Policy Assessment for the Review of the Secondary National Ambient Air Quality Standards for NOx and SOx

Second External Review Draft

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Policy Assessment for the Review of the Secondary National Ambient Air Quality Standards for NOx and SOx:

Second External Review Draft

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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EXECUTIVE SUMMARY

Introduction

This second draft Policy Assessment is an evaluation of 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), and the 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. This second draft also presents preliminary EPA staff conclusions regarding the adequacy of the current standards and various policy options that we believe are appropriate to consider as part of the current review of the secondary (welfare-based, e.g. focused on non-health effects including impacts on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility, and climate) NO_x and SO_x NAAQS.

This policy assessment is intended to help "bridge the gap" between the scientific assessment contained in the ISA and the judgments required of the EPA Administrator in determining whether, and if so, how, it is appropriate to revise the secondary NAAQS for NO_x and SO_x. 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: indicators, averaging times, forms, and levels. These elements, which serve to define each standard, must be considered collectively in evaluating the welfare protection afforded by the secondary NO_x and SO_x NAAQS.

In conducting this periodic review of the NO_x and SO_x secondary NAAQS, EPA has decided to jointly assess the scientific information, associated risks, and standards because ambient NO_x and SO_x, and their associated transformation products, such as deposited N and S, are linked from an atmospheric chemistry perspective, as well as jointly contributing to environmental effects.

Scope

This assessment primarily focuses on the effects of the deposition of ambient NO_x and SO_x on multiple ecological receptors. Highlighted effects include those associated with acidification and nitrogen nutrient enrichment. Based on these highlighted effects, EPA's objective is to develop a framework for setting standards that are ecologically relevant and that reflect the common impacts of these two pollutants as they deposit to sensitive ecosystems.

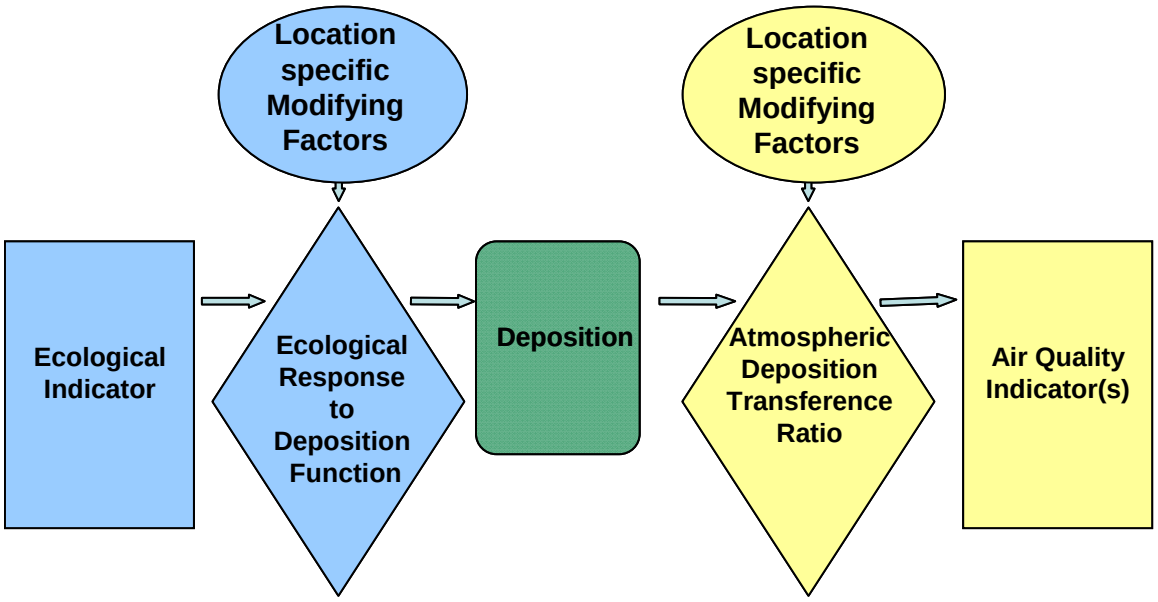
For this second draft policy assessment, we have chosen to focus much of our discussion on effects in sensitive aquatic ecosystems caused by acidifying deposition of nitrogen and sulfur, which is a transformation product of ambient NO_x and SO_x. We have a high degree of confidence in the link to aquatic acidification effects as well as more information available with which to develop an ecologically meaningful structure for the standards. We recognize in doing so that the resulting standards will not likely provide full protection against terrestrial acidification effects or against adverse nutrient enrichment effects in sensitive terrestrial and aquatic ecosystems. It is however likely that some additional protection for those ecosystems will be provided as overall NO_x and SO_x levels in the environment are decreased in response to the aquatic acidification based standards.

In the atmospheric science community, NO_x typically refers to the sum of nitrogen dio$_x$ide (NO_2), and nitric oxide (NO). In contrast, the Clean Air Act uses "NO_x" to refer to any gaseous mixture of species composed solely of nitrogen and oxygen (e.g., NO_2, NO, nitrous oxide [N_2O], nitrogen trioxide [N_2O_3], nitrogen tetroxide [N_2O_4], and dinitrogen pentoxide [N_2O_5]). The term used by the scientific community to represent the complete set of oxidized nitrogen compounds, including those listed in CAA Section 108(c), is total oxidized nitrogen (NOy). NOy includes all nitrogen oxides, including NO, NO_2, HNO_3, peroxyacetyl nitrate (PAN), $2N_2O_5$, HONO, NO_3, organic nitrates, and particulate NO_3. In the policy assessment, unless otherwise indicated, we use the term "NOy" to refer to the complete set of oxidized nitrogen compounds.

For this assessment, the full definition of SO_x includes all oxides of sulfur, including both gaseous substances (e.g., SO_2, sulfur mono$_x$ide [SO], sulfur trioxide [SO_3], thiosulfate [S_2O_3], and heptoxide [S_2O_7], as well as particulate species, such as ammonium sulfate [$(NH_4)2SO_4$]). However, throughout this document we refer to SO_x as the sum of SO_2 and sulfate to be consistent with standard monitoring instrumentation. Sulfate is referred to as SO_4 and nitrate as NO_3, recognizing that they refer to the ions that have charges of -2 for sulfate and -1 for nitrate.

Conceptual Framework

The figure below depicts the framework by which we are considering the structure of an ecologically relevant secondary standard. It is a conceptual diagram that illustrates how a level of protection related to an indicator of ecological effect(s) equates to atmospheric concentrations of NO_x and SO_x indicators. This conceptual diagram illustrates the linkages between ambient air concentrations and resulting deposition metrics, and between the deposition metric and the ecological indicator of concern. The Deposition Transference Ratios translate between NO_x and SO_x deposition metrics and ambient atmospheric concentrations of NO_x and SO_x, while the Ecological Response to Deposition Function relates the deposition metric into the ecological indicator.



Our policy assessment is structured around this conceptual model, and includes an evaluation of the effects associated with deposition of NO_x and SO_x to ecosystems, as well as an assessment of the

adequacy of the existing NO_x and SO_x standards in protecting against these effects. This policy assessment also develops a more complete understanding of the conceptual structure needed to address the variable ecosystem and atmospheric factors which modify the impacts of deposited NO_x and SO_x on ecosystems. Development of the form for the standard and options for ambient atmospheric indicators for NO_x and SO_x, averaging times, and levels of the standard are also discussed.

Ecological Effects from NO_x and SO_x Deposition

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 process of acidification, chemical components of terrestrial and freshwater aquatic ecosystems are altered in a way that leads to effects on biological organisms. Because NO_x and SO_x 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. Acidic deposition is observed to alter sulfate and nitrate concentrations in surface waters, balance of base cations, acid neutralizing capacity (ANC), inorganic aluminum, calcium, and surface water pH. These changes can result in the loss of acid-sensitive biological species such as salmonid fish species 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, biological 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 hydrology. Episodic and chronic acidification tends to occur primarily (but not exclusively) at relatively high elevations in areas that have base-poor bedrock, high relief, and shallow soils.

Based on published analyses of surface water data from freshwater ecosystem surveys and monitoring, the most sensitive lakes and streams are located in New England, the Adirondack Mountains, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), the Upper Midwest and high elevation Western ecosystems.

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 multiyear average ANC is a good overall indicator of sensitivity, capturing the ability of an ecosystem to withstand 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 (μeq/L). At annual average ANC levels between 100 and 50 μeq/L, the fitness of sensitive species (e.g., brook trout, zooplankton) begins to decline. When annual average ANC is <50 μeq/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 50 μeq/L are generally associated with death or loss of fitness of biota that are sensitive to acidification.

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 of 50. In addition, several states have set goals for improving the acid status of lakes and streams, generally targeting ANC in the range of 50 to 60 μeq/L, and have engaged in costly activities to decrease 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 are the regions most sensitive to terrestrial acidification effects from acidifying deposition. 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.

The numerous ecosystem types that occur across the U.S. have a broad range of sensitivity to N 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 N, may result in imbalance in ecosystems, with effects on ecosystem processes, structure and function. In certain N-limited ecosystems, including many ecosystems managed for commercial production, N deposition can result in beneficial increases in productivity. Nutrient enrichment effects from NO_x deposition 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 $E_x$isting NO_x and SO_x Standards to Protect Against Acidification and Nutrient Enrichment Effects

Current NO_x and SO_x secondary standards are designed to protect against direct exposure of vegetation to ambient concentrations of NO_x and SO_x. Almost all areas of the U.S. are in attainment of the current NO_x and SO_x secondary standards. The NO_x secondary standard is 0.053 parts per million (ppm), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO_2 concentrations. The SO_x secondary standard, which uses SO_2 as the atmospheric indicator, is a 3-hour average of 0.5 ppm, not to be $e_x$ceeded more than once per year.

Recent acidification status of aquatic ecosystems indicate that in the Adirondacks and Shenandoah areas, rates of acidifying deposition of NO_x and SO_x 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.

The REA only evaluated a small number of sensitive areas as case studies. However, 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.

Available ecological indicators for estuarine nutrient enrichment are not sufficiently sensitive to changes in atmospheric NO_x to be of use in assessing the adequacy of existing NO_x standards. Atmospheric NO_x can be an important contributor of N to estuarine nutrient enrichment, but additional analysis is required to develop an appropriate indicator for assessing levels of protection from nutrient enrichment effects in estuaries related to deposition of NO_x.

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 NO_x levels meeting the current standards, are known to cause changes in species composition in diatom communities indicating impaired water quality. From this we initially conclude that the existing secondary standard for NO_x does not protect such ecosystems and their resulting services from impairment.

Most terrestrial ecosystems in the US are N-limited, and therefore they are sensitive to perturbation caused by N additions. Under recent conditions, nearly all of the known sensitive mixed conifer forest ecosystems receive total N 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 N 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 Scrub Sage ecosystems in California, N 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. Because excessive N deposition and effects are observed in areas where, under recent conditions, NO_x ambient concentrations are at or below the current NO_x secondary standards, we initially conclude those standards are not adequate to protect against anticipated adverse impacts from N nutrient enrichment in sensitive ecosystems (systems where N is limiting) that are not managed for commercial agricultural and forest production.

Sulfur deposition is also linked with the formation of methylmercury. The production of methylmercury in aquatic ecosystems requires sulfate as well as mercury. The evidence is sufficient to infer a causal relationship between sulfur deposition and increased mercury methylation in wetlands and aquatic environments. However, while the production of methylmercury requires the presence of sulfate and mercury, the amount of methylmercury produced varies with oxygen content, temperature, pH, and supply of labile organic carbon. Due to limits in data, we are unable to assess the adequacy of the existing standards in protecting against effects associated with increased mercury methylation.

Conceptual Design of an Ecologically Relevant Standard

The overall concept for ecologically relevant standards recognizes that the fundamental welfare effects associated with ambient NO_x and SO_x occur through the process of deposition to sensitive ecosystems. There are four main components to the conceptual design of the standard: atmospheric and ecological indicators, deposition metrics, functions that relate indicators to deposition metrics and factors that modify the functions. In this policy assessment, the focus is on developing the conceptual design for a

standard that protects against effects associated with acidifying deposition of NO_x and SO_x in aquatic ecosystems, but this general conceptual framework is intended to apply to a broader set of potential endpoints.

For the conceptual design of an aquatic acidification standard, ANC is suggested as the ecological indicator. ANC is suggested as the ecological indicator because it 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 systems. Furthermore, ANC can be directly linked to both underlying water chemistry, e.g. pH and aluminum, and to biological impairment, specifically the number of fish species in a water body.

Acidification models represent the ecological response relationship between ANC and deposition of N and S. Acidification models are designed for the catchment scale. However, for consideration of a national standard, aggregation to a broader spatial scale is desirable; therefore a method to evaluate critical loads (the levels of deposition of N and S below which defined levels of harmful effects on specified sensitive elements of the environment do not occur) across the national landscape is presented. The atmospheric transformation functions then convert deposition to ambient concentrations of NO_x and SO_x.

Acidification models relate ANC to deposition of N and S at the catchment scale. We suggest using an acidification model that incorporates environmental variables that modify the ecological response relationship. This includes a variable to account for nitrogen uptake by ecosystems. The acidification model can be used to calculate critical loads for individual catchments based on a selected level of ANC. The load of deposition that causes a selected level of ANC varies across the nation depending on the characteristics of the catchment, such as base cation weathering rates, nitrogen retention and the level of naturally occurring organic acids.

Although critical loads for a selected level of ANC will vary catchment by catchment it is not practical for a national standard to evaluate every catchment in the U.S. Therefore, we propose two general approaches to establish critical loads. One approach is to develop a national distribution of critical loads over all levels of sensitivity, recognizing that there is a high degree of heterogeneity in acid sensitivity even at relatively small spatial scales. The second approach is to subdived the landscape of the U.S.into acid-sensitivity categories, such that within a category there are generally similar acid sensitivity characteristics. Each national acid-sensitivity category is represented by a population of catchments for which critical loads at a specified ANC limit are calculated. This second draft policy assessment explores a number of methods for developing the acid sensitivity categories.

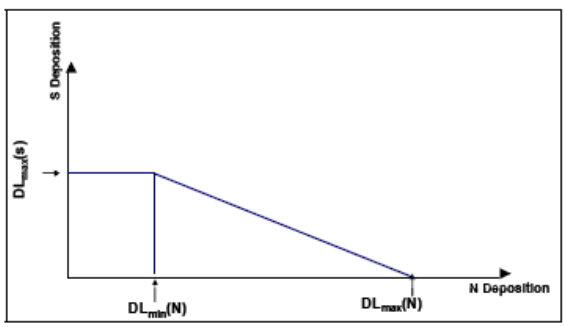
National acid-sensitivity categories should be based on features that govern ecological sensitivity to acidification. Areas that have similar underlying geology, mineral weathering rates, and hydrology should show similar sensitivity to NO_x and SO_x deposition. Ecoregions are useful geographic defiitions that holistically incorporate a number of important factors related to acid sensitivity, including geology, physiography, vegetation, climate, soils, land use, and hydrology. As such, the determination of acid-sensitivity categories begins with aggregation of lakes and streams by ecoregion. From there, acid sensitivity is further characterized using measured ANC. As noted earlier, ANC is a good indicator of the overall sensitivity of a water body to acidification. ANC measurement is also widely available in the U.S., making it a useful metric for further classifying ecoregions. The policy assessment explores several methods for using ANC to classify ecoregions using both simple and more complex methods.

Once acid-sensitivity categories are defined, a sample of catchments will be selected to represent each category. The acidification models will be used to evaluate the critical load for each catchment in the

population at the selected level of ANC. There is a distribution of critical load values within each acid-sensitivity category reflecting the range of sensitivity of catchments within each category. The goal of aggregating critical loads from multiple catchments is to develop an appropriately representative deposition value based on the distribution of critical loads, called the deposition metric, which protects a percentage of the population of water bodies within a national acid-sensitivity category from exceeding their critical load for the target value of ANC.

Distributions of catchment level critical loads are based on a combination of previously conducted steady-state critical load modeling and new critical load modeling conducted as part of this policy assessment. To ensure the population of water bodies included in the analysis were those sensitive to acidity caused by atmospheric deposition, several criteria were applied to the critical loads dataset to remove catchments in which organic acids, acid mine drainage or naturally low base cation weathering caused acidification.

Once a deposition metric is calculated, the value is modified by addition of a term to represent the amount of N that will be taken up by vegetation, immobilized in soil or degassed from the ecosystem. Next, a tradeoff curve for N and S deposition is generated for the acid sensitivity category. This function (illustrated below) is characterized by three nodes: 1) the maximum of amount of N deposition when S deposition equals zero 2) the amount of N deposition that will be captured by the ecosystem before it leaches and 3) the maximum amount of S sulfur deposition considering the N captured by the ecosystem. The function represents all pairs of N and S deposition that will equal the deposition metric for acidifying deposition for a specific target ANC.



The depositional load function

Reduced forms of nitrogen, such as ammonia, are either taken up by plants and microbes or converted to nitrate in the environment and use up the assimilative capacity of ANC at the same rate as oxidized forms of nitrogen deposition; therefore, deposition of reduced nitrogen must be accounted for in the watershed. The suggested approach is to subtract the loadings of reduced forms of nitrogen derived for a given spatial area from the deposition metric that represents a selected percentage of critical loads for a given population, such that the resultant deposition metric is for sulfur and oxidized nitrogen only. The policy assessment explores several methods for specifying the loadings of reduced nitrogen for specific geographic areas.

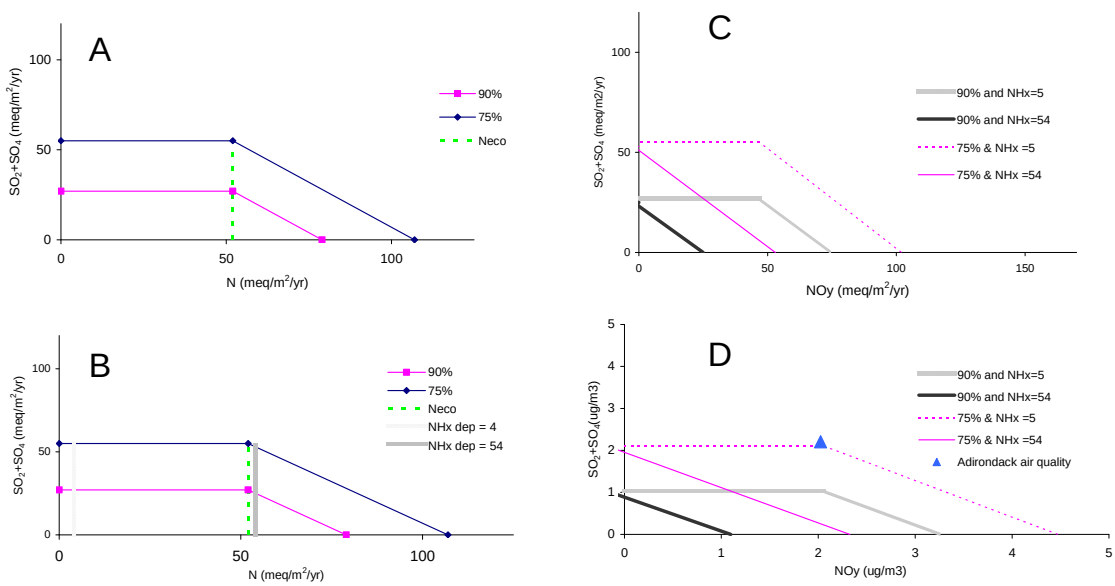
Deposition is related to ambient concentrations of NO_x and SO_x through deposition velocity, which is the rate at which an ambient pollutant is deposited. Deposition velocity varies over time and location, and is affected by land use conditions and meteorology. Our conceptual model requires conversion of deposition of N and S into ambient concentrations of NO_x and SO_x. Since the policy objective is to set an ambient air quality standard for total oxidized sulfur and nitrogen, and this is also the chemical resolution provided by the ecosystem models, it is convenient to use conversion factors based on available estimates

of concurrent deposition and ambient concentrations. The ratio of total deposition of NO_x and SO_x to ambient concentrations of NO_x and SO_x, respectively are referred to as deposition transference ratios. Applying the estimated deposition transference ratios to depositional load tradeoff curves leads to parallel tradeoff curves for ambient NO_x and SO_x (see figure below).

The national ambient air quality standard must be able to tie ANC to deposition and deposition to ambient air concentrations, incorporating ecological conditions and the contribution of reduced nitrogen. To incorporate all of these aspects, we develop an index that will provide a consistent standard nationally that is directly expressed in terms of concentrations of NO_x and SO_x. The form of this standard is referred to as the Atmospheric Acidification Protection Index (AAPI), which can be applied across the nation to convey the protection of aquatic ecosystems from acidification due to atmospheric deposition.

The AAPI represents the level of protection against the effects of acidification given local ecological conditions, the level of reduced nitrogen being deposited, and the levels of NO_x and SO_x that are limited by the standard. The AAPI is linked to a target ANC for a chosen percent of lakes and streams, and determines the combinations of NO_x and SO_x that will jointly result in the target ANC, taking into account uncertainties and other factors.

This AAPI can also be expressed as the tradeoff curves which show the combinations of NO_x and SO_x that meet the standard, generated for specific values of AAPI, and provide a representation of the standards in terms of atmospheric concentrations. These tradeoff curves will vary across the U.S. based on ecosystem sensitivity, reduced nitrogen deposition levels, and other factors. An example tradeoff curve for two different percentiles of protection at a target ANC of 50 µeq/L is provided below.



Graphs demonstrate the steps to develop a tradeoff curve for the AAPI including A) N vs. SO_2+SO_4 from the deposition metric and modified with Neco B) Two loads of NHx indicated C) after subtracting NHx load the resultant NOy vs SO_2+SO_4 curve, D) After applying the transference ratio the resultant air concentrations.

Options for Elements of the Standards

Draft Policy Assessment for the Review of the Secondary NAAQS for NO_x and SO_x: Executive Summary

Ambient air quality indicators other than NO_2 and SO_2 should be considered as the appropriate pollutant indicators for protection against the acidification effects associated with deposition of NO_x and SO_x. This consideration is based on the recognition that all forms of oxidized nitrogen and sulfur in the atmosphere contribute to deposition and resulting acidification, and as such concentrations of NO_2 and SO_2 are incomplete indicators. Furthermore, concentration of NOy is proposed as an appropriate indicator for oxides of nitrogen. The sum of concentrations of SO_2 and SO_4 is proposed as an appropriate indicator for oxides of sulfur.

Welfare effects associated with acidification result from annual cumulative deposition of nitrogen and sulfur, reflected in effects on the chronic ANC level (measured as annual or multiyear average ANC). Short-term (i.e., hours or days) episodic changes in water chemistry can also have significant biological effects. Episodic chemistry refers to conditions during precipitation or snowmelt events. Surface water chemistry has lower pH and acid neutralizing capacity (ANC) during these events than under baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed "episodic acidification." While ecosystems are also affected by episodic increases in acidity due to pulses of acidity during high rainfall periods and snowmelts, protection against these episodic acidity events can be achieved by establishing a higher chronic ANC level. Episodic acidification can result from either shorter term deposition episodes, or from longer term deposition on snowpack. Snowmelt can release stored N deposited throughout the winter, leading to episodic acidification in the absence of increased deposition during the actual episodic acidification event. Long term (3 to 5 year average) ambient NO_x and SO_x concentrations are appropriate to provide protection against low chronic ANC levels and episodic acidification.

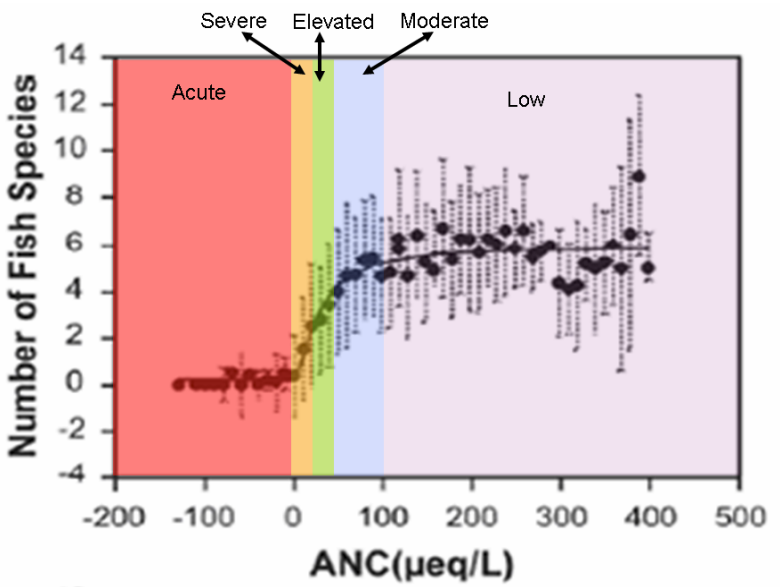
The current forms of the secondary standards for NO_x and SO_x do not take into account the combined contributions of NO_x and SO_x in the causation of effects associated with acidification of aquatic ecosystems. Based on the causal linkages between NO_x and SO_x, deposition of N and S, and the indicator of acidification, ANC, the current forms should be replaced with an atmospheric acidification protection index (AAPI), which reflects the important roles of underlying ecosystem characteristics, determinants of deposition, and deposition of reduced nitrogen in determining the potential effects from deposition of NO_x and SO_x.

The value of AAPI can be calculated for any observed values of NO_x and SO_x. However, the level of the standard for AAPI should reflect a wide number of factors, including desired level of protection indicated by a target ANC limit, the target percentile of water bodies to achieve the target ANC, and the various factors and uncertainties involved in specifying all of the other aspects of the standard, such as the acid sensitivity classification method, the specification of deposition of reduced nitrogen, nitrogen retention, the deposition transference ratios, and the averaging time. The administrator may choose an AAPI level reflecting an ANC level higher or lower than the target ANC limit to account for the combined effect of all of the components of the standard and their related uncertainties. The resulting AAPI, in the conte$_x$t of the overall standard, will reflect her informed judgment as to a standard that is sufficient but not more than necessary to protect against adverse public welfare effects.

Within the AAPI form, EPA will specify the parameter values for all elements excepting NO_x and SO_x, which will be the measured atmospheric indicators. The values for pre-industrial base cation weathering, nitrogen retention and uptake, and runoff, are based on the same inputs used to develop the deposition metrics. The values for reduced nitrogen and the deposition transference ratios will be calculated using output from the most up-to-date version of EPA's Community Multiscale Air Quality (CMAQ) model. EPA is considering methods to account for the dynamic nature of deposition of reduced nitrogen in specifying the NO_x and SO_x standards.

As demonstrated by the tradeoff curves, multiple combinations of concentrations of NO_x and SO_x can yield the same value of the AAPI. No single combination of NO_x and SO_x will produce a particular value of AAPI in all locations. Measured concentrations of annual average NO_x and SO_x necessary to meet the standards are thus expressed conditionally by the AAPI and not by fixed quantities.

A target ANC limit based on a desired level of protection is an important input to the decisions of the level of AAPI and the percent of ecosystems to be protected. Specific levels of ANC are associated with differing levels of ecosystem impairment, with higher levels of ANC resulting in fewer ecosystem impacts, and lower levels resulting in both higher intensity of impacts and a broader set of impacts. For example, the number of fish species present in a waterbody has been shown to be positively correlated with the ANC level in the water, with higher values supporting a greater richness and diversity of fish species. This relationship is illustrated in the following figure.



Number of fish species per lake or stream versus ANC level and aquatic status category for lakes in the Adirondack Case Study Area

The target ANC level specified in designing the standard is only one part in determining the overall protectiveness of the standard. The degree of protectiveness is based on all elements of the standard, including the target ANC selected by the Administrator, the size of the spatial areas over which the standard is applied, the percent of aquatic ecosystems targeted within a spatial area that is selected by the Administrator to achieve the selected ANC level, and the underlying parameters of the AAPI, including the atmospheric indicator, the critical load models used to determine pre-industrial base cation levels, the calculated values for the deposition transference ratios, and the calculated value for deposition of reduced nitrogen. There are widely varying degrees of uncertainty associated with all of these elements, some being much more certain and others being much less certain. The specified target ANC level is a crucial part of developing a standard that is requisite to protect public welfare, but it is the overall design and content of the standard that must be considered in judging the adequacy of protection it provides.

The secondary NAAQS will reflect the public welfare policy judgments of the Administrator, based on the science, as to the level of air quality which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the pollutant in the ambient air. In certain naturally acidic ecosystems, even though the ecological benchmarks are exceeded, e.g. ANC may be quite low; NO_x and

SO_x are not contributing to effects because those systems have chronic natural acidity and will not benefit from reductions in atmospheric deposition. The secondary NAAQS are not intended to provide protection in these types of naturally acidic systems. Instead, the secondary NAAQS are focused on providing protection in areas where ambient NO_x and SO_x are resulting in effects in ecosystems with low natural levels of acidification that are highly sensitive to additional inputs of acid deposition. The approaches for specifying populations of critical loads to develop deposition metrics explicitly excludes lakes and streams that are naturally acidic and those not likely to benefit from decreases in atmospheric deposition.

ANC levels below 20 μeq/L are generally associated with high probability of low pH, leading to death or loss of fitness of biota that are sensitive to acidification. Overall, there is little uncertainty that significant effects on aquatic biota are occurring at ANC levels below 20 μeq/L. Based on the field data from the Adirondacks and Shenendoah case study areas, ANC levels less than 50 μeq/L are adverse to ecosystem health, and are likely to lead to reductions in ecosystem services related to recreational fishing. However, the types of effects, specific species, and prevalence of effects across water bodies in the U.S. is more uncertain at ANC levels between 20 and 50 μeq/L. Targeting ANC levels between 50 and 100 μeq/L would provide additional protection; however, uncertainties regarding the additional reduction in adverse welfare effects are much larger for target ANC levels above 50 μeq/L.

Specifying an appropriate range of levels for an AAPI standard that is designed and specified as discussed above involves consideration of the degree to which any specific AAPI would lead to achieving the desired ANC level, and a judgment as to the degree of protection of public welfare that is warranted. Selection of a range of AAPI and selection of a specific level of AAPI within that range should incorporate a wide number of considerations, including the percent of water bodies within acid sensitive areas that the Administrator determines should be protected at the targeted ANC level.

In determining the requisite level of protection for the public welfare from effects on aquatic ecosystems, the Administrator will need to weigh the importance of the predicted risks of these effects in the overall context of public welfare protection, along with a determination as to the appropriate weight to place on the associated uncertainties and limitations of this information.

Co-Protection for Other Effects Provided by an Acidification Standard

To understand the level of protection provided by a NO_x/SO_x standard based on aquatic acidification to protect against terrestrial acidification effects, we compared the critical loads for lakes and streams that would maintain an aquatic ANC of 50 to the critical loads to maintain either a terrestrial Bc:Al ratio of 1.2 or 10 averaged across a watershed area.

Results for the Adirondacks showed that critical loads for 29 lakes at an ANC of 50 were lower for 13 of those lakes than the critical load for the terrestrial watershed areas at a Bc:Al ratio of 10 and for 21 lakes at a Bc:Al ratio of 1.2. Perhaps more significant was the result that 13 of the 16 lakes in the highly and moderately sensitive areas had a lower critical load than the Bc:Al 10 areas and 16 of 16 lakes in the highly and moderately sensitive areas had lower critical loads than the Bc:Al 1.2 areas. The Shenandoah region reflected similar results.

In general, the aquatic critical acid loads offered greater protection to the watersheds than did the terrestrial critical loads. Generally in situations where the terrestrial critical loads were more protective, the lakes or streams in the watershed were rated as having “Low Sensitivity” or “Not Sensitive” to acidifying nitrogen and sulfur deposition. Conversely, when the water bodies 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.

Initial Conclusions

In this current review, important new information has become available since the last reviews (1996 for NO_x, and 1988 for SO_x) that supports revising the current NO_x and SO_x standards. Specifically, the ISA has concluded that there are causal relationships between NO_x and SO_x acidifying deposition and effects on aquatic and terrestrial ecosystems, and the ISA and REA provide substantial quantitative evidence of effects occurring in locations that meet the current NO_2 and SO_2 standards. In addition, observational data and rigorous atmospheric modeling has become available regarding the role of both nitrogen and sulfur deposition in acidification of sensitive water bodies. This information is sufficient to inform the development of revised secondary standards for NO_x and SO_x to protect against the effects of aquatic acidification in sensitive ecosystems. Additional information is needed to set separate standards to protect terrestrial ecosystems from acidification effects. While there is also new information available on the role of nitrogen deposition on nutrient enrichment effects in sensitive terrestrial and aquatic ecosystems, and the ISA concludes there is a causal relationship between NO_x and nutrient enrichment effects, for this second draft policy assessment, we have focused on acidification effects due to the substantially greater amount of information available to inform the development of secondary standards.

We highlight the progress made in considering the joint nature of ecosystem responses to acidifying deposition of NO_x and SO_x, and note that the ability to consider revisions to the NO_x and SO_x secondary standards has been enhanced by our ability to consider a joint standard for NO_x and SO_x to protect against acidification effects. The development of an appropriate form of the standard linked to a common indicator of aquatic acidification, ANC, is also a significant step forward, as it allows for development of a standard for aquatic acidification designed to provide generally the same degree of protection across the country, while still reflecting the underlying variability in ecosystem sensitivity to acidifying NO_x and SO_x deposition.

We provide the following initial conclusions regarding the NO_x and SO_x secondary standards:

- The available effects-based evidence for aquatic and terrestrial acidification and nutrient enrichment suggests consideration of NO_x and SO_x standards that are at least as protective as the current standard. Consideration of joint standards for NO_x and SO_x is appropriate given the common atmospheric processes governing the deposition of NO_x and SO_x to sensitive ecosystems.
- On the basis of the acidification and nutrient enrichment effects that have been observed to still occur under current ambient conditions and those predicted to occur under the scenario of just meeting the current secondary NAAQS, we find support for consideration that the current secondary NAAQS are inadequate to protect the public welfare from known and anticipated adverse welfare effects from aquatic and terrestrial acidification associated with deposition of NO_x and SO_x.
- We find support for consideration that current levels of NO_x and SO_x are associated with deposition that leads to ANC values below benchmark values that cause ecological harm and losses in ecosystem services in sensitive ecosystems, including significant mortality in sensitive aquatic biota and losses in fish species richness, which is associated with reductions in recreational fishing services, among others.
- We find support for consideration that current levels of ambient NO_x and SO_x are associated with deposition that leads to Bc:Al values below benchmark values for terrestrial acidification that cause ecological harm and losses in ecosystem services in sensitive ecosystems, including losses

in tree health and growth, which are associated with reductions in timber production, among other services.

- We suggest that effects due to aquatic acidification are most suitable for defining secondary standards for NO_x and SO_x. We note that in developing a standard designed to protect against the effects of aquatic acidification due to deposition of NO_x and SO_x, the resulting standards may not provide adequate protection against known effects associated with nutrient enrichment in sensitive aquatic and terrestrial ecosystems or acidification in sensitive terrestrial ecosystems.
- Based on the causal linkages between NO_x and SO_x, deposition of N and S, and the indicator of acidification, ANC, consideration should be given to an additional secondary standard with a form defined by an atmospheric acidification protection index (AAPI), which reflects the important roles of underlying ecosystem characteristics, determinants of deposition, and deposition of reduced nitrogen in determining the potential effects from deposition of NO_x and SO_x.
- Staff has concluded, based on the evidence and risk based information, and consideration of information related to definitions of adversity, that:
  - a target level of ANC of 20 μeq/L will protect against significant losses in fish mortality in many sensitive lakes, but will place less weight on protection against losses in aquatic biodiversity, and will be less protective against potential acidification episodes,
  - a target level of ANC of 50 μeq/L will protect against significant mortality in aquatic organisms and loss of fish health and biodiversity in sensitive lakes and streams, and will give weight to considerations of uncertainties in the time to recovery of aquatic ecosystems,
  - target levels of ANC above 50 μeq/L may provide additional protection against declines in fitness of sensitive species (e.g., brook trout, zooplankton), however, overall health of aquatic communities may not be impacted.

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List of Acronyms and Abbreviations

AAPI	Atmospheric Acidification Potential Index
ADR	Adirondack Mountains of New York
Al^{3+}	aluminum
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
CAA	Clean Air Act
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network
CCS	coastal sage scrub
Chl *a*	chlorophyll *a*
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_2O	water vapor
H_2SO_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

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
Mg^{2+}	magnesium
N	nitrogen
N_2	gaseous nitrogen
N_2O	nitrous oxide
N_2O_3	nitrogen trioxide
N_2O_4	nitrogen tetroxide
N_2O_5	dinitrogen pentoxide
Na^+	sodium
NAAQS	National Ambient Air Quality Standards
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NAWQA	National Water Quality Assessment
NEEA	National Estuarine Eutrophication Assessment
NEP	net ecosystem productivity
NH_3	ammonia gas
NH_4^+	ammonium ion
$(NH_4)_2SO_4$	ammonium sulfate
NHx	category label for NH_3 plus NH_4^+
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	reduced nitrite
NO_3^-	reduced nitrate
NOAA	National Oceanic and Atmospheric Administration
NO_x	nitrogen oxides
NO_y	total 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	relative acidity
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_2O_3	thiosulfate
S_2O_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
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
$\mu g/m^3$	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., PM2.5, 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.

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

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 NOx and/or SOx 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 NH3, NH4+, NO, NO2, HNO3, N2O, NO3–, 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 NOx and/or SOx 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

The U.S. Environmental Protection Agency (EPA) is presently conducting a review of the secondary National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen (NOx) and oxides of sulfur (SOx). 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 (US EPA, 2007). The Integrated Review Plan (IRP) outlined the Clean Air Act (CAA or the Act) requirements related to the establishment and reviews of the NAAQS, the process and schedule for conducting the current review, and the key components in the NAAQS review process: an Integrated Science Assessment (ISA), Risk and Exposure Assessment (REA), and policy assessment/rulemaking. It presented key policy-relevant issues to be addressed in this review as a series of questions that frames our consideration of whether the current secondary (welfare-based) NAAQS for NOx and SOx should be retained or revised.

As part of this review, staff in the U.S. Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards (OAQPS) prepared this second draft Policy Assessment.[1] The objective of this assessment is to evaluate the policy implications of the key scientific information contained in the document *Integrated Science Assessment for Oxides of Nitrogen and Sulfur-Ecological Criteria* (USEPA, 2008; henceforth referred to as the ISA), 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; henceforth referred to as the REA). This second draft also presents staff conclusions on a range of policy options that we believe are appropriate for the Administrator to consider concerning whether, and if so how, to revise the secondary (welfare-based) NOx and SOx NAAQS.

[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.

This policy assessment is intended to help "bridge the gap" between the scientific assessment contained in the ISA and the judgments required of the EPA Administrator in determining whether it is appropriate to retain or revise the secondary NAAQS for NOx and SOx. This policy assessment considers the available scientific evidence and quantitative risk-based analyses, together with related limitations and uncertainties, and focuses on the basic components of air quality standards: indicators[2], averaging times, forms[3], and levels. These components, which serve to define each standard, must be considered collectively in evaluating the welfare protection afforded by the secondary NOx and SOx NAAQS. Our development of this policy assessment is based on the assessment and integrative synthesis of information presented in the ISA and on staff analyses and evaluations presented in this document, and is further informed by comments and advice received from an independent scientific review committee, the Clean Air Scientific Advisory Committee (CASAC), in their review of the previous integrated science assessment, risk and exposure assessment, and first draft policy assesment. To view related documents developed as part of the planning, science, and risk assessment phases of this review see http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html.

This document is organized around a conceptual framework for a combined NOx and SOx secondary NAAQS and is focused on answering key policy questions related to the implementation of that conceptual framework. Chapter 2 provides a summary of ecological effects from the deposition of ambient NOx and SOx to sensitive ecosystems, drawing from the ISA and REA. Chapter 3 places those ecological effects within the context of "public welfare" by linking effects to ecosystem services or other benchmarks of public welfare. Chapter 4 addresses the adequacy of the current NOx and SOx secondary NAAQS in addressing the impacts on public welfare from ecological effects. Chapter 5 develops the conceptual design for ecologically relevant multi-pollutant standards and presents options for developing critical components of a secondary NAAQS necessary to implement the conceptual design. Chapter 6 describes how secondary NAAQS designed to protect a specific ecological endpoint may also provide protection for other ecological endpoints. Chapter 7 provides an assessment of critical

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

[3] The "form" of a standard defines the air quality statistic that is to be compared to the level of the standard in determining whether an area attains the standard.

uncertainties and sensitivitie considered in developing the options for the components of the standard. Chapter 8 discusses issues related to monitoring of NOx and SOx. Chapter 9 provides initial staff conclusions regarding options for pollutant indicators, averaging times, forms, and ranges of levels for the secondary NOx and SOx NAAQS.

In this document we consider how the available scientific evidence and quantitative risk-based analyses, together with related limitations and uncertainties, inform the review of each element of the NAAQS: indicator, averaging times, forms, and levels. These components must be considered collectively in evaluating the welfare protection afforded by the secondary NAAQS standards. This draft document does not contain final staff conclusions as to all the necessary components of an alternative secondary standard for NOx and/or SOx but rather describes the current state of thinking with regard to potential policy options and provides an appropriate context of information for the Administrator to consider in making decisions regarding the standards.

While this policy assessment should be of use to all parties interested in the secondary NOx and SOx NAAQS review, it is written with an expectation that the reader has some familiarity with the technical discussions contained in the ISA and REA.

EPA's final Policy Assessment will address additional CASAC comments on this second draft, and will include sufficient information to inform the Administrator on critical components of the standards, and staff conclusions regarding alternative levels of the standards.

1.1 DEFINITIONS, PARAMETERS, UNITS, AND CONVENTIONS USED FOR THIS ASSESSMENT

Throughout this document numerous terms are used that address a variety of atmospheric and ecosystem processes and variables. Some of the more common terms used in the technical community are not always synonymous with definitions imbedded in the CAA. Because of this diversity of terms spanning atmospheric and ecosystem processes along with adherence to scientific and legal conventions, this section provides the terminology as a reference source for the entire report.

As discussed in detail in the REA (**REA 1.3.1**), in the atmospheric science community NOx is typically referred to as the sum of nitrogen dioxide (NO_2), and nitric oxide (NO). As defined by the Clean Air Act, the family of NOx includes any gaseous combination of nitrogen

and oxygen (e.g., NO_2, NO, nitrous oxide [N_2O], dinitrogen trioxide [N_2O_3], dinitrogen tetroxide [N_2O_4], and dinitrogen pentoxide [N_2O_5]). The term used by the scientific community to represent the complete set of reactive oxidized nitrogen compounds, including those listed in CAA Section 108(c) with the exception of N_2O, is total oxidized nitrogen (NOy), commonly defined as NO, NO_2 and the all of the oxidation products of NO and NO_2 Reactive oxidized nitrogen is defined as NOy = NO_2 + NO + HNO_3 + PAN +2N_2O_5 + HONO+ NO_3 + organic nitrates + particulate NO_3 (Finlayson-Pitts and Pitts, 2000). In this document, unless otherwise indicated, we use the term NOy as the atmospheric indicators associated with the NOx component of the proposed NOx/SOx standard .

For this assessment, SOx is defined to include all oxides of sulfur, including multiple gaseous substances (e.g., SO_2, sulfur monoxide [SO], sulfur trioxide [SO_3], thiosulfate [S_2O_3], and heptoxide [S_2O_7], as well as particulate species, such as ammonium sulfate [$(NH_4)2SO_4$]). Throughout this text we refer to sulfate as SO_4 and nitrate as NO_3, recognizing that they have charges of -2 for sulfate and -1 for nitrate. The sum of sulfur dioxide gas (SO_2) and particulate sulfate (SO_4), referred herein as (SO_2 + SO_4) is used throughout this document as the atmospheric indictor for the SOx component of the proposed NOx/SOx standard. From a measurement and modeling perspective we only consider the sum of SO_2 and particulate SO_4 as the indicator for sulfur. The sum of SO_2 and SO_4 constitute virtually all of the ambient air sulfur budget and are measured routinely in monitoring networks.

Table 1-1 provides further explanation of these indicators, some of which is repeated in Chapters 4, 5 and 8. Table 1 also provides details on the units used throughout the equations and examples in the PAD. 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 1 -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 NOy 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_2O_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., $1 \cdot HNO_3 + 2 \cdot N_20_5 + \ldots$) 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 SO_2 and SO_4 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;**	***$\mu g/m^3$*** as N or S	***ppb*** = $(MA/M_i) \cdot \rho_{air}) \cdot \mu g/m^3$ where ρ_{air} is the air density in units of (kg/m^3); $\rho_{air} = 28.97(10)^{-3} \cdot P/(R \cdot T)$ $R = 8.206(10)^{-5} m^3 atm/(mol \cdot K)$ P = atm T = degrees K MA = molecular weight of air (28.97) M_i = Atomic weight of nitrogen (14) or sulfur (32) $meq/m^3 = (1/M_i) \cdot \mu g/m^3$	

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
NO_y deposition **(SO_2 +SO_4)** ***NH_x*** Used in various conventions of: Dep_i	***meq/m²-yr as N or S***	***kg/ha-yr*** =$(M_i/q)(10)^{-2}$ · ***meq/m²-yr*** where q = charge (1 for N, 2 for S)	
$C^{\max}_{(SO4+SO2)}$	***µg/m³***		is the concentration of **(SO_2 +SO_4)** in the atmosphere consistent with $DL_S^{\max}$
$C^{\max}_{NOy}$	***µg/m³***		is the concentration of NOy in the atmosphere consistent with $DL_N^{\max}$
$C^{\min}_{NOy}$	***µg/m³***		is the concentration of NOy in the atmosphere consistent with $DL_N^{\min}$
v_i^{Dry}	***m/yr***		dry deposition velocities
v_i^{Wet}	***m/yr***		wet deposition velocities
Dep_i^{Dry}	***meq/m²-yr***		dry deposition fluxes
Dep_i^{Wet}	***meq/m²-yr***		wet deposition fluxes
Dep_i^{Total}	***meq/m²-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 NO_y to the total ambient concentration, and represents an average of the chemical species specific v_i^{Tot} (= v_i^{Dry} + v_i^{Wet}) values

1

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
Ecosystem variables			
ANC*	***μeq/L***		calculated value of ANC
ANC_{limit}	***μeq/L***		a "target" ANC level (μeq/L)
$CL_{ANClim}(i)$	***meq/m²-yr***		depositional 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 for an acid sensitive area (this is typically equal to precipitation – evapotranspiration
Qws	***m/yr***		Catchment level surface water runoff (m/yr) (this is typically equal to precipitation – evapotranspiration
N_{ECO}	***meq/m²-yr***		nitrogen retention and denitrification by terrestrial catchment
N_{leach}	***meq/m²-yr***		N leaching
$DL_{\%eco}(i)$	***meq/m²-yr***		The deposition metric, defined as the amount of deposition that protects a selected percentage of individual catchments for a population of water bodies from exceeding their $DL_{ANClim}(i)$, where *i* indicates the pollutant of interest
DL_N^{max}	***meq/m²-yr***		In the tradeoff curve for $DL_{\%eco}(i)$, the maximum of amount of N deposition when S deposition equals

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
			zero
$DL_N^{\min}$	***meq/m²-yr***		In the tradeoff curve for $DL_{\%eco}(i)$, the amount of N deposition that will be captured by the ecosystem before it leaches
$DL_S^{\max}$	***meq/m²-yr***		In the tradeoff curve for $DL_{\%eco}(i)$, the maximum amount of S sulfur deposition considering N_{ECO}

1.2 POLICY OBJECTIVES

In conducting this periodic review of the NOx and SOx secondary NAAQS, EPA has decided to jointly assess the scientific information, associated risks, and standards relevant to protecting the public welfare from adverse effects associated with oxides of nitrogen and sulfur. Although EPA has historically adopted separate secondary standards for oxides of nitrogen (NOx) and oxides of sulfur (SOx), EPA is conducting a joint secondary review of these standards because NOx, SOx, 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). There is a strong basis for considering these pollutants together, building upon EPA's and CASAC's past recognition of the interactions of these pollutants and on the growing body of scientific information that is now available related to these interactions and associated ecological effects.

EPA sets secondary standards for two criteria pollutants related to NOx and SOx: ozone and particulate matter (PM). NOx is a precursor 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. SOx is a precursor to the formation of particulate sulfate, which is a significant component of fine PM in many parts of the U.S. While there are a number

of welfare effects associated with ozone and fine PM, including ozone damage to vegetation, and visibility degradation related to PM, protection against those effects is provided by the ozone and fine PM standards. This review focuses on evaluation of the protection provided by NOx and SOx secondary standards for effects associated with direct atmospheric concentrations of NOx and SOx, and effects associated with deposition of NOx and SOx to sensitive ecosystems, including deposition in the form of particulate nitrate and sulfate in their component forms.

The ISA highlights the ecological effects associated with deposition of ambient NOx and SOx to sensitive ecosystems other than commercially managed forests and agricultural lands. This assessment primarily focuses on the effects of ambient NOx and SOx via deposition on multiple ecological receptors, but also evaluates information on gas-phase effects of NOx and SOx via stomatal exposure on vegetation, which are the effects that the current secondary standards protect against. The ISA highlighted effects including those associated with acidification and nitrogen nutrient enrichment. Based on these highlighted effects, EPA's policy objective is to develop a framework for NOx and SOx standards that incorporate factors that will lead to standards that are ecologically relevant, and that recognizes the interactions between the two pollutants as they deposit to sensitive ecosystems, with an ultimate goal of setting standards that, based on the ecological criteria described in the ISA, and consistent with the requirements of the Clean Air Act, "are 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."

In presenting policy options for the Administrator's consideration, we note that the final decision on retaining or revising the current secondary standards for NOx and SOx is largely a public welfare policy judgment based on the Administrator's informed assessment of what constitutes requisite protection against adverse effects to public welfare. A final 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 in ecosystem services. Our approach to informing these judgments, as discussed below, is consistent with the requirements of the NAAQS provisions of the Clean Air Act and with how

EPA and the courts have historically interpreted the Act. These provisions require the Administrator to establish secondary NAAQS that, in the Administrator's judgment, are requisite to protect public welfare from any known or anticipated adverse effects associated with the presence of NOx and SOx in the ambient air. In so doing, the Administrator seeks to establish standards that are neither more nor less stringent than necessary for this purpose.

For this second draft policy assessment, we have chosen to focus much of our discussion on the effects of ambient NOx and SOx on ecological impacts associated with acidifying deposition of nitrogen and sulfur, which is a transformation product of ambient NOx and SOx. We have the greatest confidence in the causal linkages between NOx and SOx and aquatic acidification effects, and we have the most complete information available with which to develop an ecologically meaningful structure for the standards.

1.3 CRITICAL POLICY ELEMENTS

Our policy objective is guided by the information in the ISA and REA, framed within the legislative requirements of the CAA. This framing leads us to focus on critical policy elements (CPE) consistent with elements of Clean Air Act language.

Sections 108 and 109 of the CAA govern the establishment and periodic review of the NAAQS and of the air quality criteria upon which the standards are based. The NAAQS are established for pollutants that are listed under section 108, based on three criteria, including whether emissions of the air pollutant cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare and whose presence in the ambient air results from numerous or diverse mobile or stationary sources. The NAAQS are based on air quality criteria that reflect the latest scientific knowledge, useful in indicating the types and extent of identifiable effects on public health or welfare that may be expected from the presence of the pollutant in ambient air. The criteria refer to criteria issued pursuant to §108 of the Clean Air Act, which 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 of welfare; and (C) any known or anticipated adverse effects on welfare."

The following critical policy elements for the design of ecologically relevant secondary standards for NOx and SOx are identified:

(CPE 1) An evaluation of the effects of ambient NOx and SOx 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.

(CPE 1.1) Evaluation of the relationship between response of ecological receptors, e.g. changes in diversity of fish species, and the response related to public welfare, e.g. loss in recreational fishing services.

(CPE 1.2) Evaluation of the extent to which identified effects are occurring under recent conditions, and the extent to which meeting the current standards would provide protection against these effects.

(CPE 2) An assessment of how best to characterize, in defining the standards, the variable ecosystem factors that affect the relationship between ecological effects and depositional loadings of N and S.

(CPE 2.1) Specification of potential indicators of ecological effects, e.g. acid neutralizing capacity (ANC) that incorporates variability in ecosystem factors.

(CPE 3) Characterization of the complex relationships between ambient concentrations of NOx and SOx and deposition of N and S in the specification of a standard.

(CPE 4) Specification of the form for the standard(s), including ambient atmospheric indicators for NOx and SOx, with consideration of averaging times, and options for levels of the standard(s).

The development of the conceptual framework for the NOx and SOx standards described in Section 1.4 will be motivated by these critical policy elements. However, in order to provide a historical context for this new framework, the next section provides a brief history of previous reviews of the NOx and SOx secondary NAAQS, as well as other relevant historical reviews of welfare effects associated with these pollutants.

1.4 HISTORICAL CONTEXT

1.4.1 History of NOx and SOx NAAQS Review

1.4.1.1 NOx NAAQS

EPA began the most recent previous review of the NOx secondary standards in 1987 and in November 1991, EPA released an updated draft AQCD for CASAC and public review and comment (56 FR 59285). This draft document provided a comprehensive assessment of the available scientific and technical information on health and welfare effects associated with NO_2 and other NO_x. CASAC reviewed the draft document at a meeting held on July 1, 1993, and concluded in a closure letter to the Administrator that the document "provides a scientifically balanced and defensible summary of current knowledge of the effects of this pollutant and provides an adequate basis for EPA to make a decision as to the appropriate NAAQS for NO_2" (Wolff, 1993). The AQCD *Air Quality Criteria for Oxides of Nitrogen* was then finalized (U.S. EPA, 1993). EPA also prepared a Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised NO_x AQCD and identified the critical elements to be considered in the review of the NO_2 NAAQS. CASAC reviewed two drafts of the Staff Paper and concluded in a closure letter to the Administrator that the document provided a "scientifically adequate basis for regulatory decisions on nitrogen dioxide" (Wolff, 1995). In October 1995, the Administrator announced her proposed decision not to revise either the primary or secondary NAAQS for NO_2 (60 FR 52874; October 11, 1995). A year later, the Administrator made a final determination not to revise the NAAQS for NO_2 after careful evaluation of the comments received on the proposal (61 FR 52852; October 8, 1996). The level for both the existing primary and secondary NAAQS for NO_2 is 0.053 ppm (100 micrograms per cubic meter [$\mu g/m^3$] of air), annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO_2 concentrations.

1.4.1.2 SOx NAAQS

Based on the 1970 SO_x criteria document (DHEW, 1970), EPA promulgated primary and secondary NAAQS for SO_2 on April 30, 1971 (36 FR 8186). The secondary standards included a standard at 0.02 ppm in an annual arithmetic mean and a 3-hour average of 0.5 ppm, not to be exceeded more than once per year. These secondary standards were established solely on the basis of 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 SO_2 exposure over the growing season, rather than from short-term peak concentrations. Therefore, EPA proposed (38 FR 11355) and then finalized (38 FR 25678) a revocation of the annual mean secondary standard. At that time, EPA was aware that SO_x air concentrations have other public welfare effects, including effects on materials, visibility, soils, and water. However, the available data were considered insufficient to establish a quantitative relationship between specific ambient SO_x concentrations and effects (38 FR 25679).

In 1979, EPA announced that it was revising the Air Quality Criteria Document (AQCD) for sulfur oxides concurrently with that for particulate matter and would produce a combined particulate matter and sulfur oxides criteria document. Following its review of a draft revised criteria document in August 1980, CASAC concluded that acid deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (1) emissions of relevant pollutants (e.g., SO_2 and oxides of nitrogen), (2) formation of acidic wet and dry deposition products, and (3) effects on terrestrial and aquatic ecosystems. CASAC also noted that acid deposition involves, at a minimum, several different criteria pollutants: oxides of sulfur, oxides of nitrogen, and the fine particulate fraction of suspended particles. CASAC felt that any document on this subject should address both wet and dry deposition, since dry deposition was believed to account for 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 nitrogen oxides and PM and SO_x. Following CASAC closure on the AQCD for SO_2 in December 1981, EPA's Office of Air Quality Planning and Standards published a Staff Paper in November 1982, but the paper did not directly assess the issue of acid deposition. Instead, EPA subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (U.S. EPA, 1984a, b), and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (U.S. EPA, 1985) (53 FR 14935 -14936). These documents, though they

were not considered criteria documents and did not undergo CASAC review, represented the most comprehensive summary of relevant scientific information completed by EPA at that point.

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

1.4.2 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 SO_2 by 10 million tons and NO_x emissions by 2 million tons from 1980 emission levels in order to achieve reductions over broad geographic regions. In this provision, Congress included a statement of findings that led them to take action, concluding that (1) the presence of acid compounds and their precursors in the atmosphere and in deposition from the atmosphere represents a threat to natural resources, ecosystems, materials, visibility, and public health; (2) the problem of acid deposition is of national and international significance; and (3) current and future generations of Americans will be adversely affected by delaying measures to remedy the problem.

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

Third, Congress 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. The Report concluded that establishing acid deposition standards for sulfur and nitrogen deposition may at some point in the future be technically feasible, although appropriate deposition loads for these acidifying chemicals could not be defined with reasonable certainty at that time.

Fourth, the 1990 Amendments also added new language to sections of the CAA pertaining to the scope and application of the secondary NAAQS designed to protect the public welfare. Specifically, the definition of "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 requested in 2000 that EPA initiate a rulemaking proceeding to enhance the air quality in national parks and wilderness areas in order to protect resources and values that are being adversely affected by air pollution. Included among the effects of concern identified in the request were the acidification of streams, surface waters, and/or soils; eutrophication of coastal waters; visibility impairment; and foliar injury from ozone.

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

The most recent 2005 NAPAP report states that "… scientific studies indicate that the emission reductions achieved by Title IV are not sufficient to allow recovery of acid-sensitive ecosystems. Estimates from the literature of the scope of additional emission reductions that are necessary in order to protect acid-sensitive ecosystems range from approximately 40-80% beyond full implementation of Title IV.… The results of the modeling presented in this Report to Congress indicate that broader recovery is not predicted without additional emission reductions" (NAPAP, 2005).[4]

Given the state of the science as described in the ISA and in other recent reports, such as the NAPAP's above, EPA believes it is appropriate, in the context of evaluating the adequacy of the current NO_2 and SO_2 secondary standards in this review, to revisit the question of the appropriateness and the feasibility of setting a secondary NAAQS to address remaining known or anticipated adverse public welfare effects resulting from the acidic and nutrient deposition of these criteria pollutants.

[4] Note that a new NAPAP report is expected to be released later in 2010. The findings of that report will be considered in the final policy assessment.

1.5 PROPOSED CONCEPTUAL FRAMEWORK FOR COMBINED NO_X SO_X STANDARDS

There is a strong basis for considering NOx and SOx 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 to ambient NOx and SOx. That framework provided a flow from ambient concentrations exposures via deposition to ecological indicators and effects (see Figure ES-2 in the REA Executive Summary). This sequence represents the process by which we can determine the risks associated with ambient concentrations of NOx and SOx. However, for the purposes of discussing a conceptual framework for design of standards to protect against those risks, a modified version of the risk framework is needed.

Figure 1-1 depicts the framework by which we are considering the structure of an ecologically meaningful secondary standard. It is a conceptual diagram that illustrates how a level of protection related to an indicator of ecological effect(s) equates to atmospheric concentrations of NOx and SOx indicators. This conceptual diagram illustrates the linkages between ambient air concentrations and resulting deposition metrics, and between the deposition metric and the ecological indicator of concern. The Atmospheric Deposition Transformation Function translates ambient atmospheric concentrations of NOx and SOx to nitrogen and sulfur deposition metrics, while the Ecological Effect Function transforms the deposition metric into the ecological indicator.

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

The details of this conceptual framework are discussed in Chapter 5, including discussions of modifying factors that alter the relationship between ambient atmospheric concentrations of NOx and SOx 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 NOx and SOx and the environment, however, such an approach may not be appropriate to provide the requisite level of protection to public welfare from effects on sensitive ecosystems. EPA is proposing in this review of the secondary standard for NOx and SOx 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.

EPA must undertake a thorough review of the air quality criteria for the pollutant at issue in reviewing a secondary NAAQS, and determine whether a current standard is requisite to protect the public welfare. Under section 108 of the CAA, air quality criteria are to "reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects" associated with the presence of the pollutant in the ambient air. It is clear from the language of the CAA that where the state of the science provides a basis for considering such effects, the review of the air quality criteria should encompass a broad analysis of "any" known or anticipated adverse effects, as well as the ways in which variable conditions such as atmospheric conditions may impact the effect of a pollutant and the ways in which other air pollutants may interact with the criteria pollutant to produce adverse effects. Specifically, section 108(a)(2) of the CAA provides that:

Air quality criteria for an air pollutant shall 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 such pollutant in the ambient air, in varying quantities. The criteria for an air pollutant to the extent practicable, shall include information on:

(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 pollutants;

(B) The types of air pollutants which, when present in the atmosphere, may interact with such pollutants to produce an adverse effect on public health or welfare; and

(C) Any known or anticipated adverse effects on welfare.

Based on this extensive review of the air quality criteria for an air pollutant, the Administrator is required to review and to revise, as appropriate, the secondary standard to ensure that the standard "is requisite to protect public welfare from any known or anticipated adverse effects associated with the presence of such air pollutant in the ambient air." CAA § 109(b) & (d). "Effects on welfare," in turn, is defined to include a broad array of effects, including effects on soil, water, crops, vegetation, and manmade materials, "whether caused by transformation, conversion, or combination with other air pollutants." CAA § 302(h). Thus, as with the sections of the CAA describing the issuance of air quality criteria, the CAA uses expansive language in describing the scope of EPA's responsibility and the range of effects that EPA should take into account in setting a standard that is requisite to protect public welfare. The term "requisite," however, indicates that section 109 is not open-ended. In considering the meaning of the term "requisite" in the context of the primary standards, the Supreme Court has agreed with EPA that such a standard is one that is "sufficient, but not more than necessary" to protect public health. Whitman v. American Trucking, 531 U.S. 457, 473 (2001).

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 NOx and SOx to terrestrial and aquatic environments can impact ecosystems through both direct and indirect mechanisms, as discussed in the REA and this document. 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 attempts to take into consideration widely acknowledged effects, such as

acidification and nutrient enrichment, which are associated with the presence of ambient SOx and NOx.

In this review, EPA is also attempting to develop a standard that takes into account the variability in effects from ambient levels of SOx and NOx. 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. One approach is to develop a secondary standard such as the one discussed in this Policy Assessment Document. Such a standard is designed to provide a generally uniform degree of protection throughout the country by allowing for varying concentrations of allowable ambient NOx and SOx, depending on atmospheric conditions and other variabilities, to achieve that degree of protection[5]. Such a standard protects 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.

[5] In concept, this approach to setting a national standard using a consistent form that may result in differing levels of atmospheric concentrations fo NOx and SOx is similar to the current proposal to use PM10 as the national indicator for protection against the health effects of PM10-2.5, as discussed in the 2010 2nd draft Policy Assessment for the PM NAAQS primary standards. In that case, EPA is proposing to recognize that the same size fraction of particles may have different toxicity depending on location, and as a result, it is more appropriate to use an indicator that reflects that varying toxicity, rather than setting one absolute level of PM10-2.5 which may not be equally protective in all locations. By proposing this form, EPA is recognizing that in attaining a PM10 standard, the resulting balance of PM10-2.5 and PM2.5 particles will differ across areas of the U.S. Likewise, setting a joint NOx/SOx standard that results in differing allowable concentrations of NOx and SOx across the U.S. based on the differing potential for NOx and SOx to result in ecological damages is appropriate in providing a requisite level of welfare protection.

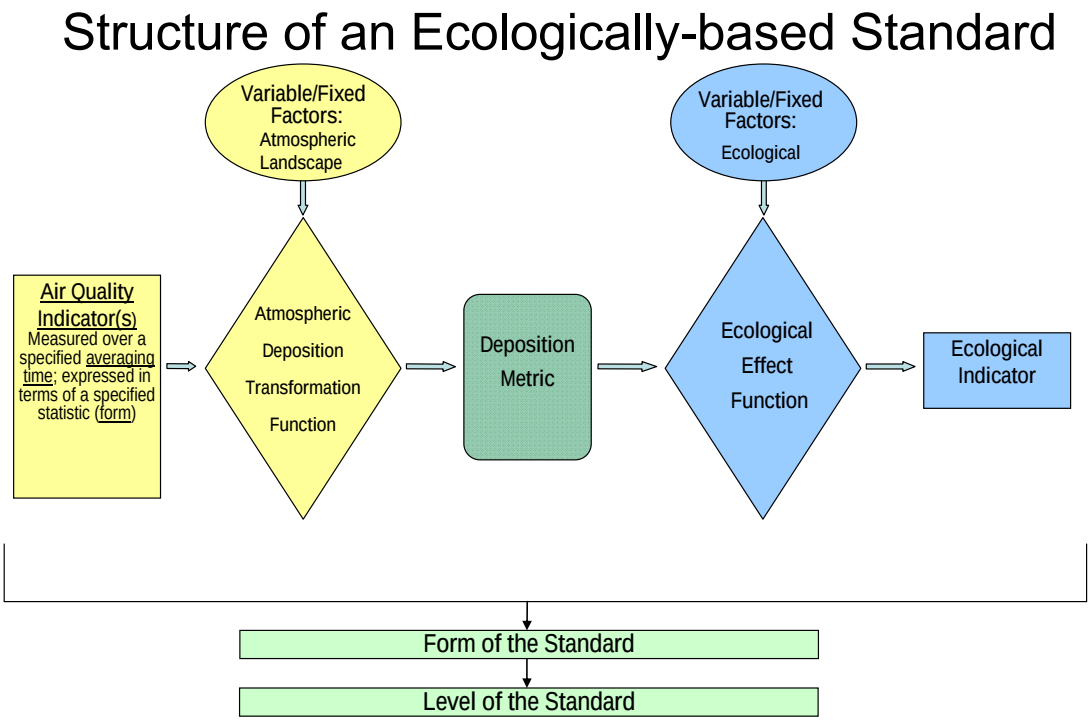

Figure 1-1. Framework of an alternative secondary standard.

1.6 POLICY RELEVANT QUESTIONS

In this policy assessment, a series of general questions frames our approach to identifying a range of policy options for consideration by the Administrator regarding secondary NAAQS for NOx and SOx. These questions are drawn from our Integrated Review Plan with modifications based on further consideration by staff and comments from CASAC and the public. Our policy assessment begins by characterizing "known or anticipated adverse effects" on public welfare within our conceptual model (CPE 1). As noted earlier, this review is focusing on effects in sensitive unmanaged ecosystems (not commercial forests or agricultural lands[6]) resulting from ambient concentrations of NOx and SOx through deposition of N and S.

[6] The decision to focus on unmanaged ecosystems is based on the weight of evidence of effects in those ecosystems. 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 N (**ISA 3.3.2.5**). In addition ,the ISA notes that agricultural and commercial forest lands are routinely fertilized with amounts of N (100 to 300 kg N/ha) that exceed air pollutant inputs even in the most polluted areas (**ISA 3.3.9**). This review recognizes that effect of N deposition in managed areas may be viewed differently than effects of N deposition in 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 Chapter 2, we draw from the information and conclusions presented in the ISA and REA to address the following questions:

1. What are the nature and magnitude of ecosystem responses to reactive nitrogen and sulfur deposition, acidification, nutrient depletion and the mobilization of toxic metals in sensitive aquatic and terrestrial ecosystems?
    a. How are these responses affected by landscape factors?
    b. What types of ecosystems are sensitive to such responses?
2. To what extent can ecosystem responses to nitrogen deposition be separated into responses related to oxidized and reduced forms of reactive nitrogen compounds?

In Chapter 3, we address the following questions related to linking effects to measures of adversity (CPE 1.1):

1. How do we characterize adversity to public welfare? What are the sources of potentially relevant characterization for this policy assessment?
2. What is the evidence of effects on ecosystem services, and how can those ecosystem services be linked to ecological indicators?
3. To what extent are identified ecosystem effects important from a public welfare perspective, and what are the important uncertainties associated with estimating such effects?

Once we have described ecological effects, we then provide an assessment of the adequacy of the existing NOx and SOx standards (CPE 1.2). We begin this assessment by drawing from the information and conclusions presented in the ISA and REA to address in Chapter 4 the following questions, which allow us to identify whether the structure of the current standards is appropriate relative to the key ecological effects assessed in the ISA and REA, including acidification and excess nutrient enrichment and whether there is adequate information and analyses available at this time to assess the extent to which potentially adverse effects on aquatic and terrestrial ecosystems can be associated with current levels of atmospheric reactive nitrogen, accounting for the contributions of oxidized and reduced forms, and SOx and with levels that are at or below the current secondary standards:

1. To what extent are effects that could reasonably be judged to be adverse to public welfare occurring under current conditions and would such effects occur if the nation met the current standards? To what extent do the current NOx and SOx secondary standards provide protection from effects associated with deposition of:
    a. Sulfur and oxidized nitrogen from atmospheric NOx, and SOx which results in acidification in sensitive aquatic and terrestrial ecosystems?
    b. Oxidized nitrogen from atmospheric NOx, which results in nutrient enrichment effects in sensitive aquatic and terrestrial ecosystems?
    c. Sulfur and oxidized nitrogen from atmospheric NOx and SOx which results in other ecological effects (e.g. mercury methylation)?
2. In what way are the structures of the current NOx and SOx secondary standards inadequate to protect against public welfare effects?

