a 50 $\mu\text{eq/L}$ threshold and the RFF scope survey. Under current and future conditions with no additional policy interventions, the RFF scope scenario assumes a small increase in unhealthy lakes from 50% to 55%, whereas the 50 $\mu\text{eq/L}$ threshold is expected to result in a small decrease from 43% to 42%.

With the program, the RFF scope survey describes a 45% decrease in unhealthy lakes, whereas the zero-out scenario projects a 31% decrease.

Table 4.4 reports the aggregate benefit estimates for the zero-out scenario using the 50 µeq/L threshold. As described above, the projected long-term decrease in the percentage of unhealthy lakes (*Δ%IL*) for this scenario is 31%. Using the range of *WTPAdr* values from the RFF scope survey and the projected number of New York households in 2010 the aggregate annual benefits of the zero-out scenario are estimated to range from \$291 million to \$829 million. Table 3.4 also reports aggregate benefit estimates for the zero-out scenarios using the 20 µeq/L and 100 µeq/L thresholds for ANC. Neither of these scenarios corresponds well with the baseline descriptions of either the base or scope version of the RFF survey. The baseline percentage of unhealthy lakes using the 20 µeq/L threshold (22%) is much lower than in either the survey version. In contrast, the percentage using the 100 µeq/L threshold (77%) is much higher. Nevertheless, the future reductions in the percentage of unhealthy lakes (22% and 26%) are closest to the reductions described in the base version of the RFF survey. Therefore, the aggregate benefits of the zero-out scenario with these thresholds are evaluated using the range of *WTPAdr* values from the RFF base survey. With the 20 µeq/L threshold, the aggregate benefits are estimated to range from \$411 million to \$916 million per year. With the 100 µeq/L threshold, the aggregate benefits are estimated to range from \$492 million to \$1.1 billion per year.

Table 4-4. Aggregate Annual Benefit Estimates of Recreational Fishing to NY Residents for the Zero-Out Scenario.

ANC Threshold	Reduction in Percentage of Unhealthy Lakes	Range of Average Household WTP per Percentage Reduction		Number of NY Households (in millions)	Range of Annual Benefits (in millions of 2007 \$)	
		*Base version WTP	**Scope version WTP		Base version	Scope version
20 µeq/L	22%	*\$2.63	\$5.87	7.162	\$410.6	\$916.4
50 µeq/L	31%	**\$1.32	\$3.76	7.162	\$291.2	\$829.4
100 µeq/L	26%	*\$2.63	\$5.87	7.162	\$491.6	\$1,097.2

*Base version WTP **Scope version WTP

These results suggest that the value of avoiding current impairments to ecosystem services from Adirondack lakes are even higher than the estimate, because the estimates assume a lag of 10 years in which no benefits accrue and because the percent of impaired lakes is slightly higher today than expected in 2020 under business-as-usual. These results imply significant value to the public in addition to those derived from recreational fishing services. Note that the

results are only applicable to improvements in the Adirondacks valued by residents of New York. If similar benefits exist in other acid-impacted areas, benefits for the nation as a whole could be substantial. The analysis provides results on only a subset of the impacts of acidification on ecosystem services and suggests that the overall impact on these services is likely to be substantial.

4.4.3 Terrestrial Acidification

In the previous chapter of this document we discussed the effects of acidifying deposition on terrestrial ecosystems, especially forests. These include the observed decline and/or dieback in red spruce and sugar maple. These species are particularly sensitive to acidifying deposition and have ranges that overlap the areas of the U.S. where some of the highest levels of acidifying deposition occur. Additionally these species are present in the case study areas examined in the REA. As a result we chose to focus on red spruce and sugar maple as the species of interest for the analysis of ecosystem services presented in this section.

A similar model to Figure 4-7 can be drawn for terrestrial acidification that links Bc:Al molar ratio to reduced tree growth to decreases in timber harvest, although we have less confidence in the significance of this linkage than we do for aquatic acidification. There are numerous services expected to be affected but the data and methods to adequately describe those losses does not as yet exist. These services include effects to forest health, water quality, and habitat, including decline in habitat for threatened and endangered species, decline in forest aesthetics, decline in forest productivity, increases in forest soil erosion and decreases in water retention (EPA, 2009; EPA, 2009; Krieger, 2001). Forests in the northeastern United States provide several important and valuable provisioning services, which are reflected in the production and sales of tree products. Sugar maples are a particularly important commercial hardwood tree species in the United States, producing timber and maple syrup that provide hundreds of millions of dollars in economic value annually (NASS, 2008). Red spruce is also used in a variety of wood products and provides up to \$100 million in economic value annually (USFS, 2006).

Forests in the northeastern United States are also an important source of cultural ecosystem services, including nonuse (existence value for threatened and endangered species), recreational, and aesthetic services (U.S. EPA, 2009; U.S. EPA, 2009). Red spruce forests are

home to two federally listed species, the spruce-fir moss spider and the rock gnome lichen. The value of these two endangered species has not been estimated.

Although we do not have the data to link acidification damages directly to economic values of lost recreational services in forests, these resources are valuable to the public. For example, most recent data from the National Survey on Recreation and the Environment (NSRE) indicate that, from 2004 to 2007, 31% of the U.S. adult (16 and older) population visited a wilderness or primitive area during the previous year, and 32% engaged in day hiking (Cordell et al., n.d.). A recent study suggests that the total annual value of off-road driving recreation was more than \$9 billion, total and value of hunting and wildlife viewing was more than \$4 billion each in the Northeastern United States in 2006 (Kaval and Loomis, 2003). Table 4-5 summarizes data from the NSRE and the Fishing, Hunting, and Wildlife Related Activity Survey (U.S. DOI, 2007) along with average WTP estimates from Kaval and Loomis to estimate the total value of these services in the northeast.

Table 4-5. Annual participation and value of outdoor (forest related) activity in the northeast.

Recreational Activity	Participation Rate (%)	Activity Days (in Thousands)	Avg. WTP Per Activity Day (\$2007)	Total Value (in millions)
Off Road Driving	16	366,336	\$25.25	\$9,250
Hunting	5.5	83,821	\$52.36	\$4,380
Wildlife Viewing	10	122,200	\$34.46	\$4,210

In addition, fall color viewing is a recreational activity that is directly dependent on forest conditions. Sugar maple trees, in particular, are known for their bright colors and are, therefore, an essential aesthetic component of most fall color landscapes. Statistics on fall color viewing are much less available than for the other recreational and tourism activities; however, a few studies have documented the extent and significance of this activity. For example, Spencer

and Holecek (2007) found that approximately 30% of residents in the Great Lakes area reported at least one trip in the previous year involving fall color viewing. In a separate study conducted in Vermont, Brown (2002) reported that more than 22% of households visiting Vermont in 2001 made the trip primarily for the purpose of viewing fall colors (Table 4-6).

Table 4-6. Summary of Studies of Fall Color Viewing .

Ecosystem Service	% Population	Population surveyed	Study Cited
Fall Color Viewing	30%	Great Lakes area residents	Spencer (2007)
	22%	Vermont visitors	Brown (2002)

Two studies have estimated values for protecting high-elevation spruce forests in the Southern Appalachians. These forests occur mostly in the Great Smoky Mountains National Park, the North Carolina Park System, the Jefferson and Pisgah National Forests, and the Blue Ridge parkway. Kramer et al. (2003) conducted a contingent valuation study estimating households' WTP for programs to protect remaining high-elevation spruce forests from damages associated with air pollution and insect infestation (Haeefele et al., 1991; Holmes and Kramer, 1995). While it is not possible to separate the relative damage attributable only to air pollution it should be noted that the insect infestation referred to in these studies is specifically damage caused by the balsam wooly adelgid to Frasier fir trees that are part of the spruce-fir ecosystem.

The survey presented respondents, who lived within 500 miles of Asheville, NC to ensure that they had some familiarity with the area, with a sheet of color photographs representing three stages of forest decline and explained that, without forest protection programs, high-elevation spruce forests would all decline to worst conditions (with severe tree mortality - an aerial survey (Dull et al. 1988) had determined that in approximately one quarter of the area greater than 70% of the standing trees were dead) and two potential forest protection programs. The first program would protect the forests along road, and trail corridors spanning approximately 1/3 of the ecosystem at risk. This level of protection may be most appealing to recreational users. The second level of protection was for the entire ecosystem and may be most appealing to those who value the continued existence of the entire ecosystem. Median household WTP was estimated to be roughly \$29 (in 2007 dollars) for the minimal program and \$44 for the more extensive program. Respondents were then asked to decompose their value for the extensive program into

use, bequest, and existence values. This resulted in values that represented components of 13% use value, 30% bequest, 57% existence value (Table 4-7).

Table 4-7. Value Components for WTP for Extensive Protection Program for Southern Appalachian Spruce-Fir Forests.

Type of Value	Proportion of WTP	Component Value In \$2007
Use	0.13	\$5.72
Bequest	0.30	\$13.20
Existence	0.57	\$25.08
Total	1	\$44.00

Another study by Jenkins, Sullivan, and Amacher (2002) estimated values for recreational users of this resource. Households in the seven state Appalachian region (North Carolina, South Carolina, West Virginia, Virginia, Tennessee, Kentucky, and Georgia) were shown photographs taken in summer 1994 at permanent test plots. These photographs depicted an unimpacted area (5% dead basal area), an area in beginning stage decline (30% dead basal area) and severe decline (75% dead basal area) intended to represent a future scenario without a forest protection program. The study estimated the mean WTP for forest protection programs at \$208 (\$2007); multiplying across the population of the seven state area gives an aggregate annual value of \$3.4 billion for avoiding a significant decline in the health of high-elevation spruce forests in the Southern Appalachian region (Table 4-8). This estimate is considerably larger than the previous study. The difference may be due to the closer proximity of the respondents in the Jenkins et al. study (the Kramer study radius of 500 miles includes respondents as far away as Michigan, New York, Missouri, Louisiana and Florida).

Table 4-8. Summary of WTP Studies for Protection of Spruce Forests in the Southern Appalachians.

WTP in \$ 2007	Aggregation	Study
\$29	Per household* for minimal program	Kramer et al. (2003)
\$44	Per household for extensive program	
\$208	Per household for forest protection program	Jenkins (2002)
\$ 3.4 b	Jenkins estimate applied to the population of the seven state**area included in the study	

* Households within a 500 mile radius of Asheville, NC

**North Carolina, South Carolina, West Virginia, Virginia, Tennessee, Kentucky, and Georgia

Forests in the northeastern United States also support and provide a wide variety of valuable regulating services, including soil stabilization and erosion control, water regulation, and climate regulation (Krieger, 2001). Forest vegetation plays an important role in maintaining soils in order to reduce erosion, runoff, and sedimentation that can adversely impact surface waters. In addition to protecting the quality of water in this way, forests also help store and help regulate the quantities and temporal discharge patterns of water in watersheds. Forests also play an important role in carbon sequestration at both regional and global scales. The total value of these ecosystem services is very difficult to quantify.

In some ecosystems where nitrogen is a growth limiting nutrient, there is the potential that atmospheric deposition of nitrogen can increase biomass production of managed and unmanaged systems with a consequent increase in carbon sequestration. The available evidence (EPA, 2008) indicates N increases ecosystem carbon content in forested ecosystems, however the magnitude of N stimulation of carbon sequestration is highly uncertain. N effects on the carbon budget of wetlands, grasslands and tundra is highly uncertain with respect to the direct relationship between atmospheric nitrogen deposition and carbon sequestration. For all ecosystem types there is the possibility of various unintended consequences, especially in non-managed systems that occur as a result increased biomass production. Consequently, data do

not exist to adequately consider the potential changes of carbon sequestration associated with atmospheric deposition of nitrogen.

4.4.4 Value Of Current Ecosystem Service Impairments Due To Terrestrial Acidification

The REA Appendix 8 describes an analysis of ecosystem service impairments associated with the impacts of terrestrial acidification on the forest product provisioning services from two commercially important tree species on unmanaged forests – sugar maple and red spruce - that are particularly sensitive to the effects of acidification. Evidence of effects due to terrestrial acidification is particularly strong for these two species whose range includes the northeastern U.S. where levels of nitrogen and sulfur deposition have historically been relatively high, however more widespread impacts that include other tree species are also possible. We acknowledge that there may be some beneficial fertilization effects of nitrogen deposition however given the complexity of the nitrogen cycle it is not possible to quantify all those effects here. There is a detailed discussion of nitrogen fertilization effects in Chapter 3.

In an exploratory study that is still under development we used data from the USFS Forest Inventory and Analysis (FIA) database, to estimate an exposure-response relationship for each species to measure the average negative effect of critical load exceedances (CLEs) of nitrogen and sulfur deposition on annual tree growth. These estimated relationships were then applied to sugar maple and red spruce stocks in the Northeast and North central regions to estimate the average percent increase in annual tree growth that would occur if all CLEs were eliminated. To estimate the aggregate-level forest market impacts of eliminating CLEs starting in the year 2000, the tree-level growth adjustments were applied using the Forest and Agricultural Sector Optimization Model (FASOM), which is a dynamic optimization model of the U.S. forest and agricultural sectors. The model results are reported as the present discounted values of future welfare changes in the forestry sector (in 5-year increments from 2000 to 2080) due to increased tree growth. Summing over this 80-year period, the total present value of these welfare gains is \$40.705 million (in 2006 dollars, using a 4% discount rate). On an annualized basis (at 4%), this is equivalent to \$1.64 million per year. These estimates can also be interpreted as the current value of impairments to forest provisioning services provided by red spruce and sugar maple due to acidification effects from nitrogen and sulfur. These results should be considered very uncertain due to the pending revision of the exposure – response curve and release of an updated version of the FASOM model. Referring back to the previous section it

is apparent that cultural services supplied by these forests, including existence and recreational use are a much larger category than the provisioning services estimated for these two species.

4.4.5 Aquatic Nutrient Enrichment

Estuaries in the eastern United States are important for fish and shellfish production. The estuaries are capable of supporting large stocks of resident commercial species, and they serve as the breeding grounds and interim habitat for several migratory species (U.S. EPA, 2009). To provide an indication of the magnitude of provisioning services associated with coastal fisheries, from 2005 to 2007, the average value of total catch was \$1.5 billion per year in 15 East Coast states. It is not known, however, what percentage of this value is directly attributable to or dependent upon the estuaries in these states. Based on commercial landings in Maryland and Virginia, the values for three key species—blue crab, striped bass, and menhaden- totaled nearly \$69 million in 2007 in the Chesapeake Bay alone.

Assessing how eutrophication in estuaries affects fishery resources requires bioeconomic models (i.e., models that combine biological models of fish population dynamics with economic models describing fish harvesting and consumption decisions), but relatively few exist (Knowler, 2002). Kahn and Kemp (1985) estimated that a 50% decline in submerged aquatic vegetation (SAV) from levels existing in the late 1970s (similar to current levels [Chesapeake Bay Program, 2008]) would decrease the net social benefits from striped bass by \$16 million (in 2007 dollars). In a separate analysis, Anderson (1989) modeled blue crab harvests under baseline conditions and under conditions with “full restoration” of SAV. In equilibrium, the increase in annual producer surplus and consumer surplus with full restoration of SAV was estimated to be \$7.9 million (in 2007 dollars) or an 11% increase from current service provision from blue crab alone. Mistiaen et al. (2003) found that reductions in dissolved oxygen (DO) cause a statistically significant reduction in commercial harvest and revenues crab harvests. For the Patuxent River alone, a simulated reduction of DO from 5.6 to 4.0 mg/L was estimated to reduce crab harvests by 49% and reduce total annual earnings in the fishery by \$275,000 (in 2007 dollars). While these values do not quantify the increase in terms of atmospheric loadings alone, the estimated 20% loading to the Potomac River watershed (REA 5.2.4) from atmospheric deposition indicates that the benefits apportioned to deposition are significant.

In addition, eutrophication in estuaries may also affect the demand for seafood. For example, a well-publicized toxic *pfisteria* bloom in the Maryland Eastern Shore in 1997 led to an estimated \$56 million (in 2007 dollars) in lost seafood sales for 360 seafood firms in Maryland in the months following the outbreak (Lipton, 1999). Surveys by Whitehead, Haab, and Parsons (2003) and Parsons et al. (2006) indicated a reduction in consumer surplus due to eutrophication-related fish kills ranging from \$2 to \$5 per seafood meal.⁸ As a result, they estimated aggregate consumer surplus losses of \$43 million to \$84 million (in 2007 dollars) in the month after a fish kill.

As mentioned in the REA (5.2.1.3), estuaries in the eastern United States also provide an important and substantial variety of cultural ecosystem services, including water-based recreational and aesthetic services. For example, FHWAR data indicate that 4.8% of the population in coastal states from North Carolina to Massachusetts participated in saltwater fishing, with a total of 26 million saltwater fishing days in 2006 (U.S. DOI, 2007). Based on estimates in Section 5.2.1.3 of the REA, total recreational consumer surplus value from these saltwater fishing days was approximately \$1.3 billion (in 2007 dollars). Recreational participation estimates for several other coastal recreational activities are also available for 1999–2000 from the NSRE. Almost 6 million individuals participated in motorboating in coastal states from North Carolina to Massachusetts. Again, based on analysis in the REA, the aggregate value of these coastal motorboating outings was \$2 billion per year. Almost 7 million people participated in birdwatching, for a total of almost 175 million days per year, and more than 3 million participated in visits to nonbeach coastal waterside areas, for a total of more than 35 million days per year (Table 4-9).

Estuaries and marshes have the potential to support a wide range of regulating services, including climate, biological, and water regulation; pollution detoxification; erosion prevention; and protection against natural hazards (MEA, 2005c). The relative lack of empirical models and valuation studies imposes obstacles to the estimation of ecosystem services affected by nitrogen deposition. While atmospheric deposition contributes to eutrophication there is uncertainty in separating the effects of atmospheric nitrogen from nitrogen reaching the estuaries from many other sources.

⁸ Surprisingly, these estimates were not sensitive to whether the fish kill was described as major or minor or to the different types of information included in the survey.

Table 4-9. Summary of Values for Current Levels of Services and Changes in Service Levels in \$2007.

Ecosystem Service	Area or Population Affected	Value (\$2007)	Species
Total Catch – Commercial Fishing	14 east coast states	\$1.5 b/yr	
	MD/VA	\$69 m/yr	blue crab, striped bass, menhaden
Change in Ecosystem Service		Value of Change (\$2007)	
50% decline in SAV	Chesapeake Bay	↓ \$16 m/yr	striped bass
Full restoration SAV	Chesapeake Bay	↑ \$ 8 m/yr	blue crab
0.4% mg/L decrease DO	Patuxent River	↓ \$275 th/yr	↓ 49% blue crab harvest
HAB	1997 MD eastern shore	↓ \$56 m	loss to seafood industry
		↓ \$43-84 m	sustained loss over months
Ecosystem Service		Participation Days	Value (\$2007)
Saltwater fishing	4.6% pop. MA-NC	26m days	\$1.3 b/yr
Motorboating	6 million		2 b/yr
Bird watching	7 million	175 m days	
Non-beach coastal visits	3 million	35 m days	

Note: Down arrows indicate a decrease in value of the magnitude specified; up arrows indicate an increase in value of the magnitude specified.

4.4.6 Value of Current Ecosystem Service Impairments Due To Aquatic Nutrient Enrichment

The aquatic nutrient enrichment case study relied on the NOAA Eutrophication Index as the indicator, which includes dissolved oxygen, HABs, loss of SAV and loss of water clarity. There are methods available to link some of the components to ecosystem services, most notably loss of SAV and reductions in DO. The REA analysis estimates the change in several ecosystem services including recreational fishing, boating, beach use, aesthetic services and nonuse services. The REA focuses on two major East Coast estuaries – the Chesapeake Bay and the Neuse River. Both estuaries receive between 20%-30% percent of their annual nitrogen loadings through atmospheric deposition and both are showing symptoms of eutrophication. The analysis uses and adapts results from several existing studies to approximate effects on several ecosystem services, including commercial fishing, recreation, aesthetic enjoyment, and nonuse values. For example, it is estimated that atmospheric nitrogen decreases the annual benefits of recreational fishing, boating, and beach use in the Chesapeake Bay by \$43-\$217 million, \$3-8 million, and \$124 million respectively, and reduces annual aesthetic benefits to nearshore residents by \$39-102 million (Table 4-10). In the Neuse River, the value of annual commercial crab fishing services would be between \$0.1-1 million higher without the contribution of atmospheric nitrogen, and recreation fishing services in the larger Albermarle Pamlico Sound estuary system (which includes the Neuse) would be \$1-8 million greater per year.

Table 4-10. Summary of Annual Damages to Services due to Atmospheric Loading.

Ecosystem Service	Annual Value (\$2007)	Waterbody Affected
Recreational Saltwater Fishing	\$43-217 b	Chesapeake Bay
	\$1-8 m	Albemarle Pamlico Sound
Beach Use	\$39-102 m	Chesapeake Bay
Boating	\$3-8 m	Chesapeake Bay
Commercial Crab Fishing	\$0.1-1 m	Neuse River

4.4.7 Terrestrial Nutrient Enrichment

For the purposes of the following section nutrient enrichment refers only to that due to NO_x deposition. Additionally these sections focus on the detrimental effects of that deposition. Staff acknowledges that NO_x deposition in managed terrestrial ecosystems has a beneficial effect, specifically increased growth (a fertilization effect). These effects are discussed in detail in Chapter 3 of this document.

The ecosystem service impacts of terrestrial nutrient enrichment in unmanaged ecosystems include primarily cultural and regulating services. In CSS areas, concerns focus on a decline in CSS and an increase in nonnative grasses and other species, impacts on the viability of threatened and endangered species associated with CSS, and an increase in fire frequency. Changes in MCF include changes in habitat suitability and increased tree mortality, increased fire intensity, and a change in the forest's nutrient cycling that may affect surface water quality through nitrate leaching (EPA, 2008).

The terrestrial nutrient enrichment case study relies on benchmark deposition levels for various species and ecosystems as indicators of ecosystem response. While it would be expected that deposition above those levels would have deleterious effects on the provision of ecosystem services in those areas, at this time it is possible only to describe the magnitude of the some of the services currently being provided. Methods are not yet available to allow estimation of changes in services due to nitrogen deposition. For the purposes of the following sections nutrient enrichment refers only to that due to NO_x deposition. Additionally these sections focus on the detrimental effects of that deposition. Staff acknowledges that a certain amount of NO_x deposition in managed terrestrial ecosystems has a beneficial effect, specifically increased growth (a fertilization effect). However no attempt has been made to quantify those beneficial effects since this document and preceding analyses are focused on unmanaged sensitive ecosystems.

The value that California residents and the U.S. population as a whole place on CSS and MCF habitats is reflected in the various federal, state, and local government measures that have been put in place to protect these habitats. Threatened and endangered species are protected by the Endangered Species Act. The State of California passed the Natural Communities Conservation Planning Program (NCCP) in 1991, and CSS was the first habitat identified for protection under the program (see www.dfg.ca.gov/habcon/nccp). It is estimated that only 10 –

15% of the original extent of CSS habitat remains (NPS.gov/cabr/naturescience/coastal-sage-scrub-and-southern-chaparral-communities.htm). Private organizations such as The Nature Conservancy, the Audubon Society, and local land trusts also protect and restore CSS and MCF habitat.

CSS and MCF are found in numerous recreation areas in California. Three national parks and monuments in California contain CSS, including Cabrillo National Monument, Channel Islands National Park, and Santa Monica National Recreation Area. All three parks showcase CSS habitat with educational programs and information provided to visitors, guided hikes, and research projects focused on understanding and preserving CSS. Over a million visitors traveled through these three parks in 2008. MCF is highlighted in Sequoia and Kings Canyon National Park, Yosemite National Park, and Lassen Volcanic National Park, where more than 5 million people visited in 2008.

The 2006 FHWAR for California (DOI, 2007) reports on the number of individuals involved in fishing, hunting, and wildlife viewing in California. Millions of people are involved in just these three activities each year. The quality of these trips depends in part on the health of the ecosystems and their ability to support the diversity of plants and animals found in important habitats found in CSS or MCF ecosystems and the parks associated with those ecosystems. Based on analyses in Section 5.3.1.3 of the REA (U.S.EPA, 2009), average values of the total benefits in 2006 from fishing, hunting, and wildlife viewing away from home in California were approximately \$947 million, \$169 million, and \$3.59 billion, respectively (Table 4-11). In addition, data from California State Parks (2003) indicate that in 2002, 68.7% of adult residents participated in trail hiking for an average of 24.1 days per year. The analyses in the REA (U.S.EPA, 2009) indicate that the aggregate annual benefit for California residents from trail hiking in 2007 was \$11.59 billion. It is not currently possible to quantify the loss in value of services due to nitrogen deposition as those losses are already reflected in the estimates of the contemporaneous total value of these recreational activities. Restoration of services through decreases in nitrogen deposition would likely increase the total value of recreational services.

Table 4-11. Summary of Current Levels of Ecosystem Services.

Activity	Participation	# of days/yr	Average WTP	Annual Aggregate Value (\$2007 in millions)
Trail Hiking	68.7% of CA population	453 m	\$25.59	115,900
Fishing	1.7 m	19 m	\$48.86	947
Wildlife Viewing	6.2 m	45 m	\$79.81	3,600
Hunting	0.28 m	3.3 m	\$50.10	169

Sources: 2006 FHWAR for California (DOI, 2007), California State Parks (2003), Kaval and Loomis (2003)

CSS and MCF are home to a number of important and rare species and habitat types. CSS displays richness in biodiversity with more than 550 herbaceous annual and perennial species. Of these herbs, nearly half are endangered, sensitive, or of special status (Burger et al., 2003). Additionally, avian, arthropod, herpetofauna, and mammalian species live in CSS habitat or use the habitat for breeding or foraging. Communities of CSS are home to three important federally endangered species: the Quino checkerspot butterfly, the kangaroo rat and the California gnatcatcher. MCF is home to one federally endangered species (mountain yellow-legged frog) and a number of state-level sensitive species. The Audubon Society lists 28 important bird areas in CSS habitat and at least 5 in MCF in California (<http://ca.audubon.org/iba/index.shtml>).⁹

The terrestrial enrichment case study in Section 5.3.1.3 of the REA and Section 3.3.5 of the ISA identified fire regulation as a service that could be affected by nutrient enrichment of the CSS and MCF ecosystems by encouraging growth of more flammable grasses, increasing fuel loads, and altering the fire cycle. Over the 5-year period from 2004 to 2008, Southern California experienced, on average, over 4,000 fires per year burning, on average, over 400,000 acres per year (National Association of State Foresters [NASF], 2009). It is not possible at this time to quantify the contribution of nitrogen deposition, among many other factors, to increased fire risk.

The CSS and MCF were selected as case studies for terrestrial enrichment because of the potential that these areas could be adversely affected by excessive N deposition. To date, the

⁹ Important Bird Areas are sites that provide essential habitat for one or more species of bird.

detailed studies needed to identify the magnitude of the adverse impacts due to N deposition have not been completed. Based on available data, this report provides a qualitative discussion of the services offered by CSS and MCF and a sense of the scale of benefits associated with these services. California is famous for its recreational opportunities and beautiful landscapes. CSS and MCF are an integral part of the California landscape, and together the ranges of these habitats include the densely populated and valuable coastline and the mountain areas. Through recreation and scenic value, these habitats affect the lives of millions of California residents and tourists. Numerous threatened and endangered species at both the state and federal levels reside in CSS and MCF. Both habitats may play an important role in wildfire frequency and intensity, an extremely important problem for California. The potentially high value of the ecosystem services provided by CSS and MCF justify careful attention to the long-term viability of these habitats.

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5 CO-PROTECTION FOR OTHER EFFECTS POTENTIALLY AFFORDED BY AN AQUATIC ACIDIFICATION STANDARD

This chapter focuses on the co-protection that a standard focused on aquatic acidification might afford for other deposition related ecological effects, including terrestrial acidification, terrestrial nutrient enrichment, and estuarine eutrophication.

5.1 POTENTIAL CO-PROTECTION FOR TERRESTRIAL ACIDIFICATION

To understand the level of co-protection an aquatic acidification standard for oxides of nitrogen and sulfur might afford for terrestrial ecosystems, an analysis was conducted to compare the critical acid loads for aquatic and terrestrial components of watersheds in the eastern United States. Aquatic critical acid loads are an integrated function of the chemistry of runoff from stream and lake waters, and the biogeochemical processes that occur within the aquatic and terrestrial components of the entire watershed. Terrestrial critical acid loads, however, are largely determined by the conditions and processes that occur in the root zone of the soil profile of the terrestrial systems of a watershed. Therefore, it is possible to have different critical acid load values for aquatic and terrestrial ecosystems within the same watershed.

For the comparative analysis of aquatic and terrestrial critical acid loads, aquatic critical acid loads were selected based on an acid neutralizing capacity (ANC) of 50 μ eq/L, and were taken directly from the Risk and Exposure Assessment (REA). The 50 μ eq/L ANC value was one of three example values modeled in the REA for aquatic acidification. The terrestrial critical acid loads in this comparative analysis were selected to protect for either a terrestrial base cation to aluminum molar ratio (Bc:Al) of 1.2 or 10.0. The Bc:Al ratio of 10.0 would be relatively more protective, as it provides greater protection against the impacts of acidification on cation availability and aluminum toxicity in the soil solution. The terrestrial critical loads were calculated using the Simple Mass Balance (SMB) method outlined in the REA and input values averaged across the area of each watershed.

Aquatic and terrestrial critical acid loads were compared in 16 watersheds from each of the two aquatic acidification case study areas, the Adirondacks and the Shenandoah, identified in the REA. For each case study area, four watersheds were randomly selected from each of the

four aquatic acidification sensitivity classes reported in the REA. Those four sensitivity classes are “highly sensitive”, “moderately sensitive”, “low sensitivity”, and “not sensitive”. In order for a watershed to be classified as one of these four classes, it had to contain at least one lake or stream with that sensitivity class designation. The Adirondacks case study area contained watersheds representing all four sensitivity classes, and the 16 watersheds that were selected for the analysis contained a total of 29 lakes. However, in the Shenandoah case study area, there were a limited number of watersheds in the “low” and “not sensitive” classes. Therefore, only one of the 16 randomly selected watersheds contained a “low” and a “not sensitive” stream. In total, there were 20 streams located in the 16 Shenandoah watersheds selected for the comparative analysis. In each of the 32 watersheds (16 Adirondacks plus 16 Shenandoah), the terrestrial critical acid loads were calculated as a single value for the entire watershed. These terrestrial critical acid loads were then compared to the aquatic critical acid loads for the lakes and streams within each watershed to determine whether the aquatic or terrestrial critical acid load provided greater protection against acidifying nitrogen and sulfur deposition. Appendix A provides a full description of the methods and results of this comparative analysis.

Results of the comparison between the example aquatic critical acid load ($ANC = 50 \mu\text{eq/L}$) and the terrestrial critical acid loads (Bc:Al 1.2 and 10.0) for the 32 watersheds are presented in Tables 5.1 and 5.2. In the 16 Adirondack watersheds, 13 of the 29 lakes had aquatic critical acid loads that were lower (more protective) than the terrestrial critical acid loads when a Bc:Al ratio of 10.0 was used. Based on terrestrial critical acid loads determined with a Bc:Al ratio of 1.2, 21 of the 29 lakes in the Adirondacks had aquatic critical acid loads lower than the terrestrial critical acid loads. More importantly, for the terrestrial critical acid loads determined with a Bc:Al ratio of 10.0, 13 of the 16 lakes in the Adirondacks classified as “highly” and “moderately” sensitive to acidification had aquatic critical acid loads lower than the terrestrial critical acid loads, and all 16 lakes in these two sensitivity classes had critical acid loads lower than the terrestrial loads determined with a Bc:Al of 1.2. The watersheds within the Shenandoah region showed similar results (Tables 5.1 and 5.2).

Table 5-1. Results of the comparison of lake and stream aquatic critical loads (ANC of 50 µeq/L) to terrestrial critical loads.

(Bc:Al molar ratios of 10.0 in soil solution) calculated for the full watershed in each of the 16 watersheds in the Adirondacks and Shenandoah case study areas. The tabular results show the number of times the aquatic acidification critical load would provide more protection than the terrestrial acidification critical load.