In Chapter 5, we follow our adequacy assessment by developing in greater detail the conceptual framework for the design of ecologically relevant multi-pollutant standards introduced in Section 1.4 above. To the extent that the available information calls into question the adequacy of protection afforded by the current standards and/or the appropriateness of the structure of the standards, we explore the extent to which available information supports consideration of alternative standards, in terms of atmospheric and ecological indicators and related averaging times, forms, and levels. This conceptual framework is designed to focus on resolving the following questions:

1. (CPE 2.1) Does the available information provide support for the use of ecological indicators to characterize the responses of aquatic and terrestrial ecosystems to oxidized nitrogen and sulfur deposition?
2. (CPE 1) Does the available information provide support for the development of appropriate ecological response to deposition relationship(s) that meaningfully relates oxidized nitrogen and sulfur deposition to relevant ecological indicators? Does a quantified relationship exist between the level of a relevant ecological indicator and an amount of nitrogen and sulfur deposition?

3. (CPE 2) What are the important variables in the ecological response to deposition relationship(s)? Are these relationships applicable nationally? What are the appropriate temporal scales for these relationships?
    a. How does ecological response to deposition relationship(s) depend upon spatially heterogeneous geologic factors (e.g. bedrock type, weathering rates) that govern sensitivity?
    b. How do we consider areas with high natural background acidification or nutrient loadings?
4. (CPE 3) Does the available information provide support for the development of appropriate functions that characterize the relationships between atmospheric NOx and SOx and the wet and dry deposition of total reactive nitrogen and sulfur?
    a. What deposition function is appropriate to use for the purpose of relating an amount of nitrogen and/or sulfur deposition in sensitive ecosystems to ambient concentrations of atmospheric reactive nitrogen, including oxides and reduced forms, and/or sulfur? What are the important variables in such a function? What are appropriate spatial and temporal scales to use in specifying such variables?

Based on the conceptual framework for the structure of the ecologically relevant multi-pollutant standards, we then address in Chapter 6 the components of the standard needed to develop options for consideration by the Administrator. Development of these options will focus on addressing the following questions:

1. (CPE 2.1) What ecological indicators are appropriate to use for the purpose of developing an alternative standard for the various ecological effects assessed in this review?
2. (CPE 5) What indicators of oxides of nitrogen and sulfur are appropriate to use for the purpose of determining whether the resultant deposition is within the target values needed to achieve the desired degree of protection? What averaging times and forms are appropriate to consider?

3. (CPE 2) What approaches are available to specify non-atmospheric components of the standard, e.g. weathering rates? Are there approaches that can simplify the structure of the standard?
4. What are the available approaches for accounting for reduced N in the structure of the standard?
5. What is the most appropriate form for the standards to reflect the relationships between ambient NOx and SOx, acidifying deposition, and the ecological indicator for acidification?

Several follow-up questions derive from our assessment of options for specifying the components of a multipollutant standard. In Chapter 6, we address the questions:

1. To what extent would a standard specifically defined to protect against one ecological effect (i.e., aquatic acidification) likely provide protection from other relevant ecological effects?
2. What are the available approaches for combining multiple indicators into a single standard, e.g. using nitrogen effects to bound the tradeoff curve for NOx/SOx for aquatic acidification effects
3. What are the available approaches to integrate potential standards for aquatic and terrestrial acidification and/or aquatic and terrestrial N enrichment?

In Chapter 7, we provide a range of explorations of uncertainties in the evidence and models as they pertain to the selection of options for components of the standard. In addition, we provide results of sensitivity analyses for components of the proposed AAPI form, as well as characterizing information on variability in those components. The chapter focuses on the following questions:

1. What are critical uncertainties in the characterization of pre-industrial levels of ANC?
2. What uncertainties are introduced through the use of steady state critical load models relative to dynamic critical loads models?
3. What are the critical uncertanties in the modeled relationship between concentrations of NOx and SOx and deposition of N and S?
4. What are the critical uncertainties in the modeled values of NHx deposition?

5. How sensitive is the form of the NOx/SOx standard to the primary components?
6. How sensitive are the atmospheric transformation ratios calculated from CMAQ to the emissions scenarios, chemical mechanisms, and meteorology in the model?
7. How well does CMAQ perform in simulating nitric oxide, nitrogen dioxide, sulfur dioxide, nitrate, ammonium and aerosol nitrate, ammonium, and sulfate relative to observations from different networks for which the data are routinely available?
8. How well does CMAQ perform in simulating wet deposition of sulfate, nitrate, and ammonium relative to observations from the National Atmospheric Deposition Program (NADP) network?

Chapter 8 provides a discussion of several important aspects of monitoring of NOx and SOx, including methods, network design, and frequency.

We conclude in Chapter 9 with a discussion of options to consider in selecting pollutant indicators, averaging times, forms, and ranges of levels for the secondary NOx and SOx standards. This discussion is informed by a consideration of the role of ecosystem services in helping to characterize what adversity to public welfare, focused on the following questions:

1. (CPE 5) What are the risks of ecosystem service impairment under alternative levels of potential standards for NOx and SOx?
2. (CPE 5) To what extent can information about ecosystem services be used to help characterize the extent to which differing levels of relevant ecological indicators reflect impacts that can reasonably be judged to be adverse from a public welfare perspective?
3. (CPE 5) Are there relevant benchmarks for adversity to public welfare that can be derived from other sources?
4. (CPE 5) Taking into consideration information about ecosystem services and other factors related to characterizing adversity to public welfare for the ecological effects being assessed in this review, what is an appropriate range of levels of protection to be achieved by alternative standards for the Agency to consider?

2 KNOWN OR ANTICIPATED ECOLOGICAL EFFECTS

In this chapter we address Critical Policy Element 1, evaluation of the effects of ambient NOx and SOx 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 NOx and SOx 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 NOx and SOx 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 NOx and SOx 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 3 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 NOx and SOx standards which are protective of U.S. ecosystems. More detailed information on the conceptual design and specific options for the proposed standards are presented in Chapters 5 and 9of this policy assessment document. While we provide a summary of effects for all four of the primary effects categories, 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.

2.1 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 buffered by high base soils, 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 (NOx, NHx and Nr) 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. 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. For the purpose of a national secondary standard, the most relevant characteristics are those that are less variable over small scales.

Acidifying deposition of NOx and SOx 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**). 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. Terrestrial and aquatic processes are often linked; therefore responses to the following questions address both types of ecosystems unless otherwise noted.

2.1.1 What is the nature of acidification related ecosystem responses to reactive nitrogen and sulfur deposition?

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.

*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., 1990b). 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 and increased inorganic Al concentrations. While ANC level does not cause direct biological harm it is a good overall indicator of the risk of acidification (Fig 2-1, See further discussion in Section 2.1.3).

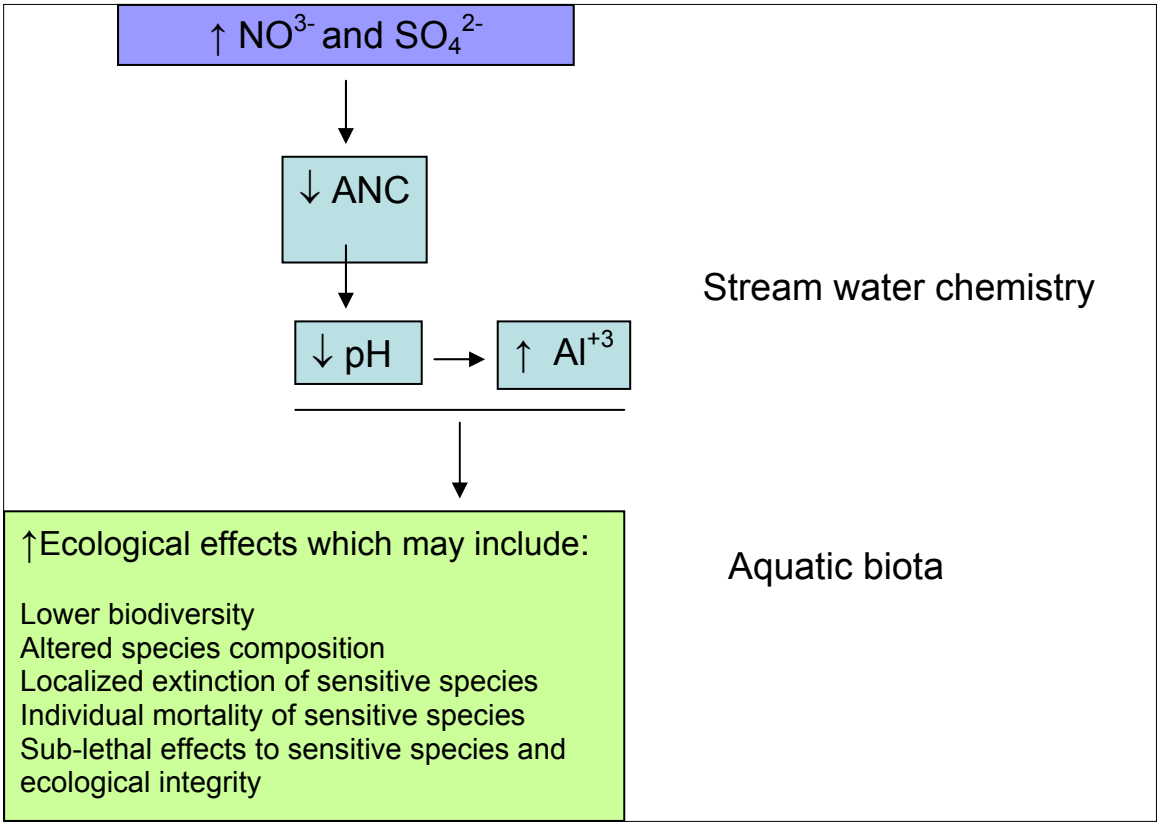

Figure 2-1. Conceptual model of direct and indirect acidification effects on aquatic biota. Acidic pollutants (NO3- and SO4-2) lower ANC, resulting in lower pH with direct toxic effects on fish. The lower pH mobilizes Al3+ from soils often resulting in higher concentration in stream water causing direct toxicity to fish.

These changes in stream water chemistry contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish, which are often sources of food for birds and other animal species in various ecosystems. These fish may also serve as a source of food and recreation for humans (see Chapter 3). 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).

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 Ca^{2+} 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 Ca^{2+} 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).

2.1.2 What types of ecosystems are sensitive to such effects? In which ways are these responses affected by atmospheric, ecological, and landscape factors?

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**).

2.1.3 What is the 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.

2.1.3.1 Aquatic

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 μeq/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 uncommon 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 **(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 (*Oncorhynchis 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 μeq/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; Wedemeger 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; ISA). 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 Figure 2-2. [Need

to indicate the source for the categorization] 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.

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.

Table 2-1. Ecological effects associated with alternative levels of acid neutralizing capacity (ANC)

The most commonly used models of acidification are presented in Table 2-2 These models are designed to be applied at the spatial scale of the watershed, with the exception of the SMART model. Steady-sate mass balance models, including the steady-state water chemistry (SSWC) model are the most commonly used method for analysis of critical loads of acid deposition. The steady-state models assume steady state conditions. The dynamic models consider how the ecosystem may change through time. These models tend to require more data than the steady-state models.

Table 2-2 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-sate 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 basesaturation 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.
Model of Acidification of Groundwater in Catchment (MAGIC)	Dynamic	MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the longterm 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 SO4 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 operates

Table 2-2 Summary several commonly used acidification models (See ISA Annex A for a more comprehensive list and discussion of acidification models)		
		on a monthly time step and 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, 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 byincorporating 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 NH4 adsorption; SO42− 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, SO4 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).

The analyses of the Adirondack Case Study Area indicated that although wet deposition rates for SO_2 and NOx have been reduced since the mid-1990s, current concentrations are still well above simulated pre-acidification (1860) conditions. Modeling predicts NO_3^- and SO_4^{2-} 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 µeq/L); 78 % of all monitored lakes in the Adirondack Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 78%, 18% are chronically acidic (**REA 4.2.4.2**).

Based on a N and S deposition scenario that maintains current emission levels to 2020 and 2050, the simulation forecast indicates there would be no improvement in water quality in the Adirondack Case Study Area. The percentage of lakes within the *Elevated* to *Acute Concern* classes remains the same from 2020 to 2050.

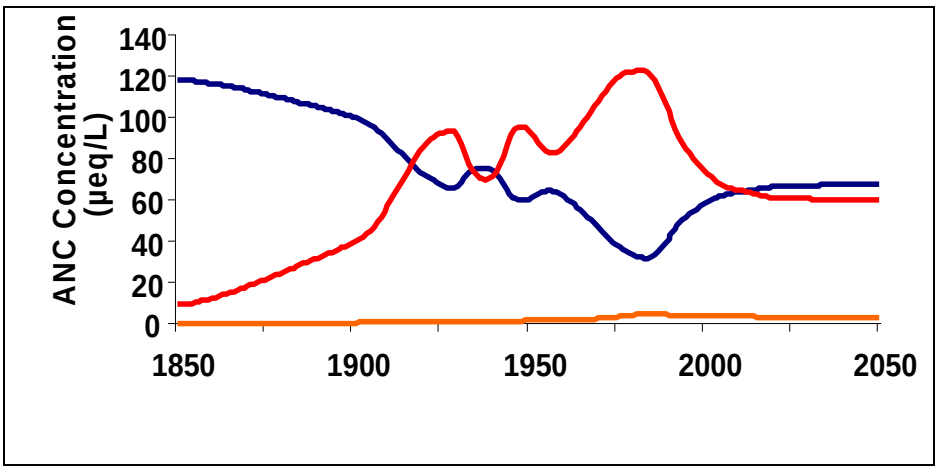

Figure 2-2. Average NO_3^- concentrations (orange), SO_4^{2-} concentrations (red), and ANC (blue) across the 44 lakes in the Adirondack Case Study Area modeled using MAGIC for the period 1850 to 2050.

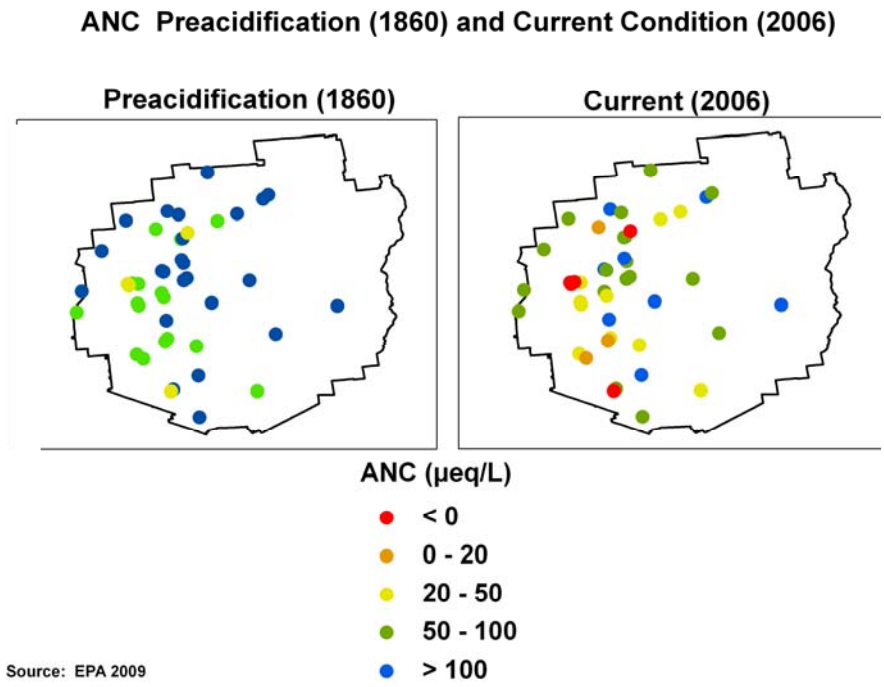

Figure 2-3. **ANC concentrations of preacidification (1860) and 2006 conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC**.

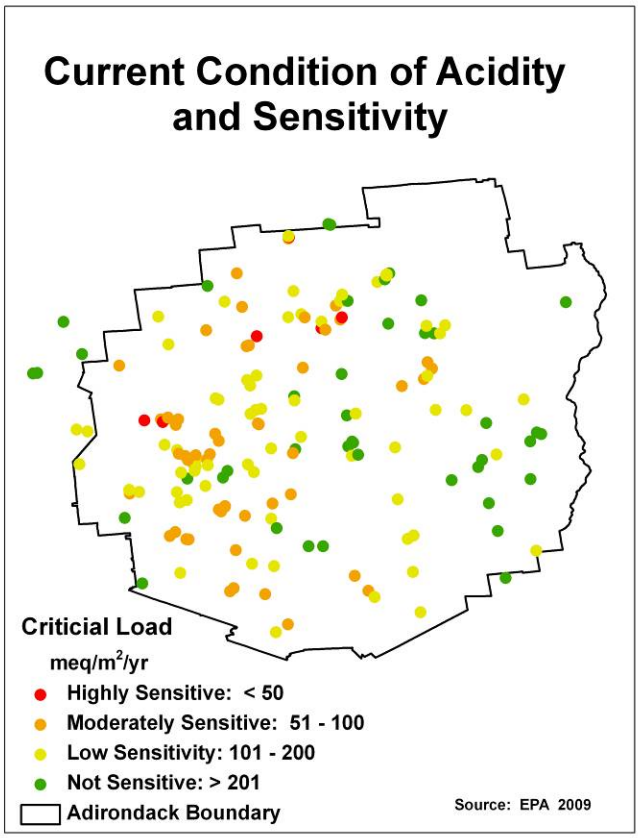

Figure 2-4. Critical loads of acidifying deposition that each surface water location can receive in the Adirondack Case Study Area while maintaining or exceeding an ANC concentration of 50 µeq/L based on 2002 data. Watersheds with critical load values <100 meq/m^2/yr (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values >100 meq/m^2/yr (yellow and green circles) are less sensitive sites.

Note that 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 NO_3- and SO_4^{2-} concentrations in surface waters. The 2006 concentrations are still above pre-acidification (1860) conditions. MAGIC modeling predicts surface water concentrations of NO_3- and SO_4^{2-} are10- 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* are 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 1995, Bulgar et al., 1999) and a decrease in fish biodiversity associated with decreasing stream ANC (Bulger et al.,1995; Dennis and Bulger, 1995; 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**).

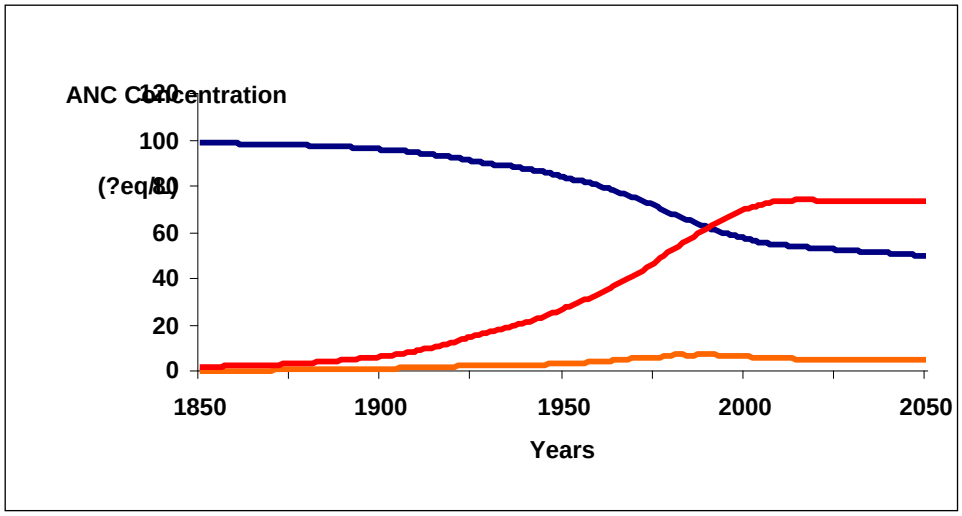

Figure 2-5. **Average NO_3^- concentrations orange), SO_4^{2-}concentrations (red), and ANC (blue) levels for the 60 streams in the Shenandoah Case Study Area modeled using MAGIC for the period 1850 to 2050.**

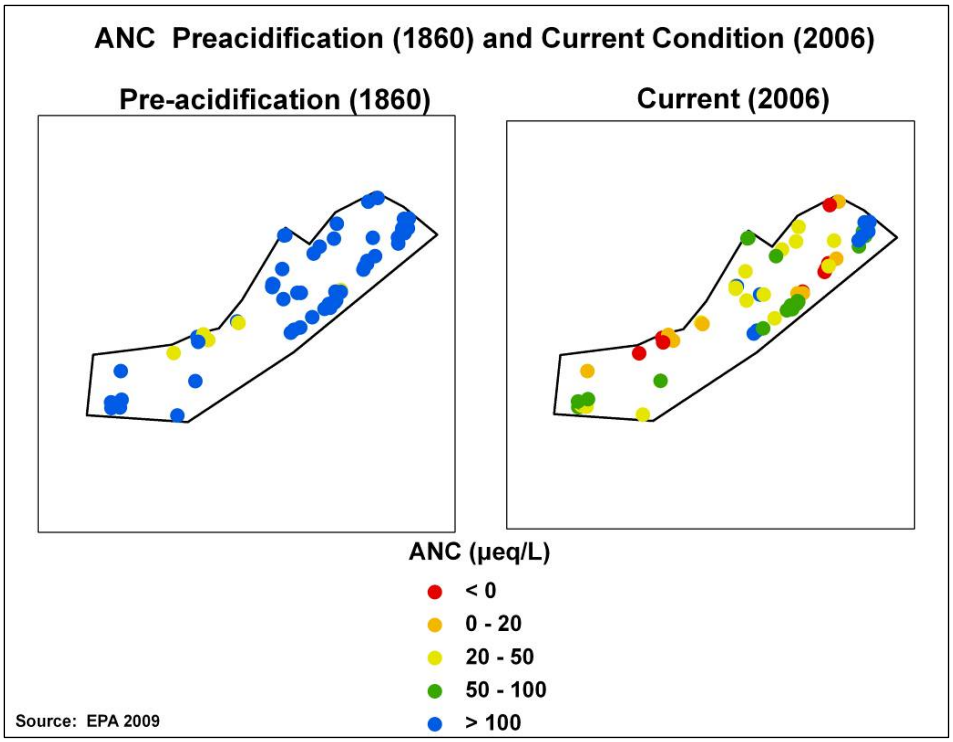

Figure 2-6. **ANC levels of 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 60 streams in the Shenandoah Case Study Area modeled using MAGIC**.

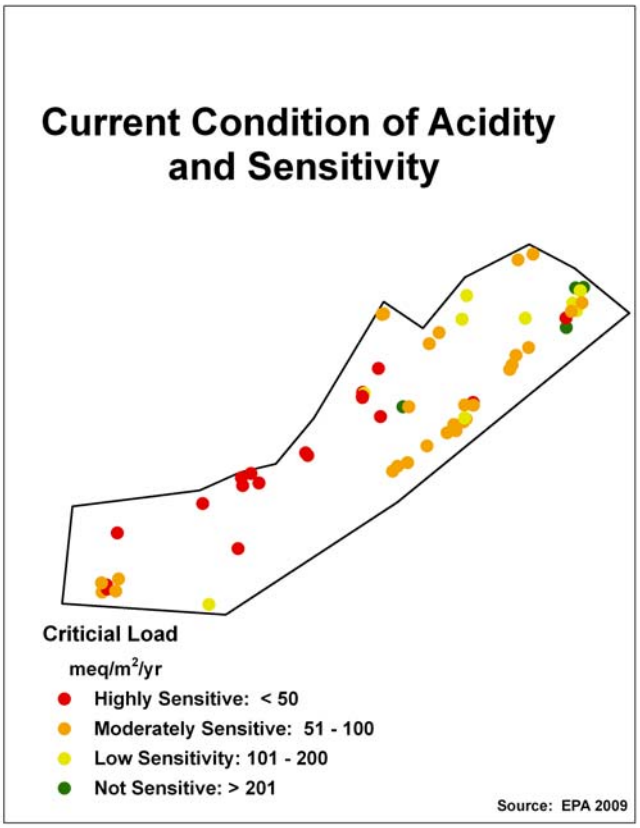

Figure 2-7. Critical loads of surface water acidity for an ANC of 50 µeq/L for Shenandoah Case Study Area streams. Each dot represents an estimated amount of acidifying deposition (i.e., critical load) that each stream's watershed can receive and still maintain a surface water ANC >50 µeq/L. Watersheds with critical load values <100 meq/m^2/yr (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values >100 meq/m^2/yr (yellow and green circles) are less sensitive sites.

2.1.3.2 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 Ca^{2+}, Mg^{2+} 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 eq ha^{-1} 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**).

2.1.4 What are the 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 (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.

2.1.4.1 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 was derived from multiple site calibrations. The 95% confidence interval for pre-acidification of lakes was an average of 15 μeq/L difference in ANC concentrations or 10% and 8 μeq/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 (**Figure 7.1-6 REA**).

2.1.4.2 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**).

2.2 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, (e.g. NHx) 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. We address the issue of incorporating the relative contributions of oxidized and reduced nitrogen into the standards in Chapters 5 and 8.

2.2.1 What is the nature of terrestrial and freshwater ecosystem responses to reactive nitrogen and/ sulfur deposition?

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 steam water as two of the primary indictors of N enrichment. Several N-addition studies indicate that NO_3- leaching is induced by chronic additions of N (Edwards et al., 2002b; 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 μeq/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. In the West, this has lead 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.

2.2.2 What types of ecosystems are sensitive to such effects? How are these responses affected by atmospheric, ecological, and landscape factors?

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; Rueth et al., 2003; Egerton-Warburton and Allen 2000; Williams et al., 1996; and additional studies summarized in **Table 4-4 ISA**). 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 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.

2.2.3 What is the magnitude of ecosystem responses to nitrogen deposition?

2.2.3.1 Terrestrial

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 2-8. 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 2-9, depicts the sites where empirical effects of terrestrial nutrient enrichment have been observed and site proximity to elevated atmospheric N deposition.

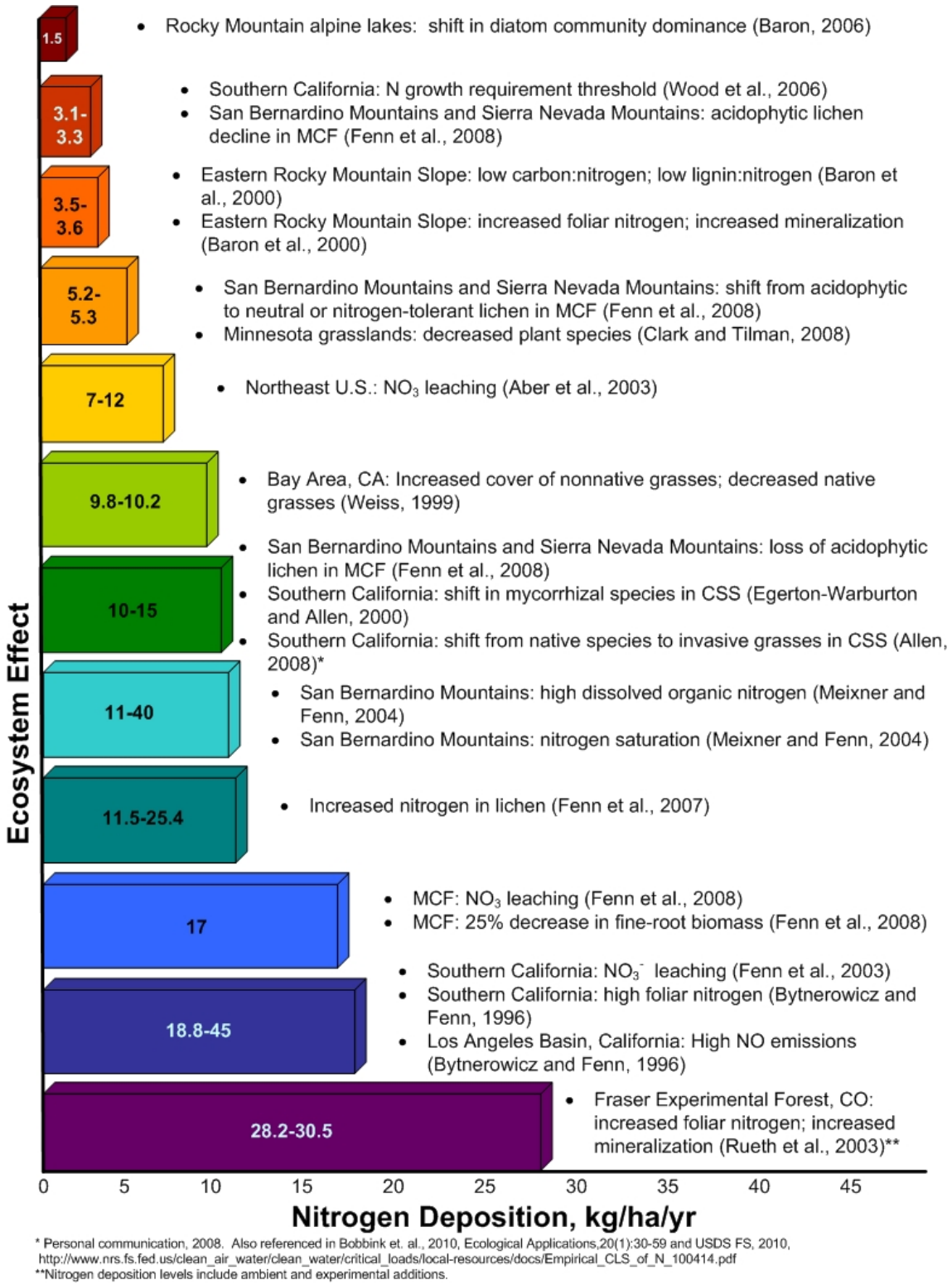

Figure 2-8. Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators (REA 5.3.1.2) MCF-Mixed Conifer Forest, CSS-Coastal Sage Scrub

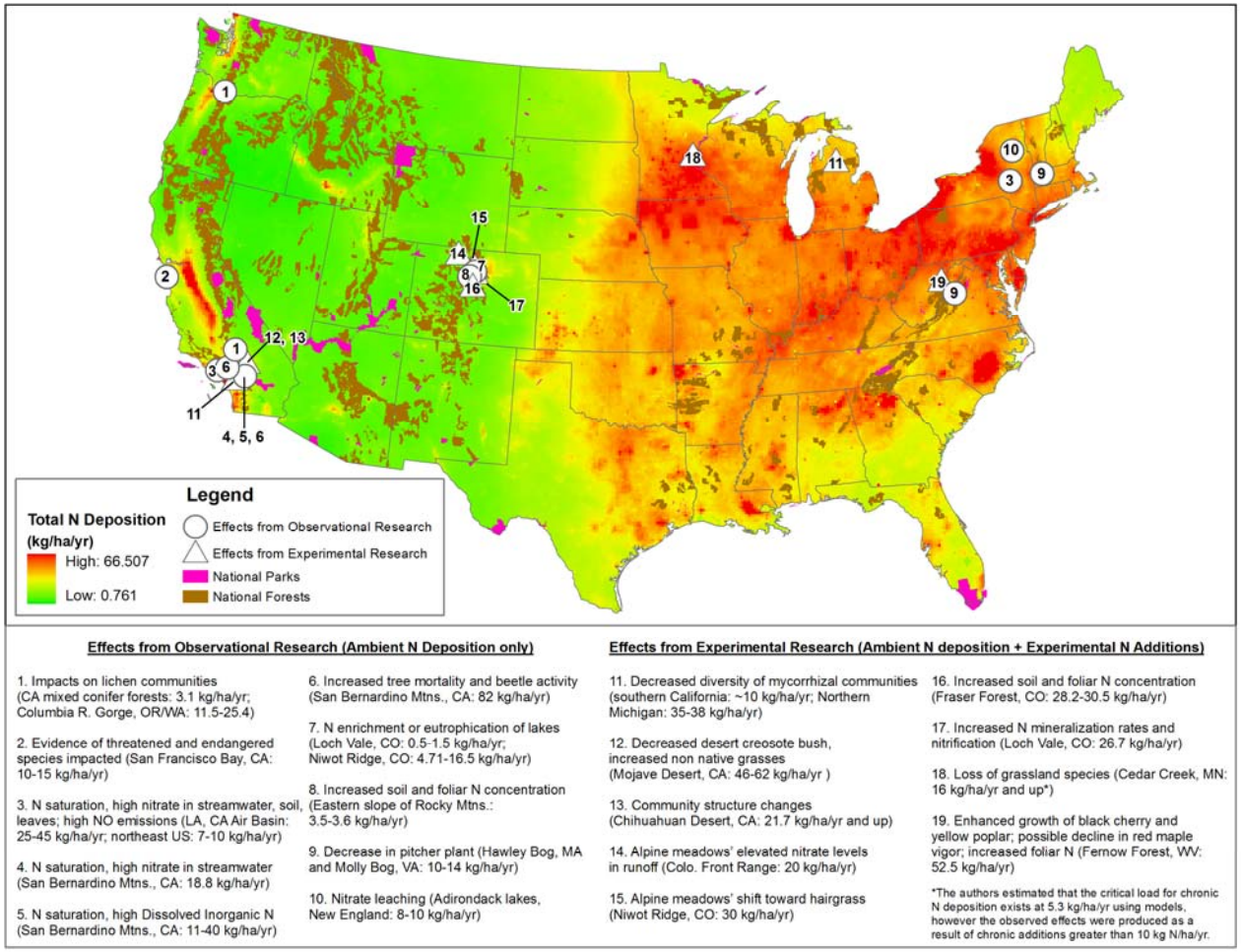

Figure 2-9 Observed effects from ambient and experimental atmospheric nitrogen deposition loads in relation to using CMAQ 2002 modeling results and NADP monitoring data. Citations for effect results are from the ISA, Table 4.4 (U.S. EPA, 2008) 1= Fenn et. al. (2008), 2=Weiss (1999), 3=Bytnerowicz and 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.

2.2.3.2 Freshwater

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. (2008) 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**).

2.2.3.3 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 sources of N 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.

What is the nature of estuary responses to reactive nitrogen deposition?

*In the ISA, the evidence is sufficient to infer a **causal** relationship between Nr 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.

What types of ecosystems are sensitive to such effects? How are these responses affected by atmospheric, ecological, and landscape factors?

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.

What is the magnitude of ecosystem responses to eutrophication?

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.

2.2.4 What are the 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 2.1.4 of this chapter (**REA 7.0**).

2.2.4.1 Aquatic

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 RETrival (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**).

2.2.4.2 Terrestrial

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.

2.3 WHAT ECOLOGICAL EFFECTS ARE ASSOCIATED WITH GAS-PHASE NO_X AND SO_X?

Acidifying deposition and nitrogen enrichment are the main focus of this policy assessment; however, there are other known ecological effects are attributed to gas-phase NOx and SOx. Acute and chronic exposures to gaseous pollutants such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitric oxide (NO), nitric acid (HNO_3) 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 NOx or SOx, 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 NOx and SOx occur at levels well above ambient concentrations observed in the U.S. **(ISA 3.4.2.4).**

2.3.1 What is the 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 SO_2 and injury to vegetation* (**ISA 4.4.1 and 3.4.2.1**). Acute foliar injury to vegetation from SO_2 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 SO_2 exposure concentration and time of exposure.

The evidence is sufficient to infer a ***causal*** *relationship between exposure to NO, NO_2 and PAN and injury to vegetation* (**ISA 4.4.2 and 3.4.2.2**). At sufficient

concentrations, NO, NO_2 and PAN can decrease photosynthesis and induce visible foliar injury to plants. *Evidence is also sufficient to infer a* ***causal*** *relationship between exposure to HNO_3 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.

2.3.2 What types of ecosystems are sensitive to such effects? How are these responses affected by atmospheric, ecological, and landscape factors?

Vegetation in ecosystems near sources of gaseous NOx and SOx or where ambient concentrations of SO_2, NO, NO_2, PAN and HNO_3 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 NOx and SOx and specific plant response are impacted by internal factors such as rate of stomatal conductance and plant detoxtification 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 aperature. The aperature 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 SO_2 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).

2.3.3 What is the magnitude of ecosystem responses to gas phase effects of NOx and SOx?

The phytotoxic effects of gas phase NOx and SOx are dependent on the exposure concentration and duration and species sensitivity to these pollutants. Effects to vegetation associated with NOx and SOx, are therefore, variable across the U.S. and tend to be higher near sources of photochemical smog. For example, SO_2 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 SO_2 than many foliose and crustose species (Hutchinson et al., 1996).

The ISA states there is very limited new research on phytotoxic effects of NO, NO_2, PAN and HNO_3 at concentrations currently observed in the United States with the exception of some lichen species (**ISA 4.4**). Past and current HNO_3 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 HNO_3 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 NOx and SOx occur at levels well above ambient concentrations observed in the U.S. **(ISA 3.4.2.4).**

2.4 SUMMARY

In summary, NOx and SOx 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.

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3 CONSIDERATIONS OF ADVERSITY TO PUBLIC WELFARE

3.1 How do we characterize adversity to public welfare? What are the relevant factors and how are they addressed in this document?

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 NOy and SOx 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. In subsequent sections we will discuss each of these concepts as they relate to adversity.

3.1.1 What are the benchmarks for adversity from other sources?

3.1.1.1 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 3-1).

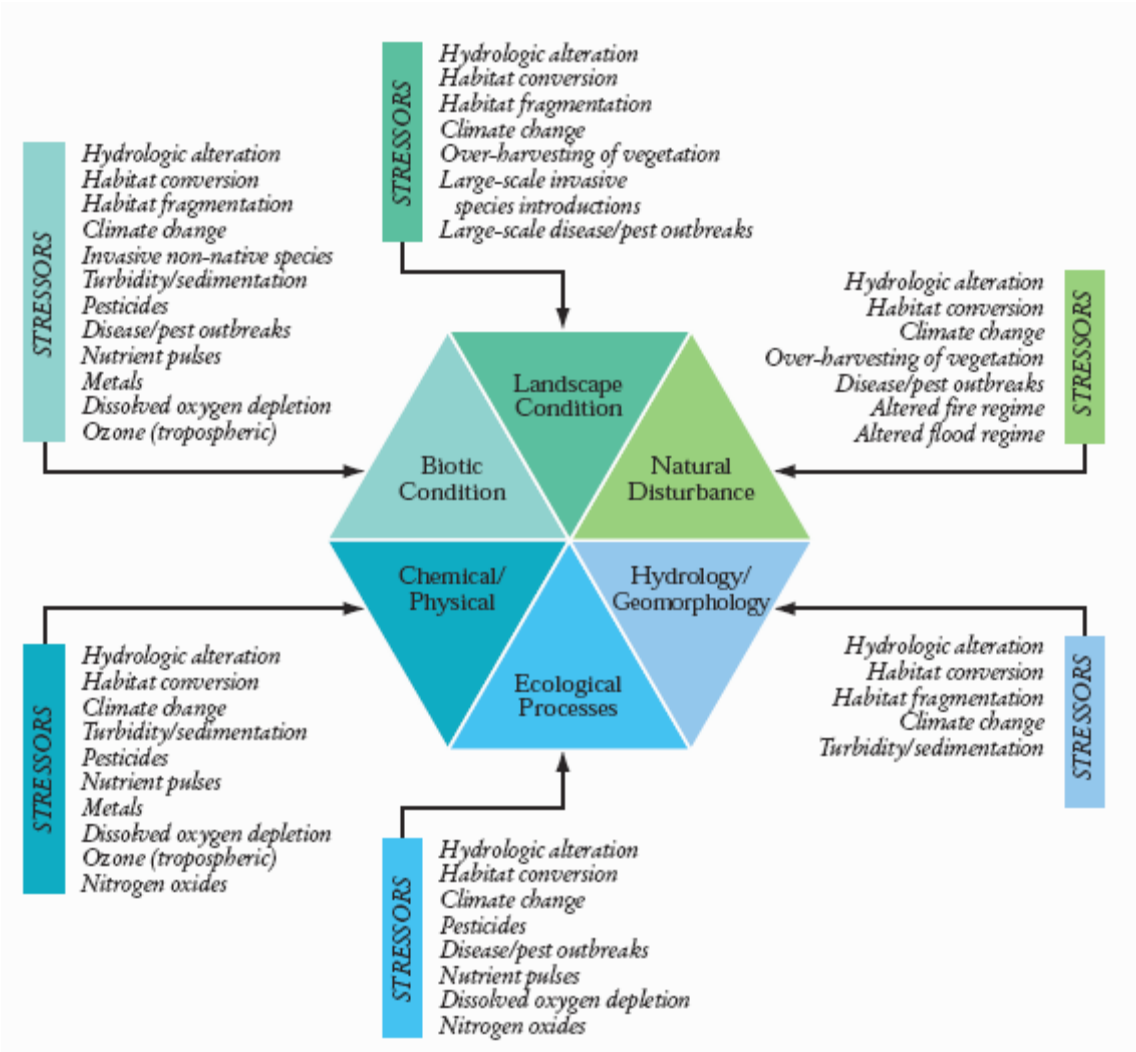

Figure 3-1. Common anthropogenic stressors and the essential ecological attributes they affect. Modified from Young and Sanzone (2002)

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 O_3-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.

3.1.2 Other EPA Programs and Federal Agencies

Various federal laws and policies exist to protect ecosystem health. How other federal agencies and EPA 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.

3.1.21. 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)).

3.1.2.2 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 $CaCO_3$ for freshwater aquatic life except where natural concentrations are less. Alkalinity is the sum total of components in the water that tend to elevate the pH of the water above a value of about 4.5.

As mentioned in the Redbook, alkalinity is expressed as $CaCO_3$ in mg/L. Alkalinity differs slightly from ANC in that ANC includes other buffering compounds (Na, Mg, and K) as well and includes buffering capacity of particulates in the water sample. Since alkalinity is expressed as mg/L and ANC is expressed as μeq/L, alkalinity must be multiplied by 20 to be converted to μeq/L. Thus a recommended criterion of 20 mg/L alkalinity is equivalent to an ANC of 400 μeq/L.

3.1.2.3 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."

3.1.2.3 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).

3.1.2.4 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.

3.1.25Chesapeake 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. 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 NOy 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.

3.1.2.6 Critical Loads

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. Researchers often use the term "critical loads" to describe when particular detrimental effects are realized, as is the case in Figure 2-1.

Harmful effects due to acidification have been defined here as those that occur below a given ANC for aquatic systems and below a given Bc:Al ratio for terrestrial systems. However, the level at which an effect becomes adverse to public welfare is determined by the Administrator, informed by available scientific information.

3.1.2.7 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. These critical loads are determined through a policy process. Indeed 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 and acidification that protect 95% of forests, seminatural vegetation or surface waters in Europe. For comparison to the U.S maps presented in this document the units of deposition convert to a range of 3.2 kg $ha^{-1}a^{-1}$ to > 24 kg $ha^{-1}a^{-1}$.

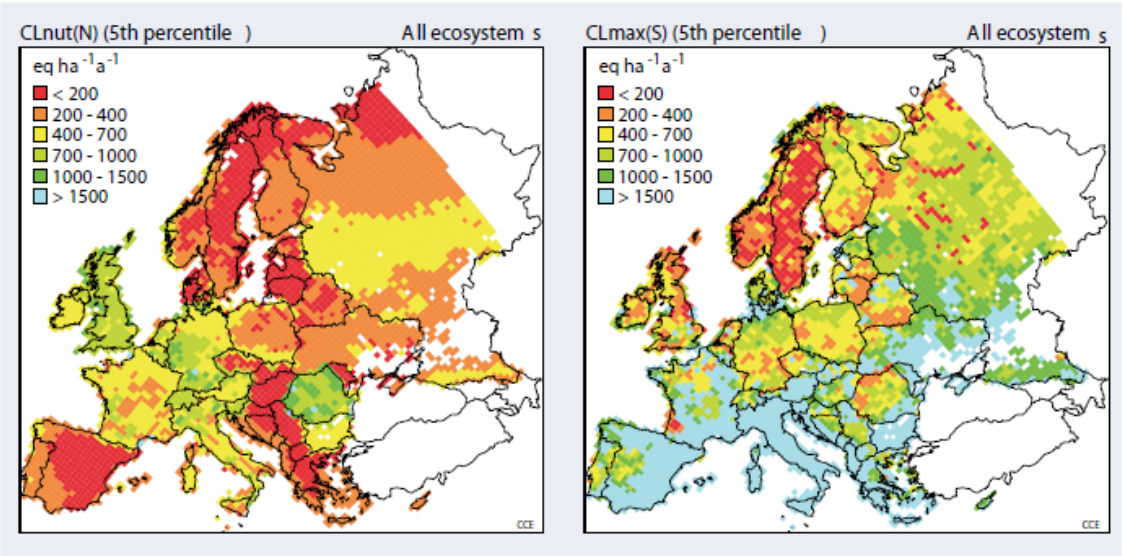

Figure 3-2 European maps of eutrophication (left) and acidification (right) which protect 95% of natural areas in 50x50 km^2 European Monitoring and Evaluation Programme grid. Red shaded areas illustrate grid cells where deposition needs to be lower than 200 eq ha^{-1} a^{-1} to reach this protection target.

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

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 20 µeq/L for the protection of brown trout.

Individual countries have also set ANC targets for other species for example Norway uses a critical limit of 30μeq/L for Atlantic salmon (Jenkins et al, 2003).

3.2 What are ecosystem services and how does this concept relate 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), 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 NOy and SOx concentrations and deposition may impact that resource. The relationship between ecosystem services and public welfare effects is illustrated in Table 3-1.

Table 3-1. Crosswalk between Ecosystem Services and Public Welfare Effects

Public Welfare Effect	Ecosystem Service	Service Category
Soils	Nutrient Cycling	Supporting
Water	Drinking water, Recreation, Aesthetic	Provisioning, Cultural
Crops	Food, Fuel Production, Forest Products	Provisioning
Vegetation	Food, Recreation, Aesthetic, Nonuse	Provisioning, Cultural
Wildlife	Recreation, Food, Nonuse	Cultural, Provisioning
Climate	Climate Control	Regulating
*Personal Comfort and Wellbeing		

*All ecosystem services contribute to personal comfort and wellbeing.

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 3-3.

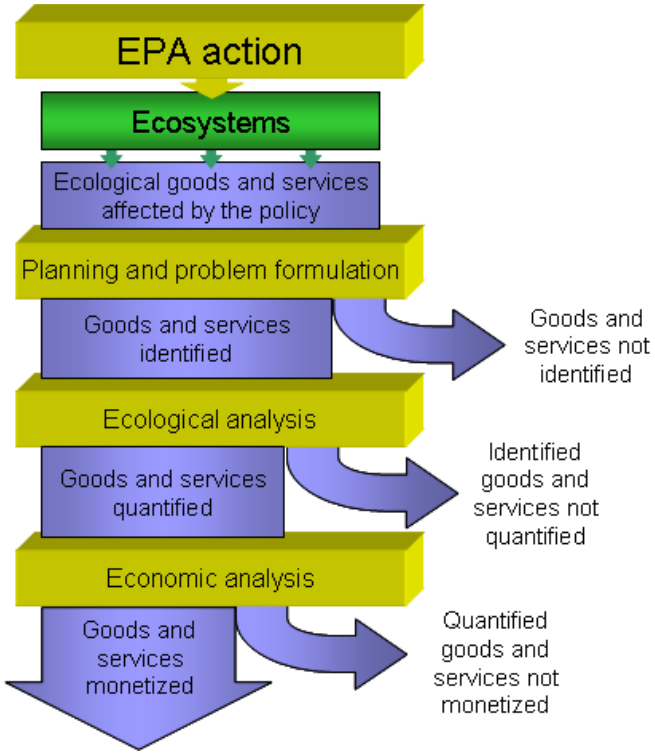

Figure 3-3. Representation of the benefits assessment process indicating where some ecological benefits may remain unrecognized, unquantified, or unmonetized. (Source: EBASP USEPA 2006).

A conceptual model integrating the role of ecosystem services in characterizing known or anticipated adverse effects to public welfare is shown in Figure 3-3. 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 NO_y and SO_x 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 and summarized in Chapter 2 of this document) 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 3-3 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, 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.

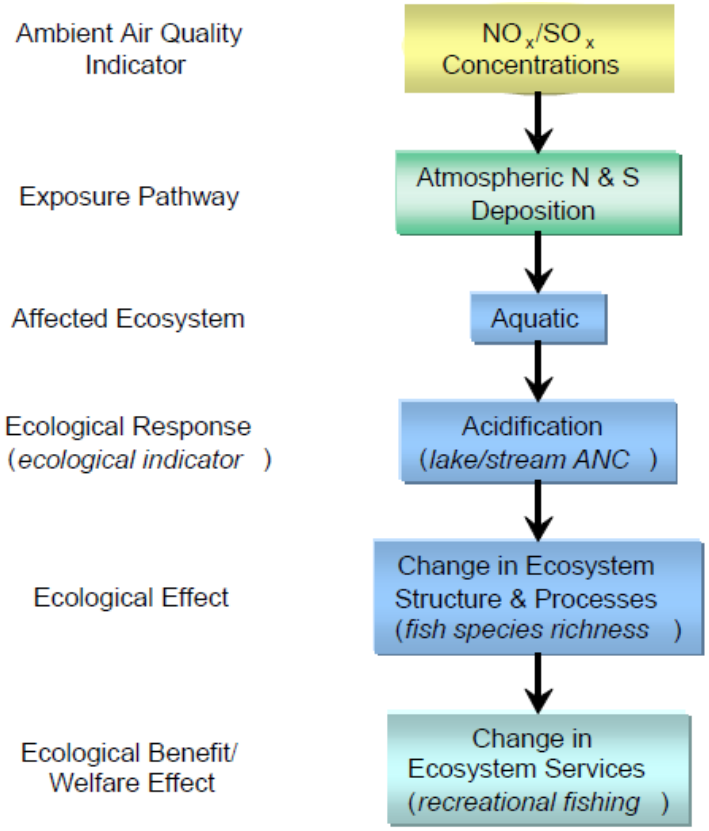

Figure 3-4. Conceptual model showing the relationships among ambient air quality indicators and exposure pathways and the resulting impacts on ecosystems, ecological responses, effects and benefits to characterize known or anticipated adverse effects to public welfare.

These concepts can also be applied to the programs described in section 3.1. 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 and nitrogen deposition levels are illustrated in Figures 3-5 and 3-6. Please note that the scale of deposition levels is different for the two maps to allow greater differentiation of the deposition in the western U.S.

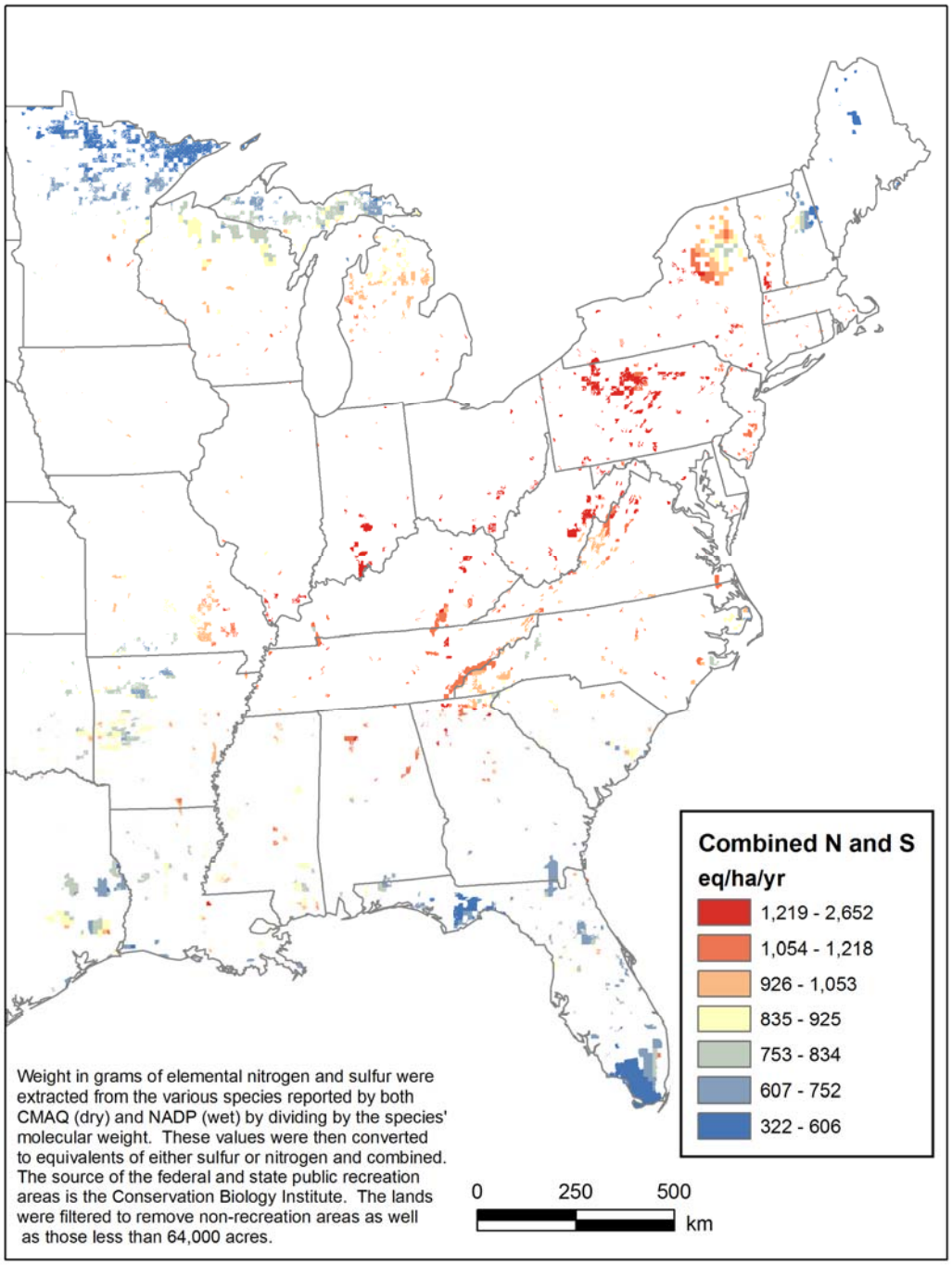

Figure 3-5. Locations of Eastern U.S. Public Lands relative to deposition of nitrogen and sulfur in sensitive aquatic areas. **Source 2005 CMAQ and NADP.**

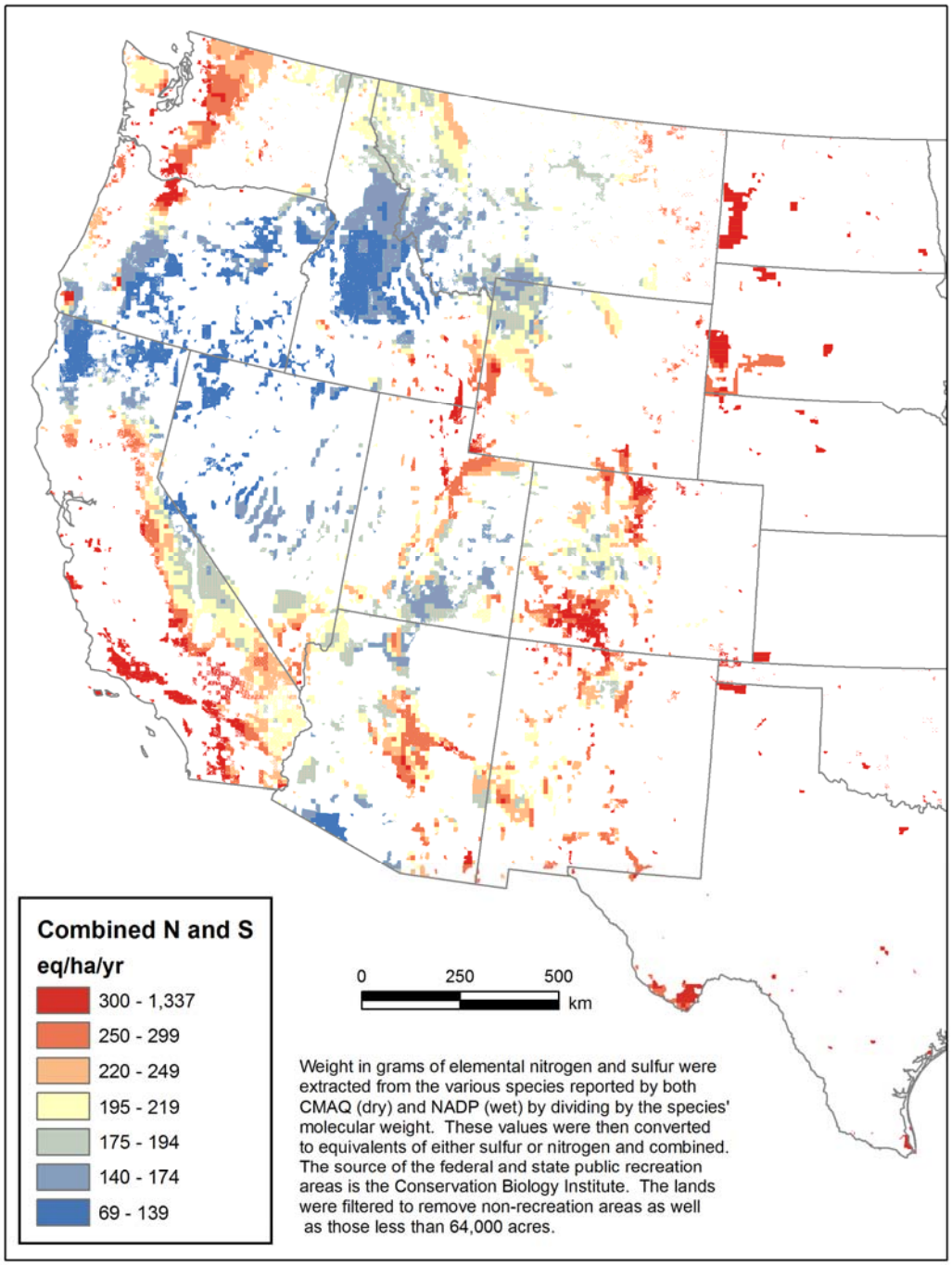

Figure 3-6. Location of Western U.S. Public Lands relative to deposition of nitrogen and sulfur. Source 2005 CMAQ and NADP.

3.3 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 NOy and SOx 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]

3.3.1 Ecosystem Services and Links to Public Welfare

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 provide measures of changes in public welfare.

3.3.2 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. In economics revealed and stated

[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.

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 places is crucial for characterizing the associated change in an ecosystem service, and will also affect the value the public places on that change.

3.3.3 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 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.

3.3.44 Collective Action as an Indicator of Public Preferences

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

[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).

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.[3] 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 (NGOs) 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.

3.3.4.1 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.

[3] 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.

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.

3.3.4.2 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, as well as, wild 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.[4] "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.)

3.3.4.3 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

[4] 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.

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 is 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."

3.3.4.4 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.) There are many such examples, where all three of these types of groups partner on the same project.

3.3.4.5 Using Information on Collective Actions to Estimate Welfare Impacts

The fact that collective action activities are being undertaken by communities, 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.[5] However, 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. For example, groups suffer from the problem of free-ridership. When there are free-riders we know that the activity of the group understates the preferences of the community for an improvement in environmental quality, however it is difficult to estimate the magnitude of its impact on the total activity of the group.

3.4 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 3-7. 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.

[5] 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.

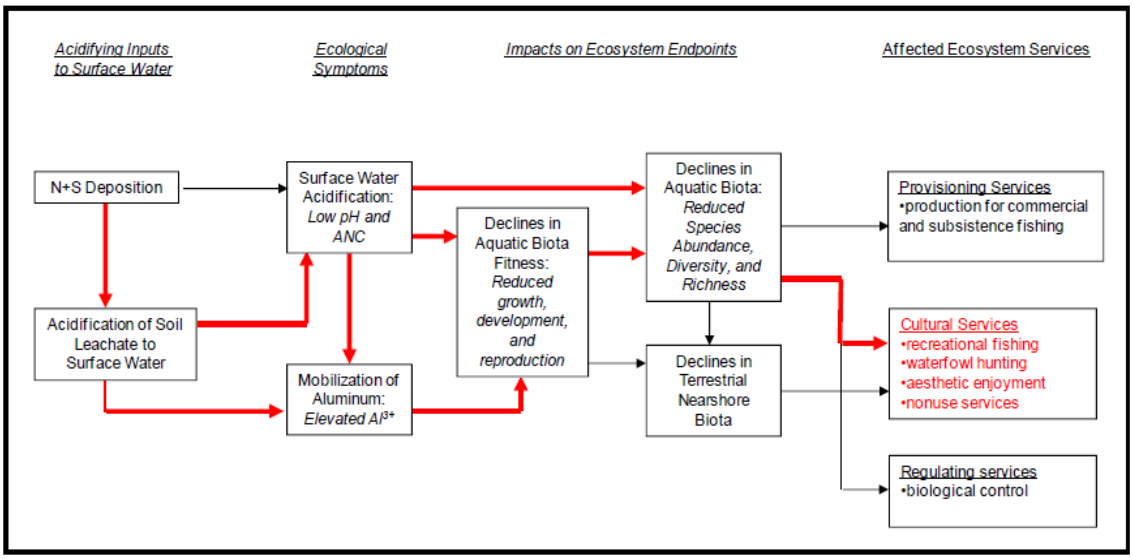

Figure 3-7. Conceptual model linking ecological indicator (ANC) to affected ecosystem services. The red arrows highlight the path to monetization of recreational fishing effects.

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.

For the purposes of the following sections nutrient enrichment refers only to that due to NOy deposition. Additionally these sections focus on the detrimental effects of that deposition. Staff acknowledges that a certain amount of NOy deposition in managed terrestrial ecosystems may have 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.

3.4.1 Evidence for Adversity Related to 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 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, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), northern Florida, 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.

3.4.1.1 What is the value of the impaired recreational fishing and other cultural services?

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 NOy/SOx 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 enrichment[6]. 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

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

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 extrapolated to the full universe of Adirondack lakes. Table 3-2 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 3-2. Count of Impacted Lakes

ANC Threshold (in µeq/L)	Year	Lake Count
20	2005	0
20	2020	107
20	2050	95
20	2100	74
50	2005	0
50	2020	244
50	2050	222
50	2100	200
100	2005	0
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 3 – 3

summarizes the results and the present value of benefits and annualized benefits at 3 and 7% discount rates.

Table 3-3. Present Value and Annualized Benefits, Adirondack Region

ANC Threshold (in μeq/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 NOy/SOx 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 50μeq/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 3-4. 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.

Table 3-4. Aggregate Annual Benefit Estimates 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 $)	
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

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.

[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.

3.4.2 Evidence for Adversity Related to 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 3-6 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 (ISA, 2009; REA, 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 (ISA, 2009; REA, 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 3-5 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 3-5. 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.

Two studies have estimated values for protecting high-elevation spruce forests in the Southern Appalachians. 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 (Haefele et al., 1991; Holmes and Kramer, 1995). The survey presented respondents 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) and two potential forest protection programs. Median household WTP was estimated to be roughly $29 (in 2007 dollars) for the minimal program and $44 for the more extensive program. Another study by Jenkins, Sullivan, and Amacher (2002) estimated 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 3-6. Summary of Studies of Select Terrestrial Ecosystem Services

Fall Color Viewing	30%	Great Lakes area residents	Spencer (2007)
	22%	Vermont visitors	Brown (2002)
Protection of spruce		Southern Appalachians	
	$29	WTP per household for minimal program	Kramer et al. (2003)
	$44	WTP per household for extensive program	
	$3.4 b	Aggregate annual value	Jenkins (2002)

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.

3.4.2.1 What is the value of current ecosystem service impairments? 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 4.

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.

3.4.3 Evidence for Adversity Related to 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 pfiesteria 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.

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 3-7. 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	

3.4.3.1 Value of aquatic ecosystem service impairments from current levels 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. 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 3-8. 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

3.4.4 Evidence for Adversity Related to Terrestrial Nutrient Enrichment

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.

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 (seewww.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-chaparrel-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. 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 vale of these recreational activities. Restoration of services through decreases in nitrogen deposition would likely increase the total value of recreational services.

Table 3-9. 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 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.

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

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4 ADDRESSING THE ADEQUACY OF THE CURRENT STANDARDS

Based on the information in Chapters 2 and 3, we conclude that there is support in the available effects-based evidence for consideration of secondary standards for NO_X and SO_X that are protective against adverse ecological effects associated with deposition of NO_X and SO_X to sensitive ecosystems. Having reached this general conclusion, we then to the extent possible evaluate the adequacy of the current NO_X and SO_X secondary standards 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 NO_X and SO_X deposition levels, 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.

4.1 Are The Structures Of The Current NO_x And SO_x Secondary Standards Based On Relevant Ecological Indicators Such That They Are Adequate To Determine And Protect Public Welfare Against Adverse Effects On Ecosystems?

The current secondary NO_X and SO_X standards are intended to protect against adverse effects to public welfare. For NO_X, the current secondary standard was set identical to the

primary standard[1], e.g. an annual standard set for NO_2 to protect against adverse effects on vegetation from direct exposure to ambient NO_X. For SO_X, 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 SO_2. 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 NO_2 and SO_2 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 SO_2, NO, NO_2 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 SOx and NOx. 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 NO_X and SO_X standards are associated with deposition of N and S caused by atmospheric concentrations of NO_X and SO_X (see Chapter 2). 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 NO_2 and SO_2 concentrations as indicators, the current standards address only a fraction of total atmospheric NO_X and SO_X, and do not take into account the effects from deposition of total atmospheric NO_X and SO_X. By addressing short-term concentrations, the current SO_2 standard, while protective against direct foliar effects from gaseous SO_X, 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 SO_2 standard.

[1] The current primary NO_2 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 NO_2. The current secondary standard remains as it was set in 1971.

The levels of the current standards also are not well suited to dealing with deposition-based effects of NOx and SOx. Current standards are specified as allowable single atmospheric concentration levels for NO_2 or SO_2. This type of structure does not take into account variability in the atmospheric and ecological factors that may alter the effects of NO_X and SO_X 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 NO_X and SO_X 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 … 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 most areas of the U.S. are in attainment with the current NO_2 and SO_X standards, it is possible to evaluate current conditions, and evaluate the impact on public welfare from the current effects on ecosystems from NO_X and SO_X deposition in areas that attain the current standards that use NO_2 and SO_2 as indicators. In addition, this chapter qualitatively addresses the adequacy of the structures of the existing standards relative to ecologically relevant standards for NO_X and SO_X, and sets up arguments for developing an ecologically relevant structure for the standards as described in Chapter 5.

4.2 To What Extent Are The Structures Of The Current NO_X AND SO_X Secondary Standards Meaningfully Related To Relevant Ecological Indicators Of Public Welfare Effects?

The current secondary standard for NO_X, set in 1971, using NO_2 as the atmospheric indicator, is 0.053 parts per million (ppm) (100 micrograms per cubic meter of air [μg/m3]),

annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO_2 concentrations. This standard was selected to provide protection to the public welfare against acute injury to vegetation from direct exposure and resulting phytoxicity. During the last review of the NO_X standards, impacts associated with chronic acidification and eutrophication from NOx deposition were acknowledged, but the relationships between atmospheric concentrations of NOx 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 (USEPA 1995).

The current secondary standard for SO_X, set in 1971, uses SO_2 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 SO_X secondary standard, impacts associated with chronic acidification were acknowledged, but the relationships between atmospheric concentrations of SOx and levels of acidification, along with the complex interactions between SO_X and NO_X in acidification processes, were cited as critical uncertainties which made the setting of secondary NAAQS to protect against acidification inappropriate at that time (USEPA 1982).

In the previous separate reviews of the NO_X and SO_X secondary standards, EPA acknowledged in each review the additional impacts of NO_X and SO_X 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 NO_X and SO_X. 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 NO_2 and SO_2 as measured by the current standards. Even though the NO_2 standard uses an annual average of NO_2, it is focused on the annual average of 1-hour NO_2 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. NO_2 and SO_2 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 NO_X and SO_X 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 NO_X and SO_X can be in found in Chapters 5 and 6 below. The third issue is that the current standards reflect separate assessments of the two individual pollutants, NO_2 and SO_2, rather than assessing the joint impacts of deposition of NO_X and SO_X 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 NO_X and SO_X 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 NO_X and SO_X should be a critical element of the conceptual framework for ecologically relevant standards. There are also important interactions between NO_X and SO_X 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 NO_X and SO_X. 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 NO_X and SO_X. 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.

4.3 To What Extent Do Current Monitoring Networks Provide A Sufficient Basis For Determining The Adequacy of Current Secondary NO_X and SO_X Standards?