Case Study Area	Watershed Sensitivity to Aquatic Acidification			
	Highly Sensitive	Moderately Sensitive	Low Sensitivity	Not Sensitive
Adirondacks	7 of 7	6 of 9	0 of 7	0 of 6
Shenandoah	14 of 14	5 of 5	0 of 1	0 of 1

Table 5-2. Results of the comparison of lake and stream aquatic critical loads (ANC of 50 µeq/L) to terrestrial critical loads.

(Bc:Al molar ratios of 1.2 in soil solution) calculated for the full watershed in each of the 16 watersheds in the Adirondacks and Shenandoah Case Study Areas. The tabular results show the number of times the aquatic acidification critical load would provide more protection than the terrestrial acidification critical load.

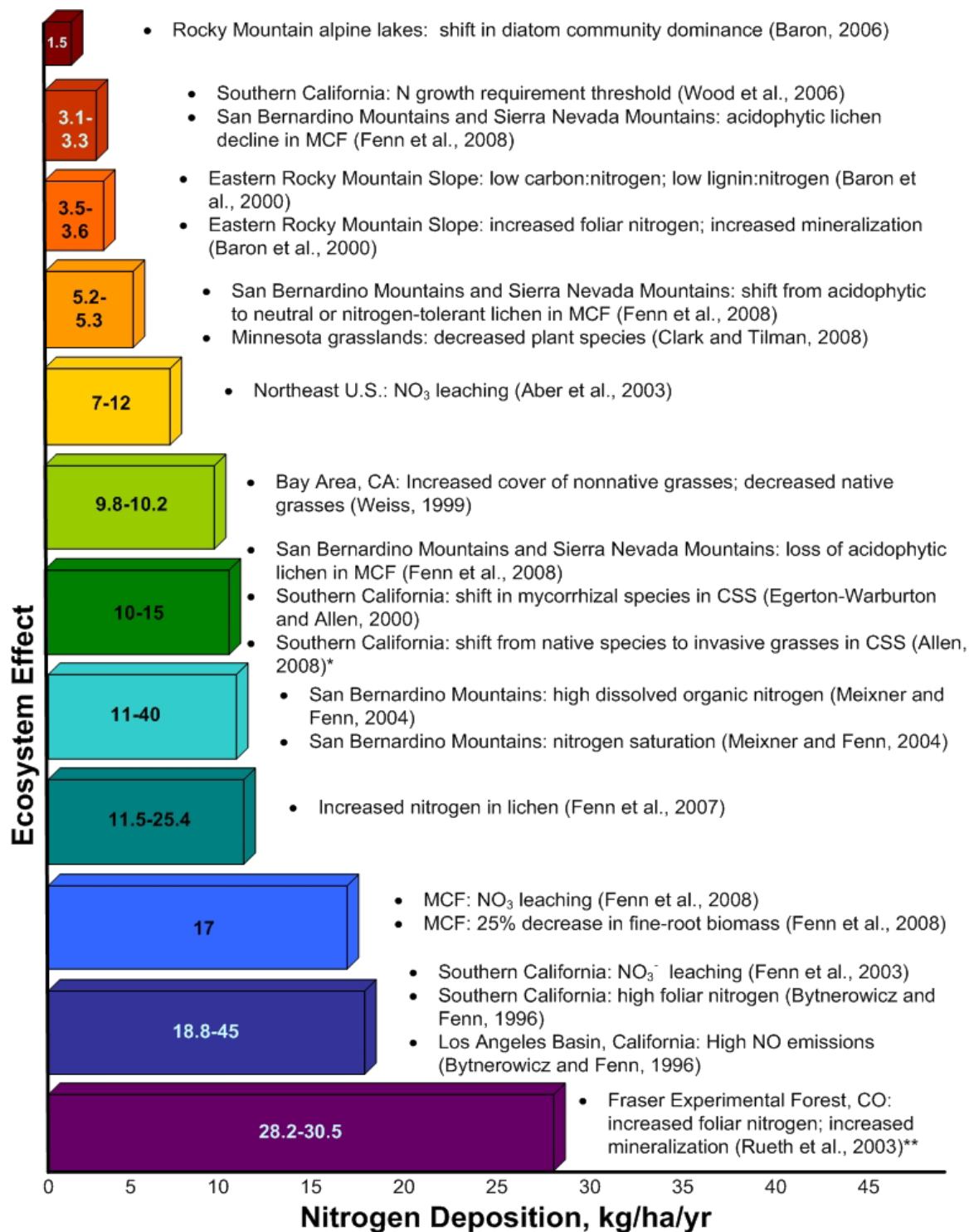
Case Study Area	Watershed Sensitivity to Aquatic Acidification			
	Highly Sensitive	Moderately Sensitive	Low Sensitivity	Not Sensitive
Adirondacks	7 of 7	9 of 9	5 of 7	0 of 6
Shenandoah	14 of 14	5 of 5	0 of 1	0 of 1

In summary, terrestrial and aquatic critical acid loads were compared for watersheds in the Adirondack and Shenandoah case study areas. Results indicated that, in general, the aquatic critical acid loads were lower and therefore offered greater protection to the watershed than did the terrestrial critical acid loads. In situations where the terrestrial critical acid loads were lower (i.e., more protective) than the aquatic critical acid loads, the lakes or streams in the watershed were often rated as having “low sensitivity” or “not sensitive” to acidifying nitrogen and sulfur deposition. Conversely, when the waterbodies were more sensitive to deposition (“highly sensitive” or “moderately sensitive”), the aquatic critical acid loads generally provided a greater level of protection against acidifying nitrogen and sulfur deposition in the watershed. It is uncertain whether these results would be consistent for the rest of the country.

5.2 POTENTIAL CO-PROTECTION FOR TERRESTRIAL NUTRIENT ENRICHMENT

Whereas critical loads have been modeled for aquatic acidification protection, for terrestrial nutrient enrichment protection, there are only empirical benchmarks developed from field studies of specific ecosystems or species. To understand the level of co-protection an aquatic acidification standard for oxides of nitrogen and sulfur might afford for nutrient over-enrichment effects to terrestrial ecosystems, a critical load developed for a lake in an ecoregion can be compared to nitrogen deposition benchmarks found in the scientific literature. Figure 5.1 below summarizes the terrestrial nutrient enrichment effects summarized in the REA.

For each depositional load that is considered for aquatic acidification, it can be compared against the chart in Figure 5.1 to understand the level of protection offered in individual parts of the country where these studies were conducted. For example, if a maximum nitrogen depositional load was selected for California of 80 meq/(m²-yr) or ~11 kg N/(ha-yr), this could be compared directly to the benchmarks in Figure 5.1 that describe California ecosystems (meq/(m²-yr) divided by 7.14 equals kg/(ha-yr)). Comparing this maximum nitrogen deposition number to the benchmarks in Figure 5.1, shows that the depositional load would provide some protection against leaching in the San Bernardino Mountains (11-40 kg/(ha-yr)), but would have to be lower to protect California coastal sage scrub in Southern California (3.1-3.3 kg/(ha-yr)), and lichens in mixed conifer forests (3.1-5.3 kg/(ha-yr)).



* Personal communication, 2008. Also referenced in Bobbink et al., 2010, Ecological Applications, 20(1):30-59 and USDS FS, 2010, http://www.nrs.fs.fed.us/clean_air_water/clean_water/critical_loads/local-resources/docs/Empirical_CLS_of_N_100414.pdf

**Nitrogen deposition levels include ambient and experimental additions.

Figure 5.1 Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators (REA 2009).

5.3 POTENTIAL CO-PROTECTION FOR AQUATIC NUTRIENT ENRICHMENT

The REA found that deposition of reactive nitrogen contributed to eutrophication of estuaries; however, it was also noted that atmospheric deposition of nitrogen is only part of the total nitrogen load to the estuaries. This makes it difficult to understand the co-protection that an aquatic acidification standard for oxides of nitrogen and sulfur might afford. One way to approach this issue is to assume any reduction in atmospheric nitrogen load to an enriched estuary will be a benefit. A second approach would be to see how far the reduction in nitrogen likely to result from an aquatic acidification standard would go towards meeting the total nitrogen load reduction goals set by the estuary programs.

As described in the REA, the Chesapeake Bay is one national estuary that is suffering from eutrophication. In issuing his Executive Order on the Chesapeake Bay (EO 13508), President Obama recognized that the Bay watershed is one of our nation's greatest treasures and must be protected and restored. To that end, EPA is proposing a nitrogen total maximum daily load (TMDL) for the Chesapeake Bay. The TMDL will contain a specific air allocation for nitrogen deposition. The allocations that were provided to the states included assumptions that air deposition levels of nitrogen would be reduced to 14.9 million pounds per year to the tidal waters and to 323 million pounds to the watershed by the year 2020. According to the Chesapeake Bay Program Office, the tidal waters have a surface area of 4,479 square miles and the watershed is 64,216 square miles. This means that in 2020, the TMDL currently calls for nitrogen deposition levels to the combined bay and watershed to be reduced to 337.9 million pounds/68,695 square miles/yr, which is equivalent to 8.6 kg/ha/yr or 61 meq/m²/yr. As in Section 5.2, if we use as an example a maximum nitrogen depositional load of 80 meq/m²/yr or ~11 kg N/ha/yr, this number would not meet the Chesapeake Bay TMDL as currently envisioned.

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6 ADDRESSING THE ADEQUACY OF THE CURRENT STANDARDS

Based on the information in Chapters 3 and 4, we conclude that there is support in the available effects-based evidence for consideration of secondary standards for oxides of nitrogen and sulfur that are protective against adverse ecological effects associated with deposition of oxides of nitrogen and sulfur to sensitive ecosystems. Having reached this general conclusion, we then to the extent possible evaluate the adequacy of the current standards for oxides of nitrogen and sulfur by considering to what degree risks to sensitive ecosystems would be expected to occur in areas that meet the current standards. Staff conclusions regarding the adequacy of the current standards are based on the available ecological effects, exposure and risk-based evidence. In evaluating the strength of this information, staff have taken into account the uncertainties and limitations in the scientific evidence. This chapter addresses key policy relevant questions that inform our determination regarding the adequacy of the structure and levels of the current secondary standards. The chapter begins with a discussion of the structure of the current standards, followed by a presentation of information on recent air quality relative to the existing standards, recent deposition levels of oxides of nitrogen and sulfur, evaluation of recent deposition levels relative to levels where adverse ecological effects have been observed, and a set of conclusions regarding the adequacy of the current structure and levels of the standards. Acidification occurs over extended periods and the ability of both terrestrial and aquatic systems to recover is dependent upon not only the decrease in acidic deposition, but the ability of these ecosystems to generate cations needed for nutrients and base cation supply. As a result, given the same decrease in deposition, ecosystems with high levels of base cation replacement will recover faster than those with low levels.

6.1 APPROPRIATENESS OF THE CURRENT STANDARD

The current secondary oxides of nitrogen and sulfur standards are intended to protect against adverse effects to public welfare. For oxides of nitrogen, the current secondary standard was set identical to the primary standard¹, e.g. an annual standard set for NO₂ to protect against adverse effects on vegetation from direct exposure to ambient oxides of nitrogen. For oxides of

¹ The current primary NO₂ standard has recently been changed to the 3 year average of the 98th percentile of the annual distribution of the 1 hour daily maximum of the concentration of NO₂. The current secondary standard remains as it was set in 1971.

sulfur, the current secondary standard is a 3-hour standard intended to provide protection for plants from the direct foliar damage associated with atmospheric concentrations of SO₂. It is appropriate in this review to consider whether the current standards are adequate to protect against the direct effects on vegetation resulting from ambient NO₂ and SO₂ which were the basis for the current secondary standards. The ISA concluded that there was sufficient evidence to infer a causal relationship between exposure to SO₂, NO, NO₂ and PAN and injury to vegetation. Additional research on acute foliar injury has been limited and there is no evidence to suggest foliar injury below the levels of the current secondary standards for oxides of nitrogen and sulfur. There is sufficient evidence to suggest that the levels of the current standards are likely adequate to protect against direct phytotoxic effects.

The ISA however, has established that the major effects of concern for this review of the oxides of nitrogen and sulfur standards are associated with deposition of N and S caused by atmospheric concentrations of oxides of nitrogen and sulfur (see Chapter 3). As discussed in the following sections, the current standards are not directed toward depositional effects, and none of the elements of the current NAAQS – indicator, form, averaging time, and level – are suited for addressing the effects of N and S deposition. Thus, by using atmospheric NO₂ and SO₂ concentrations as indicators, the current standards address only a fraction of total atmospheric oxides of nitrogen and sulfur, and do not take into account the effects from deposition of total atmospheric oxides of nitrogen and sulfur. By addressing short-term concentrations, the current SO₂ standard, while protective against direct foliar effects from gaseous oxides of sulfur, does not take into account the findings of effects in the ISA, which notes the relationship between annual deposition of S and acidification effects which are likely to be more severe and widespread than phytotoxic effects under current ambient conditions, and include effects from long term deposition as well as short term. Acidification is a process which occurs over time, as the ability of an aquatic system to counteract acidic inputs is reduced as natural buffers are used more rapidly than they can be replaced through geologic weathering. The relevant period of exposure for ecosystems is therefore not the exposures captured in the short averaging time of the current SO₂ standard.

The levels of the current standards also are not well suited to dealing with deposition-based effects of oxides of nitrogen and sulfur. Current standards are specified as allowable single atmospheric concentration levels for NO₂ or SO₂. This type of structure does not take into

account variability in the atmospheric and ecological factors that may alter the effects of oxides of nitrogen and sulfur on public welfare. Consistent with section 108 of the CAA, the ISA includes in the air quality criteria consideration of how these variable factors impact the effects of ambient oxides of nitrogen and sulfur on public welfare. See CAA section 108 (a)(2)(A) requiring air quality criteria to include information on “those variable factors (including atmospheric conditions) which of themselves or in combination with other factors may alter the effects on public health or welfare of such air pollutant.” Secondary standards are intended to address a wide variety of effects occurring in different types of environments and ecosystems. Ecosystems are not uniformly distributed either spatially or temporally in their sensitivity to air pollution. Therefore, failure to account for the major determinants of variability, including geological and soil characteristics related to the sensitivity to acidification as well as atmospheric and landscape characteristics that govern rates of deposition, may lead to standards that do not provide requisite levels of protection across ecosystems. Finally, given the mismatch of all of the other elements of the current secondary NAAQS with deposition-based effects, the form of those standards will also be mismatched.

Because all areas of the U.S. are in attainment with the current NO₂ and SO₂ standards, it is possible to evaluate current conditions, and evaluate the impact on public welfare from the current effects on ecosystems from oxides of nitrogen and sulfur deposition in areas that attain the current standards that use NO₂ and SO₂ as indicators. In addition, this chapter qualitatively addresses the adequacy of the structures of the existing standards relative to ecologically relevant standards for oxides of nitrogen and sulfur, and sets up arguments for developing an ecologically relevant structure for the standards as described in chapter 7.

6.2 STRUCTURES OF THE CURRENT OXIDES OF NITROGEN AND SULFUR SECONDARY STANDARDS AND RELEVANT ECOLOGICAL INDICATORS OF PUBLIC WELFARE EFFECTS

The current secondary standard for NO_x, set in 1971, using NO₂ as the atmospheric indicator, is 0.053 parts per million (ppm) (100 micrograms per cubic meter of air [$\mu\text{g}/\text{m}^3$]), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO₂ concentrations. This standard was selected to provide protection to the public welfare against acute injury to vegetation from direct exposure and resulting phytotoxicity. During the last review of the oxides of nitrogen standards, impacts associated with chronic acidification and eutrophication from

oxides of nitrogen deposition were acknowledged, but the relationships between atmospheric concentrations of oxides of nitrogen and levels of acidification and eutrophication and associated welfare impacts were determined to be too uncertain to be useful as a basis for setting a national secondary standard (U.S. EPA ,1995).

The current secondary standard for oxides of sulfur, set in 1971, uses SO₂ as the atmospheric indicator, is a 3-hour average of 0.5 ppm, not to be exceeded more than once per year. This standard was selected to provide protection to the public welfare against acute injury to vegetation. In the last review of the oxides of sulfur secondary standard, impacts associated with chronic acidification were acknowledged, but the relationships between atmospheric concentrations of oxides of sulfur and levels of acidification, along with the complex interactions between oxides of nitrogen and sulfur in acidification processes, were cited as critical uncertainties which made the setting of secondary NAAQS to protect against acidification inappropriate at that time (U.S. EPA, 1982).

In the previous separate reviews of the oxides of nitrogen and sulfur secondary standards, EPA acknowledged in each review the additional impacts of oxides of nitrogen and sulfur on public welfare through the longer term impact of the pollutants once deposited to ecosystems. However, the previous reviews cited numerous uncertainties as the basis for not directly addressing those impacts in the setting of secondary standards. In addition, these previous reviews did not consider the common pathways of impact for both nitrogen and sulfur acting on the same ecosystem endpoints.

Three issues arise that call into question the ecological relevance of the current structure of the secondary standards for oxides of nitrogen and sulfur. One issue is the exposure period that is relevant for ecosystem impacts. The majority of deposition related impacts are associated with depositional loads that occur over periods of months to years. This differs significantly from exposures associated with hourly concentrations of NO₂ and SO₂ as measured by the current standards. Even though the NO₂ standard uses an annual average of NO₂, it is focused on the annual average of 1-hour NO₂ concentrations, rather than on a cumulative metric or an averaging metric based on daily or monthly averages. A second issue is the choice of atmospheric indicators. NO₂ and SO₂ are used as the component of oxides of nitrogen and sulfur that are measured, but they do not provide a complete link to the direct effects on ecosystems from deposition of oxides of nitrogen and sulfur as they do not capture all relevant chemical

species of oxidized nitrogen and oxidized sulfur that contribute to deposition. The ISA provides evidence that deposition related effects are linked with total nitrogen and total sulfur deposition, and thus all forms of oxidized nitrogen and oxidized sulfur that are deposited will contribute to effects on ecosystems. This suggests that more comprehensive atmospheric indicators should be considered in designing ecologically relevant standards. Further discussions of the need for more ecologically relevant atmospheric indicators as well as the relative contributions to deposition from various species of oxides of nitrogen and sulfur can be found in Chapter 2. The third issue is that the current standards reflect separate assessments of the two individual pollutants, NO₂ and SO₂, rather than assessing the joint impacts of deposition to ecosystems, recognizing the role that each pollutant plays in jointly affecting ecosystem indicators, functions, and services. The clearest example of this interaction is in assessment of the impacts of acidifying deposition on aquatic ecosystems.

Acidification in an aquatic ecosystem depends on the total acidifying potential of the deposition of both N and S from both atmospheric deposition of oxides of nitrogen and sulfur as well as the inputs from other sources of N and S such as reduced nitrogen and non-atmospheric sources. It is the joint impact of the two pollutants that determines the ultimate effect on organisms within the ecosystem, and critical ecosystem functions such as habitat provision and biodiversity. Standards that are set independently are less able to account for the contribution of the other pollutant. This suggests that interactions between oxides of nitrogen and oxides of sulfur should be a critical element of the conceptual framework for ecologically relevant standards. There are also important interactions between oxides of nitrogen and sulfur and reduced forms of nitrogen, which also contribute to acidification and nutrient enrichment. Although the standards do not directly address reduced forms of nitrogen in the atmosphere, e.g. they do not require specific levels of reduced nitrogen, it is important that the structure of the standards address the role of reduced nitrogen in determining the ecological effects resulting from deposition of atmospheric oxides of nitrogen and sulfur. Consideration will also have to be given to account for loadings coming from non-atmospheric sources as ecosystems will respond to these sources as well.

In addition to the fundamental issues discussed above, the current structures of the standards do not address the complexities in the responses of ecosystems to deposition of oxides of nitrogen and sulfur. Ecosystems contain complex groupings of organisms that respond in

various ways to the alterations of soil and water that result from deposition of nitrogen and sulfur compounds. Different ecosystems therefore respond in different ways depending on a multitude of factors that control how deposition is integrated into the system. For example, the same levels of deposition falling on limestone dominated soils have a very different effect than those falling on shallow glaciated soils underlain with granite. One system may over time display no obvious detriment while the other may experience a catastrophic loss in fish communities. This degree of sensitivity is a function of many atmospheric factors which control rates of deposition as well as ecological factors which control how an ecosystem responds to that deposition. The current standards do not take into account spatial and seasonal variations not only in depositional loadings but also in sensitivity of ecosystems exposed to those loadings.

The 2005 ambient conditions indicate that the current SO₂ and NO₂ secondary standards are not exceeded (Figures 6-1 and 6-2) in locations where ecological effects have been observed, and where critical loads of nitrogen and sulfur are exceeded.

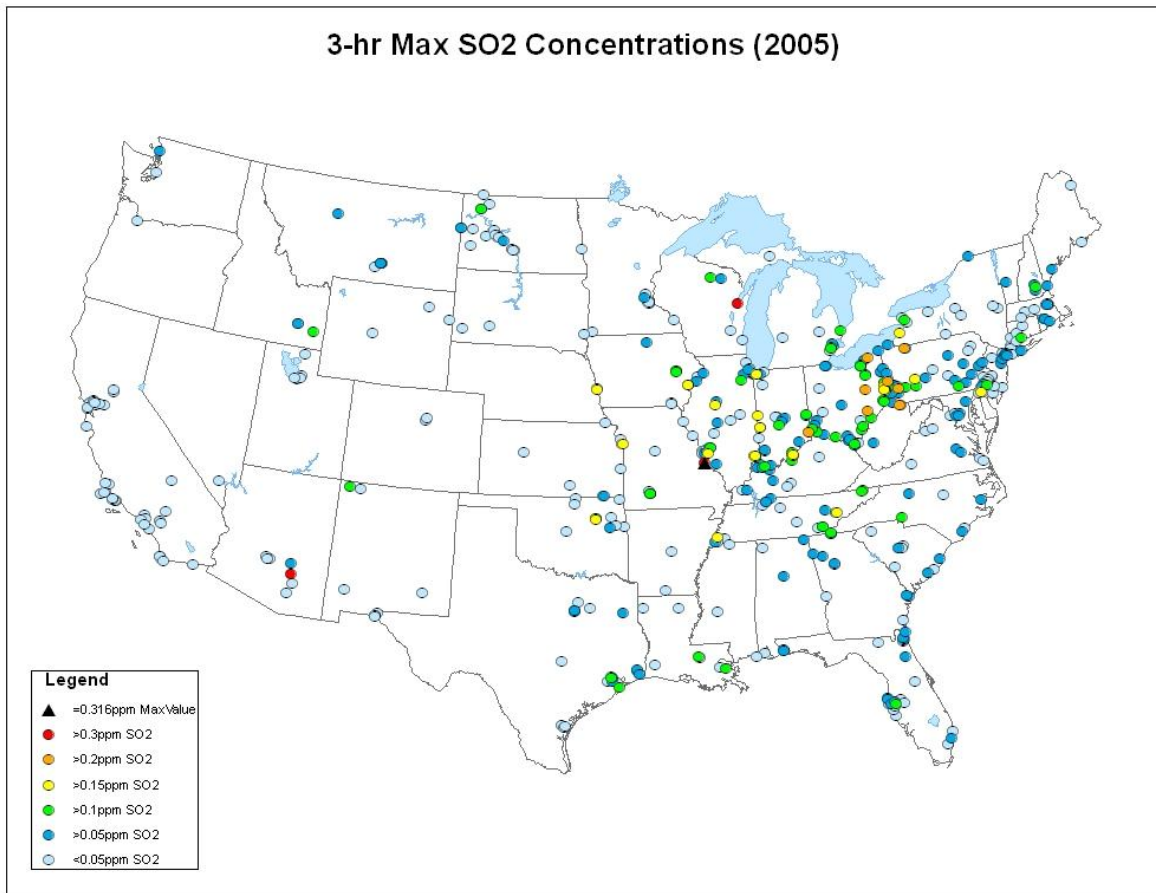


Figure 6-1. Three hour average maximum 2005 SO₂ concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base. The current SO₂ secondary standard based on the maximum 3 hour average value is 500 ppb, a value not exceeded. While there are obvious spatial gaps, the majority of these stations are located to capture maximum values generally in proximity to major sources and high populations. Lower relative values are expected in more remote acid sensitive areas. See Table 2-1 for unit conversions

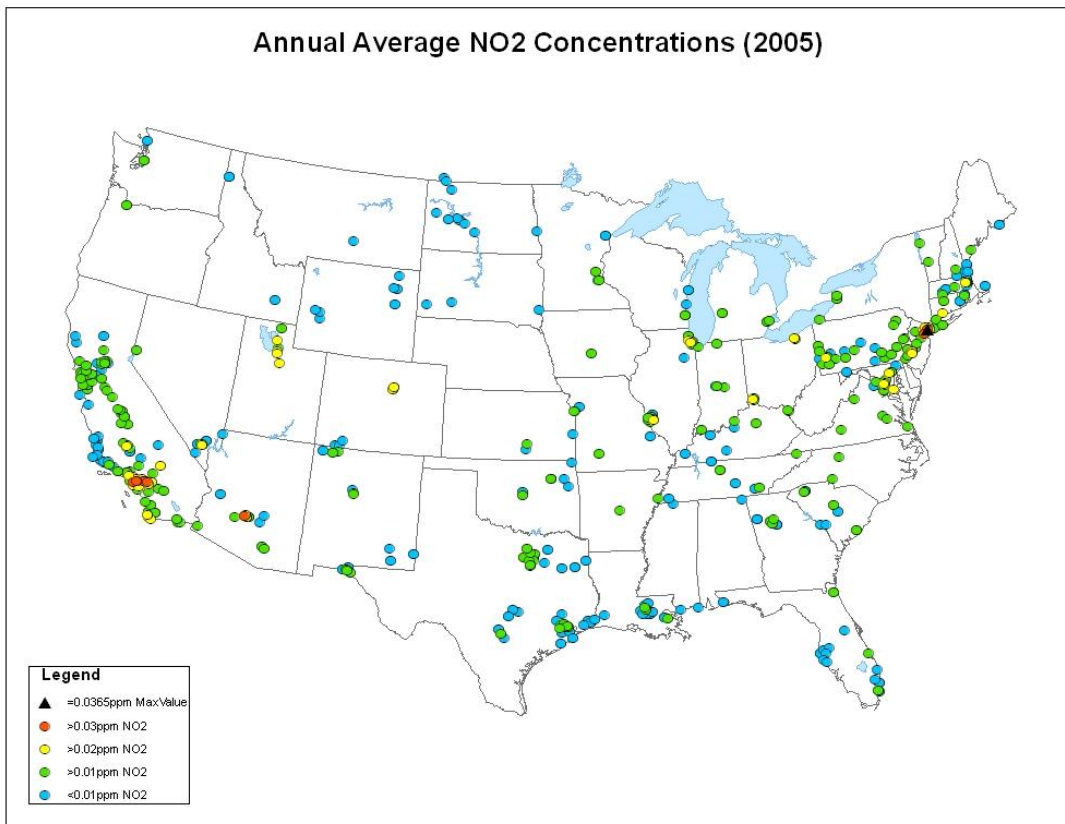


Figure 6-2 Annual average 2005 NO₂ concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base. The current NO₂ secondary standard is 53 ppb, a value well above those observed. While there are obvious spatial gaps, the stations are located in areas of relatively high concentrations in highly populated areas. Lower relative values are expected in more remote acid sensitive areas. See Table 2-1 for unit conversions

6.3 ADVERSE EFFECTS ON THE PUBLIC WELFARE OCCURRING UNDER CURRENT AIR QUALITY CONDITIONS FOR NO₂ AND SO₂

In the previous sections we have established that all areas of the U.S. were at concentrations of SO₂ and NO₂ below the levels of the current standards. In many locations, SO₂ and NO₂ concentrations are substantially below the levels of the standards. This pattern suggests that levels of deposition and any effects on ecosystems due to deposition of oxides of nitrogen and sulfur under recent conditions are occurring even though areas meet or are below current standards. In this section we focus on summarizing the evidence of effects occurring at deposition levels consistent with recent conditions.

The ISA summarizes the available studies of relative nitrogen contribution and finds that in much of the U.S., oxides of nitrogen contribute from 50 to 75 percent of total atmospheric deposition relative to total reactive nitrogen that includes oxidized and reduced nitrogen species (ISA Section 2.8.4). Although the proportion of total nitrogen loadings associated with atmospheric deposition of nitrogen varies across locations (N deposition in the eastern U.S. includes locations with greater than 9 kg N/ha-yr, and in the central U.S. high deposition locations with values on the order of 6 to 7 kg N/ha-yr), the ISA indicates that atmospheric N deposition is the main source of new anthropogenic N to most headwater streams, high elevation lakes, and low-order streams. Atmospheric N deposition contributes to the total N load in terrestrial, wetland, freshwater, and estuarine ecosystems that receive N through multiple pathways. In several large estuarine systems, including the Chesapeake Bay, atmospheric deposition accounts for between 10 and 40 percent of total nitrogen loadings (U.S. EPA, 2000).

Atmospheric concentrations of oxides of sulfur account for nearly all S deposition in the US. For the period 2004–2006, mean S deposition in the U.S. was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg S/ha-yr, in the Ohio River Valley where most recording stations reported 3 year averages >10 kg S/ha-yr. Numerous other stations in the East reported S deposition >5 kg S/ha-yr. Total S deposition in the U.S. west of the 100th meridian was relatively low, with all recording stations reporting <2 kg S/ha-yr and many reporting <1 kg S/ha-yr. S was primarily deposited in the form of wet SO₄²⁻ followed in decreasing order by a smaller proportion of dry SO₂ and a much smaller proportion of deposition as dry SO₄²⁻.

New scientific evidence exists to address each of the areas of uncertainty raised in the previous reviews. Based on the new evidence, the current ISA concludes that:

- (1) The evidence is sufficient to infer a causal relationship between acidifying deposition (to which both oxides of nitrogen and sulfur contribute) and effects on biogeochemistry related to terrestrial and aquatic ecosystems; and biota in terrestrial and aquatic ecosystems.
- (2) The evidence is sufficient to infer a causal relationship between N deposition, to which oxidized and reduced nitrogen contribute, and the alteration of A) biogeochemical cycling of N and carbon in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems; B) biogenic flux of methane (CH₄), and N₂O in terrestrial and wetland ecosystems; and C) species richness, species composition, and biodiversity in terrestrial, wetland, freshwater aquatic and coastal marine ecosystems.
- (3) The evidence is sufficient to infer a causal relationship between S deposition and increased Hg methylation in wetlands and aquatic environments.

Subsequent to the previous review of the secondary standard for oxides of nitrogen, a great deal of information on the contribution of atmospheric deposition associated with ambient oxides of nitrogen has become available. In Chapter 3 of the REA a thorough assessment is provided of the contribution of oxidized nitrogen to nitrogen deposition throughout the U.S., and the relative contributions of ambient oxidized and reduced forms of nitrogen. Staff concludes that based on that analysis, ambient oxides of nitrogen are a significant component of atmospheric nitrogen deposition, even in areas with relatively high rates of deposition of reduced nitrogen. In addition, staff concludes that atmospheric deposition of oxidized nitrogen contributes significantly to total nitrogen loadings in nitrogen sensitive ecosystems.

As discussed throughout the REA document, there are several key areas of risk that are associated with ambient concentrations of oxides of nitrogen and sulfur. As noted earlier, in previous reviews of the secondary standards for oxides of nitrogen and sulfur, the standards were designed to protect against direct exposure of plants to ambient concentrations of the pollutants. A significant shift in understanding of the effects of oxides of nitrogen and sulfur has occurred since the last reviews, reflecting the large amount of research that has been conducted on the effects of deposition of nitrogen and sulfur to ecosystems. The most significant risks of adverse

effects to public welfare are those related to deposition of oxides of nitrogen and sulfur to both terrestrial and aquatic ecosystems. These risks fall into two categories, acidification and nutrient enrichment, which were emphasized in the REA are most relevant to evaluating the adequacy of the existing standards in protecting public welfare from adverse ecological effects.

6.3.1 Acidification in sensitive aquatic and terrestrial ecosystems

The focus of the REA case studies was on determining whether deposition of sulfur and oxidized nitrogen in locations where ambient oxides of nitrogen and sulfur were at or below the current standards was resulting in acidification and related effects. This review has focused on identifying ecological indicators that can link atmospheric deposition to ecological effects associated with acidification. Oxides of nitrogen and sulfur contribute to acidification in both aquatic and terrestrial ecosystems, although the indicators of effects differ. Although there are some geographic areas with both terrestrial and aquatic ecosystems that are vulnerable to acidification, the case study areas do not fully overlap. The locations of the case studies evaluated in the REA are shown on Figure 6-3.

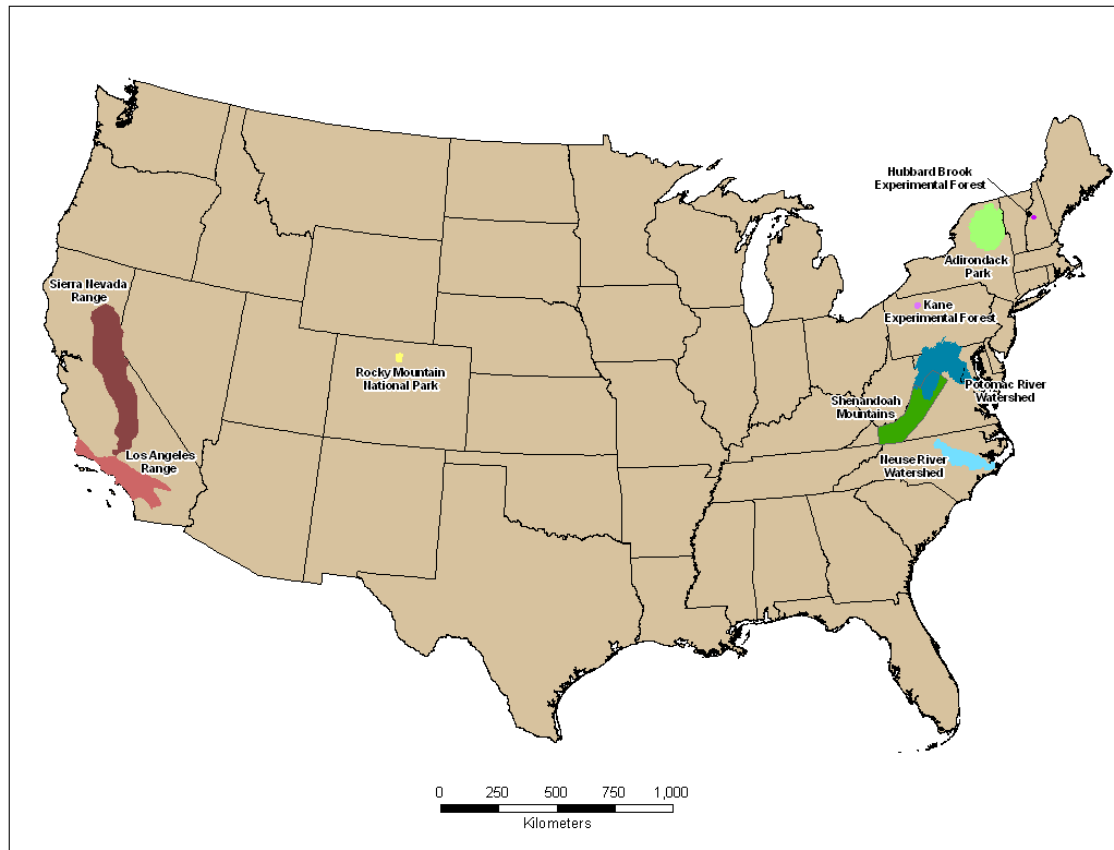


Figure 6-3 National map highlighting the nine case study areas evaluated in the REA.

Aquatic Acidification

Based on the case studies conducted for lakes in the Adirondacks and streams in Shenandoah National Park, staff concludes that there is significant risk to acid sensitive aquatic ecosystems at atmospheric concentrations of oxides of nitrogen and sulfur at or below the current standards. This conclusion is based on application of the MAGIC model to estimate the effects of deposition at levels consistent with atmospheric oxides of nitrogen and sulfur concentrations that are at or below the current standards. An important ecological indicator for aquatic acidification effects is acid neutralizing capacity (ANC) of a waterbody, and the case study focused on evaluating whether locations were likely to be below critical values of ANC given deposition levels associated with oxides of nitrogen and sulfur atmospheric concentrations that meet the current standards. In addition, the case studies assessed the ecological effects and some of the known ecosystem services that are associated with different levels of ANC in order to associate levels of ANC with measures of public welfare that may be adversely affected by

deposition levels consistent with atmospheric concentrations of oxides of nitrogen and sulfur that meet the current standards.

Staff concludes that the evidence and risk assessment support strongly a relationship between atmospheric deposition of oxides of nitrogen and sulfur and loss of ANC in sensitive ecosystems, and that ANC is an excellent indicator of aquatic acidification. Staff also concludes that at levels of deposition associated with oxides of nitrogen and sulfur concentrations at or below the current standards, ANC levels are expected to be below benchmark values that are associated with significant losses in fish species richness (REA Section 4).

Many locations in sensitive areas of the U.S. have ANC levels below benchmark levels for ANC classified as severe, elevated, or moderate concern (see Figure 2-1). The average current ANC levels across 44 lakes in the Adirondack case study area is 62.1 $\mu\text{eq/L}$ (moderate concern). However, 44 percent of lakes had deposition levels exceeding the critical load for an ANC of 50 $\mu\text{eq/L}$, and 28 percent of lakes had deposition levels exceeding the critical load for an ANC of 20 $\mu\text{eq/L}$ (REA Section 4.2.4.2). This information indicates that almost half of the 44 lakes in the Adirondacks case study area are at an elevated concern levels, and almost a third are at a severe concern level. These levels are associated with greatly diminished fish species diversity, and losses in the health and reproductive capacity of remaining populations. Based on assessments of the relationship between number of fish species and ANC level in both the Adirondacks and Shenandoah areas, the number of fish species is decreased by over half at an ANC level of 20 $\mu\text{eq/L}$ relative to an ANC level at 100 $\mu\text{eq/L}$ (REA Figure 4.2-1). At levels below 20 $\mu\text{eq/L}$, populations of sensitive species, such as brook trout, may decline significantly during episodic acidification events. When extrapolated to the full population of lakes in the Adirondacks area using weights based on the EMAP probability survey (REA 4.2.6.1), 36 percent of lakes exceeded the critical load for an ANC of 50 $\mu\text{eq/L}$ and 13 percent of lakes exceeded the critical load for an ANC of 20 $\mu\text{eq/L}$.

Many streams in the Shenandoah case study area also have levels of deposition that are associated with ANC levels classified as severe, elevated, or moderate concern. The average ANC under recent conditions for the 60 streams evaluated in the Shenandoah case study area is 57.9 $\mu\text{eq/L}$, indicating moderate concern. However, 85 percent of streams had recent deposition exceeding the critical load for an ANC of 50 $\mu\text{eq/L}$, and 72 percent exceeded the critical load for an ANC of 20 $\mu\text{eq/L}$. As with the Adirondacks area, this information suggests that significant

numbers of sensitive streams in the Shenandoah area are at risk of adverse impacts on fish populations under recent conditions. Many other streams in the Shenandoah area are likely to experience conditions of elevated to severe concern based on the prevalence in the area of bedrock geology associated with increased sensitivity to acidification suggesting that effects due to stream acidification could be widespread in the Shenandoah area (REA 4.2.6.2).

In the ISA it is noted that significant portions of the U.S. are acid sensitive, and that current deposition levels exceed those that would allow recovery of the most acid sensitive lakes in the Adirondacks (ISA Executive Summary). In addition, because of past loadings, areas of the Shenandoah are sensitive to current deposition levels (ISA Executive Summary). Parts of the West are naturally less sensitive to acidification and subjected to lower deposition (particularly SO_x) levels relative to the eastern United States, and as such, less focus in the ISA is placed on the adequacy of the existing standards in these areas, with the exception of the mountainous areas of the West, which experience episodic acidification due to deposition.

While most (99 percent) stream kilometers in the U.S. are not chronically acidified under current conditions, a recent survey found sensitive streams in many locations in the U.S., including the Appalachian mountains, the Coastal Plain, and the Mountainous West (ISA Section 4.2.2.3). In these sensitive areas, between 1 and 6 percent of stream kilometers are chronically acidified.

The ISA notes that “consideration of episodic acidification greatly increases the extent and degree of estimated effects for acidifying deposition on surface waters.” (ISA Section 3.2.1.6) Some studies show that the number of lakes that could be classified as acid-impacted based on episodic acidification is 2 to 3 times the number of lakes classified as acid-impacted based on chronic ANC. These episodic acidification events can have long term effects on fish populations (ISA Section 3.2.1.6). Under recent conditions, episodic acidification has been observed in locations in the eastern U.S. and in the mountainous western U.S. (ISA Section 3.2.1.6).

It can therefore be concluded that recent levels of oxides of nitrogen and sulfur are associated with deposition that leads to ANC values below benchmark values known to cause ecological harm in sensitive aquatic systems, including lakes and streams in multiple areas of the U.S. These changes are known to have impacts on ecosystem services including recreational fishing which is discussed along with other services in Chapter 3. While other ecosystem

services (e.g. habitat provisioning, subsistence fishing, and biological control as well as many others) are potentially affected by reductions in ANC, confidence in the specific translation of ANC values to these additional ecosystem services is much lower.

Terrestrial Acidification

Based on the case studies on sugar maple and red spruce habitat, staff concludes that there is significant risk to sensitive terrestrial ecosystems from acidification at atmospheric concentrations of NO_x and SO_x at or below the current standards. This conclusion is based on application of the simple mass balance model to deposition levels associated with NO_x and SO_x concentrations at or below the current standards. The ecological indicator selected for terrestrial acidification is the base cation to aluminum ratio (BC:Al), which has been linked to tree health and growth. The results of the REA strongly support a relationship between atmospheric deposition of NO_x and SO_x and BC:Al, and that BC:Al is a good indicator of terrestrial acidification. At levels of deposition associated with NO_x and SO_x concentrations at or below the current standards, BC:Al levels are expected to be below benchmark values that are associated with significant effects on tree health and growth. Such degradation of terrestrial ecosystems could affect ecosystem services such as habitat provisioning, endangered species, goods production (timber, syrup, etc.) and many others.

Many locations in sensitive areas of the U.S. have BC:Al levels below benchmark levels classified as providing low to intermediate levels of protection to tree health. At a BC:Al ratio of 1.2 (intermediate level of protection), red spruce growth can be reduced by 20 percent. At a BC:Al ratio of 0.6 (low level of protection), sugar maple growth can be decreased by 20 percent. The REA did not evaluate broad sensitive regions. However, in the sugar maple case study area (Kane Experimental Forest), recent deposition levels are associated with a BC:Al ratio below 1.2, indicating between intermediate and low level of protection, which would indicate the potential for a greater than 20 percent reduction in growth. In the red spruce case study area (Hubbard Brook Experimental Forest), recent deposition levels are associated with a BC:Al ratio slightly above 1.2, indicating slightly better than an intermediate level of protection (REA Section 4.3.5.1).

Over the full range of sugar maple, 12 percent of evaluated forest plots exceeded the critical loads for a BC:Al ratio of 1.2, and 3 percent exceeded the critical load for a BC:Al ratio

of 0.6. However, there was large variability across states. In New Jersey, 67 percent of plots exceeded the critical load for a BC:Al ratio of 1.2, while in several states on the outskirts of the range for sugar maple (e.g. Arkansas, Illinois) no plots exceeded the critical load for a BC:Al ratio of 1.2. For red spruce, overall 5 percent of plots exceeded the critical load for a BC:Al ratio of 1.2, and 3 percent exceeded the critical load for a BC:Al ratio of 0.6. In the major red spruce producing states (Maine, New Hampshire, and Vermont), critical loads for a BC:Al ratio of 1.2 were exceeded in 0.5, 38, and 6 percent of plots.

The ISA reported one study (McNulty, 1997) that estimated 15 percent of U.S. forest ecosystems exceeded the critical loads for acidity for N and S deposition by >250 eq/ha/year under current conditions (ISA Section 4.2.1.3). Staff concludes that this represents a significant portion of sensitive terrestrial ecosystems.

It can therefore be concluded that recent levels of NO_x and SO_x are associated with deposition that leads to BC:Al values below benchmark values that cause ecological harm in some sensitive terrestrial ecosystems. While effects are more widespread for sugar maple, there are locations with low to intermediate levels of protection from effects on both sugar maple and red spruce. While there are many other ecosystem services, including timber production, natural habitat provision, and regulation of water, climate, and erosion, potentially affected by reductions in BC:Al, linkages of BC:Al values to these additional ecosystem services is on the whole not well understood.

6.3.2 Nutrient enrichment effects in sensitive aquatic and terrestrial ecosystems

Nutrient enrichment effects are due to nitrogen loadings from both atmospheric and non-atmospheric sources. Evaluation of nutrient enrichment effects requires an understanding that nutrient inputs are essential to ecosystem health and that specific long term levels of nutrients in a system affect the types of species that occur over long periods of time. Short term additions of nutrients can affect species competition, and even small additions of nitrogen in areas that are traditionally nutrient poor can have significant impacts on productivity as well as species composition. Most ecosystems in the United States are nitrogen-limited, so regional decreases in emissions and deposition of airborne nitrogen compounds could lead to some decrease in growth of the vegetation that surrounds the targeted aquatic system but as discussed below evidence for this is mixed. Whether these changes in plant growth are seen as beneficial or

adverse will depend on the circumstances (e.g. managed ecosystems). However, as noted earlier, this review of the standards is focused on unmanaged ecosystems. Changes to unmanaged systems may be adverse or beneficial depending on desired ecosystem services. In assessing adequacy of the current standards, we are focusing on the adverse effects of nutrient enrichment in unmanaged ecosystems. However, the following discussion provides a brief assessment of effects in managed ecosystems.

Nitrogen is a fundamental nutrient for primary production in both managed and unmanaged ecosystems. Impacts of nutrient enrichment in managed ecosystems may be positive or negative depending on the levels of nutrients from other sources in those areas. Positive growth effects can result when crops or commercial forests are not receiving enough nitrogen. Nutrients deposited on crops from atmospheric sources are often referred to as passive fertilization. Most productive agricultural systems require external sources of nitrogen in order to satisfy nutrient requirements. Nitrogen uptake by crops varies, but typical requirements for wheat and corn are approximately 150 kg/ha-yr and 300 kg/ha-yr, respectively (NAPAP, 1990). Typical estimated rates of passive nitrogen fertilization are in the range of 0 to 5.5 kg/ha-yr (NAPAP, 1991).

Information on the effects of changes in passive nitrogen deposition on forestlands and other terrestrial ecosystems is very limited. The multiplicity of factors affecting forests, including other potential stressors such as ozone, and limiting factors such as moisture and other nutrients, confound assessments of marginal changes in any one stressor or nutrient in forest ecosystems. The ISA notes that only a fraction of the deposited nitrogen is taken up by the forests, most of the nitrogen is retained in the soils (ISA 3.3.2.1). In addition, the ISA indicates that forest management practices can significantly affect the nitrogen cycling within a forest ecosystem, and as such, the response of managed forests to NO_x deposition will be variable depending on the forest management practices employed in a given forest ecosystem (ISA Annex C C.6.3) Increases in the availability of nitrogen in N-limited forests via atmospheric deposition could increase forest production over large non-managed areas, but the evidence is mixed, with some studies showing increased production and other showing little effect on wood production (ISA 3.3.9). Because leaching of nitrate can promote cation losses, which in some cases create nutrient imbalances, slower growth and lessened disease and freezing tolerances for forest trees, the net effect of increased N on forests in the U.S. is uncertain (ISA 3.3.9).

In managed agricultural ecosystems, nitrogen inputs from atmospheric NO_x comprise a small fraction (less than 3 percent) of total nitrogen inputs, which include commercially applied fertilizers as well as applications of composted manure. And because of the temporal and spatial variability in atmospheric deposition of NO_x, it is unlikely that farmers would alter their fertilization decisions based on expected nitrogen inputs from NO_x. And, in some locations, farmers need less nitrogen inputs due to production of excess nitrogen through livestock. In these locations, nitrogen production through livestock waste exceeds the absorptive capacity of the surrounding land, and as such, excess nitrogen from deposition of NO_x in those locations reduces the capacity of the system to dispose of excess nitrogen, potentially increasing the costs of waste management from livestock operations (Letson and Gollehon, 1996). A USDA Economic Research Service report found that in 1997, 68 counties with high levels of confined livestock production had manure nitrogen levels that exceed the assimilative capacity of the entire county's crop and pasture land (Gollehon et al., 2001). In those locations, additional nitrogen inputs from NO_x deposition will result in excess nitrogen, leading to nitrogen leaching and associated effects that adversely affect ecosystems.

Aquatic Nutrient Enrichment

The REA case studies focused on coastal estuaries and revealed that while current ambient loadings of atmospheric NO_x are contributing to the overall depositional loading of coastal estuaries, other non-atmospheric sources are contributing in far greater amounts in total, although atmospheric contributions are as large as some other individual source types. The ability of current data and models to characterize the incremental adverse impacts of nitrogen deposition is limited, both by the available ecological indicators, and by the inability to attribute specific effects to atmospheric sources of nitrogen. The REA case studies used as the ecological indicator for aquatic nutrient enrichment an index of eutrophication known as the Assessment of Estuarine Trophic Status Eutrophication Index (ASSETS EI). This index is a six level index characterizing overall eutrophication risk in a waterbody. This indicator is not sensitive to relatively large changes in nitrogen deposition. In addition, this type of indicator does not reflect the impact of nitrogen deposition in conjunction with other sources of nitrogen.

For example, if NO_x deposition is contributing nine tenths of the nitrogen loading required to move a waterbody from an ASSETS EI category of "moderate" to a category of

“poor”, zeroing out NO_x deposition will have no impact on the ASSETS EI value. However, if an area were to decide to put in place decreases in nitrogen loadings to move that waterbody from “poor” to “moderate,” the area would have to reduce the full amount of the loadings through other sources if atmospheric deposition were not considered. Thus, the adverse impact of atmospheric nitrogen is in its contribution to the overall loading, and reductions in NO_x will decrease the amount of reductions from other sources of nitrogen loadings that would be required to move from a lower ASSETS EI category to a higher category. NO_x deposition can also be characterized as reducing the *risk* of a waterbody moving from a higher ASSETS EI category to a lower category, by reducing the vulnerability of that waterbody to increased loadings from non-atmospheric sources.

Based on the above considerations, staff preliminarily concludes that the ASSETS EI is not an appropriate ecological indicator for estuarine aquatic eutrophication. Staff further concludes that additional analysis is required to develop an appropriate indicator for determining the appropriate levels of protection from N nutrient enrichment effects in estuaries related to deposition of NO_x. As a result, staff is unable to make a determination as to the adequacy of the existing secondary NO_x standard in protecting public welfare from N nutrient enrichment effects in estuarine aquatic ecosystems.

Additionally, nitrogen deposition can alter species composition and cause eutrophication in freshwater systems. In the Rocky Mountains, for example, deposition loads of 1.5 to 2 kg/ha-yr which are well within current ambient levels are known to cause changes in species composition in diatom communities indicating impaired water quality (ISA Section 3.3.5.3). It then seems apparent then that the existing secondary standard for NO_x does not protect such ecosystems and their resulting services from impairment.

Terrestrial Nutrient Enrichment

The scientific literature has many examples of the deleterious effects caused by excessive nitrogen loadings to terrestrial systems. Several studies have set benchmark values for levels of N deposition at which scientifically adverse effects are known to occur. These benchmarks are discussed more thoroughly in Chapter 5 of the REA. Large areas of the country appear to be experiencing deposition above these benchmarks for example, Fenn et al. (2008) found that at 3.1 kg N/ha-yr, the community of lichens begins to change from acidophytic to tolerant species;

at 5.2 kg N/ha-yr, the typical dominance by acidophytic species no longer occurs; and at 10.2 kg N/ha-yr, acidophytic lichens are totally lost from the community. Additional studies in the Colorado Front Range of the Rocky Mountain National Park support these findings and are summarized in Chapter 6.0 of the *Risk and Exposure Assessment*. These three values (3.1, 5.2, and 10.2 kg/ha-yr) are one set of ecologically meaningful benchmarks for the mixed conifer forest (MCF) of the Pacific coast regions. Nearly all of the known sensitive communities receive total nitrogen deposition levels above the 3.1 N kg/ha-yr ecological benchmark according to the 12 km, 2002 CMAQ/NADP data, with the exception of the easternmost Sierra Nevadas. MCFs in the southern portion of the Sierra Nevada forests and nearly all MCF communities in the San Bernardino forests receive total nitrogen deposition levels above the 5.2 N kg/ha-yr ecological benchmark.

Coastal Sage Scrub communities (CSS) are also known to be sensitive to community shifts caused by excess nitrogen loadings. Wood et al. (2006) investigated the amount of nitrogen utilized by healthy and degraded CSS systems. In healthy stands, the authors estimated that 3.3 kg N/ha-yr was used for CSS plant growth (Wood et al., 2006). It is assumed that 3.3 kg N/ha-yr is near the point where nitrogen is no longer limiting in the CSS community. Therefore, this amount can be considered an ecological benchmark for the CSS community. The majority of the known CSS range is currently receiving deposition in excess of this benchmark. Thus, staff concludes that recent conditions where NO_x ambient concentrations are at or below the current NO_x secondary standards are not adequate to protect against anticipated adverse impacts from N nutrient enrichment in sensitive ecosystems.

6.3.3 Other Ecological Effects (Eg. Mercury Methylation) Associated With Deposition of Atmospheric Oxides Of Nitrogen and/or Sulfur

It is stated in the ISA (ISA Sections 3.4.1 and 4.5) that mercury is a highly neurotoxic contaminant that enters the food web as a methylated compound, methylmercury. Mercury is principally methylated by sulfur-reducing bacteria and can be taken up by microorganisms, zooplankton and macroinvertebrates. The contaminant is concentrated in higher trophic levels, including fish eaten by humans. Experimental evidence has established that only inconsequential amounts of methylmercury can be produced in the absence of sulfate. Once methylmercury is present, other variables influence how much accumulates in fish, but elevated mercury levels in

fish can only occur where substantial amounts of methylmercury are present. Current evidence indicates that in watersheds where mercury is present, increased oxides of sulfur deposition very likely results in additional production of methylmercury which leads to greater accumulation of MeHg concentrations in fish (Munthe et al, 2007; Drevnick et al., 2007).

The production of meaningful amounts of methylmercury (MeHg) requires the presence of SO_4^{2-} and mercury, and where mercury is present, increased availability of SO_4^{2-} results in increased production of MeHg. 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 (ISA Section 3.4). In watersheds where changes in sulfate deposition did not produce an effect, one or several of those interacting factors were not in the range required for meaningful methylation to occur (ISA 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 addressed qualitatively in Chapter 6 of the Risk and Exposure Assessment.

With respect to sulfur deposition and mercury methylation, the final ISA determined: *The evidence is sufficient to infer a causal relationship between sulfur deposition and increased mercury methylation in wetlands and aquatic environments.* However, staff did not conduct a quantitative assessment of the risks associated with increased mercury methylation under current conditions. As such, staff is unable to make a determination as to the adequacy of the existing SO_2 standards in protecting against welfare effects associated with increased mercury methylation.

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7 CONSIDERATION OF ALTERNATIVE STANDARDS FOR AQUATIC ACIDIFICATION

Having reached the conclusion that the current NO₂ and SO₂ standards are not adequate to provide appropriate protection against deposition-related effects associated with oxides of nitrogen and sulfur, staff considers alternative standards that are multi-pollutant and multimedia in nature to address such effects on public welfare. The inherently complex and variable linkages between ambient concentrations of nitrogen and sulfur oxides, the related deposited forms of nitrogen and sulfur, and the ecological responses that are associated with public welfare effects call for consideration of an ecologically relevant design of a standard that reflects these linkages. Such a standard will necessarily be more complex than the NAAQS that have been set historically to address effects associated with direct exposure to a single pollutant. Nonetheless, an ecologically relevant multi-pollutant, multimedia standard to address deposition-related effects is still appropriately defined in terms of the same basic elements that are used to define any NAAQS – indicator, form, averaging time, and level – with the form incorporating additional structural elements that reflect these multi-pollutant and multimedia attributes. These structural elements include the use of an ecological indicator, tied to the ecological effect we are focused on, that accounts for ecologically relevant factors other than ambient air concentrations. All of these elements are needed to enable a linkage from ecological indicator to ambient air indicators to completely define an ecologically relevant standard.

More specifically, in this chapter we focus on the development of an ecologically relevant standard to address effects associated with acidifying deposition of oxides of nitrogen and sulfur in sensitive aquatic ecosystems. This focus is consistent with the information presented in the ISA and REA which highlighted the sufficiency of the quantity and quality of the available evidence and assessments associated with aquatic acidification relative to the information and assessments available for other deposition-related effects, including terrestrial acidification and aquatic and terrestrial nutrient enrichment. Based on its review of these documents, CASAC agreed with the conclusion that aquatic acidification should be the focus for developing a new multi-pollutant, multimedia standard in this review. In reaching conclusions about a standard designed to address aquatic acidification effects, we also recognize that such a standard may also provide some degree of protection against other deposition-related effects, drawing from information presented above in chapter 5.

Our development of an alternative standard for aquatic acidification recognizes the need for a nationally applicable standard for protection against adverse effects of aquatic acidification to public welfare, while recognizing the complex and heterogeneous interactions between ambient air concentrations of nitrogen and sulfur oxides, the related deposition of nitrogen and sulfur, and associated ecological responses. Our approach also recognizes that while a standard is national in scope and coverage, the effects to public welfare from aquatic acidification will not occur to the same extent in all locations in the U.S., given the inherent variability of aquatic systems to the effects of acidification. As noted above in chapters 3 and 4, many locations in the U.S. are naturally protected against acid deposition due to underlying geological conditions. Likewise, some locations in the U.S., including lands managed for commercial agriculture and forestry, are not likely to be negatively impacted by current levels of nitrogen and sulfur deposition. As a result, while the alternative standard we are considering would apply everywhere, it is structured to account for differences in the sensitivity of ecosystems across the country. This allows for appropriate protection of sensitive aquatic ecosystems, which are relatively pristine and wild and generally in rural areas, and the services provided by such sensitive ecosystems, without requiring more protection than is needed elsewhere.

In this chapter we present our reasoning for developing a standard that employs (1) NO_y and SO_x as the atmospheric indicators; (2) a form that takes into account variable factors, such as atmospheric and ecosystem conditions that modify the amounts of deposited oxides of nitrogen and sulfur; the distinction between oxidized and reduced forms of nitrogen; effects of deposited nitrogen and sulfur on aquatic ecosystems in terms of the ecological indicator ANC; and the representativeness of water bodies within a defined spatial area; (3) a multi-year averaging time, and (4) a standard level defined in terms of a target ANC level that, in the context of the above form, identifies the allowable levels of concentrations of NO_y and SO_x in the ambient air. In developing such a standard, we have defined an index, termed an aquatic acidification index (AAI), directly expressed in terms of atmospheric concentrations of oxides of nitrogen and sulfur, that can be applied across the country to convey the allowable levels of oxides of nitrogen and sulfur in the ambient air based on various factors such as the sensitivity of an area and the desired degree of protection from aquatic acidification caused by atmospheric deposition.

In considering such an alternative standard for aquatic acidification, we focus on each element of the standard, including alternative indicators (section 7.1), forms (section 7.2), averaging times (section 7.3), and levels (section 7.4). We then consider implications of various combinations of alternative forms and levels, by characterizing areas that currently would likely not meet such standards (section 7.5). A summary of staff conclusions with regard to the current standards and alternative standards that are appropriate for consideration in this review is presented in section 7.6.

7.1 INDICATORS

In considering alternative ambient air indicators, we primarily focus on the important attribute of association. Association in a broad sense refers to how well an ambient air indicator relates to the ecological effects of interest by virtue of the conceptual or process-based framework, linking indicator and effects as well as through empirical evidence. We also consider how measurable or quantifiable an indicator is to enable its use as an effective indicator of relevant ambient air concentrations.

As discussed above in chapter 6, staff concludes that indicators other than NO_2 and SO_2 should be considered as the appropriate indicators of oxides of nitrogen and sulfur in the ambient air for protection against the acidification effects associated with deposition of oxides of nitrogen and sulfur. This conclusion is based on the recognition that all forms of nitrogen and sulfur in the ambient air contribute to deposition and resulting acidification, and as such, NO_2 and SO_2 are incomplete indicators. In principle, the indicators should represent the species associated with oxides of nitrogen and sulfur in the ambient air that can contribute acidifying deposition. This includes both the species of oxides of nitrogen and sulfur that are directly emitted as well as species transformed in the atmosphere that retain the nitrogen and sulfur atoms from directly emitted oxides of nitrogen and sulfur. We emphasize the individual atoms associated with oxides of nitrogen and sulfur because the acidifying potential is specific to nitrogen and sulfur, and not other atoms (e.g., H, C, O) whether derived from the original source of oxides of nitrogen and sulfur emissions or from atmospheric transformations. For example, the acidifying potential of each molecule of NO_2 , NO , HNO_3 or PAN is identical, as is the potential for each molecule of SO_2 or ion of particulate sulfate, SO_4 . Each atom of sulfur affords twice the acidifying potential of any atom of nitrogen.

The next two sub-sections address indicators for oxides of sulfur and nitrogen, respectively. The discussion on sulfur is brief, reflecting a general lack of issues or alternatives for this pollutant, while the discussion on oxides of nitrogen addresses several related issues and alternatives.

7.1.1 Ambient air indicators for oxides of sulfur

Oxides of sulfur include the gases sulfur monoxide (SO), sulfur dioxide (SO₂), sulfur trioxide (SO₃), disulfur monoxide (S₂O), and particulate-phase sulfur compounds that result from gas-phase sulfur oxides interacting with particles. However, the sum of SO₂ and SO₄ does represent virtually the entire ambient air mass of sulfur that contributes to acidification. In addition to accounting for virtually all the potential for acidification from oxidized sulfur in the ambient air, there are reliable methods to monitor the concentrations of SO₂ and particulate SO₄. In addition, much of the data used to develop the technical basis for the standard is based on monitoring or modeling of these species.¹ Staff concludes that the sum of SO₂ and SO₄, referred to as SO_x, are appropriate ambient air indicators of oxides of sulfur because they represent virtually all of the acidification potential of ambient air oxides of sulfur and there are reliable methods suitable for measuring SO₂ and SO₄.

7.1.2 Ambient air indicators for oxides of nitrogen

Total reactive oxidized nitrogen, NO_y, defined in chapter 2, incorporates basically all of the oxidized nitrogen species that have acidifying potential and as such, NO_y should be considered as an appropriate indicator for oxides of nitrogen. NO_y is an aggregate measure of NO_x (defined as NO and NO₂) and all of the reactive oxidized products of NO_x. That is, NO_y is a group of nitrogen compounds in which all of the compounds are either an oxide of nitrogen or the nitrogen atoms in the compounds that came from oxides of nitrogen. NO_y is especially relevant as an acidification indicator in that it both relates to the oxides of nitrogen in the ambient air and also represents the acidification potential of all oxidized nitrogen species in the ambient air, whether an oxide of nitrogen or derived from oxides of nitrogen.

¹ As discussed above in chapter 2, we note that SO₂ and particulate SO₄ are routinely measured in ambient air monitoring networks, although only CASTNET filter packs do not intentionally exclude particle size fractions. The CMAQ treatment of SO_x is the simple addition of both species, which are treated explicitly in the model formulation. All particle size fractions are included in the CMAQ SO_x estimates.