Staff have closely evaluated whether levels of N and S allowed by current standards are requisite to protect public welfare. Doing so requires relating atmospheric concentrations with deposition, exposure pathways, and measured effects on ecologic receptors. A combination of monitoring and air quality model applications is useful in linking atmospheric concentrations to ecological effects. There are over 1000 ground level monitoring platforms (Figures 4-1 and 4-2 and Table 4 -1) that provide measurements of some form of atmospheric nitrogen or sulfur. 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.. Total reactive oxidized atmospheric nitrogen, NO_Y, is defined as NO_X (NO and NO_2) and all oxidized NO_X products: $NO_y = NO_2 + NO + HNO_3 + PAN + 2N_2O_5 + HONO + NO_3$ + organic nitrates + 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

Table 4-1. 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

Table 4-1 Summary of Monitoring Networks (continued)

Network	Number of Sites	Species Measured	Sampling Frequency	Comments
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/NOx	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, NO2, NOX or NOY in 2009 identified in AQS
NOY	59	NO_y	Hourly	All Monitoring Sites with Measurements of NOY in 2009 identified in AQS, regardless of Monitoring Type
IMPROVE	214	Nitrates	24-hour	MPROVE Monitoring Sites with Measurements of Nitrates (88306) identified in AQS
CASTNET	88	Nitrates	Weekly Ave.	EPA & NPS

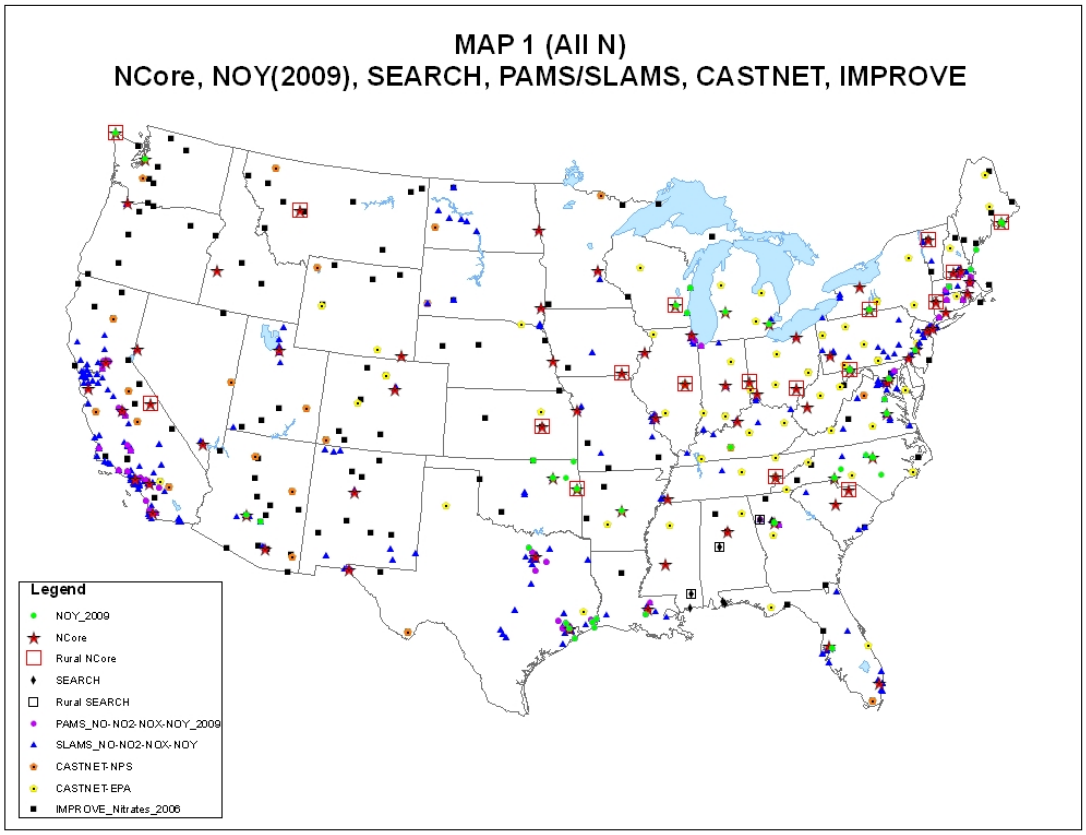

Figure 4-1 Routinely operating surface monitoring stations measuring forms of atmospheric nitrogen.

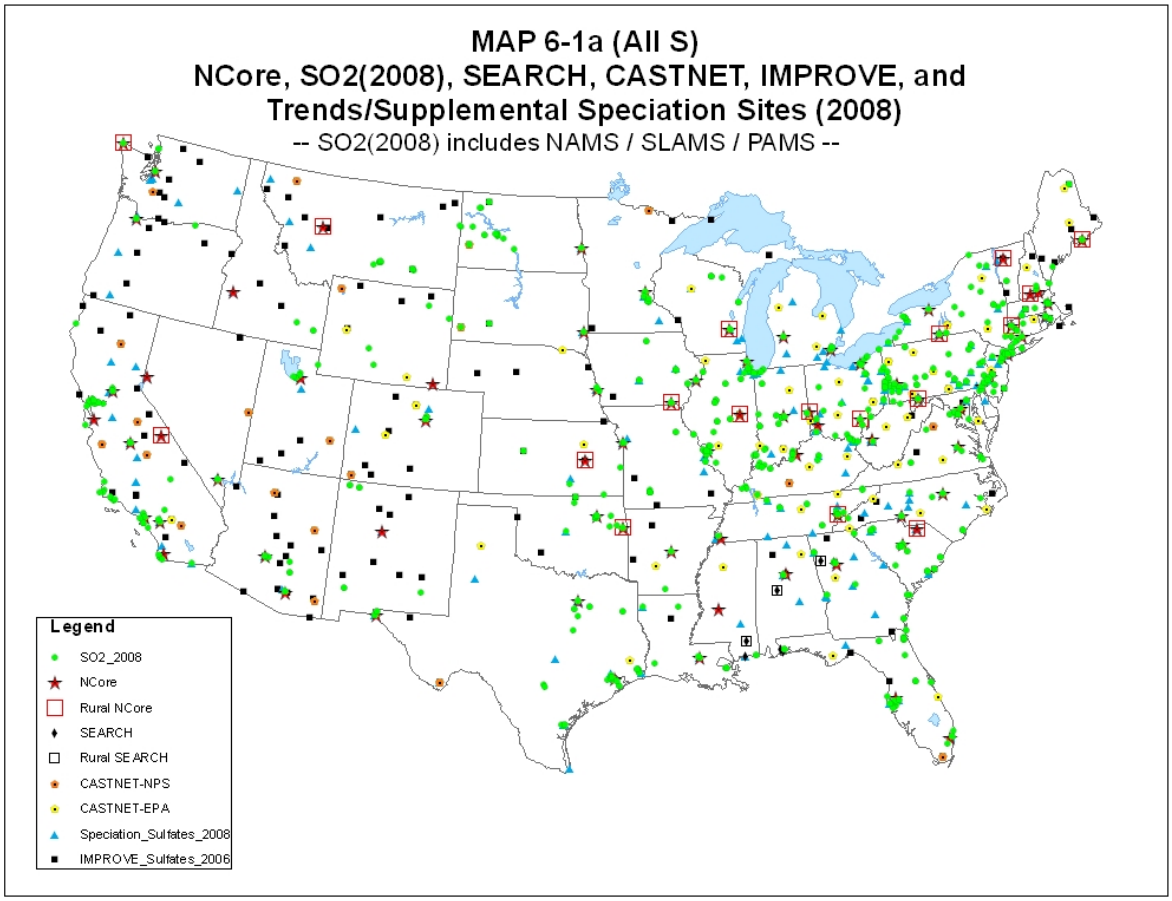

Figure 4-2 Routinely operating surface monitoring stations measuring forms of atmospheric sulfur. All site locations measure both SO_2 and sulfate except for the green SO_2 only sites**.**

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. Total reduced nitrogen (NH_X) includes ammonia, NH_3, plus ammonium, NH_4 (EPA, 2008). 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. 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 SO_2, 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 SO_2, 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 NO_2, 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 4-3). The NCore network (Scheffe et al., 2009) is a multiple pollutant network with co-located measurements of key trace gases (CO, SO_2, O_3, 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

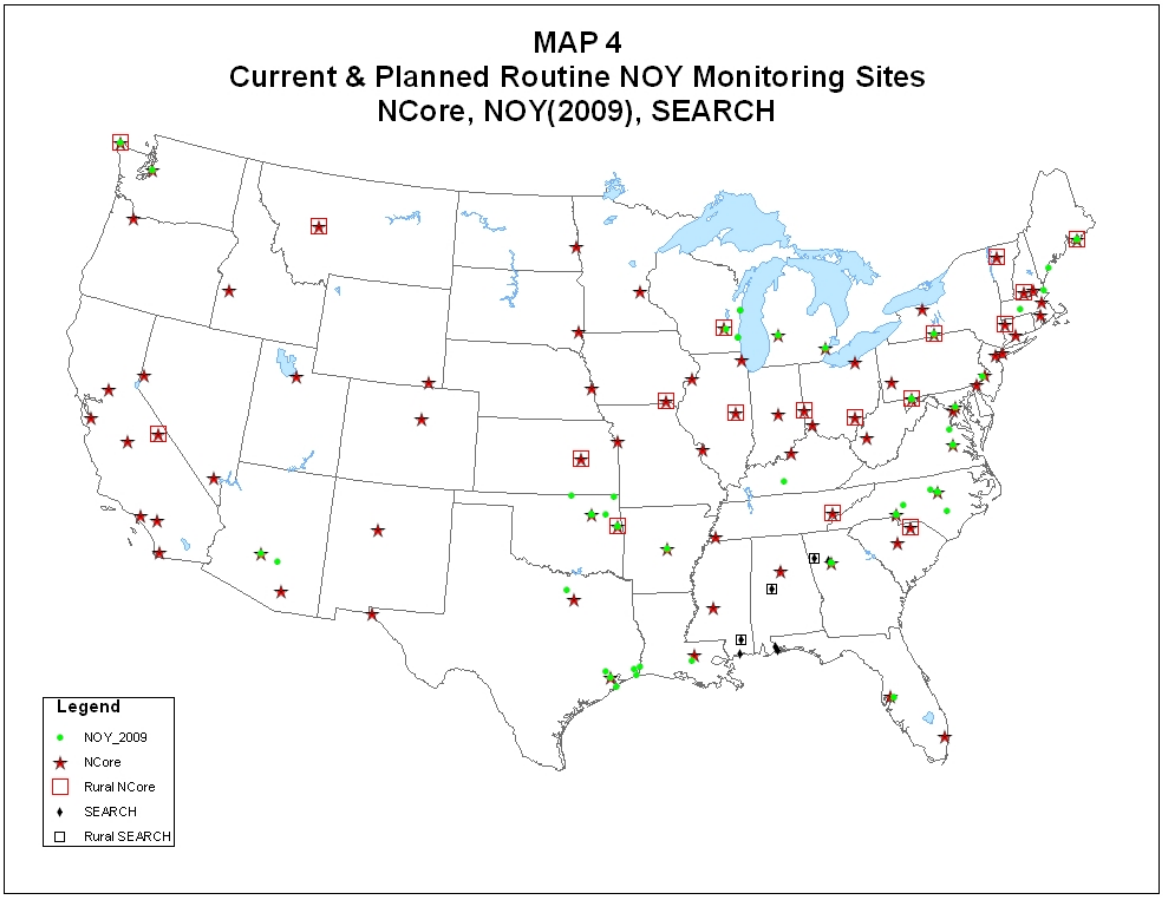

Figure 4-3. Anticipated network of surface based NO_Y stations based on 2009 network design plans. The NCore stations are scheduled to be operating by January, 2011.

measurements of ammonia and possibly true NO_2 are under consideration. True NO_2 is noted to differentiate from the NO_2 determined through routine regulatory networks that have known variable positive bias for NO_2. 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.

There are significant measurement gaps for characterizing NO_Y, NH_X and SO_2 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 NO_2) 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. Note that the NO_X monitors used for NAAQS primary compliance purposes capture varying amounts of transformed nitrogen species; however, the method provides biased low estimates with significant airshed induced variability relative to true NO_Y. With the exception of the SEARCH network in the Southeast, there are virtually no routine networks that measure ammonia, although EPA is considering options for ammonia sampling in CASTNET and NCORE networks. Ammonium is reported in EPA chemical speciation networks, although the values are believed to be biased low due to ammonia volatization.

CASTNET provides mostly rural measurements of SO_2, total nitrate, and ammonium, and affords an existing infrastructure useful for future monitoring in support of a potential NOx and SOx secondary standard. However, the lack of NO_Y, SO_X and NH_X measurements in sensitive ecosystems will require attention in the N/S secondary standard proposal.

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).

4.3.1 To what extent does the NADP monitoring network provide an adequate characterization of deposition and what are the major limitations?

The National Atmospheric Deposition Program (NADP) includes approximately 250 sites (Figure 4-4) 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. The organic bound nitrogen is not analyzed routinely in NADP samples. 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.

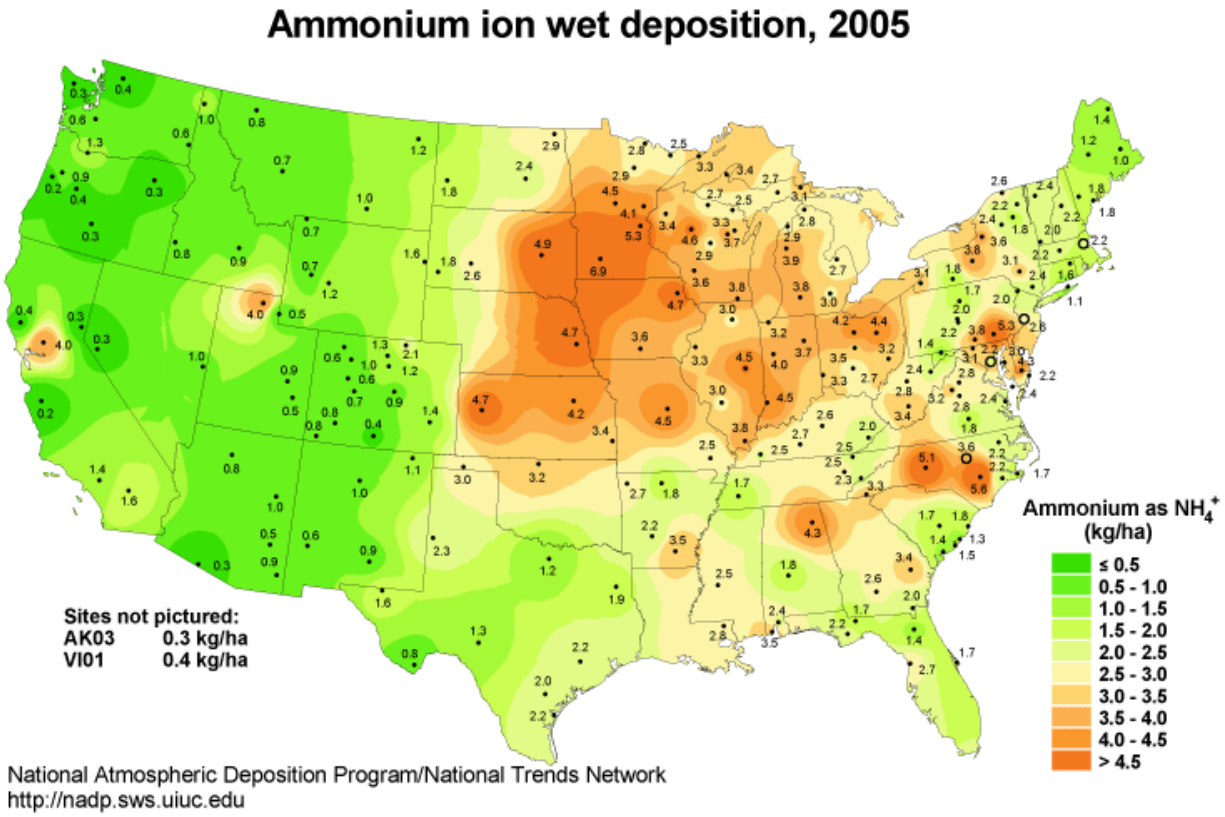

Figure 4-4. Location of approximately 250 National Atmospheric Deposition Monitoring (NADP) National Trends Network (NTN) sites illustrating annual ammonium deposition for 2005. Weekly values of precipitation based nitrate, sulfate and ammonium are provided by NADP**.**

4.3.2 What are the relative strengths and important gaps in existing atmospheric monitoring networks to address a combined NO_X/SO_X secondary standard?

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 virtually offer no support for a secondary NO_X/ SO_X standard 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 on a 2.5μ 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 offgassing from nylon filters.

Although this summary of existing networks suggests significant challenges in meeting the monitoring needs of a new NO_X/ SO_X standard, 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 SO_2 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 e developed in the second PAD.

4.3.3 How do we characterize deposition through monitoring and models?

Routinely available directly measured precipitation to quantify wet deposition of sulfur and nitrogen species is provided through the NADP. 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 (EPA, 1999) 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). 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.

4.3.2.1 Why are we using CMAQ to model deposition? How are we using it? Why is CMAQ the right model to use? What is the spatial and temporal resolution of CMAQ? What are the model years? What are the limitations to CMAQ?

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 Chapter 7 of this PA. Currently, there are efforts to improve a number of nitrogen related processes in CMAQ, recognizing comparatively less uncertainty with the treatment of sulfur. Active areas of model process improvement are in the treatment of lightning generated NO_X and the transference of nitrogen between atmospheric and terrestrial and aquatic media, often referred to as bi-directional flux. Lightning NOx potentially provides a significant contribution to wet deposition as the resulting NO_X is rapidly entrained into aqueous cloud processes. Both the thermodynamics of soil processes and mass transfer of nitrogen species across the surface-atmosphere interface is governed by an assortment of temperature, moisture, advection and concentration patterns. These processes and mass transfer relationships are coupled within the emissions, meteorological, and chemical simulation processes and associated surface/vegetation and terrain information incorporated in or accessed by the CMAQ. In addition to research activities to improve the characterization of nitrogen-related processes in CMAQ, efforts are also underway to improve the general characterization of ammonia emissions

which remains as an area of large uncertainty due to limited source data and the ubiquitous nature of these emissions. Another challenge for regional/national air quality modeling is properly representing the effects on pollutant concentrations, precipitation and therefore deposition of variable terrain features, particularly steep mountain-valley gradients and the interfaces to wide open basins encountered in the Western United States.

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.

4.4 What Is Our Best Characterization of Atmospheric Concentrations Of NO_Y and SO_X, and Deposition Of N And S?

Air quality models and blending of model results and observations are used to characterize current environmental state conditions due to the relative sparseness of monitoring coverage in sensitive ecosystems as well as gaps in coverage for specific atmospheric species of N and S most relevant to deposition, such as NO_Y, in available monitoring platforms.

4.4.1 What are the current atmospheric concentrations of reactive nitrogen, NO_Y, reduced nitrogen, NH_X, sulfur dioxide, SO_2, and sulfate, SO_4?

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 the major sources 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 are largely 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 SO2 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 4-5 through 4-11 respectively. Given the considerable gaps in air quality observation networks as discussed in the REA and ISA (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 4-12 and 4-13 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 4-14) are typically are less than 40 ppb. The spatial patterns for the 2005 modeled and observed NO_Y and SO_2 concentrations are similar to the 2002 CMAQ-based maps provided in

the REA, largely capturing the influence of major source regions throughout the nation. A spreading of the oxidized sulfur fields (Figures 4-5 and 4-6), relative to SO_2, is consistent with sulfate transformation and associated air mass aging and transport. Ammonia and ammonium concentration patterns (Figure 4-4) 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 (see Chapter 7) does reduce NH_3 spatial gradients. Total deposition for nitrogen and sulfur (Figures 4-15 and 4-16) basically follow the patterns of ambient air concentrations. The contribution of reduced nitrogen to total nitrogen deposition (Figure 4-17) illustrates the strong influence of agricultural based ammonia emissions, particularly in upper midwest and eastern North Carolina.

The 2005 ambient conditions indicate that the current SO_2 and NO_2 secondary standards are not exceeded (Figures 4-18 and 4-19) in locations where ecological effects have been observed, and where critical loads of nitrogen and sulfur are exceeded. This information is consistent with the fact that NO_2 accounts for only a fraction of NOy, and thus decreases in NO and NO_2 emissions that result in attaining the current secondary NO_2 standard would not be expected to fully address deposition of NO_Y in acid sensitive areas that generally are not represented by urban oriented NO_2 monitoring locations. The map in Figure 4-20 further illustrates this point by showing that the contribution of NO_2 to NO_Y is often less than 50% in rural areas. Neither NO_Y nor NO_2 concentrations correlate well with total oxidized nitrogen deposition (Figure 4-21), based on the annual average values in each 12 km CMAQ grid cell. The lack of correlation between NO_Y and nitrogen deposition is largely due to the inclusion of NO_Y species with low deposition velocity, primarily NO_2. While NO_2 does not reflect the majority of oxidized nitrogen in rural environments, the species remains a significant contributor to the total ambient NO_Y budget. In contrast, species with high deposition velocities such as nitric acid correlate well with oxidized nitrogen deposition. The temporal correlations between NO_Y and deposition are likely to be similar to the nitric acid to deposition relationship when averaged over larger a spatial area as the influence of species with low deposition velocities is

minimized in rural locations associated with acid sensitive areas. Those relationships will be explored in the final PAD.

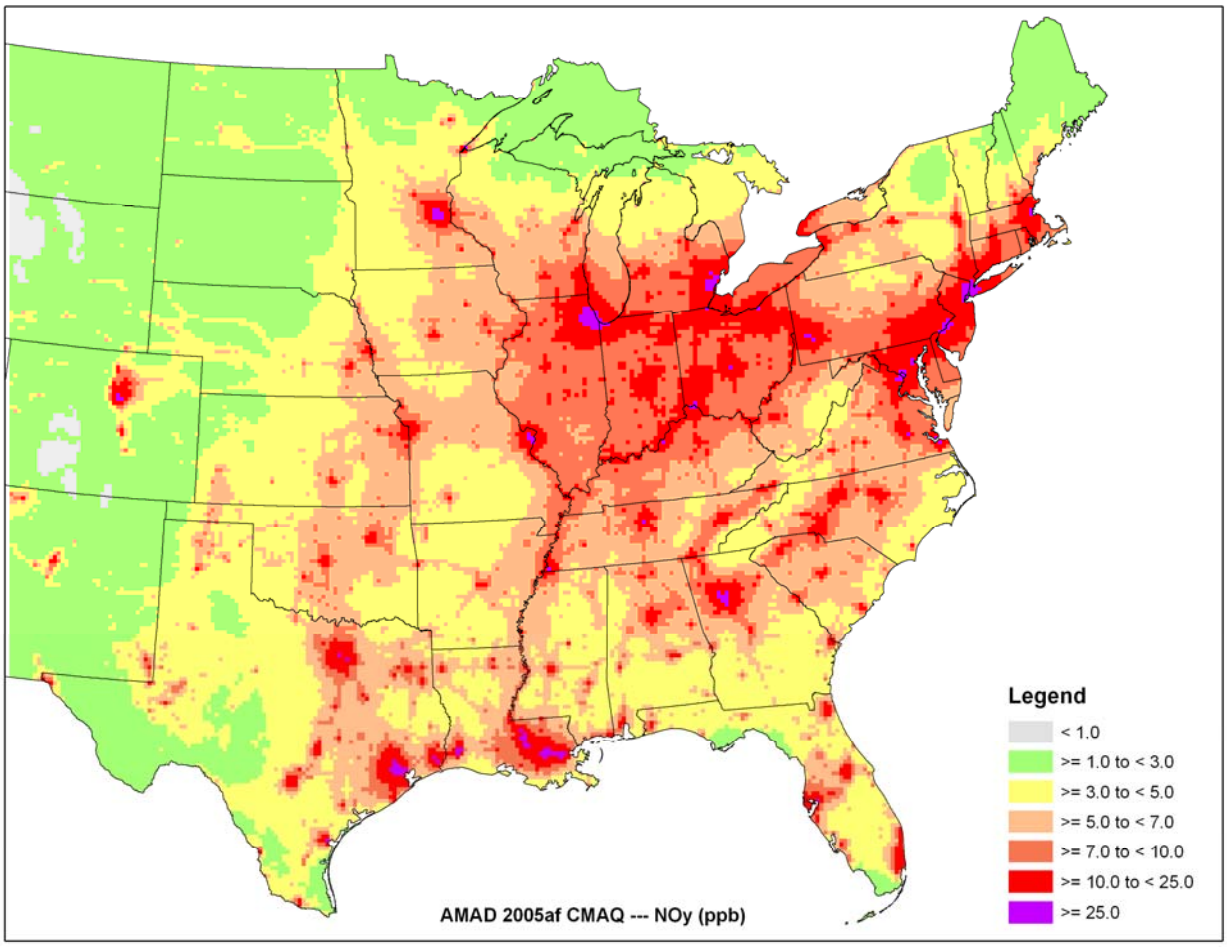

Figure 4-5. 2005 CMAQ modeled annual average NO_Y (ppb; see Table 1-1 for unit conversions).

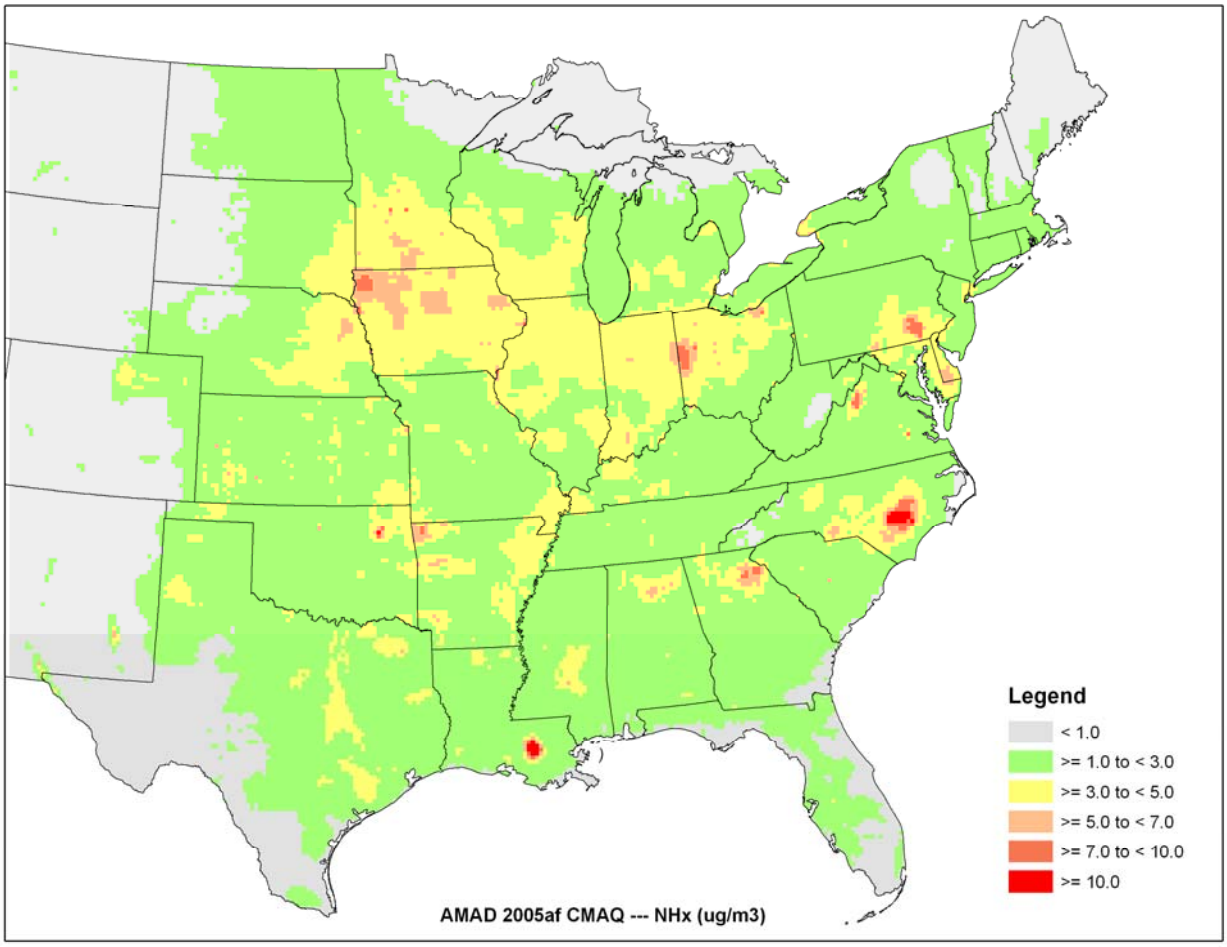

Figure 4-6. 2005 CMAQ modeled annual average total reduced nitrogen (NH_X) (as ug/m^3 nitrogen – see Table 1-1 for unit conversions)

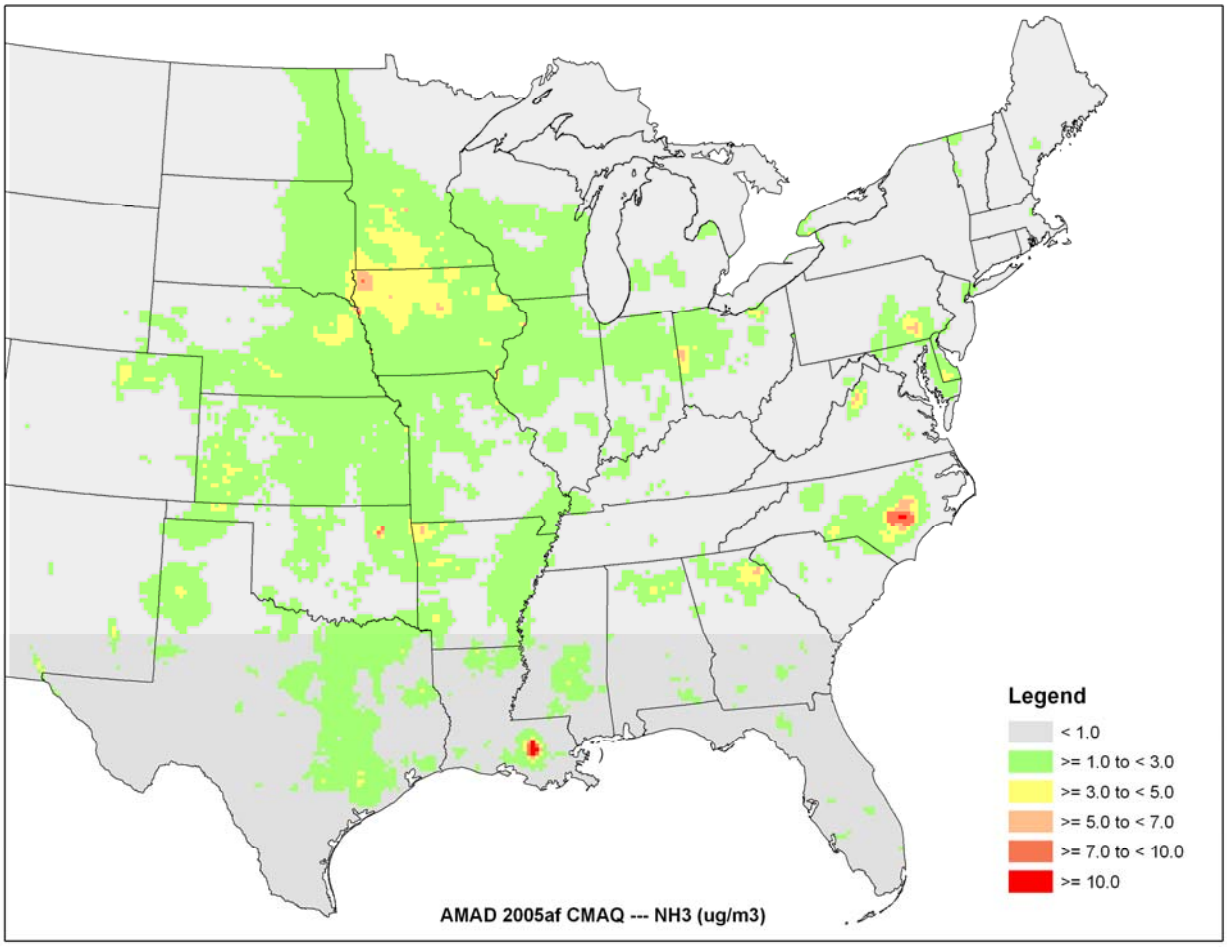

Figure 4-7. 2005 CMAQ modeled annual average ammonia, NH_3, (as ug/m^3 N; see Table 1-1 for unit conversions)

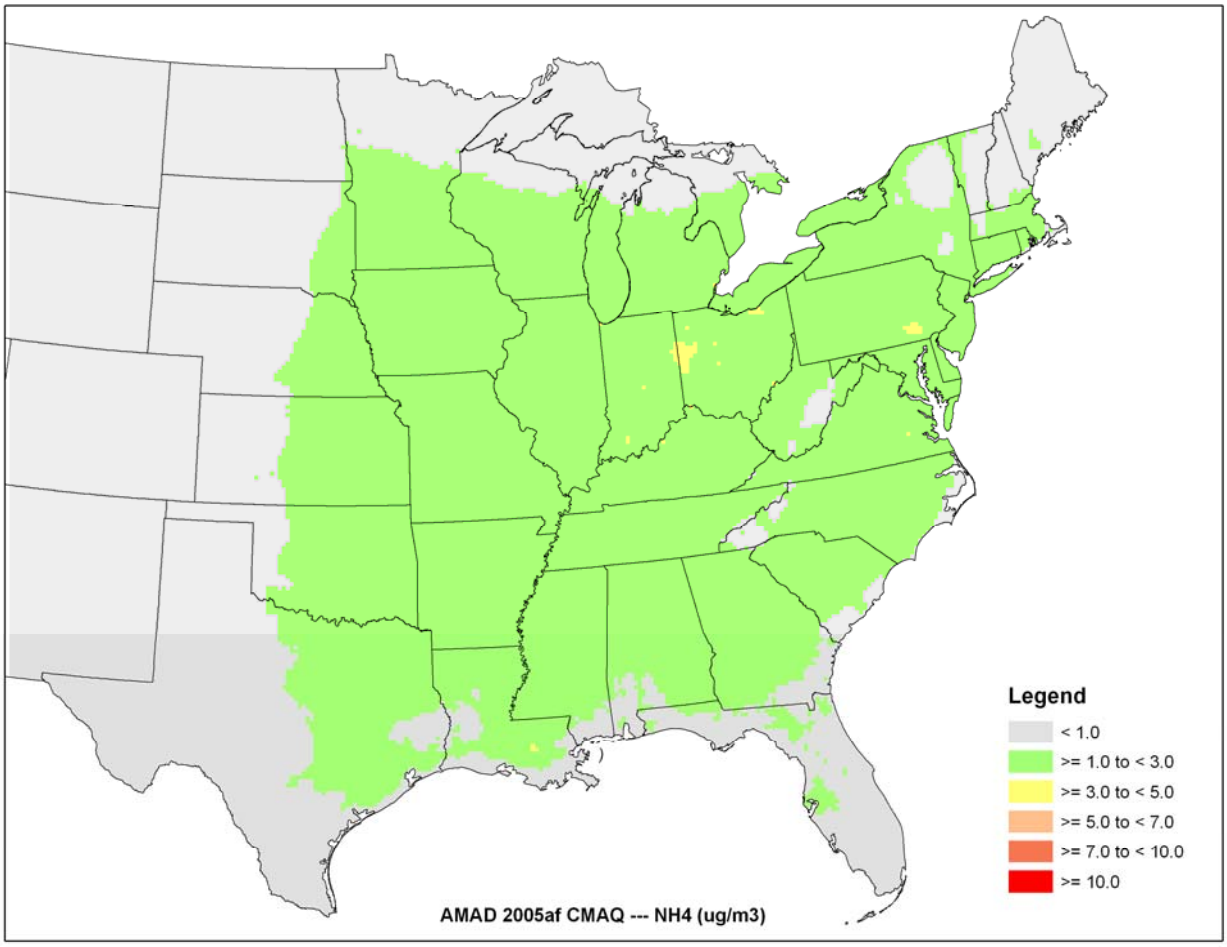

Figure 4-8. 2005 CMAQ modeled annual average ammonium, NH_4, (as ug/m^3 N; see Table 1-1 for unit conversions)

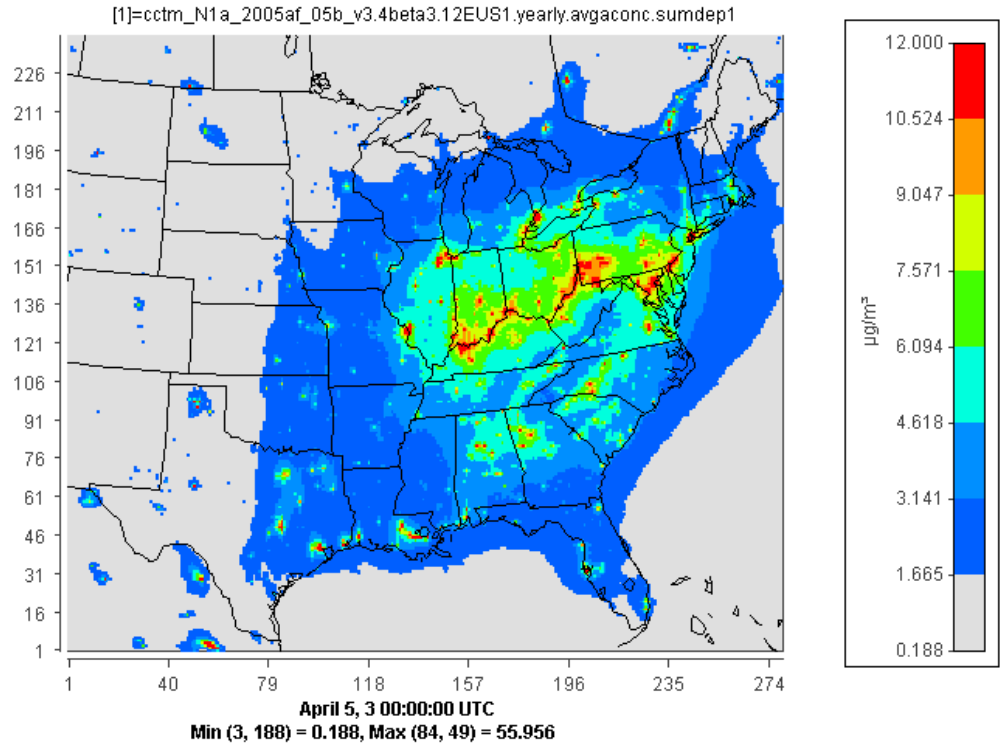

Figure 4-9. 2005 CMAQ modeled annual average SO_X, (as ug/m^3 S from SO_2 and SO_4; see Table 1-1 for unit conversions).

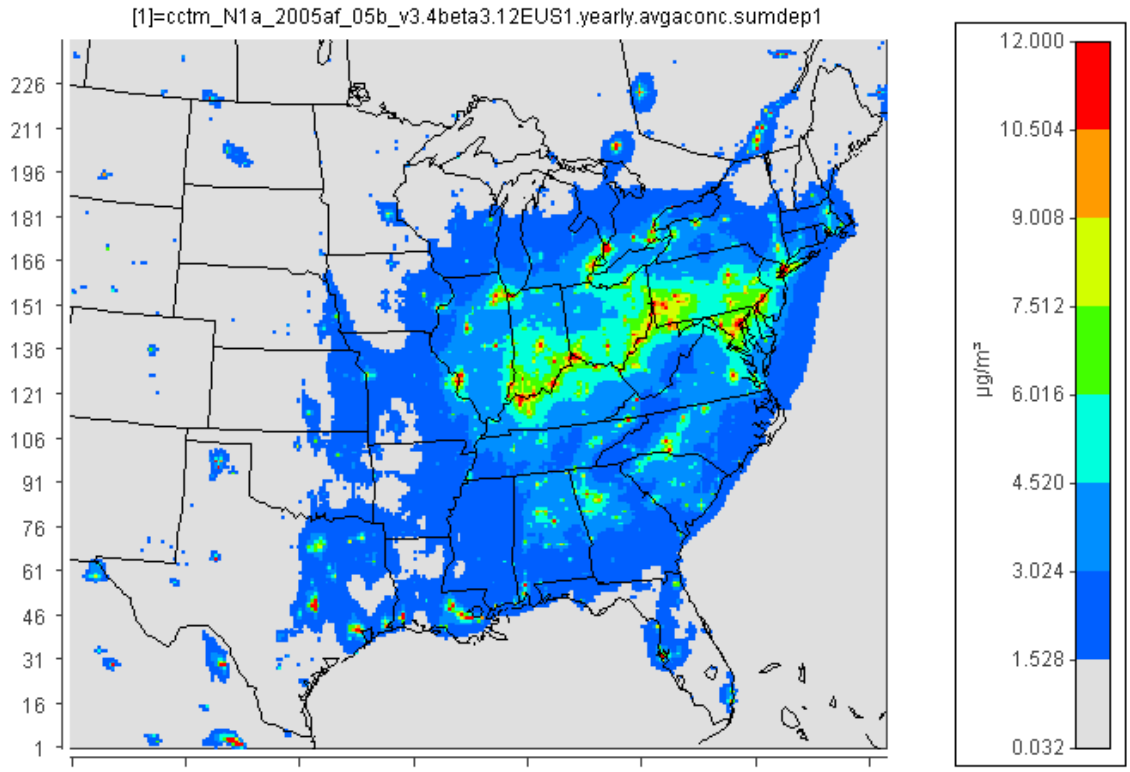

Figure 4-10. 2005 CMAQ modeled annual average SO_2 (as ug/m^3 S; see Table 1-1 for unit conversions)

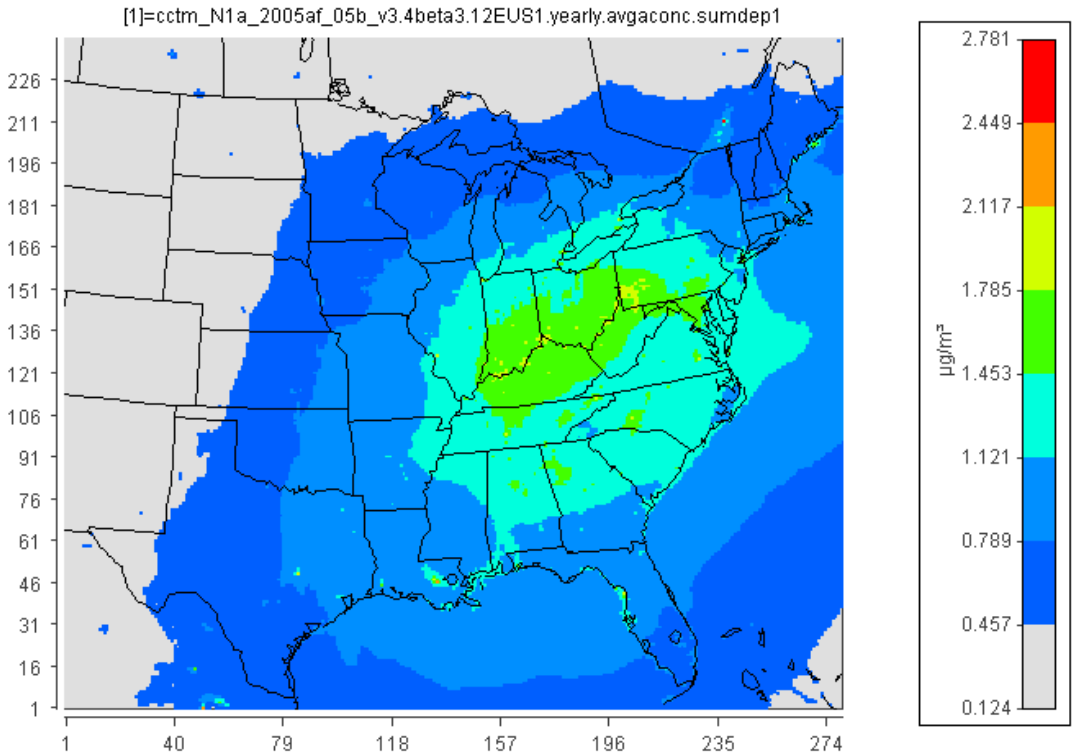

Figure 4-11. 2005 CMAQ modeled annual average SO_4 (as ug/m^3 S; see Table 1-1 for unit conversions).

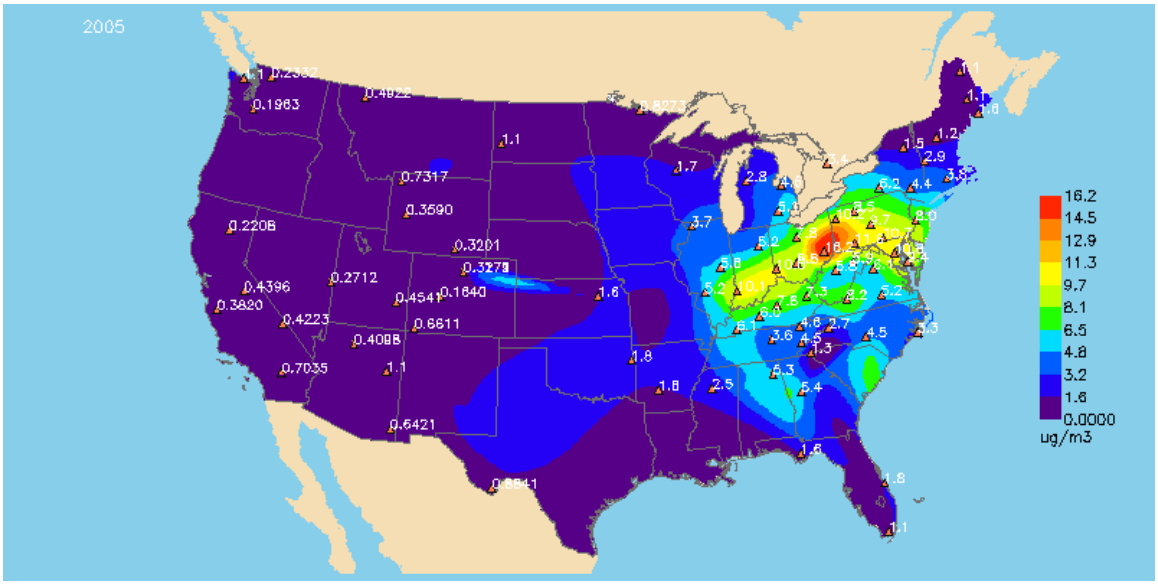

Figure 4-12. 2005 annual average sulfur dioxide concentrations based on CASTNET generated by the Visibility Information Exchange Web Sysytem (VIEWS). See Table 1-1 for unit conversions

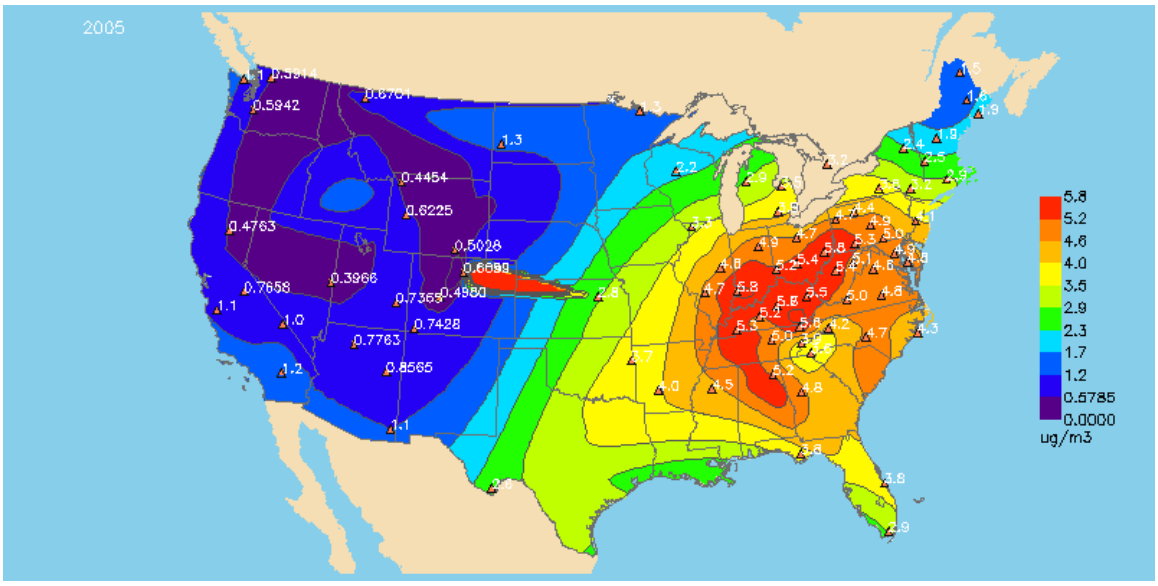

Figure 4-13 2005 annual average sulfate concentrations based on CASTNET generated by the Visibility Information Exchange Web Sysytem (VIEWS). [interpolating relative sparse data can produce unrealistic concentration plumes as demonstrated in the central U.S.] see Table 1-1 for unit conversions.

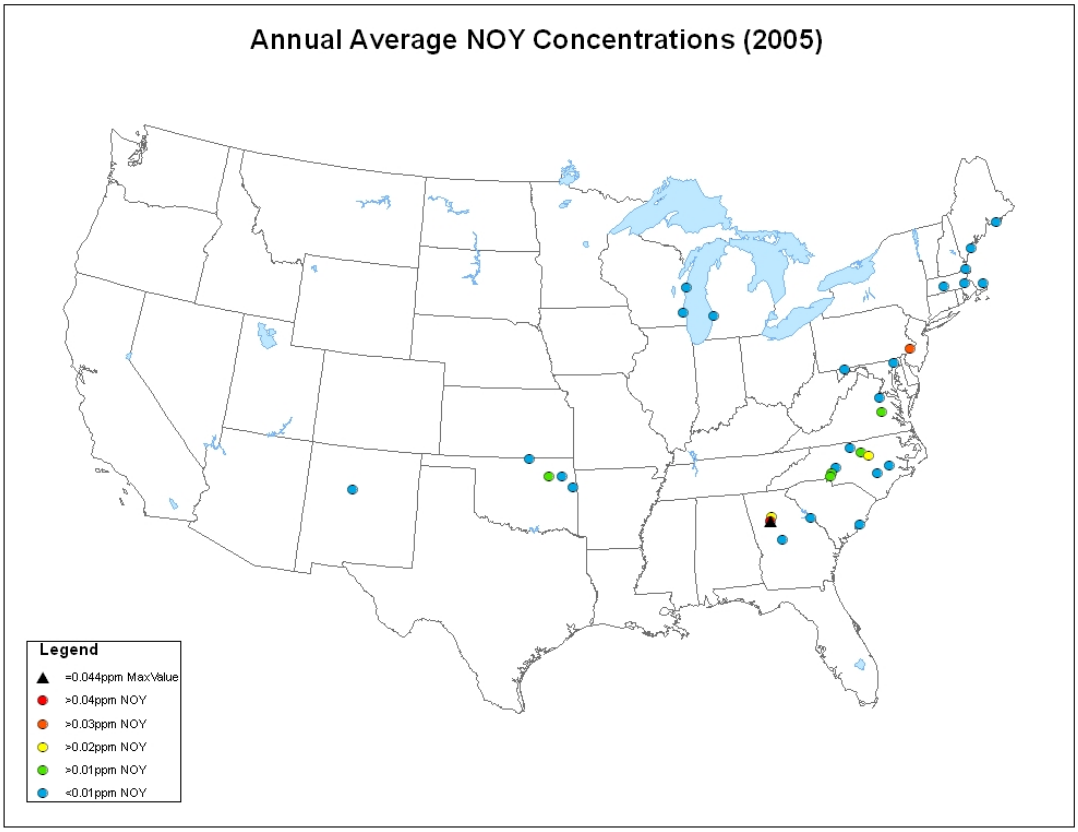

Figure 4-14. Annual average 2005 NO_Y concentrations from reporting stations in the Air Quality System (AQS). see Table 1-1 for unit conversions.

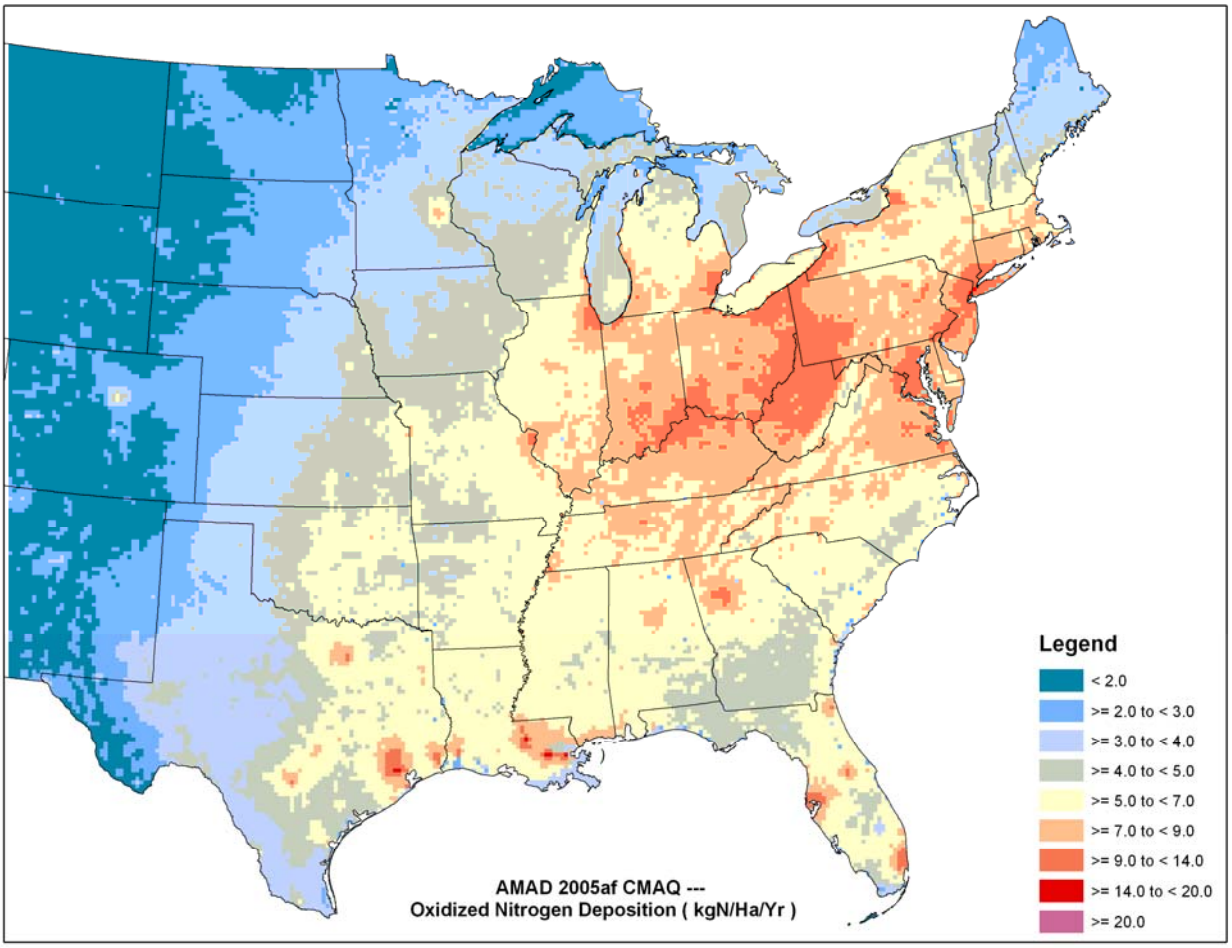

Figure 4-15. 2005 CMAQ modeled oxidized nitrogen deposition (kgN/ha-yr). see Table 1-1 for unit conversions

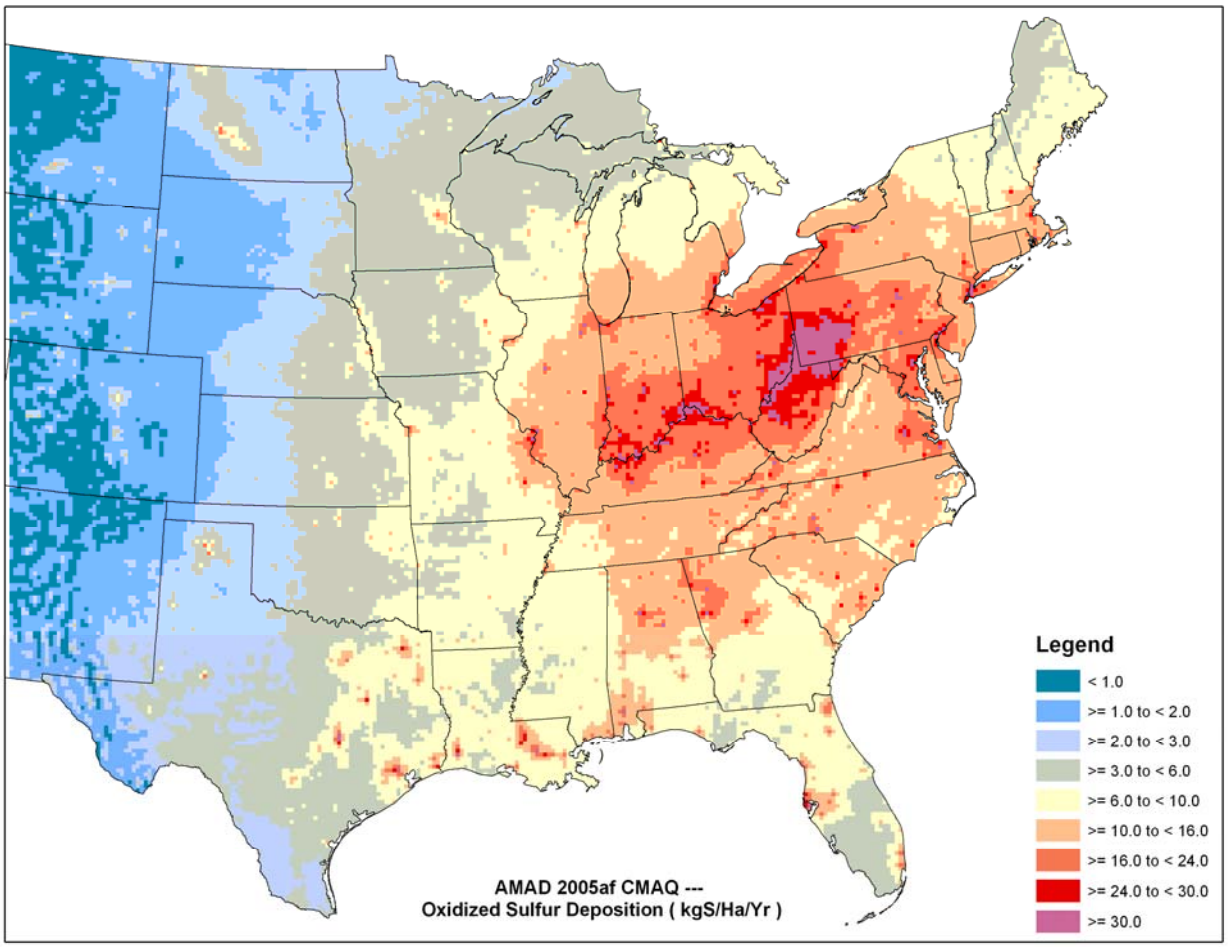

Figure 4-16. 2005 CMAQ modeled oxidized sulfur deposition (kgS/ha-yr). see Table 1-1 for unit conversions

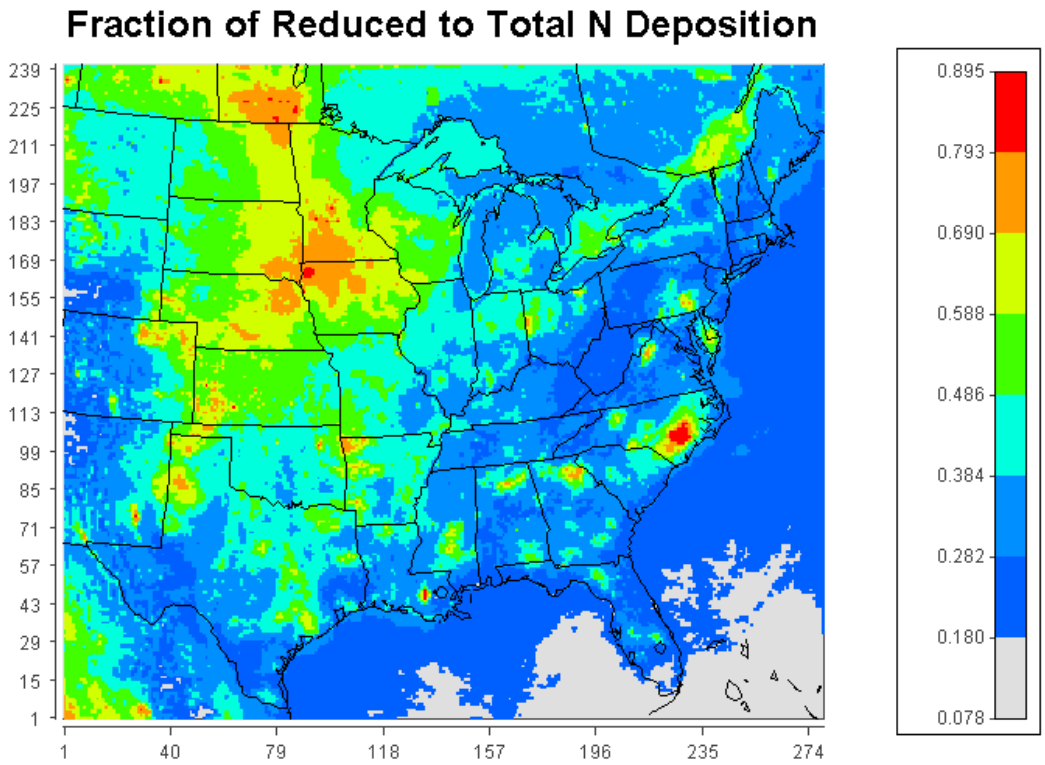

Figure 4-17. 2005 CMAQ derived annual average ratio of reduced to total nitrogen deposition.

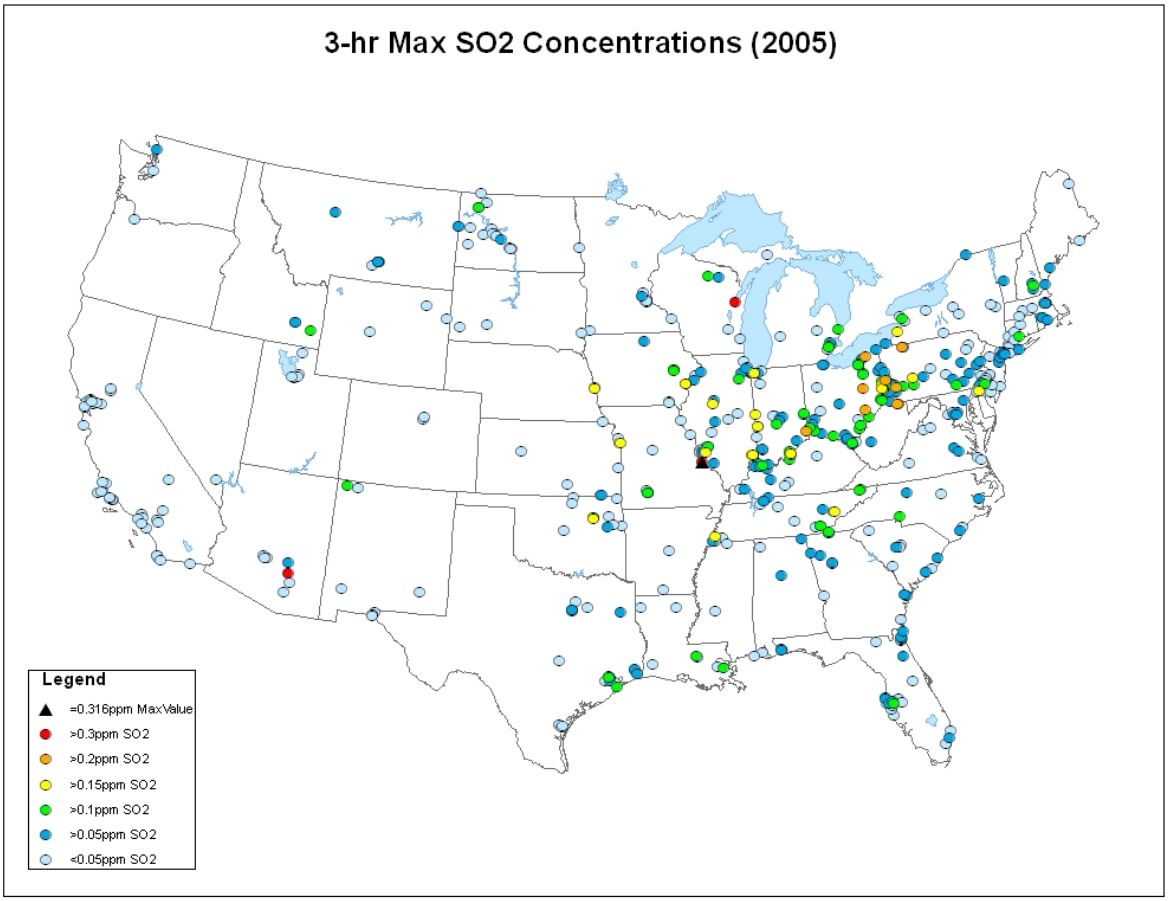

Figure 4-18. Three hour average maximum 2005 SO_2 concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base. The current SO_2 secondary standard based on the maximum 3 hour average value is 500 ppb, a value not exceeded. While there are obvious spatial gaps, the majority 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 1-1 for unit conversions

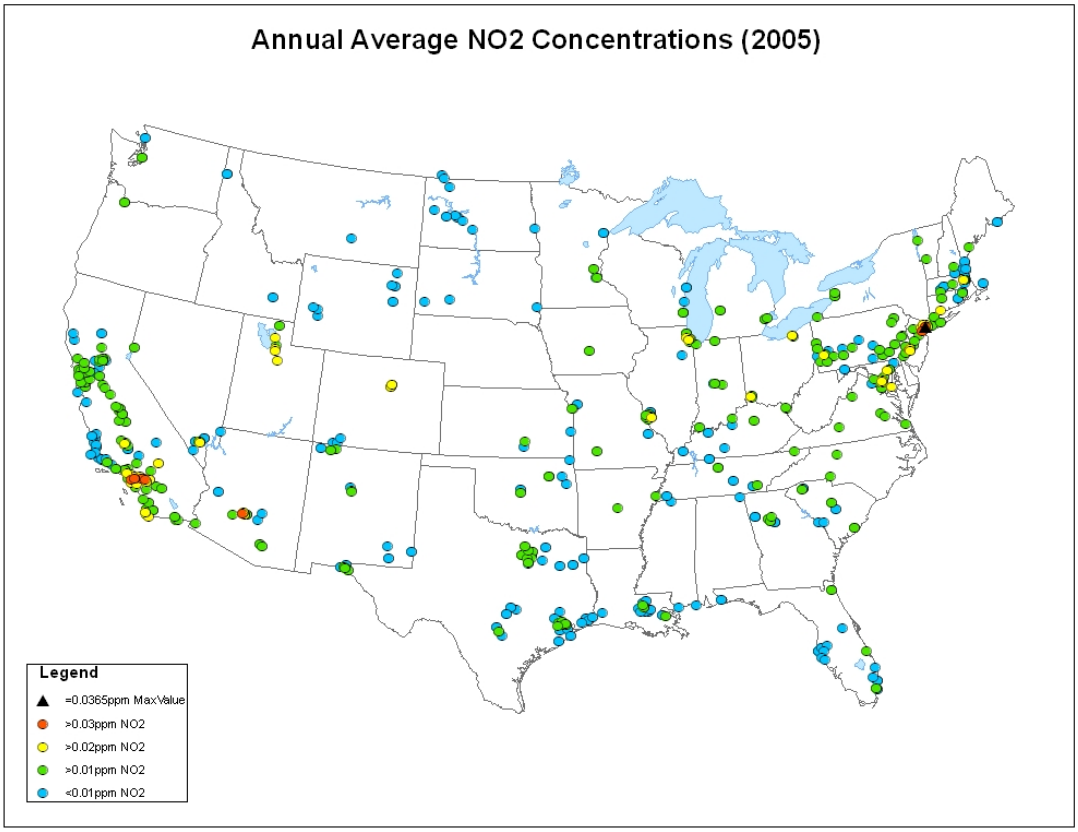

Figure 4-19 Annual average 2005 NO_2 concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base. The current NO_2 secondary standard is 53 ppb, a value well above those observed. While there are obvious spatial gaps, the stations are located in areas of relatively high concentrations in highly populated areas. Lower relative values are expected in more remote acid sensitive areas. see Table 1-1 for unit conversions

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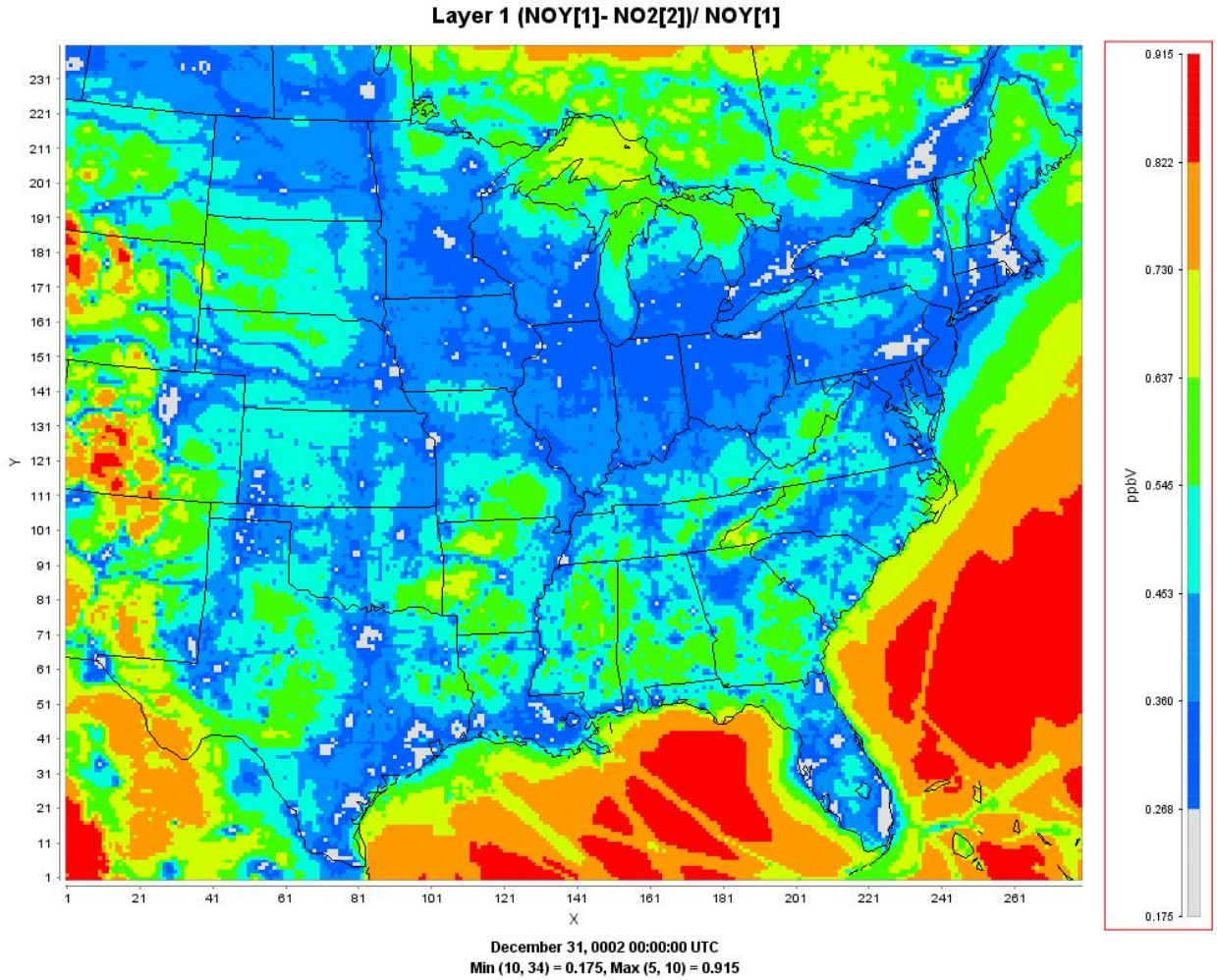

Figure 4-20 2005 CMAQ derived annual average ratio of (NO_Y – NO_2)/NO_Y. The fraction of NO_2 contributing to total NO_Y generally is less than 50% in the Adirondack and Shenandoah case study areas. The ratio (dimensionless – scale units of ppbv are an automated output) reflects the relative air mass aging associated with transformation of oxidized nitrogen beyond NO and NO_2 as one moves from urban to rural locations.