There are currently available reliable methods of measuring NO_y. The term “aggregate” measure means that the NO_y as measured is not based on measuring each individual species of NO_y and calculating an NO_y value by addition (as performed in CMAQ processing), but rather produces a measurement, as described in chapter 2, in which all of the individual NO_y species are processed by the measurement technique to produce a single aggregate measure of all of the nitrogen atoms that were associated with any NO_y species. Consequently, the NO_y measurement effectively provides the sum of all individual species, but the identity of the individual species is lost. As discussed above, the accounting for the individual nitrogen atoms is an accounting of the ambient air acidification potential of oxides of nitrogen and their transformation products and therefore the most relevant indicator for aquatic acidification effects associated with oxides of nitrogen.

However, the loss of the information on individual species has motivated consideration of alternative or more narrowly defined indicators for oxides of nitrogen. Considering a subset of NO_y species is based on the following lines of reasoning. First, the actual dry deposition of nitrogen is determined on an individual species basis by multiplying the species concentration times a species-specific deposition velocity and then summed to develop an estimate of total dry deposition. Consequently, the use of individual ambient species has the potential to be more consistent with the underlying science of deposition and, therefore, has the potential to allow for a more rigorous evaluation of dry deposition with specialized field studies. In addition, there has been a suggestion of focusing only on the most quickly depositing NO_y species, such as nitric acid and HNO₃, as contributions from other NO_y species such as NO₂ may be negligible. These alternative indicators are considered below.

- **What are the relative merits of using the sum of each individual NO_y species as the indicator for oxides of nitrogen?**

Dry deposition of NO_y is treated as the sum of the deposition of each individual species in advanced process-based air quality models like CMAQ, as described in chapter 2. Conceptually one could extend this process-based approach by using all NO_y species individually as separate indicators for oxides of nitrogen and requiring, for example, measurements of each of the species, including the dominant species of HNO₃, particulate nitrate, true NO₂, NO, and PAN. The potential attraction of using individual species would be the reliance on actual deposition velocities that have more physical meaning in comparison to a

model constructed aggregate deposition of NO_y, which is difficult to evaluate with observations because of the assimilation of many species with disparate deposition behavior. The major drawback of using individual NO_y species as the indicators is the lack of reliable measurement techniques, especially for PAN and NO₂ in rural locations, which renders the use of virtually any individual NO_y species, except for NO and perhaps particulate nitrate, as functionally inadequate from a measurement perspective.

- **What are the relative merits of using a subset of NO_y species as the indicators for oxides of nitrogen?**

If certain species provide relatively minor contributions to total NO_y deposition, then we could consider excluding them as part of the indicator. As discussed in chapter 2, each nitrogen species within the array of NO_y species has species-specific dry deposition velocities. For example, the deposition velocity of nitric acid is much greater than the velocity for nitrogen dioxide and, consequently, for a similar ambient air concentration, nitric acid contributes more deposition of acidifying nitrogen relative to nitrogen dioxide. In transitioning from source-oriented urban locations to rural environments, the ratio of the concentrations of nitric acid and PAN to nitrogen dioxide increases.

Based on the reasoning that a larger fraction of the deposited NO_y is accounted for by total nitrate (the sum of nitric acid and particulate nitrate), a surrogate for more rapidly depositing fraction of NO_y, combined with the availability of reliable total nitrate measurements through CASTNET, consideration has been given to using total nitrate as the indicator for oxides of nitrogen. The use of total nitrate as it could be incorporated within the form of the standard is described in appendix E. One can reason that nitrate correlates well with total reactive oxidized nitrogen deposition relative to NO_y (as discussed in chapter 2), given the inherent noise associated with variable contributions of low deposition velocity species (e.g., NO₂) that may have relatively high ambient concentrations. However, modeling simulations suggest that NO_y may be a more robust indicator in terms of absolute changes in ambient air concentrations, relative to nitric acid², of relating changes in an ambient air indicator to changes in nitrogen deposition driven by changes in ambient concentrations of oxides of nitrogen (Figure 2-32).

²Nitric acid concentrations are significantly higher than particulate nitrate and served as a more convenient regression variable without affecting the correlations.

In summary, the disadvantages of using a subset of NO_y species such as total nitrate or nitric acid as an indicator are that a significant portion of ambient mass with the potential for acidifying deposition is not captured. This conclusion relates to species with high and low deposition velocities. For example, nitrogen dioxide (low deposition velocity) alone is an inadequate indicator by itself because it generally corresponds to less than 50% of the ambient air contribution to nitrogen deposition, yet is a necessary piece of the aggregated total NO_y indicator because it can contribute significantly to deposited nitrogen.

- **What are staff conclusions with regard to an appropriate indicator for oxides of nitrogen?**

Staff concludes that total reactive oxidized nitrogen, NO_y, is the appropriate ambient indicator based on its direct relationship to deposition associated with aquatic acidification and its direct relationship to oxides of nitrogen in the ambient air. Because NO_y represents all of the potentially acidifying oxidized nitrogen species in the ambient air, it is appropriately associated with the deposition of potentially acidifying oxides of nitrogen. In addition, there are reliable methods available to measure NO_y. Measurement of each individual species of NO_y, or the measurement of only a subset of species of NO_y is less appropriate, because a subset would fail to account for significant portions of the oxidized reactive nitrogen that relates to acidification, and because there are not reliable measurements methods available to measure all of the individual species of NO_y.

NO_y also is a useful measurement for model evaluation purposes. Model evaluation considerations are especially important, recognizing the unique role that CMAQ provides as described below in section 7.2. Both of these data uses, NAAQS indicator and model evaluation, are best served through characterizing the total mass of all relevant species, which in the case of oxidized nitrogen, is best reflected through NO_y.

In reaching this conclusion, we note that the use of NO_y, as well as SO₂ and SO₄, as the ambient air indicators for a new aquatic acidification standard for oxides of nitrogen and sulfur was introduced in the first draft of this PA and was generally supported by CASAC in its review of that document (Russell and Samet, 2010a).

7.1.3 Monitoring Considerations

Monitoring considerations specific to the indicators discussed above are briefly summarized here, while other monitoring related issues are addressed in more detail above in

chapter 2. With respect to the oxides of sulfur indicators, SO₂ and SO₄, and oxides of nitrogen indicator, NO_y, we recognize that reliable monitoring methods are currently available. Protocols for monitor operations and quality assurance would be provided in conjunction with the establishment of a standard that utilized these ambient indicators for oxides of nitrogen and sulfur.

With regard to the design of appropriate monitors for particulate sulfate, staff concludes that an instrument design that does not intentionally omit any size fraction of the entire range of sulfate particle diameters is appropriate to consider for measuring sulfate. This inclusion of all particle diameters considers that while most of the potential depositing mass is largely incorporated in those particles with aerodynamic diameters less than 2.5 μ, particles with larger diameters deposit much more quickly and can be an important contributor to sulfate deposition in certain areas.

Further, with regard to monitoring instrumentation for SO₂, staff concludes that available SO₂ continuously operating instruments with the ability to capture low concentrations such as those deployed in NCore are appropriate to consider. In addition, consideration should be given to the CASTNET filter pack (FP) SO₂ measurement technique for the purpose of this secondary standard, since the 1-week averaging period employed by the CASTNET sampler is adequate for the purposes of a standard based on annual average calculations (as discussed below in section 7.3).

7.2 FORM

Based on the evidence of the aquatic acidification effects caused by NO_y and SO_x, staff concludes that it is appropriate to develop a new form that is ecologically relevant for addressing deposition-related effects, specifically for aquatic acidification effects. EPA staff has developed a conceptual design for the form of the standard that includes three main components: ecological indicators, deposition metrics that relate to ecological indicators, and a function that relates ambient indicators to deposition metrics. Collectively, these three components link the ecological indicator to ambient indicators, as illustrated in Fig 7-1.

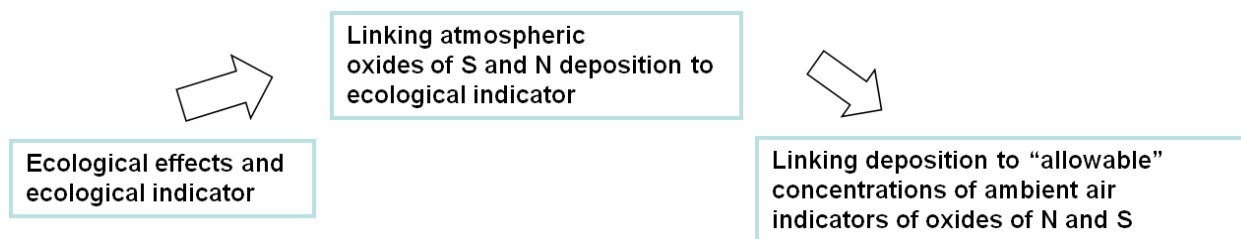


Figure 7-1. Conceptual design of the form of an aquatic acidification standard for oxides of nitrogen and sulfur.

The simplified flow diagram in Figure 7-1 compresses the various atmospheric, biological, and geochemical processes associated with acidifying deposition to aquatic ecosystems (Figure 2-1) into a simplified conceptual picture. The ecological indicator (left box) is related to atmospheric deposition through biogeochemical ecosystem models (middle box), which associate a target deposition load to a target ecological indicator. Once a target deposition is established, associated allowable air concentrations are determined (right box) through the relationships between concentration and deposition that are embodied in air quality models such as CMAQ. In sections 7.2.1 – 7.2.3 we describe the development and rationale for each of these components. Section 7.2.4 ties together these three components and develops the full expression of the form of the standard using the concept of a national “aquatic acidification index” that represents a target ANC level as a function of ambient air concentrations. Section 7.2.5 addresses spatial aggregation issues associated with defining each of the terms of this index within a spatial area.

The aquatic acidification index (AAI)³ is designed to be an ecologically relevant form of the standard that determines the allowable levels of ambient NO_y and SO_x based on a target ANC limit for the U.S. The intent of the AAI is to weight atmospheric concentrations of oxides of nitrogen and sulfur by their propensity to contribute to acidification through deposition, given the fundamental acidifying potential of each pollutant, and to take into account the ecological factors that govern acid sensitivity in different ecosystems. The index also accounts for the contribution of reduced nitrogen to acidification. Thus, the AAI encompasses those attributes of specific relevance to protecting ecosystems from the acidifying potential of ambient air concentrations of NO_y and SO_x.

³ This index was previously termed the aquatic acidification protection index (AAPI) in earlier documents.

Staff notes two important concepts illustrated by the O₃ and PM₁₀ NAAQS that lend support to using this index as the form of a NAAQS. First, in recent reviews of the secondary ozone standards, EPA has considered use of a form of the standard that reflects ecologically relevant exposures, by using a cumulative index which weights exposures at higher concentrations greater than those at lower concentrations based on scientific literature demonstrating the cumulative nature of O₃-induced plant effects and the need to give greater weight to higher concentrations (EPA, 2007; See 75 FR 2938, 2999 January 19, 2010). Staff also notes that PM₁₀ is the indicator for the coarse PM NAAQS standard (PM₁₀ = PM_{2.5} + PM_{10-2.5}). Although the standard has a single level (150 µg/m³), the actual amount of coarse PM that is allowed varies depending on how much fine PM (PM_{2.5}) is present. By its nature, the PM₁₀ NAAQS provides the appropriate protection from exposure to coarse PM across locations using PM₁₀ as the indicator, by allowing the level of coarse PM to vary appropriately across locations. The form for a standard for oxides of nitrogen and sulfur developed in this assessment builds on this concept by using an index that weights the ambient concentrations to reflect their relationship to acidification and provides the appropriate protection across the country by allowing ambient air concentrations of oxides of nitrogen and sulfur to vary appropriately based on ecosystem sensitivity and other relevant factors.

7.2.1 Ecological indicator

Ecological effects and ecological indicator

In considering alternative ecological indicators, we again primarily focus on the important attribute of association. In the case of an ecological indicator for aquatic acidification, association refers to the relationship between the indicator and adverse effects as discussed in chapter 3. Because of the conceptual structure of the form of this standard (Figure 7-1), this particular ecological indicator must also link up in a meaningful and quantifiable manner with acidifying atmospheric deposition. In effect, the ecological indicator for aquatic acidification is the bridge between the biological impairment we are focused on and deposition of NO_y and SO_x.

This section presents the staff's rationale for selecting acid neutralizing capacity (ANC) as the appropriate ecological indicator for consideration. Recognizing that ANC is not itself the

causative or toxic agent for adverse aquatic acidification effects, the rationale for using ANC as the relevant ecological indicator is based on the following:

- ANC is directly associated with the causative agents, pH and dissolved aluminum, both through empirical evidence and mechanistic relationships;
 - Empirical evidence shows very clear and strong relationships between adverse effects and ANC;
 - ANC is a more reliable indicator from a modeling perspective, allowing use of a body of studies and technical analyses related to ANC and acidification to inform the development of the standard; and
 - ANC literally embodies the concept of acidification as posed by the basic principles of acid base chemistry and the measurement method used to estimate ANC and, therefore, serves as a direct index to protect against acidification.
- **What ecological indicators are appropriate to relate the effects of acidifying deposition to aquatic systems?**

Ecological indicators of acidification in aquatic ecosystems can be chemical or biological components of the ecosystem that are altered by the acidifying effects of nitrogen and sulfur deposition. A desirable ecological indicator for aquatic acidification is one that is measurable or estimable, linked causally to deposition of nitrogen and sulfur, and linked causally, either directly or indirectly to ecological effects known or anticipated to adversely affect public welfare.

As summarized in chapter 2, atmospheric deposition of NO_x and SO_x causes aquatic acidification through the input of strong acid anions (e.g. NO_3^- and SO_4^{2-}) that ultimately shifts the water chemistry equilibrium toward increased hydrogen ion levels (or decreased pH). The anions are deposited either directly to the aquatic ecosystem, or indirectly via transformation through soil nitrification processes and subsequent drainage from terrestrial ecosystems. In other words, when these anions are mobilized in the terrestrial soil, they can leach into adjacent water bodies. Aquatic acidification is indicated by changes in the surface water chemistry of ecosystems. In turn, the alteration of surface water chemistry has been linked to negative effects on the biotic integrity of freshwater ecosystems. There is a suite of chemical indicators that could be used to assess the effects of acidifying deposition on lake or stream acid-base chemistry. These indicators include acid neutralizing capacity (ANC); alkalinity (ALK); base neutralizing capacity, commonly referred to as acidity (ACY); surface water pH; trivalent aluminum, Al^{+3} ;

concentrations of major anions (SO_4^{2-} , NO_3^-); cations (Ca^{2+} , Mg^{+2} , K^+); or sums of cations or anions.

Indicators such as specific anions, cations, or their groupings, while relevant to acidification processes, are not robust acidification indicators as it is the relative balance of cations and anions that is more directly associated with acidification. That balance is captured by ANC and ALK. Acidity, ACY, is the corollary of ANC from the perspective of how much strong base it takes to reach an equivalence point. Because ACY is not used in most ecosystem assessments, the body of information relating ACY to effects is too limited to serve as a basis for an appropriate ecological indicator. Aluminum and other metals are causative toxic agents that directly impair biological functions. However, aluminum, or metals in general, have high variability in concentrations that can be linked to effects, often at extremely low levels which in some cases approach detectability limits, exhibit rapid transient responses, and are often confounded by the presence of other toxic metals. These concerns limit the use of metals as reliable and measurable ecological indicators. Hydrogen ion (H^+) concentrations, using their negative logarithmic values, or pH, are well correlated with adverse effects, as discussed in chapter 3, and determine the solubility of metals such as aluminum (figure 3-1). However, pH also is not a preferred acidification indicator due to its highly transient nature and other concerns, which are discussed below in the context of why ANC is a preferred indicator.

ANC and ALK are very similar quantities and are used interchangeably in the literature and for some of the analyses presented in this document. Both ANC and ALK are defined as the amount of strong acid required to reach a specified equivalence point (Stumm and Morgan, 1981). For acid base solutions, an equivalence point can be thought of as the point to which the addition of strong acids (i.e., titration) is no longer neutralized by the solution⁴. This explains the term acid neutralizing capacity, or ANC, as ANC truly relates directly to the capacity of a system to neutralize acids. The differences between ANC and ALK are based on operational definitions and subject to various interpretations as described by Hemond, 1992. ANC is a preferred over ALK as the body of scientific evidence has focused on ANC and effects

⁴ The common equivalent point that defines ANC or ALK is based on a solution of water, absent dissolved organic carbon (DOC), that is open to the atmosphere for CO_2 exchange and dissolved inorganic carbon (DIC) exists in the form of bicarbonate ion, HCO_3^- , carbonate ion, CO_3^{2-} and carbonic acid, H_2CO_3 . In such a solution, when the titration with strong acid brings the pH down to the equivalence point at a pH of 4.5, all inorganic carbon is fully protonated as carbonic acid, H_2CO_3 .

relationships. ALK is more widely associated with more general characterizations of water quality such as the relative hardness of water associated with carbonates.

Having reasoned that ANC is a preferred indicator to ALK, ACY, individual metals or groupings of ions, we consider the relative merits of ANC compared to pH, which is a well recognized indicator of acidity and a more direct causative agent with regard to adverse effects. First, the linkage between ANC and pH is considered in recognition of the causative association between pH and effects.

- **What is the mechanistic basis for and empirical evidence of the association between pH and ANC?**

ANC directly is not the causative toxic agent impacting aquatic species diversity. The scientific literature generally emphasizes the links between pH and adverse effects as described in chapter 3. It is important, therefore, to establish that ANC and pH are well related from a mechanistic perspective as well through empirical evidence. ANC and pH are co-dependent on each other based on the requirement that all solutions are electrically neutral, meaning that any solution must satisfy the condition that all negatively charged species must be balanced by all positively charged species. ANC is defined in chapter 2 (equation 2-11) as the difference between strong anions and cations:

$$\text{ANC} = 2([\text{CA}^{2+}] + [\text{Mg}^{2+}]) + [\text{K}^+] + [\text{NH}_4^+] - (2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-]) \quad (7-1)$$

While the chemistry can be complex, the co-dependency between ANC and pH is explained by recognizing that positively charged hydrogen, H^+ , is incorporated in the charge balance relationships related to the overall solution chemistry which also defines ANC. The positive, directional co-dependency (i.e., ANC and pH increase together) is further explained in concept as ANC reflects how much strong acid (i.e., how much hydrogen ion) it takes to titrate to an equivalence point.

Strong observed correlations between pH and ANC (Fig 7-2) support these mechanistic relationships. There generally is an S-shaped relationship between pH and ANC, which suggests that the linear part of the ANC and pH relationship is useful in guiding the discussion on ranges of ANC (section 7.4) which relates most closely to adverse effects. The asymptotic parts of the

ANC-pH curve reflect the inherent buffering capacity of ANC as hypothetical additions of acid would not result in significant pH change over those flat portions of the curve.

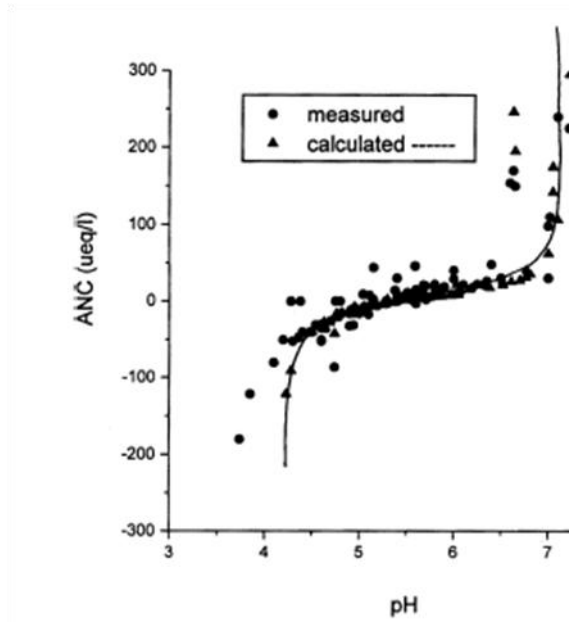


Figure 7-2. The relationship between pH and ANC under equilibrium conditions with mineral phase gibbsite. Triangles indicate calculated values while circles indicate measurements (Bi and Liu 2001).

- **What does the available evidence show concerning associations between ANC and aquatic acidification effects?**

As discussed in chapter 3, there are well established examples of ANC correlating strongly with a variety of ecological effects which are summarized in Table 3-1. Because pH and ANC are well correlated (Figure 7-2) and linearly dependent over the pH ranges (4.5 – 6) where adverse ecological effects are observed (Figure 3-3), evidence of clear associations exist between ANC and adverse ecological effects (Figures 7-3 and 7-4). In large measure, these figures, as well as the related effects discussions in chapter 3, speak directly to the appropriateness of ANC with respect to its use as an ecological indicator.

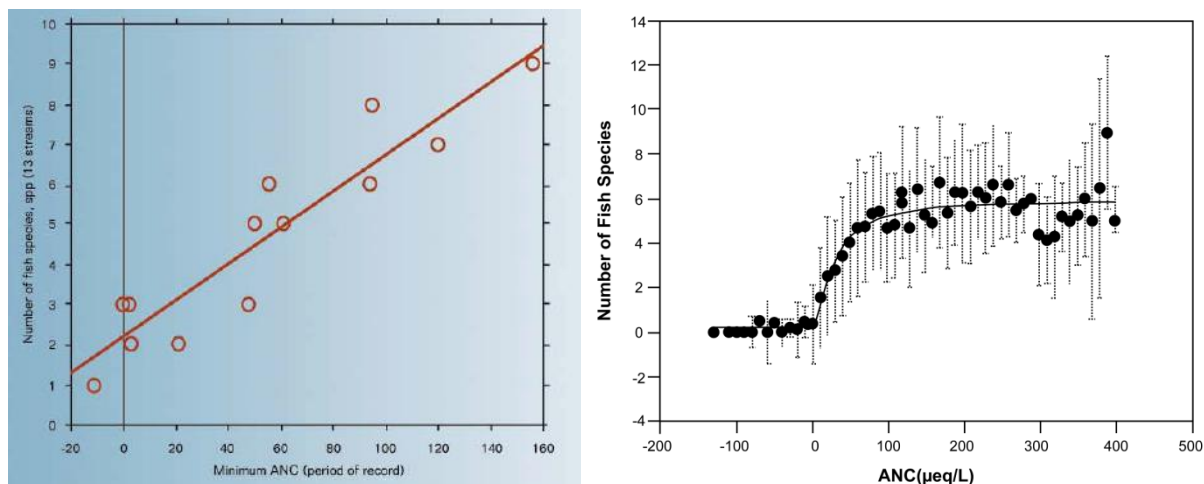


Figure 7-3 and 7-4. (Left) Relationship between ANC and number of fish species present in aquatic freshwater ecosystems in Shenandoah National Park (Source: Arthur Bulger, University of Virginia, reproduced from NAPAP, 2005.). (Right) Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 $\mu\text{eq/L}$ ANC categories, based on data collected by the Adirondack Lakes Survey Corporation Source: Sullivan et al. (2006).

- **Why is ANC a more appropriate ecological indicator than pH?**

The previous two discussions established a clear association between ANC and ecological effects, while acknowledging a more direct causal relationship between pH and effects. Nonetheless, ANC is preferred as an ecological indicator based on its superior ability to provide a linkage with deposition in a meaningful and quantifiable manner, a role that is served far more effectively by ANC than by pH. While both ANC and pH are clearly associated with the effects of concern, ANC is superior in linking these effects to deposition.

The basis for this conclusion is that acidifying atmospheric deposition of nitrogen and sulfur is a direct input of potential acidity (ACY), or, in terms of ANC, such deposition is relevant to the major anions in equation 7-1 that reduces the capacity of a water body to neutralize acidity. Consequently, there is a well defined linear relationship between potential acidifying deposition and ANC. This ANC-deposition relationship facilitates the linkage between ecosystem models that calculate an ecological indicator and the atmospheric deposition of NO_y and SO_x . On the other hand, there is no direct linear relationship between deposition and pH. There certainly is a relationship, as acid inputs from deposition lower pH, but the relationship can be extremely nonlinear and there is no direct connection from a modeling or mass balance perspective between the amount of deposition entering a system and pH. The term

“mass balance” underlies the basic formulation of any physical modeling construct, atmospheric or aquatic systems, and refers to the accounting of the flow of mass into a system, the transformation to other forms, and the loss due to flow out of a system and other removal processes. ANC is a conserved property. This means that ANC in a water body can be accounted for by knowledge of how much ANC initially exists, how much flows in and is deposited, and how much flows out. In contrast, hydrogen ion concentration in the water, the basis for pH, is not a conserved property as its concentration is affected by several factors such as temperature, atmospheric pressure, mixing conditions of a water body, and the levels of other several chemical species in the system. The disadvantage of pH lacking conservative properties is that there is a very complex connection between changes in ambient air concentrations of NO_y and SO_x and pH.

The discussion of basic water chemistry of natural systems in chapter 2 provides further details on why pH is not a conserved quantity and is subject to rapid transient response behavior that makes it difficult to use as a reliable and functional ecological indicator. For now, we can use the observed pH-to-ANC relationship (Figure 7-2) to partially explain the concern with pH responding too abruptly. In the region where pH ranges roughly from 4.5 to 6 and is of greatest relevance to effects (as seen in Figure 3-3), there clearly is more sensitivity of pH to changes in ANC in the ANC range from approximately 0 to 50 µeq/L. We focus on this part of the ANC-to-pH relationship when we say that ANC associates well with pH in a fairly linear manner. However, the pH range from 4.5 to 6 also includes one of the very steepest parts of the slope relating pH as a function of ANC (Figure 7-2), where ANC ranges down below 0 µeq/L, which is subject to very rapid change in ANC, or deposition inputs. This part of the relationship coincides with reduced levels of ANC and hence with reduced ability to neutralize acids and moderate pH fluctuations. This response behavior can be extended to considering how pH would change in response to deposition, or ambient concentrations, of NO_y and SO_x, which can be viewed as “ANC-like” inputs.

In summary, because ANC clearly links both to biological effects of aquatic acidification as well as to acidifying inputs of NO_y and SO_x deposition, staff concludes that ANC is an appropriate ecological indicator for relating adverse aquatic ecosystem effects to acidifying atmospheric deposition of SO_x and NO_y, and is preferred to other potential indicators. In reaching this conclusion, we note that in its review of the first draft PA, CASAC concluded that

“information on levels of ANC protective to fish and other aquatic biota has been well developed and presents probably the lowest level of uncertainty in the entire methodology” (Russell and Samet, 2010a). In its more recent review of the second draft PA, CASAC agreed “that acid neutralizing capacity is an appropriate ecological measure for reflecting the effects of aquatic acidification” (Russell and Samet, 2010b; p. 4).

7.2.2 Linking ANC to deposition.

Linking atmospheric SO_x and NO_y deposition to ecological indicator

- **What does the available evidence show concerning the linkage of ANC to acidifying deposition?**

There is evidence to support a quantified relationship between deposition of nitrogen and sulfur and ANC. This relationship was analyzed in the REA for two case study areas, the Adirondack and Shenandoah Mountains, based on time-series modeling and observed trends.

Modeled long-term trends over time

In the REA analysis, long-term trends in surface water nitrate, sulfate and ANC were modeled using Model of Acidification of Groundwater in Catchment (MAGIC) for the two case study areas. These data were used to compare recent surface water conditions (2006) with preindustrial conditions (i.e. preacidification 1860). The results showed a marked increase in the number of acid impacted lakes, characterized as a decrease in ANC levels, since the onset of anthropogenic nitrogen and sulfur deposition (see chapter 2).

Observed recent trends over time

In the REA, more recent trends in ANC, over the period from 1990 to 2006, were assessed using monitoring data collected at the two case study areas. In both case study areas, nitrate and sulfate deposition decreased over this time period. In the Adirondack Mountains, this corresponded to a decreased concentration of nitrate and sulfate in the surface waters and an increase in ANC (REA, section 4.2.4.2). In the Shenandoah Mountains, there was a slight decrease in nitrate and sulfate concentration in surface waters corresponding to modest increase

in ANC from 50 ueq/L in 1990 to 67 ueq/L in 2006 (REA, section 4.2.4.3 and Appendix 4, section 3.4).

- **What ecosystem modeling approaches should be considered to link ANC and deposition?**

In the REA, the quantified relationship between deposition and ANC was investigated using ecosystem acidification models, also referred to as acid balance models or critical loads models (chapter 2 above; REA, chapter 4 and Appendix 4). These models quantify the relationship between deposition of nitrogen and sulfur and the resulting ANC in surface waters based on an ecosystem's inherent generation of ANC and ability to neutralize nitrogen deposition through biological and physical processes. A critical load is defined as the amount of acidifying atmospheric deposition of nitrogen and sulfur beyond which a target ANC is not reached. Relatively high critical load values imply that an ecosystem can accommodate greater deposition levels than lower critical loads for a specific target ANC level. Ecosystem models that calculate critical loads form the basis for linking deposition to ANC.

As discussed in chapter 2, both dynamic and steady state models calculate ANC as a function of ecosystem attributes and atmospheric nitrogen and sulfur deposition, and can be used to calculate critical loads. Steady state models are time invariant and reflect the long term consequences associated with an ecosystem reaching equilibrium under a constant level of atmospheric deposition. Dynamic models are time variant and take into account the time dependencies inherent in ecosystem hydrology, soil and biological processes. Dynamic models like MAGIC can provide the time series response of ANC to deposition whereas steady state models provide a single ANC relationship to any fixed deposition level. Dynamic models naturally are more complex than steady state models as they attempt to capture as much of the fundamental biogeochemical processes as practicable, whereas steady state models depend on far greater parameterization and generalization of processes that is afforded, somewhat, by not having to accounting for temporal variability.

- **What is an appropriate modeling approach to link ANC and deposition for development of a nationally applicable NAAQS?**

Steady state models are capable of addressing the question of what does it take to reach and sustain a specific level of ANC, which is the question most relevant to the development of a NAAQS. Dynamic models are also capable of addressing that question, but can also address the

question of how long it takes to achieve that result. In determining an appropriate modeling approach for the development of a NAAQS, we consider both the relevance of the question addressed as well as the ability to perform modeling that provides relevant information for geographic areas across the country.

Dynamic models require a large amount of catchment level-specific data relative to steady state models. Because of the time invariant nature of steady state models, the data requirements that integrate across a broad spectrum of ecosystem processes is achievable and available now at the national level. In contrast, the data needs to support dynamic models for national-scale analyses simply are not available at this time. Water quality data exist for developing a national data base for modeling nearly 10,000 catchments in the contiguous U.S. In addition, the information provided by steady state modeling would be sufficient to develop and analyze alternative NAAQS and the kind of protection they would afford. While it would be an important goal to also obtain information about how much time it would take for a target ANC level to be achieved, the absence of such information does not preclude developing and evaluating alternative NAAQS using the AAI structure. Based on the above considerations, staff concludes that at this time steady state critical load modeling is an appropriate tool for linking long-term ANC levels to atmospheric deposition of nitrogen and sulfur for development of an AAI that has national applicability.

- **How does a steady state critical load model establish a linkage between ANC and associated levels of nitrogen and sulfur deposition?**

The steady state critical load model is used to define the amount of atmospheric deposition of nitrogen (N) and sulfur (S) beyond which a target ANC is not achieved and sustained. It is expressed as:

$$CL_{ANClim}(N + S) = ([BC]_0^* - [ANC_{lim}])Q + Neco \quad (7-2)$$

Where:

$CL_{ANClim}(N + S)$ is the critical load of deposition, with units of equivalent charge/(area-time);

$[BC]_0^*$ is the natural contribution of base cations from weathering, soil processes and preindustrial deposition, with units of equivalent charge/volume;

Q is the catchment level runoff rate governed by water mass balance and dominated by precipitation, with units of distance/time;

$[ANC_{lim}]$ is the target ANC value, with units of equivalent charge/volume; and

$Neco$ is the amount of nitrogen deposition that is effectively neutralized by a variety of biological (e.g., nutrient uptake) and physical processes, with units of equivalent charge/(area-time).

Equation 7- 2 is a modified expression that adopts the basic formulation of the SSWC and FAB steady state models that are described in chapter 2. More detailed discussion of the rationale, assumptions and derivation of equation 7- 2, as well as all of the equations in this chapter, are included in Appendix B. For now, the equation simply reflects the amount of deposition, $CL_{ANClim}(N + S)$, associated with a sustainable long-term ANC target, $[ANC_{lim}]$, given the natural system ANC generation, $[BC]_0^*$, and the capacity of the natural system to neutralize nitrogen deposition, $Neco$. We note that this expression of critical load is valid when nitrogen deposition is greater than $Neco$. The runoff rate, Q , allows for balancing mass in the two environmental mediums – atmosphere and catchment.