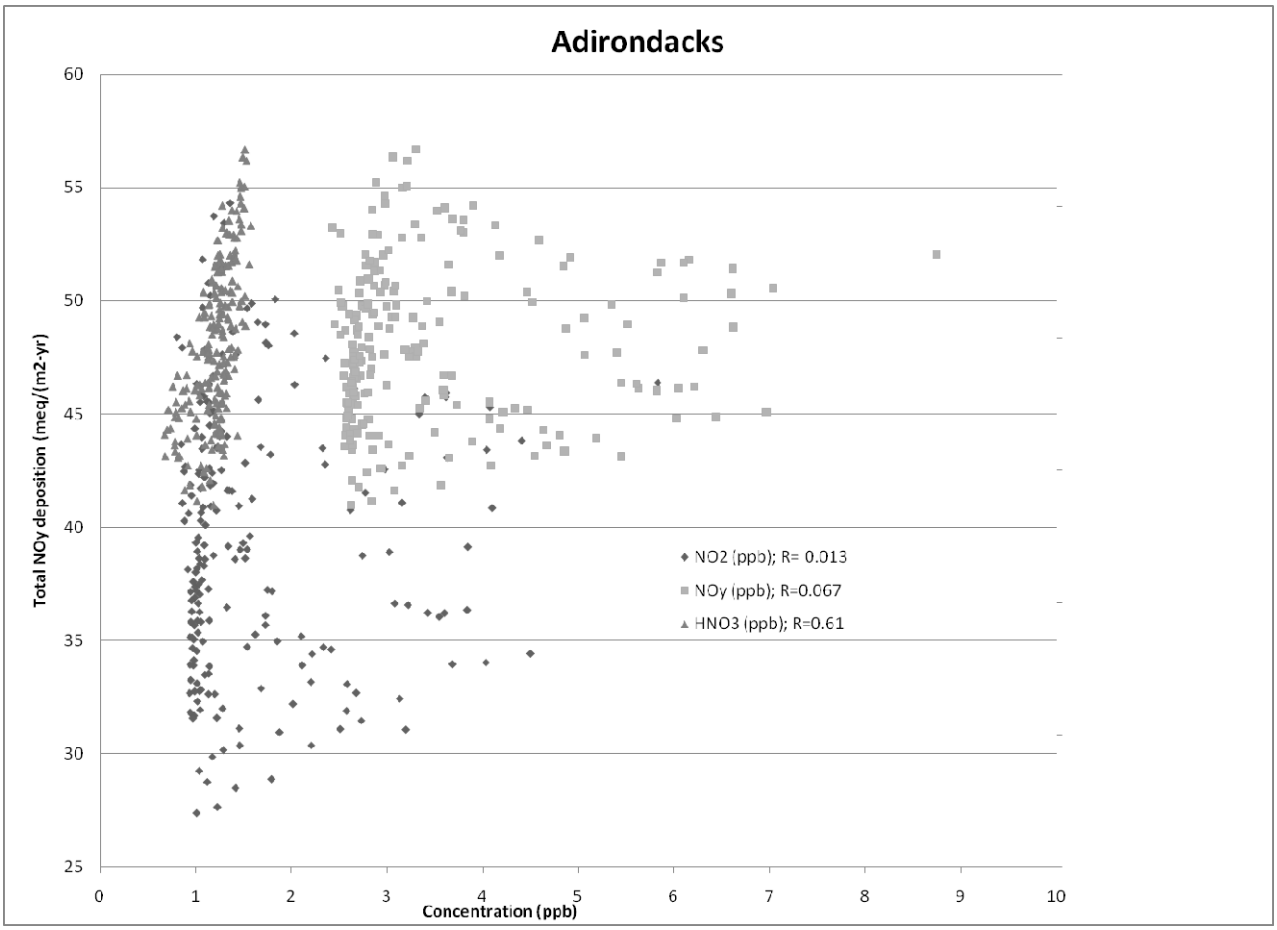

Figure 4-21 Scatter plots of total oxidized nitrogen deposition with average annual NO_2, HNO_3 and NO_Y concentrations on each 12 km^2 grid based on 2005 CMAQ results for the Adirondack region.

4.5 Are Adverse Effects On The Public Welfare Occurring Under Current Air Quality Conditions For NO_2 And SO_2 And Would They Occur If The Nation Met The Current Secondary Standards?

In the previous sections we have established that almost all areas of the U.S. were at concentrations of SO_2 and NO_2 below the levels of the current standards. In many locations, SO_2 and NO_2 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 NOx and SOx 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., NO_X contributes 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 SOx 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 SO_4^{2-} followed in decreasing order by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry SO_4^{2-}.

New scientific evidence exists to address each of the areas of uncertainty raised in the previous reviews (summarized above in section 1.4). 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 NO_X and SO_X 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 NO_X and NH_X 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 (CH_4), and N_2O 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 NO_X secondary standard, a great deal of information on the contribution of atmospheric deposition associated with ambient NO_X has become available. In Chapter 3 of the REA a thorough assessment is provided of the contribution of NO_X to nitrogen deposition throughout the U.S., and the relative contributions of ambient NO_X and reduced forms of nitrogen. Staff concludes that based on that analysis, ambient NO_X is 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 NO_X and SO_X. As noted earlier, in previous reviews of the NO_X and SO_X secondary standards, 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 NO_X and SO_X 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 NO_X and SO_X to both terrestrial and aquatic ecosystems. These risks fall into two categories: acidification and nutrient enrichment. These made up the emphasis of the REA, and are most relevant to evaluating the adequacy of the existing standards in protecting public welfare from adverse ecological effects.

4.5.1 To what extent do the current NO_X and SO_X secondary standards provide protection from adverse effects associated with deposition of atmospheric NO_X and SO_X which results in 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 NO_X and SO_X was 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. NO_X and SO_X 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 4-20.

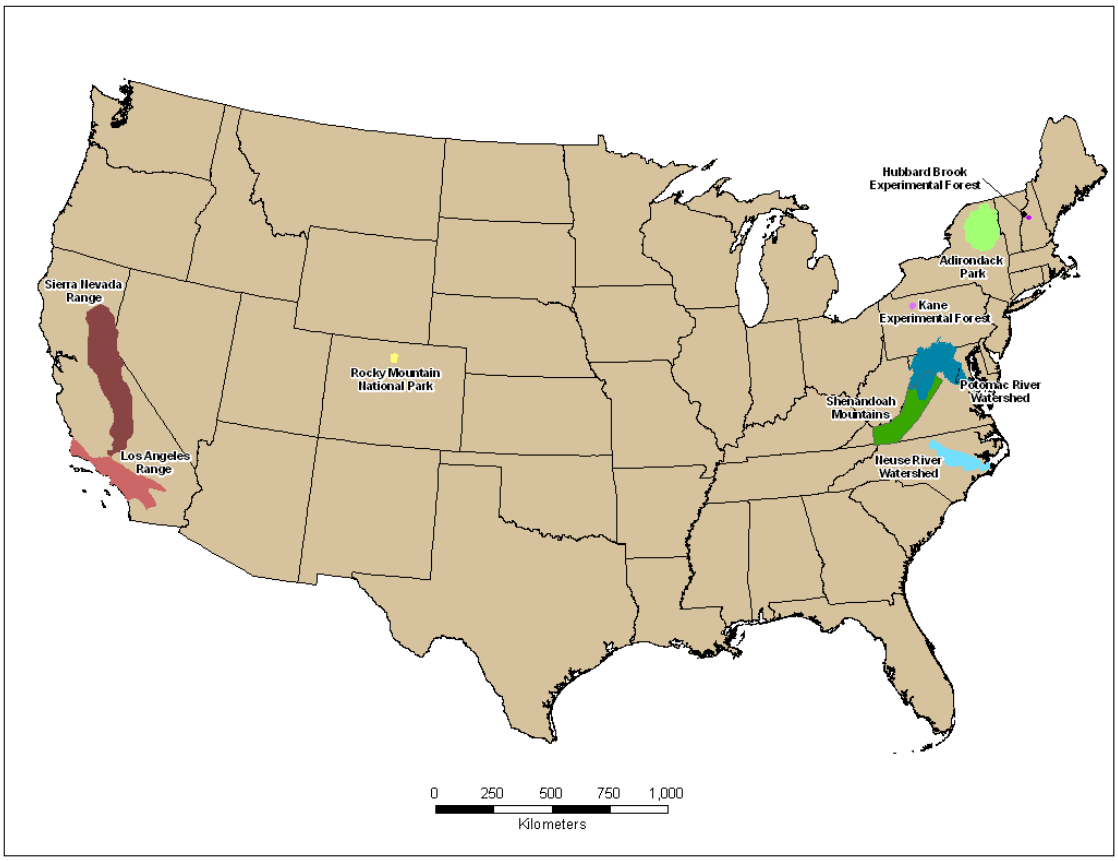

Figure 4-22 National map highlighting the nine case study areas evaluated in the REA.

4.5.1.1 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 NO_X and SO_X 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 NO_X and SO_X 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 NOx and SOx 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 NO_X and SO_X that meet the current standards.

Staff concludes that the evidence and risk assessment support strongly a relationship between atmospheric deposition of NO_X and SO_X 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 NO_X and SO_X 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 μeq/L (moderate concern). However, 44 percent of lakes had deposition levels exceeding the critical load for an ANC of 50 μeq/L, and 28 percent of lakes had deposition levels exceeding the critical load for an ANC of 20 μeq/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 μeq/L relative to an ANC level at 100 μeq/L (**REA Figure 4.2-1**). At levels below 20 μeq/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 μeq/L and 13 percent of lakes exceeded the critical load for an ANC of 20 μeq/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 μeq/L, indicating moderate concern. However, 85 percent of streams had recent deposition exceeding the critical load for an ANC of 50 μeq/L, and 72 percent exceeded the critical load for an ANC of 20 μeq/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 ES**). In addition, because of past loadings, areas of the Shenandoah are sensitive to current deposition levels (**ISA ES**). 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) of 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 NO_X and SO_X 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.

4.5.1.2 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.

4.5.2 To what extent does the current NO_X secondary standard provide protection from adverse effects associated with deposition of atmospheric NO_X, which results in 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. The 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. In certain limited situations, additions of nitrogen can increase rates of growth, and these increases can have short term benefits in certain managed ecosystems. As noted earlier, this review of the standards is focused on unmanaged

ecosystems. As a result, 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.

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 effects can occur when crops or commercial forests are not receiving enough nitrogen nutrients. Nutrients deposited on crops from atmospheric sources are often referred to as passive fertilization. Nitrogen is a fundamental nutrient for primary production in both managed and unmanaged ecosystems. 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). These rates compare to estimated rates of passive nitrogen fertilization 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 NOx 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 NOx 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 NOx, 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 some 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 effect ecosystems.

4.5.3 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 indictor 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 NOx 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.

4.5.4 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 the12 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.

4.6 To What Extent Do The Current NO_X And/Or SO_X Secondary Standards Provide Protection From Other Ecological Effects (Eg. Mercury Methylation) Associated With The Deposition Of Atmospheric NO_X, And/Or SO_X?

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 SO_X 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 are 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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5 OPTIONS FOR ELEMENTS OF THE STANDARD

The elements of the standard include the ambient air indicator, the form, the averaging time and the level. The "indicator" of a standard defines the chemical species or mixture of criteria air pollutants that is to be measured in determining whether an area attains the standard. The "form" of a standard defines the air quality statistic that is to be compared to the level of the standard in determining whether an area attains the standard. The "averaging time" defines the period of time over which the air quality indicator is averaged, e.g. annual average. The "level" is the specific quantity to which the air quality statistic will be compared.

Historically, EPA has established NAAQS so that the locally-monitored ambient concentration of an air pollutant indicator is compared against a specified numerical level of atmospheric concentration, using a specified statistical form and averaging time. For example, the current secondary standard for oxides of nitrogen uses ambient concentrations of NO_2 as the indicator. Attainment is determined by comparing the annual arithmetic mean of the measured maximum daily1-hour NO_2 concentrations, for a calendar year, against the level of 0.053 ppm. As discussed in Chapters 4, a standard using this kind of approach for defining indicator, form, averaging time, and level is not the most appropriate way to protect sensitive ecosystems from effects associated with ambient concentrations of NO_X and SO_X. This is because the ecological effects of NO_X and SO_X are a result of deposition of these air pollutions. The inherently complex and variable linkages between ambient concentrations of NO_X and SO_X, their deposited forms of nitrogen and sulfur, and the ecological responses that are associated with public welfare effects call for consideration of a more complex and ecologically relevant design of the standard that reflects these linkages. In this chapter, we present a set of potential options for defining the elements of the NO_X and SO_X secondary standard including indicator, form, averaging time, and certain aspects of the level, with additional discussion of the options for specifying a range of levels is discussed in Chapter 9.

After review of the ISA and REA, CASAC concluded that aquatic acidification should be the focus for developing a multi-pollutant standard, based on the quantity and quality of available data. CASAC also recommended that, in addition to aquatic acidification, the EPA

should consider multiple ecological indicators and made the following statement in their letter to the EPA on August 28, 2009:

> "...the Panel finds the information in the current REA sufficient to inform setting separate standards for terrestrial acidification, eutrophication of western alpine lakes and terrestrial nutrient enrichment. However, the Panel believes that setting a standard for coastal nutrient enrichment would be difficult because of the substantial inputs of non-atmospheric sources of N to these systems."

As a result of our assessment of the science, and reflecting the comments of CASAC, this policy assessment is focused on developing a standard specifically designed to protect against the effects of aquatic acidification in sensitive ecosystems, while recognizing that such a standard may also provide co-protection against effects of terrestrial acidification, eutrophication of high elevation western lakes and terrestrial nutrient enrichment. Co-protection against these effects is discussed in Chapter 6.

Our development of options for the standards recognizes the need for nationally applicable standard for protection against adverse effects to public welfare, while recognizing the complex and heterogeneous interactions between atmospheric concentrations of NOy and SOx, deposition from of NOy and SOx, and ecological response. Our approach also recognizes that while a standard is national in scope and coverage, the effects to public welfare from aquatic acidification may not occur to the same extent in all locations in the U.S. – in fact, protection may vary among locations according to sensitivity. As noted in Chapters 2, 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, our design for the standards is intended to protect sensitive ecosystems and the services provided by those sensitive ecosystems.

In this chapter we present our reasoning for suggesting a standard that employs (1) NOy and SOx as the atmospheric indicators, (2) a multi-year averaging time, (3) a form of a secondary standard that takes into account variable factors, such as atmospheric and ecosystem conditions that modify the amounts of deposited NO_X and SO_X, and the associated effects of deposited N and S on ecosystems, and (4) a target ANC level and target percentages of water bodies to protect to the target ANC level. Our goal in developing the form of the standard is to create an

index, directly expressed in terms of atmospheric concentrations of NOy and SOx, which can be applied across the nation to convey the allowable levels of ambient NOy and SOx, based on various factors such as the sensitivity of an area and the desired degree of protection from acidification caused by atmospheric deposition. This chapter is structured around questions related to the various elements of a standard. The chapter begins in section 5.1 with a discussion of atmospheric indicators. In Section 5.2 the averaging times for the atmospheric indicators is presented. In Section 5.3 a suggested ecologically relevant form of the standard is presented. In Section 5.4 the issues regarding the spatial area over which a standard might be evaluated are discussed, along with related issues regarding spatial averaging within areas. Section 5.5 provides a discussion of specific target ANC levels. Section 5.6 discusses the selection of target percentages of water bodies to protect to this ANC level. As noted previously, additional discussion related to options for ranges of the level of the standard are discussed in Chapter 9.

5.1 What atmospheric indicators of oxidized nitrogen and sulfur are appropriate for use in a secondary NAAQS that provides protection for public welfare from exposure related to deposition of NOx and SOx?

Staff concludes that indicators other than NO_2 and SO_2 should be considered as the appropriate pollutant indicators for protection against the acidification effects associated with deposition of NO_X and SO_X. **This conclusion is based on the recognition that all forms of oxidized nitrogen and sulfur in the atmosphere contribute to deposition and resulting acidification, and as such NO_2 and SO_2 are incomplete indicators. Furthermore, staff concludes that NOy** (total oxidized nitrogen) should be considered as an **appropriate indicator for oxides of nitrogen. NOy is** defined as NOx (NO and NO_2) and all oxidized NOx products: **including NO, NO_2, and all other oxidized N-containing compounds transformed from NO and NO_2** (Finlayson-Pitts and Pitts, 2000). **As described in Chapter 4, this set of compounds includes** $NO_2 + NO + HNO_3 + PAN + 2N_2O_5 + HONO + NO_3$ + organic nitrates + particulate NO_3. **SOx includes sulfur monoxide (SO), sulfur dioxide, sulfur trioxide (SO_3), and disulfur monoxide (S_2O), and particulate-phase S compounds that result from gas-phase sulfur oxides interacting with particles. Staff concludes that** $SO_2 + SO_4$ **should be considered as an appropriate indicator for oxides of sulfur.**

In principle, measured NOy based on catalytic conversion of all oxidized species to NO, followed by chemiluminescence NO detection is consistent with this definition. We recognize the caveats associated with instrument conversion efficiency and possible inlet losses which are discussed in Chapter 8. The development of the function that converts atmospheric concentrations of NOy and SOx to N and S deposition incorporates NOy estimates based on the Community Multi-scale Air Quality (CMAQ) model (EPA, 1999). CMAQ treats the dominant NOy species (NO, NO_2, nitric acid, PAN and particulate NO_3) as explicit species while the minor contributing non-PAN organic nitrogen compounds are aggregated. From a measurement and modeling perspective we only consider the sum of SO_2 and particulate SO_4 as the indicator for sulfur. The sum of SO_2 and SO_4 constitute virtually all of the ambient air sulfur budget and are measured routinely in monitoring networks. In addition to accounting for virtually the entire oxidized sulfur budget, SO_2 and particulate SO_4 are routinely measured in ambient air monitoring networks, although only CASTNET filter packs capture the entire particle size range. The CMAQ treatment of SOx is the simple addition of both species which are treated explicitly in the model formulation. All particle size fractions are included in the CMAQ SOx estimates. Consistent with units and the charge balance relationships applied in ecosystem acidification models, only mass as sulfur or nitrogen is considered when aggregating the species constituting NOy or SOx.

5.2 What is the appropriate averaging time for the air quality indicators NOy and SOx to provide protection of public welfare from adverse effects from aquatic acidification?

Based on the review of the scientific evidence, welfare effects associated with acidification result from event based to annual cumulative deposition of N and S. Annual cumulative deposition of N and S reflects the chronic acid base balance of the surface water as indicated by the ANC level (measured as annual ANC). Also, critical loads for acidity are in terms of annual cumulative deposition of N and S. Aquatic acidification can occur over both long- and short-term timescales. 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 significant biological effects. Short-term change in chemistry is termed "episodic acidification."

Some streams may have chronic or base flow chemistry that is suitable for aquatic biota, but may be subject to occasional acidic episodes with lethal consequences.

Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the eastern United States. Episodic acidification can result from several mechanisms related to changes in hydrologic flow paths. For example, snow can store N deposited throughout the winter, snowmelt releases this stored N in a pulse that leads to episodic acidification in the absence of increased deposition during the actual episodic acidification event. However, inputs of nitrogen and sulfur from snowpack and atmospheric deposition largely cycle through soil. As a result short-term direct deposition inputs are not important in episodic acidification. As noted in Chapter 3 of the ISA, protection against episodic acidity events can be achieved by establishing a higher chronic ANC level (See 5.3.2.1). Protection against a low chronic ANC level is provided by reducing overall annual average deposition levels for nitrogen and sulfur. This supports the conclusion that long term NOy and SOx concentrations are appropriate to provide protection against low chronic ANC levels, which protects against both long term acidification and acute acidic episodes.

Staff suggests a 3 to 5 year averaging time of the cumulative annual average for the air quality indicators NOy and SOx, to account for interannual variations.

5.3 What form(s) of the standard are most appropriate to provide protection of sensitive ecosystems from the effects of acidifying deposition related to ambient NOx and SOx concentrations?

Based on the evidence of the aquatic acidification effects caused by NOy and SOx, staff concludes that it is appropriate to consider changes to the form of the existing NO_X and SO_X secondary standards to provide protection to ecosystems. EPA staff has developed a conceptual design for the form of the standard that includes four main components: atmospheric and ecological indicators, deposition metrics, functions that relate indicators to deposition metrics and factors that modify the functions. These components of the design are illustrated in Fig 5.1. The rectangles represent indicators. Ecological indicators are chemical or biological components of the ecosystem that can be linked to N and S deposition based on scientific evidence. Air quality indicators are the chemical species of the criteria air pollutants that best represent the atmospheric pollutants that cause ecological harm in the criteria pollutant categories of oxides of

nitrogen and oxides of sulfur (selection of air quality indicators was discussed in Section 5.1). Diamonds indicate functions in which two variables are related. The ecological effect function is the relationship between the ecological indicator and deposition. The atmospheric deposition transference ratio is the relationship between deposition and the atmospheric concentration of an air quality indicator. The ovals represent factors which will modify the functions. Modifying factors can vary across the landscape, such as soil depth, catchment size, etc. The spatial heterogeneity of modifying factors can be challenging to characterize, and therefore in some cases we present multiple options for how to incorporate them into the design.

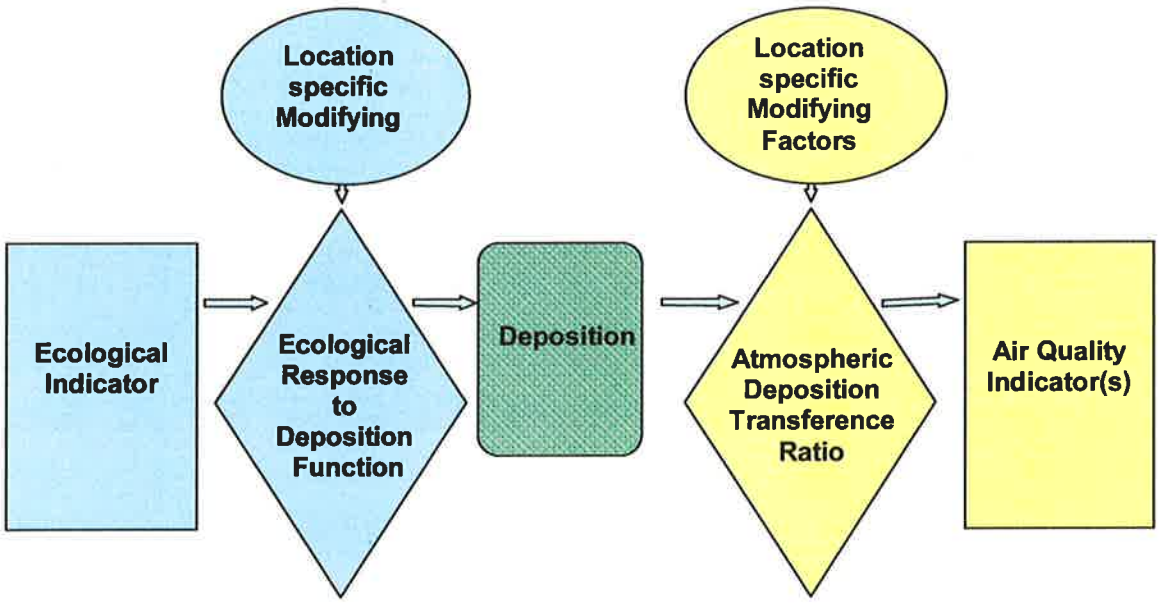


Figure 5-1 Conceptual design of the form of NO_X and SO_X secondary standard

5.3.1 Conceptual Design of the Form: General Overview

A summary of the design of the form based on aquatic acidification is given here to help provide context and support for the more detailed discussions that follow. The conceptual design for a form that is specifically based on aquatic acidification effects is illustrated by Fig 5.2. Starting on the left side of the figure, ANC is a chemical indicator of sensitivity to aquatic acidification that is tied to the probability of biological harm that may occur to the system from aquatic acidification. ANC is often considered the best chemical indicator of sensitivity to aquatic acidification (Section 5.3.2.1). Ambient NOy and SOx add to the total deposition of N and S that lead to aquatic acidification. NHx is a component comprising a varying fraction of the

total N deposition. The load of N and S deposition that causes a specific level of ANC will vary depending on the characteristics of the receiving ecosystem, but can be quantified at the catchment scale with acid-base balance acidification models. The acidification models that characterize the relationship between ANC and N and S deposition that are most appropriate to inform the NAAQS are discussed in Sections 5.3.2.

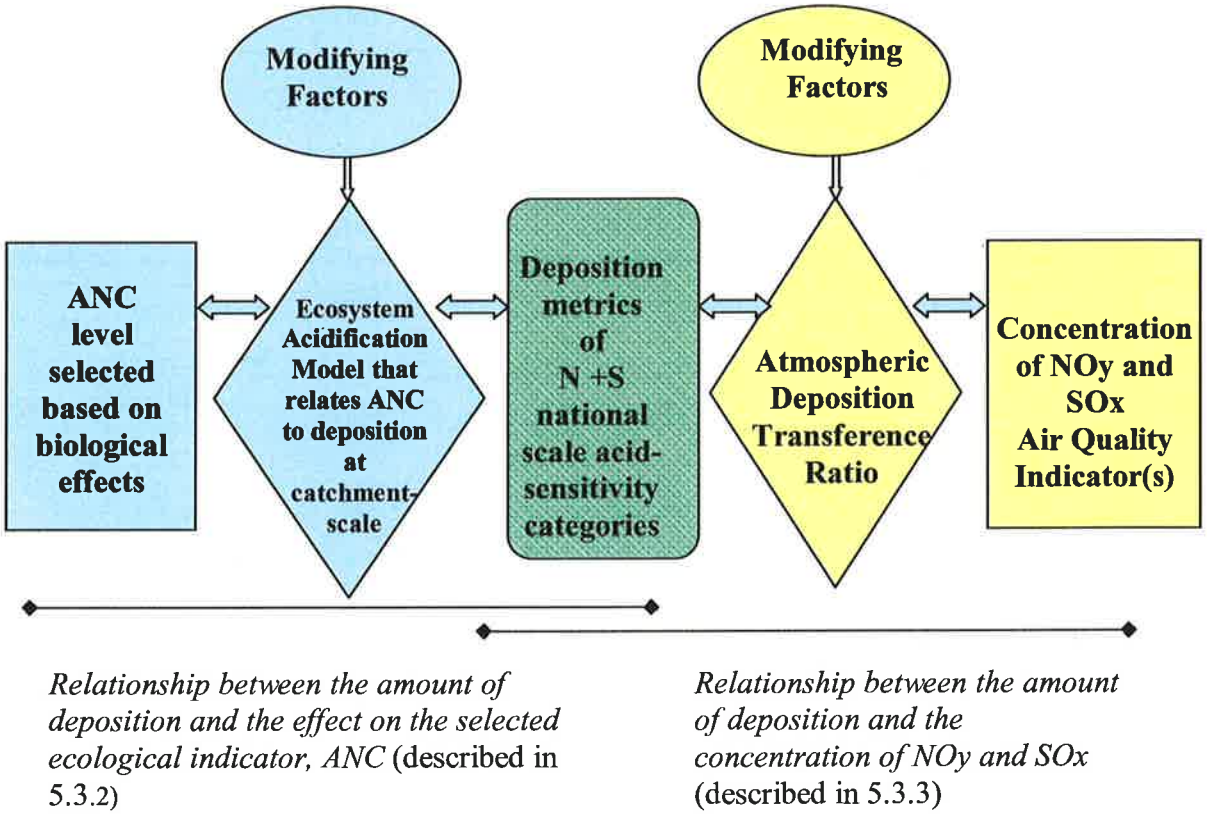


Figure 5-2. Conceptual design of the form of the standard based on aquatic acidification.

Catchment scale modeling is necessary to understand the sensitivity of individual waterbodies to acid deposition. Secondary NAAQS, however, are intended to be requisite to protect public welfare from known or anticipated adverse effects. One aspect of adversity to public welfare is a consideration of the requisite amount of protection for sensitive populations or groups of catchments. In so doing, the Administrator seeks to establish standards that are neither more nor less stringent than necessary for this purpose. In order to establish such a standard for the entire country, it is necessary to look across variability both in effect and

exposure. In addition, there are uncertainties in our estimates of risk and exposure for individual waterbodies. Therefore, we propose to examine various alternative spatial groupings of sensitive populations of waterbodies to inform the development of requisite protection. EPA staff proposes to categorize the landscape nationally, such that within a category there are generally similar acid-sensitivity characteristics. Each national acid-sensitivity category is represented by a population of catchments for which critical loads at a specified ANC limit are calculated.

In our proposed approach, for each acid-sensitive category of the landscape the distribution of critical loads from a population of catchments would be evaluated to develop a deposition metric. The deposition metric would be defined as the amount of deposition that reasonably assures a specified percentage of individual catchments in a population would achieve a target ANC level.

The level of the ANC target is tied to the described degree of protection for aquatic biota. It will be selected as one element of the set of information that informs the Administrator's selection of the allowable level(s) of ambient NOy and SOx under the secondary standard. Options for target ANC levels are discussed in Section 5.5. Taken together, the secondary standard would be set with a goal of specifying allowable ambient levels of NOy and SOx such that there is a desired degree of confidence that a targeted percentage of aquatic ecosystems would achieve a specified ANC level within each acid-sensitivity category (see Chapter 9).

Finally, the deposition of reduced N should be taken into account because reduced forms of N are often quickly converted to NO_3^- by the processes of nitrification. For this reason, the amount of reduced N needs to be accounted for in the standard because some fraction of the acid buffering capacity of an ecosystem is used up by reduced nitrogen, leaving less protection against deposition from NOy and SOx. Spatial characterization of reduced N is discussed in Section 5.3.2. The deposition tradeoff curves are then multiplied by the deposition to concentration transference ratio to calculate the atmospheric concentration tradeoff curves. Development of these functions is discussed in Section 5.3.3. Thus far we have summarized our conceptual design by walking through the components of the standard shown in Fig 5.2 from the left to the right, and a more detailed illustration of these steps is given by Fig 5.3.

The bidirectional arrows shown in Fig 5.2 emphasize that the order in which one considers the links between ANC and deposition resulting from of NOy and SOx is conceptually important. Moreover, different questions may be answered by working through Fig 5.2 right to

left versus the left to right. For example, if the amount of N and S deposited to a given catchment is known, the level of ANC that would result may be calculated. The calculated ANC could then be compared to a benchmark value of ANC. Working through Fig 5.2 from the right to the left is the basis for the Atmospheric Acidification Protection Index (AAPI, Fig 5.3 and Section 5.3.4). The AAPI is essentially a function that determines the allowable levels of ambient NOy and SOx based on the target ANC limit, given uncertainties in the parameters used to calculate an ANC equivalent at the national scale, and weighing other factors such as time to recovery for ecosystems, based on populations of catchments that represent acid-sensitive areas in the U.S. The AAPI is designed to be a more ecologically relevant form of the standard relative to the current form . The intent of the AAPI is to weight atmospheric concentrations of NOx and SOx by their propensity to contribute to acidification through deposition, given the fundamental acidifying potential of each pollutant, and the ecological factors that govern acid sensitivity in different ecosystems, as well as the contribution of reduced nitrogen. Thus the AAPI is more relevant to protecting ecosystems from acidifying deposition compared to simple ambient concentration forms which do not reflect factors that affect acidifying potential.

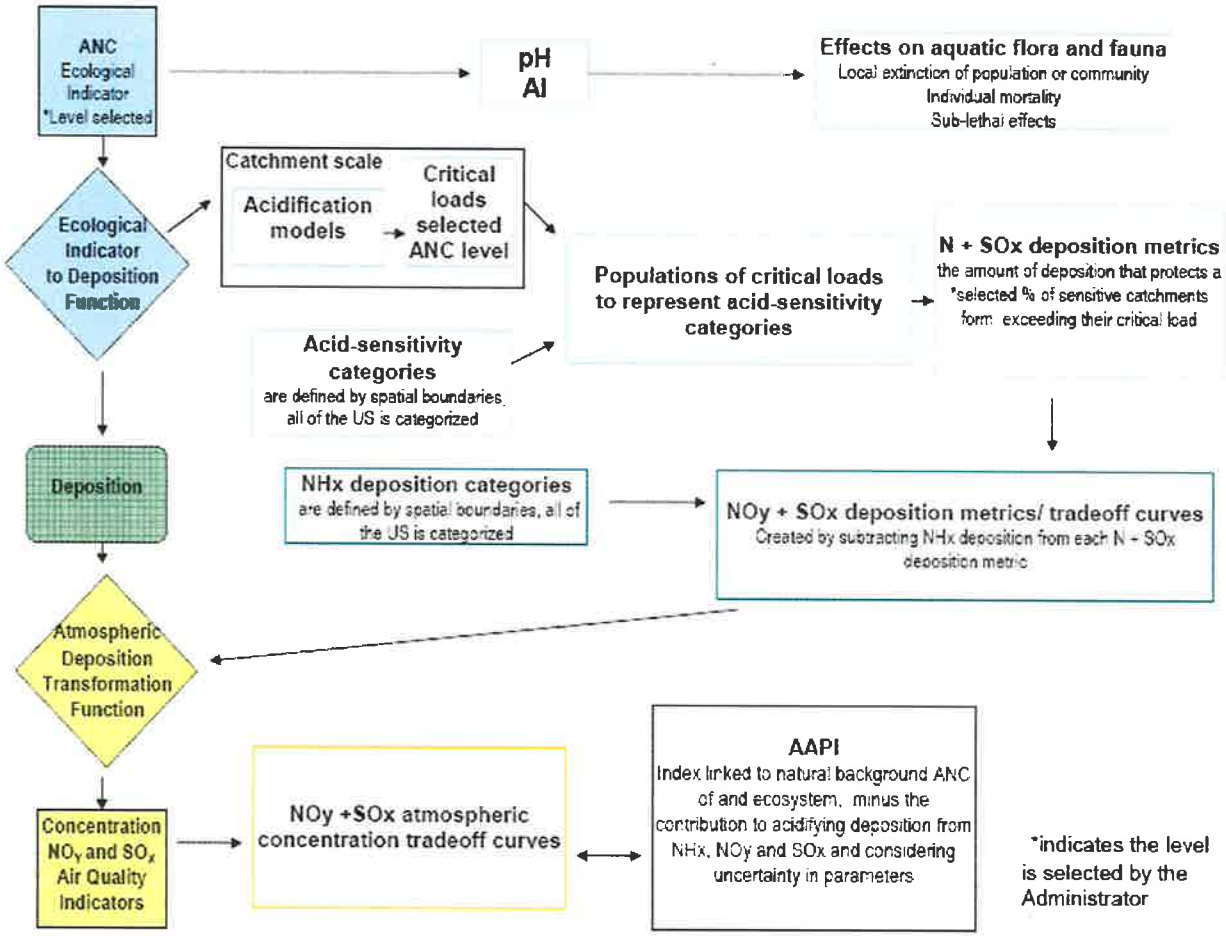


Figure 5-3 Detailed conceptual design of the form of the standard based on aquatic acidification.

Staff notes two important concepts illustrated by the O_3 and PM_{10} 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 O_3-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 PM_{10} is the indicator for the coarse PM NAAQS standard ($PM_{10} = PM_{2.5} + PM_{10-2.5}$). Although the standard has a single level (150 $\mu g/m^3$), 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 PM_{10}NAAQS provides the appropriate level of protection from exposure to coarse PM across locations using a related index of PM (PM_{10}) as the indicator, while allowing the, level of coarse PM to vary across locations. The proposed form for the NOx and SOx standard builds on the concept of using a related index (the AAPI) to provide a homogeneous level of protection across the nation, while allowing ambient air concentrations of NOx and SOx to vary based on ecosystem sensitivity and other relevant factors.

5.3.2 Conceptual design of the form: Linking the ecosystem indicator to deposition

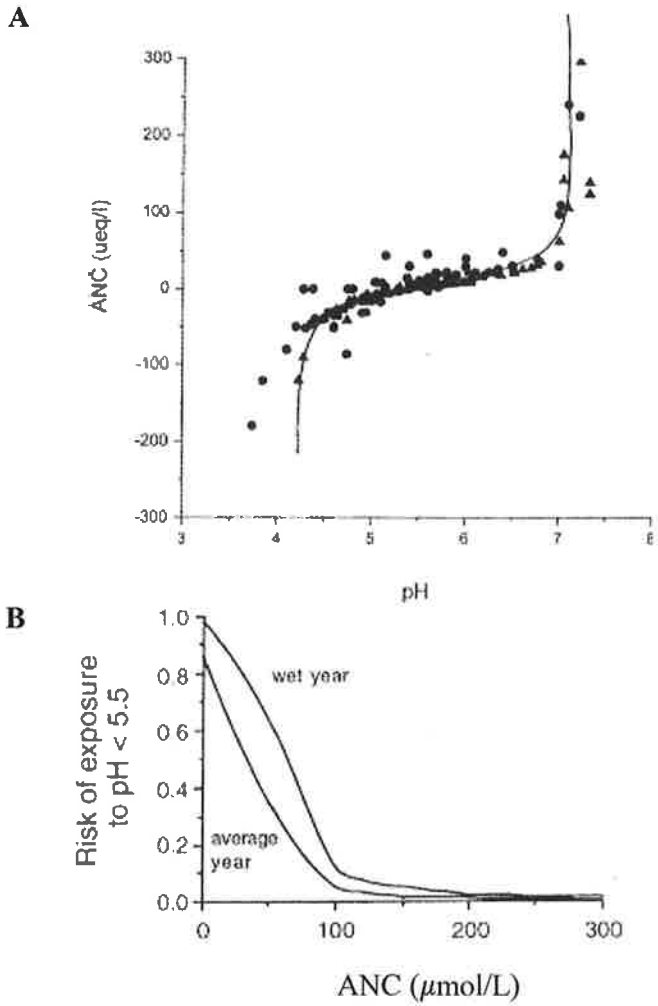
The relationship between the ecosystem indicator, acidification models, and deposition metric components of the form are discussed in this section. The relationship between deposition metric and atmospheric concentrations is discussed in Section 5.3.3. and the derivation of the AAPI equation is presented in Section 5.3.4.

5.3.2.1 Ecological Indicator: *Does the available information provide support to use ANC as the ecological indicator in the conceptual design of the NOy and SOx standard based on aquatic acidification?*

Ecological indicators of acidification in aquatic ecosystems can be chemical or biological components of the ecosystem that are altered by the acidifying effects of N and S deposition. A desirable ecological indicator for aquatic acidification is one that is

measurable or estimable, linked causally to deposition of N and S, 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 NOy and SOx causes aquatic acidification through the input of strong acid anions (e.g. NO_3^- and SO_4^{2-}) or chemical forms that are transformed by the ecosystem into strong acid ions. The anions are deposited either directly to the aquatic ecosystem, or indirectly via drainage from terrestrial ecosystems. In other words, when these anions are mobilized in the terrestrial soil, they can leach into adjacent waterbodies. 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 are 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), surface water pH and concentrations of SO_4^{2-}, NO_3^-, Al, and Ca^{2+}; the sum of base cations; and the base cation surplus. ANC is the most widely used chemical indicator of acid sensitivity and has been found in various studies to be the best single indicator of the likelihood of biological response and health of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006). The utility of the ANC criterion lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al. For example, there is an extensive literature documenting threshold pH levels for various aquatic species mortality and health. ANC and pH are directly related under equilibrium conditions (Fig 5.4A). In the field there is a relationship between decreasing ANC and increasing risk to exposure of a threshold pH level (Fig 5.4B). ANC is also used because it integrates overall acid status (**ISA 3.2.3 and REA 5.2.1**) and the acid-related stress for biota that occupies the water that can be directly related to biological impairment, including the number of fish species (**ISA 3.2.3**).



ANC

Figure 5-4. **A.** 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). **B.** The relationship between precipitation (wet and average year), ANC and the risk to exposure of a pH below 5.5 (Gerritsen et al. 1996).

EPA staff thus concludes that the available information provides support for the use of ecological indicators to characterize the responses of aquatic ecosystems to acidification effects associated with N and S deposition, and that ANC is the most supportable indicator.

***5.3.2.2* Relating the ecological indicator to atmospheric deposition:** *Does a quantified relationship exist between the ecological indicator and atmospheric deposition of nitrogen and sulfur?*

There is evidence to support a quantified relationship between deposition of N and S, and ANC. This relationship was analyzed in the REA to determine current risk for two case study areas, the Adirondack and Shenandoah Mountains, with three techniques (1) a time series analysis to evaluate long-term trends using MAGIC modeling to reconstruct past trends, (2) a time series analysis using monitoring data to evaluate recent observed trends and (3) a critical load approach using water chemistry data from the Temporally Integrated Monitoring of Ecosystems (TIME) program and Long-term Monitoring (LTM) to calculate critical loads with the SSWC and FAB aquatic acidification models. A technical summary of the methods used in the REA are provided in Appendix A.

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 N and S deposition (**REA appendix 4 section 5**)

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 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 4.2.4.3 and REA appendix 4 section 3.4**).

Critical loads

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 (REA Chapter 4 and REA Appendix 4)**. These models quantify the relationship between deposition of N and S and the ability of an ecosystem to counterbalance or buffer the deposition. The ecosystem acidification models simulate a variety of water and soil acidification responses at the laboratory, plot, hillslope, and catchment scales. For example, the level of deposition that causes a specified level of an ecosystem endpoint could be calculated (e.g. a critical load for ANC=50μeq/L). A summary of acidification models is given in ISA appendix A and further discussed in section 5.3.2.3. In the REA analysis, critical loads and their exceedances were calculated for four values of ANC (i.e., ANC of 0, 20, 50, and 100 μeq/L) for 169 lakes in the Adirondack Mountains and 60 streams in the Shenandoah Mountains.

In summary, EPA staff concludes from the REA analysis, in combination with information presented in the ISA, that a quantitative relationship exists between the level of surface water ANC and an amount of nitrogen and sulfur deposition. These relationships are shown by long-term trends going back to preindustrial conditions in the 1860s, recent trends since the 1990s and critical loads modeling.

5.3.2.3 Relating the ecological indicator to deposition: *How do steady state models compare to dynamic models?*

Models are important tools to evaluate how multiple environmental factors alter the relationship between ANC atmospheric deposition. There are two general types of acidification models: steady-state and dynamic. These models make different assumptions, indicate different time horizons for their critical loads and they have different data requirements.

Basic approach of steady-state vs. dynamic acidification models

The basic principle of the steady-state approach of aquatic acidification models is to determine the maximum acid input that will result in adequate biogeochemical

conditions to sustain ecosystem health. Adequate biogeochemical conditions is a subjective term that relates to a particular benchmark (e.g. ANC = 20, 50, 100), representing different degrees of protection of aquatic ecosystems against acidic deposition. 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 soil minerals is often a major source of base cation supply to an ecosystem. It is considered one of the governing factors of ecosystem critical loads.

A dynamic model includes 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.

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 a 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 model 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-yer 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 be on what results during equilibrium conditions.

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. 1985). Data required to conduct dynamic modeling are not available for as many places as the data required to conduct steady-state modeling.

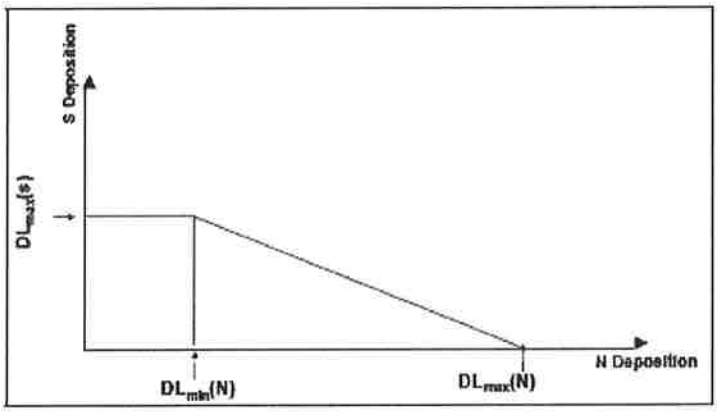
Comparison of two steady-state models: FAB and SSWC

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 exceedence 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 Fig 5.5: 1. the maximum of amount of N deposition when S deposition equals zero (DLmax (N)); 2. the amount of N deposition that will be captured by the ecosystem before it leaches (DLmin(N)); and 3. the maximum amount of S deposition considering the N captured by the ecosystem (DLmax (S)). The function represents many unique pairs of N and S deposition that will equal the critical load for acidifying deposition. The slope portion of the function will vary according to attributes of the water body that is modeled, including lake size and in-lake retention.**



Figurer 5-5 Illustration of a generalized N + S deposition tradeoff curve that is calculated by using the FAB approach

The EPA staff concludes that the available information supports using the steady-state acidification models to characterize the relationship between the ANC ecological indicator and total nitrogen and sulfur deposition. The steady state models take a simple

mass balance approach to characterizing ecosystem acidification and data is available for over 8,000 locations to conduct steady-state modeling.

5.3.2.4 Relating the ecological indicator to deposition: *What is the appropriate ecosystem acidification model to represent the relationship between nitrogen and sulfur deposition, and the ecological indicator?*

A combination of the SSWC and FAB models is proposed by EPA staff for catchment scale modeling for use in developing critical loads to specify the form of the standards. A modified SSWC model is used because there is high confidence in the availability and quality of the input data that is required by this model. The SSWC model for aquatic acidification is expressed as equation 1.

$$CL_{ANC\lim}(N+S) = ([BC]_O^* - [ANC_{\lim}])Q \qquad (1)$$

Where,

$CL_{ANClim}(N+S)$ = depositional load of S and N that does not cause the ecosystems to exceed a given ANC_{lim} (meq/m$^{2/}$yr)

$[BC]_0^*$ = the preindustrial concentration of base cations (μeq/L)

ANC_{limit} = a ANC limit (μeq/L)

Q= surface water runoff (m/yr) (this is typically equal to precipitation – evapotranspiration

This model is further constrained by a quantity of N which would be taken up, immobilized or denitrified by ecosystems and used to adjust the quantity of deposition required to meet a specified critical load. This term is represented as CLmin(N) in the FAB model and illustrated in Fig. 5.5. For application in the form of the standard and in the following discussion, the parameter is designated with the abbreviation N_{eco}. The acid-base model constrained by N_{eco} is expressed by equation 2.

$$CL_{ANC\lim}(N+S) = ([BC]_O^* - [ANC_{\lim}])Q + N_{eco} \qquad (2)$$

Where,

N_{eco}= nitrogen retention and denitrification by terrestrial catchment and nitrogen retention in the lake

Two options to derive the term N_{eco} were considered, each yielding different results. The first approach is to calculate the long-term amount of N an ecosystem can immobilize and denitrify before leaching (i.e. N saturation) that is derived from the FAB model [denoted as DLmin(N) in the FAB model]. This approach requires the input of multiple ecosystem parameters and is expressed by eq 3.

$$N_{eco} = fNupt + N_{ret} + (1-r)(N_{imm} + N_{den}) \quad (3)$$

Where,

N_{upt}= nitrogen uptake by the catchment (meq/m^2/yr)

N_{imm}= nitrogen immobilization by the catchment (meq/m^2/yr)

N_{den}=denitrification of nitrogen in the catchment (meq/m^2/yr)

N_{ret} = in-lake retention of nitrogen (meq/m^2/yr)

f =forest cover in the catchment (dimensionless parameter)

r = fraction lake/catchment ratio (dimensionless parameter)

The second approach for estimating N_{eco} is to take the difference between N deposition and measured N leaching in a catchment as expressed by eq 4.

$$N_{eco} = Dep_N^{Total} - N_{leach} \quad (4)$$

CASAC has advised EPA to use the second approach to derive the Neco term:,

> "In principal, Equation 3, captures many of the major landscape and ecological factors that influence the processing of atmospherically deposited N <u>within</u> an ecosystem, including biological and abiotic retention of N (immobilization, uptake and sedimentation), and gaseous loss (denitrification) after N has been deposited and/or transported. This approach opens the "black box" and attempts to estimate some of the component parts of N processing and loss. It is best modeled as a dynamic process because such factors as age

> and stage of vegetation, soil moisture, moisture regime, and nutrient demand will affect various components of N cycling. For many ecosystems, complete supporting data may not be available.
>
> Equation 4 is basically a mass balance approach that keeps track of inputs and outputs. It does not include the detailed biogeochemical processes identified in Equation 3. Data for this latter approach may be much more readily available than the approach using Equation 3. Watershed N retention can be estimated using this approach (e.g., Lovett et al. 2000, and many others), but the processes involved in the retention are not detailed. This approach is most effectively used when hydrologic boundaries (e.g., watershed) are defined. Hence, the Panel recommends that the mass-balanced (i.e., Equation 4) approach should be used." (CASAC, April 29, 2010)

(A comparison of calculating Neco using both methods is provided in Appendix A)

Two methods to calculate pre-industrial base cation weathering: F factor and MAGIC

The preindustrial concentration of base cations ($[BC]_0^*$) is calculated to represent conditions prior to industrialization (~about 1860). It incorporates the main source of base cations to an ecosystem including preindustrial weathering from soil and pre-industrial base cation deposition. It is therefore considered one of the governing factors of critical loads. $[BC]_0^*$ is commonly calculated using one of two approaches: dynamic modeling (i.e. MAGIC) and calculation by the F-factor approach (Henriksen and Posch 2001). Staff propose that the base cation weathering rates may be calculated by either method.

In this section, critical load estimates obtained from two steady-state approaches were compared. The exercise is not intended to provide an assessment of the accuracy of the two models, but rather to provide a means for evaluating the relative performance of the two different models. The EPA conducted analysis compared steady-state CL values based on Henriksen and Posch (2001) F-factor approach and output from the MAGIC model. The primary purpose of the F-factor is to obtain estimates of preindustrial surface water base cation concentrations ($[BC]_0^*$) for equation 1. The MAGIC (Cosby et al., 1985) model can also be used to derive preindustrial surface water base cation concentrations. MAGIC is a process-based model designed to mimic the geochemical effects of mineral weathering, soil cation exchange, and other watershed processes. Once the model has been calibrated for a watershed, it can be run to simulate how surface

water chemistry changes with time and to predict preindustrial cation concentrations ($[BC]_0^*$) to be used in the steady-state SSWC CL model in equation 1.

The comparison of CLs between the F-factor and MAGIC approached was done for two regions, streams in Southern Appalachia and lakes in the Adirondack Mountains. For 67 streams and 99 lakes, $[BC]_0^*$ were determined for both approaches and CLs were calculated using the same value of Q. The results are show in Fig 5.6. For this analysis, the steady-state MAGIC model yielded critical load values that show the same trend for both regions, but were on average 16 meq S /m^2-yr for the Adirondack Lakes and 5 meq S/m^2-yr for Southern Appalachia streams higher than those from the SSWC F-factor approach. The two models converge at low critical, but diverge as the buffering potential for watersheds increase. This is **particularly the case for CL values above 80 meq/m^2-yr for lakes in the Adirondack Mountains. These results are consistent with similar comparison of critical load done by Holdren et al. 1992. Holdren et al 1992 found on average that the MAGIC model yielded CL values that were on average 29** meq S /m^2-yr higher than those from the SSWC model. Holdren et al 1992 also found that as the buffering potential for watersheds increased, as indicated by increasing CLs, the results from the two models gradually diverge.

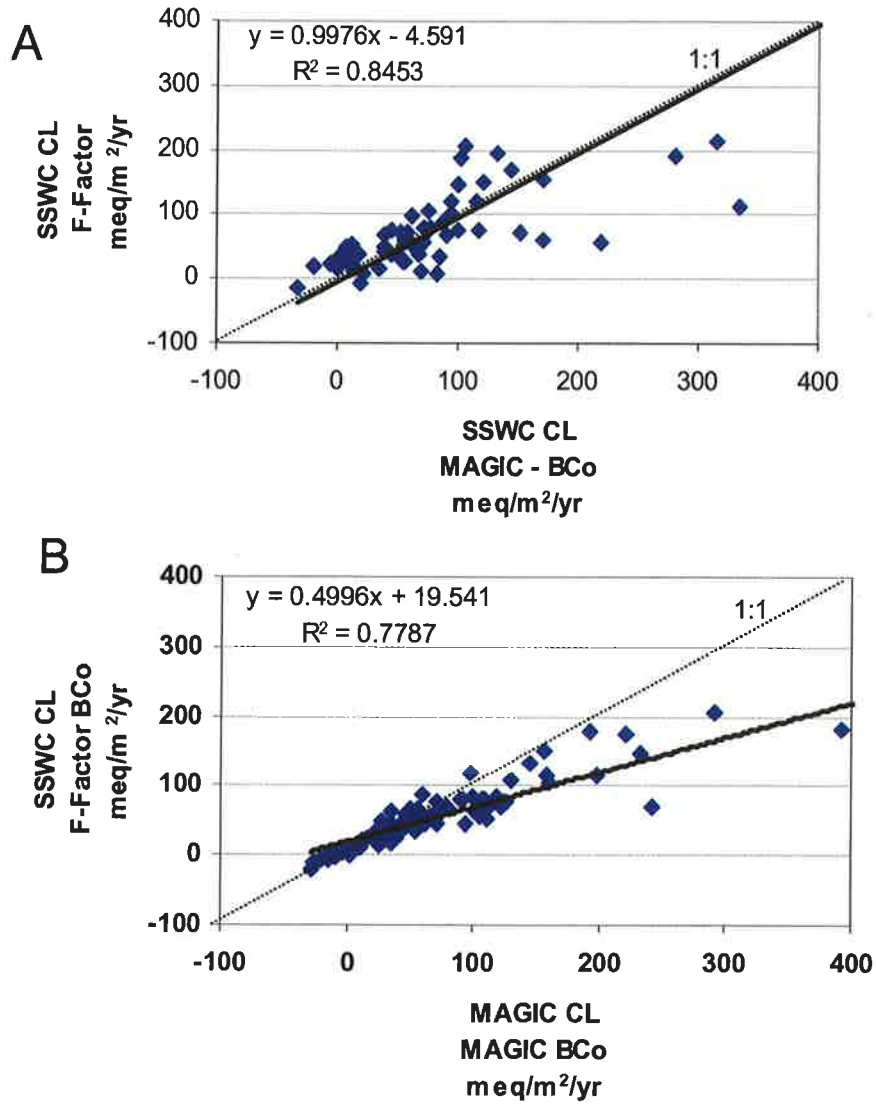


Figure 5-6 **Relationship between CLs using pre-industrial base cation weathering ($[BC]_0^*$ =BC_o) calculated by MAGIC versus the F-factor methods: A)** 67 streams in the Southern Appalachian and **B)** 99 lakes in the Adirondacks Mountains.

5.3.2.5 Relating the ecological indicator to deposition: *How can we aggregate critical loads, derived from catchment-scale acidification models for a target ANC, across broader areas to develop a deposition metric that adequately for a nationally representative acid-sensitivity category?*

Acidification models are considered the best way to describe the relationship between ANC and deposition. It is important to emphasize that the acidification models are only

applied at the spatial scale of the catchment. Response to N and S deposition will vary among catchments. However, modeling every catchment in a region (i.e. a spatial area that includes a large population of individual catchments) is implausible at this time due to the data limitations. A method to extrapolate watershed-scale analysis to a region was developed in the REA. In that method, the critical loads (combined N+S load for a selected ANC level) developed for the case study sites were applied over a region using water chemistry data. Critical load exceedance (i.e., the amount of actual deposition above the critical load, if any) was calculated for each waterbody in the region to quantify the number of lakes or streams that receive levels of deposition exceeding the CL. Lakes and streams with positive exceedance values, where actual deposition was above its critical load, were not protected at that critical limit (e.g. ANC= 20, 50, 100 μeq/L; **REA Appendix 4**).

The relationship between ANC and N and S deposition is also applicable nationally. Areas that have similar geologic underpinnings, mineral weathering rates, and hydrology should show similar sensitivity to NOy and SOx deposition. Weathering rate of geologic parent material is the main source of base cations to an ecosystem, and it is therefore considered one of the governing factors of ecosystem critical loads. Landscape features that are linked to ecosystem acid-sensitivity include lithology, elevation, percent forested watershed, and watershed area (Sullivan et al. 2007).

How do we use catchment scale acidification modeling to inform the NAAQS? The goal is to have a national applicable standard, but still take into account catchment base processes. As previously noted, acidification models are parameterized for catchments and their critical loads vary at the spatial scale of the catchment. However, aggregating critical loads from multiple catchments will allow for an appropriately representative deposition value, which provides adequate protection of ecosystems and can be applied over larger spatial areas. For this reason, EPA Staff proposes evaluating a population of waterbodies that are sensitive to acidification to calculate a benchmark depositional load (called the deposition metric) in which a specified percentage of the population does not exceed their critical load for a selected ANC limit. This approach uses the distribution of critical loads from a population to derive a value that is intended to provide protection

over a spatial area that is larger than the individual catchment for which a single critical load may be calculated. The deposition metric is expressed by the following equation:

$$DL_{\%ECO}(N+S) = \left\{\left([BC]_O^* - [ANC_{\lim}]\right)Q\right\}_{\%ECO} \qquad (5)$$

The change from the CL term to the DL term reflects the change from a critical load for deposition to a specific catchment to a deposition load that applies across a population of catchments in a broader area. N_{ECO} would then be added to $DL_{\%ECO}$ to calculate the N and $SO_2 + SO_4^{-2}$ tradeoff curves (section 5.3.2.8)

5.3.2.6 Deposition metric: *What critical load data is available and what populations of catchments are excluded? For any acid sensitive category, how is the distribution of critical loads evaluated in developing the deposition metric?*

Steady state critical loads calculated for ANC that were used in this analysis were either previously published in the literature or calculated using the SSWC method from water quality data collected by national monitoring programs. A map of critical loads is presented in Fig. 5.7.

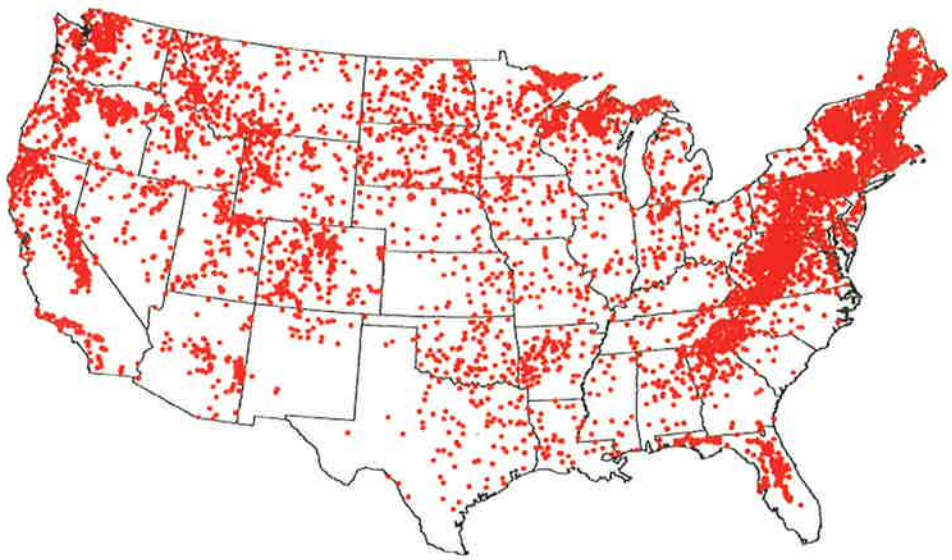


Figure 5-7 Sites of CLs calculated by SSWC that are used in the Policy Assessment analysis

To ensure the population of water bodies included in the analysis were those sensitive to acidity caused by atmospheric deposition, several criteria were applied to the CL dataset to remove watersheds in which organic acids, acid mine drainage or naturally low base cation weathering caused acidification.

- The pre-industrial ANC was calculated for each site in which there was sufficient data. Certain pre-industrial ANC values, defined as ANC< the target ANC(e.g. 50 μeq/L), indicate natural acidity due to naturally low BC weathering and were removed from the data set.
- All CL $\leq$10 meq/m^2/yr were removed. This is a second screen to remove catchments that may be naturally acidic for which pre-industrial ANC values could not be calculated.
- To remove catchments that are dominated by acidity caused by acid mine drainage, if the concentration of $SO_4^{-2}$of the water was >400 ueq/L twice or

more than expected by S deposition the catchment was considered to be dominated by acid-mine drainage and removed from the dataset.

- The cause of aquatic acidity was considered to be dominated by organic acids if the concentration of DOC in the water was > 10mg/L, sites exceeding 10 mg/L were excluded from the dataset.

The latitude and longitude of each site was used to determine its membership to an acid-sensitive category. Multiple methods for defining an acid sensitive category are presented in section 5.3.2.7. The distribution of critical loads from a population that represents an acid-sensitivity category was then evaluated. A deposition value that protects a specified percentage of the ecosystems (called the deposition metric) would be selected. Each acid-sensitivity category would have a deposition metric that protects the same percentage of ecosystems (see Section 5.4-5.6 for a comprehensive discussion of the levels). The deposition metric would be a value representing a specified percentile of the distribution, such as the 95th percentile. The distributions of critical loads for many definitions of acid sensitive areas are skewed to the right, which implies that a central estimate using the mean, would not be projected to achieve the target ANC of the majority of acid-sensitive ecosystems; therefore it may be preferable to calculate the deposition metric to target protecting a higher percentage of catchments. For example, if the 75% or 90% of the aquatic ecosystems are targeted for protection, then the deposition metric that represents the critical load for the 75^{h} or 90th percentile of the population would be selected.

5.3.2.7 ***Landscape categorization:*** *How is the U.S. landscape categorized based on acid-sensitivity?*

Two general approaches are suggested. The first approach is to have one population of water bodies represent the entire nation and select a deposition metric from this one large population. In this approach the U.S is not subdivided into acid-sensitivity categories. The second approach is to subdivide the U.S. into acid-sensitivity categories based on criteria that are known to be associated with acid-sensitivity and for which national-scale data sets are available. A population of catchments could then be

identified to represent each acid-sensitive category. Several categorization possibilities are discussed under the second approach.

Option 1: No subdivision of the U.S.

Option 1 is a simple approach in which the U.S. is not subdivided into acid-sensitivity categories and the total population of critical loads represents the entirety of the U.S. The deposition metric would be selected by evaluating the distribution of CL from the entire population after screening out preindustrial ANC< 50 μeq/L and CL <10 meq/m^2/yr, as described in section 5.3.2.6. Deposition metrics that protect 90%, 75% and 50% of the population are given as examples in Table 5.1. Figure 5.8 shows the cumulative distribution of critical loads of waterbodies at ANC=50 μeq/L. Note that for an ANC=50 μeq/L the greatest CL is 4179 meq/m^2/yr, while 50% of the waterbodies have CLs less than 118 meq/m^2/yr, thus indicating the skewed distribution of the data set.

Table 5.1. Descriptive statistics of the national CL data set.

ANC μeq/L	# CL	Mean Neco	After excluding sites for sulfate>400, DOC >10, pre-industrial ANC < target ANC, then excluding sites with CL<10, the resulting CL in analysis n=	CL mean (meq/m2/yr)	CL Ster	Example deposition metrics		
						DL %90 (meq/m^2/yr)	DL %75 (meq/m^2/yr)	DL %50 (meq/m^2/yr)
50	7497	52	5280	257	5	27	55	118
20	7497	52	5613	259	4	33	62	124

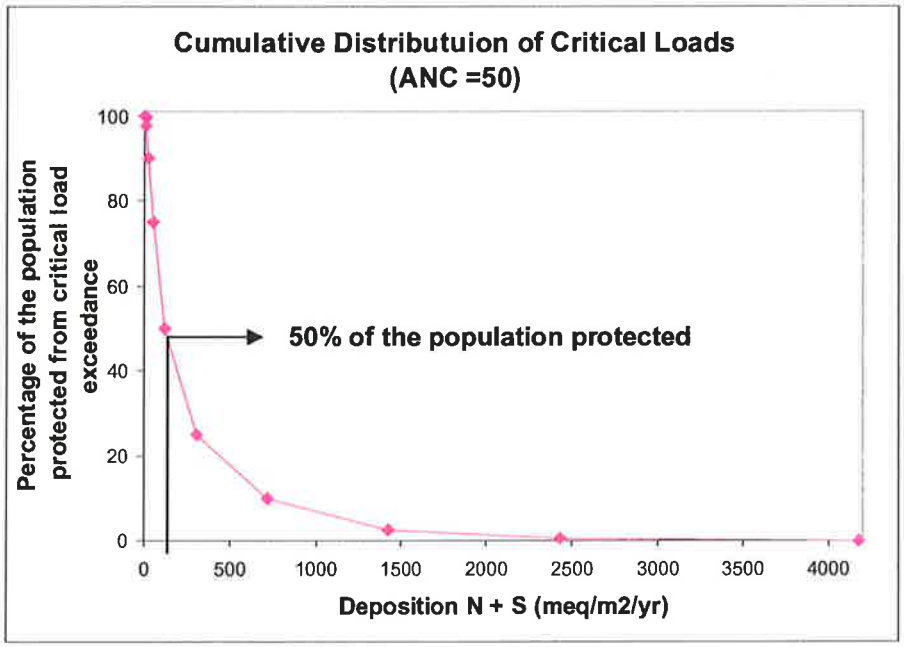


Figure 5-8 Cumulative distribution of the critical loads for ANC =50 μeq/L considered in the analysis (n =5281)

The benefit to this approach is that it provides one deposition metric for the entire country, making it simple and easy to calculate and convey. The main weakness of this approach is the degree of uniformity in protection across the nation, as that it may over-protect areas of the nation that are least sensitive to acidification and under protect in areas that are most sensitive. The extent of possible over or under protected is discussed at the end of this section.

Option 2: Acid-sensitivity categorization of the landscape

In Option 2, four approaches to categorize the U.S based on criteria that influence acid-sensitivity are presented: 1) binary categorization (sensitive vs. less-sensitive), 2) 5 categories of sensitivity (based on cluster analysis), 3) one less-sensitive category and sensitive ecoregions considered individually and 4) all ecoregions considered individually. The extent to which current critical loads represent the categories as defined by each approach is discussed. Each approach presented uses the concept of ecoregions to define spatial boundaries of sensitive ecosystems and ANC to determine acid-

sensitivity. Numerous options were explored, but we have chosen to focus this discussion on those options recommended by the staff as most likely to be useful in setting the standards. Other parameters for which to base acid-sensitivity categorization that were explored include bedrock geology, soil base cation weathering, dissolved organic carbon and alkalinity. Staff suggests moving forward with ANC because it is the best indicator of acid-sensitivity integrating natural buffering capacity, historic load and current load, and there is good national coverage of ANC measurement from almost every ecoregions (level 3). A brief summary of ecoregions and ANC data that were used in the analysis is presented here, prior to the presentation of the options.

Ecoregions

Ecoregions are "areas of similarity regarding patterns in the mosaic of biotic, abiotic, aquatic, and terrestrial ecosystem components, with humans being considered part of the biota" (McMahon and others 2001). EPA staff proposed considering Omernik's ecoregions in this analysis of acid-sensitivity (maps may be downloaded at www.epa.gov/wed/pages/ecoregions.htm). These ecoregions are categorized using a holistic; "weight-of-evidence" approach where the importance of factors may vary. The method used to map ecoregions 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 (Wiken 1986; Omernik 1987, 1995). 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".

To evaluate the effectiveness of ecoregions, they must be tested against measures that relate to their purpose (Omernik 2004). The first publication of the ecoregions based on Omernik's weight-of-evidence approach was published in 1987 (Omernik 1987). Current maps 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 (CEC 1997). At Level II, the continent is subdivided into 52 ecoregions (CEC 1997). Level III, is a further subdivision of Level II,

and divides N. America into 120+ categories. Level IV is a subdivision of Level III, it is the finest scale of Omernik's ecoregions mapping and development of these maps is currently in progress. Ecoregion level 3 are used here to categorize the landscape.

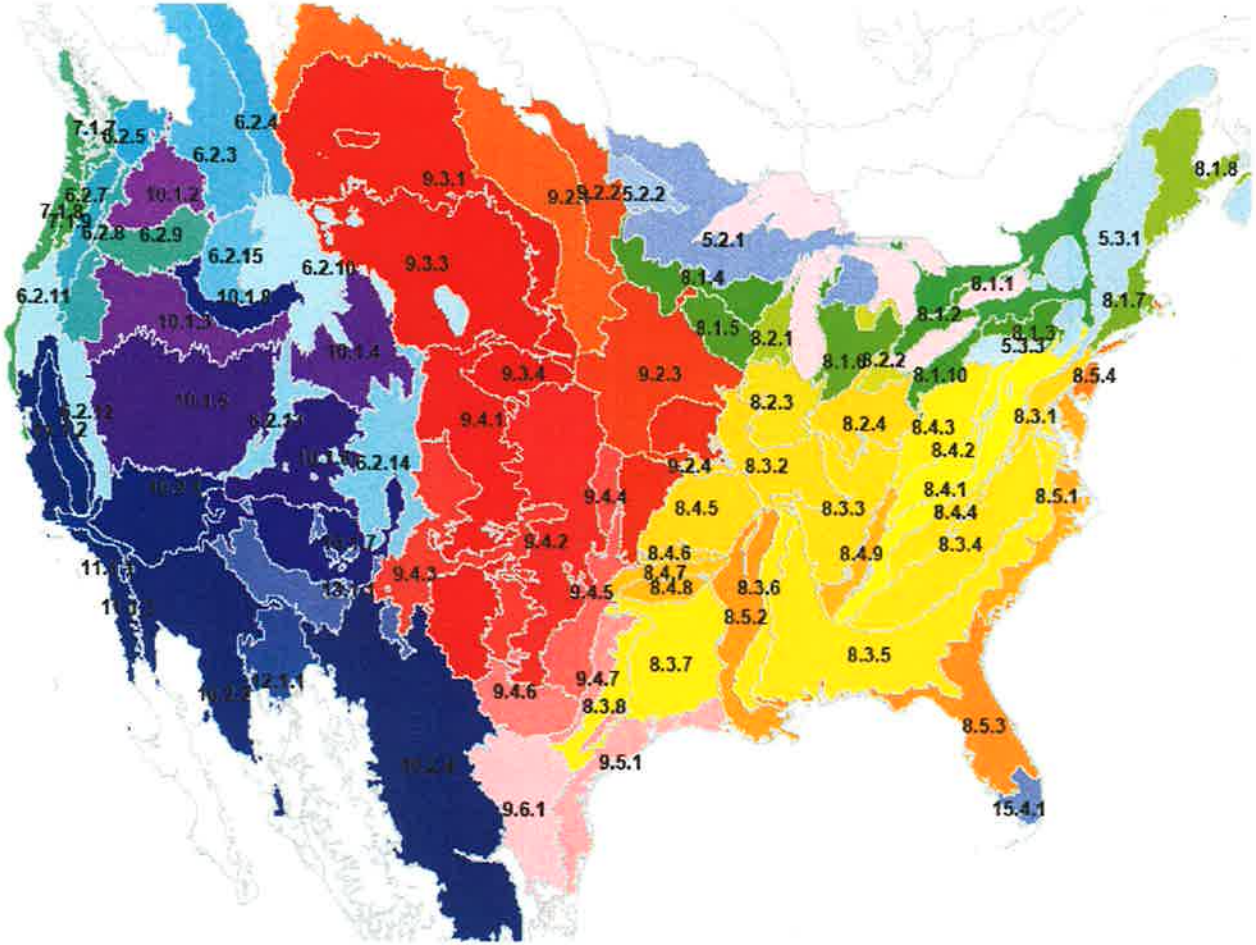


Figure 5-9 Map that illustrates Omernick's ecoregions (level 3).

ANC data

Water chemistry data on ANC was collected from several national monitoring networks. The data sources are summarized on Table 5.2. These data sources included approximately 11,000 observations. For sites with more than one year of data, the measurements were averaged over the past 5 years. For example, if data for 2008, 2007, 2006, 2005, 2004, and 2003 were available, then the years from 2004-2008 were averaged. If it had data from 1990 and 2002 they were not averaged because the 1990 point was beyond the cutoff date.

Table 5-2 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
EPALong 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	1997-1998	EPA-600-388-021a

Table 5-2 Summary of data sources considered for the evaluation of national ANC		
Program	**Dates of observations**	**Reference**
EMAP _MAIA)		
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/

Option 2a: Categorize the U.S. into 2 categories (sensitive or less--sensitive) based on ANC and ecoregions

In this approach, ANC, considered the best indicator of acidification, is used to determine which ecoregions in the U.S. are sensitive to acidification. All ecoregions in the U.S. are then categorized as either sensitive or less-sensitive. A deposition metric is calculated for each category. The data sources used in this analysis are described first, followed by a more detailed description of the analysis.

Defining acid-sensitivity of ecoregions based on ANC

This analysis compared whether mean ANC differed between ecoregions when the entire dataset versus a subset of the dataset containing observations that ranged from -50 to 200 μeq/L was used in the analysis. The sample size and mean ANC value for each ecoregion is presented in table 5.3. In the data subset, the values ranging from -50 to 200 μeq/L were selected to focus on acid-sensitive areas, all ANC observations that were greater than 200 μeq/L were excluded from the dataset because ANC above this level indicates that an eco-system is not very sensitive to acidification. All observation less than -50 μeq/L were also deleted from the dataset. This is because ANC values below -50 μeq/L are typically not the result of acidification resulting from deposition (Kauffman et al. 1992). Both analyses indicate that ecoregions 5, 6, 7 and 8 have the among the lowest mean ANC values compared to the other five ecoregions. After observations outside of the -50 to 200 μeq/L are removed, ecoregions 12, 13, are15 are represented by five or less observations, indicating there are few sites measured with ANC values within the range of acid-sensitivity due to deposition. Therefore ecoregions 5 through 11 are considered sensitive and all other ecoregions are considered less sensitive.

Next only those level three subdivisions of the ecoregions with 10 or more observations between -50 to 200 μeq/L were considered sensitive. Fig 5.10 lists the level three ecoregions which are indicated to be sensitive by ANC data.

Table 5-3 National ANC data. Observations from 6318 sites remained after filtering data to remove sites with an average value of ANC<-50 and >200 μeq/L. Color shaded boxes indicate ecoregions that are considered sensitive based on the ANC values. Kruskal-Wallis Test indicated ecoregions has a significant effect on ANC.

	All ANC data		ANC data between -50 and 200 μeq/L	
Ecoregion level 1	*# sites*	*Mean ANC*	*# sites*	*Mean ANC*
5	3519	212	2603	57
6	1952	892	754	90
7	177	775	30	68
8	5051	605	2680	77
9	1098	4694	94	149
10	592	2677	112	134
11	209	2663	35	93
12	19	2496	1	198
13	102	2869	3	146
15	12	406	5	164

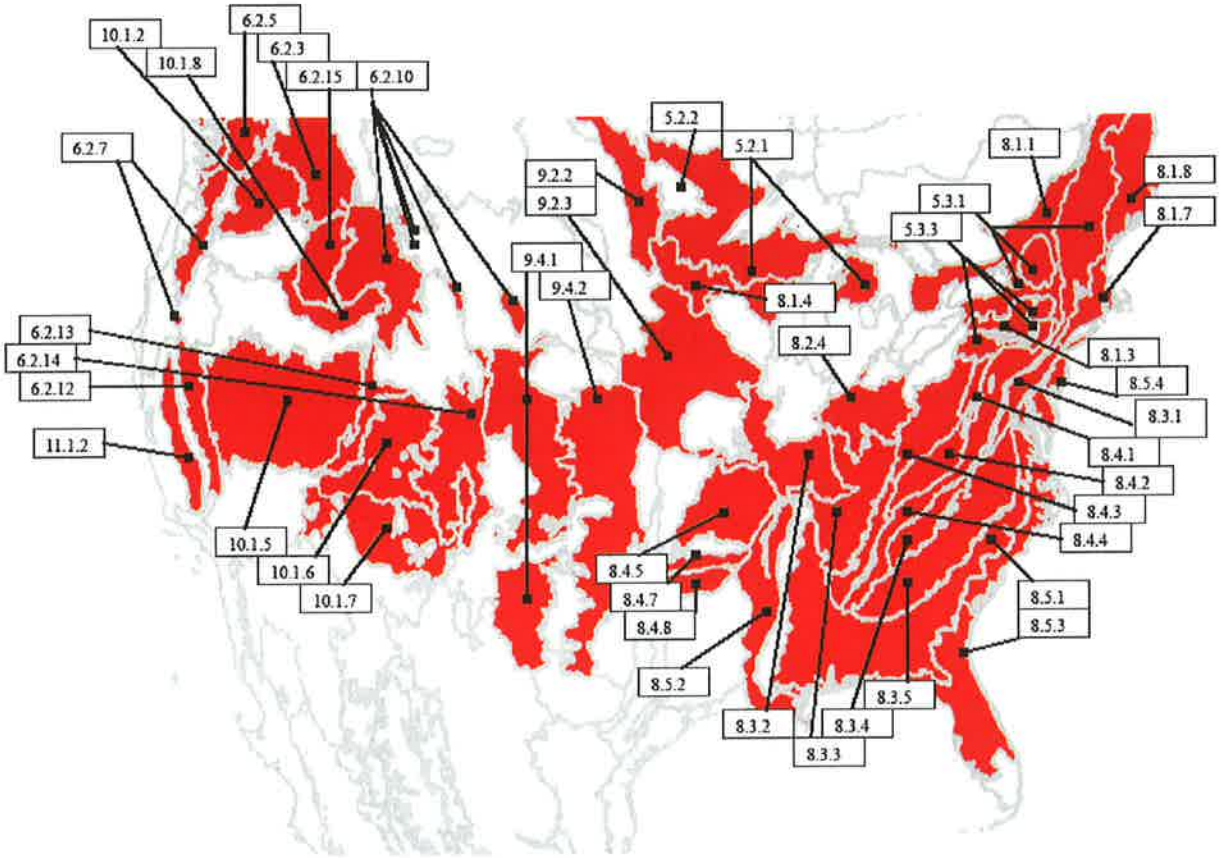


Figure 5-10 Map of sensitive ecoregions (red) using binary categorization approach (sensitive vs. less-sensitive) with ANC observations between -50 and 200 μeq/L

Table 5-4. Descriptive statistics of the CL populations that result when the US is divided into two categories, sensitive and less-sensitive based on ANC data.

ANC μeq/L	Sensitivity class	CL in class n=	Mean Neco	Neco St er	CL mean (meq/m2/yr)	CL St er	Example deposition metrics		
							DL %90 (meq/m^2/yr)	DL %75 (meq/m^2/yr)	DL %50 (meq/m^2/yr)
50	sensitive	4553	55	0.4	219	4	26	51	106
50	less-sensitive	727	37	0.9	496	21	53	117	277
20	sensitive	4881	55	0.3	222	4	32	58	114
20	less-sensitive	732	37	0.9	508	21	63	122	291

Dividing the U.S. into two categories (sensitive and less-sensitive) provides a mechanism to reduce possible over-protection that may occur in less-sensitive regions via Option 1, which does not distinguish between areas that are sensitive and not-sensitive. In Option 2a, the sensitivity category is considered one area, in which one deposition metric could be calculated by evaluating all the CL data from the sensitive ecoregions. This would result in two deposition metrics for the U.S., one for sensitive areas and one for less-sensitive areas. The ecoregions in the sensitive category could be subdivided (See Option 2c).

Option 2b: Cluster Analysis

This approach uses ANC to categorize the acid-sensitivity of ecoregions based on a quantitative cluster analysis. Additional analysis simultaneously considering multiple criteria including ALK, DOC and soil BC weathering datasets were considered, however they are not suggested mainly due to limitation in the national coverage of these datasets, and in the case of soil BC weathering, uncertainty in the method of calculation.

Cluster analysis is a method of grouping objects together based on a chosen similarity metric that is determined from a set of variables of interest. In this analysis ecoregions are grouped based on the distributions of ANC from waterbodies. Numerous algorithms exist for performing cluster analysis. We employed the *k*-means method, which involves assigning a pre-determined number of clusters (n) to the dataset and minimizing the Euclidean distances between the cluster centers and the watersheds. Distance in this case refers to the water quality variables, not geographic distance. The process was repeated for a number of different n values (2 to 40), and a combination of fit statistics and graphical examination of the resulting clusters was used to settle on a final solution. The 5 cluster solution was chosen in this way, which has an R^2 of 0.71 and is shown in Fig 5.11. In selecting the number of clusters, we balanced goals of a parsimonious number of clusters with ability of the clusters to explain a large portion of the variance in ANC across ecoregions.

The deposition metrics based on the CL ANC=50 μeq/L are presented for each cluster in Table 5.5. In general the sensitivity indicated by the mean ANC level of the clusters matches the deposition metrics, with the exception of Cluster 3 and 4 which have deposition metrics indicating they should switch places in regards to sensitivity indicated by the deposition metrics of the 90th, 75th and 50th percentile. This reflects the skewed nature of the distributions of ANC within ecoregions, where ecoregions may be matched more closely on alternative percentiles of

the distribution than others. There are 5 ecoregions which do not have cluster membership (Table 5.6); this indicates there was insufficient ANC data in these ecoregions for classification. There are 8 ecoregions that do not have CL data, but do have cluster membership (Table 5.6.). These ecoregions would be represented by the deposition metric in their cluster.

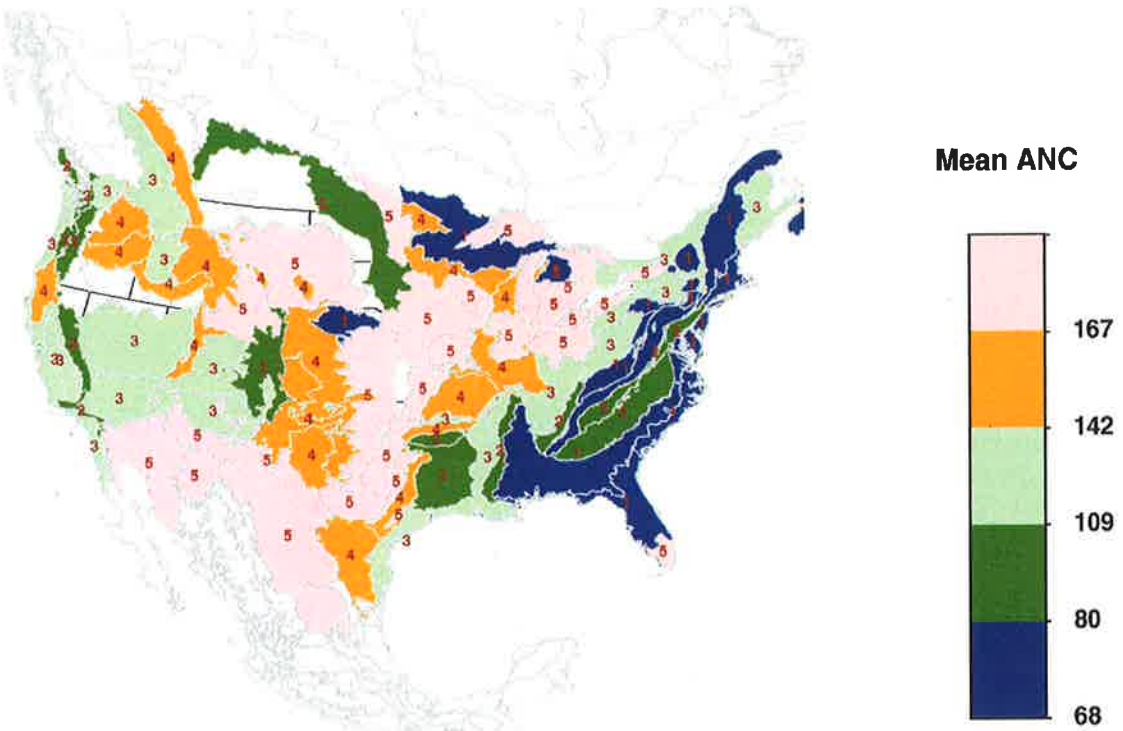


Fig 5.11. Map of sensitive ecoregions based on clusters of log ANC values between -50 and 200 μeq/L

Table 5-5. Descriptive statistics of the CL populations that result when the US is divided into 5 clusters based on log ANC values between -50 and 200 μeq/L.

Target ANC =	Sensitivity class (mean ANC)	CL n=	Mean Neco (meq/m²/yr)	Neco St er	CL mean (meq/m2/yr)	CL St er	Example deposition metrics		
							DL %90 (meq/m²/yr)	DL %75 (meq/m²/yr)	DL %50 (meq/m²/yr)
50	5 (167)	216	51	2	354	20	72	114	269
50	4 (142)	655	39	0.7	393	17	30	64	193
50	3 (109)	784	41	0.8	416	18	48	99	232
50	2 (80)	1113	52	1.0	183	6	26	52	111
50	1 (68)	2432	61	0.5	197	6	24	46	90

Option 2c: One less-sensitivity category and individual sensitive ecoregions

This option builds on option 2a. Like option 2a, the CLs from the ecoregions (level 3) considered less-sensitive would be combined into one population to represent the less-sensitive category. The ecoregions (level 3) considered sensitive using the ANC approach described in option 2a would be represented by the CLs only from the same ecoregions. There are 43 ecoregions (level 3) considered sensitive using option 2a. The deposition metrics of the sensitive ecoregions are presented in Table 5.6.

Table 5-6. Descriptive statistics of the populations of CL ANC=50 μeq/L values that result for each ecoregion

Sensitivity class		Eco-region level 3	Neco mean	CL N=	CL mean (meq/m^2/yr)	CL St er	Example deposition metrics		
Cluster 5	ANC						DL %90 (meq/m^2/yr)	DL %75 (meq/m^2/yr)	DL %50 (meq/m^2/yr)
4	X	10.1.2	28	22	177	40	26	37	122
na		10.1.3	37	41	95	18	18	27	52
5		10.1.4	19	16	244	47	34	50	258
3	X	10.1.5	27	43	266	53	16	41	107
3	X	10.1.6	36	5	106	37	22	23	119
3	X	10.1.7	23	3	74	8	61	61	71
4	X	10.1.8	39	7	158	58	16	73	134
3		10.2.1							
5		10.2.2	19	2	75	1	73	73	
5		10.2.4							
3		11.1.1	20	16	705	211	62	127	293
3	X	11.1.2	22	5	279	97	58	88	262
3		11.1.3	14	19	367	69	41	72	337
5		12.1.1	32	3	88	41	45	45	48
5		13.1.1	38	52	189	21	36	76	120
5		15.4.1							
1	X	5.2.1	45	469	158	10	16	26	56
4	x	5.2.2							
1	X	5.3.1	55	735	177	9	36	58	101
1	X	5.3.3	79	159	113	9	28	52	90
4	X	6.2.10	35	202	230	20	26	50	112
4		6.2.11	20	86	956	92	138	360	744
2	X	6.2.12	17	105	172	24	17	28	68
4	X	6.2.13	37	78	245	45	21	33	59
2	X	6.2.14	22	186	145	12	20	43	91

Table 5-6. Descriptive statistics of the populations of CL ANC=50 μeq/L values that result for each ecoregion

Sensitivity class		Eco-region level 3	Neco mean	CL N=	CL mean (meq/m^2 /yr)	CL St er	Example deposition metrics		
Cluster 5	ANC						DL %90 (meq/m^2 /yr)	DL %75 (meq/m^2 /yr)	DL %50 (meq/m^2/yr)
3	X	6.2.15	38	86	155	19	16	35	76
3	X	6.2.3	47	73	353	35	46	119	228
4		6.2.4	61	28	956	92	102	653	990
3	X	6.2.5	21	133	425	33	90	163	308
2	X	6.2.7	21	88	376	29	60	116	284
na		6.2.8	25	30	323	44	73	127	260
4		6.2.9	32	108	244	17	65	117	197
2		7.1.7	16	29	423	64	21	185	325
3		7.1.8	12	68	1098	100	273	368	945
2		7.1.9	4	11	662	100	260	357	523
3	X	8.1.1	72	43	716	102	133	280	541
3	X	8.1.3	72	88	255	20	104	144	216
na		8.1.2							
4	X	8.1.4	65	45	328	41	26	46	333
5		8.1.5	24	9	961	125	158	794	946
5		8.1.6	90	23	731	49	381	617	703
1	X	8.1.7	72	169	223	18	49	86	148
3	X	8.1.8	35	143	177	16	51	70	108
3		8.1.10	81	9	935	152	351	542	1011
4		8.2.1	77	3	667	101	482	482	687
5		8.2.2							
5		8.2.3							
5	X	8.2.4	104	9	892	76	642	674	937
2	X	8.3.1	50	41	306	33	113	138	218
5	X	8.3.2	82	12	659	132	329	338	466
3	X	8.3.3	67	17	1022	147	429	558	719
2	X	8.3.4	75	168	174	7	74	100	155
1	X	8.3.5	63	75	182	244	15	34	76
2		8.3.6	78	6	399	242	52	98	166
2		8.3.7	65	31	211	35	60	104	160
4		8.3.8	69	4	261	149	32	55	156
1	X	8.4.1	68	510	321	22	31	53	98
1	X	8.4.2	82	200	160	16	24	36	82
3	X	8.4.3	85	19	346	59	119	168	316
2	X	8.4.4	78	379	98	5	21	38	68
4	X	8.4.5	70	24	938	96	243	642	907
3		8.4.6	73	14	102	28	25	42	67
4	X	8.4.7	67	23	129	22	33	64	94

Table 5-6. Descriptive statistics of the populations of CL ANC=50 μeq/L values that result for each ecoregion

Sensitivity class		Eco-region level 3	Neco mean	CL N=	CL mean (meq/m^2/yr)	CL St er	Example deposition metrics		
Cluster 5	ANC						DL %90 (meq/m^2/yr)	DL %75 (meq/m^2/yr)	DL %50 (meq/m^2/yr)
2	X	8.4.8	68	25	141	28	30	65	94
2		8.4.9	61	23	309	82	53	101	167
1	X	8.5.1	44	16	159	39	111	121	245
3		8.5.2	73	13	942	159	223	461	987
1	X	8.5.3	59	53	116	25	13	25	52
1	X	8.5.4	64	43	62	6	22	33	59
2		9.2.1	53	2	122	24	98	98	122
5	x	9.2.2							
5	X	9.2.3	21	13	425	40	249	337	392
5		9.2.4	72	16	365	26	190	309	361
na		9.3.1	55	2	211	101	110	110	211
5		9.3.3	32	21	278	73	78	106	139
1		9.3.4	38	3	79	15	49	49	87
4	X	9.4.1	38	11	30	3	17	20	27
5	X	9.4.2	59	15	148	18	58	102	138
4		9.4.3	30	2	36	6	30	30	36
?		9.4.4	66	6	419	55	268	315	398
5		9.4.5	69	28	257	21	118	175	237
5		9.4.6	52	5	265	80	78	134	199
5		9.4.7	83	2	263	179	84	84	263
3		9.5.1	62	6	1096	386	258	378	838
4		9.6.1							

Option 2d: All ecoregions

In this approach, each ecoregion (level 3) is represented by CLs that are located from sites within the spatial boundaries of the same ecoregion (level 3). Eighty-five ecoregions (level 3) occur in the conterminous U.S., 76 of those are represented by CLs in this analysis. The remaining 9 ecoregions (level 3) for which CLs are not available could be represented by deposition metrics that are calculated using all of the CL data as described in option 1. This approach yields 77 deposition metrics.

Comparison

In this section, Option 1 and 2a-d are compared to help inform the decision of which option is most appropriate. Table 5.7 summarizes the number of deposition metrics that would result from each option. Option 1 has only one deposition metric. This approach would be

easiest to communicate and implement. However there is some concern that this approach may under protect the most sensitive areas and over protect the least sensitive areas. Several analyses have been made to determine if and to what extent this concern may be valid.

Table 5-7 Summary of the number of deposition metrics that would result from the options for how to categorized the landscape based on acid-sensitivity

Acid-sensitivity categorization approach	#deposition metrics for less-sensitive areas	# of tradeoff curves for sensitive areas	Total N + S deposition metrics
Op#1 No subdivision of the U.S.	n/a	1	1
Op#2a Binary categorization (sensitivity based on 10 or more observations of ANC between -50 and 200 μeq/L)	1	All sensitive areas could be represented by the same population of critical loads	2
Op#2b 5 Cluster (based on centroid of data between ANC between -50 and 20 μeq/L 0)	n/a	The U.S. is categorized into 5 clusters of acid sensitivity based on ANC. Each ecoregions is assigned a cluster id, and the CLs from sites within each cluster are pooled to create the population for that cluster.	5
Op#2c 1 sensitive category and individual eco-region categories	1	43 ecoregions (level 3) are considered sensitive, there is CL data available for 40 ecoregions at ANC= 50, the 3 ecoregions which do not have CL data could be represented by values calculated from the entire sensitive population population.	44
Op#2d All ecoregions	n/a	85 ecoregions (level 3) occur in the US, of these there is CL data for 76 therefore they could be represented by CLs only from their ecoregions. The 9 ecoregions without CLs could be represented by the entire population.	77

A comparison of the values for the 90%-tile deposition metric at ANC=50 μeq/L is given for

option 1(no-subdivision/all data), 2a (sensitive vs. less-sensitive classification) and 2b (5 clusters based on log ANC) in Fig 5.12. The deposition metric for option 1 is 27 meq/m^2/yr. When compared to the deposition metrics from option 2a, it would under protect the sensitive category by 1 meq/m^2/yr and over-protect the less-sensitive category by 27 meq/m^2/yr. When option 1 is compared to option 2b, clusters 1 and 2 would be slightly under protected by 3 and 1 meq/m^2/yr, respectively. Clusters 3, 4 and 5 would be over protected by between 3 to 35 meq/m^2/yr.

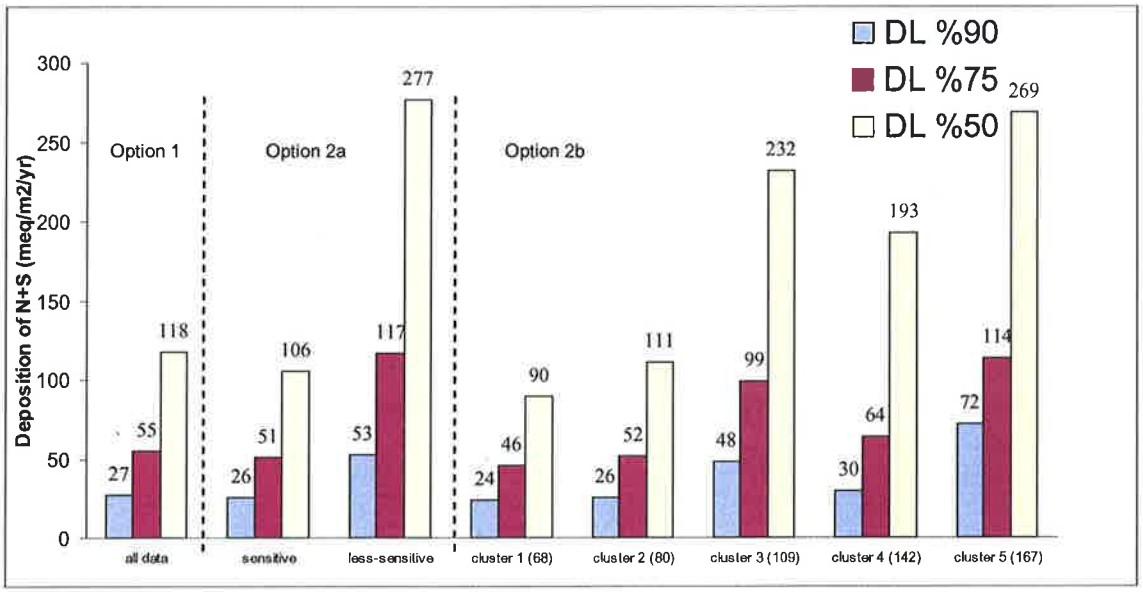


Figure 5-12 Deposition metrics for 90%,75% and 50% of the population for options, 1 (all data), 2a (binary classification), and 2b (clusters based on log ANC)

A second method to compare the options 1 and 2a is presented in Fig 5.13. Sites that would not be protected at a 90%-tile deposition metric at ANC=50 μeq/L are shown. In both options 10% of the total population is not going to be protected from exceeding the CL, by comparing these maps we see that the spatial distribution of sites that are not protected between the two options is similar. In option 2a, there are 10% of total sites that will not be protected in both the sensitive and the less-sensitive ecoregions. This means that eventhough a region is considered less sensitive, 10% of the water bodies would not meet the target ANC because more deposition would be allowed. Considering the analyses represented by Fig 5.11 and 5.12, how much benefit is gained by subdividing the landscape into acid sensitivity classes?

One nation

Sites for which N+S critical loads are not protected when one deposition metric to protect 90% of the population is selected. Red indicates sites not protected

Binary categorization: sensitive and non-sensitive

Sites for which N+S critical loads are not protected when the two deposition metrics are selected to protect 90% of each population. Red indicates sites not protected in the sensitive areas and green indicates sites that are not protected in the less-sensitive areas

Figure 5-13 Comparison of sites that are protected if the nation is not subdivided and if the nation is subdivided into a sensitive and non-sensitive category

Option 2c and 2d provide more spatial detail than the other options. Option 2c uses one deposition metric for all ecoregions categorized as less-sensitive areas according to option 2a, while each ecoregion considered sensitive (using log ANC) is represented only by CLs located within the boundaries of the ecoregion. Option 2d uses only CLs from within an ecoregions to represent that ecoregions. A strength of option 2d is that it provides the finest level of spatial detail consistent with available data. A weakness is that some ecoregions are represented by a small sample size of critical loads, which may not accurately convey the population of critical loads for waterbodies across the entire ecoregion. The cumulative distribution of the 90 %-tile deposition metric of the CLs at ANC=50 μeq/L of all ecoregions (level 3) is shown in Fig 5.14. This figure helps to visualize how option 2d compares to the other options. The deposition to protect 90% of the population in the most sensitive ecoregions is 13 meq/m^2/yr. In comparison to option 1, the deposition to protect 90% of the population is 29 meq/m^2/yr. If the national value were chosen, then although 90% of the total population would be protected, only ~76% of

the ecoregions would have 90% of their populations protected. This illustrates that the sample size and distribution of critical loads varies among ecoregions.

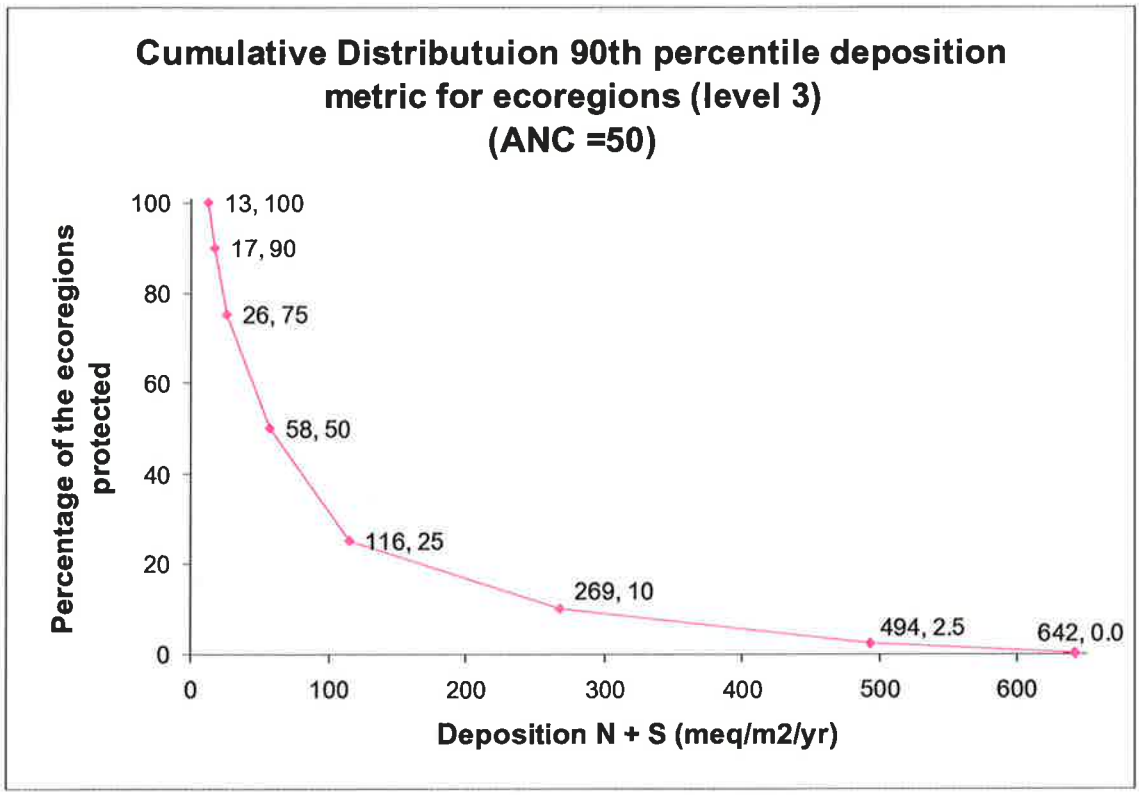


Figure 5-14. Cumulative distribution of the 90% deposition metric for ecoregions is shown. The x and y values are given next to each data point.

Neco

Neco is added to the deposition metric to develop the N and S tradeoff curves (See Section 5.3.2.8). Staff suggests that the spatial boundaries used to determine the acid-sensitivity categories for calculating deposition metrics are also used to calculate Neco values.

5.3.2.8 Deposition metric: Developing N and S tradeoff curves from the deposition metrics for the acid sensitive categories

Acid sensitivity categories define the spatial area of a population. Therefore the membership of an individual catchment to a population that represents and acid sensitivity category will vary depending on which approach for categorizing acid-sensitivity across the landscape is selected for the NAAQS. For each category that is established, there will be a single, specified value for a deposition metric. This deposition metric will be based on the population of catchments in that

specific category. Therefore both the number and the values of the deposition metrics can change based on how finely the U.S. is subdivided into acid sensitivity categories.

The deposition metric for a category will be a single, specified value for the deposition of N and S. That deposition load can be achieved by various combinations of N and S loading, and these combinations can be expressed as an N and S deposition tradeoff curve. Thus for each category a specific deposition load and a resulting N and S tradeoff curve can be developed. Regardless of which option is chosen for spatially dividing the U.S. into acid-sensitivity categories, the number of N and S deposition tradeoff curves is the same as the number of deposition metrics (Table 5.7). For each category, the assigned value for Neco is added to the deposition metric to develop the N and S tradeoff curve. Fig. 5.15 provides an example for two of the categorization options – Option 1, with a tradeoff curve for the single national category, reflecting the entire population of critical loads, and Option 2a, with a tradeoff curve for the sensitive and not sensitive binary landscape categorization.

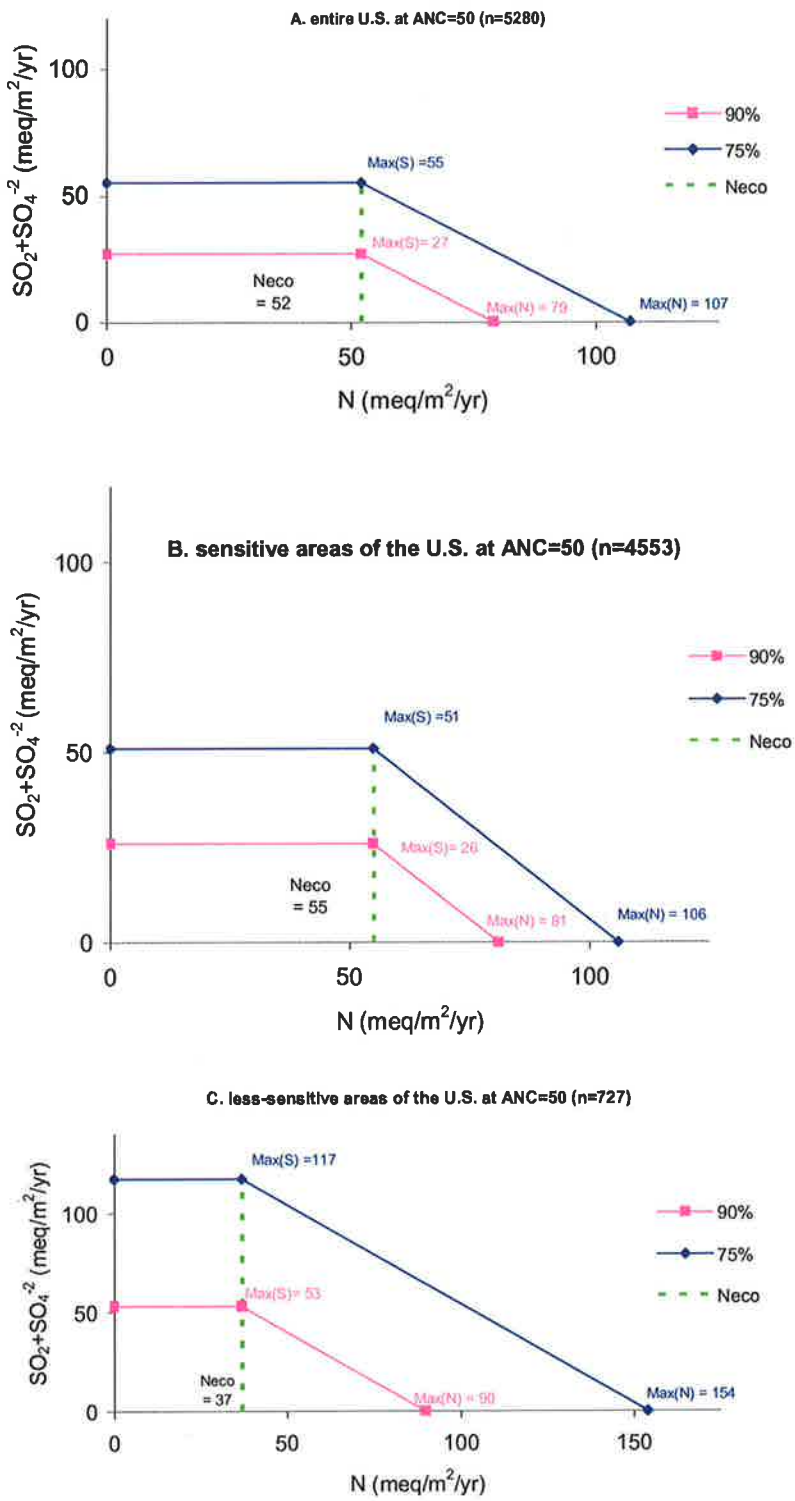


Figure 5-15 Examples of N + (SO_2 +SO_4^{-2}) deposition tradeoff curves for option 1 (A) and option 2a(B and C).

5.3.9 **Deposition metric:** How is reduced nitrogen appropriately considered in the deposition metric?

N deposition is composed of NHx deposition and NOy deposition. Deposition from NH_X can contribute to acidification. However, the criteria pollutant listed by EPA pursuant to section 108 (a) of the Act is oxides of nitrogen, which does not include NHx. The NAAQS is for oxides of nitrogen and sulfur, hence the form of the NAAQS needs to account for the deposition effects of these oxides. To accomplish this, the loadings of reduced forms of nitrogen derived for a given spatial area would be subtracted from the N +S deposition metric after N_{ECO} is added, such that the resultant deposition metric is for sulfur and oxidized nitrogen only. Subtraction of reduced nitrogen from the deposition metric based on nitrogen and sulfur is expressed by equation

$$DL_{\%ECO}(NO_Y + S) = DL_{\%ECO}(N + S) + N_{Eco} - Dep_{NHx}^{Total} \qquad (6)$$

Staff propose the value of reduced nitrogen is initially set using deposition of NHx modeled using the CMAQ, evaluated for the period 2002-2005. The average values of NHx deposition for the 83 ecoregions (level 3) in the U.S. ranges from 4 -54 meq/m^2/yr. This would mean that each acid-sensitivity category would have one N+S deposition metric, one N_{ECO} value and one NHx deposition value. **Staff is considering the most appropriate spatial averaging extent for NHx. Figure 5.16 shows spatially interpolated values of reduced nitrogen deposition based on 12km CMAQ modeling in the Eastern U.S. It is clear that in some locations, there is significant heterogeneity in NHx deposition within ecoregion 3 boundaries. Given this information, two possible approaches to estimating reduced nitrogen values are possible: 1) average reduced nitrogen deposition within an ecoregion, acknowledging that this will lead to uncertainties in the level of protection associated with levels of ambient NOy and SOx, or 2) allow for additional spatial refinement of sensitive areas to reflect the heterogeneity of NHx deposition.**

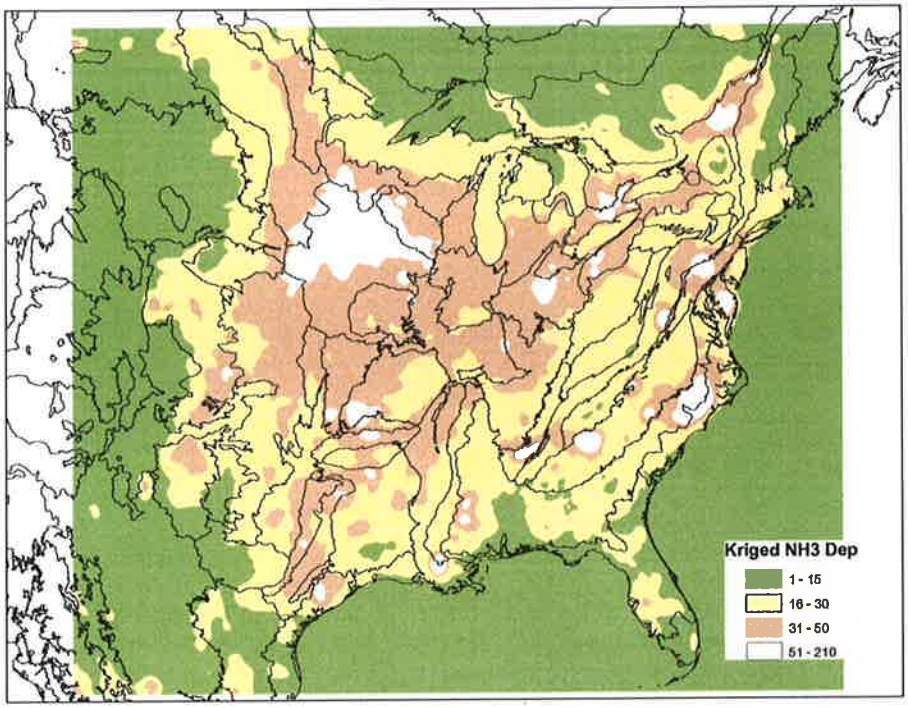


Figure 5-16. A U.S. map of NH_3 deposition (meq/m^2/yr) overlaying ecoregions (level 3) boundaries

The deposition from NOy and SOx is converted to atmospheric concentrations of NOy and SOx by the methods described in section 5.2.3 and an example is given in fig 5.19. This figure also shows air quality in the Adirondack region relative to the NOy and SOx tradeoff curves for option 1 and option 2a. In option 1 the Adirondacks air quality is slightly out of attainment for a 75%-tile deposition metric based on CL at ANC=50. In option 2a the Adirondack air quality is out of attainment for the curve for the sensitive areas, but in attainment for the less-sensitive areas.

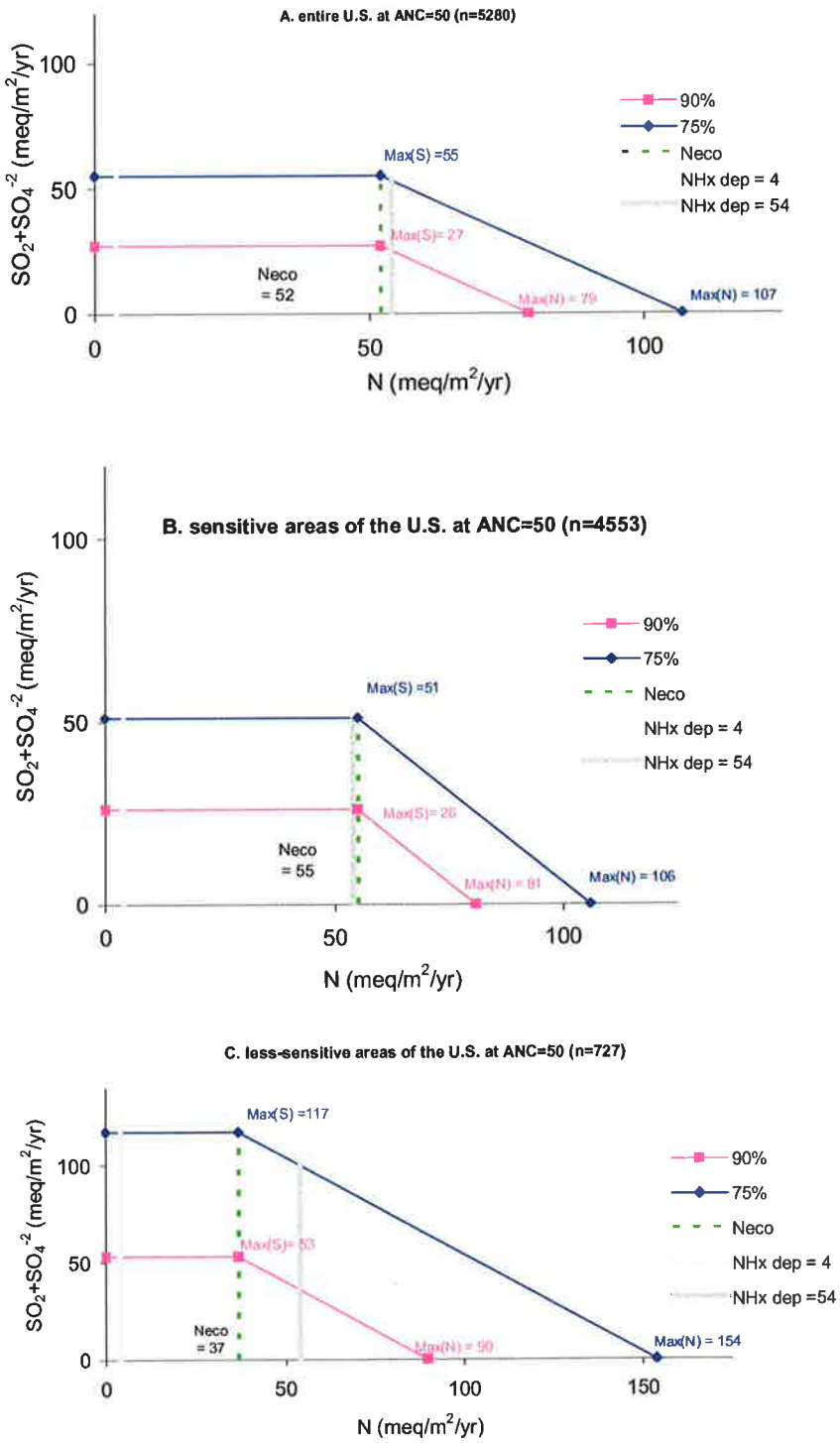


Figure 5-18. Examples of N + (SO_2 +SO_4^{-2}) deposition tradeoff curves for option 1 (A) and option 2a(B and C). Deposition metrics that correspond to protection 75% or 90% of ecosystems are given with the high and low value for average NHx deposition in ecoregions indicated by vertical grey lines.

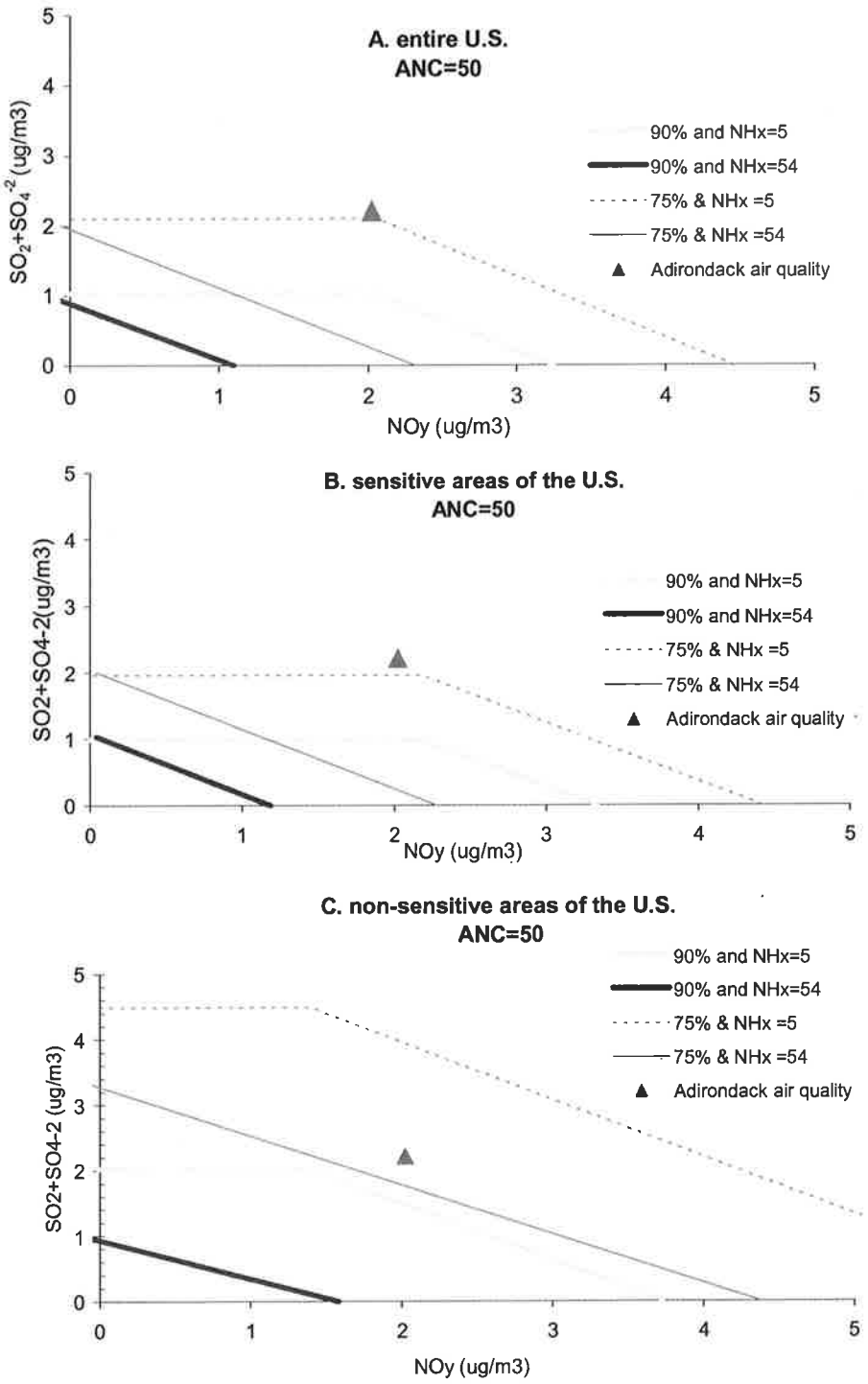


Figure 5-19. Examples of NOy + (SO_2 +SO_4^{-2}) deposition tradeoff curves for option 1 (A) and option 2a(B and C). Deposition metrics that correspond to protection 75% or 90% of the ecosystems considering both the high and low value for NHx deposition

5.3.3 Conceptual Design: Linking Deposition to Atmospheric Concentration

5.3.3.1 Background

Atmospheric pollutants deposit onto land and water surfaces through at least two major mechanisms: direct contact with the surface (dry deposition), and transfer into liquid precipitation (wet deposition). A third mechanism involving impaction of fog droplets onto the surface (occult deposition) also exists, but has been shown to be very small relative to wet deposition (Fuhrer 1986; Thalmann 2001) and so is not considered in calculations below. The magnitude of each deposition process is related to the ambient concentration through the time-, location-, process- and chemical species-specific *deposition velocity* (Seinfeld and Pandis,1998):

$$Dep_i^{Dry} = v_i^{Dry} \cdot C_i^{Amb} \quad (7)$$

$$Dep_i^{Wet} = v_i^{Wet} \cdot C_i^{Amb} \quad (8)$$

where v_i^{Dry} and v_i^{Wet} are the dry and wet deposition velocities, Dep_i^{Dry} and Dep_i^{Wet} are the dry and wet deposition fluxes, C_i^{Amb} is the ambient concentration, and the *i* subscript indicates the pollutant species under study. The total deposition of each pollutant is

$$Dep_i^{Tot} = Dep_i^{Dry} + Dep_i^{Wet} \quad (9)$$

Substituting Equations 7 and 8 into Equation 9 yields

$$Dep_i^{Tot} = v_i^{Dry} \cdot C_i^{Amb} + v_i^{Wet} \cdot C_i^{Amb} \quad (10)$$

The total deposition of sulfur or nitrogen would therefore be:

$$Dep_\alpha^{Tot} = \sum_i (v_i^{Dry} + v_i^{Wet}) \cdot m_i \cdot C_i^{Amb} \quad (11)$$

where m_i is the molar ratio of the atom of interest (α, which refers to either sulfur or nitrogen atoms in SO_x or NO_y) to the *i*'th pollutant. Note that only species in SO_x and NO_y (see Table 1) will be input to these equations; NH3 and NH4 are not currently included as listed pollutants (see Chapter 8 for an expanded discussion of the role of NHx).

5.3.3.2 Aggregation Issues

A relationship for converting sulfur or nitrogen deposition to "equivalent" ambient concentrations, which is part of specifying ambient air quality standards, is

provided in equation 11. A major issue to consider during such conversion is the treatment of spatial, temporal and chemical resolutions of the deposition data and the resulting standards. Since the objective is to specify allowable levels of total ambient SO_x and NO_y (as S and N),, and this is also the chemical resolution provided by the ecosystem models, it is convenient to use a relationship with the following form:

$$Dep_i^{Tot} = T_i \cdot C_i^{Amb} \qquad (12)$$

where T_i is what we term the "transference ratio", which can be considered an aggregated, "effective" deposition velocity that relates total deposition of sulfur or nitrogen to the total ambient concentration, and represents an average of the chemical species specific v_i^{Tot} ($= v_i^{Dry} + v_i^{Wet}$) values in Equation 11. In other words, the transference ratio is effectively the aggregate deposition velocity that would have been required to obtain a level of deposition given a level of atmospheric concentrations. The SO_x and NO_y concentrations are the result of applying the m_i values to the C_i^{Amb} values in Equation 11. Although T_i values are representative of pure nitrogen and sulfur, they are derived from concentrations and depositions of the individual pollutants, so that the resulting value is appropriately weighted by the relative levels of each pollutant actually present in the environment.

The deposition velocities (and, by extension, the T_i values) provide relationships between depositions and concentrations that are concurrent. Since the deposition critical loads derived from ecosystem models that are in need of conversion to atmospheric concentrations are in terms of annual deposition, the ambient concentrations will also be aggregated to the annual level through averaging. Data used to derive annual T_i values will also need to have the same spatial representativeness as the depositional loads derived from ecosystem models. However, many of the calculations involving relationships between concentrations and depositions will be in terms of the masses of the N and S atoms within NOy and SOx removed from the other atoms in the pollutant species, which we will refer to as "oxidized S" and "oxidized N". This is done both because these quantities are the outputs of the ecosystem models discussed in Section XXX, and it removes potential ambiguities that might be introduced by different species mixtures.

5.3.3.3 Air Quality Simulation Models

Ideally, T_t values would be derived for each area of interest from concurrently collected sulfur and nitrogen deposition and concentration measurements. However, no monitoring network currently exists that can provide such information. We therefore suggest using output of the Community Multi-scale Air Quality (CMAQ) model (EPA, 1999) for initial calculation of T_t values.

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. Its comprehensive structure is ideal for providing T_t values that appropriately address the chemical and temporal aggregation issues discussed above, and weighted spatial averages of the gridded data can be used for areas that span multiple grid cells. The major potential drawback to using CMAQ output is that the data is simulated rather than measured.

CMAQ does not directly calculate or use T_t values; instead the following procedures are used in the code to model deposition:

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, all of which is conceptually contained in the v^{wet} parameter in Equation 8.

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. Some bias has been found between CMAQ's wet deposition predictions and measured values (Morris et al., 2005); recent analyses suggest that poor simulation of precipitation

could be responsible for this (Davis and Swall, 2006), which can potentially be dealt with by recalculating wet deposition using precipitation measurements. Although the model is continually undergoing improvement, CMAQ is EPA's state-of-the-science computational framework for calculating deposition velocities, and was therefore the logical first choice as a source for T_t values.

5.3.3.4 Oxidized Sulfur and Nitrogen Pollutant Species

Ideally, all possible NOy and SOx air pollutant species that contribute to ecological adversity would be considered for T_t values. The pollutant list is constrained by the source of T_t values, which is currently CMAQ output. The oxidized sulfur and nitrogen species currently available in CMAQ whose data will be used for T_t values, are listed in Table 1.

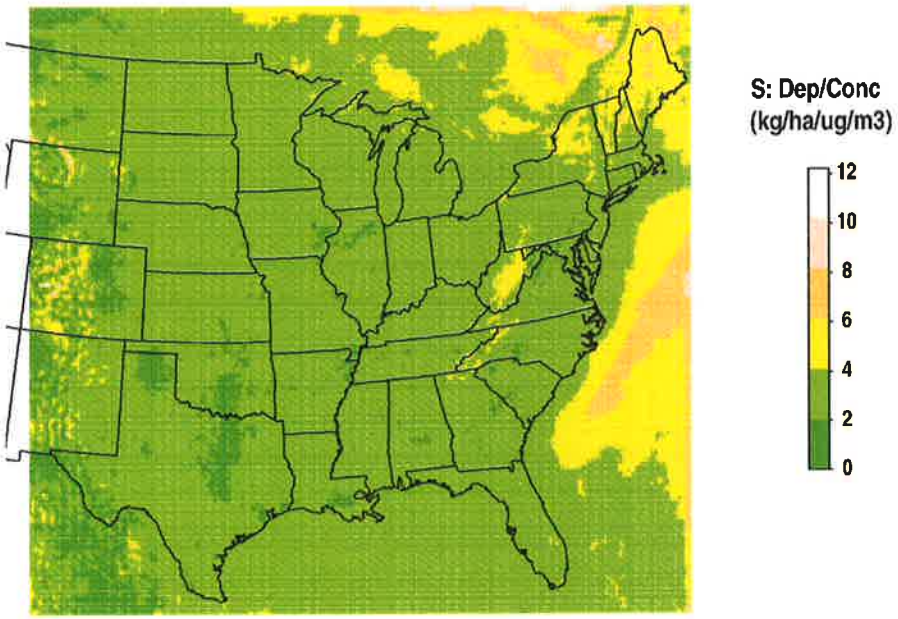
One issue that needs explicit consideration is the contributions of particles larger than $PM_{2.5}$ to sulfur and nitrogen deposition. A recent review of particle deposition measurements (Grantz, Garner, and Johnson, 2003) showed that coarse particles generally deposit far more sulfate and nitrate in forest ecosystems than fine particles. However, CMAQ does not currently provide simulations of coarse particulate sulfate and nitrate. This is an issue that needs to be addressed by developers of either the model or the future SOx/NOy measurement network to set scientifically sound standards. This issue is explored further in the discussion of monitoring in Section XXX.

5.4.5 Example Calculations

Figure 5.20 shows annual inverse T_t values[1] calculated for each 12 km grid in the eastern and western domains for a 2002 CMAQ v4.6 simulation, which is the quantity that would be used for conversion of deposition load tradeoff curves. Figure 5.21 shows an example application of these ratios for a lake in the Adirondacks. Deposition load tradeoff curves for this lake (see Section 5.5 for their calculation) are multiplied by the inverse T_t value from the appropriate gridcell in Fig. 5.22 to convert those depositions to ambient concentrations of sulfur and nitrogen.

[1] Inverse T_t values represent the multiplier needed to convert deposition levels into atmospheric concentrations of NOy and SOx.

A CMAQ v4.7 simulation for multiple years (2002-2005) recently became available, which was used to examine the inter-annual variability of inverse T_t values. The grid-specific coefficients of variation (CV) are shown in Fig. 5.22. Fig. 5.22 shows that CV values are relatively small (< 25%) in the Adirondacks and Shenandoah case study areas. This suggests that a 3-year average of the ratios may be a sufficiently stable representation of deposition velocities for converting the deposition load curves to ambient concentrations.



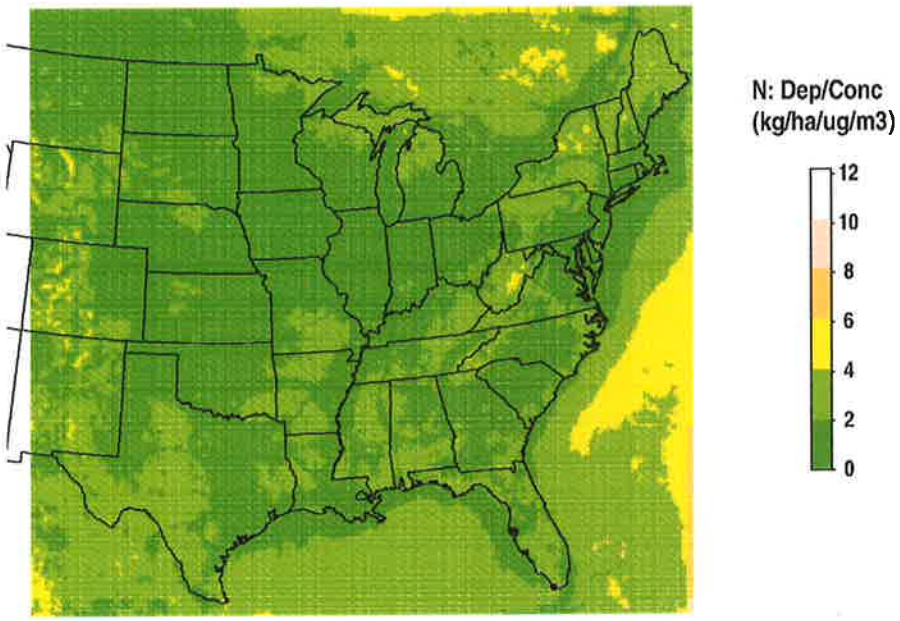


Figure 5-20 2005 T_t values for each grid cell in the eastern U.S. domain. The top map shows values for sulfur and the bottom is for nitrogen.

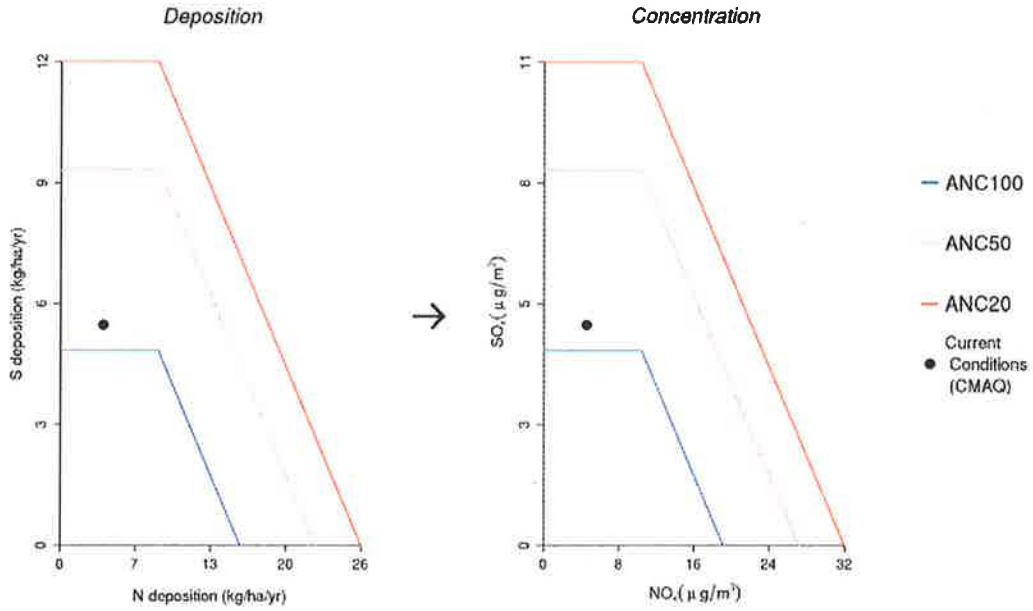
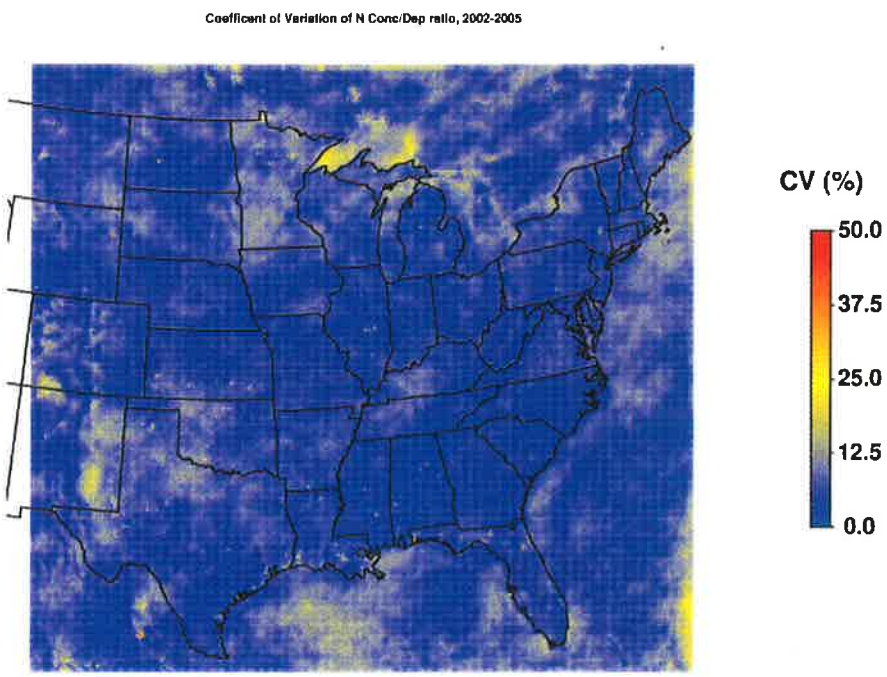
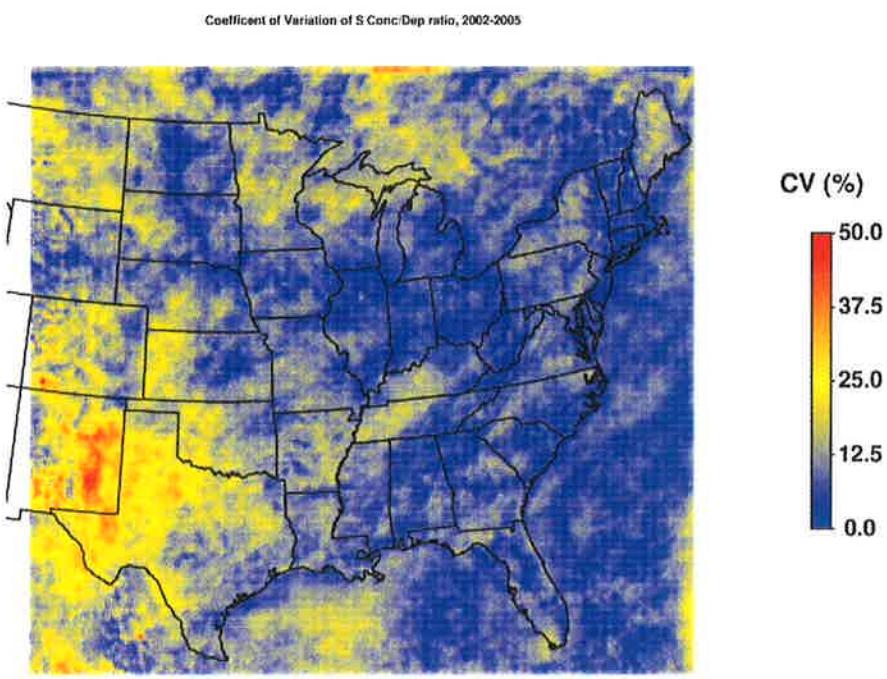


Figure 5-21. Schematic Diagram illustrating the procedure for converting deposition tradeoff curves of sulfur and nitrogen to atmospheric concentrations of SOx and NOy.



a)



b)

Figure 5-22 Inter-annual coefficients of variation (CV) of a) NO_y and b) SOx T_t values, based on a series of 2002-2005 CMAQ v4.7 simulation.