In considering the contributions of SO_x or NO_y species to acidification, it is useful to think of every depositing nitrogen atom as supplying one equivalent charge unit and every sulfur atom as depositing two charge units. We use equivalent charge per volume as a normalizing tool in place of the more familiar metrics such as mass or moles per volume. This allows for a clearer explanation of many of the relationships between atmospheric and ecosystem processes that incorporate mass and volume unit conventions somewhat specific to the environmental media of concern (e.g., m³ for air and liter for liquid water). Equivalent charge reflects the chemistry equilibrium fundamentals that assume electroneutrality, or balancing charge where the sum of cations always equals the sum of anions. This fundamental relationship is behind, but only partially explains, the simple ANC equation (7-1) introduced earlier:

$$ANC = \text{sum of major cations} - \text{sum of major anions.}$$

At this stage we use the terms S and N in the $CL_{ANClim}(N + S)$ term to broadly represent all species of sulfur or nitrogen that can contribute acidifying deposition. This follows conventions used in the scientific literature that addresses critical loads, and it reflects all

possible acidifying contributions from any sulfur or nitrogen species. For all practical purposes, S reflects SO_x as described in section 7.1, the sum of sulfur dioxide gas and particulate sulfate. However, N includes both oxidized forms, consistent with the ambient indicator, NO_y, in addition to reduced nitrogen species, ammonia and ammonium ion, referred to as NH_x. NH_x is included in the critical load formulation because it contributes to potentially acidifying nitrogen deposition. Consequently, from a mass balance or modeling perspective, the form of the standard must account for NH_x as described below. The data requirements for equation 7-2 are addressed later in section 7.2.5 after we complete the discussion of form.

- **How is reduced nitrogen deposition, NH_x, considered separately from oxidized forms of nitrogen?**

Equation 7-2 relates total nitrogen deposition to ANC. However, for the AAI form of the standard it is important to separately identify and include the direct relationship between ambient air indicators of oxides of nitrogen and sulfur and ANC, as illustrated in Figure 7-1. This can be done by separating total nitrogen deposition, N, into oxidized, NO_y, and reduced, NH_x, components:

$$CL_{ANClim}(NO_y + NH_x + SO_x) = ([BC]_0^* - [ANC_{lim}])Q + Neco \quad (7-3)$$

We can define a critical load in terms of NO_y and SO_x that takes into account the available supply of NH_x deposition:

$$CL_{ANClim}(NO_y + SO_x) = ([BC]_0^* - [ANC_{lim}])Q + Neco - NH_x \quad (7-4)$$

Where NH_x represents the combined wet and dry deposition of ammonia, NH₃, and ammonium ion, NH₄. By separating out NH_x deposition from the aggregated critical load, the amounts of combined NO_y and SO_x deposition for the critical load are identified.

7.2.3 Linking deposition to allowable concentrations

Linking deposition to “allowable” concentrations of ambient air indicators of oxides of N and S

The last major component of the simplified form illustrated in Figure 7-1 addresses the linkage between deposition and allowable concentrations of ambient air indicators, NO_y and SO_x.

- **How do we link deposition to allowable concentrations?**

To link ambient air concentrations with deposition, we define a transference ratio, T, as the ratio of total wet and dry deposition to concentration, consistent with the area and time period over which the standard is defined. Since we intend to express deposition of NO_y and SO_x in terms of NO_y and SO_x concentrations, we define two transference ratios:

$$T_{SO_x} = \text{Dep}(SO_x)/[SO_x], \text{ and}$$

$$T_{NO_y} = \text{Dep}(NO_y)/[NO_y]$$

Where;

Dep(SO_x or NO_y) is the combined dry and wet deposition of SO_x or NO_y, and
[SO_x or NO_y] is the ambient air concentration of SO_x or NO_y.

Before discussing the rationale, assumptions and information to develop the transference ratios, we reconstruct equation 7-4 in concentration terms using transference ratios:

$$CL_{ANClim}(NO_y + SO_x) = ([BC]_0^* - [ANClim])Q + Neco - NHx \quad (7-4)$$

Consider the $CL_{ANClim}(NO_y + SO_x)$ term as representing the combinations of NO_y and SO_x deposition that would meet a critical load:

$$\text{Dep}(NO_y) + \text{Dep}(SO_x) = ([BC]_0^* - [ANClim])Q + Neco - NHx \quad (7-5)$$

Express the deposition of NO_y and SO_x in concentration terms and rewrite (7-5):

$$[NO_y]T_{NO_y} + [SO_x]T_{SO_x} = ([BC]_0^* - [ANClim])Q + Neco - NHx \quad (7-6)$$

Rearrange to define critical load in terms of NO_y and SO_x concentration;

$$CL (N + S) = ([BC]_0^* - [ANC_{lim}])Q + Neco = [NOy]T_{NOy} + [SOx]T_{SOx} + NHx \quad (7-7)$$

Equation 7-7 traces back to the original critical load expression, equation 7-2, with two refinements: depositions are translated to ambient air concentrations through the transference ratios, and reduced nitrogen deposition, NHx, is separated from total nitrogen deposition to allow for an expression that relates the ambient air indicators, NOy and SOx, and ANC. The rationale underlying transference ratios follows.

- **What approaches are considered for developing transference ratios?**

Transference ratios are a modeled construct, and therefore we are not able to compare directly these ratios with explicit measurable quantities. There is an analogy to deposition velocity, as a transference ratio is basically an aggregated weighted average of the deposition velocities of all contributing species across dry and wet deposition, and transference ratio units are expressed as distance/time. However, wet deposition commonly is not interpreted as the product of a concentration times a velocity. Direct wet deposition observations are available which integrate all of processes, regardless of how well they may be understood, related to wet deposition into a measurable quantity. There has been a history of nomenclature and conventions using terms such as washout ratios that incorporate the essence of transferring ambient mass to rain and cloud droplets, as summarized in Seinfeld and Pandis (1998). There are reasonable analogies between the processes governing dry and wet deposition, from a fundamental mass transfer perspective. In both cases there is a transfer of mass between the dry ambient phase and another medium, either a surface or vegetation in the case of dry deposition, or a rain droplet or cloud in the case of wet precipitation. The specific thermodynamic properties and chemical/biological reactions that govern the transfer of dry mass to plants or aqueous droplets differ, but either process can be based on conceptualizing the product of a concentration, or concentration difference, times a mass transfer coefficient which is analogous to the basic dry deposition model: dry deposition = concentration x velocity. Indeed, Seinfeld and Pandis (1998) utilize the concept of a wet deposition velocity in explaining wet deposition processes, and this rationale is captured in more detail in Appendix F.

Transference ratios require estimates of wet deposition (NOy and SOx), dry deposition (NOy and SOx) and concentrations of NOy and SOx. Possible sources of information include

model estimates or a combination of model estimates and observations, recognizing that dry deposition is a modeled quantity that can use observed or modeled estimates of concentration. The limited amount of NO_y measurements in acid sensitive areas as well as the combination of representative NO_y, SO₂ and SO₄ observations generally preclude the use of observations for a standard that is applicable nationally.

One could consider a blending of observations and models to take advantage of their relative strengths, for example, combining the NADP wet deposition observations, modeled dry deposition, and a mix of modeled and observed concentrations, using the model for those species not measured or measured with very sparse spatial coverage. A potential disadvantage of mixing and matching model estimates is to lose consistency afforded by using just modeling alone. A modeling platform like CMAQ is based on adhering to consistent treatment of mass conservation, by linking emission inputs with air concentrations and concentrations to deposition. Inconsistencies from combining processes from different analytical platforms increase the chance that mass (of nitrogen or sulfur) would unintentionally be increased or decreased as the internal checking that assures mass conservation is lost. Transference ratios incorporate a broad suite of atmospheric processes and consequently an analytical approach that instills consistency in the linkage of these processes is preferable to an approach lacking such inherent consistency. This contention does not mean that observations alone, if available, could not be used, but suggests that the inconsistencies in combining models and observations for the purposes of developing transference ratios has the potential for creating unintended artifacts.

While there is a reasonable conceptual basis for the concept of an aggregated deposition velocity we are calling a transference ratio, there is very limited ability to compare observed and calculated ratios. This is because the deposition velocity is dependent on individual species, and the mass transfer processes of wet and dry removal, while conceptually similar, are different. Consequently, there does not exist a meaningful approach to measure such an aggregated or lumped parameter. Therefore, at this time our evaluation of transference ratios is based on sensitivity studies, analysis of variability, and comparisons with other models, as described in Appendix F.

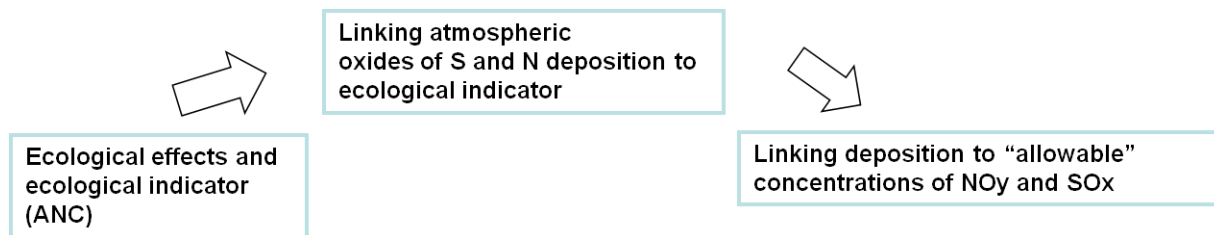
The interannual variability, as well as the sensitivity to emission changes of roughly 50%, result in changes of transference ratios of approximately 5 - 10%. Part of the reason for this inherent stability is due to the co-dependence of concentration and deposition. For example, as

concentrations are reduced as a result of emissions reductions, deposition in turn is reduced since deposition is a direct linear function of concentration leading to negligible impact on the deposition-to-concentration ratio. The same line of reasoning explains why an overestimate of concentration likely does not induce a bias in the transference ratio. While it is important to continue to improve the model's ability to match ambient concentrations in time and space, the bias of a modeled estimate of concentration relative to observations does not necessarily result in a bias in a calculated transference ratio. In effect, this consideration of bias cancellation reduces the sensitivity of transference ratios to model uncertainties and affords increased confidence in the stability of these ratios. Based on the series of sensitivity and variability analyses, staff concludes that the transference ratios are relatively stable and provide a sound metric for linking deposition and concentration in the form of the standard.

Transference ratios are dependent on the platform they are constructed upon. Comparisons of transference ratios constructed from different modeling platforms do exhibit significant differences. While this divergence of results may be explained by a variety of differences in process treatments, input fields and incommensurabilities in species definitions and spatial configurations, it does suggest two very important conclusions. First, the idea of using multiple platforms for different parts of the country may be problematic as there does not exist a reliable approach to judge acceptance which is almost always based on comparisons to observations. Second, since transference ratios are based on concentrations and deposition, as the uncertainties in each of those components are reduced, the relative uncertainty in the ratios also is reduced. This means that basic improvements in the model's ability to reproduce observed wet deposition and ambient concentration fields enhance the relative confidence in the constructed transference ratios. Similarly, as in-situ dry deposition flux measurements become available that enable a more rigorous evaluation and diagnosis of modeled dry deposition processes, the expected improved treatment of dry deposition also would increase confidence in transference ratios. Finally, deposition is directly related to ambient air concentrations. Models like CMAQ rely on the concentration-to-deposition linkage to calculate deposition, which is the foundation for broadly based and robust assessments addressing atmospheric deposition. In principle, the use of a modeled constructed transference ratio is based on the same premise by which we use models to estimate deposition in the first place.

The shortage of widely available ambient air observations and the fact that estimates of dry deposition requires modeling, collectively suggests that a unified modeling platform is the best approach for constructing transference ratios. Staff has considered CMAQ and other models (see chapter 2), such as CAMx and the Canada’s AURAMS - A Unified Regional Air-quality Modeling System (Smythe et al., 2008), and concludes that CMAQ is the preferred modeling platform for constructing transference ratios for purposes of this NAAQS review. This conclusion reflects our view that for the purposes of defining transference ratios, a modeling platform should (1) be a multiple pollutant model recognizing the myriad of connections across pollutant categories that directly and indirectly impact nitrogen and sulfur characterization, (2) include the most comprehensive scientific treatments of atmospheric processes that relate directly and indirectly to characterizing concentrations and deposition, (3) have an infrastructure capability that accommodates the inclusion of improved scientific treatments of relevant processes and important input fields, and (4) undergo frequent reviews regarding the adequacy of the underlying science as well as the appropriateness in applications. The CMAQ platform exhibits all these characteristics. It has been (and continues to be) extensively evaluated for several pollutant categories, is supported by a central infrastructure of EPA scientists, with considerable interfacing with the scientific research communities in academia and industry, whose mission is to improve and evaluate the CMAQ platform. More directly, CMAQ, and its predecessor versions, has a long track record going back to the NAPAP in the 1980’s of specific improvements in deposition processes, which are described in Appendix F.

7.2.4 Completing the link from ecological indicator to ambient air indicators



- **How is a target long-term ANC level linked to appropriate terms of ecosystem attributes, reduced nitrogen deposition, and ambient air indicators?**

The two previous sections described the links between long-term ANC and deposition (7.2.2) and deposition and ambient air concentration (7.2.3) provided by equation 7-7:

$$CL = ([BC]_0^* - [ANC_{lim}])Q + N_{eco} = [NO_y]T_{NO_y} + [SO_x]T_{SO_x} + NH_x \quad (7-7)$$

Equation (7-7) represents a relationship that defines the ambient air concentrations of NO_y and SO_x that would not exceed a specified critical load. The terms on the right side of equation 7-7 represent the maximum amount of acidifying deposition, expressed in terms of the concentrations of ambient air indicators, NO_y and SO_x, as well as the deposition of NH_x, that would not exceed a specified critical load. The difference between actual total acidifying deposition and the critical load is referred to as “exceedance deposition,” DEP_{ex}, where:

$$DEP_{ex} = [NO_y]T_{NO_y} + [SO_x]T_{SO_x} + NH_x - CL \quad (7-8)$$

Thus, exceedance deposition is the amount of acidifying deposition in excess of the amount of deposition that would just achieve a specified critical load.

We define a related term, “ANClim exceedance,” ANClim_{ex}, that is directly proportional to deposition exceedance by dividing by the runoff rate, Q_r, representative of the area over which all the atmospheric terms are defined:

$$ANClim_{ex} = DEP_{ex}/Q_r = \{[NO_y]T_{NO_y} + [SO_x]T_{SO_x} + NH_x - CL\}/Q_r \quad (7-9)$$

ANClim exceedance (ANClim_{ex}) is the difference between a target ANC (ANClim) and a calculated ANC for an area. Thus, we can calculate an ANC value (ANCalc) by the following equation:

$$ANCalc = ANClim - \{[NO_y]T_{NO_y} + [SO_x]T_{SO_x} + NH_x - CL\}/Q_r \quad (7-10)$$

The terms in equation 7- 10 are then rearranged to highlight the connection from the ecological indicator, ANC, to ambient air indicators, NOy and SOx, in terms of a representative critical load (CL_r) for an area:

$$ANC_{calc} = \{AN_{Clim} + CL_r/Q_r\} - NHx/Q_r - T_{NOy} [NOy]/Q_r - T_{SOx}[SOx]/Q_r \quad (7-11)$$

Equation 7-11 is the basic expression of the standard which translates the simple conceptual diagram into an explicit expression that relates ANC as a function of the ambient air indicators, NOy and SOx. Based on equation 7-11, we define an aquatic acidification index (AAI) that is more simply stated in terms that emphasize the ambient air indicators:

$$AAI = F1 - F2 - F3[NOy] - F4[SOx] \quad (7-12)$$

where the AAI represents the long term (or steady state) ANC level associated with ambient air concentrations of NOy and SOx. The AAI is the potential the atmosphere affords in influencing ecosystem ANC. The factors F1 through F4 convey three attributes: a relative measure of the ecosystem's ability to neutralize acids (F1), the acidifying potential of reduced nitrogen deposition (F2), and the deposition-to-concentration translators for NOy (F3) and SOx (F4). Specifically:

$$F1 = AN_{Clim} + CL_r/Q_r ;$$

$$F2 = NHx/ Q_r = NHx \text{ deposition divided by } Q_r;$$

$$F3 = T_{NOy}/ Q_r ; T_{NOy} \text{ is the transference ratio that converts deposition of NOy to ambient air concentrations of NOy; and}$$

$$F4 = T_{SOx}/ Q_r ; T_{SOx} \text{ is the transference ratio that converts deposition of SOx to ambient air concentrations of SOx.}$$

All of these factors include representative Q_r to maintain unit (and mass) consistency between AAI and the terms on the right side of equation 7-12.

We note that the F1 factor incorporates an ecosystem's ability to generate acid neutralizing capacity through base cation supply ($[BC]^*_0$) and to neutralize acidifying nitrogen deposition through *Neco*, both of which are incorporated in the CL term. Because *Neco* can only

neutralize nitrogen deposition (oxidized or reduced) there may be rare cases where Neco exceeds the combination of reduced and oxidized nitrogen deposition. Consequently, to ensure that the AAI equation is applicable in all cases that may occur, we recognize that equation 7-12 is conditional on total nitrogen deposition, $\{NHx + F3[NOy]\}$, being greater than Neco. In rare cases where Neco is greater than $\{NHx + F3[NOy]\}$, F2 and F3 would be set equal to 0. In such cases, CL_r would be defined only in terms of acidifying deposition of sulfur:

$$CL_r(S) = ([BC]_0^* - [ANC_{lim}])Q, \text{ only when } Neco \geq \{NHx + F3[NOy]\} \quad (7-13)$$

The consequence of setting F2 and F3 to zero and eliminating Neco from the CL expression is simply to constrain the AAI calculation just to SOx as nitrogen would have no bearing on acidifying contributions in this case.

Staff concludes that equation 7-12, which defines an AAI, is ecologically relevant and appropriate for use as the form of a national standard designed to provide protection for aquatic ecosystems from the effects associated with acidifying deposition associated with concentrations of oxides of nitrogen and sulfur in the ambient air. We note, however, that equation 7-12 does not, in itself, define the spatial areas over which the terms of the equation would apply. To specify values for factors F1 through F4, it is necessary to define spatial areas over which these factors are determined. Thus, it is necessary to identify an approach for spatially aggregating water bodies into ecologically meaningful regions across the U.S., as addressed in the next section.

7.2.5 Spatial Aggregation

One of the unique aspects of this review is the need to consider the spatial areas over which values for the factors in the AAI equation that defines the form of the standard are quantified. Ecosystems across the U.S. exhibit a wide range of geological, hydrological and vegetation characteristics that influence greatly the ecosystem parameters, Q, BC_0^* and Neco that are incorporated in the AAI. Variations in ecosystem attributes naturally lead to wide variability in the sensitivities of water bodies in the U.S. to acidification, as well as in the responsiveness of water bodies to changes in acidifying deposition. Consequently, variations in ecosystem sensitivity must be taken into account in developing a national standard. In developing a

national secondary standard to protect public welfare, our focus is on protecting sensitive populations of water bodies, not on each individual water body, which is consistent with our approach to protecting public health through primary standards that focus on susceptible populations, not on each individual.

In this section, we first describe alternative approaches to defining ecologically relevant regions across the U.S. Once spatially aggregated regions are established, we then consider approaches to characterizing each region as acid sensitive or relatively non-acid sensitive based on alkalinity and ANC data. This characterization facilitates a more detailed analysis of those regions that are relatively more acid sensitive. We also use this characterization to avoid over-protection in relatively non-acid sensitive regions that would receive limited benefit from reductions in the deposition of oxides of nitrogen and sulfur with respect to aquatic acidification effects. Further, we discuss approaches to developing representative values of each of the terms in the AAI equation (factors F1 through F4) for each ecologically relevant region. These following sections generally address spatial aggregation approaches applicable to the United States. The approaches discussed below, however, are limited to the contiguous United States since there is insufficient data available for Hawaii, Alaska and the territories to consider applying such approaches at this time. Other approaches to apply to these areas are discussed below.

Stated more simply, this section discusses appropriate ways to divide the country into ecologically relevant regions; to characterize each region as either acid sensitive or relatively non-acid sensitive; and to determine values of factors F1 through F4 for each region, taking into consideration the acid sensitivity of each region. For each such region, the AAI would be calculated based on the values of factors F1 through F4 specified for that region.

Approaches to spatial aggregation

In considering approaches to spatial aggregation, staff focused on methods that have been developed to define ecologically relevant regions, referred to as ecoregions, which are meaningfully related to the factors that are relevant to aquatic acidification. As noted above, we did not focus on looking at each individual water body. We first considered the broadest aggregation possible that looked at the entire nation as one region. We recognize that aggregating over the entire nation would preclude taking into account the inherent variability in atmospheric and ecological factors that fundamentally modify the relationships that are central to

the development of an ecologically relevant AAI. As a consequence, we conclude it is appropriate to consider approaches that divide the country into ecologically relevant regions for the purpose of defining appropriate spatial areas over which AAI factors would be specified and the AAI would be calculated.

- **What approaches are available to define ecologically relevant regions in the U.S.?**

Ecoregions are areas of similarity regarding patterns in vegetation, aquatic, and terrestrial ecosystem components. Available ecoregion categorization schemes include EPA's Omernik classifications (<http://www.epa.gov/wed/pages/ecoregions.htm>, Omernik, 1987), the National Ecological Observatory Network (NEON, <http://www.neoninc.org/>) domains, and Bailey's ecoregions developed for the United States Forest Service (USFS).

The NEON domains are under development and the current design is based on 20 eco-climatic regions, each with similarities in vegetation, landforms, and climate. One goal of NEON, which is supported by the U.S. National Science Foundation, is to develop a baseline of ecological data for use in variety of applications, especially to observe the effects of changing climates on ecosystem parameters and performance. Bailey's ecoregions also group regions based on similar vegetation and climatic conditions. There are no apparent advantages of NEON or Bailey's scheme relative to the Omernik classification system. The lack of more resolved spatial groupings as well as being in the developmental stage limits the utility of the NEON domains at this time. Neither Bailey's scheme nor NEON has undergone a level of peer review and scientific scrutiny comparable to that achieved with the Omernik scheme. Omernik's scheme is well documented and used frequently in the ecosystem community which has resulted in readily accessible data and an increased knowledge base of its utility.

Omernik's ecoregions are categorized using a holistic, "weight-of-evidence" approach in which the relative importance of factors may vary from region to region. The method used to map ecoregions is described in Omernik (1987), as one that is:

“. . . based on the premise that ecological regions can be identified through the analysis of the patterns and the composition of biotic and abiotic phenomena that affect or reflect differences in ecosystem quality and integrity (Omernik, 1987). These phenomena include geology, physiography, vegetation, climate, soils, land use, wildlife, and hydrology. The relative importance of each characteristic varies from one ecological region to another regardless of the hierarchical level.”

The first publication of the ecoregions based on Omernik's weight-of-evidence approach was published in 1987 (Omernik, 1987). Current maps found in <http://www.epa.gov/wed/pages/ecoregions.htm> are refinements and revisions of the 1987 publication. Hierarchical levels were developed and a Roman numeral classification scheme was adopted to distinguish coarser (more general) and finer (more detailed) categorization. Level I is the coarsest level, dividing North America into 15 ecoregions. At level II, the continent is subdivided into 52 ecoregions. Level III is a further subdivision of level II, and divides North America into 120+ ecoregions. Level IV is a subdivision of level III, and development of maps for this level is currently in progress.

- **What ecoregion categorization scheme is most applicable for the purpose of defining the AAI?**

For the reasons discussed above, staff concludes that Omernik's ecoregion classification is the most appropriate method to consider for the purposes of this review as it offers several levels of spatial delineation, has undergone an extensive scientific peer review process, and has explicitly been applied to delineating acid sensitive areas within the United States. Further, we conclude that ecoregion level III (Figure 7-5) resolution with 84 defined regions in the contiguous United States⁵ is the most appropriate level to consider for this purpose. The spatial resolution afforded by Level III strikes an appropriate balance relative to the reasoning that supports staff conclusions on indicators, as discussed above in section 7.1. We conclude that the most detailed level of resolution (level IV) is not appropriate given (1) the limited data availability to address nearly 1000 subdivisions within that level and (2) the currently evolving nature of level IV regions. Further, we conclude that level III regions are preferred to level II in that level III regions, but not level II regions, are largely contiguous in space which allows for a more coherent development of information to quantify the AAI factors and to characterize the concentrations of NO_y and SO_x in the ambient air within each region.

Appendix C includes a description of each level III ecoregion. While the use of ecoregions is an appropriate spatial aggregation scheme for this NO_y/SO_x standard focused on aquatic acidification, many of the same ecoregion attributes may be applicable in subsequent NAAQS reviews that may address other deposition-related aquatic and terrestrial ecological effects. Because atmospheric deposition is modified by ecosystem attributes, the types of

⁵ We note that an 85th area within Omernik's Ecoregion Level III is currently being developed for California.

vegetation, soils, bedrock geology, and topographic features that are the basis of this ecoregion classification approach also will be key attributes for other deposition-related effects (e.g., terrestrial acidification, nutrient enrichment) that link atmospheric concentrations to an aquatic or terrestrial ecological indicator. Just as this aquatic acidification standard links atmospheric and ecosystem processes, future NO_y/SO_x standards that consider other deposition-related effects may well include ecosystem-based processing of deposition inputs as they translate to a defined ecological indicator.

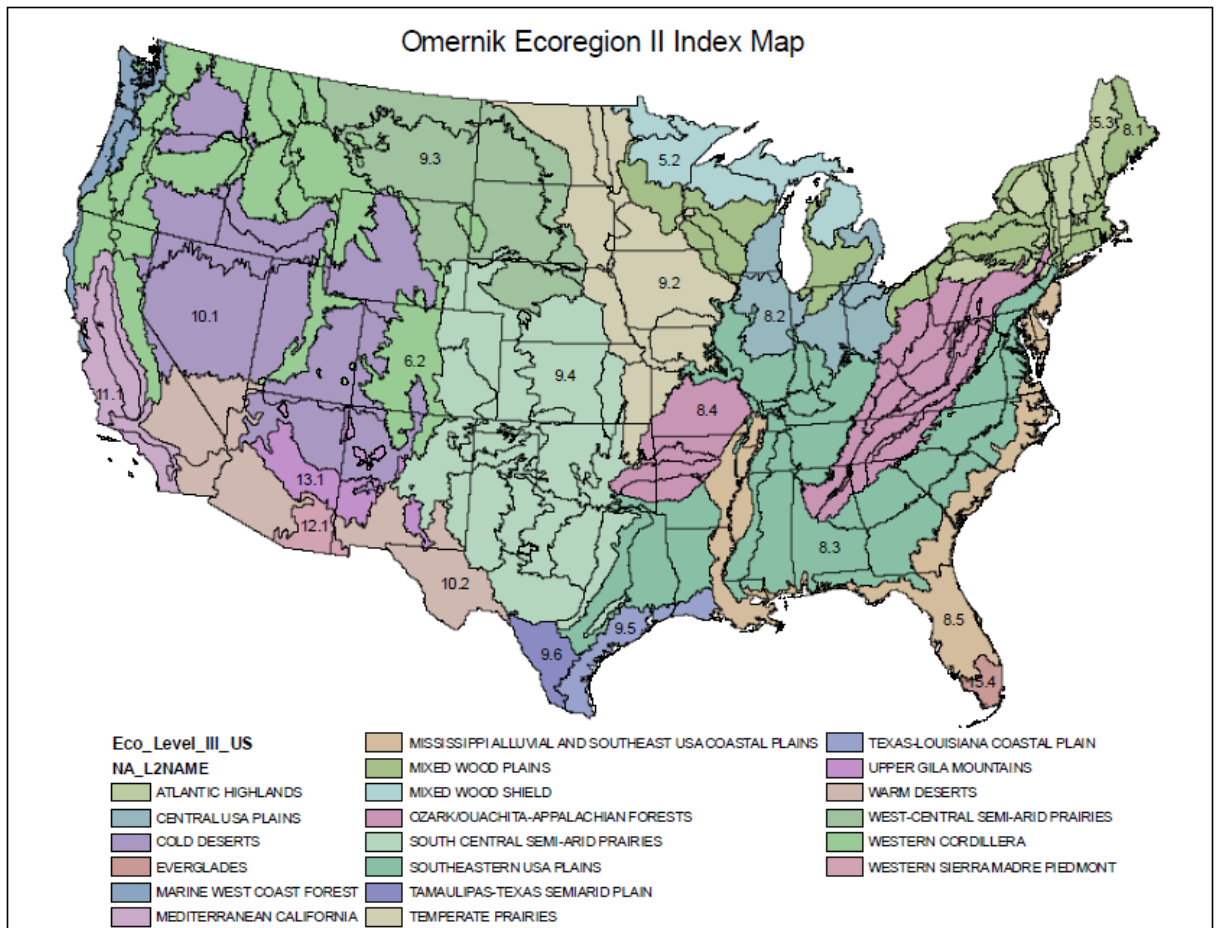


Figure 7-5. Omernik Ecoregion II areas with ecoregion III subdivisions (<http://www.epa.gov/wed/pages/ecoregions>). There are 20 Ecoregion II categories, each of which are further subdivided into a total of 84 Level III categories.

Characterizing ecoregion level III sensitivity

Staff has used Omernik's original alkalinity data (chapter 2) and more recent ANC data (as discussed above in chapter 2) to delineate two broad groupings of ecoregions: acid sensitive and relatively non-acid sensitive ecoregions. This delineation was performed to enable greater focus on those regions with water bodies that generally have greater acid sensitivity and to avoid over-protection in regions with generally less sensitive water bodies. Our approach to delineating acid sensitive and relatively non-acid sensitive regions, which is discussed more fully below in section 7.5, included an initial numerical-based sorting scheme using ANC data. Following this initial delineation, we reviewed other water quality parameters to identify naturally acidic conditions associated with low base cation supply or high organic acid levels, which would support characterizing a region as relatively less-acid sensitive, which is addressed later in section 7.5. In addition, we considered the degree to which ecoregions exceed representative critical loads based on current and future deposition levels, which provided insight into the likelihood that a region is naturally acidic and unlikely to be responsive to changes in concentrations of NO_y and SO_x in the ambient air and thus to changes in related deposition levels. These reviews based on analyzing available data were supplemented by considering to what extent a region is characterized as a relatively pristine, rural undeveloped area that is not predominantly managed for agricultural or forest products, as described in chapter 1. This last consideration allows for the application of common sense judgments to avoid over-protection, which cannot be arrived at through data analysis alone. The overall objective is to produce a logical and practical grouping of ecoregions that experience adverse conditions with respect to aquatic acidification and are likely to respond to changes in concentrations of NO_y and SO_x in the ambient air and to the related deposition levels.

The initial delineation of acid sensitive and relatively non-acid sensitive regions used ANC data to determine the number of water bodies within the region with long-term ANC values suggestive of acid sensitivity, so as to screen out regions with an overabundance of high ANC values. In our review of this ANC data, we identified regions that have greater than 5% of water bodies with data with ANC values less than 200 µeq/L and that have greater than 1% of water bodies with ANC values less than 100 µeq/L. Applying these criteria yielded 29 acid sensitive ecoregions (Figure 7-6). The resulting acid sensitive ecoregions resemble the patterns of acid sensitivity in the original Omernik alkalinity map (Figure 2-39) and in the similar ANC map

(Figure 2-40), which is an expected outcome as Figure 7-6 is derived from ANC and ALK data. The patterns reveal the simple observation that collection of ANC data has been targeted to areas of suspected or known acid sensitivity.