5.3.3 AAPI

In sections 5.3.2 and 5.3.3, the form of the standard is expressed as an approach for linking ecosystems, N and S deposition and ambient air concentrations of NOx and SOx to conceptually identify levels of NOx and SOx that are protective of ecosystems via NOx and SOx tradeoff curves. The tradeoff curves will differ among acid-sensitivity categories because they are derived from a specific percentage of ecosystems protected within an overall sensitive area. In this section, the form of the standard is expressed as the AAPI equation, which is an index, set to one level, which can be applied across the nation to convey the potential of an ecosystem to become acidified from atmospheric deposition. Moreover, the AAPI calculates the target ANC for a percentage of aquatic ecosystems within a particular acid sensitive area when atmospheric concentrations of NOx and SOx are input

5.3.4.2 Definition and Derivation of the AAPI

The definition of the AAPI considered here is:

> Annual Average AAPI: Natural background ANC minus the contribution to acidifying deposition from NHx, minus the acidifying contribution of deposition from NOy and SOx.

In order to derive the AAPI, we start with the basic framework of critical loads discussed in section 5.3. The approach used to calculate N and S deposition values for a specified ANC at a catchment-scale is expressed in Equation 2 from section 5.3.

$$CL_{ANC\lim}(N+S) = ([BC]_O^* - [ANC_{\lim}])Q + N_{eco} \qquad (2)$$

To develop an equation that allows us to set a single value for the standard across the U.S., rearrange equation (2) to solve for ANC (place ANC on the left hand side of the equation):

$$Q \cdot ANC_{\lim} = N_{ECO} + [BC]_O^* \cdot Q - \left[Dep_N^{Total} + Dep_S^{Total}\right] \qquad (13)$$

$$ANC_{\lim} = \frac{1}{Q} N_{ECO} + [BC]_O^* - \frac{1}{Q}\left[Dep_N^{Total} + Dep_S^{Total}\right] \quad (14)$$

Building from equation 14, total nitrogen deposition is split into oxidized and reduced nitrogen because we need to be able to specify the standards in terms of oxides of nitrogen, and so the contribution of reduced nitrogen has to be separated.

$$ANC_{\lim} = \left[\frac{1}{Q} \cdot N_{ECO} + [BC]_O^*\right] - \frac{1}{Q}\left[Dep_{NOy}^{Total} + Dep_S^{Total}\right] - \frac{1}{Q} \cdot Dep_{NHx}^{Total} \quad (15)$$

Where,

Dep_{NHx}^{Total} = the depositional load of reduced nitrogen, NHx.

In order to judge whether a catchment meets the ANC_{limit} given observed NOy and SOx levels, the associated depositional loadings of NOy and S can be compared directly against calculated deposition tradeoff curves, atmospheric concentrations of NOy and SOx can be compared against the atmospheric concentration tradeoff curves or, loadings of NOy and SOx can be input into the following equations to obtain the calculated value of ANC, equal to ANC*:

$$ANC^* = \left[\frac{1}{Q} \cdot N_{ECO} + [BC]_O^*\right] - [L(NOy) + L(SOx)] - L(NHx) \quad (16)$$

Where,

ANC*= the calculated value of ANC given loadings of N and S for comparison against an ANC_{limit}.

L(NOy+S)= the load of NOy+S anions based on observed atmospheric concentrations of NOy and SOx

L(NHx) = the load of reduced nitrogen deposition

[Note that L(N) = L(NOy+NHx)]

In equation 16, the ANC* will vary based on the deposition load inputs of NOx, NHx and S at the site of interest. The deposition loads caused by NOx and S and NHx are inputs, leading to

$$ANC^* = \left[\frac{1}{Q} \cdot N_{ECO} + [BC]_O^*\right] - \frac{1}{Q}\left[Dep_{NOy}^{Total} + Dep_S^{Total}\right] - \frac{1}{Q} \cdot Dep_{NHx}^{Total} \qquad (17)$$

If ANC* < ANC_{lim}, then the deposition of N and S exceeds the deposition load to maintain ANC_{limit}. ANC* is still representative of the calculated ANC based on specific catchment level estimates of $[BC]_0^*$, N_{ECO}, Q and NH_x.

The AAPI is equivalent to the equation for calculating ANC* when the catchment specific values are replaced by spatially aggregated values that represent an acid sensitive areas (based on a percentile of water bodies targeted for an ANC level selected by the Administrator), NH_x is replaced by average values for aggregate ecosystem areas, and aggregated deposition velocities translate NOy and SOx into deposition:

$$AAPI = \left[\frac{1}{Q} \cdot N_{eco} + [BC]_O^*\right]_{\%eco} - \frac{1}{Q} Dep_{\alpha NHx}^{Total} - \frac{1}{Q}\left[T_{NOy} \cdot C_{NOy}^{amb} + T_{SOx} \cdot C_{SOx}^{amb}\right] \quad (18)$$

Where C_{NOy}^{amb} and C_{SOx}^{amb} are concentrations of NOy and SOx, respectively, T_{NOy} and T_{SOx} are the transfer ratios to convert ambient concentrations to deposition for NOy and SOx, respectively (See section 5.3.3 for further description of calculation of these ratios)

Note that while equation (18) is used to calculate the value of AAPI for any observed values of NOx and SOx, the level of the standard for AAPI selected by the administrator should reflect a wide number of factors, including desired level of protection indicated by a target ANC_{limit}, the specified percentile of waterbodies projected to achieve the target ANC, and the various factors and uncertainties involved in specifying all of the other aspects of the standard, such as the classification of landscape areas, the specification of reduced nitrogen deposition, the methodology to determine deposition of NOx and SOx, and the averaging time. As such the administrator may choose an AAPI level higher or lower than the target ANC_{limit} to reflect the combined effect of the all of the components of the standard and their related uncertainty, such

that the chosen AAPI, in the context of the overall standard, reflects her informed judgment as to a standard that is sufficient but not more than necessary to protect against adverse public welfare effects.

5.3.4.2 How are AAPI parameters determined?

Other than ambient levels of NOx and SOx, which would be measured values, EPA would determine and specify all of the values for the AAPI parameters, as discussed below. $T_{\alpha NOy}$ and $T_{\alpha SOx}$ are calculated from CMAQ by dividing the annual average NOy, SOx concentration by the total NOy or SOx deposition, respectively, for each grid cell and then aggregating all grid cells in a level three ecoregion. The $T_{\alpha NOy}$ and $T_{\alpha SOx}$ are spatially variable, and for the purposes of setting the standard, are determined based on the ratios of total sulfur and nitrogen depositions to concentrations from CMAQ model outputs (as described in section 5.3).

NHx is spatially variable and determined based on monitored and/or CMAQ modeled outputs. The average NHx deposition across grid cells within an acid sensitive region will be used to represent the depositional load of NHx. (See section 5.3)

There will be multiple combinations of concentrations of NOy and SOx that result in a specific value of the AAPI. There will be no single combination of NOy and SOx that solves for a particular value of AAPI in all locations. Measured concentrations of annual average NOy and SOx necessary to meet the standards are thus expressed conditionally by the equality in the AAPI equation (18), and not by fixed quantities.

In order to provide a set of values for elements of the form, the T_{NOy}, T_{SOx} and NHx, values for specific areas would be estimated based on the best available monitoring and/or modeling data. Given the limited availability of measured deposition velocities, staff concludes that the calculated deposition ratios based on the CMAQ modeling from 2005 provides the best available source of estimates of T_{NOy} and T_{SOx}. Evaluation of the stability of these estimates of deposition ratios over time suggests that in most acid sensitive areas, deposition ratios are quite stable, with a coefficient of variation less than 25 percent across a four year period. While there are a limited number of sites that directly measure deposition of reduced nitrogen, staff

concludes that the most widely available and defensible estimates of reduced nitrogen deposition (NHx) are the estimates obtained from the CMAQ modeling from 2005.[2]

For each acid sensitive area the natural background ANC is a calculated value and is determined by the expression $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$ from equation 18. The three components are: $[BC]_0^*$, the pre-industrial weathering rate; N_{eco}, which represents the amount of deposited nitrogen that is removed via ecosystem uptake, denirification and immobilization; and Q, the runoff parameter. These components act in combination, so that the 95th percentile of the distribution of values for each variable may not equal the 95th percentile value for the combination of the variables. Therefore the value for the combination of these variables will be determine from the critical load which represents the selected % of protection given the distribution of critical loads in the population.

It is important to note for this form of the standard that the same AAPI can be obtained with different combinations of ambient NOy and SO_x concentrations. The implication of the form of the standard expressed in equation (18) is that there will be a tradeoff curve that reflects the combinations of NOy and SOx that satisfy equation (18) for any specific value of the standard. The shape of the tradeoff curve will depend on the specific values of $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$, T_{NOy}, T_{SOx} and NHx for a limited number of specific areas classified based on acid-sensitivity. As discussed in Section 5.3, all parts of the U.S. would be classified into areas based on acid-sensitivity. Within each such area, EPA would specify the parameter values of AAPI, leading to a specific tradeoff curve for each area.

The levels of NOy and SOx that meet an AAPI standard expressed for a given $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$, T_{NOy}, T_{SOx} and NHx:

$$\left[T_{NOy}\cdot C_{NOy}^{amb}+T_{SOx}\cdot C_{SOx}^{amb}\right]=Q\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}-Dep_{NHx}^{Total}-Q\cdot AAPI \quad (19)$$

[2] Note to readers: Maps of CMAQ 2005 estimates of NHx deposition will be included in the second draft policy assessment, along with an evaluation of the representativeness of the 2005 NHx deposition for characterizing conditions over a multiyear period.

Note that $\left[T_{NOy} \cdot C_{NOy}^{amb} + T_{SOx} \cdot C_{SOx}^{amb}\right]$ is essentially the critical load of NOy and S expressed in terms of atmospheric concentrations. The pairs of NOy and SOx that will meet a given AAPI limit are related through the following equations

$$NO_y^* = C_{\min}\left(NO_y\right) \tag{20}$$

$$SO_x^* = C_{\max}(SOx) \forall NO_y < C_{\min}(NO_y) \tag{21}$$

$$SO_x^* = C_{\max}(SOx) + \left[\frac{C_{\max}(SOx)}{(C_{\min}(NO_y) - C_{\max}(NO_y))}\right] \cdot NO_y^* \forall NO_y > C_{\min}(NO_y) \tag{22}$$

Where,

NO_y^* is the coordinate point for NOy

SO_x^* is the coordinate point for SOx

$C_{\max}(SOx)$ is the concentration of SOx in the atmosphere consistent with DLmax (S)

$C_{\max}(NOy)$ is the concentration of NOy in the atmosphere consistent with DL max (N)

$C_{\min}(NO_y)$ is the concentration of NOy in the atmosphere consistent with DL min (N)

$$C_{\max}\left(SOx\right) = \frac{1}{T_{\alpha S}} DL_{\max}(S) \tag{23}$$

$$C_{\min}\left(NO_Y\right) = \frac{1}{T_{\alpha NO\,y}} DL_{\min}\left(N - NHx\right) \forall NHx < DL_{\min}\left(N\right) \tag{24}$$

$$= 0 \forall NHx > DL_{\min}\left(N\right)$$

$$C_{\max}\left(NO_Y\right) = \frac{1}{T_{\alpha N}} DL_{\max}\left(N\right) \tag{25}$$

Where DLmax(S), DLmax (N), and DLmin(N).are based on the critical load within a sensitive areas that protects a specified percentile (e.g. 95%) of water bodies in the area.

Note that C_{min}(NOy) is a conditional function determined by the relationship between total nitrogen buffering capacity in an ecosystem and the amount of reduced nitrogen deposition. When reduced nitrogen deposition exceeds the buffering capacity of an ecosystem, then all atmospheric oxidized nitrogen contributes to acidification. When reduced nitrogen deposition is less than the buffering capacity of an ecosystem, then some amount of NOy is buffered (i.e. is reflected in C_{min}(NOy) but that amount reflects the contribution of NHx to total nitrogen (the amount of buffering capacity used up by reduced nitrogen). In this case, some fraction of the atmospheric oxidized nitrogen may not contribute to acidification.

Recall that these three variables are conditional on the chosen level of AAPI, and reflect the depositional loadings that are associated with an equivalent level of ANC, e.g. for an AAPI of 50, the $DL_{max}(S)$, $DL_{max}(N)$, and $DL_{min}(N)$ are associated with an ANC of 50. Also recall than $DL_{max}(S)$ for a given ANC is a function of the "natural" flux of base cations to a watershed, runoff, and the amount of sulfur retention within a waterbody; $DL_{min}(N)$ is the minimum amount of deposition of total nitrogen (NHx + NOx) that catchment processes can effectively remove without contributing to the acidic balance; and $DL_{max}(N)$ for a given ANC is a function of $DL_{min}(N)$ and the "natural" flux of base cations to a watershed, runoff, and the amount of nitrogen retention within a waterbody, assuming S is zero. In our framework, $DL_{min}(N)$ is calculated from the FAB critical load modeling (equation 5 from Attachment A of the REA) or estimated through measured or modeled values of total nitrogen deposition and nitrate leaching.

As discussed in sections 5.3, the specific estimation of of $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$, T_{NOy}, T_{SOx} and NHx in a specific sensitive area will depend on the spatial scale of the sensitive area. Sensitivity can be assessed at the level of individual catchments, however, this presents practical limitations for establishing meaningful standards, as there are thousands of catchments within the U.S. Binning classes of sensitivity within larger spatial areas can provide a more manageable set of values of $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$, T_{NOy}, T_{SOx} and NHx. These parameters can be estimated in several ways for the larger spatial areas. Mean or median values can be generated across catchments, however, this would lead to parameter estimates that do not reflect conditions in the more sensitive lakes in the region. Alternatively, in order to provide a desired level of protection in these larger defined spatial areas, estimates based on higher percentiles of the distributions of parameters across catchments can be generated, e.g. the 75th or 95th percentile values of of $\left[\frac{1}{Q}\cdot N_{eco}+[BC]_O^*\right]_{\%eco}$, T_{NOy}, T_{SOx} and NHx could be used to provide protection for the more vulnerable aquatic ecosystems, however this would potentially lead to over-protection for less vulnerable ecosystems in the area. The Administrator may consider the balance between protection of particularly sensitive ecosystems and the overall protection for ecosystems in an area as an important element to consider in making decisions about the target level of ANC and the percent of aquatic ecosystems within an area targeted to achieve the specified ANC level.

5.4 Options for specifying the targets for the ecological indicator for aquatic acidification (ANC)

As discussed earlier in this chapter, ANC is the ecological indicator best suited to reflect the sensitivity of aquatic ecosystems to acidification (5.3). ANC is an indicator of the effects expected to occur given the natural buffering capacity of an ecosystem and the loadings of nitrogen and sulfur resulting from atmospheric deposition. **As noted by CASAC in their review of the first draft of this Policy Assessment, "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."**

A target ANC limit is an important starting point in deciding the appropriate level of AAPI, and is a necessary component in determining the critical loads for N and S from which the tradeoff curves for ambient NOy and SOx are derived. In fact, the target ANC together with the selected percent of waterbodies to be protected to that target ANC (see section 5.4) uniquely determines the set of critical loads of N and S across the set of acid sensitivity categories.

In reaching staff conclusions regarding the range of target ANC levels that is appropriate to evaluate further in the context of setting a NOx and SOx standard with the AAPI form, considering effects on public welfare due to aquatic acidification**, we use three types of information: 1) direct information on levels of biological impairment related to alternative levels of ANC (and related levels of pH), 2) target ANC values and their rationales as identified by states or regions in setting critical loads to protect regional water bodies, and 3) information on ecosystem service losses associated with alternative ANC values.**

In addition, we evaluate risk-based information derived from the Risk Assessment, focused on case studies of acid sensitive lakes and streams in the Adirondacks and Shenendoahs. As part of our risk-based considerations, we have considered estimates of risks under current conditions in which current NOx and SOx air quality standards are met in the case study areas.

It is important to note that the choice of a target ANC level starts with an evaluation of the conditions that exist if a certain ANC occurs in fact. There is a significant body of science to inform that evaluation, as discussed below. However the development of a NAAQS based on the AAPI form does not assume or guarantee that any specific ANC level will in fact occur for any specific body of water. A critical issue for the Administrator to address in setting a NAAQS based on the AAPI is to consider and weigh the varying degrees of uncertainty in establishing the elements of the AAPI. These uncertainties impact the likelihood that a specific AAPI standard would in fact achieve a target ANC level for a specified percentage of a population of water bodies. Thus it is appropriate to first look at target ANC from the perspective of what we understand the impacts would be if a certain ANC level were realized. Hence, the discussion below focuses on evaluation of the ecological impacts at various target ANC levels, assuming the ANC level occurs in fact. Judgments made based on that evaluation then become the foundation for further judgments that would be made in the process of establishing the specific level of an AAPI, taking into account the degree of uncertainty in projecting the actual ANC levels that would result from any specific APPI standard.

5.4.1 What levels of impairment are related to alternative target levels of ANC?

As discussed in Chapters 2, 3, and 4, specific levels of ANC are associated with differing levels of risk of ecosystem impairment, with higher levels of ANC resulting in lower risk of ecosystem impacts, and lower 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[3], 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.

[3] Biological effects are primarily attributable to a combination of low pH and high inorganic Al concentration. Such conditions occur more frequently during rainfall and snowmelt that cause high flows of water and less commonly during low-flow conditions, except where chronic acidity conditions are severe. Higher ANC values are generally associated with lower risk of low pH during rainfall and snowmelt events.

Because there is a direct correlation between ANC and pH levels, we can inform the selection of target ANC in part through information on effects of pH as well as direct studies of ANC. Figure 5-23 demonstrates the relationship between the measure of risk to the aquatic ecosystems, ANC, and pH, the causal indicator of effect in aquatic ecosystems (Chapter 2). Levels of pH are closely associated with ANC in the pH range of 4.5 to 7. Within this range, higher ANC levels are associated with higher pH levels. At a pH level of 4.5, further reductions in ANC appear to be uncorrelated with pH, as pH levels remain at 4.5 while ANC values fall substantially. Likewise, at a pH value of 7, ANC values continue to increase with no corresponding increase in pH. As pH is the primary causal indicator of acidification related effects, this suggests that ANC values below -50 μeq/L (the apparent point on the function where pH reaches a minimum) are not likely to result in further damage, while ANC values above 50 μeq/L (the apparent point on the function where pH reaches a maximum) are not likely to confer additional protection. As a result, our focus will be on ANC values in the range of -50 to 50 μeq/L.

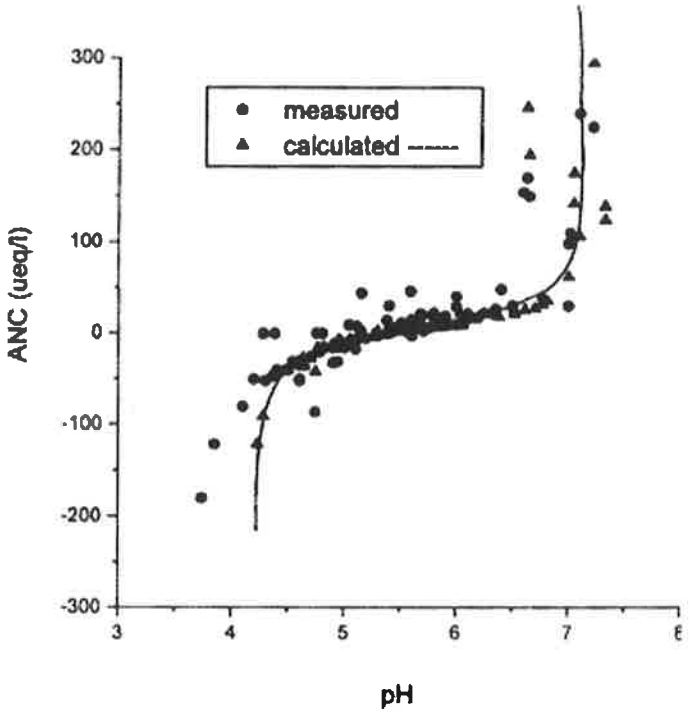


Figure 5-23. Relationship between ANC and pH levels (reproduced from Bi et al, 2001)

Within this ANC range, the role of ANC is to protect against the likelihood of decreased pH (and associated increases in Al). Gerritson et al (1996) demonstrate that the probability of pH decreasing to a given threshold level is affected by the ANC level. In general, the higher the ANC, the lower the probability of decreasing to the threshold. Figure 5-24, reproduced from Gerritson et al (1996) shows that for two common fish species, the probability of exposure to pH levels below threshold values declines as ANC levels increase. This suggests that greater protection against threshold values of pH that cause biological damage would be achieved by target ANC values set high enough to have a low probability of the system going below a threshold pH level.

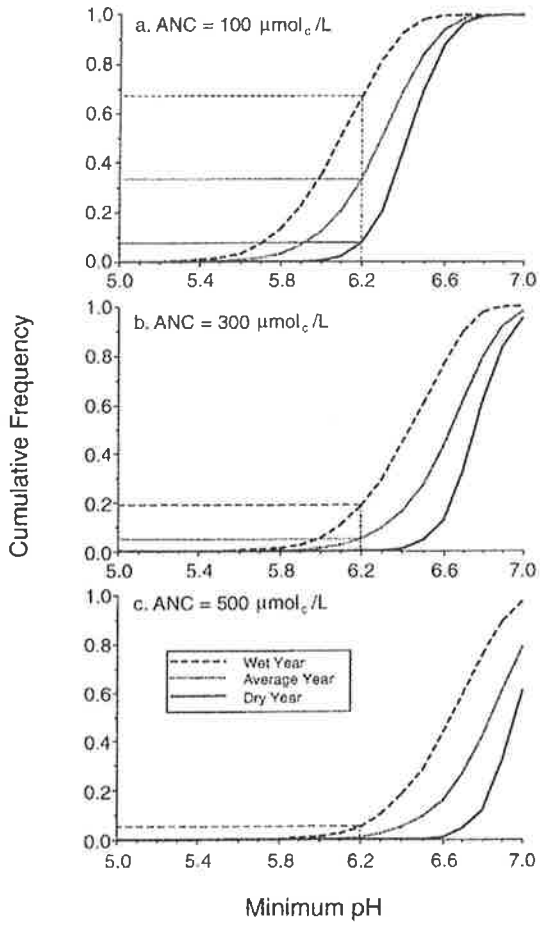


FIG. 5. Cumulative distributions of minimum pH per event for streams with ANC = 100, 300, and 500 μmol$_c$/L, respectively, during April in wet, average, and dry years.

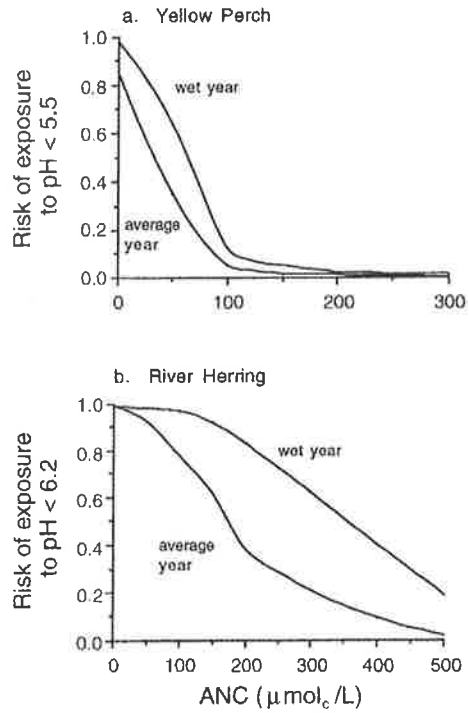


FIG. 6. Risk of exposure to one or more streamwater pH depressions below critical during average and dry years. (a) Yellow perch. (b) River herring (blueback herring and alewife).

Figure 5-24 Summary of results from Gerritson et al 1996. Blue back herring larval mortality occurs at pH 6.2. The higher the ANC the less likely it is that the pH will dip below 6.2 Source Gerritsen et al. 1996

Damages to aquatic ecosystems can be measured using several different metrics, including health of fish populations (measured using the condition factor, an index of fish length and weight which indicates loss in available energy due to acidification), biodiversity (e.g. number of fish species), and community structure (e.g. ratios of higher trophic level to lower trophic level species). The next two sections discuss the evidence for a range of damage types occurring at different levels of pH and ANC.

Evidence of effects due to low pH levels:

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 2, typically at pH <4.5 and an ANC <0 μeq/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 Shenendoah 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 study (Woodward, 1991) concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of inorganic Al was pH 5.0.

One important indicator of acid stress is increased fish mortality. Table 5-9 summarizes the evidence of mortality related to different levels of pH for a number of fish species.

Table 5-9. 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

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 5-10, 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.

Table 5-10 Threshold response of increased mortality of fish to low pH listed from least sensitive to most sensitive

Study	Species	Increased Mortality Threshold, pH	Study Conditions
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	

Source: Baker et al 1990, reproduced from the ISA, Table B-23.

The highest pH threshold for any of the studies reported in Table 5-10 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 lifestages of fish.

Non-lethal effects have been observed at pH levels as high as 6. A study in the Shenendoah National Park found that the condition factor, a measure of fish health expressed as fish weight/length^3 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; Cosby et al., 2006; 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 5-25.

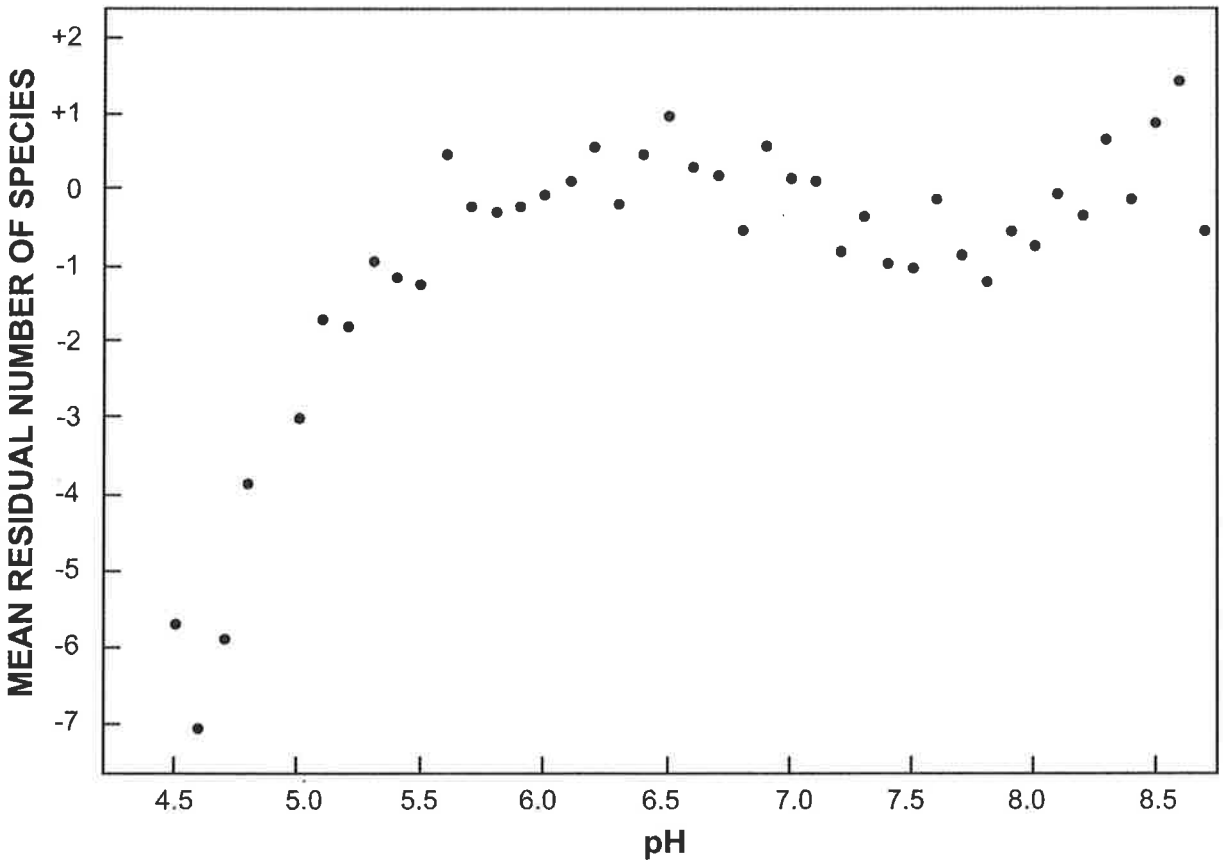


Figure 5-25. Mean residual number of species per lake for lakes in Ontario, by pH interval. The residual number of species for a lake is the deviation of the observed number from the number predicted by lake area.

Source: Matuszek and Beggs (1988).

A study in the Adirondacks found that among the studied lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH higher than 6.5 (Baker et al., 1990b; Driscoll et al., 2001).

Biological responses at differing pH levels are summarized in Table B-13 of the ISA, reproduced here in Table 5-11.

Table 5-11 General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.

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

pH Decrease	General Biological Effects
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass). Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.

Evidence of changes in biological endpoints in response to changes in pH indicates that while the time to full response varies, and the pH level at which recovery occurs varies, there is clear evidence that increasing pH levels leads to improvements in a number of measures of ecosystem health. In a study in Ontario, there was varied response to increases in pH across studied lakes, with little increase in phytoplankton diversity in one lake as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian, 1996), while in another lake, profound change began at pH 5.5.

Fish populations have recovered in acidified lakes when the pH and ANC have been increased through liming or reduction of acidifying deposition (Beggs and Gunn, 1986; Dillon et al., 1986; Gunn et al., 1988; Hultberg and Andersson, 1982; Keller and Pitblado, 1986; Kelso and Jeffries, 1988; Raddum et al., 1986).

In considering the range of pH values to evaluate further in the context of impacts on public welfare, the overall weight of evidence regarding the full range of biological effect indicators, including mortality, fish health, and biodiversity supports further consideration of a target pH level of no less than 5.5, with some support for pH target levels of 6 to 6.5.

Evidence of effects directly or indirectly related to low ANC levels:

The number of fish species present in a waterbody has been shown to be positively correlated with the ANC level in the water, with higher values supporting a greater richness and diversity of fish species (Figure 5-26 and 5-27). The diversity and distribution of phyto-zooplankton communities are also positively correlated with ANC.

When comparing lower ANC to higher ANC streams, the lower ANC streams demonstrated severe mortality in young fish due to a sharp drop in pH and increase in Al

concentrations. The higher ANC stream maintained a pH level greater than 6.6 with correspondingly low Al concentrations (MacAvoy et al 1995). In streams with chronically low ANC, pH levels were in the range of 5.3 to 5.6, and a steady decline in trout populations was observed.

Within the range where ANC is the limiting indicator, (e.g. ANC range from -50 to 100 μeq/L) the relationship between ANC and ecosystem impacts ranges from linear to non-linear, with a sigmoidal shape. Evidence shows a linear relationship in streams in the Eastern U.S., and a non-linear relationship in lakes in the Northeastern U.S. (Figures 5-26 and 5-27).

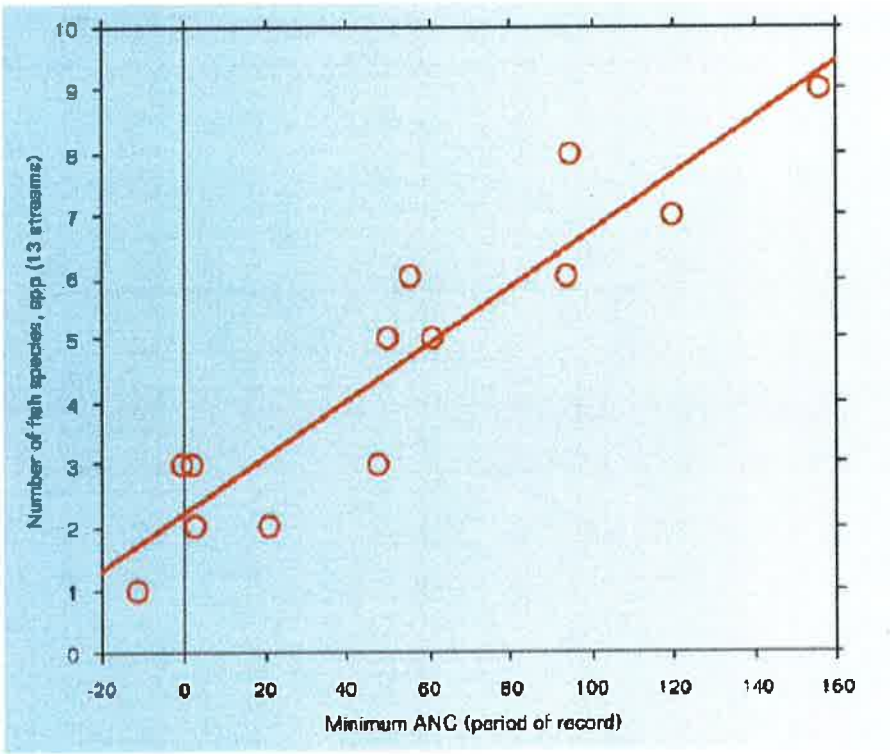
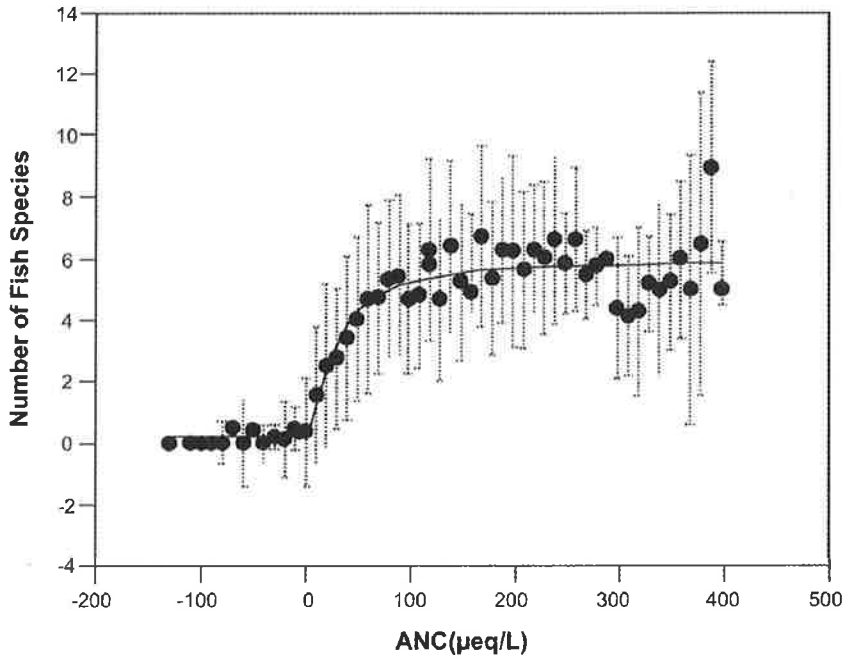


Figure 5-26 Relationship between ANC and number of fish species present in aquatic freshwater ecosystems in Shenandoah National Park (Source: Arthur Bulger, University of Virginia, reproduced from NAPAP, 2005.)



Source: Sullivan et al. (2006)

Figure 5-27. Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 μeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

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**).

For freshwater systems, ANC levels can be grouped into five major classes: <0, 0–20, 20–50, 50–100, and >100 μeq/L, with each range representing a probability of ecological damage to the community. The five categories of ANC and expected ecological effects are described Table 2-1 in Chapter 2 and are supported by a large body of research completed throughout the eastern United States (Sullivan et al., 2006).

In a study in Maryland, Gerritsen et al. (1996) found that at an ANC less than 40 to 70 μeq/L, Yellow perch had a risk of exposure to its critical pH =5.5 of greater than 50 percent. Figures from that study, reproduced in Figure 5-24 above, show the relationships between ANC and the probability of exceeding benchmark pH levels that have been associated with mortality in the Yellow perch and River herring. These figures demonstrate two important principles, 1) as ANC levels fall, the distribution of pH shifts to the left, with increasing probability of low pH

levels, and 2) as ANC levels fall, the probability of exceeding mortality thresholds increases, but this relationship varies by fish species.

The specific relationship between ANC and the probability of exceeding benchmark pH levels varies by water body and fish species. However, based on Figure 5-23, ANC levels matching the target pH levels of 5.5 to 6.5 discussed in the previous section range from approximately 0 to 50 μeq/L. In considering the range of ANC values to evaluate further in the context of impacts on public welfare, the overall evidence on effects at lower ANC levels described in Table 2-1, supports further consideration of a range of ANC from 20 to 50 μeq/L. While Figure 5-23 suggests some probability that ANC levels down to 0 μeq/L are correlated with pH levels of 5.5, the specific relationship between ANC and fish species diversity shown in Figure 5-27 indicates that at an ANC of 0 μeq/L, there is significant damage to ecosystems with almost complete loss of fish species, which indicates that an ANC of 0 μeq/L is not an appropriate target level to protect against significant damage to ecosystems.

Evidence and Risk Based Conclusions regarding target ANC levels

ANC values less than or equal to 0 μeq/L are chronically acidic and can lead to complete loss of species, and major changes in the ability of waterbodies to support diverse biota, especially in water bodies that are highly sensitive to episodic acidification. Biota are generally not harmed when ANC values are >100 μeq/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 μeq/L. This suggests that at ANC greater than 100, little risk from acidification exists in many aquatic ecosystems. At ANC levels below 100 μeq/L, overall health of an aquatic community can be maintained; however, fish fitness and community diversity begin to decline. At ANC levels between 100 and 50 μeq/L, the likelihood that fitness of sensitive species (e.g., brook trout, zooplankton) will begins to decline is increased. When ANC concentrations are <50 μeq/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 health of fish populations, affecting reproductive ability and fitness. ANC levels below 20 μeq/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 5.2.2.1 and REA 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 μeq/L. Overall, there is little uncertainty that significant effects on aquatic biota are occurring at ANC levels below 20 μeq/L.

Based on the field data from the Adirondacks and Shenendoah case study areas, ANC levels less than 50 μeq/L are adverse to ecosystem health, and are likely to lead to reductions in ecosystem services related to recreational fishing. However, the types of effects, specific species, and prevalence of effects across water bodies in the U.S. is more uncertain at ANC levels between 20 and 50 μeq/L. ANC levels between 50 and 100 μeq/L are potentially adverse to ecosystem health, and may result in losses in ecosystem services, but the effects are less severe and greater uncertainty exists as to the magnitude of ecosystem service impacts.

Consideration of the appropriate levels of ANC to target in the standard to reduce the likelihood of effects from aquatic acidification can be based upon the above presented categories of aquatic status in Table 2-1. Using this information as well as information provided by both the ISA and REA, the lowest two categories (0 and <20 μeq/L) would appear inadequate to protect against catastrophic loss of ecosystem function. While ecological effects occur at ANC levels below 50 μeq/L, the degree and nature of those effects is less significant than at levels below 20 μeq/L. Levels between 50 and 100 μeq/L would provide additional protection; however, uncertainties regarding the additional reduction in adverse welfare effects are much larger for target ANC levels above 50 μeq/L.

The target ANC level specified in designing the standard is only one part in determining the overall protectiveness of the standard. The degree of protectiveness is based on all elements of the standard, including the target ANC, the size of the spatial areas over which the standard is applied, the percent of aquatic ecosystems targeted within a spatial area that is selected by the Administrator in light of the selected ANC level, the atmospheric indicator, the calculated values for the deposition transformation ratios (T_{NOx} and T_{SOx}), and the calculated value for reduced nitrogen deposition (NHx). There are widely varying degrees of uncertainty associated with all of these elements, some being

much more certain and others being much less certain. The specified target ANC level is a crucial part in determining the adequacy of protection provided by an AAPI, but it is the overall design and content of the standard that must be considered in judging the adequacy of protection it provides.

Consideration of the target ANC should also reflect that an adequate level of ANC should protect against episodic as well as long term effects. Selecting a higher chronic ANC level can provide greater protection against short term peaks in acidification. In addition, selection of ANC values in the lower end of the range of 20 to 50 μeq/L provides less protection against these short term episodic effects. Selection of target ANC values in the upper end of the range from 20 to 50 μeq/L provides additional protection against episodic peaks in acidification.

When considering a standard to protect against aquatic acidification, it is necessary to take into account both the time period desired for recovery as well as the potential of recovery. 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 μeq/L. Therefore, for these waterbodies, no reduction in input is likely to achieve an ANC of 50 μeq/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 waterbodies, the time to recovery would be largely dependent on future inputs of acidifying deposition.

The concept of target ANC is based on the long-term response of aquatic ecosystems. The time required for a waterbody to achieve the target ANC given a decrease in emissions such that the critical load for that target ANC is not exceeded is often decades if not centuries. In recognition of the potential desire to achieve 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. Similarly, one might also consider specifying a target ANC that will yield an intermediate ANC level within a specified time horizon. For example, if there is a desire to obtain an ANC of 20 μeq/L by 2030, it might be necessary to use the depositional loadings equivalent to obtaining a target ANC of 50 μeq/L which will ultimately be realized many years later. The depositional loading associated with the interim ANC target is called the target load. The implication of this is that an important component of the decision on the level of the AAPI is the timeframe in which the desired ANC value is to be achieved. There is a great deal of heterogeneity in the response time among waterbodies, and as such, specific quantification of the relationship between the critical loads and target loads is not possible.

5.4.2 Additional information on Target ANC levels

A number of regional organizations, states, and international organizations have developed critical loads frameworks to protect against acidification of sensitive aquatic ecosystems. In considering the appropriate range of target ANC levels, 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 3 provides a detailed discussion of how critical loads have been developed and used in other contexts. This section summarizes the specific target ANC values and their rationales.

The UNECE has developed critical loads in support of international emissions reduction agreements. As noted in Chapter 3, critical loads were established to protect 95 percent of surface waters in Europe from an ANC less than 20μeq/L, based on protection of brown trout. Individual countries have set alternative ANC targets, for example, Norway targets an ANC of 30 μeq/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 μeq/L (or higher). Vermont has set

an explicit ANC target of 50 μeq/L. Tennessee has established site specific target ANC values based on assessments of natural acidity, with a default value of 50 μeq/L when specific data is not available.

Taken together, these policy responses to concerns about ecological effects associated with acidification indicate that target ANC values between 20 and 50 μeq/L have been selected by states and other nations to provide adequate protection of lakes and streams in some of the more sensitive aquatic ecosystems.

5.4.3 Adversity of ecological impacts associated with alternative target ANC levels

The point at which effects on public welfare become adverse is not specifically defined in the Clean Air Act. In Chapter 3 we explained that 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. Consideration of adversity in the context of the secondary NOx and SOx standards can be informed by information about losses in ecosystem services associated with acid deposition, and the potential economic value of those losses (Chapter 3).

Ecosystem service losses at alternative levels of ANC are difficult to enumerate. However, in general there are categories of ecosystem services (discussed in detail in Chapter 3) 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 μeq/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 a value of $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 an ANC of 20 to 50 μeq/L, the study implies benefits to the New York population of $400 to $900 million per year (in constant 2007$) for achievement of an ANC of 20 μeq/L, and $300 to $800 million per year for achieving an ANC of 50 μeq/L. 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 WTP include resident's benefits for potential birdwatching 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 public welfare, impacts associated with ANC greater than 50 μeq/L are adverse to public welfare.

5.5 Options for specifying the targets for the deposition metric

This section outlines the steps necessary to aggregate critical loads to form a depositionl metric ($DL_{\%ECO}$) for a broad geographic area at a desired level of protection. In this chapter, evaluate $DL_{\%ECO}$ for several of the options for categorization of landscape sensitivity based on acid-sensitivity that are presented in section 5.3. The options include one $DL_{\%ECO}$ for the entire population of lakes and streams at a given level of protection, creating two categories (sensitive and less-sensitive) with a distinct $DL_{\%ECO}$ for each, and a cluster approach which creates multiple categories of sensitivity for which $DL_{\%ECO}$ are calculated. Regardless of the method of aggregation, the question becomes how to choose a $DL_{\%ECO}$ value to represent the population of CL for waterbodies. For the purpose of comparison, we have chosen to calculate the $DL_{\%ECO}$ from the 90 percentile CL, 75 percentile CL and 50 percentile CL for each method of aggregation. Using this method, the target $DL_{\%ECO}$ becomes that value which represents protection for 90%, 75% or 50% of the population of waterbodies for a desired level of ANC and would not offer the same degree of protection to those waterbodies with CL less than the chosen $DL_{\%ECO}$. While we would not expect the same degree of protection for these waterbodies, they would likely receive some benefit from the reduced deposition necessary to meet the selected $DL_{\%ECO}$. This chapter will therefore also present comparisons between the percentage of waterbodies that would be protected at given $DL_{\%ECO}$ from an ANC <50 μeq/L and those that would likely be protected from an ANC <20 μeq/L at the same $DL_{\%ECO}$. These comparisons are described below.

Table 5.12 shows a comparison between the percent of waterbodies that would be protected from ANC<50 using 90%, 75% and 50% $DL_{\%ECO}$ for the one population approach and those that, while not protected from an ANC <50 μeq/L would be protected from an ANC<20 μeq/L. The selection of the $DL_{\%ECO}$ for ANC at 50 μeq/L representing 90% of the waterbodies would likely protect 97% of all waterbodies from having an ANC<20 μeq/L. If the 75% $DL_{\%ECO}$ for ANC 50 μeq/L was chosen, 83% of waterbodies would likely be protected from an ANC<20 μeq/L and if the 50% $DL_{\%ECO}$ was chosen only 56% of waterbodies would likely be protected

against an ANC <20 μeq/L. This is an important distinction as severe degradation is likely to occur in lakes and streams with ANC<20 μeq/L.

Table 5-12. Comparison of percentage protection from ANC values less than 50 and less than 20 using DL that result when the US is considered one population.

Percentile protection	$DL_{\%ECO}$ (meq/m^2/yr)	Total number of Sites in Analysis	Total Number of Sites protected from ANC <50	Total % Sites protected from ANC <50	Total Number of Sites protected from ANC <20	Total % Sites protected from ANC <20
90%	27	5280	4778	90	5145	97
75%	55	5280	3973	75	4394	83
50%	118	5280	2654	50	2947	56

Table 5.13 shows a comparison between the percent of waterbodies that would be protected from ANC<50 μeq/L using 90%, 75% and 50% $DL_{\%ECO}$s for subdividing the U.S. into two acid-sensitivity categories and those that, while not protected from an ANC <50 would likely be protected from an ANC<20 μeq/L. **Sensitive Category**: The selection of the $DL_{\%ECO}$ for ANC50 μeq/L representing 90% of the sensitive waterbodies would likely protect 98% of all waterbodies from having an ANC<20 μeq/L. If the 75% $DL_{\%ECO}$ for ANC 50 μeq/L for sensitive waterbodies was chosen, 84% of waterbodies would likely be protected from an ANC<20 μeq/L and if the 50% $DL_{\%ECO}$ were chosen only 57% of waterbodies would likely be protected against an ANC <20 μeq/L. **Less-sensitive Category:** The selection of the $DL_{\%ECO}$ for ANC50 representing 90% of the non-sensitive waterbodies would likely protect 92% of all waterbodies from having an ANC<20 μeq/L. If the 75% $DL_{\%ECO}$ for ANC 50 μeq/L for sensitive waterbodies was chosen, 77% of waterbodies would likely be protected from an ANC<20 μeq/L and if the 50% $DL_{\%ECO}$ were chosen only 52% of waterbodies would likely be protected against an ANC <20 μeq/L.

Table 5-13. Comparison of percentage protection from ANC values less than 50 and less than 20 using DL that result when the US is divided into two categories, sensitive and less sensitive based on ANC data.							
	Percentile protection	$DL_{\%ECO}$ **(meq/m^2/yr)**	**Total number of Sites in Analysis**	**Total Number of Sites protected from ANC <50**	**Total % Sites protected from ANC <50**	**Total Number of Sites protected from ANC <20**	**Total % Sites protected from ANC <20**
Sensitive	90%	26	4553	4104	90	4451	98
	75%	51	4553	3428	75	3841	84
	50%	106	4553	2284	50	2575	57
Less sensitive	90%	53	727	655	90	672	92
	75%	117	727	546	75	560	77
	50%	277	727	364	50	377	52

The sensitive category can be further subdivided into ecoregions (Option 2c in section 5.3) and the deposition metrics would be calculated only from sites within the ecoregions. The $DL_{\%ECO}$ values calculated for each ecoregion (level 3) are presented in Table 5.14s. The $DL_{\%ECO}$ s calculated for the sensitive category of waterbodies (the CLs from all ecoregions considered sensitive are pooled together) are compared against the $DL_{\%ECO}$ developed for each ecoregions within the sensitivity category for both ANC 50 μeq/L and ANC 20 μeq/L and for each percentile (90, 75 and 50).

[Placeholder for additional discussion on percentile values]

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6. CO-PROTECTION FOR OTHER EFFECTS USING STANDARDS TO PROTECT AGAINST ACIDIFICATION

Discussion in this Policy Assessment on the NO_X and SO_X secondary standard has, to this point, centered on the level of protection of aquatic ecosystems against acidification from atmospheric deposition of NO_X and SO_X. This chapter focuses on the co-protection such a standard could achieve for other ecological effects, including terrestrial acidification, terrestrial nutrient enrichment, and estuarine eutrophication.

6.1 To What Extent Would A Standard Specifically Defined To Protect Against Aquatic Acidification Likely Provide Protection From Terrestrial Acidification?

To understand the level of co-protection a NO_X and SO_X secondary standard based on aquatic acidification can provide for terrestrial ecosystems, EPA staff conducted an analysis 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 to protect for an acid neutralizing capacity (ANC) of 50μeq/L, and were taken directly from the Risk and Exposure Assessment (REA) (2009). The 50μeq/L ANC value was one of three values modeled in the REA (2009) 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 is more conservative, 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 (2009) 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 (2009). For each Case Study Area, four watersheds were randomly selected from each of the four aquatic acidification sensitivity classes reported in the REA (2009). 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 B of this Policy Assessment document provides a full description of the methods and results of this comparative analysis.

Results of the comparison between the aquatic critical acid load (ANC = 50 μeq/L) and the terrestrial critical acid loads (Bc:Al 1.2 and 10.0) for the 32 watersheds are presented in **Tables 6.1 and 6.2**. 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 (Table 6.1).

Table 6-1. 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
Shenandoh	14 of 14	5 of 5	0 of 1	0 of 1

Table 6-2. 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
Shenandoh	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.

6.2 To What Extent Would A Standard Specifically Defined To Protect Against Aquatic Acidification Likely Provide Protection From Terrestrial Nutrient Enrichment?

The figure below summarizes the terrestrial nutrient enrichment effects from nitrogen discussed in the REA (2009). The REA reported these benchmarks as kg/ha/yr. To convert to meq/m2/yr each benchmark number must be multiplied by 7.14. The range in meq/m2/yr thus becomes 10.7 meq/m2/yr for the low end benchmark of changes to diatom community structure to 321 meq/m2/yr at the high end benchmark associated with nitrate leaching, high foliar nitrogen, and high NO emissions in southern California.

For each depositional load that is considered for aquatic acidification, whether it is a national number or a sensitivity based number, it can be compared against the chart in figure 6.1 to understand the level of protection offered in individual parts of the country where these studies were conducted. For example referring back to the figure under option 1 in section 5.3.2, the depositional load selected to encompass 90% of the critical loads on a national basis to protect for an ANC of 50 is described as a tradeoff curve between sulfur and nitrogen. If sulfur were zero then the maximum nitrogen deposition would be 79 meq/m2/yr or 11 kg/ha/yr. Comparing this maximum nitrogen deposition number to the benchmarks in figure 6.1 shows that the depositional load would provide some protection against leaching in northeast forests, but would have to be lower to protect California coastal sage scrub, lichens in mixed conifer forests, alpine lake communities, and Minnesota grasslands.

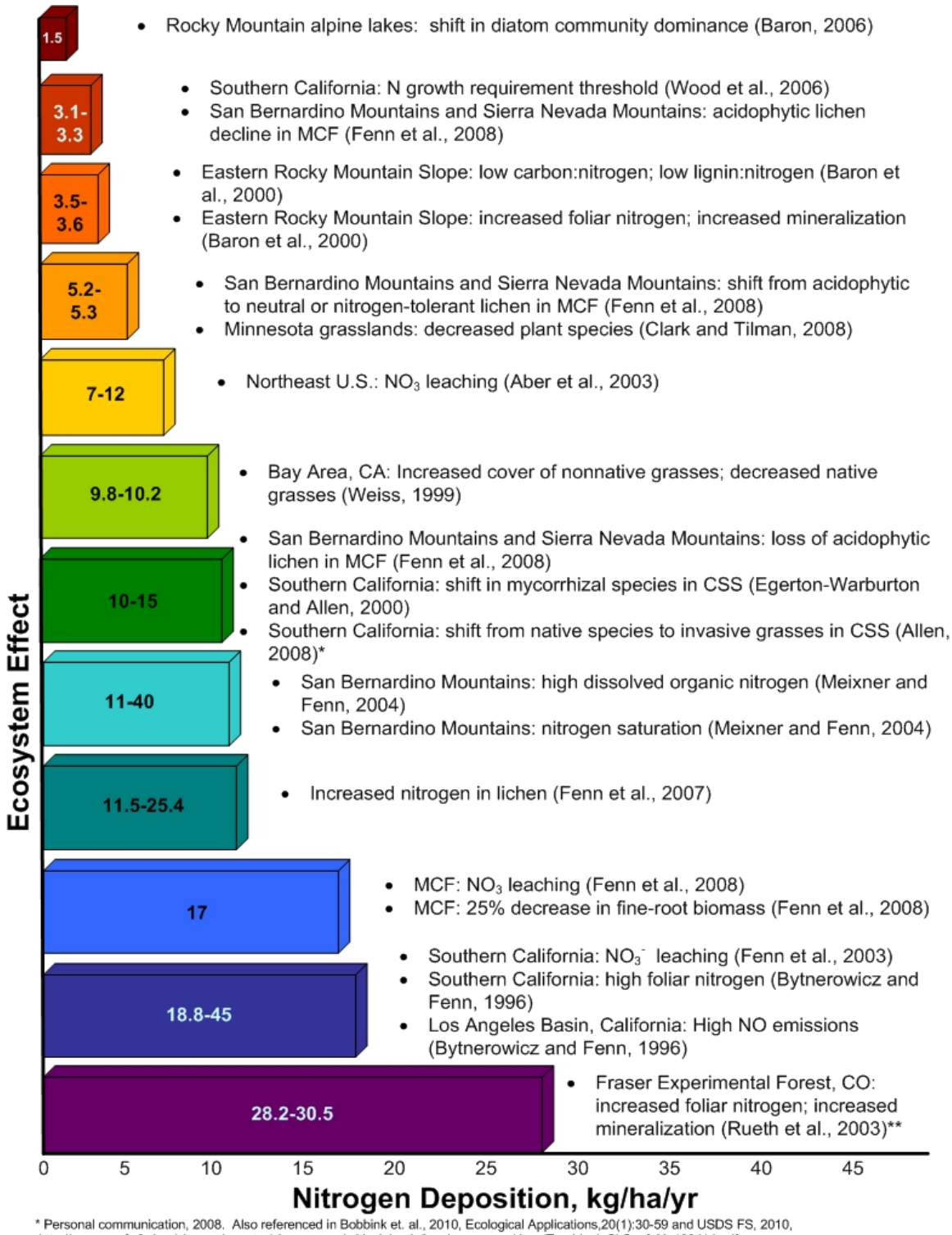

Figure 6-1 Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators.

6.3 To What Extent Would A Standard Specifically Defined To Protect Against Aquatic Acidification Likely Provide Protection From Aquatic Nutrient Enrichment?

The REA (2009) 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. Due to the complications of separating out the effects of atmospheric deposition from the effects of other nitrogen loads, CASAC did not recommend that a secondary NAAQS be set to specifically protect against estuarine eutrophication at this time.

As described in the REA (2009), the Chesapeake Bay is one national estuary that is suffering from eutrophication. In issuing his Executive Order on the Chesapeake Bay, 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 6.2, this number can be compared to the maximum depositional load of 79 meq/m2/yr. If sulfur were zero on the national tradeoff curve from the figure under option 1 of section 5.3.2, then the allowed depositional load of 79 meq/m2/yr would not meet the Chesapeake Bay TMDL as currently envisioned.

6.4 REFERENCE

US EPA (United States Environmental Protection Agency). 2009. *Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Sulfur*. Final. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Research Triangle Park, NC. September.

7 EVALUATION OF UNCERTAINTY AND VARIABILITY IN THE CONTEXT OF AN AAPI STANDARD, INCLUDING MODEL EVALUATION, SENSITIVITY ANALYSES, AND ASSESSMENT OF INFORMATION GAPS

7.1 INTRODUCTION AND PURPOSE

This chapter provides discussions of results of analyses and assessments intended to address the relative confidence associated with many of the individual and combined components of the linked atmospheric-ecological effects system described in Chapter 5, as well as important uncertainties in the scientific evidence that should be considered in developing options for the standard. This chapter is intended to integrate a variety of analyses related to the sensitivity of the models and model components to uncertainty and variability, and place the results of those analyses within the context of the conclusions that can be drawn regarding the components of the AAPI. These components include ecosystem effects; dose-response relationships; underlying ecosystem sensitivity to acid deposition, biogeochemical, atmospheric and deposition processes; and characterization of ecosystem services. While several processes are imbedded in the AAPI equation introduced in Chapter 5, the level of the AAPI, as in all NAAQS, is to include consideration of information on uncertainty and variability. Consequently, knowledge of the relative confidence and natural variability in the structural components of the AAPI are considered in staff conclusions on options for ranges of the level of the standard. This chapter is not intended to be a comprehensive treatment of all uncertainties that exist relative to the overall review of the standards, instead, it focused on those that are most relevant in evaluating choices regarding the AAPI form of the standard and options regarding the indicator, averaging time, and ranges of levels of the AAPI-based NOx and SOx standard.

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 overall AAPI to the components of the equation proposed to calculate the AAPI can help

demonstrate how important uncertainty and variability in those components are in assessing the protection of ecosystems provided by an AAPI standard. To evaluate the potential interactions between uncertain and/or variable AAPI 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. In addition to informing considerations of the AAPI level, 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 AAPI components are especially useful to inform monitoring network design, the spatial boundaries of acid sensitive regions, and averaging periods relevant to NAAQS implementation.

*Use of confidence assessment results to inform setting of the AAPI level***.**

The analyses summarized in this chapter largely address parameters related to atmospheric/deposition and biogeochemical characterization, which are incorporated in the AAPI. General uncertainty related discussions are provided for elements in the standard setting process including dose-response relationships, effects, economic valuation metrics, as well as for several specific processes (e.g., organic nitrogen) which are directly represented in the AAPI. Confidence related information is not used to make decisions on inclusion or exclusion of a parameter in the AAPI model. Instead, we develop the overall approach using the best available information and most practical approaches, with an understanding of the level of confidence associated with both individual components and the overall resulting AAPI. The overarching principle in setting the level of the AAPI is consideration of the impact that associated NOx and SOx levels will have on the level of protection from adverse effects on public welfare. Information on uncertainty in different elements of the form of the standard and the scientific evidence informing those elements is used to evaluate our confidence that the standard has a high likelihood of protecting public welfare. One way of considering confidence levels is to identify components of the standard for which we have low confidence and adjust the level of the AAPI to ensure that, given the uncertainty in those components, we have a high likelihood of achieving a target level of protection. This approach to considering confidence levels places greater weight on ensuring a high likelihood of achieving protection, and places less weight on

concerns about providing more that requisite protection. Conversely, low confidence in components of the standard could also be considered to increase the likelihood that more than requisite protection could result, and consequently, the AAPI could be adjusted downward to account for lower confidence that the level of protection is requisite. To the extent that the available information suggests that a particular process or parameter creates a positive or negative bias (as opposed to broader uncertainty with no clear direction) would lead to recommending correspondingly higher or lower AAPI level. The Clean Air Act (CAA) language requires the secondary standards to be set to provide a requisite level of protection against known or anticipated effects, which can be interpreted to include effects which have large uncertainty but for which the expectation of adverse effects on public welfare exists with reasonable confidence.

Significant emphasis is placed on evaluations of CMAQ due to the unique role that atmospheric models hold in the linked AAPI system. The AAPI as currently formulated relies on CMAQ for both the initial characterization of reduced nitrogen deposition, and the deposition transformation ratios (T_{NOx} and T_{SOx}) which characterize the relationships between atmospheric concentrations of NOx and SOx and deposition of N and S. 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 guide implementation strategies for monitoring network design and emission inventory improvement. Sensitivity of CMAQ derived deposition transformation ratios to changes in emissions, and treatment of chemistry [not yet completed] and variability over time provide insight into the stability of these parameters that are used in a relatively static manner in the AAPI, and into how well proposed 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. The MAGIC critical load simulations also provide information on the temporal trajectory of ANC, including the expected time necessary to reach a desired ANC, which can help inform the level of the AAPI, recognizing that there may be additional consideration given to reaching a target ANC within a specific timeframe, e.g. by 2030 or 2040. [[not yet completed]

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. As a result, these uncertainties are more difficult to explicity account for in development of the standards. In the case of the equation describing the AAPI, while the degree of uncertainty in some elements can be characterized, sometimes quantitatively, a formal uncertainty analysis using statistical sampling techniques (e.g., Monte Carlo simulation) to identify the relative and combined influences of parameter uncertainty was not performed. However, we did evaluate the sensitivity of the AAPI to its components using two related assessments: analysis of variance (ANOVA) and elasticity calculations. The results of these assessments are addressed in section 7.5.

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, e.g. the AAPI level, 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 PAD are intended to provide insight into the relative stability of the AAPI and associated NOx and SOx tradeoff curves and confidence in modeled parameterizations. Sensitivity analyses are especially useful in the

absence of observed data to challenge models. For example, the NOy and SOx transference ratios are a model construct that is difficult, if not impossible, to compare to observations. The sensitivity of these ratios to changing meteorology, emissions and chemical mechanism treatments 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 AAPI results) of AAPI parameters. Toward that end, ANOVA and elasticity analyses were applied to determine the relative sensitivity of AAPI results associated with individual and combined AAPI parameters.

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 AAPI and trade-off curves, variability is considered in guiding the design of monitoring and modeling analyses supporting implementation activities.

7.2 Uncertainty associated with ecosystem effects and dose – response relationships.

Chapter 2 provides a brief summary of uncertainties based on the REA and is reproduced here to centralize all uncertainty discussions. 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 ANC and atmospheric deposition. 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.

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 was derived from multiple site calibrations. The 95% confidence interval for pre-acidification of lakes was an average of 15 μeq/L difference in ANC concentrations or 10% and 8 μeq/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 (**Figure 7.1-6 REA**).

Chapter 2 also reviews the basic evidence underlying effects on fish mortality, aquatic species diversity and more extended food web disruptions leading to adverse impacts on birds associated with aquatic acidification. There is high confidence associated with causality between acidification and these ecological effects. Also, there is extremely high confidence in the relationship between the ecological indicator, ANC, and the more direct chemical properties (lower pH and increased Al) associated with acidification.

7.3 Uncertainty in benefits estimates

Descriptions of the current provision of ecosystem services presented for each of the effect areas analyzed for this review followed by estimations of the damages incurred to selected services due to nitrogen and sulfur deposition. The current services are presented to give the reader a sense of the magnitude of the benefit the public receives from these ecosystems under current conditions. The data used in these descriptive passages is generally derived from government (either federal or state) sources we are reasonably certain to be of the highest quality. Where monetary values are placed on the these services we have generally used widely cited studies, particularly meta analyses that provide an average value that smoothes the variation in WTP estimates. These estimates underestimate the total value of these services as they use benefit estimates for a marginal increase in these services. It is likely that the total benefits of these services are greater because their marginal value likely is lower than the average value. While reductions in sulfur and nitrogen emissions would increase the size of the benefits from these services, for many of them it is unknown how significant the increase will be.

The analyses of damages incurred are more uncertain and are limited to those areas where data and tools were available. Only some services were analyzed which in some cases meant that the results were limited to one or two services and in the case of terrestrial nutrient enrichment no services had sufficient data available to attempt an estimate of damage. This means that the estimates presented are a very small part of the total damage incurred due to deposition.

Aquatic Acidification

Recreational Fishing Model.

The analysis of recreational fishing damages presented in Chapter 3 is subject to the assumptions necessary to perform the analysis. The original analysis performed for the REA was based on projecting future benefits of increased recreational fishing based on a complete cessation of all nitrogen and sulfur emissions. These decisions under or over estimate the current damages to public welfare incurred from nitrogen and sulfur deposition. The magnitude of the bias in results is unknown in either direction however the majority of the assumptions influence

the estimates downward. These include the use of emissions estimates that include projected decreases due to implementation of Title IV regulations in 2020. These emissions estimates are lower than current emissions and therefore lead to underestimation of damages. Because the models only value this improvement for New York residents (without accounting for out-of-state visitors) the damages are underestimates of the benefits of these improvements in the Adirondacks region.

The use of projected population in the REA analyses contributes to an overestimate of current damages since current population is smaller than future population. Further, these estimates are extrapolated from a 44 lake subset and applied to all Adirondack lakes. The representativeness of this sample is unknown. This analysis also does not account for any change in fishing demand (possible overestimate) and income (possible underestimate).

Banzhaf, et al Benefits Transfer.

The approach using the WTP estimates from the Banzhaf study is subject to the same uncertainties described above and some additional considerations. Specifically there is some uncertainty regarding which types of ecosystem services are reflected in the study's estimates of the improvements in ecosystem services of reducing acidification, particularly provisioning and regulating services. The values likely include recreational fishing services, which means *they cannot be added to the recreational fishing model results,* and other cultural services including other recreation and nonuse services. The inclusion in the survey of other ecosystem changes (birds, trees, etc.) leads to an overestimation of WTP for remediation of lake acidification alone. Finally, assumptions were required to align the Banzhaf survey scenarios to the likely results of complete removal of all nitrogen and sulfur emissions. These are reasonably close but not exact and may not be applicable to another baseline.

Conclusion.

While these estimates are subject to uncertainty we are reasonably confident that they represent a good first-order approximation of the damages to recreational fishing due to nitrogen and sulfur deposition. Additionally it should be noted that the Banzhaf survey results represent a broader picture (though by no means complete) of the damages to ecosystem services in the Adirondacks. Finally, we would again like to emphasize that these estimates represent only a

small sample of the damages incurred to a broad range of ecosystem services affected and the areas of the nation where acidic deposition is an ongoing issue.

7.4 CMAQ Application and Evaluation

7.4.1 Overview of CMAQ model application

The CMAQ model is a comprehensive, peer-reviewed (Aiyyer et al., 2007), 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 deposition over urban, regional, and larger spatial scales (Dennis et al., 1996; U.S. EPA, 1999; Bryun and Schere, 2006). CMAQ is run for user-defined input sets of meteorological conditions and emissions. For this analysis, we are using predictions from several existing CMAQ runs. These runs include annual simulations for 2002 using CMAQv4.6 and annual simulations for each of the years 2002 through 2005 using CMAQv4.7 (Foley et al., 2010). CMAQv4.6 was released by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) in October 2007. CMAQv4.7 along with an updated version of CMAQ's meteorological preprocessor (MCIPv3.4, Otte and Pleim, 2010)[1] were released in October 2008[2]. The 2002 simulation with CMAQv4.6 was performed for both the Eastern and Western domains. The horizontal spatial resolution of the CMAQ grid cells in these domains is 12 x 12 km. The 2002 through 2005 simulations with CMAQv4.7 were performed for the eastern 12-km domain and for the continental United States domain, which has a grid resolution of 36 x 36 km. The CMAQv4.6 and v4.7 annual simulations feature year-specific meteorology, as well as year-specific emissions inventories for key source sectors, such as utilities, on-road vehicles, nonroad vehicles, wild fires, and natural biogenic sources. Emissions for other sectors of the inventory for each of the years modeled rely on inventories for 2002. Details on the development of emissions, meteorology, and other inputs to the 2002 CMAQv4.6 runs can be found in a separate report (U.S. EPA, 2008). Inputs for the CMAQv4.7 runs for 2002 through 2005 were derived using procedures similar to those for the CMAQv4.6 2002 runs.

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

[2] The differences in nitrogen and sulfur deposition in the case study areas between CMAQ v4.6 and v4.7 for 2002 are small, as described in Chapter 3.

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

7.4.2 CMAQ Evaluation, Sensitivity and Variability Analyses

Past results. A variety of comparisons of modeled estimates to observations were included in the REA (EPA, 2009), and some of the highlights are summarized here in addition to new work on ammonia characterization and wet deposition. Readers are encouraged to review the earlier report. Ambient air concentrations and wet deposition observations are paired against modeled estimates. In contrast, dry deposition is always a modeled value, either derived from ambient or modeled ambient concentrations. Given the interest in relevant nitrogen and sulfur species, CASTNET observations were used extensively. Comparisons of modeled annual average total nitrate (sum of nitric acid and particulate nitrate), ammonium, sulfate, and sulfur dioxide to observations for the 2002 base year are provided in Figures 7-1 through 7-4. Normalized mean bias statistics for 2002-2005 base years are provided in Table 7-1.

CMAQ overpredicts SO_2 and underpredicts SO_4. Although model performance is good for total SO_x, the inclusion of co-located SO_2 and sulfate measurements required for future secondary NO_x/SO_x NAAQS comparisons will help diagnose issues with the model's ability to partition these two species. CMAQ generally overpredicts total nitrate and slightly underpredicts ammonium and the model captures the monthly temporal patterns of sulfate, total nitrate and ammonium when all sites are aggregated (Figures 7-5 to 7-7). There are some basic incommensurabilities between model estimates and observations that complicate interpretation of model to observation comparisons, most notably the representation of space as a model represents a volume average of roughly 144 km^2, which depends on the time varying vertical depth of the lowest modeled layer. Most surface based observations rely on point sampling and the extent to which a point is representative of broader volume space varies with meteorology, distribution of emissions and surface characteristics.

Table 7-1. Normalized Mean Bias Statistics for Predicted and Observed Pollutant Concentration

Pollutant Concentrations	2002	2003	2004	2005
SO_2	45%	39%	47%	41%
SO_4^{2-}	-13%	-9%	-13%	-17%
TNO_3	22%	26%	22%	24%
NH_4^+	4%	11%	7%	2%

Ammonia.

Characterizing ammonia deposition is of increasing importance for assessing ecosystem responses to nitrogen deposition. Nitrogen deposition includes both deposition of NOy and deposition of reduced nitrogen (ammonia + ammonium). Ecosystem effects are due to total nitrogenand, as such, the recommended AAPI form of the standard directly includes reduced nitrogen to account for its role in using up an ecosystems ability to absorb nitrogen. The proposed form of the standard uses CMAQ modeled deposition of reduced nitrogen.

Because of a shortage of routinely available ammonia observations, model evaluation studies have relied on ammonium measurements from CASTNET as the only routine source of reduced nitrogen observations. Clearly, the lack of ammonia observations must be addressed in future implementation scenarios as there is relatively greater uncertainty in characterizing ammonia relative to SO_x and NO_y. Recently, Dennis et al. (2011) explored the sensitivity of CMAQ (addressed below) to varying treatments affecting ammonia deposition velocity. As part of that study, CMAQ ammonia estimates were compared with ammonia observations at two sites in North Carolina (Figure 7-8).

Wet deposition.

Modeled wet deposition in CMAQ is a function of the volume of predicted precipitation within a grid cell and the pollutant concentrations scavenged from the atmosphere during precipitation events. As a result, errors in modeled precipitation and in emission inputs can lead to significant bias and error in the wet deposition predictions compared to observed values. EPA

(Dennis and Foley, 2010) has corrected CMAQ wet deposition predictions by scaling the model output based on observation-based gridded precipitation data generated by the Parameter-elevation Regressions on Independent Slopes Model (PRISM, 2004). The precipitation adjusted deposition fields are more highly correlated with observed values for all wet deposited nitrogen and sulfur species compared to the base model output (Figures 7-9). In addition, the adjusted fields are better able to capture the spatial heterogeneity of accumulated wet deposition due to orographic effects on precipitation amounts.

Adjusting the wet deposition values to account for over-predictions in the model precipitation inputs revealed compensating errors for nitrate and ammonium. The negative bias seen in these species after the precipitation adjustment is believed to be due to missing emissions sources. A second bias adjustment was performed for nitrate and ammonium based on observed levels at the NADP/NTN sites (Figure 7-10). The final adjusted spatial fields of annual total wet deposition values are more consistent with observed wet deposition values. Ongoing studies suggest that much of this bias can be reduced in the Eastern half of the US by including nitrogen oxide produced by lightning and accounting for the bi-directional flux of ammonia. Once these model improvements are incorporated in CMAQ a second bias adjustment may not be needed in the East.

7.4.3 Variability and sensitivity of CMAQ generated components.

7.4.3.1 Ambient Concentration to Deposition Transformation ratios.

The deposition transference ratios[3] introduced in Chapter 5 are referenced as T_{SOx} and T_{NOy}, to distinguish these parameters from an exact linkage to deposition velocity, which is uniquely associated with individual atmospheric species. Deposition transference ratios are defined as the annual wet and dry deposition of all oxidized species (NO_y for T_{NOy}, SO_2 plus SO_4 for T_{SOx}) divided by the average annual concentration of NO_y, for T_{NOy}, or SO_4 plus SO_2, for T_{SOx}. The units for T_{NOy} and T_{SOx} are distance/time. Deposition transference ratios provide a mechanism to associate ambient concentrations to deposition loads and to determine if an area's

[3] In the first draft of the Policy Assessment, the deposition transformation ratios were labeled V_{NOx} and V_{SOx}. For this draft, based on recommendations from CASAC, we have renamed these ratios T_{NOx} and T_{SOx}.

air concentrations of NO_y and SO_x meet a NAAQS level using the AAPI form. A deposition transformation ratio is an aggregate representation of the deposition process generated through modeling which does not lend itself to a traditional analysis relating observations and predictions. Furthermore, there is an implicit assumption that the response of deposition transformation ratios to changes in meteorology and emissions is relatively stiff, as these ratios are an attribute of the system that channels ambient air response associated with decreases in emissions of NO_x and SO_x to changes in deposition. The stiffness of the deposition transference ratios would suggest that the relationship between ambient concentrations and deposition is strictly a constant proportion, not impacted by the mixture and level of emissions or by changes in meteorology. To better understand the implications of this assumption, we investigated the relative variability of the modeled deposition transformation ratios across time and space, and the stability of the ratios relative to emissions and meteorological inputs was conducted to guide EPA in determining how uncertainties in this parameter may eventually impact AAPI related calculations.

7.4.3.2 Spatial and Interannual Variation of T_S and T_N.

Generally small spatial and inter-annual variability exist in the deposition transformation ratios for the 2002 -2005 model years (Figure 7-11). The inter-annual variability, calculated at the grid cell level, as measured by the median coefficient of variation is around 10% and the absolute values of the ratios remain stable (Figure 7-12), suggesting that year to year changes in meteorology have minimal impact on the ratios. Spatial homogeneity of deposition transformation ratios within the two acid sensitive areas we evaluated in the REA (Adirondacks and Shenendoah) (Figure 7-11) is consistent with a relatively homogeneous ambient concentration environment overlaid upon a landscape of similar vegetation and surface conditions. Such spatial homogeneity within case study areas provides confidence that an area wide application AAPI will not be strongly dependent on the exact boundaries chosen to define an acid sensitive area.

7.4.3.3 T_{SOx} and T_{NOy} Sensitivity to emission changes.

The response of T_{SOx} and T_{NOy} to emission changes was explored by analyzing available base case 2005 and 2030 CMAQ simulations. The 2030 case reflected expected changes in emissions associated with simulated implementation of a variety of national rules and represents Eastern U.S. domain wide NOx and SOx emission reductions of 48% and 40%, respectively. Median changes in deposition transference ratios tended to be around zero (figure 7-12), with the Adirondack region exhibiting slightly higher response than the Shenandoah region and remainder of the Eastern U.S. domain.

7.4.3.4 T_{SOx} and T_{NOy} sensitivity to different chemical mechanisms.

[Intended to be added in the final PA]

7.4.3.5 Ammonia sensitivity.

The role of NH_x deposition is incorporated in the AAPI expression as a parameter that influences the level of allowable concentrations of NO_y and SO_x, due to its role as part of the total reactive nitrogen budget which affects acidification.. Characterizing ammonia deposition is challenging due to the variety of surface and vegetation types that influence ammonia dry deposition velocities as well the potential for bi-directional flux of ammonia. In addition, ammonia emission estimates remain relatively more uncertain than emissions of NO_x and SO_2 given the complexity of meteorology and agricultural practices that influence the spatial and temporal patterns of ammonia releases. An exploration of the sensitivity of ammonia to three different treatments of deposition processes in CMAQ was performed by EPA (Dennis et al., 2010) to test the inclusion of a bi-directional NH_3 flux algorithm and elucidate the relative importance associated with advection, deposition and chemical transformation on ammonia patterns. These treatments included a (1) base case of current CMAQ treatment using existing ammonia deposition velocity schemes and uni-directional deposition, (2) modified the base case by replacing ammonia deposition velocity calculations with SO_2 deposition velocities (SO_2 interacts with surfaces and vegetation similarly to NH_3, but with reduced velocity) as a lower bound and (3) introducing a bi-directional flux algorithm to the base case (retaining NH3 deposition velocities). Based on modeled process analysis that delineates the effects of deposition, chemical transformation and advection (horizontal and vertical) on emitted ammonia, the results (Figure 7-13) suggest that ammonia patterns, especially when a bi-directional flux process is incorporated, are more indicative of a transported pollutant where emissions influence can span hundreds of kilometers, markedly different from some earlier perspectives where ammonia often was thought of as near source phenomenon due to high deposition velocities. The process analysis illustrates the importance of vertical advection which enables the movement of ammonia into traditional mesoscale flow patterns. The effect is enhanced by the reintroduction of deposited ammonia through bi-directional flux into the ambient environment.

From a monitoring perspective, a design that addresses the regional characterization of NOy and SO_x would be consistent with characterizing NH_x. Not only would ammonia and ammonium measurements be useful for estimating dry deposition through deposition modeling approaches such as those used in CASTNET, but they would serve as important diagnostic data

to continually assess the effectiveness of NH_x deposition processes in models like CMAQ. This is especially important as we recognize a large uncertainty in the bi-directional formulation associated with the estimation of Γ, the emissions potential due to the existence of compensation points. Nonetheless, we can learn much about the NH_3 budget in spite of these uncertainties.

High priority research is ongoing to improve the bi-directional parameterization and the estimates of the leaf and soil gammas across different cropping regions and throughout the year. We are developing a software tool to estimate the soil Γ associated with fertilizer application. When we have a spatially and temporally varying Γ_g, we will investigate the emissions budgets for fertilized fields, as well as reexamine the animal operation emission budgets, as this will be of interest. Work to examine the seasonality of single cell budgets and their range of influence is continuing. Current and future CMAQ applications to ecosystem deposition will incorporate bi-directional flux treatment of ammonia.

7.4.3.6 CMAQ uncertainties and the AAPI

The AAPI relies on CMAQ for the sulfur and nitrogen transference ratios and NH_x deposition. The model evaluation results, including the ammonia and wet precipitation treatments, reflect a continual process of model improvement designed to ingest the latest science within a framework links a myriad of atmospheric and surface processes across multiple pollutant species. While this document focuses in on the more direct processes affecting N and S deposition, these modifications are incorporated with the philosophy that the best science is being adopted and they in turn support the overall improvement of the models' treatment of all processes. The inclusion of better chemistry and physics of a particular process acts as an internal diagnostic tool for other processes that are linked throughout the model framework through basic conservation of mass principles. With respect to the AAPI, the CMAQ model must be relied on to provide the spatial flexibility attendant with a national standard. As the model continually adopts the best science, confidence in relevant CMAQ generated AAPI parameters is raised for both near term and future scenarios.

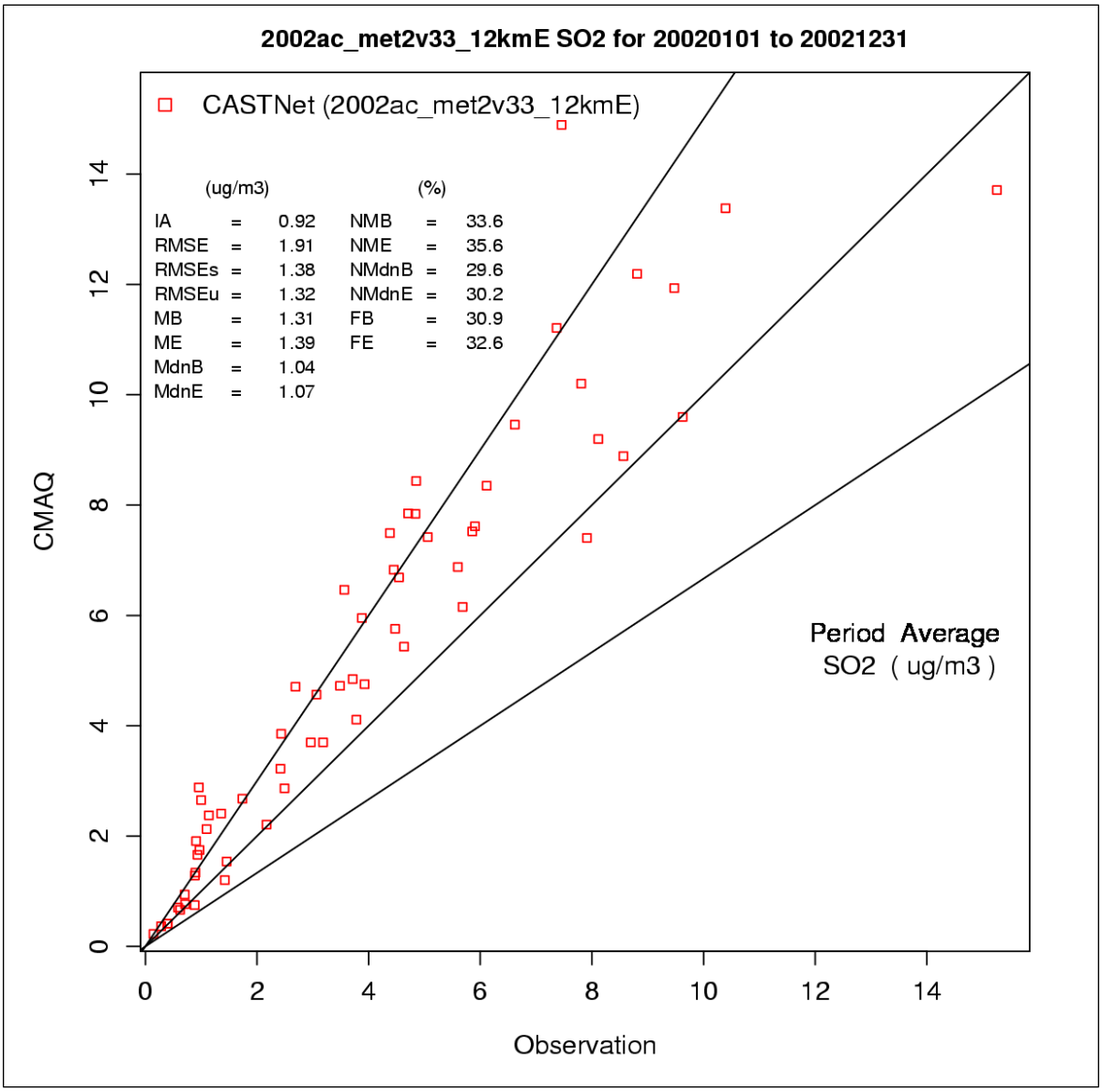


Figure 7-1 **2002 CMAQv4.6 annual average SO_2 predicted concentrations versus observations at CASTNet sites in the eastern domain (note, units are in actual mass for SO_2, including oxygen)**.

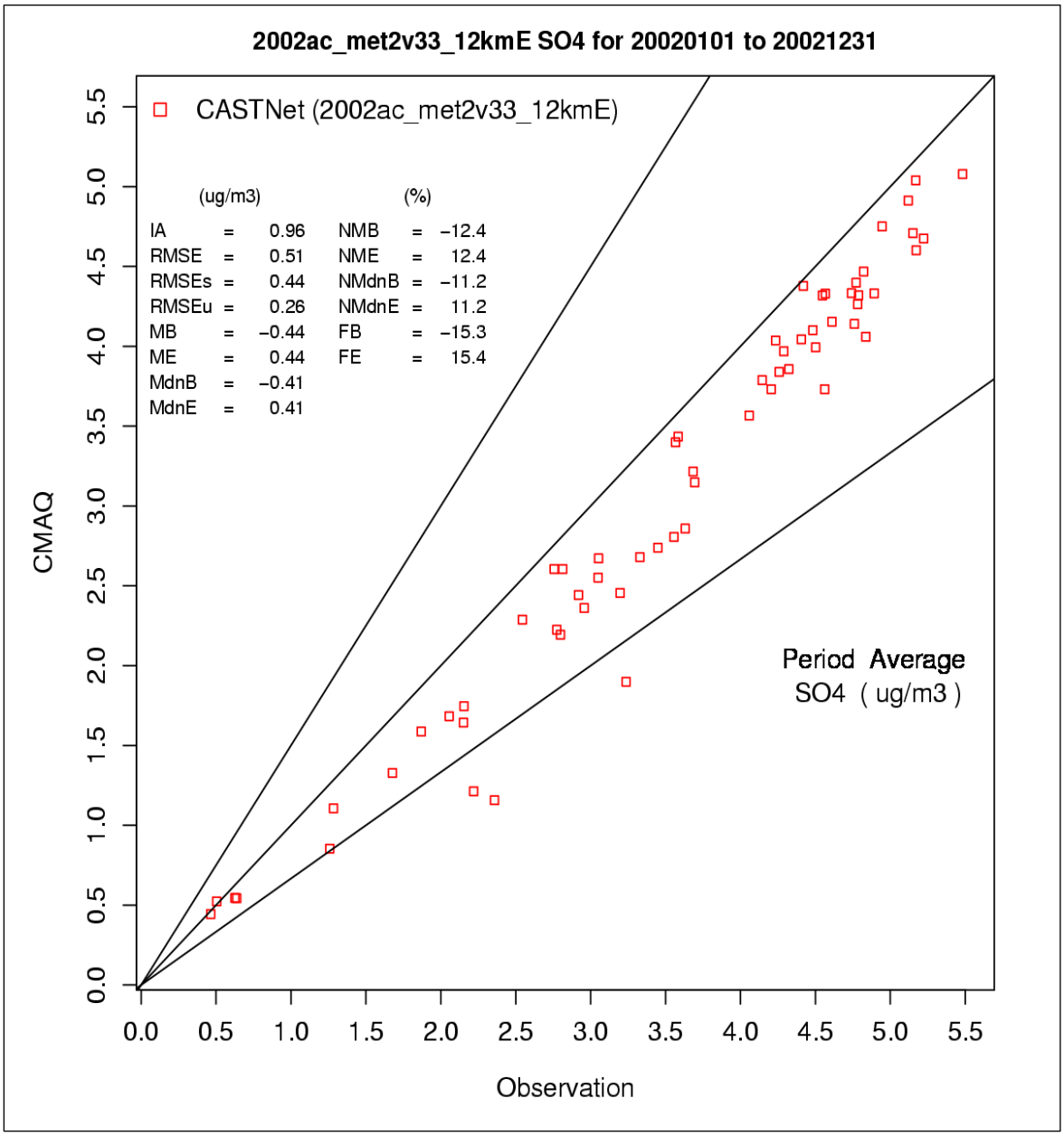


Figure 7-2 2002 CMAQv4.6 annual average SO^{2-}_4 predicted concentrations versus observations at CASTNet sites in the eastern domain (note, units are in actual mass for SO_4, including oxygen).

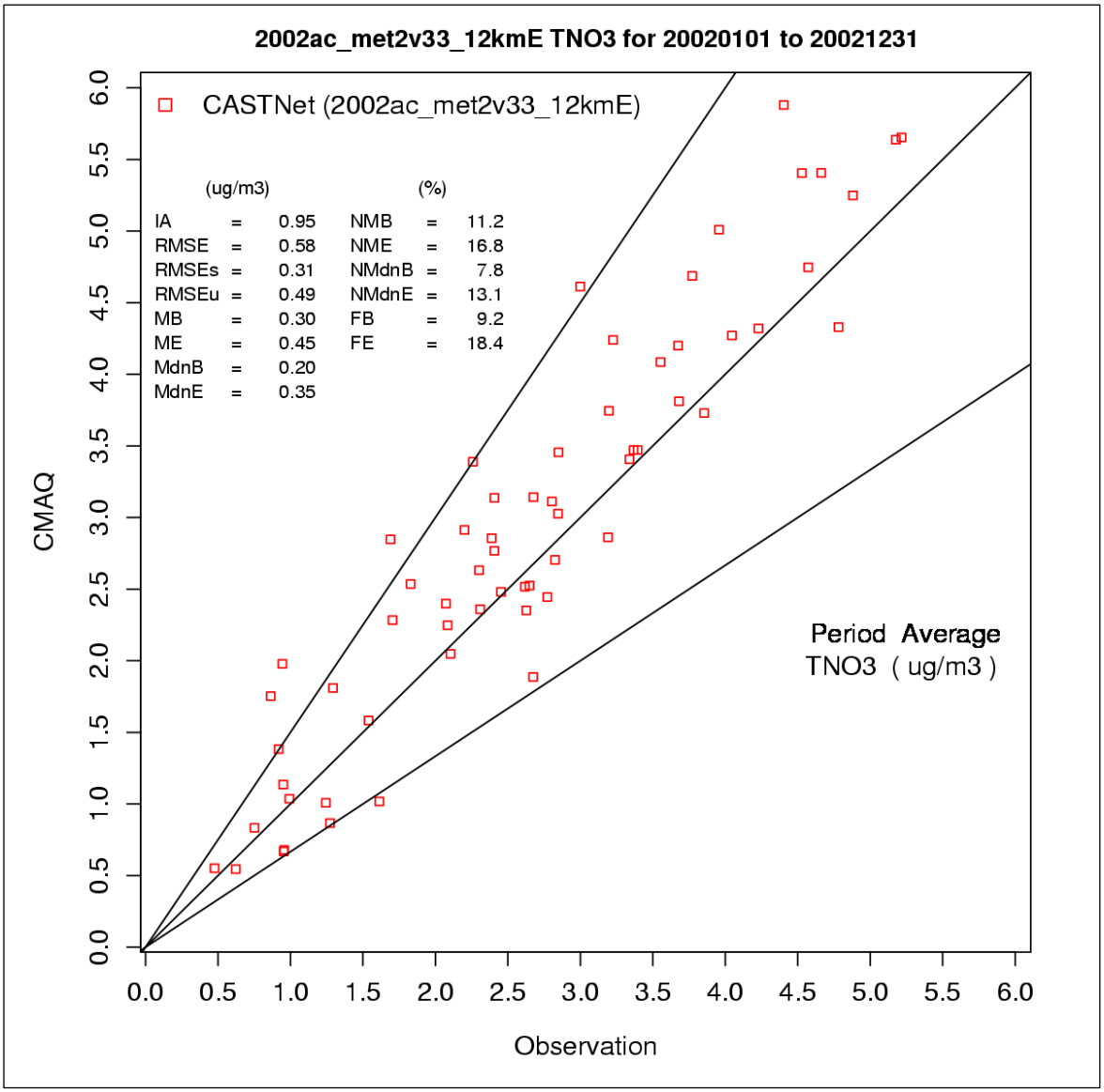


Figure 7-3 **2002 CMAQv4.6 annual average TNO_3 predicted concentrations versus observations at CASTNet sites in the eastern domain (note, units are in actual mass for NO_3, including oxygen).**

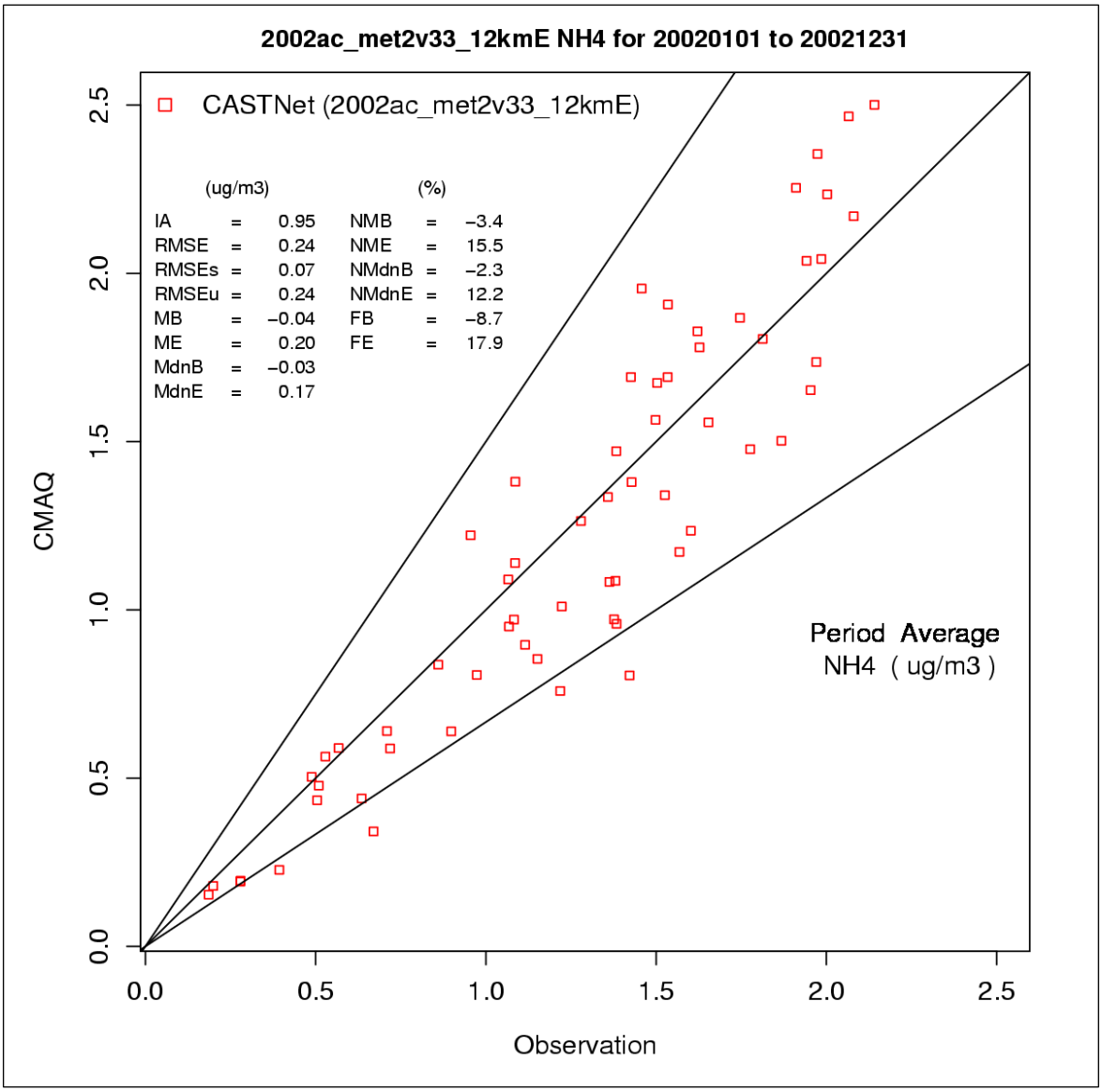


Figure 7-4. 2002 CMAQv4.6 annual average NH_4^+ predicted concentrations versus observations at CASTNet sites in the eastern domain (note, units are in actual mass for NH_4, including hydrogen).

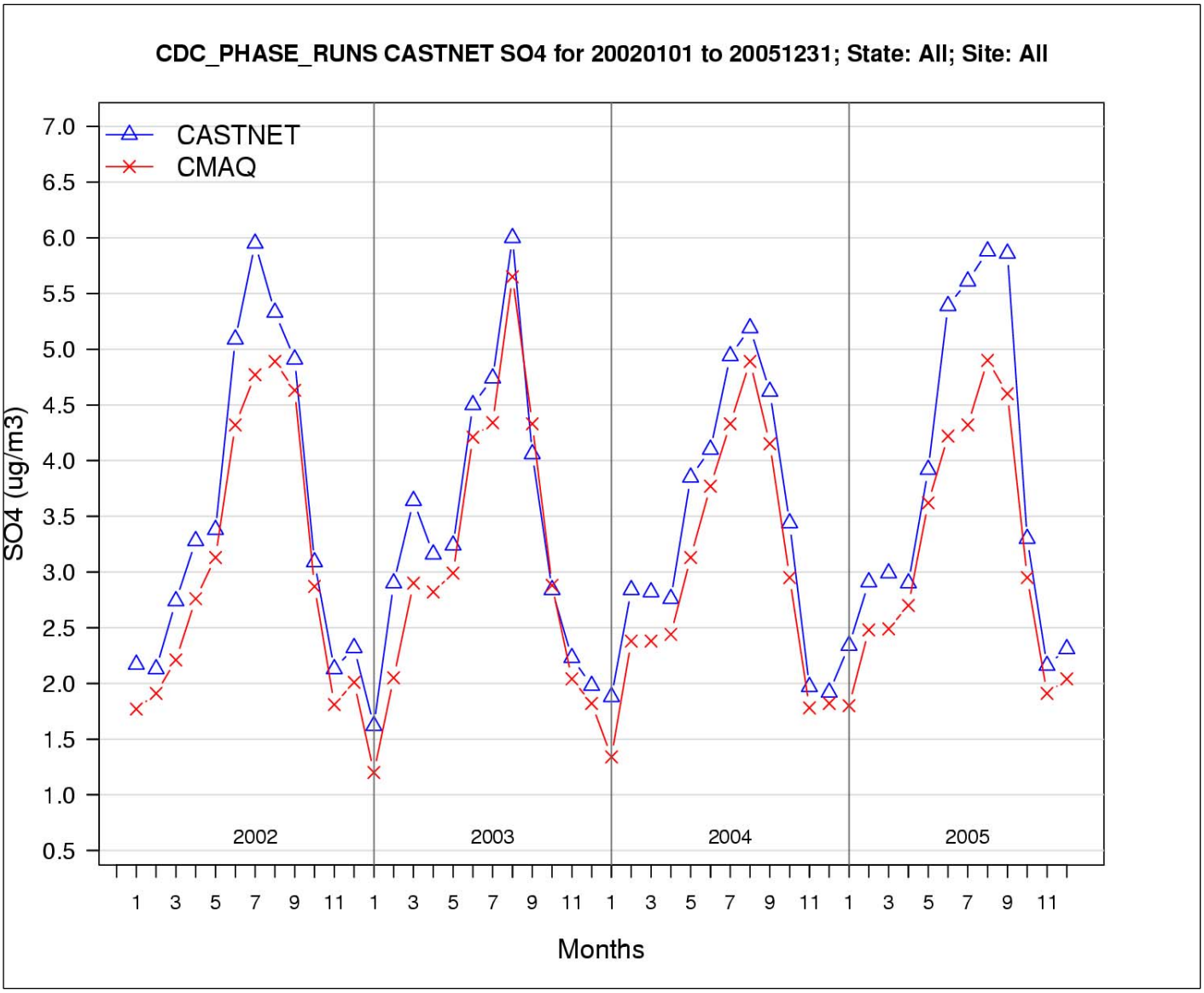


Figure 7-5. 2002–2005 Domain-wide average SO_4^{2-} predicted concentrations and observations by month at CASTNet Sites in the eastern domain(note, units are in actual mass for SO_4, including oxygen) .

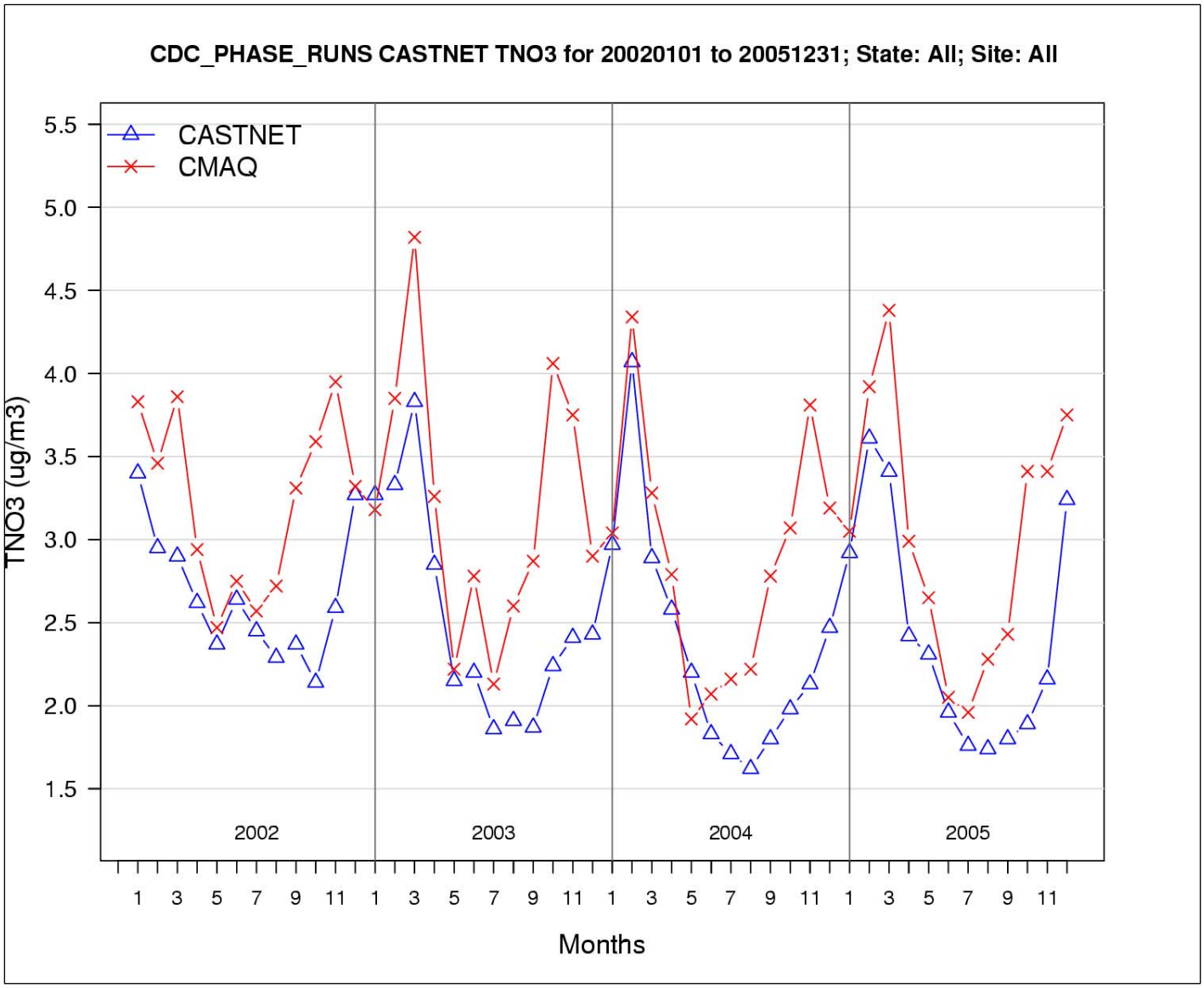


Figure 7-6. 2002–2005 Domain-wide average TNO_3 predicted concentrations and observations by month at CASTNet sites in the eastern domain (note, units are in actual mass for NO_3, including oxygen).

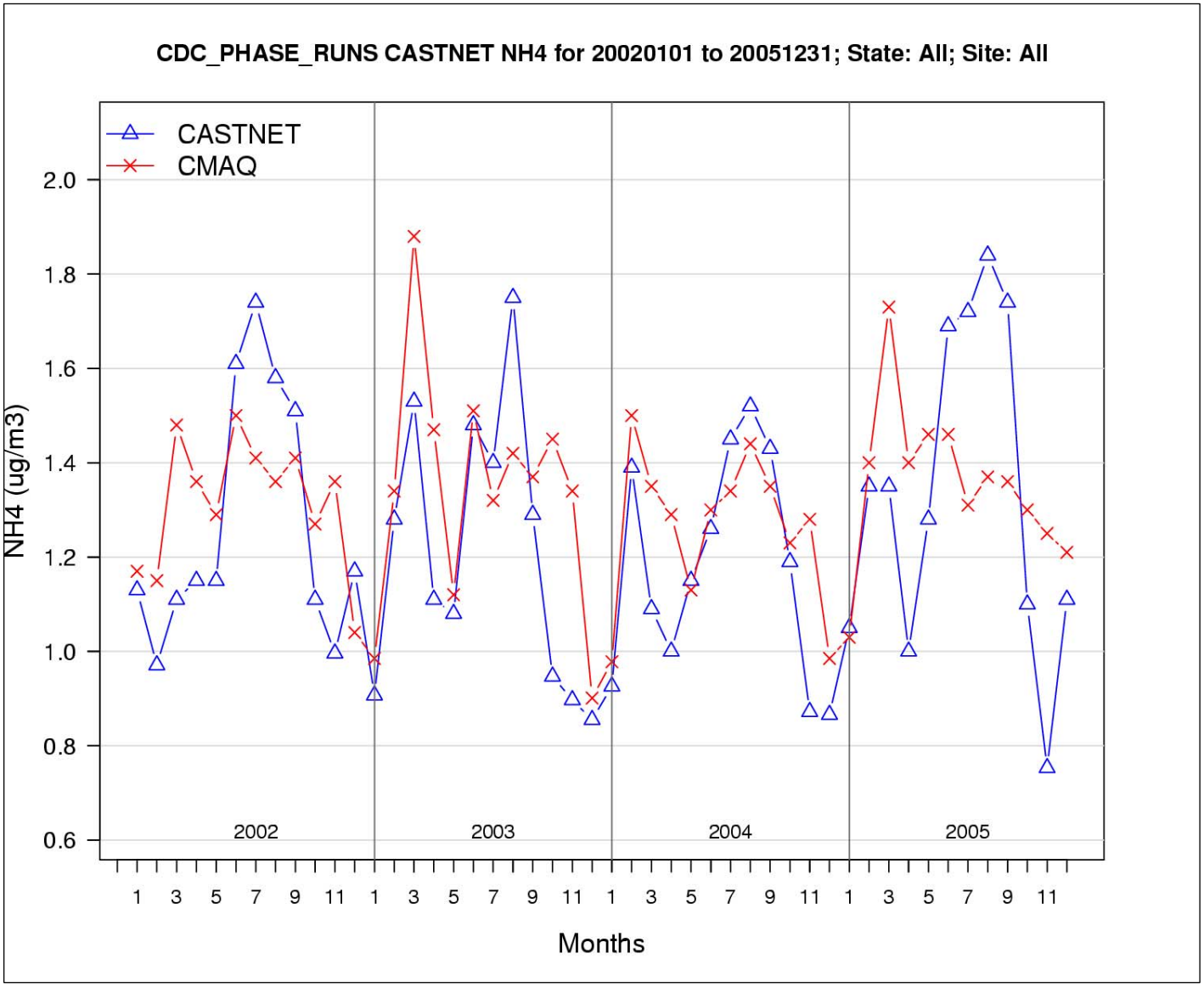


Figure 7-7 2002–2005 Domain-wide average NH_4^+ predicted concentrations and observations by month at CASTNet sites in the eastern domain (note, units are in actual mass for NH_4, including hydrogen).

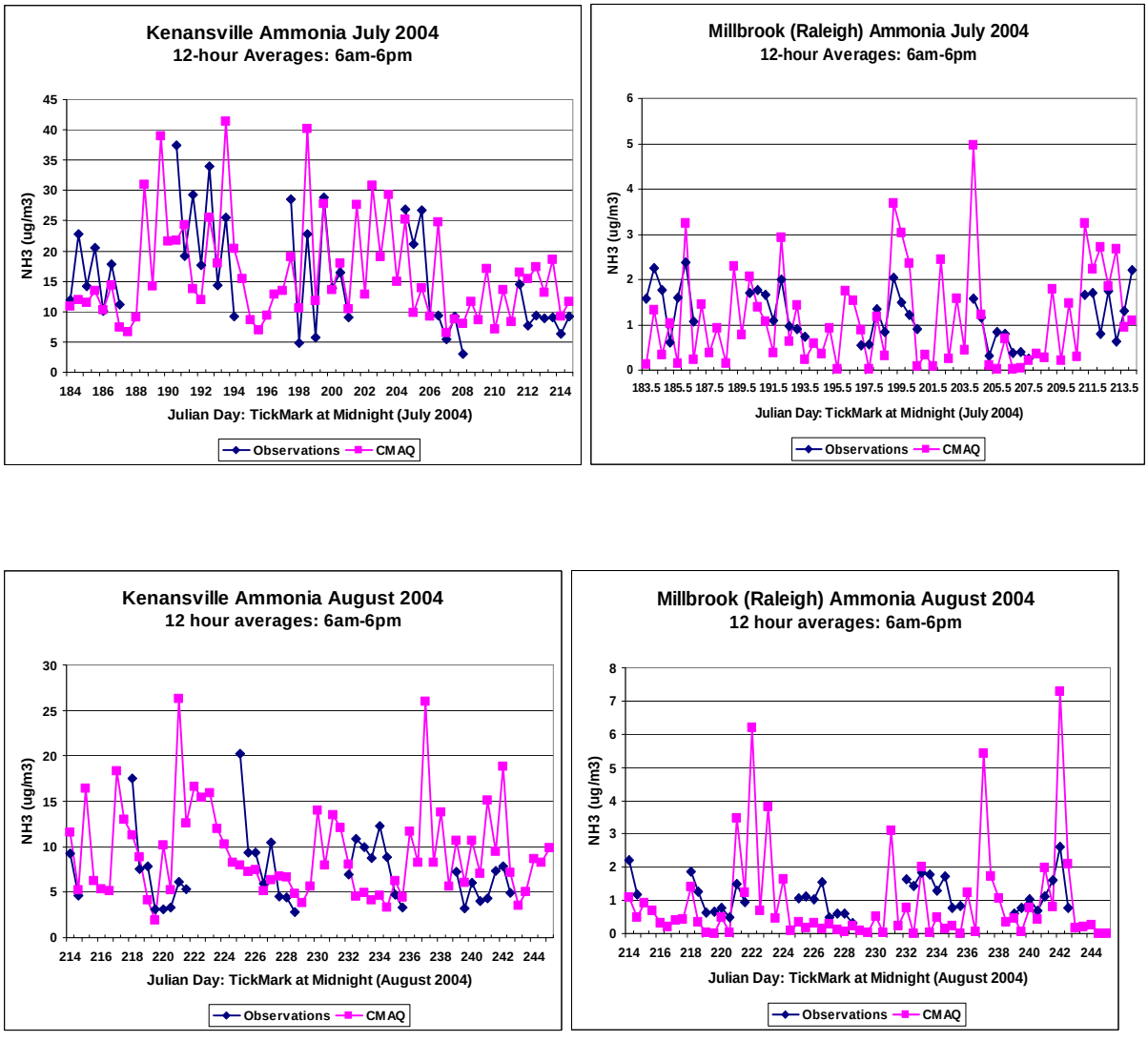


Figure 7-8. Comparison of CMAQ predictions and measurements for 12-hour (6am-6pm) average NH_3 concentrations, with a monitoring cycle of 4 days on and 4days off, at a high emission site (Kenansville) and a low emission urban site (Raleigh) in North Carolina compared to CMAQ for July 2004 (top) and August 2004 (bottom), from Dennis et al., 2010 (note, units are in actual mass for NH_3, including hydrogen).

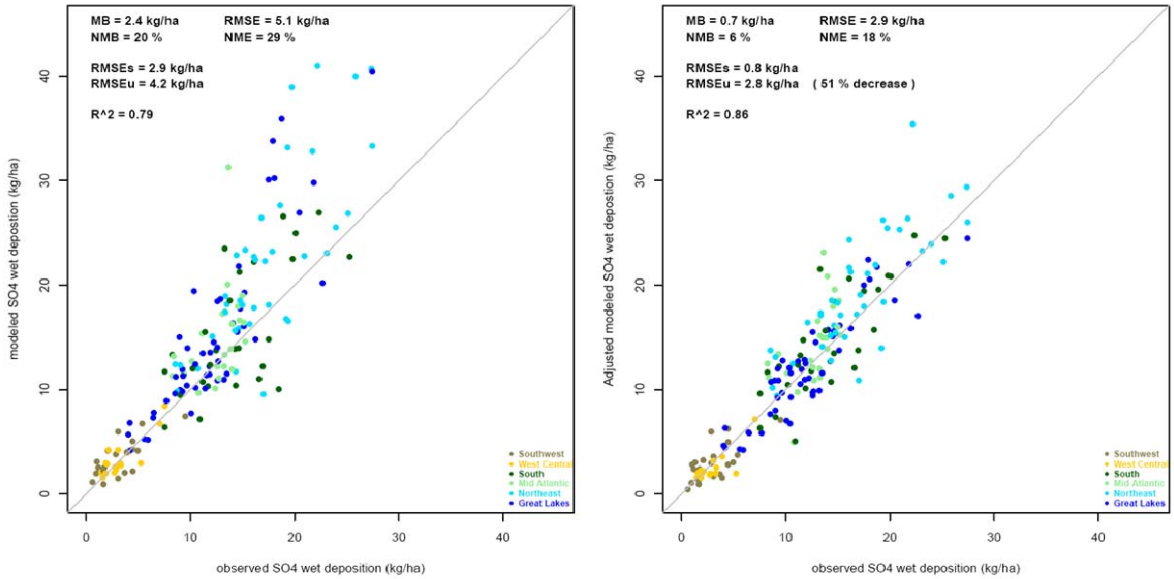


Figure 7-9 Unadjusted (left) and PRISM (right) adjusted CMAQ annual wet deposited sulfate for 2002 (note, units are in actual mass for SO_4, including oxygen).

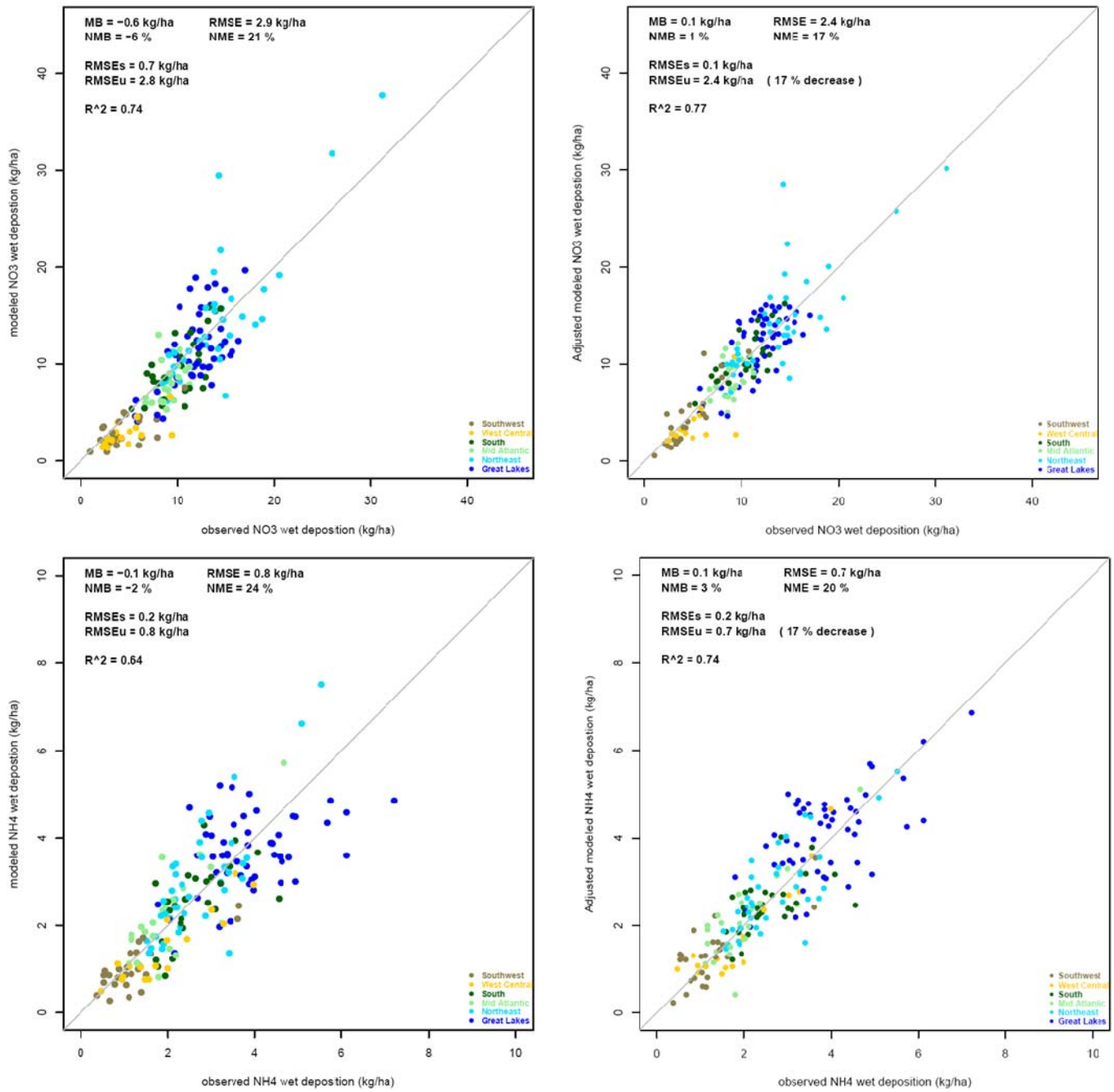
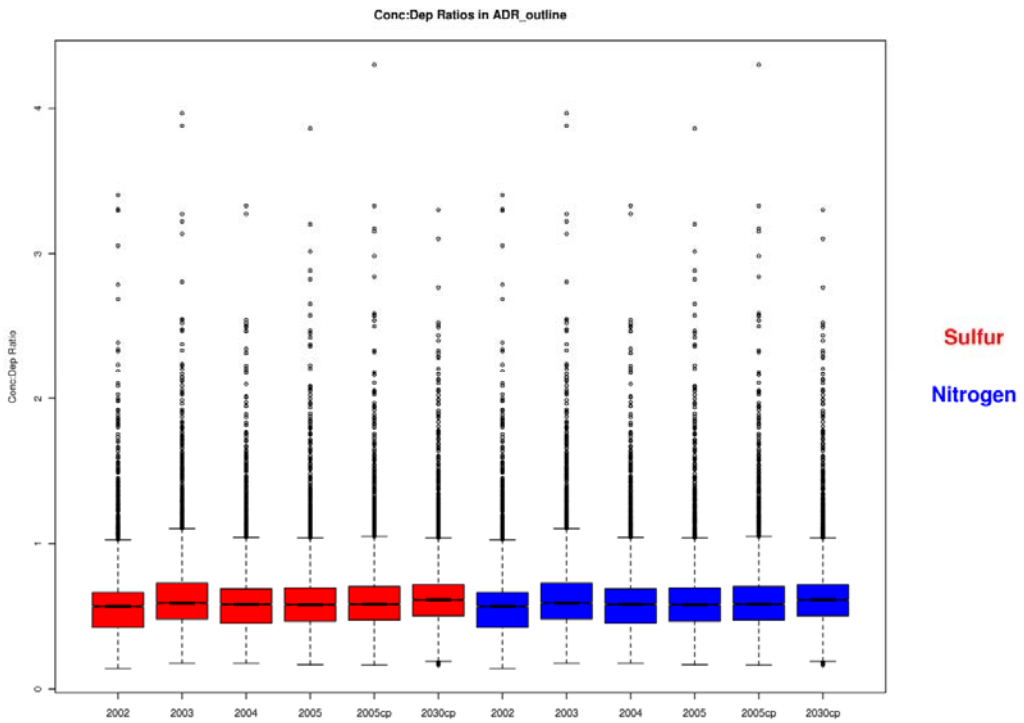


Figure 7-10 Unadjusted (left) and PRISM and bias (right) adjusted CMAQ annual wet deposition of nitrate (top) and ammonium (bottom) (note, units are in actual mass for NH_4 and NH_3, including hydrogen).



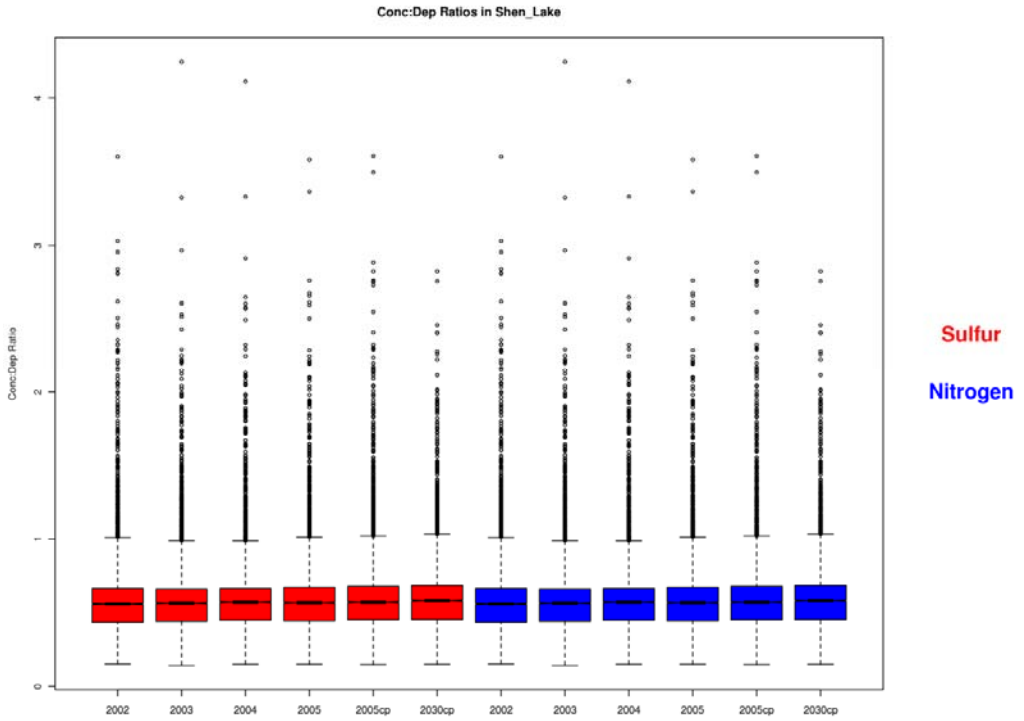


Figure 7-11 Spatial and interannual variability of inverse deposition transference ratios, $1/T_{SOx}$ and $1/T_{NOy}$, for Adirondack (top) and Shenandoah case study areas.

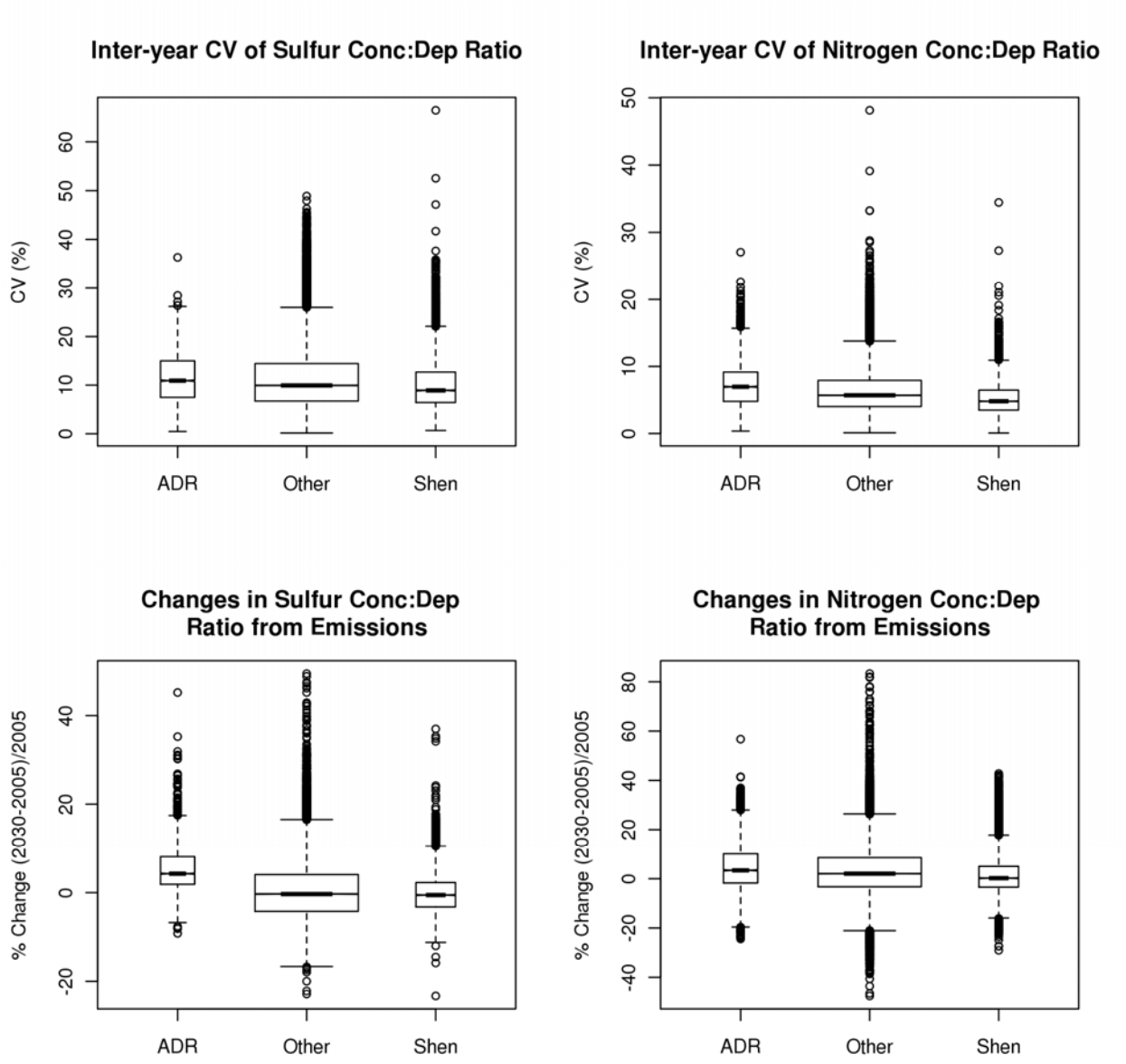


Figure 7-12. Summary of inter-annual and emissions sensitivity variability of sulfur and nitrogen deposition transference ratios.

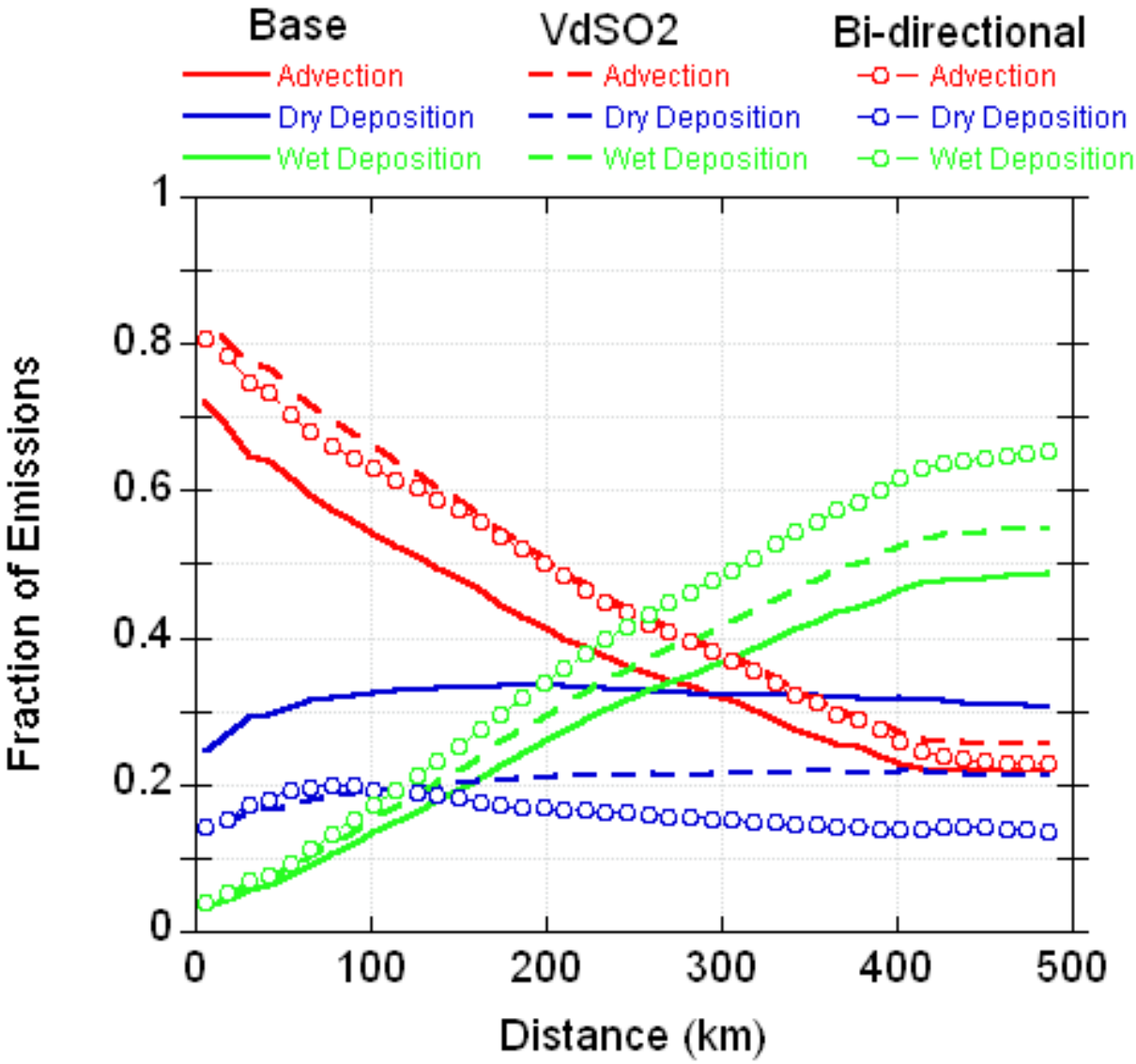


Figure 7-13. Cumulative regional NH3 budget of advection, wet- and dry deposition, calculated for an expanding box starting at the high-emitting Sampson County NC cell (from Dennis et al, 2010)

7.5. Sensitivity of AAPI to component parameters

An elasticity analysis was applied to investigate sensitivity of the AAPI to its components (Appendix A). The means, medians and quartiles of the AAPI component variables were based on the range variable values across ecoregions that overlapped with the CMAQ domains. Elasticities measure the percent change in the AAPI for a 1% change in the AAPI parameters: Q, Neco, NH_x, BC_0^*, T_{NOy}, T_{SOx}, NO_y, and (SO_2 + SO_4).

$$AAPI = \frac{1}{Q} N_{eco} + BC_0^* - \frac{1}{Q} NHx - \frac{1}{Q}\left[T_{NOy} \cdot NOy + T_{SOx} \cdot (SO_4 + SO_2)\right]$$

The elasticity results identified significance for all the AAPI parameters. Detailed results are provided in Appendix A. Base cation weathering, BC_0^*, and hydraulic flow rate, Q, exerted strong influence on AAPI, an expected result given the explicit dependency evident in the AAPI expression. The transference rations for NOy (T_{NOy}) and SOx (T_{SOx}) exhibited relatively less influence on AAPI calculations than all other parameters when evaluated at means of the variables. However, in some locations, when evaluated at other values of the variables, AAPI can be more sensitive to the deposition transformation ratios.

These results suggest focusing on the uncertainties in the non-atmospheric inputs, including base cation weathering and runoff rates, and the implications of those uncertainties in setting an AAPI that will have a high likelihood of providing the targeted level of protection. An analysis of variance (ANOVA) analysis of the AAPI parameters will be added to the final PA.

7.6 Uncertainty in Critical Load and ANC modeling

7.6.1 MAGIC modeling

An extensive uncertainty analysis of the MAGIC model was conducted as part of the REA, and documented in Appendix 4 of the REA. This uncertainty analysis included comparison of MAGIC outputs with observed water chemistry and ANC values. The uncertainty analysis also included an approach for generating confidence intervals for predicted ANC, using ensembles of model results based on alternative model calibration methods.

The model performance comparisons documented in Appendix 4 of the REA show close correspondence between simulated and observed annual average surface water SO_4, NO_3, and ANC during the model calibration period for 44 lakes in the Adirondacks Case Study Area and 60 streams in the Shenendoah Case Study Area. These comparisons are reproduced in Figures 7-14 and 7-15. Comparisons in the ability of MAGIC to reproduce the temporal pattern of ANC for individual lakes was also assessed, and the model does reasonably well at matching the pattern of ANC, although the fit is not as good as during the model calibration period.

The estimated confidence bounds on predicted ANC suggest that the 95 percent upper confidence bound is on average 10 percent higher in lakes, and 5 percent higher in streams. This suggests relatively low uncertainty introduced by the MAGIC modeling assumptions. MAGIC modeling is used in developing the estimates of base cation weathering for comparison to the F-factor approach described in Chapter 5.

7.6.2 SSWC modeling

As stated in Appendix 4 of the REA, uncertainties in some elements of the SSWC modeling are not well understood. The version of the SSWC model used here uses the F-factor approach to estimate the preindustrial base cation supply for a given catchment. While this approach has been widely applied in Canada and Europe, it has only been used in a few cases within the United States and its assumptions and parameters have not been fully evaluated for aquatic systems. The natural or preindustrial catchment supply of base cations (i.e. weathering rates) has the most influence on the critical load calculation and also has the largest uncertainty (Li and McNulty, 2007). The uncertainty and ability to accurately estimate this parameter has not fully been evaluated and its uncertainty is unknown. It is important to note that for the United States, there is only one study for surface waters critical loads that compared steady-state and dynamic models and different steady-state approaches (MAGIC and F-factor) (Holdren et al. 1992) other than what is presented in Chapter 5. Holdren et al. 1992 compared critical loads calculated by the steady-state MAGIC and the SSWC F-factor model for lakes in the Northeast. In this study, steady-state MAGIC model yielded critical load values that show the same general trend and on average were 14 kg/(ha-yr) SO_4 higher than those from the SSWC F-factor approach, which is consistent with results, presented in Chapter 5. The two models converge at

low critical, but diverge as the buffering potential for watersheds increase, as indicated by increasing critical loads.

The REA conducted an uncertainty assessment using Monte Carlo simulation methods to characterize the uncertainty in estimated critical loads using the SSWC, varying a number of important inputs including runoff rates, water chemistry variables, and acid deposition. The coefficients of variation (CV) for the estimated critical loads (standard deviation divided by the mean) were calculated for each lake in the study as a measure of relative uncertainty.

The results of this uncertainty analysis show that the coefficients of variation are on average very low for target ANC values within the range we are recommending (20 to 50 μeq/L). The CVs for critical loads are only 5% and 9% for critical load limits of 20 and 50 μeq/L, respectively. Although the average CV is relatively small for the population of sites modeled, individual site CV can vary from 1% to 45%. This difference is due to the high degree of uncertainty in site specific parameters for particular sites.

These analyses suggest that uncertainties introduced in the AAPI directly by the SSWC Factor model are likely to be moderate. Additional uncertainties are introduced by the generalization of the F-factor approach to estimate critical loads in locations where F-factors have not been developed.