In addition, the acid sensitive ecoregions generally are characterized as areas with mountainous, high elevation terrain or water bodies in Northern latitudes (Northern areas of Minnesota, Wisconsin and Michigan; and New England). The northern non-mountainous regions share attributes (growing season, vegetation, soils and geology) similar to mountainous regions and typically are located in rural areas, often in tracts of designated wilderness, park and recreation areas. Of the 29 acid sensitive ecoregions, the following six ecoregions are located in two Level II ecoregions (i.e., Southeastern Plains (8.3) and Mississippi Alluvial and Southeast Coastal Plains (8.5); Figure 7-6) and are characterized by relative lowland plains or transitional lands between plains and hills: Piedmont (8.3.4), Southeastern Plains (8.3.5), South Central Plains (8.3.7), Middle Atlantic Coastal Plain (8.5.1), Southern Coastal Plains (8.5.3) and Atlantic Coastal Pine Barrens (8.5.4). These coastal plains and transition areas are noted here and are discussed in more detail below in section 7.5 in considering alternative criteria for delineating acid sensitive and relatively non-acid sensitive ecoregions.

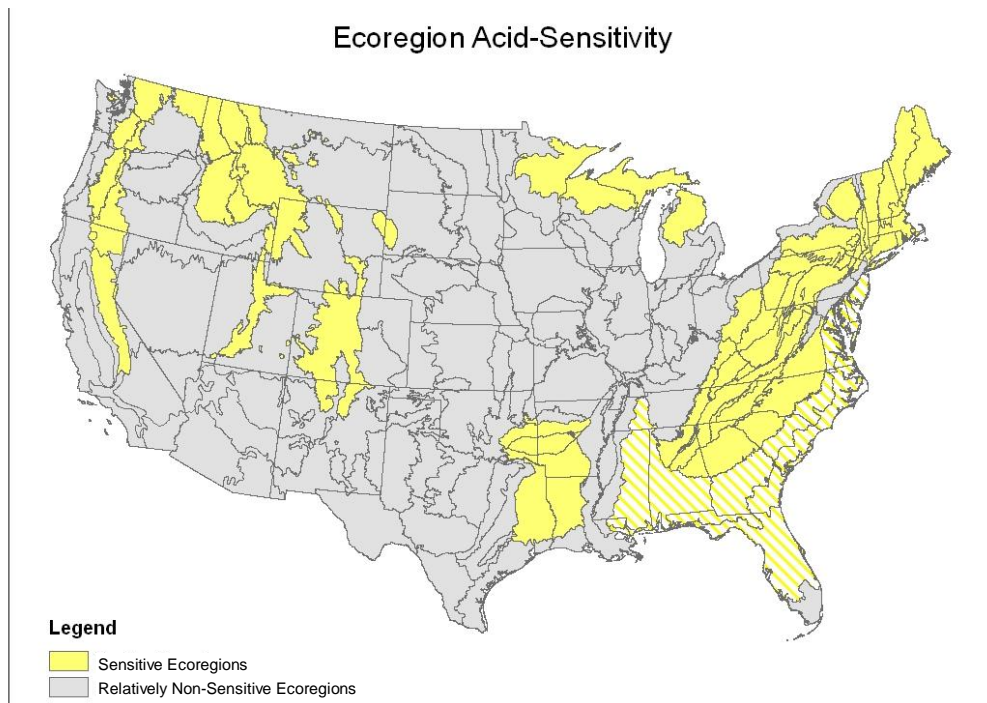
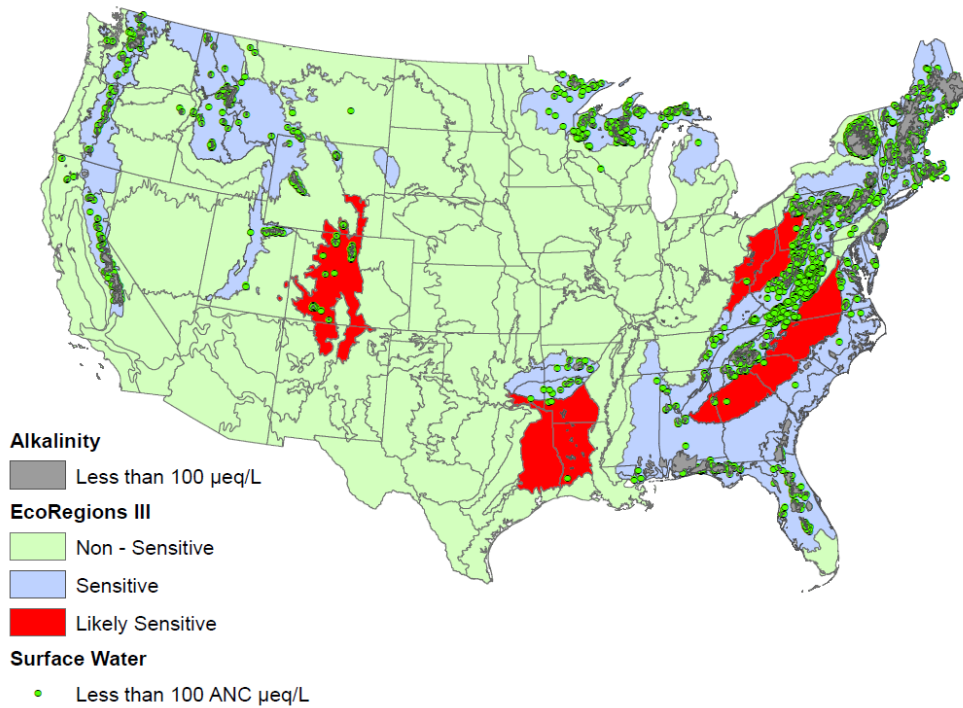


Figure 7-6. The top panel captures some of the data details used in delineating acid sensitive and relatively non-acid sensitive regions, which are shown in the bottom panel. The red areas in the top panel reflect acid sensitive areas with small samples sizes (less than 20) of water quality data. The four cross-hatched acid sensitive regions in the bottom panel are low elevation coastal plains type areas as discussed in sections 7.2 and 7.5.

Establishing representative factors for the AAI equation

Having concluded that the Omernik level III ecoregions are an appropriate approach to spatial aggregation for the purpose of an aquatic acidification standard, we use those ecoregions to define each of the factors in the AAI equation (equation 7-12 developed above in section 7.2.4):

$$AAI = F1 - F2 - F3[NOy] - F4[SOx] \quad (7-12)$$

Where:

$$F1 = AN_{Clim} + CL_r/Q_r;$$

$$F2 = NHx/Q_r; \text{ NHx is the deposition divided by } Q_r;$$

$$F3 = T_{NOy}/Q_r; T_{NOy} \text{ is the transference ratio that converts deposition of NOy to ambient air concentrations of NOy; and}$$

$$F4 = T_{SOx}/Q_r; T_{SOx} \text{ is the transference ratio that converts deposition of SOx to ambient air concentrations of SOx.}$$

The factors F1 through F4 in equation 7-12 are defined for each ecoregion by specifying ecoregion-specific values for each factor based on monitored or modeled data that are representative of each ecoregion. The F1 factor is also defined by a target ANC value (AN_{Clim}), as discussed below in section 7.4.

To specify ecoregion-specific representative values for the term CL_r in factor F1, we first create a distribution⁶ of calculated critical loads for the water bodies in the ecoregion for which we have sufficient water quality and hydrology data.⁷ We then define the representative critical load to be a specific percentile, the nth percentile, of the distribution of critical loads in the ecoregion. Thus, for example, using the 90th percentile means that within an ecoregion, 90 percent of the water bodies would be expected to have higher calculated critical loads than the representative critical load. The choice of an appropriate range of percentile values to consider is discussed below in response to the next question. To specify ecoregion-specific representative

⁶ In this PA, the distribution of critical loads was based on CL values calculated with Neco at the lake level. Consideration should be given to using a distribution of CLs without Neco and adding the ecoregion average Neco value to the nth percentile critical load. This would avoid cases where the lake level Neco potentially could be greater than total nitrogen deposition.

⁷ We judge the data to be sufficient for this purpose if data are available from more than 10 water bodies in an ecoregion.

values for the term Q_r , which is used in factors F1 through F4, we use the median value of the distribution of Q values that are available for water bodies within each ecoregion.

To specify ecoregion-specific representative values for the remaining terms in the AAI equation, NH_x , T_{NO_y} , T_{SO_x} , NO_y , and SO_x , we use data averaged over the ecoregion. Each of these terms is based on 2005 CMAQ model simulations over 12-km grids, discussed above in chapter 2. The CMAQ simulation provides estimates of deposition of NH_x , NO_y , and SO_x , as well as ambient air concentrations of NO_y and SO_x . All of these terms are based on annual average model outputs for each grid cell, which are spatially averaged across all the grid cells contained in each ecoregion to calculate a representative annual average value for each ecoregion. The transference ratios, T_{NO_y} and T_{SO_x} , are calculated as the annual deposition spatially averaged across the ecoregion and divided by the annual ambient air concentration spatially averaged across the ecoregion. We conclude that this approach of using spatially averaged values is appropriate, largely due to the relatively rapid mixing of air masses due to gaseous-based advection and dispersion processes that typically results in relatively homogeneous air quality patterns for regionally dispersed pollutants. In addition, there is greater confidence in using spatially averaged modeled atmospheric fields than in using modeled point-specific fields.

Of these terms, NH_x deposition perhaps exhibits greater spatial variability, as well as overall uncertainty, than the other terms. On this basis, we conclude that it would also be appropriate to consider allowing the use of alternative approaches to specifying the value of NH_x . One such approach might involve the use of more localized and/or contemporaneous modeling in areas where this term is likely to be particularly variable and important. Such an alternative approach could allow for more localized changes over time in the concentration of NH_x to be reflected in the calculated AAI value for an ecoregion. Other approaches might involve the use of monitored NH_x data as the concentration variable applied in dry deposition modeling.

The ecoregion-specific values for factors F1 through F4 would be codified as part of a standard that is defined in terms of the AAI. For the purpose of calculating AAI values that reflect recent air quality in the absence of NO_y and SO_x monitoring data in each ecoregion, we use the annual average NO_y and SO_x concentrations that result from the 2005 CMAQ model simulation. For the purpose of applying a standard defined in terms of the AAI in the future,

NO_y and SO_x would be determined by measuring the annual average concentrations of NO_y and SO_x in the ambient air. The measured values of NO_y and SO_x would then be used in equation 7-12, together with the values for F1 through F4 that are specified for each ecoregion, to calculate an annual AAI for an ecoregion.

- **What range of nth percentile values is appropriate to consider as part of the definition of the form of the standard?**

The nth percentile value chosen as part of the definition of the form of the standard is an important parameter that directly impacts the representative critical load specified for each ecoregion, and therefore the degree of protectiveness of the standard. A higher percentile corresponds to a lower critical load and, therefore, to lower allowable ambient air concentrations of NO_y and SO_x and the related deposition to achieve a target AAI level. In conjunction with specifying the values of factors F1 through F4 as discussed above, alternative forms for consideration can be appropriately characterized in part by identifying a range of alternative percentile values for consideration. Consequently, we assess alternative standards below (section 7.5) by specifying alternative combinations of percentile values, as discussed here, and target ANC values, which would equate to standard levels, discussed below in section 7.4, within the ranges identified as appropriate to consider in this review.

In identifying percentile values that are appropriate to consider, we take into consideration the characterization of the ecoregions as acid sensitive or as relatively non-acid sensitive, as discussed above. In considering ecoregions characterized as acid sensitive, we judge that it is appropriate to focus on the upper part of the distribution of critical loads, so as to ensure that the ecoregion would be represented by relatively more acid sensitive water bodies within the ecoregion. Specifying the form in this way would help to define a standard that would be protective of the population of acid sensitive water bodies within an ecoregion, recognizing that even ecoregions characterized as acid sensitive may contain a number of individual water bodies that are not acid sensitive. We also recognize that there is no basis for independently evaluating the degree of protectiveness afforded by any specific percentile value, since it is the combination of form and level, in conjunction with the indicator and averaging time, which determine the degree of protectiveness. In light of this, we conclude that it is appropriate to consider initially a range of percentile values, from well above the 50th percentile, or median, of the distribution to somewhat below the highest value. For purposes of this policy assessment, we

have considered percentile values in the range of the 70th to the 90th percentile. We conclude that it would not be appropriate to represent an ecoregion with the highest or near highest critical load so as to avoid potential extreme outliers that can be seen to exist at the extreme end of the data distributions, which would not be representative of the population of acid sensitive water bodies within the ecoregion. Also, in considering ecoregions that are inherently acid sensitive, we have limited the lower end of our range of consideration to the 70th percentile, a value well above the median of the distribution.

With regard to relatively non-acid sensitive ecoregions, we recognize that while such ecoregions are generally less sensitive to acidifying deposition from oxides of nitrogen and sulfur, they may contain a number of water bodies that are acid sensitive. This category includes ecoregions that are well protected from acidification effects due to natural production of base cations and high ANC levels, as well as naturally acidic systems with limited base cation production and consequently very low critical loads. Therefore, the use of a critical load that would be associated with highly sensitive water bodies in a naturally acidic system would impose a high degree of relative protection in terms of allowable ambient air concentrations of oxides of nitrogen and sulfur and related deposition, while potentially affording little or no public welfare benefit from attempting to improve a naturally acidic system. Based on these considerations, we conclude it is appropriate to consider the use of a range of percentile values that extends lower than the range identified above for acid sensitive ecoregions. Consideration of a lower percentile would avoid representing a relatively non-acid sensitive ecoregion by a critical load associated with relatively more sensitive water bodies. In particular, we conclude it is appropriate to focus on the median or 50th percentile of the distribution of critical loads so as to avoid over-protection in such ecoregions. Recognizing that relatively non-acid sensitive areas generally are not sampled to the extent that acid sensitive regions are, it also is appropriate to consider using the median critical load of all relatively non-acid sensitive areas.

- **How do we calculate AAI factors in data-limited ecoregions?**

The initial delineation of acid sensitive and relatively non-acid sensitive ecoregions was based on available ANC and alkalinity data. Areas not meeting the ANC criteria described above are categorized as relatively non-acid sensitive. The development of a reasonable distribution of critical loads for water bodies within an ecoregion for the purpose of identifying

the n^{th} percentile representative critical load requires additional data, including more specific water quality data for major cations and anions. This means that the water bodies that can be used to develop a distribution of critical loads is generally a subset of those water bodies for which ANC data are available. Consequently, there are certain ecoregions with sparse data that are not suitable for developing a distribution of critical loads.

As noted above, we judge that it is not appropriate to develop such distributions based on data from less than ten water bodies within an ecoregion. Such ecoregions, which included only relatively non-acid sensitive ecoregions, were characterized as being data-limited. We identified 12 such ecoregions, and for these ecoregions we considered alternative approaches to specifying values for the terms CL_r and Q_r for the purpose of determining values for each of the factors in the AAI equation. For these data-limited ecoregions, we judge that it is appropriate to use the median values of CL_r and Q_r from the distributions of these terms for all other relatively non-acid sensitive ecoregions, rather than attempting to use severely limited data to develop a value for these terms based solely on data from such an ecoregion. We note that this data limitation is not a concern in specifying values for the other terms in the AAI equation for such ecoregions, since those terms are based on data from the 2005 CMAQ model simulation, which covers all ecoregions across the contiguous United States.

Data coverage for Hawaii, Alaska, and the U.S. Territories

The above methods apply to those ecoregions within the contiguous U.S. For those areas outside the continental U.S., there is currently a lack of available data to characterize the sensitivity of such areas, as well as a lack of water body-specific data and CMAQ-type modeling to specify values for the terms F1 through F4 in the AAI equation. Thus, we have considered possible alternative approaches to specifying values for factors F1 through F4 in the AAI equation for these areas.

One such approach could be to specify area-specific values for the factors based on values derived for ecoregions with similar acid sensitivities, to the extent that relevant information can be obtained to determine such similarities. Such an approach would involve conducting an analysis to characterize similarities in relevant ecological attributes between ecoregions in the contiguous U.S. and these areas outside the contiguous U.S. so as to determine the appropriateness of utilizing ecoregion-specific values for the CL_r and Q_r terms from one or more ecoregions within the contiguous U.S. This approach would also involve conducting

additional air quality modeling for these areas that are outside the geographical scope of the currently available CMAQ model simulations, so as to develop the other information necessary to specify values for factors F2 through F4 for these areas.

A second approach could rely on future data collection efforts to establish relevant ecological data within these areas that, together with additional air quality modeling, could be used to specify area-specific values for factors F1 through F4. Until such time as relevant data become available, these areas could be treated the same as data-limited ecoregions in the contiguous U.S. that are relatively non-acid sensitive.

Staff concludes that either approach would introduce substantial uncertainties that arise from attempting to extrapolate values based on similarity assumptions or arbitrarily assigning values for factors in the AAI equation that would be applicable to these areas outside the contiguous U.S. In light of such uncertainties, we conclude that it would also be appropriate to consider relying on the existing NO₂ and SO₂ secondary standards in these areas for protection of any potential direct or deposition-related ecological effects that may be associated with the presence of oxides of nitrogen and sulfur in the ambient air. In staff's view, relying on existing secondary standards in these areas is preferable to using a highly uncertain approach to allow for the application of a new standard based on the AAI in the absence of relevant area-specific data.

7.3 AVERAGING TIME

Aquatic acidification can occur over both long- and short-term timescales. Long-term cumulative deposition of nitrogen and sulfur is reflected in the chronic acid-base balance of surface waters as indicated by measured annual ANC levels. Similarly, the use of steady state critical load modeling, which generates critical loads in terms of annual cumulative deposition of nitrogen and sulfur, means that the focus of ecological effects studies based on critical loads is on the long-term equilibrium status of water quality in aquatic ecosystems. Much of the evidence of adverse ecological effects associated with aquatic acidification, as discussed above in chapter 3, is associated with chronically low ANC levels. Protection against a chronic ANC level that is too low is provided by reducing overall annual average deposition levels for nitrogen and sulfur.

Reflecting this focus on long-term acidifying deposition, we developed the AAI that links ambient air indicators to deposition-related ecological effects, in terms of several factors, F1

through F4. As discussed above, these factors are all calculated as annual average values, whether based on water quality and hydrology data or on CMAQ model simulations. In the context of a standard defined in terms of the AAI, staff concludes that it is appropriate to consider the same annual averaging time for the ambient air indicators as is used for the factors in the AAI equation.

We also recognize that short-term (i.e., hours or days) episodic changes in water chemistry, often due to changes in the hydrologic flow paths (Chen et al. 1984), can have important biological effects in aquatic ecosystems. Such short-term changes in water chemistry are termed “episodic acidification.” Some streams may have chronic or base flow chemistry that is generally healthy for aquatic biota, but may be subject to occasional acidic episodes with potentially lethal consequences. Thus, short-term episodic ecological effects can occur even in the absence of long-term chronic acidification effects.

Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the eastern United States. Episodic acidification can result from several mechanisms related to changes in hydrologic flow paths. For example, snow can store nitrogen deposited throughout the winter and snowmelt can then release this stored nitrogen, together with nitrogen derived from nitrification in the soil itself, in a pulse that leads to episodic acidification in the absence of increased deposition during the actual episodic acidification event. We note that inputs of nitrogen and sulfur from snowpack and atmospheric deposition largely cycle through soil. As a result, short-term direct deposition inputs are not necessarily important in episodic acidification. Thus, as noted in chapter 3 of the ISA, protection against episodic acidity events can be achieved by establishing a higher chronic ANC level.

Taken together, the above considerations support the conclusion that it is appropriate to consider the use of a long-term average for the ambient air indicators NO_y and SO_x for an aquatic acidification standard defined in terms of the AAI. The use of an annual averaging time for NO_y and SO_x concentrations would be appropriate to provide protection against low chronic ANC levels, which in turn would protect against both long-term acidification and acute acidic episodes.

We have also considered interannual variability in both ambient air quality and in precipitation, which is directly related to the deposition of oxides of nitrogen and sulfur from the ambient air. While ambient air concentrations show year-to-year variability, we note that often

the year-to-year variability in precipitation is considerably greater, given the highly stochastic nature of precipitation. The use of multiple years over which annual averages are determined would dampen the effects of interannual variability in both air quality and precipitation. For the ambient air indicators, the use of multiple-year averages would also add stability to calculations used to judge whether an area meets a standard defined in terms of the AAI. Consequently, staff concludes that an annual averaging time based on the average of each year over a consecutive 3 to 5 year period is appropriate to consider for the ambient air indicators NO_y and SO_x. In reaching this conclusion, we note that in its comments on the second draft PA, CASAC agreed that a 3 to 5 year averaging time was appropriate to consider (Russell and Samet, 2010b; p.4).

7.4 LEVEL

As discussed above in section 7.2.1, ANC is the ecological indicator best suited to reflect the sensitivity of aquatic ecosystems to acidifying deposition from oxides of nitrogen and sulfur in the ambient air. ANC is an indicator of the aquatic acidification expected to occur given the natural buffering capacity of an ecosystem and the loadings of nitrogen and sulfur resulting from atmospheric deposition. Thus, in this PA we have developed a new standard for aquatic acidification that is based on the use of chronic ANC as the ecological indicator as a component in the AAI.

The level of the standard would be defined in terms of a single, national value of the AAI. The standard would be met at a monitoring site when the multi-year average of the annual values of the AAI was equal to or *above* the specified level of the standard,⁸ where the annual values of the AAI would be calculated based on the AAI equation using the assigned ecoregion-specific values for factors F1 through F4 and monitored annual average NO_y and SO_x concentrations. Since the AAI equation is based on chronic ANC as the ecological indicator, the level chosen for the standard would reflect a target chronic ANC value. The assigned F factors for each ecoregion would be determined by EPA based on water quality and hydrology data, CMAQ modeling, the selected percentile value that is used to identify a representative critical load within the ecoregion, and the level of the standard. The combination of the form of the standard (section 7.2), defined by the AAI equation and the assigned values of the F factors in

⁸ Unlike other NAAQS, where the standard is met when the relevant value is at or *below* the level of the standard since a lower standard level is more protective, in this case a higher standard level is more protective.

the equation, other elements of the standard including the ambient air indicators (section 7.1) and their averaging time (section 7.3), and the level of the standard determines the allowable levels of NO_y and SO_x in the ambient air within each ecoregion. All of the elements of the standard together determine the degree of protection from adverse aquatic acidification effects associated with oxides of nitrogen and sulfur in the ambient air. The level of the standard plays a central role in determining the degree of protection provided and is discussed below.

We focus primarily on information that relates degrees of biological impairment associated with adverse ecological effects to aquatic ecosystems to alternative levels of ANC in reaching staff conclusions regarding the range of target ANC levels that is appropriate to consider for the level of the standard. We develop the rationale for identifying a range of target ANC levels that is appropriate to consider by addressing questions related to the following areas:

- (1) associations between ANC and pH levels to provide an initial bounding for the range of ANC values to be considered;
 - (2) evidence that allows for the delineation of specific ANC ranges associated with varying degrees of severity of biological impairment ecological effects;
 - (3) the role of ANC in affording protection against episodic acidity;
 - (4) implications of the time lag response of ANC to changes in deposition;
 - (5) past and current examples of target ANC values applied in environmental management practices; and
 - (6) data linking public welfare benefits and ANC.
- **What range of pH levels is useful to help inform an initial bounding of target ANC levels?**

As discussed above in chapter 3, specific levels of ANC are associated with differing levels of risk of biological impairment in aquatic ecosystems, with higher levels of ANC resulting in lower risk of ecosystem impacts, and lower ANC levels resulting in risk of both higher intensity of impacts and a broader set of impacts. While ANC is not the causal agent determining biological effects in aquatic ecosystem, as discussed above in section 7.2, it is a useful metric for determining the level at which a water body is protected against risks of acidification. There is a direct correlation between ANC and pH levels which, along with dissolved aluminum, are more closely linked to the biological causes of ecosystem response to acidification.

Because there is a direct correlation between ANC and pH levels, we can inform the selection of target ANC levels in part through information on effects of pH as well as direct studies of effects related to ANC. Levels of pH are closely associated with ANC in the pH range of approximately 4.5 to 7 (Figure 7-2). Within this range, higher ANC levels are associated with higher pH levels. At a pH level of approximately 4.5, further reductions in ANC generally do not correlate with pH, as pH levels remain at approximately 4.5 while ANC values fall substantially. Similarly, at a pH value of approximately 7, ANC values can continue to increase with no corresponding increase in pH. As pH is the primary causal indicator of aquatic acidification related effects, this suggests that ANC values below approximately $-50 \mu\text{eq/L}$ (the apparent point in the relationship between pH and ANC where pH reaches a minimum) are not likely to result in further damage, while ANC values around and above approximately $100 \mu\text{eq/L}$ (the apparent region in the relationship where pH reaches a maximum) are not likely to confer additional protection. As a result, our initial focus is on target ANC values in the range of -50 to $100 \mu\text{eq/L}$.

- **What specific ANC ranges are related to varying degrees of effects on aquatic ecosystems?**

As discussed above in chapter 3 and section 7.2, the number of fish species present in a water body has been shown to be positively correlated with the ANC level in the water, with higher values supporting a greater richness and diversity of fish species (Figures 7-3 and 7-4). The diversity and distribution of phyto-zooplankton communities also are positively correlated with ANC.

Within the ANC range from approximately -50 to $100 \mu\text{eq/L}$, linear and sigmoidal relationships are observed (shown in Figures 7-3 and 7-4, respectively) between ANC and ecosystem effects. On average, fish species richness is lower by one fish species for every $21 \mu\text{eq/L}$ decrease in ANC in Shenandoah National Park streams (ISA, section 3.2.3.4). As shown in Table 3-3, ANC levels have been grouped into five categories related to expected ecological effects, including categories of acute concern ($<0 \mu\text{eq/L}$), severe concern ($0-20 \mu\text{eq/L}$), elevated concern ($20-50 \mu\text{eq/L}$), moderate concern ($50-100 \mu\text{eq/L}$), and low concern ($>100 \mu\text{eq/L}$). This categorization is supported by a large body of research completed throughout the eastern United States (Sullivan et al., 2006).

Water bodies with ANC values less than or equal to 0 $\mu\text{eq/L}$ are chronically acidic. Such ANC levels can lead to complete loss of species and major changes in the ability of water bodies to support diverse biota, especially in water bodies that are highly sensitive to episodic acidification. Based on the above considerations, staff has focused on target ANC levels no lower than 0 $\mu\text{eq/L}$.

Biota generally are not harmed when ANC values are $>100 \mu\text{eq/L}$, due to the low probability that pH levels will be below 7. In the Adirondacks, the number of fish species also peaks at ANC values $>100 \mu\text{eq/L}$. This suggests that at ANC levels greater than 100 $\mu\text{eq/L}$, little risk from acidification exists in many aquatic ecosystems. At ANC levels below 100 $\mu\text{eq/L}$, overall health of aquatic communities can be maintained, although fish fitness and community diversity begin to decline. At ANC levels ranging from 100 down to 50 $\mu\text{eq/L}$, there is increasing likelihood that the fitness of sensitive species (e.g., brook trout, zooplankton) will begin to decline. When ANC concentrations are below 50 $\mu\text{eq/L}$, the probability of acidification increases substantially, and negative effects on aquatic biota are observed, including large reductions in diversity of fish species and changes in the health of fish populations, affecting reproductive ability and fitness. We recognize that while there is evidence that ANC levels above 50 can confer additional protection from adverse ecological effects associated with aquatic acidification in some sensitive ecosystems, the expectation that such incremental protection from adverse effects will continue up to an ANC level of 100 is substantially reduced. In staff's view, the above considerations support a focus on target ANC levels up to a level greater than 50 $\mu\text{eq/L}$ but below 100 $\mu\text{eq/L}$, such as up to a level of 75 $\mu\text{eq/L}$.

In considering the available scientific evidence, as summarized here and discussed in more detail in the ISA and REA, we note that in its review of the second draft PA CASAC expressed the following views about the range of biological responses that corresponds to this range of ANC levels (i.e., 0-100 $\mu\text{eq/L}$):

“There will likely be biological effects of acidification at higher ANC values within this range, and there are relatively insensitive organisms that are not impacted at ANC values at the low end of this range. Adverse effects of acidification on aquatic biota are fairly certain at the low end of this range of ANC and incremental benefits of shifting waters to higher ANC become more uncertain at higher ANC levels. There is substantial confidence that there are adverse effects at ANC levels below 20 $\mu\text{eq/L}$, and reasonable confidence that there are adverse effects below 50 $\mu\text{eq/L}$. Levels of 50 $\mu\text{eq/L}$ and higher would provide additional protection, but the Panel has less confidence in the significance

of the incremental benefits as the level increases above 50 $\mu\text{eq/L}$.” (Russell and Samet, 2010b; pp. 15-16)

The above considerations, including the views of CASAC, provide support for focusing on target ANC levels in the range of 20 to 75 $\mu\text{eq/L}$.

- **What is the role of ANC in protecting against low pH levels and episodic acidity?**

Across the broad range of ANC values from 0 to 100 $\mu\text{eq/L}$, ANC affords protection against the likelihood of decreased pH (and associated increases in Al). In general, the higher the ANC within this range, the lower the probability of reaching low pH levels where direct effects such as increased fish mortality (Table 3-1) occur. Accordingly, greater protection would be achieved by target chronic ANC values set high enough to avoid pH depression to levels associated with elevated risk.

The specific relationship between ANC and the probability of reaching pH levels of elevated risk varies by water body and fish species. ANC levels below 20 $\mu\text{eq/L}$ are generally associated with high probability of low pH, leading to death or loss of fitness of biota that are sensitive to acidification (ISA, section 5.2.2.1; REA, section 5.2.1.2). At these levels, during episodes of high acidifying deposition, brook trout populations may experience lethal effects. In addition, the diversity and distribution of zooplankton communities decline sharply at ANC levels below 20 $\mu\text{eq/L}$. Overall, there is little uncertainty that significant effects on aquatic biota are occurring at ANC levels below 20 $\mu\text{eq/L}$.

It is clear that at ANC levels approaching 0 $\mu\text{eq/L}$ (Table 3-1), there is significant impairment of sensitive aquatic ecosystems with almost complete loss of fish species. Avoiding ANC levels approaching 0 $\mu\text{eq/L}$ is particularly relevant to episodic spikes in acidity that occur during periods of rapid snow melt and during and after major precipitation events. Since the ANC range we are discussing here reflects average, long-term sustained values, consideration should be given to protecting against episodic drops in ANC values to a level as low as 0 $\mu\text{eq/L}$. The above considerations do not provide support for a target chronic ANC level as low as 0 $\mu\text{eq/L}$ for a standard that would protect against significant harm to aquatic ecosystems, including harm from episodic acidification. In staff’s view, these considerations also support a lower end of the range for consideration no lower than 20 $\mu\text{eq/L}$.

We note that CASAC agreed with this view in its comments on the second draft PA (Russell and Samet, 2010b; p. 16). CASAC noted that “there are clear and marked biological effects at ANC values near 0 $\mu\text{eq/L}$, so this is probably not an appropriate target value” for the AAI. With regard to the likelihood of impairment of aquatic ecosystems due to episodic acidification, in terms of specific target levels for chronic ANC, CASAC expressed the following view:

“Based on surface waters studied in the Northeast, decreases in ANC associated with snowmelt [are] approximately 50 $\mu\text{eq/L}$. Thus, based on these studies, a long term ANC target level of 75 $\mu\text{eq/L}$ would generally guard against effects from episodic acidification down to a level of about 25 $\mu\text{eq/L}$.” (Russell and Samet, 2010b; p. 26)

- **What are the implications of considering ecosystem response time?**

When considering a standard level to protect against aquatic acidification, it is appropriate to take into account both the time period to recovery as well as the potential for recovery in acid sensitive ecoregions. Ecosystems become adversely impacted by acidifying deposition over long periods of time and have variable time frames and abilities to recover from such perturbations. Modeling presented in the REA (REA, section 4.2.4) shows the estimated ANC values for Adirondack lakes and Shenandoah streams under pre-acidification conditions and indicates that for a small percentage of lakes and streams, natural ANC levels would have been below 50 $\mu\text{eq/L}$. Therefore, for these water bodies, reductions in acidifying deposition are not likely to achieve an ANC of 50 $\mu\text{eq/L}$ or greater. Conversely, for some lakes and streams the level of perturbation from long periods of acidifying deposition has resulted in very low ANC values compared to estimated natural conditions. For such water bodies, the time to recovery would be largely dependent on future inputs of acidifying deposition.

Setting a standard level in terms of a target chronic ANC level is based on the long-term response of aquatic ecosystems. The time required for a water body to achieve the target ANC level given a decrease in ambient air concentrations of NO_y and SO_x and related acidifying deposition such that the critical load for that target ANC is not exceeded is often decades if not centuries. In recognition of the potential public welfare benefits of achieving the target ANC in a shorter time frame, the concept of target loads had been developed. Target loads represent the depositional loading that is expected to achieve a particular level of the ecological indicator by a given time. For example, to achieve an ANC level of 20 $\mu\text{eq/L}$ by 2030, it might be necessary to

specify a higher target ANC level of, for example, 50 $\mu\text{eq/L}$, such that the depositional loading would be reduced more quickly than would occur if the depositional loading was based on achieving a target ANC level of 20 $\mu\text{eq/L}$ as a long-term equilibrium level. In this example, the target ANC of 50 $\mu\text{eq/L}$ would ultimately be realized many years later.

The above considerations have implications for selecting an appropriate standard level, in that the standard level affects not only the ultimate degree of protection that would be afforded by the standard, but also the time frame in which such protection would be realized. However, we recognize that there is a great deal of heterogeneity in response times among water bodies and that there is only very limited information from dynamic modeling that would help to quantify recovery time frames in areas across the country. As a consequence, we recognize that quantification of a general relationship between critical loads associated with a specific long-term target ANC level and target loads associated with achieving the target ANC level within a specific time frame is not currently possible. Thus, while the time frame for recovery is an important consideration in selecting an appropriate range of levels to consider, we conclude that it can only be considered in a qualitative sense at this time.

- **What ANC target levels have been set by other organizations to protect against aquatic acidification?**

A number of regional organizations, states, and international organizations have developed critical load frameworks to protect against acidification of sensitive aquatic ecosystems. In considering the appropriate range of target ANC levels for consideration in this review, it is informative to evaluate the target ANC levels selected by these different organizations, as well as the rationale provided in support of the selected levels. Chapter 4 provides a detailed discussion of how critical loads have been developed and used in other contexts. This section summarizes such specific target values and their rationales.

The UNECE has developed critical loads in support of international emissions reduction agreements. As noted in chapter 4, critical loads were established to protect 95 percent of surface waters in Europe from an ANC less than 20 $\mu\text{eq/L}$ based on protection of brown trout. Individual countries have set alternative ANC targets; for example, Norway targets an ANC of 30 $\mu\text{eq/L}$ based on protection of Atlantic salmon.

Several states have established target ANC or pH values related to protection of lakes and streams from acidification. While recognizing that some lakes in the Adirondacks will have a

naturally low pH, the state of New York has established a target pH value of 6.5 for lakes that are not naturally below 6.5. As noted above, this level is associated with an ANC value that is likely to be between 20 and 50 $\mu\text{eq/L}$ or possibly higher. New Hampshire and Vermont have set ANC targets of 60 $\mu\text{eq/L}$ and 50 $\mu\text{eq/L}$, respectively. Tennessee has established site-specific target ANC values based on assessments of natural acidity, with a default value of 50 $\mu\text{eq/L}$ when specific data are not available.

Taken together, these policy responses to concerns about ecological effects associated with aquatic acidification indicate that target ANC values between 20 and 60 $\mu\text{eq/L}$ have been selected by states and other nations to provide protection of lakes and streams in some of the more sensitive aquatic ecosystems.

- **What relevant information is available that links public welfare benefits to alternative target ANC levels?**

The point at which effects on public welfare become adverse is not defined in the CAA. Characterizing a known or anticipated adverse effect to public welfare is an important component of developing any secondary NAAQS. According to the CAA, welfare effects include:

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

While the text above lists a number of welfare effects, the NAAQS is aimed at protection from adverse effects to public welfare. Consideration of adversity to public welfare in the context of the secondary NAAQS for oxides of nitrogen and sulfur can be informed by information about losses in ecosystem services associated with acidifying deposition and the potential economic value of those losses, as discussed above in chapter 4.

Ecosystem service losses at alternative ANC levels are difficult to enumerate. However, in general there are categories of ecosystem services, discussed in chapter 4, that are related to the specific ecosystem damages expected to occur at alternative ANC levels. Losses in fish populations due to very low ANC (below 20 $\mu\text{eq/L}$) are likely associated with significant losses in value for recreational and subsistence fishers. Many acid sensitive lakes are located in areas with high levels of recreational fishing activity. For example, in the northeastern U.S., where

nearly 8 percent of lakes are considered acidic, more than 9 percent of adults participate in freshwater fishing, with an estimated value of approximately \$5 billion in 2006. This suggests that improvements in lake fish populations are likely associated with significant recreational fishing value.

Inland surface waters also provide cultural services such as aesthetic and existence value and educational services. To the extent that piscivorous birds and other wildlife are harmed by the absence of fish in these waters, hunting and birdwatching activities are likely to be adversely affected. A case study of the value to New York residents of improving the health of lakes in the Adirondacks found significant willingness to pay for those improvements. When scaled to evaluate the improvement in lake health from achieving ANC values of 20 to 50 $\mu\text{eq/L}$, the study implies benefits to the New York population roughly on the order of \$600 million per year (in constant 2007\$). The survey administered in this study recognized that participants were thinking about the full range of services provided by the lakes in question – not just the recreational fishing services. Therefore the estimates of willingness to pay include resident's benefits for potential hunting and birdwatching activities and other ancillary services. These results are just for New York populations. If similar benefits exist for improvements in other acid sensitive lakes, the economic value to U.S. populations could be very substantial, suggesting that, at least by one measure of impact on public welfare, impacts associated with ANC less than 50 $\mu\text{eq/L}$ may be adverse to public welfare.

- **What are staff conclusions with regard to a range of standard levels that is appropriate to consider to protect against deposition-related aquatic acidification effects associated with oxides of nitrogen and sulfur in the ambient air?**

Based on all the above considerations, staff concludes that consideration should be given to a range of standard levels from 20 to 75 $\mu\text{eq/L}$. The available evidence indicates that target ANC levels below 20 $\mu\text{eq/L}$ would be inadequate to protect against substantial ecological effects and potential catastrophic loss of ecosystem function in some sensitive aquatic ecosystems. While ecological effects occur at ANC levels below 50 $\mu\text{eq/L}$ in some sensitive ecosystems, the degree and nature of those effects are less significant than at levels below 20 $\mu\text{eq/L}$. Levels at and above 50 $\mu\text{eq/L}$ would be expected to provide additional protection, although uncertainties regarding the potential for additional protection from adverse ecological effects are much larger for target ANC levels above about 75 $\mu\text{eq/L}$ as effects are generally appreciably less sensitive to changes in ANC at such higher levels.

In reaching this conclusion, staff took into consideration the extent to which a target ANC level within this range would protect against episodic as well as long-term ecological effects. Levels in the mid- to upper part of this range would be expected to provide greater protection against short-term, episodic peaks in aquatic acidification, while lower levels within this range would give more weight to protection from long-term rather than episodic acidification. Similarly, levels in the mid- to upper part of this range would be expected to result in shorter time periods for recovery given the lag in ecosystem response in some sensitive ecosystems relative to levels in the lower part of this range. We also note that this range encompasses target ANC values that have been established by various States and regional and international organizations to protect against acidification of aquatic ecosystems.

We recognize that the level of standard together with the other elements of the standard, including the ambient air indicators, averaging time, and form, determine the overall protectiveness of the standard. Thus, consideration of a standard level should reflect the strengths and limitations of the evidence and assessments as well as the inherent uncertainties in the development of each of the elements of the standard. The implications of considering alternative standards, defined in terms of alternative combinations of levels and percentile values that are a critical component of the form of the standard, are discussed below in section 7.5. Key uncertainties in the various components of the standard are summarized and considered below in section 7.6.

7.5 Considerations associated with alternative standards

To provide some perspective on the implications of various alternative standards, staff assessed the number of acid sensitive ecoregions that would likely not meet a set of alternative standards. The alternative standards considered in this assessment were based on combinations of alternative levels, within the range of 20 to 75 $\mu\text{eq/L}$ identified above in section 7.4, and alternative forms, characterized by alternative representative percentile values within the range of the 70th to 90th percentile identified above in section 7.2.5. These alternative standards are also defined in terms of the other elements of the standard: ambient air indicators NO_y and SO_x identified above in section 7.1; other elements of the form of the standard, including ecoregion-specific values for factors F1 through F4 in the AAI equation, specified as discussed above in section 7.2; and an annual averaging time for NO_y and SO_x, as discussed above in section 7.3. With regard to the averaging time, we did not consider multi-year averaging of the calculated

annual AAI values due to data limitations, including, for example, the lack of CMAQ modeling for multiple consecutive years. In this assessment, we characterize an ecoregion as likely not meeting a given alternative standard if the calculated AAI value is less than the level of the standard, recognizing that higher AAI values are more protective than lower values.

The results of this assessment are presented below for each of the 29 ecoregions characterized as acid sensitive. Calculated annual AAI values, which in essence are “design values” at the ecoregion level, are shown below in Table 7-1 for each acid sensitive ecoregion for each alternative standard considered. Based on these AAI values, Table 7-2 then summarizes the number of acid sensitive ecoregions that would likely not meet each of the alternative standards considered. We also calculated AAI for all ecoregions categorized as relatively non-acid sensitive, as shown in Table D-5 in Appendix D. In all cases, these ecoregions were likely to meet all of the alternative standards considered in this assessment.

As described above in section 7.2, the AAI values presented here are based in part on data from 2005 CMAQ model simulations, which was used to generate values for F2 through F4 in the AAI equation as well as to estimate ambient air concentrations of NO_y and SO_x that reflect recent air quality in the absence of currently available monitored concentrations in sensitive ecoregions across the country. Water quality and hydrology data from water bodies within each ecoregion were also used in calculating the AAI values. Such data were initially used to calculate critical loads for each water body with sufficient data within an ecoregion so as to identify the nth percentile critical load representative of the ecoregion used in calculating the F1 factor for the ecoregion. In developing the distribution of critical loads for each ecoregion, three approaches were considered to define the water bodies included in the distribution. These approaches included using (1) all water bodies with available data, (2) screening out water bodies with SO₄⁻² levels > 400 µeq/L as an indicator acid mine drainage activities and (3) adding additional screening to eliminate water bodies with DOC values >10mg/L or critical loads less than 10 meq/m²-yr, as indicators of naturally acidic systems. Here, we present results of analyses that did not include any screens as there were only marginal differences in the results with or without applying the screens. The inclusion of all water bodies also provided useful diagnostic information. Because the representative critical load for an ecoregion is an important quantity that reflects the nth percentile sensitivity, consideration should be given to alternative methods such as using an interpolated nth percentile value based on the distribution of critical

loads rather than using a water body-specific critical load based on its rank order within the distribution.

Table 7-1a. Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of **20 µeq/L.** (highlighted values indicate regions not likely to meet an alternative standard)

		70 th	75 th	80 th	85 th	90 th
6.2.4	Canadian Rockies	933.4	740.3	685.6	551.0	84.5
6.2.3	Columbia Mountains/Northern Rockies	353.5	267.3	190.3	136.5	106.3
6.2.7	Cascades	90.2	72.2	46.2	31.3	19.1
8.5.4	Atlantic Coastal Pine Barrens	-154.6	-172.7	-174.6	-182.4	-193.6
5.3.1	Northern Appalachian and Atlantic Maritime Highlands	58.3	49.0	33.6	21.3	6.4
6.2.10	Middle Rockies	180.0	122.1	99.0	81.6	69.4
8.1.3	Northern Appalachian Plateau and Uplands	227.0	173.4	165.7	120.4	85.6
8.1.7	Northeastern Coastal Zone	42.0	22.6	9.3	-4.4	-23.6
5.3.3	North Central Appalachians	-60.8	-74.4	-87.4	-97.8	-112.5
8.1.8	Maine/New Brunswick Plains and Hills	89.7	84.4	71.0	65.5	48.5
6.2.5	North Cascades	138.4	130.7	112.9	93.8	65.8
5.2.1	Northern Lakes and Forests	51.4	38.7	25.9	14.1	3.8
6.2.15	Idaho Batholith	66.8	62.0	59.3	48.0	41.6
8.4.1	Ridge and Valley	-72.3	-95.1	-117.6	-143.7	-177.8
8.4.2	Central Appalachians	-78.3	-109.0	-147.0	-169.5	-186.2
8.4.3	Western Allegheny Plateau	412.4	280.7	47.4	-20.8	-97.9
6.2.13	Wasatch and Uinta Mountains	297.8	255.3	230.6	174.6	136.6
8.5.1	Middle Atlantic Coastal Plain	-17.2	-29.5	-64.0	-131.6	-169.4
6.2.12	Sierra Nevada	49.1	38.2	28.1	22.2	12.6
6.2.14	Southern Rockies	120.6	98.5	85.7	67.6	50.8
8.4.4	Blue Ridge	-65.5	-73.5	-83.3	-93.1	-104.9
8.3.5	Southeastern Plains	-51.2	-59.2	-73.1	-91.0	-106.7
8.3.4	Piedmont	131.6	102.7	72.7	45.7	11.8
8.4.9	Southwestern Appalachians	35.3	-18.5	-29.4	-69.8	-121.5
8.4.6	Boston Mountains	65.1	65.1	27.7	8.7	-24.4
8.4.7	Arkansas Valley	90.1	82.5	66.2	50.7	-1.0
8.5.3	Southern Coastal Plain	-31.2	-61.8	-105.1	-143.2	-154.9
8.4.8	Ouachita Mountains	89.3	74.6	64.6	51.3	-3.3
8.3.7	South Central Plains	287.1	279.6	213.3	136.4	47.3

Table 7-1b. Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of 35 µeq/L. (highlighted values indicate regions not likely to meet an alternative standard)						
		70%	75%	80%	85%	90%
6.2.4	Canadian Rockies	934.4	736.5	692.4	556.9	80.9
6.2.3	Columbia Mountains/Northern Rockies	342.8	257.3	188.0	122.5	106.8
6.2.7	Cascades	92.1	74.7	47.8	30.7	21.4
8.5.4	Atlantic Coastal Pine Barrens	-160.7	-173.7	-174.3	-180.7	-192.9
5.3.1	Northern Appalachian and Atlantic Maritime Highlands	58.8	46.2	32.1	20.1	3.4
6.2.10	Middle Rockies	179.1	121.7	99.2	81.0	63.3
8.1.3	Northern Appalachian Plateau and Uplands	225.5	173.7	163.9	121.4	87.3
8.1.7	Northeastern Coastal Zone	42.3	23.2	8.9	-6.1	-24.2
5.3.3	North Central Appalachians	-59.8	-71.8	-88.7	-95.3	-114.3
8.1.8	Maine/New Brunswick Plains and Hills	89.5	84.6	72.1	65.9	47.1
6.2.5	North Cascades	144.4	125.1	110.3	86.5	71.6
5.2.1	Northern Lakes and Forests	52.7	39.6	25.7	14.3	1.0
6.2.15	Idaho Batholith	60.2	56.7	53.7	49.6	39.8
8.4.1	Ridge and Valley	-72.3	-94.0	-116.3	-144.8	-175.4
8.4.2	Central Appalachians	-80.3	-107.3	-143.2	-173.0	-182.0
8.4.3	Western Allegheny Plateau	415.2	281.4	46.2	-22.1	-94.1
6.2.13	Wasatch and Uinta Mountains	287.3	243.0	221.8	184.4	126.3
8.5.1	Middle Atlantic Coastal Plain	-16.2	-32.0	-61.4	-133.2	-163.4
6.2.12	Sierra Nevada	47.4	40.5	30.6	21.8	13.8
6.2.14	Southern Rockies	120.2	102.3	87.3	66.4	53.1
8.4.4	Blue Ridge	-65.4	-71.6	-82.4	-93.6	-104.6
8.3.5	Southeastern Plains	-55.5	-63.4	-72.1	-96.2	-107.9
8.3.4	Piedmont	131.2	96.1	72.6	43.7	14.0
8.4.9	Southwestern Appalachians	31.1	-12.2	-29.1	-71.4	-121.3
8.4.6	Boston Mountains	65.1	65.1	28.9	8.7	-21.2
8.4.7	Arkansas Valley	89.3	85.7	71.4	50.6	-2.0
8.5.3	Southern Coastal Plain	-29.1	-61.7	-106.5	-138.6	-150.8
8.4.8	Ouachita Mountains	89.5	78.9	67.4	49.3	-4.8
8.3.7	South Central Plains	291.9	275.4	210.4	133.1	47.3

Table 7-1c. Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of **50 µeq/L.** (highlighted values indicate regions not likely to meet an alternative standard)

		70%	75%	80%	85%	90%
6.2.4	Canadian Rockies	935.5	732.7	699.2	562.7	79.4
6.2.3	Columbia Mountains/Northern Rockies	327.0	262.1	192.3	132.6	106.4
6.2.7	Cascades	93.0	72.5	51.7	29.2	23.9
8.5.4	Atlantic Coastal Pine Barrens	-166.7	-174.0	-174.7	-176.5	-192.7
5.3.1	Northern Appalachian and Atlantic Maritime Highlands	57.0	44.0	30.8	17.0	1.1
6.2.10	Middle Rockies	178.2	119.5	97.5	81.6	56.9
8.1.3	Northern Appalachian Plateau and Uplands	223.9	174.1	162.2	122.4	89.0
8.1.7	Northeastern Coastal Zone	42.1	23.9	8.7	-7.2	-24.8
5.3.3	North Central Appalachians	-58.7	-69.2	-87.5	-95.5	-115.8
8.1.8	Maine/New Brunswick Plains and Hills	90.1	84.8	73.4	65.1	45.8
6.2.5	North Cascades	148.3	123.8	116.8	93.0	69.7
5.2.1	Northern Lakes and Forests	54.0	39.8	24.7	14.1	-0.2
6.2.15	Idaho Batholith	59.3	53.6	43.9	40.6	37.5
8.4.1	Ridge and Valley	-75.2	-94.4	-116.8	-144.0	-172.8
8.4.2	Central Appalachians	-82.0	-105.5	-140.5	-172.1	-182.1
8.4.3	Western Allegheny Plateau	418.0	282.2	43.2	-23.4	-90.3
6.2.13	Wasatch and Uinta Mountains	276.9	230.6	199.4	194.2	109.5
8.5.1	Middle Atlantic Coastal Plain	-15.2	-34.6	-58.8	-134.8	-157.4
6.2.12	Sierra Nevada	44.9	39.0	32.0	24.3	13.7
6.2.14	Southern Rockies	124.1	112.6	85.2	67.9	58.1
8.4.4	Blue Ridge	-65.3	-72.9	-82.7	-92.5	-102.8
8.3.5	Southeastern Plains	-57.5	-65.2	-77.2	-102.6	-112.7
8.3.4	Piedmont	125.8	99.6	74.2	40.1	14.8
8.4.9	Southwestern Appalachians	26.9	-6.0	-28.8	-73.1	-121.1
8.4.6	Boston Mountains	65.1	65.1	30.0	8.7	-17.9
8.4.7	Arkansas Valley	88.8	88.4	76.6	50.5	0.7
8.5.3	Southern Coastal Plain	-27.5	-55.8	-101.9	-134.7	-151.7
8.4.8	Ouachita Mountains	89.8	83.1	70.3	47.2	-6.2
8.3.7	South Central Plains	296.7	271.2	209.4	129.8	47.3

Table 7-1d. Calculated AAI values for acid sensitive ecoregions across the range of nth percentiles for an alternative level of **75 µeq/L.** (highlighted values indicate regions not likely to meet an alternative standard).

		70%	75%	80%	85%	90%
6.2.4	Canadian Rockies	937.2	726.3	710.5	572.5	63.5
6.2.3	Columbia Mountains/Northern Rockies	316.6	268.7	201.8	130.5	40.3
6.2.7	Cascades	89.4	70.1	49.9	36.2	11.3
8.5.4	Atlantic Coastal Pine Barrens	-166.7	-173.5	-176.4	-176.7	-205.6
5.3.1	Northern Appalachian and Atlantic Maritime Highlands	56.3	43.4	27.6	14.6	-25.3
6.2.10	Middle Rockies	176.6	125.2	98.0	83.1	32.7
8.1.3	Northern Appalachian Plateau and Uplands	225.3	174.6	159.3	128.5	-35.2
8.1.7	Northeastern Coastal Zone	43.0	25.0	8.1	-5.2	-47.4
5.3.3	North Central Appalachians	-56.9	-73.1	-85.3	-92.8	-128.1
8.1.8	Maine/New Brunswick Plains and Hills	87.9	83.2	71.7	62.5	15.2
6.2.5	North Cascades	145.6	125.1	116.0	95.4	24.4
5.2.1	Northern Lakes and Forests	54.9	41.0	26.2	12.8	-17.4
6.2.15	Idaho Batholith	55.7	44.9	38.8	30.1	13.6
8.4.1	Ridge and Valley	-73.1	-95.5	-116.5	-142.2	-203.2
8.4.2	Central Appalachians	-81.7	-106.4	-137.9	-169.5	-263.2
8.4.3	Western Allegheny Plateau	422.7	283.4	41.2	-25.6	-183.9
6.2.13	Wasatch and Uinta Mountains	259.6	210.6	186.2	168.0	71.9
8.5.1	Middle Atlantic Coastal Plain	-13.5	-38.8	-54.4	-137.4	-218.4
6.2.12	Sierra Nevada	45.9	39.6	30.8	23.9	-6.9
6.2.14	Southern Rockies	127.1	112.6	92.2	78.3	46.6
8.4.4	Blue Ridge	-64.8	-74.7	-83.3	-92.9	-116.5
8.3.5	Southeastern Plains	-59.8	-68.9	-89.3	-109.0	-142.1
8.3.4	Piedmont	126.1	98.6	70.2	37.6	-50.6
8.4.9	Southwestern Appalachians	19.9	4.4	-28.4	-75.8	-374.4
8.4.6	Boston Mountains	65.0	65.0	31.9	8.8	-12.5
8.4.7	Arkansas Valley	93.8	87.0	85.3	50.4	-7.4
8.5.3	Southern Coastal Plain	-31.0	-60.7	-94.4	-132.0	-182.4
8.4.8	Ouachita Mountains	90.2	90.2	75.1	43.8	-44.9
8.3.7	South Central Plains	304.7	264.3	220.8	124.3	20.9

Table 7-2. Summary of the number of acid sensitive ecoregions (out of 29) not likely to meet alternative standards based on a 2005 CMAQ simulation.

Sort by Percentile			Sort by ANC		
ANC	Percentile	Number	ANC	Percentile	Number
75	90	25	75	90	25
50	90	22	75	85	21
35	90	19	75	80	19
20	90	19	75	75	16
75	85	21	75	70	15
50	85	19	50	90	22
35	85	16	50	85	19
20	85	13	50	80	16
75	80	19	50	75	13
50	80	16	50	70	11
35	80	14	35	90	19
20	80	10	35	85	16
75	75	16	35	80	14
50	75	13	35	75	10
35	75	10	35	70	9
20	75	9	20	90	19
75	70	15	20	85	13
50	70	11	20	80	10
35	70	9	20	75	9
20	70	8	20	70	8

As expected, the number of ecoregions that likely would not meet alternative standards increases with increasing percentile values and standard levels (Table 7-2). Out of 29 acid sensitive ecoregions, the number of ecoregions that would likely not meet the alternative standards considered ranges from 25 for the most protective alternative standard considered (75 µeq/L, 90th percentile) to 8 for the least protective alternative standard (20 µeq/L, 70th percentile). It is apparent that both the percentile and the level chosen have a strong influence, over the ranges considered, in determining the number of areas that would likely not meet this set of alternative standards.

In considering these results, we note first that there are two groupings of ecoregions that would likely not meet almost all combinations of level and form (Table 7-2; Appendix D maps and Tables). The first group broadly reflects Coastal Plains, including Southern Coastal Plain, 8.5.3; Southeastern Plains, 8.3.5; Middle Atlantic Coastal Plain, 8.5.1; and Atlantic Coastal Pine

Barrens, 8.3.4. The second group is made up of southern Appalachian mountain areas, including North Central Appalachians, 5.3.3; Ridge and Valley, 8.4.1; Central Appalachians, 8.4.2; Blue Ridge, 8.4.4; and Southwestern Appalachians, 8.4.9. In addition, these two groupings exhibit the highest amounts of exceedance relative to alternative standards.

The Northern Appalachian and Atlantic Maritime Highlands (5.3.1), which includes the Adirondacks, and the Northern Lakes and Forests (5.2.1) of the upper midwest exhibit similar patterns with respect to in the role of level and percentile in identifying regions not likely to meet alternative standards, although there are considerably fewer cases compared to the regions in the Coastal Plains and Appalachians.

In the mountainous west, the Sierra Nevada (6.2.12), Idaho Batholith (6.2.15) and the Cascades (6.2.7) ecoregions likely do not meet alternative standards in fewer cases relative to eastern regions, with the Sierra Nevada ecoregion exhibiting relatively greater sensitivity compared to all western regions. Only in the upper part of the ranges of level and percentile do regions in the northern and central Rockies likely not meet alternative standards.

In considering these findings, it is clear that the standard as defined by the AAI behaves in an intuitively logical manner. That is, an increase in ecoregions likely not to meet the standard is associated with higher alternative levels and percentiles, both of which contribute to a lower regionally representative critical load. Moreover, the areas of known adverse aquatic acidification effects are identified, mostly in high elevation regions or in the northern latitudes -- the Adirondacks, Shenandoahs, northern midwest lakes and the mountainous west. These results reflect the first application of a nationwide model that integrates water quality and atmospheric processes at a national scale and provides findings that are consistent with our basic understanding of the extent of aquatic acidification across the U.S. What is particularly noteworthy is that this model is not initialized with a starting ANC based on water quality data, which likely would result in a reproduction of water quality observations. Rather, this standard reflects the potential of the changes in atmospheric concentrations of NO_y and SO_x to induce long-term sustained changes in surface water systems. The fact that the patterns of adversity based on applying this standard are commensurate with what is observed in surface water systems provides confidence in the basic underlying formulation of the standard.

However, the Coastal Plains and Appalachian mountain regions merit further inspection as they stand out as areas with the largest relative exceedances from a national perspective. We

considered water quality data from these regions as well as an emissions sensitivity CMAQ simulation to diagnose the behavior of these regions. The maps and tables in appendix D include paired comparisons of the CMAQ 2005 and emissions sensitivity simulations. The emissions sensitivity simulation reflects domain-wide reductions in NO_y and SO_x emissions of 48% and 42%, respectively, relative to 2005 base year emissions. We assume that this emissions sensitivity simulation is indicative of future conditions.

The emissions sensitivity results project that most the four Coastal Plains regions likely not meeting alternative standards in the 2005 base year would likely continue not to meet the standards in the future. In contrast, many of the regions that likely do not meet the alternative standards based on recent air quality, especially at alternative levels of 20 and 35 µeq/L, would likely meet such standards in the future year scenario for the Appalachian mountain regions. It is apparent that the AAI calculations are especially sensitive to changes in SO_x emissions as the Appalachian regions have the highest SO_x concentrations and deposition rates (as discussed in chapter 2), and we observe that the AAI equation responds as expected to reductions in SO_x. On the other hand, the Coastal Plains regions, especially the Atlantic Coastal Pine Barrens, have extremely low critical loads relative to the eastern U.S., such that even the least protective alternative standards are likely not met despite significant projected reductions in SO_x and NO_y emissions. The emissions sensitivity scenario is a prospective application of the standard, in the sense that rules derived from the air quality management process result in reductions of NO_y and SO_x emissions. Expected emission changes over the next two decades should be far greater than the 42 and 48% SO_x and NO_y reductions used in this analysis, with a consequent further reduction in ecoregions that would likely not meet alternative standards.

Relative to other ecoregions, water quality data for these Coastal Plains regions indicates low natural base cation supply, low runoff rates and a large percentage of water bodies with dissolved organic carbon (DOC) concentrations exceeding 5mg/L. Because of both low natural base cation supply and runoff rates, indicating poor drainage, critical loads are near the bottom of a national distribution (Table D-3). Elevated DOC and low base cation supply are indicative of naturally acidic conditions where acidity is dominated by natural sources of organic acids and, consequently, reductions in strong anions (NO₃⁻ and SO₄⁻²) resulting from reduced emissions may provide only marginal benefits. Low base cation supply is not the cause of acidity, although it is directly related to low ANC. In contrast, the Appalachian mountain regions generally have

low DOC levels, average runoff rates, moderately low base cation supply and highly elevated sulfate concentrations. Collectively, those attributes do not suggest naturally acidic conditions as the availability of anthropogenic contributions of mineral acids is likely responsible for observed low ANC values in those regions. Therefore, regions with limited base cation supply have extremely low critical loads and when accompanied by elevated DOC levels are indicative of naturally acidic systems.

The Sierra Nevada region is an interesting case study as it has the lowest critical load values nationally (Table D-2). Water quality data indicate extremely low sulfate, as expected given the relatively low SO₂ emissions in the western U.S. Extremely low base cation supply and low Neco, which mitigates the effect of nitrogen deposition, explain the low critical load values. Low Neco values appear to associate well with high elevation western U.S. regions, perhaps reflecting the more arid and reduced vegetation density relative to eastern U.S. regions. The proximity to high level nitrogen emissions combined with very low base cation supply explains the cases where the Sierra region likely does not meet alternative standards. Because Neco values are low in the Sierras, the system responds effectively to reductions of NO_x emissions as illustrated in the maps and tables of Appendix D. Although Neco affords protection from the acidifying effects of nitrogen deposition, the availability of excessive nitrogen neutralization capacity also means that reductions in nitrogen are not as effective as reductions in SO_x in reducing the calculated AAI.

In reviewing these results, it is clear that the alternative combinations of level and form presented provide context for considering the impact of different standards. Since the AAI equation has been newly developed in this assessment, these exceedance examples help to address the question of whether the AAI equation responds in a reasonable manner with regard to identifying areas of concern and to prospective changes in atmospheric conditions likely to result from future emissions reduction strategies. In staff's view, the behavior of the AAI calculations is both reasonable and explainable, which serves to increase our confidence in considering a standard defined in terms of the AAI in this review.

Further, these analyses provide additional insight in regard to categorizing the sensitivity of ecoregions as acid sensitive or relatively non-acid sensitive, as introduced earlier in section 7.2.5. In the earlier discussion, the Coastal Plains regions were highlighted as appearing markedly different than other acid sensitive regions located in mountainous and Northern latitude

areas. In presenting considerations that inform delineation of acid sensitive categories, we interpret these exceedance analyses as suggesting that the Coastal Plains regions behave in a markedly different manner relative to other acid sensitive regions. In considering this information, we note that the underlying assumption in developing an aquatic acidification standard is that it is designed to afford protection from deposition-related risk beyond that which arises from natural conditions. The lack of response of these regions to significant changes in acidifying deposition would be consistent with the regions being categorized as relatively non-acid sensitive. The basis of this standard relies on the association between changes in emissions, air concentrations, deposition and water quality. The concept of delineating relatively non-acid sensitive areas is intended for those areas where this basic tenet of association is not adhered to. Such is the case for extremely well buffered systems with high ANC, which was used in the initial sensitivity categorizations discussed above in section 7.2, as well as for extremely poorly buffered systems with low natural base cation supply and naturally acidic conditions. This analysis suggests that the following should appropriately be considered in delineating an ecoregion as relatively non-acid sensitive: (1) the level of natural base cation supply, (2) DOC concentrations, (3) representative critical loads, and (4) responsiveness to deposition change. We conclude that the combination of these considerations is more insightful than using just a single attribute, as “natural” acidity is dependent on more than one variable.

Consideration also should be given to other attributes, such as the dominant land use (e.g., agriculture, commercial and residential development) and percentage of wild or protected lands, both of which reflect the intent that this standard be focused on relatively pristine environments. In light of all the above considerations, we conclude that it would be reasonable and appropriate to categorize the Coastal plains ecoregions as relatively non acid–sensitive for purposes of this standard.

A categorization of relatively less-acid sensitive should not be interpreted as implying that such areas would likely not receive benefits from programs designed to address acid sensitive areas. Since the relatively non-acid sensitive areas generally are in lower elevation locations, they would generally benefit from the reduction of emissions designed to improve nearby sensitive areas in two ways. First, because of the rural location of many acid sensitive areas, they often are located are in so-called transport or regional air pollution corridors. The regional behavior of NO_y and SO_x in the atmosphere is influenced strongly by emission

strategies designed to reduce ambient ozone and PM_{2.5}, both of which are influenced by the same transport and atmospheric chemistry processes impacting acid sensitive regions. The emissions sensitivity simulation illustrates the expected benefits associated with addressing regional scale air pollution in a multiple pollutant context, recognizing that the CMAQ simulation originally was used for assessing ozone and PM_{2.5}. From an analogous hydrological perspective, the reduction of acid anions flowing from higher elevation acid sensitive areas eventually translates to reduced strong anion contributions, and therefore higher ANC, into the transitional plateaus, plains and coastal areas.

7.6 SUMMARY OF SYSTEM UNCERTAINTIES

7.6.1 Overview

This section summarizes discussions of results of analyses and assessments, presented more fully in Appendices F and G, intended to address the relative confidence associated with many of the individual and combined components of the linked atmospheric-ecological effects system described throughout this chapter. These components include ecosystem effects; dose-response relationships; underlying ecosystem sensitivity to acid deposition, biogeochemical, atmospheric and deposition processes; and characterization of ecosystem services.

Uncertainty and sensitivity analyses are used to inform the relative confidence in the components and models that are used in defining the standard. Assessments of variability in the data used to determine parameters of the standard increases the level of understanding about the likelihood that alternative parameterizations of the standard will achieve targeted levels of protection when applied to sensitive ecosystems across the U.S. Assessments of the sensitivity of the calculated AAI to the components in the AAI equation can help demonstrate how important uncertainty and variability in those components are in assessing the protection of ecosystems provided by the standard. To evaluate the potential interactions between uncertain and/or variable AAI components, a multifactor sensitivity analysis is also conducted. The ranges of component values evaluated in the multifactor sensitivity assessment are guided by individual variability and uncertainty analyses of specific components. An additional objective of these “confidence” related analyses and discussions is to help guide research and data collection efforts intended to reduce uncertainty for future NAAQS reviews and implementation efforts. Spatial and temporal variability analyses of AAI components are especially useful to inform

monitoring network design, spatial boundaries of acid sensitive areas, and consideration of multi-year averaging periods.

Significant emphasis is placed on evaluations of CMAQ due to the unique role that atmospheric models hold in specifying terms in the AAI equation. The AAI as developed in this PA relies on CMAQ model simulations for both the initial characterization of reduced nitrogen deposition and the deposition transformation ratios (T_{NO_x} and T_{SO_x}) which characterize the relationships between atmospheric concentrations of NO_y and SO_x and deposition of nitrogen and sulfur. Included are interpretations of model evaluation results from the REA (EPA, 2009) as well as more recent results related to wet deposition and the treatment of ammonia deposition. Comparison of model results to observations provides a general sense of the confidence we have that the models capture the spatial, temporal and compositional texture of the relevant atmospheric and deposition species that drive the linked atmospheric-ecosystem processes. Both model evaluation results and assessments of spatial and temporal variability can guide strategies for monitoring network design. Sensitivity of CMAQ-derived deposition transformation ratios to changes in atmospheric concentrations and variability over time provide insight into the stability of these parameters that are used in a relatively static manner in the AAI, and into how well alternative averaging times capture the overall spatial and temporal trends in the parameters.

We evaluate the sensitivity of critical load modeling components by comparing dynamic (MAGIC) and hybrid steady state model results, looking at terminal results of MAGIC. This approach was viewed as a test of the more reduced form approximations used in steady state modeling relative to more sophisticated treatment in MAGIC.

For the purposes of this discussion, we characterize *uncertainty* regarding models and their outputs as referring to the lack of knowledge regarding both the actual values of model input variables (parameter uncertainty) and the model characterization of physical systems or relationships (model uncertainty). In any application, uncertainty is, ideally, reduced to the maximum extent possible, but significant uncertainty often remains. It can be reduced by improved measurement and improved model formulation. Model evaluation results provide some insight into the relative uncertainty associated with the ability of models to capture key environmental state characteristics. Confidence regarding the fundamental science supporting causal determinations about the effects of acid deposition, and the translation of those effects into ecosystem services and values is less amenable to quantification.

Sensitivity refers to the influence on modeled results due to perturbations in input variables or change of process formulations. Sensitivity analysis can provide a sense of how important different parameters and inputs might be to the outcomes of interest, ie., the calculated AAI value, but cannot by themselves indicate how important specific parameters actually are, because they do not incorporate information on the range of parameter values or the likelihood associated with any specific parameter value. Sensitivity results in this assessment are intended to provide insight into the relative stability of the AAI and confidence in modeled parameterizations. Sensitivity analyses are especially useful in the absence of observed data to challenge models. For example, the NO_y and SO_x transference ratios are a model construct that is difficult, if not impossible, to compare to observations. The sensitivity of these ratios to changing meteorology and emissions is evaluated in reference to the stability of these ratios under changing conditions. Low sensitivity here implies that the choice to use long-term averages of modeled ratios is justified. Sensitivity analyses also are used to discern the relative influence on calculated AAI values of other parameters in the AAI equation. Toward that end, elasticity analyses were applied to determine the relative sensitivity of AAI results associated with individual and combined AAI parameters. A Monte Carlo type simulation was also conducted to inform characterization of overall uncertainty associated with the AAI equation.

Variability refers to the heterogeneity in a population or variable of interest that is inherent and cannot be reduced through further data collection and research. In the context of the AAI, characterization of variability can be used to guide the design of an appropriate monitoring network.

7.6.2 Summary of results and conclusions

Uncertainty and natural variability exist in all of the components of the AAI developed in this PA, and should be considered in establishing a standard for aquatic acidification. A summary of the relative uncertainties of these components is provided in Table 7-3. On balance, the confidence level in the information and processes associated with the linkages from ecological effects to atmospheric conditions through deposition and ecosystem modeling is very high.

An analysis of the cumulative effects of uncertainty on the AAI was conducted and is described in Appendix G. In summary, this included bootstrapping analyses of the parameters in

the AAI equation to translate error in individual measurements to the regional values used in the equation. The parameters that are averages of grid-level CMAQ modeled values, *Ndep* and *NHx*, had bootstrapped uncertainty values of approximately $\pm 20\%$ (Figures G-1 and G-5). The transference ratios include two different grid-level CMAQ modeled values and had much higher uncertainty, exceeding 100% (Figures G-3 and G-4). The calculation of *Neco* also includes two different input values, the CMAQ derived *Ndep* values and lake-specific nitrogen leaching values. The *Neco* results also had high uncertainty values, ranging from -65% to approximately 200% (Figure G-2). The critical load value for the region is affected by the *Q* and *BCo* values at the individual lakes within a region. Uncertainty in these parameters gave a regional uncertainty range for the critical load of $\pm 35\%$ (Figure G-6).

The results of the bootstrapping analyses were used to complete a cumulative analysis of uncertainty in a subsequent Monte Carlo style analysis. This analysis is illustrated in the form of the tradeoff curve for the concentrations of *NOy* and *SOx* (Figure G-7). The results in the two regions analyzed were similar. There was a range of uncertainty, with 50% of the distribution within $\pm 20\%$ of the observed value. Most importantly, the mean value of the results was very close to the observed value in both regions. This indicates that there is no systematic bias in the results despite what can be relatively high levels of uncertainty in the input parameters.

The considerable body of evidence is conclusive with regard to causality between aquatic acidification and biological and ecological effects. Confidence in the linkage associating aquatic acidification and ANC is extremely high, as the aquatic chemistry describing this relationship, while nonlinear, is relatively simple with regard to chemical species and reactions. The relationships between deposition and ANC, while complicated by a variety of biogeochemical and hydrological processes and data requirements within watersheds, are well established and the critical load models have been thoroughly vetted through the scientific community with a demonstrated level of successful evaluation. The linkages between ambient concentrations of relevant species and deposition are best handled through air quality modeling systems like CMAQ. The relationship between concentrations and deposition is well characterized by these models, which are constrained by mass balance principles. While much of the physical and chemical processing that determines concentrations and consequent deposition is interwoven with numerous fundamental processes characterizing mass transport and atmospheric chemical oxidation, the science is relatively mature with years of applications and continued evolution of

the models. The specific processes guiding nitrogen and sulfur chemistry and deposition are relatively simple. More challenging is the ability to parameterize processes at the air-surface interface which guide the estimation of deposition velocities and the re-emission of certain species, as well as many of the area-wide natural processes and agricultural practices which influence emissions of oxidized and reduced forms of nitrogen.

The variety of uncertainty, variability, and sensitivity analyses included in Appendices F and G have been conducted under the assumption that the basic model construct is well established, as discussed immediately above. Throughout these discussions there is no apparent directional bias in the uncertainty regarding the biological, chemical and physical processes incorporated in the AAI. From the perspective of valuation of ecosystem services, the estimates generally are believed to be biased low, meaning the values of reaching a target level of protection are underestimated. However, quantification of these values is perhaps the most uncertain of all aspects considered.

Table 7-3. Summary of Qualitative Uncertainty Analysis of Key Components of the AAI

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
Major elements (and sub-models) of the ecological effects to ambient concentration framework					
Biological/ecosystem response to acidification	Clear associations between aquatic acidification (pH, elevated Al) and adverse ecosystem effects (fish mortality, decreased species diversity)	Both	Low	Low (regionally)	The ecosystem level responses are well studied at regional levels. The uncertainty increases at larger scales due to an increasing number of factors influencing the patterns (e.g. latitudinal species gradient, specie-area relationships).
Linkage between direct acidification species and ecological indicator (ANC)	The relationships across ANC, pH and dissolved Al are controlled by well defined aquatic equilibrium chemistry	Both	Low	Low	ANC is the preferred ecosystem indicator as it has a direct relationship with pH and the deposition species relevant to the NOx/SOx standard.
Linkage between ecological indicator and adverse ecological effects	Direct nonlinear associations between ANC and fish mortality and species diversity	Both	Low-medium	Low	Although the pH dependency on ANC is nonlinear, it is always directionally consistent. In extremely low and high ANC environments the relationship is of minimal value as catchments are in relatively “less sensitive” regimes due to natural conditions or extreme anthropogenic influence (i.e., acid mine drainage). In sensitive areas of concern the relationship essentially is similar to the relationships between direct acidification species and adverse effects.
Deposition to ANC linkage through Critical Load approach	Mass-balance Steady State critical load model is applied to determine critical load values. MAGIC model is used to validate steady State model. The Steady State critical load model formulation is used as the foundation for deriving the AAPI equation.	Both	Low	Low	The model formulation is well conceived and based on a substantial amount of research and applications available in the peer reviewed literature. There is greater uncertainty associated with the availability of data to support certain model components.

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
Atmospheric concentrations to deposition	Deposition is a direct function of ambient concentration, influenced by several processes, and handled in the AAPI through air quality modeling.	Both	Low	Low	The model design is appropriate given the spatial and temporal complexities that influence deposition velocity, as well as the variety of atmospheric species that generally are not measured. Greater uncertainty resides in the information (e.g., ammonia emissions) driving these calculations and availability of observations to evaluate model behavior.
Ecological indicator to changes in the value of ecosystem services	Definitions of public welfare may include economic considerations, based on the tradeoffs people would make to avoid the negative impacts of acidification, through effects on the values of ecosystem services. Empirical estimates of valuation for limited ecosystem service categories are used to inform the discussions of adversity associated with alternative ANC levels.	Negative	Medium-high	Low-medium	<p>There are many studies that estimate the value of increasing services that may be affected by changes in acidification and eutrophication. However, few of these studies focus on the particular impact of acidification and eutrophication on the quality of these services and preferences for avoiding these impacts.</p> <p>Those studies that do are often limited to analyzing the impacts on a narrow population or particular change in environmental quality. The monetized benefits to fishers and to New York residents for ecosystem improvements in the Adirondacks associated with improvements to the ecological indicator are significant underestimates of the total benefits in the U.S. This is because those living outside New York would value improvements to the Adirondacks and similar natural environments elsewhere.</p> <p>The methodologies used in the studies that underlie the estimates of the value of changes in ecosystem services in the Adirondacks region are sound and have been subject to peer review. The method of aligning the improvements valued in the Banzhaf et al. study with estimates of eliminating current damages leads to may lead to an over or underestimate of the benefits. The range of this difference is difficult to know a priori, but the total improvements in the share of lakes that improve above an ANC threshold of 20 µeq/L are consistent.</p>

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
Sub-components and data of individual models					
Atmospheric Components					
Dep _{SOx}	Annual deposition of sulfur mass from dry deposition of (SO ₂ and SO ₄) and wet SO ₄ derived from CMAQ 12km horizontal grid resolution averaged over 5 years	Both	Low	Low	The treatment of SO _x deposition in EPA air quality models has evolved over the last two decades. There is general consensus that the overall mass balance of S is treated well with difficulties in spatial pairing of observations and modeled results of wet deposition. This spatial pairing has improved with the more recent PRISM adjustments.
Dep _{NOy}	Annual deposition of oxidized nitrogen mass from dry deposition of (all NO _y species) and wet NO ₃ derived from CMAQ 12 km horizontal grid resolution averaged over 5 years	Both	Low	Low-medium	The treatment of oxidized nitrogen deposition in EPA air quality models has evolved over the last two decades. There is general consensus that the overall mass balance of oxidized N is treated well. However, the broad range of deposition velocities across NO _y species, and especially uncertainties regarding the deposition of significant species such as NO ₂ pose ongoing challenges. Similarly, a shortage of NO _y species measurements as well a lack of techniques to directly measure dry deposition impede progress on improving parameterization of N dry deposition.
Dep _{NHx}	Annual deposition of reduced nitrogen mass from dry deposition of (NH ₃ and SO ₄) and wet NH ₄ derived from CMAQ 12km horizontal grid resolution averaged over 5 years	Both	Low	Medium	NH _x deposition also is quantified through CMAQ applications. The well dispersed nature of agricultural based emissions that are influenced strongly by meteorological and surface /soil characteristics continues to challenge characterization of ammonia emissions. Recent incorporation of a bi-directional flux process in CMAQ improves consistency with available scientific understanding and yields improved time and space pairing of limited observations with model results. A lack of both ammonia and ammonium ambient observations continues to compromise our ability to characterize uncertainty in our treatment of NH _x . As with all dry deposition estimates, technologies for direct measurements are not available routinely. Both NH _x deposition and NO _x deposition are assigned low values of magnitude based on a general dominating role of sulfur deposition.

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
Wet deposition (generically – N and S species)	Wet component of total deposition as described in the Dep terms, above	Both	Low	Low	Wet deposition remains an attribute of relatively high confidence based on the ability to directly measure chemical components in precipitation samples. However, given the stochastic nature of precipitation, models have a difficult time in matching observations. The use of 5 year averages and post-processing PRISM adjustments have reduced uncertainty in spatial pairing of observations and modeled estimates.
Dry deposition (generically – N and S species)	Dry component of total deposition as described in the Dep terms, above	Both	Medium	Medium-high	The absence of direct dry deposition measurements combined with the significant variability in the parameters that influence dry deposition velocity reduces the confidence level in dry deposition relative to wet deposition.
Deposition Transference Ratios	CMAQ derived ratio of total oxidized deposition to concentration averaged over one year	Both	Low	Unknown	Transference ratios enable the connection between deposition and the policy relevant ambient air indicators, NO _y and (SO ₂ + SO ₄). They are strictly a model construct and cannot be evaluated in a traditional model to observation context. The low sensitivity of these ratios to emission changes and inter annual meteorology combined with low spatial variability indicate that these ratios are necessarily stable.
C _{NO_y}	Ambient concentrations of NO _y through observations.	Negative	Low	Low-medium	Adequate spatial coverage of NO _y observations does not exist, but will be addressed in the proposed rule. The monitoring technology only over the last 5 years has been perceived as “routine” based on incorporation in the NCore network. However, FRM status for NO _y instruments currently is not available. The negative bias direction is a standard caveat to any instrument relying on internal air stream conversion of atmospheric species prior to detection.
C _{SO_x}	Ambient concentrations of NO _y through observations.	Both	Low	Low	A lack of adequate spatial coverage is the primary concern for SO ₂ + SO ₄ observations. FRM status is not available for SO ₄ ; although the long track record of accurate and precise CASTNET FP measurements indicates that achieving FRM status is a low hurdle.

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
Ecosystem Components					
BC ₀ *	Pre-industrial base cation concentrations	Negative	Medium-high	High	Both the F-factor approach and process based MAGIC modeling were used to generate BC ₀ *. Excellent agreement between both approaches was established in the Shenandoah streams. The more comprehensive data requirements of MAGIC limit its widespread use to the Adirondacks, although for consistency the F-factor approach was applied nationwide. The analyses also illustrated greater divergence at higher critical loads, or areas with greater acid buffering capacity and high base cation levels. These conditions often are screened out of our population distribution analyses, and when included do not affect the location within the distribution of the more sensitive water bodies. Since MAGIC (the preferred approach) tends to overestimate BC ₀ * relative to the F factor approach, and the F-factor is more widely applied nationally, the BC ₀ * estimates are viewed as conservative leading to a slight positive bias in estimating critical loads. Although we have many modeled estimates of BC ₀ *, there is a lack of direct measurements of BC weathering rates.
Neco		Positive	Low	Medium	The term Neco, as defined, has a relatively medium confidence level and is a direct function of the uncertainty inherent in the deposition estimates from CMAQ and surface measurements of NO ₃ . However, this “measurement” difference approach reflects the average of all influencing processes (denitrification, uptake, and immobilization) over the time period of measurements. Consequently, there is an inherent assumption of a relatively static system (Neco is applied in a steady state model) that generally is not tested. In concept, a true steady state vision of Neco would be based on a mature forested ecosystem. The relative bias of Neco is related, largely, to the relative productivity of the forest. The challenge in determining any potential bias in Neco is to determine the relative “maturation age” of an ecosystem which requires

Source	Description	Potential influence of uncertainty in element		Knowledge-Base uncertainty	Comments
		Direction (negative implies less relative protection)	Magnitude		
					knowledge of future land use activities. In areas of high land use restrictions of a recovering forest, Neco would be assumed to be overestimated. The relative magnitude of Neco often is mitigated by the dominance of SO _x in controlling acidification processes in many systems. Furthermore, it is unclear to what extent any stored N will be released back into the system, which is assumed to not occur in the linked system model.
Q	Annual runoff rate (distance/time) for a catchment.	Both	Low	High	Data used to calculate Q was compiled in 1985. Streamflow data were collected at over 12,000 gauging stations during 1951-80; 5,951 stations were selected for the analysis. See Gebert et al. (1987) for a complete description of how the runoff was determined from the streamflow data. Appropriate maps of the data can show the geographical distribution of runoff in tributary streams for the years 1951-80 and can describe the magnitudes and variations of runoff nationwide. The data was prepared to reflect the runoff of tributary streams rather than in major rivers in order to represent more accurately the local or small scale variation in runoff with precipitation and other geographical characteristics. Gerbert, W.A., Graczyk, D.J., and Krug, W.R., 1987, Average annual runoff in the United States, 1951-80: U.S. Geological Survey Hydrologic Investigations Atlas HA-710, scale 1:7,500,000.
DOC	Surface water dissolved organic carbon	Negative	Low	Medium	Water bodies with high DOC levels (> 10mg/l) were screened out of the critical load calculations in order to avoid naturally acidic systems. However, the inherent assumption of $ANC = \sum \text{strong CA} - \sum \text{strong AN}$ does not explicitly account for contributions of weak organic acids. Consequently, a small positive bias pervades the critical load calculations (i.e., the CL estimates are high). The knowledge base value of M reflects a general shortage of DOC data.

7.7 SUMMARY OF STAFF CONCLUSIONS ON SECONDARY STANDARDS FOR OXIDES OF NITROGEN AND SULFUR

This section summarizes staff conclusions with regard to the adequacy of the current NO₂ and SO₂ secondary standards and potential alternative standards that are appropriate to consider to provide requisite protection from adverse public welfare effects, including effects on sensitive ecosystems, associated with the presence and deposition of oxides of nitrogen and sulfur in the ambient air. In reaching these conclusions, staff has considered these standards in terms of the basic elements of the NAAQS: indicator, averaging time, form, and level (as discussed above in sections 7.1 to 7.4, respectively). Staff conclusions are based on the available scientific and technical information as assessed and presented in the ISA (US EPA, 2008), the REA (US EPA, 2009), and as summarized and interpreted throughout this documents and its appendices. In so doing, we have considered the advice of CASAC and public comments on earlier drafts of this document.

In this assessment, we emphasize a policy approach that incorporates a multi-pollutant, multi-media framework, taking into consideration the combined effects of oxides of nitrogen and oxides of sulfur and the linkages between relevant atmospheric processes and associated ecosystem effects. As such, we have taken into account both evidence-based and impact assessment-based considerations to inform our conclusions related to the adequacy of the current NO₂ and SO₂ secondary standards and alternative standards that are appropriate for consideration in this review. In so doing, we are seeking to identify as broad an array of policy options as is supportable by the available information, recognizing that the selection of a specific approach to reaching final decisions on secondary standards for oxides of nitrogen and sulfur will reflect the judgments of the Administrator as to standards that are requisite to protect the public welfare from adverse effects associated with the presence of oxides of nitrogen and sulfur in the ambient air.

We recognize that selecting from among alternative standards will necessarily reflect consideration of the qualitative and quantitative uncertainties inherent in the relevant evidence and in the quantitative impact assessment of exposure and risks to sensitive ecosystems. In reaching staff conclusions on alternative standards that are appropriate to consider, we are mindful that the CAA requires secondary standards to be set that are requisite to protect public

welfare from known and anticipated adverse effects, such that the standards are to be neither more nor less stringent than necessary.

Based on the currently available information, staff reaches the following conclusions regarding secondary standards for protecting against adverse public welfare effects, including effects on sensitive ecosystems, associated with the presence and deposition of oxides of nitrogen and sulfur in the ambient air:

- (1) With regard to the *adequacy of the current standards*, currently available scientific evidence and assessments clearly call into question the adequacy of the protection afforded by the current NO₂ and SO₂ secondary standards from *deposition-related effects on sensitive ecosystems* related to oxides of nitrogen and sulfur in the ambient air, including acidification and nutrient enrichment in aquatic and terrestrial ecosystems. In addition, the elements of the current NO₂ and SO₂ standards are not ecologically relevant, and are thus not appropriate, for standards that are designed to provide such protection. Nonetheless, based on the current evidence, the current standards likely do afford adequate protection from the *direct effects involving injury to vegetation* associated with atmospheric exposure to oxides of nitrogen and sulfur.
 - (a) Thus, consideration should be given to establishing a new ecologically relevant standard(s) to provide increased protection from deposition-related effects of oxides of nitrogen and sulfur on sensitive ecosystems.
 - (b) Consideration should also be given to retaining the current NO₂ and SO₂ secondary standards to continue to provide protection from the direct effects of oxides of nitrogen and sulfur on vegetation.
- (2) With regard to *establishing a new ecologically relevant standard(s)*, consideration should be given to establishing a multi-pollutant standard that addresses the combined effects of oxides of nitrogen and oxides of sulfur specifically to provide increased public welfare protection from aquatic acidification in sensitive ecosystems. This conclusion is based in general on the evaluation and assessments in the ISA and REA showing that both oxides of nitrogen and sulfur are major contributors to aquatic acidification and that acidification of aquatic ecosystems is best characterized and understood in terms of the combined rather than individual effects of oxides of nitrogen and sulfur. In addition, there is a well developed body of scientific evidence linking the deposition of ambient oxides of nitrogen and sulfur to acidification in sensitive aquatic ecosystems and showing that a significant number of water bodies currently experience levels of acidification associated with the deposition of atmospheric nitrogen and sulfur that could reasonably be judged to be adverse from a public welfare perspective in areas where the current standards were met.
 - (a) While there are other important ecosystem effects attributable to deposition of oxides of nitrogen and/or oxides of sulfur, such as terrestrial acidification and nutrient enrichment of aquatic and terrestrial systems, we conclude that the available information and assessments are only sufficient to support the development of a national standard specifically to address aquatic acidification at this time.

- (b) Nonetheless, we recognize an aquatic acidification standard as developed in this assessment is likely to provide some degree of co-protection for these other deposition-related effects, particularly for terrestrial acidification, in at least some acid sensitive watersheds.
- (3) With regard to ambient air *indicators* for an aquatic acidification standard that would address the combined contributions of oxides of nitrogen and sulfur, consideration should be given to using total reactive oxidized nitrogen, NO_y , as the indicator for oxides of nitrogen and the sum of gaseous sulfur dioxide (SO_2) and particulate sulfate (SO_4), referred to in this assessment as SO_x , as the indicator for oxides of sulfur. This conclusion takes into consideration the available evidence that demonstrates a strong linkage between concentrations of NO_y and SO_x in the ambient air, the deposition of nitrogen and sulfur from NO_y and SO_x , and acidification effects in aquatic ecosystems.
- (a) Consideration could also be given to defining the indicator for oxides of nitrogen as some subset of NO_y species, including those NO_y species that deposit relatively more quickly than other species and/or those that comprise the dominant mass of NO_y . Based on our assessment, however, we conclude that the advantages of using total aggregated NO_y make it the preferred choice.
- (b) In considering an indicator for oxides of nitrogen, we recognize that aquatic acidification results from and is best understood in terms of the deposition of total nitrogen, in both oxidized and reduced forms. Since the pollutant that is the focus of this review is oxides of nitrogen, not reduced forms of nitrogen, we conclude that it is appropriate to consider reduced forms of nitrogen separately, as a factor in the form of the standard, rather than as part of the indicator of the standard.
- (4) With regard to the *form* of such a multi-pollutant, deposition-related standard, consideration should be given to an ecologically relevant form that characterizes the relationships between the ambient air indicators for oxides of nitrogen and sulfur, the related deposition of nitrogen and sulfur, and the associated aquatic acidification effects in terms of a relevant ecological indicator. Based on the available information and assessments, consideration should be given to using acid neutralizing capacity (ANC) as the most appropriate ecological indicator for this purpose, in that it provides the most stable metric that is highly associated with the water quality properties that are directly responsible for the principal adverse effects associated with aquatic acidification: fish mortality and reduced aquatic species diversity.

We have developed such a form, termed an aquatic acidification index (AAI), using a simple equation to calculate an AAI value in terms of the ambient air indicators of oxides and nitrogen and sulfur and the relevant ecological and atmospheric factors that modify the relationships between the ambient air indicators and ANC. Recognizing the spatial variability of such factors across the U.S., we conclude it is appropriate to divide the country into ecologically relevant regions, characterized as acid-sensitive or relatively non-acid-sensitive, and specify the value of each of the factors in the AAI equation for each such region.

With regard to approaches to defining such ecologically relevant regions, consideration should be given to using Omernik ecoregions, level III, as the appropriate set of regions over which to define the AAI. There are 84 such ecoregions that cover the continental U.S. This set of ecoregions is based on grouping a variety of vegetation, geological, and hydrological

attributes that are directly relevant to aquatic acidification assessments and that allow for a practical application of an aquatic acidification standard on a national scale.

With regard to an equation that would define the AAI, consideration should be given to the following equation:

$$AAI = F1 - F2 - F3[NO_y] - F4[SO_x]$$

Factors F1 through F4 would be defined for each ecoregion by specifying ecoregion-specific values for each factor based on monitored or modeled data that are representative of each ecoregion. The F1 factor is also defined by a target ANC value. More specifically:

- (a) F1 reflects a relative measure of an ecosystem's ability to neutralize acidifying deposition. The value of F1 for each ecoregion would be based on a representative critical load for the ecoregion associated with a single national target ANC level, as well as on a representative runoff rate. The representative runoff rate, which is also used in specifying values for the other factors, would be the median value of the distributions of runoff rates within the ecoregion. The representative critical load would be derived from a distribution of critical loads calculated for each water body in the ecoregion for which sufficient water quality and hydrology data are available. The representative critical load would be defined by selecting a specific percentile of the distribution.

In identifying a range of percentiles that are appropriate to consider for this purpose, we have considered regions categorized as acid sensitive separately from regions categorized as relatively non-acid sensitive. In delineating these categories, consideration should be given to alternative approaches that take into account a range of relevant ecological and atmospheric factors. For acid sensitive regions, we conclude that consideration should be given to selecting a percentile value from within the range of the 70th to the 90th percentile. The lower end of this range was selected to be appreciably above the median value so as to ensure that the critical load would be representative of the population of relatively more acid sensitive water bodies within the region, while the upper end was selected to avoid the use of a critical load from the extreme tail of the distribution which is subject to a high degree of variability and potential outliers. For relatively non-acid sensitive regions, we conclude that consideration should be given to selecting the 50th percentile to best represent the distribution of water bodies within such a region, or alternatively to using the median critical load of all relatively non-acid sensitive areas, recognizing that such areas are far less frequently evaluated than acid sensitive areas. Using either of these approaches would avoid characterizing a generally non-acid-sensitive region with a critical load that is representative of relatively acid sensitive water bodies that may exist within a generally non-acid sensitive region.

- (b) F2 reflects the deposition of reduced nitrogen. Consideration should be given to specifying the value of F2 for each region based on the averaged modeled value across the region, using national CMAQ modeling that has been conducted by EPA. Consideration could also be given to alternative approaches to specifying this value, such as allowance for the use of air quality modeling conducted by States using more refined model inputs.

- (c) F3 and F4 reflect transference ratios that convert ambient air concentrations of NO_y and SO_x, respectively, into related deposition of nitrogen and sulfur. Consideration should be given to specifying the values for F3 and F4 for each region based on CMAQ modeling results averaged across the region. We conclude that specifying the values or the transference ratios based on CMAQ modeling results alone is preferred to an alternative approach that combines CMAQ model estimates with observational data.
 - (d) The terms [NO_y] and [SO_x] reflect ambient air concentrations measured at monitoring sites within each region.
- (5) With regard to *averaging time*, consideration should be given to averaging calculated annual AAI values over 3 to 5 years to provide reasonable stability in the resulting index value, in light of the relatively high degree of interannual variability expected in an index that is strongly related to the amount and pattern of precipitation that occurs within a region from year to year.
- (6) With regard to the *level* of a standard based on the above indicators, alternative forms, and averaging times, consideration should be given to a level within the range of 20 to 75 µeq/L. In reaching this conclusion, staff has considered the available information that links specific ANC levels to various types of acidification-related effects, and the uncertainties inherent in such linkages, and the severity of such effects, in sensitive ecosystems, as well as the extent to which such effects could reasonably be judged to be important from a public welfare perspective. This range also reflects consideration of the extent to which such a standard would protect against not only long-term but also episodic acidification, as well as the time lag in ecosystem response to changes in deposition that may result from such a standard. Relatively more protection from both long-term and episodic acidification would be provided by a standard in the mid- to upper part of this range, which would also accelerate the time frame in which the target ANC level would likely be reached in some sensitive ecosystems. This range also encompasses target ANC values that have been established by various States and regional and international organizations to protect against acidification of aquatic ecosystems.

Based on the evidence and assessments in the ISA and REA, we conclude that a target ANC value of 20 µeq/L is a reasonable lower end of this range, so as to protect against chronic acidification-related adverse impacts on fish populations which have been characterized as severe at ANC values below this level. Further, we conclude that a target ANC value of 75 µeq/L is a reasonable upper end of this range in recognition that the potential for additional protection at higher ANC values is substantially more uncertain in light of evidence that acidification-related effects are far less sensitive to increases in ANC above this value.

- (7) An aquatic acidification standard, as defined above, would be interpreted as follows: the standard would be met at a monitoring site when the measured annual-average concentrations of NO_y and SO_x are such that the value of the annual AAI, averaged over 3 to 5 years, is equal to or greater than the level of the standard, when using the region-specific values of factors F1 through F4 for the ecoregion in which the monitor is located.

7.8 REFERENCES

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