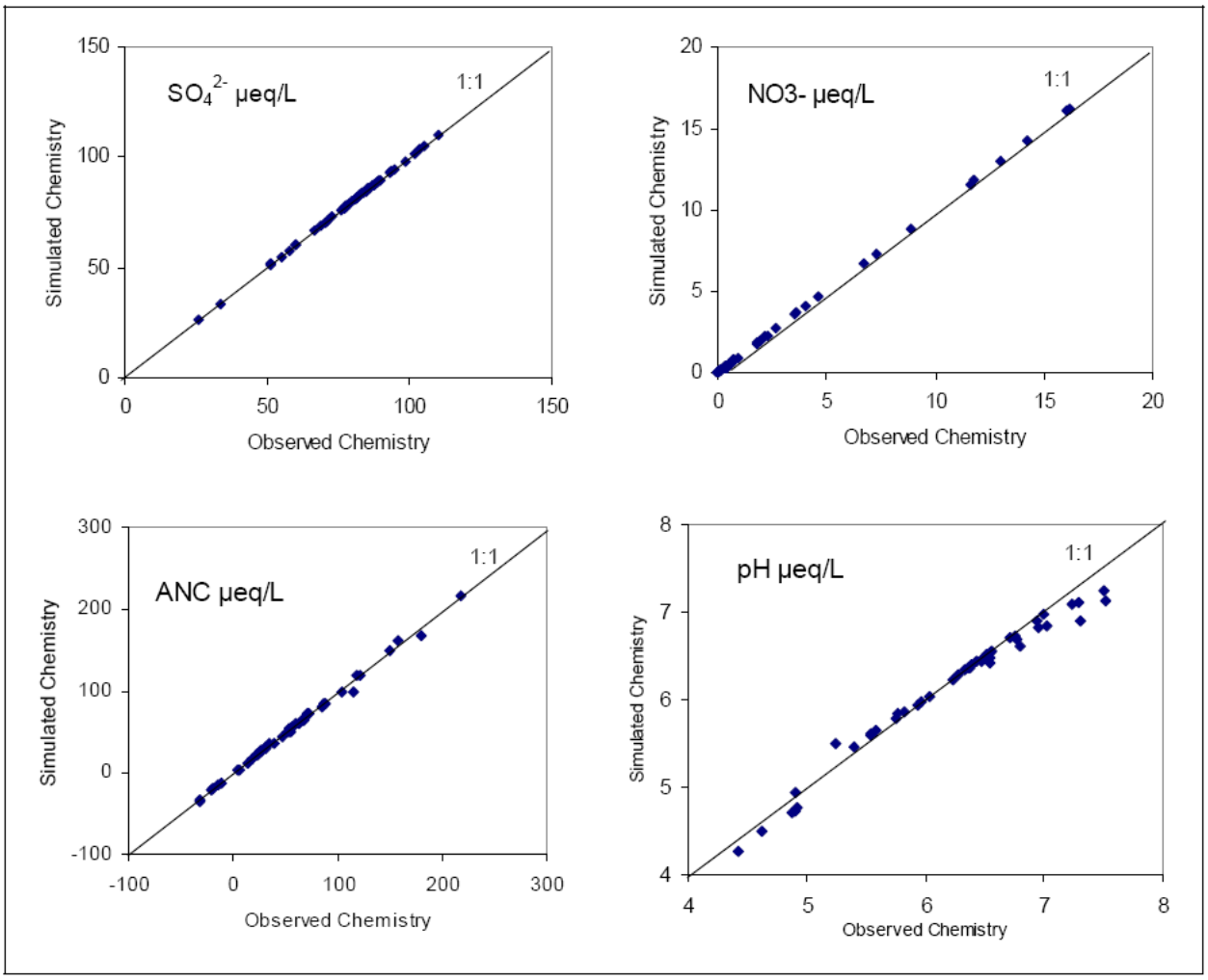


Figure 7-14 Simulated versus observed annual average surface water SO42-, NO3-, ANC, and pH during the model calibration period for each of the 44 lakes in the Adirondacks Case Study Area. The black line is the 1:1 line. (Source: reproduced from REA, Appendix 4, Figure 1.1-1)

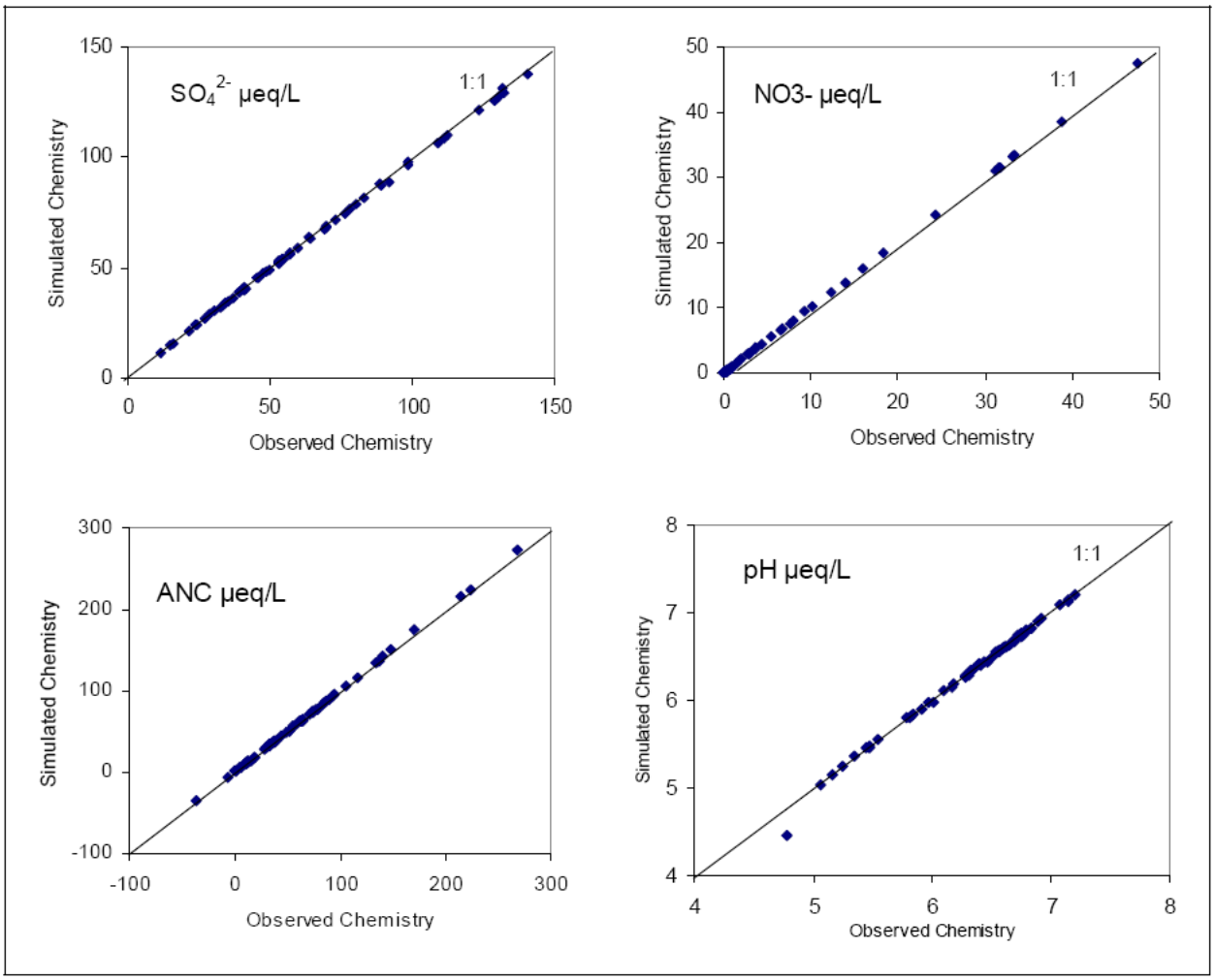


Figure 7-15. Simulated versus observed annual average surface water SO42-, NO3-, ANC, and pH during the model calibration period for each of the 60 streams in the Shenandoah Case Study Area. The black line is the 1:1 line. (Source: reproduced from REA, Appendix 4, Figure 1.1-2)

7.7. Modeling and Data Gaps (To be expanded in final PA)

Atmospheric and deposition processes. The previous section introduced two important enhancements regarding the treatment of wet precipitation and the bi-directional flux of ammonia. The interest in deposition of sulfur and nitrogen raises the potential importance of occult (cloud and fog related processes) deposition associated with mists and clouds, which may be particularly relevant for aquatic acidification of high elevation watersheds. Occult deposition currently is in the early stages of development within the CMAQ framework.

Lightning generated NOx emissions have been an active area of research over the last decade and approaches that incorporate lightning count data and estimated NOx generation based on satellite measurements and aircraft campaigns have been tested in modern air quality models, including CMAQ. Lightning NOx is hypothesized to increase upper tropospheric ozone levels and wet nitrogen precipitation, with relatively negligible impact on near surface ambient nitrogen patterns. It is anticipated that CMAQ will incorporate lightning NOx for EPA assessments in the 2012 timeframe.

Interest in organic bound nitrogen has increased based on NADP measurements suggesting that organic nitrogen contributes as much as 30% of the total nitrogen in precipitation samples. Significant uncertainties regarding the origin and composition of organic nitrogen (Altieri et al., 2009) suggest a need for research to improve our understanding of organic nitrogen prior to developing parameterizations in air quality models. Questions regarding the the relative contribution of anthropogenic or natural sources as well as the effects of re-entrainment from the surface require attention.

Atmospheric Observations. Chapter 4 addresses the current state of atmospheric observations relative to the NOx/SOx secondary standard and Chapter 8 addresses preliminary recommendations for monitoring methods. This new standard poses measurement resource challenges as the current networks, with the exception of CASTNET and some National Park Service (NPS) efforts, are deficient in spatial coverage relevant to anticipated acid sensitive areas and the specific measurement needs related to NOy, speciated NOy and ammonia and ammonium.

Source emissions. Anthropogenic emissions of nitrogen oxides (NO and NO_2) and sulfur dioxide generally are believed to be well characterized as the major contributors of NOx and SO_2 from energy generation and transportation sectors have a history of continuous improvements of emissions modeling as well as direct emission measurements for major power generating units. Greater uncertainty resides in natural emissions of NOx from lightning processes (discussed above) and soil and agricultural related phenomena. Both NOx and ammonia emissions are subject to re-emission after deposition as part of the complex cycling of nitrogen in soils and biota. Characterizing the variety of agricultural practices that impact both ammonia and NOx is complicated by the dispersed nature of agriculture processes as well as the

influence of various meteorological factors on relevant biogeochemical processes controlling transformation and removal of nitrogen species.

Ecosystem processes and surface water observations. [To be completed in final PA] The critical load modeling approaches that produced the N/S deposition tradeoff curves require a variety of input data depending on the approach chosen. In general terms, the availability of watershed related deposition, soil and vegetation characteristics and surface water chemistry determine the approach taken. There is a relatively extensive source of data for critical load modeling in the Eastern U.S., as illustrated by the frequent reliance on the Adirondack and Shenandoah Case studies. For this PA, critical load estimates were developed for national level coverage, largely through SSWC modeling relying on surface water data. Several ecoregions included an extremely small sample size of critical load estimates that challenged the development of a national scale assessment of acid sensitive areas. A more thorough characterization of nitrogen retention, dissolved organic carbon, soil chemistry in all acid sensitive areas would lead to reduced uncertainties in applying the AAPI as well as future considerations for standards that incorporate terrestrial acidification and nutrient enrichment effects.

7.8. Summary and Conclusions

Uncertainty and natural variability exist in all of the components of the structure of the NOx and SOx standard introduced in this PA, and should be considered in establishing the level of the AAPI. A summary of the relative uncertainties of these components is provided in table 7-1 (To be added). 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. 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 is best handled through air quality modeling systems like CMAQ. The relationship between concentrations and deposition loads is well characterized by these models, which are constrained by mass balance principles. While much of the physical and chemical processing that determine 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 this chapter have been conducted under the assumption that the basic model construct is solid, as discussed immediately above, and are used to inform conclusions regarding the level of the AAPI that incorporate consideration of uncertainty. These analyses are also useful in guiding implementation efforts related to future monitoring, emissions and model process improvements. The influence of uncertainty on the level of the AAPI can be thought of as reducing or increasing relative stringency of the level to increase the likelihood that requisite protection of public welfare is provided. Throughout these discussions there is no apparent directional bias in the uncertainty regarding the biological, chemical and physical processes incorporated in the AAPI. 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. Consequently, the level of the AAPI should be relatively high in a buffering context to account for the existence of uncertainties in several components. In addition to, but related to these uncertainties discussions, are considerations of time lag to reach a target level ANC due to ecosystem response dynamics, as well the uncertainties in the severity and prevalence of episodic events. Both of these considerations suggest support for an AAPI that is somewhat higher than the target ANC supported by the specific evidence and risk information.

1 **Table 7-2. Summary (Incomplete) of Qualitative Uncertainty Analysis of Key Modeling Elements in the NOx/SOx AAPI.**

Source	Description	Potential influence of uncertainty on risk estimates		Knowledge-Base uncertainty*	Comments (KB: knowledge base, INF: influence of uncertainty on AAPI estimates)
		Direction	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	
Linkage between direct acidification species to 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 indictor and adverse ecological effects	Direct 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 modeling	Both MAGIC and Steady State critical load models are applied to determine critical load models. The Steady State critical load model formulation is used as the foundation for deriving the	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 on risk estimates		Knowledge-Base uncertainty*	Comments (KB: knowledge base, INF: influence of uncertainty on AAPI estimates)
		Direction	Magnitude		
	AAPI equation.				
Atmospheric concentrations to Deposition	Deposition is a direct function of ambient concentration, influenced by several processes, and handled in this PA 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 driving (e,g,, ammonia emissions) these calculations and availability of observations to evaluate model behavior.
Sub-components and data of individual models					
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, NOy 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.
Additional elements to be added (.BCo, NECO, Q, DOC, benefits, ambient obs, surface water obs, emissions, ...)					

7.9 REFERENCES:

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8 AMBIENT AIR MONITORING

Ambient air measurements of nitrogen and sulfur species support implementation of this proposed NAAQS secondary standard and improve the information basis for subsequent reviews. These uses extend beyond the basic need to measure the proposed NAAQS indicators, NO_Y, SO_2 and SO_4, in approximate priority order:

- Direct NAAQS comparisons.
- Reduced nitrogen, NH_3 and NH_4, to evaluate CMAQ and other air quality models ability to characterize NH_X deposition, a component of the AAPI expression.
- Model and process improvement - In combination with NAAQS indicators and NHx, additional speciated NO_Y components including HNO_3, PAN, NO_2, and NO to continually assess air quality model behavior and associated deposition processes.
- Subsequent NAAQS reviews of the secondary NO_X/SO_X standard as well as related primary and secondary standards reviews (ozone, NO_2, SO_2 and PM).
- Accountability – Assessing the effectiveness of implemented programs addressing emission strategies to meet attainment of the proposed NAAQS using all noted measurements.

8.1 What Are The Appropriate Ambient Air Indicators To Consider In Developing The Standards?

The recommendation of NO_Y, SO_2 and SO_4 as the ambient air indicators for the proposed NO_X/SO_X standard was introduced in the first draft of the PAD and endorsed by CASAC (CASAC, 2010). Essentially, NO_Y, which is an aggregate of all reactive oxidized nitrogen compounds and the two sulfur species represent the oxidized ambient air species of relevance to the criteria pollutants NO_X and SO_X with potential to adversely affect acid-base balance in aquatic systems. Contributions of reduced nitrogen, which would not be part of the indicator for the standard under the approach suggested in this PAD, are provided by CMAQ.

Why not use each individual species as indicators?

One could consider using all NO_Y species as NAAQS indicators, requiring, for example, measurements of the dominant species: HNO_3, particulate nitrate, true NO_2, NO, and PAN. Conceptually, each species would be paired with a species - specific deposition velocity in the AAPI expression to transfer individual deposition values to ambient values. The attraction of using individual species would be the reliance on actual deposition velocities that have more physical meaning in comparison to model constructed transference ratios which aggregate dry and wet deposition and all nitrogen species. The transference ratio approach does retain the necessary conservation of mass which underlies virtually all parameterization schemes, but loses some degree of physical relevance due to use of modeled outputs – an admittedly unique construct. The major drawback of using individual species as NAAQS indicators is the lack of routinely available measurement techniques and an associated resource burden even if adequate techniques were available. Currently, technology for measuring true NO_2, HNO_3, and PAN generally is not available for routine network applications. In addition to this practical consideration, there is another important reason for using the aggregated transference ratios. Because the standard, and the explicit Clean Air Act authority, is based on ambient air there must be an effective link connecting deposition and concentrations of the criteria pollutants in the ambient air. The use of individual species conceptually allows for a more physically meaningful approach to characterize and calculate deposition. However, the transference ratios also enable incorporation of the contributions of wet precipitation in the ambient air indicators. There is no practical alternative that allows for the disentangling of wet deposition as a function of ambient air concentrations as that relationship is best addressed through the coupling of numerous meteorological and chemical processes imbedded in the air quality modeling platform. One could consider wet precipitation as a separate parameter and isolate dry precipitation in the AAPI equation. But doing so would lose the important connection between wet precipitation of nitrogen and the same emission sources responsible for dry deposition.

Finally, one might advocate for direct measurements of dry deposition of individual NO_Y species. Again, technologies simply are not ready for consideration in routine network applications. And, it is arguably practical to model dry deposition even if direct dry deposition measurement technologies were available. One reason for this is that there is significant spatial

heterogeneity in the factors (vegetation and surface type, micrometeorology) that define deposition velocity. Consequently, direct dry deposition measurements would have limited spatial representativeness in comparison to ambient air observations. The model conceptually accounts for the spatial variance, at the level of horizontal grid cell resolution, of the factors defining deposition velocity on a species by species basis. However, one also could reason that a well placed direct measurement of dry deposition is more realistic than a modeled result that relies on numerous assumptions. The development of technologies to measure direct dry deposition will benefit the diagnosis and improvement of process formulations in models.

Consideration has been given to change the atmospheric indicator from NO_Y to total nitrate (the sum of nitric acid and particulate nitrate). The rationale for that approach is that a larger fraction of the deposited NO_Y is accounted for by total nitrate, which currently is measured in CASTNET with high confidence. One can reason adequately that nitrate may correlate well with total oxidized nitrogen deposition relative to NO_Y (as discussed in Chapter 4), given the inherent noise associated with variable contributions of low deposition velocity species of ambient level significance (e.g., NO_2). The disadvantages of using total nitrate as an indicator are that significant ambient mass with the potential for deposition is not captured, and NO_Y is a preferred measurement for model evaluation and accountability purposes. Accountability refers to assessing if emissions reductions have the intended consequences on ambient air and deposition levels in the context of, "Aare our emissions reductions strategies working as planned?" All three of these concerns relate to the benefit of closing mass balances in whatever environmental medium is being characterized. In addition, the use of nitrate alone would create an increased distancing from the listed criteria pollutant oxides of nitrogen as NO_Y does include NO and NO_2.

8.2 Reactive Oxidized Nitrogen and Sulfur Species.

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 (Figure 8-1). The dominant ambient air NO_Y species are NO, NO_2, HNO_3, P-NO_3 and PAN. Near source urban environments typically have a relatively higher fraction of NOx compared to the products of NO_X reactions, nitrates and PAN, which are relatively more dominant in rural locations (Figures 8-2 – 8-5).

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 that nitric acid is the most dominant contributing species from a deposition perspective (Figure 8-1), with significant contributions from particulate nitrate, PAN and NO_2. The original source of emissions (NO accounts for 90-95% of all emitted NO_X) provides very small (< 5%) contributions to ambient air and virtually nothing to deposition. The combination of nitric acid and particulate nitrate consistently contribute greater than 50% of the oxidized nitrogen dry deposition load, whereas PAN and NO_2 contribute roughly 15-25% of the deposition load. These broad summary statements speak to some of the monitoring considerations addressed earlier, particularly the case for monitoring for total nitrate. However, caution should be exercised when considering not measuring a considerable fraction of the ambient NO_Y burden reflected in 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 8-2), that in some locations NO_2 deposition may be similar to nitric acid contributions.

A sampling of co-located NO_Y species observations in rural Eastern Canada (Figure 8-2), particularly in Egbert, Ontario, illustrates the concern of the general assumption that NO_2 may not contribute significantly to NO_Y deposition in rural locations. While it may be true that in general NO_2 is of less of concern in rural areas relative to urban areas, that does not dismiss the potential for significant misrepresentation of total nitrogen budget in certain rural locations.

The results also raise the question of potential efficiencies gained from not cycling between NO and NO_Y analyses, which is the standard configuration in commercial NOy instruments, acknowledging the limited use of NO data in rural, acid sensitive environments (note that NO present in the air would still be captured in the NO_Y measurement).

These examples are used to support the rationalization of using NO_Y as an appropriate atmospheric indicator in applying the AAPI. However, while it may be required to measure NO_Y for explicit AAPI calculations to determine compliance with a NOx/SOx standard, there should be additional measurements of true NO_2, HNO_3, p-NO_3 and PAN to allow for diagnostic evaluations of both air quality models and the NO_Y measurement itself. This recommendation would leverage existing CASTNET filter pack (FP) observations necessary to capture particulate sulfate (discussed below) and therefore require the addition of true NO_2 measurements and periodic sampling for PAN.

Sulfur Species. Although sulfur dioxide and particulate sulfate contribute approximately 60 and 40 %, respectively, to ambient SOx concentrations, sulfur dioxide is the dominant contributor to SO_X deposition (Figure 8-6), which is consistent with CASTNET observational studies (Sickles and Shadwick, 2007). Measurement technology issues are not as complex for SOx as they are for NO_Y and individual NO_Y species. Issues related to particle size fraction and averaging period for SOx are discussed below.

Reduced Nitrogen.

The AAPI does not include reduced nitrogen (ammonia gas and ammonium ion) as an ambient air indicator. However, reduced nitrogen deposition is an explicit AAPI component which is estimated through air quality modeling. As discussed in the Chapter 7, 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. (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.

8.3 What measurements would be used to characterize NOy and SOx ambient air concentrations for the purposes of the AAPI based standard?

Ambient NOy, SO_2 and particulate sulfate (SO_4) concentrations would be used as the indicators in determining compliance with the standard. All of these indicators are measured in different places within the current routine monitoring networks (section 3.2). However, there are issues requiring resolution associated with Federal Reference or Equivalency Measurement (FRM/FEM) status of measurement techniques that to date have served as supplemental information, which will require resolution. A FRM for SO_2 exists, but not for NO_Yor 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. Acquiring FRM status may require better characterization of the conversion efficiencies, mass loss and clear guidance on operating and siting procedures. Particulate sulfate 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 $PM_{2.5}$ 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. With minor exceptions, the $PM_{2.5}$ fraction generally accounts for over 80% of the ambient sulfate mass. Unfortunately, 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 (Grantz et al., 2003).

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 FP for SO_2 measurements as a resource saving option, 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. Some concerns have been raised about the possibility of exclusion of coarse particles from NO_Y samplers operating at low flow conditions as well as potential difficulties of reducing organically bound and mineralized nitrate. Insight into conversion and capture efficiency characteristics will be advanced both by research catalyzed by the need to support this standard and through ongoing and future network operations.

8.4 What additional complementary measurements are recommended?

We recommend that there be 3-4 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-NO_3, PAN, true 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 $PM_{2.5}$ 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.

8.5 What sampling frequency would be required?

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 varaibility 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 ($PM_{2.5}$ 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.

8.6 What are the spatial scale issues associated with monitoring for compliance, and how should these be addressed?

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 at length in Chapter 5. 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 effectively serves 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 serves a similar role that existing CASTNET sites provide in estimating dry deposition.

8.7 What specific monitoring methods would be used?

Federal reference and/or equivalent methods (FRM/FEM) are presently available only for SO_2. 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. NO_Y measurement is 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).

One of the challenges associated with specifying performance attributes for p-SO_4 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 NO_2, 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-SO_4 or NO_Y.

p-SO_4. The routinely operating methodology for particulate sulfate (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 $PM_{2.5}$ speciation (exclusion of particles larger than 2.5 µ 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 $PM_{2.5}$ 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 advantages of using the FP method will be the availability of important co-measured species (e.g., SO_2, total nitrate, ammonium). While EPA will 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 SO_2 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.

SO_2. Sulfur dioxide is a NAAQS pollutant and a FRM is available. See 75 FR at 35554-56 and 35593-95 (June 22, 2010) (adopting a second FRM for SO_2). As part of the NCore network development effort, trace gas SO_2 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 an additional 5-1 10 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 certificaton for NO_Y presents more considerable challenges given the limited history of routinely operating instruments. The process EPA is pursuing for certification status for NO_Y will be addressed in the final PA.

8.8 REFERENCES

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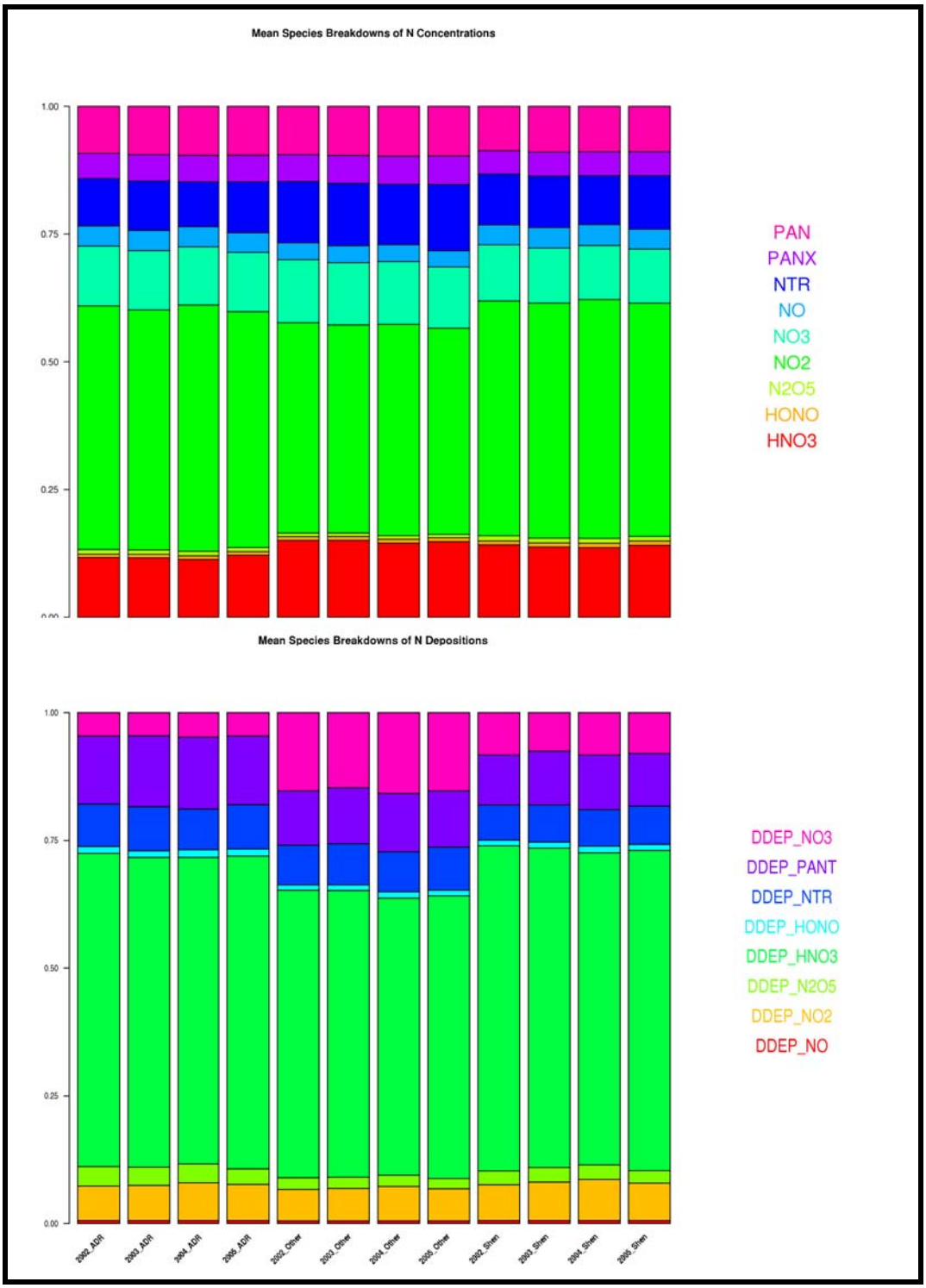

Figure 8-1 Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and deposition (below) of individual NOy species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.

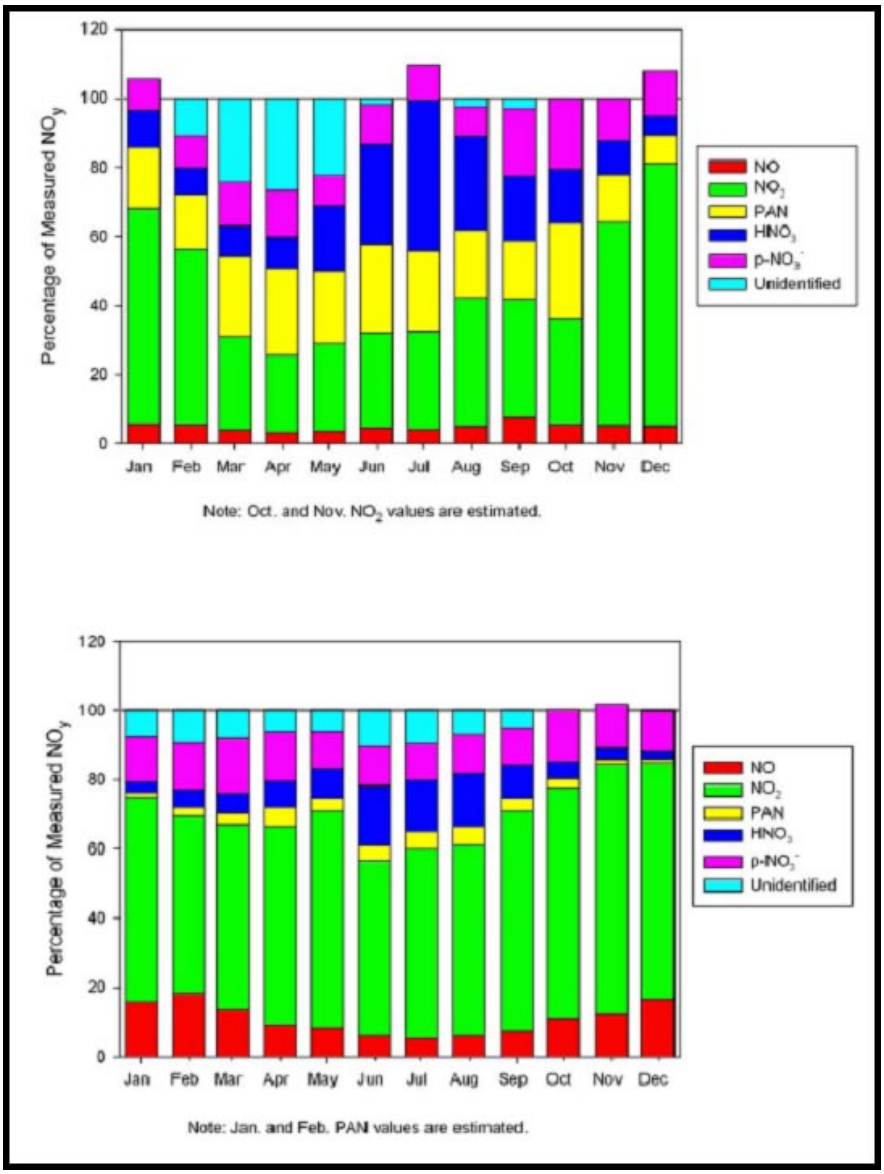

Figure 8-2 Examples of the Relative Abundance of Several NO_y Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured NO_y Concentration -- Kejimkujik, NS, (top) and Egbert, ON, (bottom) during 2003. Although both sites are in rural locations, the Kejimkujik, NS site represents more aged air masses as it lies considerably further downwind from major sources of NOx relative to the Egbert site. (*Source: NARSTO, 2010*)

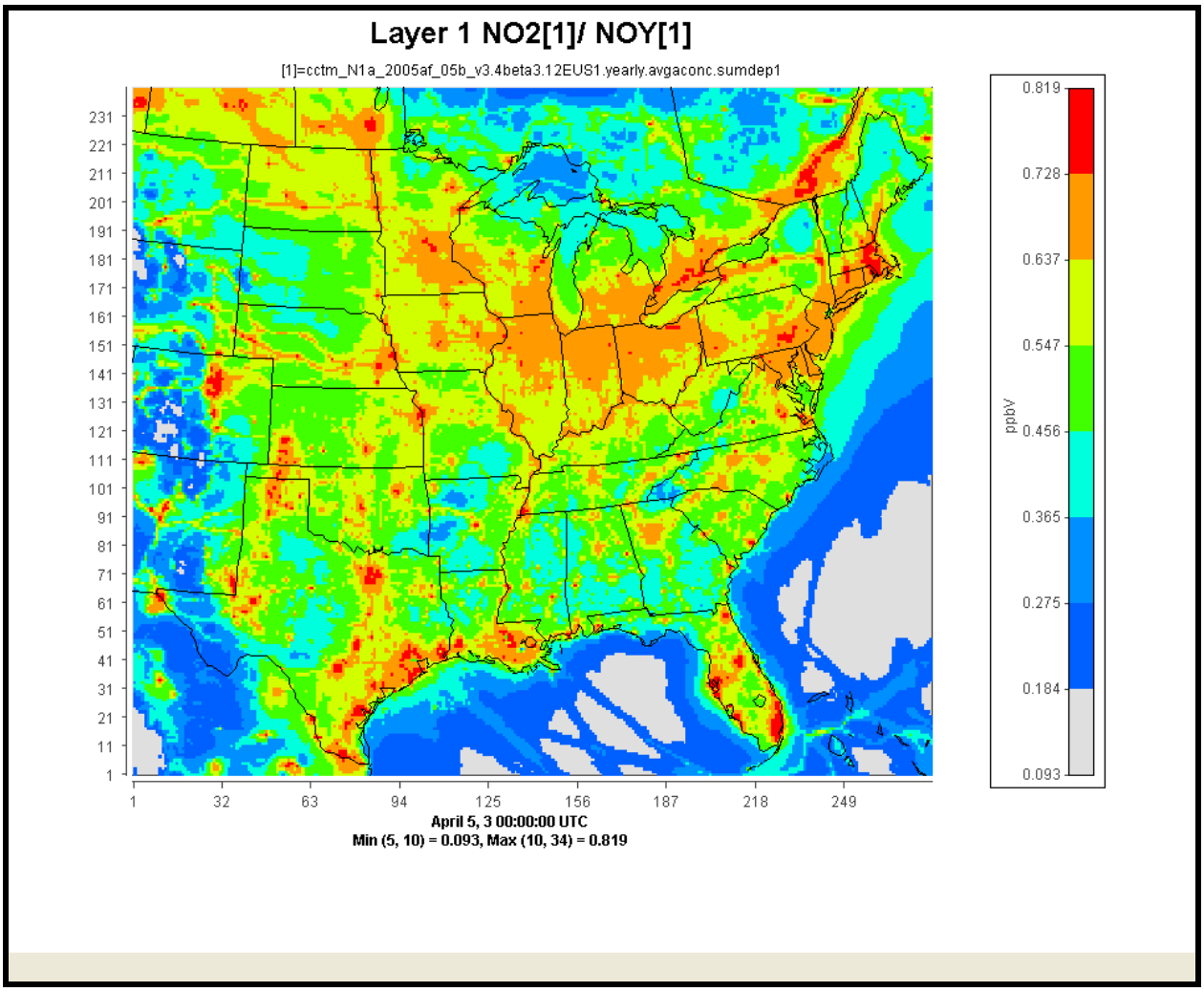

Figure 8-3 Annual average fraction of NOy ambient air contributed by NO_2 based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

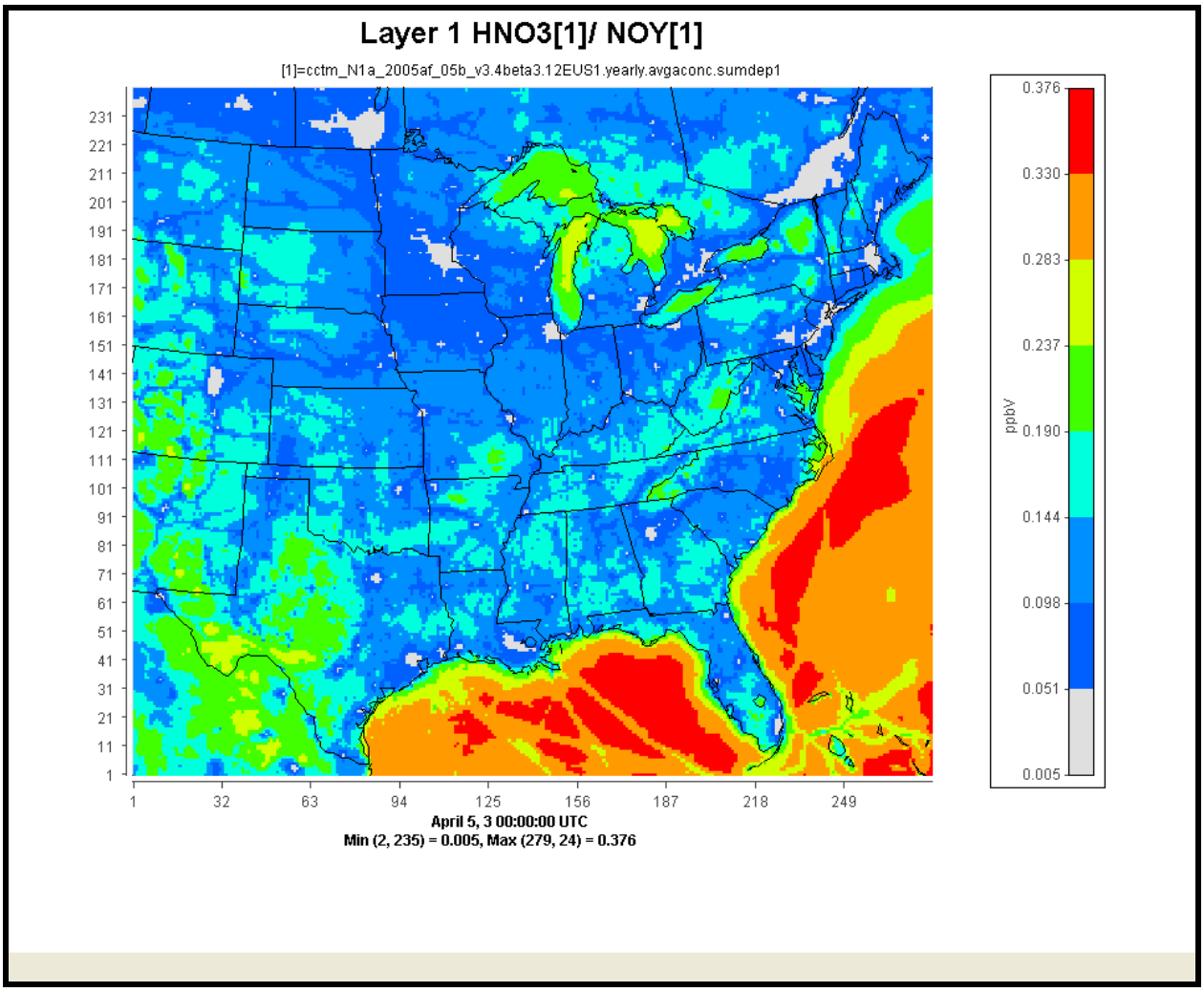

Figure 8-4 Annual average fraction of NOy ambient air contributed by HNO_3 based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

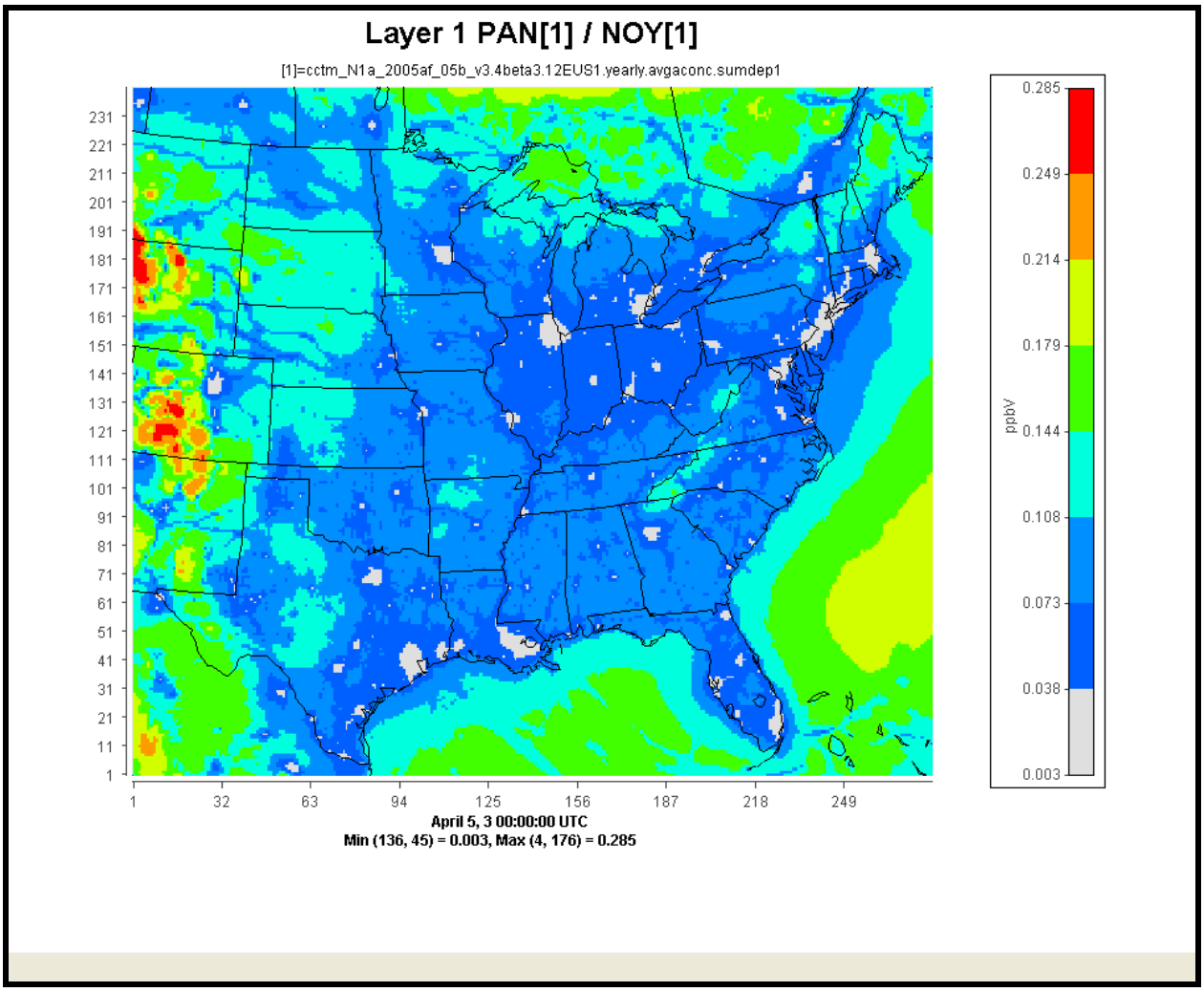

Figure 8-5 Annual average fraction of NOy ambient air contributed by PAN based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

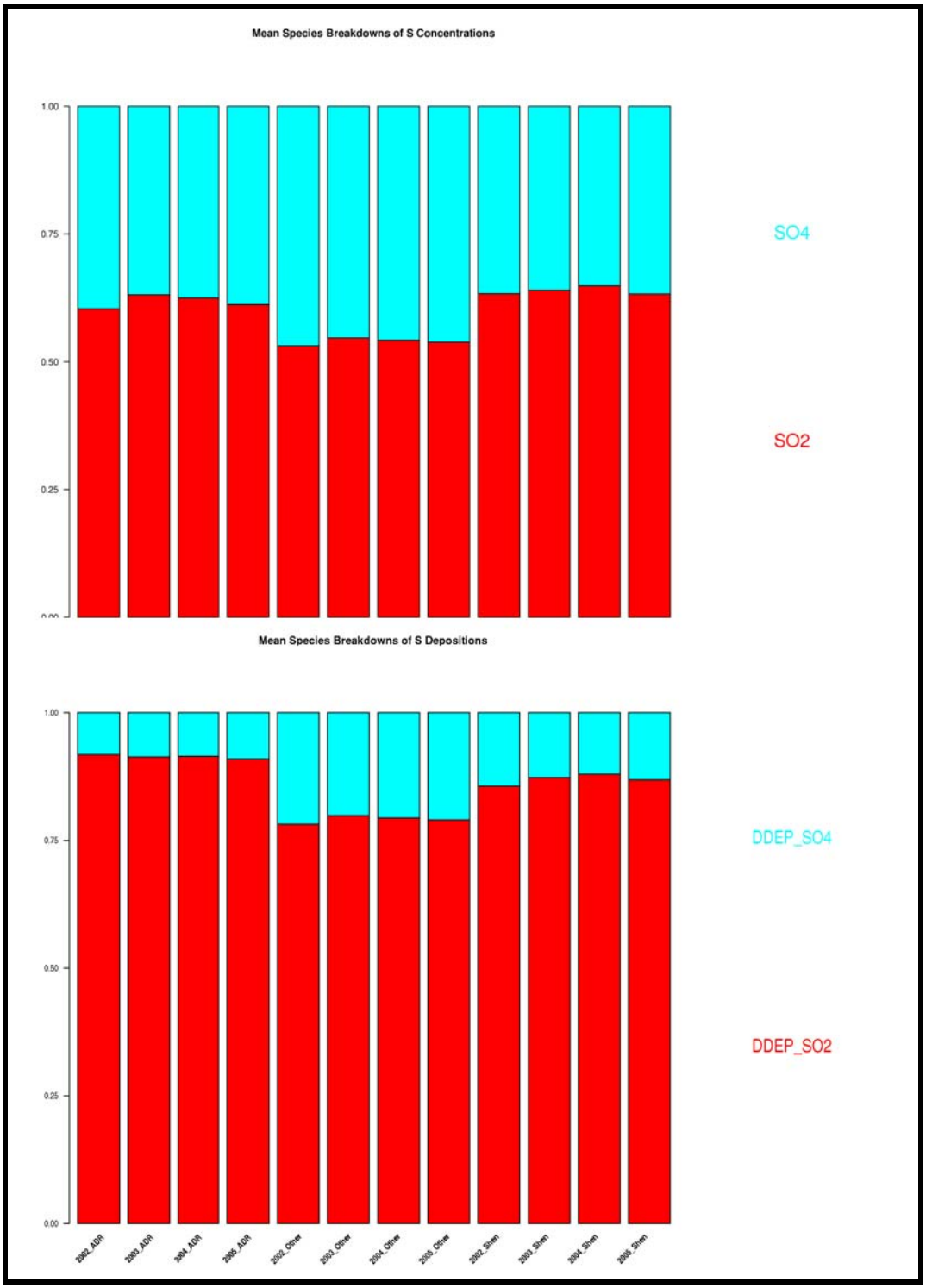

Figure 8-6 Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and deposition (below) of individual SOx species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.

9 INITIAL CONCLUSIONS

Staff initial conclusions on the elements of the secondary NO_X and SO_X standards for the Administrator's consideration in making decisions on the secondary NO_X and SO_X standards are summarized below, together with supporting conclusions from previous chapters. We recognize that selecting from among alternative policy options will necessarily reflect consideration of qualitative and quantitative uncertainties inherent in the relevant evidence and in the assumptions of the quantitative exposure and risk assessments. Any such standard should protect public welfare from any known or anticipated adverse effects associated with the presence of the pollutant(s) in the ambient air, "whether caused by transformation, conversion, or combination with other air pollutants." CAA § 302(h). . In providing these options for consideration, we are mindful that the Act requires standards that, in the judgment of the Administrator, are requisite to protect public welfare. The standards are to be neither more nor less stringent than necessary. Our focus in this review on ecosystems that are both sensitive to acidification and responsive to atmospheric acid deposition is intended to ensure that the resulting standards are appropriately protective and not more protective than necessary in ecosystems that are not adversely affected by acid deposition.

To evaluate whether the current secondary NAAQS is adequate or whether consideration of revisions is appropriate, the conclusions and options for the Administrator to consider in this review are based on effects-, exposure- and risk-based considerations. The exposure and risk assessments reflect the availability of new tools, assessment methods, and a larger and more diverse body of evidence than was available in the last reviews. We have taken a weight of evidence approach that evaluates information across the variety of research areas described in the ISA and in addition includes assessments of air quality, exposures, and qualitative and quantitative risks associated with alternative air quality scenarios.

Staff notes that since the last review, additional policy-relevant developments have occurred that may also warrant consideration by the Administrator when making decisions about what is requisite to protect public welfare. The NRC report (described in Chapter 5) states: "Whatever the reason that led EPA to use identical primary and secondary NAAQS in the past, it is becoming increasingly evident that a new approach will be needed in the future. There is

growing evidence that the current forms of the NAAQS are not providing adequate protection to sensitive ecosystems and crops" (NRC, 2004).

The last review raised the following key issues as a rationale for not setting a separate standard for NO_X to protect against acidification and nutrient enrichment effects in sensitive ecosystems:

1) Lack of enough consistent information to support a revision of the current secondary standard to protect these aquatic systems.

2) Lack of adequate quantitative evidence on the relationship between deposition rates and environmental impacts

3) Significant uncertainties with regard to the long-term role of nitrogen deposition in surface water acidity and with regard to the quantification of the magnitude and timing of the relationship between atmospheric deposition and the appearance of nitrogen in surface water.

In this current review, staff concludes that important new information has become available since the last review that supports revising the current NO_X and SO_X standards. Specifically, the ISA has concluded that there are causal relationships between NO_X and SO_X acidifying deposition and effects on aquatic and terrestrial ecosystems, and the ISA and REA provide substantial quantitative evidence of effects occurring in locations that meet the current NO_2 and SO_2 standards. In addition, substantial new information, based on observational data and rigorous atmospheric modeling, has become available regarding the role of both nitrogen and sulfur deposition in acidification of sensitive water bodies. This information is sufficient to inform the development of revised secondary standards for NO_X and SO_X to protect against the effects of acidification. While there is also new information available on the role of nitrogen deposition on nutrient enrichment effects in terrestrial and aquatic ecosystems, and the ISA concludes there is a causal relationship between NO_X and nutrient enrichment effects, for this draft policy assessment, staff have focused on aquatic acidification effects due to the substantially greater amount of information available to inform the development of secondary standards for those effects. This is consistent with the available science and data, and also with the recommendations of CASAC, which stated that "EPA Staff is advised to focus on an AAPI standard driven by aquatic effects concerns." There is not sufficient information at this time to develop secondary standards directly focused on protection of sensitive terrestrial ecosystems from acidification or sensitive terrestrial and aquatic ecosystems from adverse effects from

nutrient enrichment. Establishing standards that are multipollutant and ecologically relevant is an inherently complex process. We note that the aquatic acidification based standards are an important step in providing additional protections for sensitive ecosystems. While they do not provide complete protection for all sensitive ecosystems against all adverse effects, they will likely result in reductions in NO_Y and SO_2 across broad regions of the U.S., resulting in decreased deposition and related effects for both terrestrial and aquatic ecosystems across all types of effects (see Chapter 6 for a broader discussion of this issue).

Staff highlights the progress made in considering the joint nature of ecosystem responses to acidifying deposition of NO_X and SO_X, and notes that the ability to consider revisions to the NO_X and SO_X secondary standards has been enhanced by our ability to consider a joint standard for NO_X and SO_X to protect against aquatic acidification effects. The development of an appropriate form of the standard linked to a common indicator of aquatic acidification, ANC, is also a significant step forward, as it allows for development of a standard for aquatic acidification designed to provide generally the same degree of protection across the country, while still reflecting the underlying variability in ecosystem sensitivity to acidifying NO_X and SO_X deposition.

9.1 CONSIDERATION OF ALTERNATIVE STANDARDS

We begin by noting that the existing evidence continues to support existing NO_2 and SO_2 standards to protect against adverse effects associated with direct exposure of vegetation to gas phase NO_X and SO_X. 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 SOx and NOx. There is sufficient evidence to suggest that the levels of the current standards are likely adequate to protect against direct phytotoxic effects. As such, staff concludes that retaining the existing NO_2 and SO_2 standards to continue protection against these effects is appropriate. However, as discussed in Chapter 4, we also conclude that the existing secondary NO_X and SO_X standards are not adequate to provide protection of aquatic and terrestrial ecosystems against the effects of acidifying deposition. In response to this conclusion, staff considers a second overarching question:

What additional NO_X and SO_X standards are supported by the currently available scientific evidence and risk-based information, as reflected in the ISA and REA?

To inform the answer to this overarching question, we have posed a series of more specific questions to aid in considering how the current NO_X and SO_X standards might be revised to provide requisite public welfare protection.

Chapter 5 provided a conceptual framework for a secondary standard that is designed to provide protection of ecosystems against the effects associated with deposition of ambient concentrations of NO_X and SO_X. Chapter 5 also provided a discussion of potential options for the elements of a standard based on that conceptual framework, with a focus on the form of the standards. While we recognize the potential for significant impacts of current levels of NO_X and SO_X on terrestrial ecosystems and the effect of current levels of NO_X on nutrient enrichment in sensitive aquatic ecosystems, we conclude that the currently available information is insufficient to develop either individual or joint standards to protect against these effects. We note that development of a standard for protection against terrestrial acidification may be appropriate using the same structure as we are proposing for aquatic acidification, using the Bc:Al ratio as the ecological indicator. However, the data needed to parameterize the form of such a standard is not sufficient at this time. As a result, we conclude that the current state of knowledge supports a standard to protect against the adverse effects associated with acidification of aquatic ecosystems. Such a standard is likely to provide some level of protection against other endpoints associated with deposition of N and S, but is not likely to adequately protect all sensitive terrestrial ecosystems or all N nutrient sensitive aquatic ecosystems.

Building on the options discussed in Chapter 5, this section offers staff conclusions regarding the elements of the standard, including the indicators for NO_X and SO_X, the form of the standard, the averaging times, and presents for consideration options for target ANC levels associated with protection against specific ecological effects in aquatic ecosystems. Ultimately, the levels of AAPI considered by the Administrator should incorporate consideration of target levels of ANC, percent of waterbodies protected within defined spatial areas, and trajectories for ecosystem recovery, as well as uncertainties in the components of the AAPI. Associated with these elements of the AAPI are sets of NOy/(SO2+SO4) tradeoff curves which determine the

levels of ambient NO_y and SO2+SO4 which will satisfy the level of the standard. The expression of these trade-off curves embodies the depositional load for a specified spatial area that is equivalent to the critical load for the waterbody in that area that represents a selected percentile (e.g. 95th percentile) of critical loads across waterbodies in the area, such that the selected percent of waterbodies in that area are expected to achieve an ANC at the target level. If a target load for a specific temporal period (e.g. by 2030) is evaluated instead of the critical load, then the depositional load represents the amount of deposition that is expected to achieve a target ANC value by a specific year for the selected percent of waterbodies in the area. The equivalent AAPI for an area can be calculated by inputting the values for each parameter of the AAPI equation for the selected percentile waterbody and the observed values of NO_y and SO2+SO4.

These elements will be considered collectively in evaluating the protection from welfare effects associated with aquatic acidification afforded by alternative standards under consideration. In considering the currently available scientific and technical information, we consider both the information available in the last review and information that is newly available since the last review as assessed and presented in the ISA and RA prepared for this review (US EPA, 2008; US EPA, 2009).

9.1.1. Indicators

Staff concludes that the appropriate indicators for NO_X and SO_X, as described in detail in Chapter 5, are total NO_y and the sum of SO2 and SO4, respectively. Total NO_y includes all nitrogen oxides, including e.g. total reactive oxidized atmospheric nitrogen, defined as NO_X (NO and NO_2) and all oxidized NO_X products: $NO_y = NO_2 + NO + HNO_3 + PAN + 2N_2O_5 + HONO + NO_3$ + organic nitrates + particulate NO_3. The sum of SO2 and SO4 constitutes virtually the entire ambient air sulfur budget and SO2 and SO4 are measured routinely in existing monitoring networks.

9.1.2. Averaging times

As noted in Chapter 2 and Chapter 5, episodes of acidification and chronic acidification levels are associated with deposition over longer periods of time due to the storage and release of deposited nitrogen and sulfur in soils, snow, and ice. As a result, while episodic acidification may occur on much shorter timeframes, e.g. days to weeks, the cause of these episodes is largely due to shifts in hydrological flow paths, and the impact of these episodes is still determined by long term deposition of NO_y and SO2+SO4 and associated long-term ANC, and thus the appropriate averaging time for ambient NO_y and SO2+SO4 will be longer term. The averaging time for ambient concentrations of NO_y and SO2+SO4 should be reflective of the long-term cumulative nature of deposition. CASAC supports using a three to five year averaging period "to help smooth out the year-to-year climatic variation in air concentration and deposition estimates." (CASAC, 2010)

9.1.3. Form

The "form" of a standard defines the air quality statistic that is to be compared to the level of the standard in determining whether an area attains the standard. As discussed extensively in chapter 5, staff concludes that the current forms of the NO_X and SO_X secondary standards are not appropriate for addressing ecosystem acidification effects, and also concludes that a form that combines NO_X and SO_X levels with information on ecosystem sensitivity and nitrogen retention and uptake is most appropriate to maximize the likelihood of protecting sensitive ecosystems from the effects of acidification, without requiring standards that are more than requisite to provide that protection. Specifically, staff concludes that the Atmospheric Acidification Protection Index form as described in Chapter 5 is best suited to provide for protection against adverse effects due to acidifying deposition related to NO_X and SO_X.

Within the AAPI, it is also appropriate to consider the specification of values of non-air quality parameters of the AAPI, including pre-industrial base cation weathering, nitrogen retention and uptake, runoff, and levels of reduced nitrogen deposition. As discussed in Chapter 5, staff is proposing that the pre-industrial base cation weathering, nitrogen retention and uptake, and runoff values be determined by assessing the critical loads associated with a specific percentile of the waterbodies within defined spatial boundaries (as noted in Chapter 5, consideration is being given to a number of different methods for defining spatial boundaries).

The values of pre-industrial base cation weathering, nitrogen retention and uptake, and runoff values for a selected percentile waterbody are then used as the values in the form of the standard as realized for the specific ecoregion.

The value of reduced nitrogen is initially set using deposition of NHx modeled using the CMAQ, evaluated for the period 2002-2005. Staff is considering the most appropriate spatial averaging extent for reduced nitrogen. Figure 9-1 shows spatially interpolated values of reduced nitrogen deposition based on 12km CMAQ modeling in the Eastern U.S. It is clear that in some locations, there is significant heterogeneity in reduced nitrogen deposition within ecoregion III boundaries. Given this information, two possible approaches to estimating reduced nitrogen values in the AAPI algorithm are 1) average reduced nitrogen deposition within an ecoregion, acknowledging that this will lead to uncertainties in the level of protection associated with levels of ambient NO_Y and SO_X, or 2) allow for additional spatial refinement of sensitive areas to reflect the heterogeneity of reduced nitrogen deposition. This will result in multiple parameterizations of the AAPI within a single ecoregion.

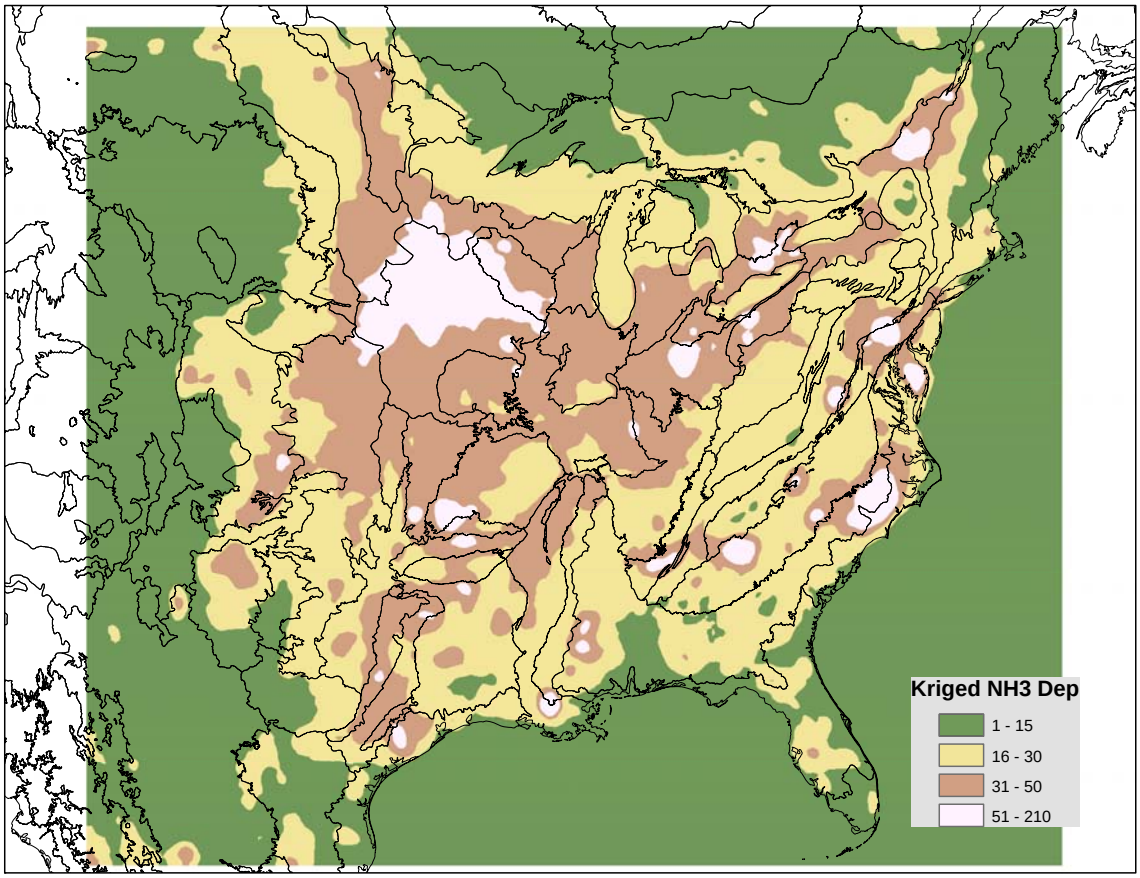

Figure 9-1. Spatially interpolated CMAQ estimates of deposition of reduced nitrogen (2002-2004 average)

Unlike other parameters in the AAPI, reduced nitrogen is expected to change significantly over time because of the largely anthropogenic sources of reduced nitrogen deposition. In order to address this potential, we are exploring methods for specifying the standards in a way that would provide for updating the values of reduced nitrogen in the AAPI based on new modeling of reduced nitrogen deposition, following requirements for modeling established by EPA.

9.1.4. Considerations in Defining Options for the AAPI Standard

Conclusions regarding an appropriate range of levels of the AAPI standard will be informed by considerations of the levels of the target ecological indicator ANC (related to levels of protection from effects of chronic and episodic acidification), relationships between target ANC levels and trajectories of recovery over time, and uncertainties in the various elements of the AAPI that affect the likelihood that the level of protection intended by a particular target ANC will be realized when atmospheric concentrations of NO_y and SO2+SO4 fall below the tradeoff curve for that target ANC. Chapter 5 provides an assessment of the information related to selection of a target ANC, and the rationale for focusing additional considerations on specific target ANC levels, including 20 and 50 µeq/L.

The "levels" of the ambient indicators are determined by the selection of a level for the AAPI, as they represent the quantities of the ambient indicators that will result in the specified level of the AAPI. Those levels will vary for different locations depending on the non-atmospheric related characteristics of the ecosystem, the level of reduced nitrogen in the ecosystem, and the atmospheric transformation ratios (T_{NOy} and $T_{(SO2+SO4)}$).

The secondary NAAQS will reflect the public welfare policy judgments of the Administrator, based on the science, as to the level of air quality which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the pollutant in the ambient air. The exposure and risk assessment provide information regarding the effects associated with a number of different welfare endpoints at different levels of air quality, expressed in terms of the joint multiyear mean concentrations of NO_y and SO2+SO4 determined such that specific levels of ecosystem protection (for example, ANC greater than 50 µeq/L) are met. Staff also recognizes that in certain naturally acidic ecosystems, even though the ecological benchmarks are exceeded, e.g. ANC may be quite low; NO_y and SO2+SO4 are not contributing to effects because those systems have chronic natural acidity and will not benefit from reductions in atmospheric deposition. The secondary NAAQS are not intended to provide protection in these types of naturally acidic systems. As a result, in our determination of appropriate lakes and streams to include in the populations of critical loads that determine protective NO_y and SO2+SO4 levels, we apply filters to remove lakes and streams that are naturally acidic or acidified due to mine drainage. The secondary NAAQS are focused on providing protection in

areas where ambient NO_y and SO2+SO4 are resulting in effects in ecosystems with low natural levels of acidification that are highly sensitive to additional inputs of acid deposition.

Staff concludes that ecosystem effects of NO_y and SO2+SO4 deposition in aquatic ecosystems are an important public welfare effect of concern, based on the types and extent of ecosystem services likely to be affected by deposition, as well as the location of some aquatic ecosystems within state and national protected lands, including Class I national parks and wilderness areas (Chapter 3).

9.1.4.1 Target ANC Level

In reaching staff conclusions regarding target ANC levels that are appropriate to consider for an AAPI-based standard, staff take into account the currently available scientific information including: evidence from field and laboratory studies, including evidence of effects in highly sensitive ecosystems and estimates of risk reductions associated with alternative annual standard levels, as well as the related limitations and uncertainties associated with this information as presented and discussed more fully in the ISA and RA (US EPA, 2008; US EPA, 2009). In developing conclusions regarding the target ANC, we evaluated both evidence and risk based information. In addition, we consider information on target ANC and pH levels used by other organizations that have established critical loads for protection of aquatic ecosystems from effects of acidification.

We conclude that it is appropriate to define NO_X and SO_X standards that will provide generally consistent protection for acid sensitive lakes and streams across the country. In order to do so, we focus attention on considering target ANC levels that will lead to a level of AAPI that provides the same protection for sensitive aquatic ecosystems throughout the U.S. The result of focusing on a nationally protective level of AAPI is a set of varying NO_y/(SO2+SO4) tradeoff curves across the U.S. reflecting that NO_y and SO2+SO4 affect acidification in different ways depending on underlying ecosystem characteristics and levels of reduced nitrogen, such that the same AAPI is calculated with differing levels of NO_y and SO2+SO4. This approach recognizes that changes in air quality to meet the standards may reflect differing combinations of NO_y and SO2+SO4 leading to the same level of the AAPI.

Based on our analyses of risks of impacts on aquatic species diversity and fitness and on the basis of the scientific effects literature, we conclude that achieving a target ANC of 50 μeq/L

would substantially decrease the effects of acidification due to NO_y and SO2+SO4 on aquatic ecosystems, decreasing the risk of losses in biodiversity and mortality in fish and other aquatic organisms, and improving the overall health of aquatic ecosystems. Additionally, it is anticipated that achieving a target ANC of 50 µeq/L would provide increased protection from NO_y and SO2+SO4 in areas with higher levels of variability in ecosystem sensitivity due to variability in meteorology, bedrock geology, topography, land use characteristics, or reduced nitrogen deposition.

It is recognized, however, that a achieving a target ANC of 50 µeq/L would likely not protect the most sensitive aquatic ecosystems or species within those ecosystems from the effects of NO_y and SO2+SO4. At ANC levels below 100 µeq/L, while overall health of an aquatic community can be maintained, ANC levels are expected to be such that fish fitness and community diversity begin to decline**.** At ANC levels between 100 and 50 µeq/L, ANC levels are expected to be such that the fitness of sensitive species (e.g., brook trout, zooplankton) also begins to decline.

9.1.4.2 Target Percent of Waterbodies to Meet a Target ANC Level

The appropriate range of levels of AAPI is also informed by the selection of a target percent of protection for waterbodies within particular acid sensitivity classes or ecoregions (see Chapter 5). More specifically, the greater percentage of waterbodies that are to be protected generally indicates a greater likelihood that sensitive waterbodies will achieve a target ANC level, and as such, in setting the level of the standard, there will be less need to reflect uncertainty in the likelihood that those sensitive waterbodies will be protected.

It is also important to consider that while the target ANC level will not be met in all sensitive waterbodies if a target percent less than 100 is selected, all waterbodies will realize some level of protection due to decreases in NOy and SO2+SO4 to meet the target ANC in targeted waterbodies.

Additional analyses of the implications of alternative target percentages of waterbodies are underway and are expected to be completed for inclusion in the final PA.

9.1.4.2 Additional Considerations Related to Developing Options for the AAPI Form of the Standard

In developing options for the standard, consideration should of the degree to which any specific AAPI would lead to achieving the desired ANC level, and a judgment as to the degree of protection of public welfare that is warranted. These considerations should incorporate a wide number of factors, including the percent of water bodies within acid sensitive areas that the Administrator determines should be protected at the targeted ANC level, as well as consideration of achieving desired levels of protection within generational timeframes, e.g., 20 to 40 years, concerns about protection against episodic acidification events, and uncertainties in the modeling of critical loads, nitrogen uptake and retention, reduced nitrogen deposition, and relationships of atmospheric concentrations to deposition. In considering options for the standard that would reflect consideration for providing requisite welfare protection against know or anticipated effects, we believe that while the available information is insufficient to set separate standards for terrestrial acidification and aquatic and terrestrial nutrient enrichment effects, it is also appropriate to consider the evidence of those effects and the likelihood for co-protection provided by standards targeted at protection against effects of aquatic acidification (Chapter 6).

Chapter 7 provided a summary and synthesis of critical uncertainties and implications for the standards. While many uncertainties cannot be quantitatively assessed, and as such cannot be used to recommend specific quantitative changes to the AAPI, there are several uncertainty analyses which give some insight into the magnitude and direction of the uncertainty. For example, uncertainty analysis of the MAGIC model of critical loads indicates that modeled pre-industrial ANC (which informs the distribution of critical loads on which NO_y and SO2+SO4 levels are based by establishing the natural ability of an aquatic ecosystem to neutralize acid inputs) has 95 percent confidence intervals that are 10 percent higher (or lower) than the mean estimate for lakes, and 5 percent higher (or lower) than the mean estimate for streams. Similar uncertainty exists regarding overall uncertainty in the models used to generate critical loads for determining the NO_y and SO2+SO4 tradeoff curves.

The deposition of reduced nitrogen is a critical input to the AAPI and has a large expected uncertainty due to the use of CMAQ modeling which relies on uncertain chemistry and uncertain inventories of ammonia emissions. Much of the uncertainty introduced by reduced nitrogen deposition can be decreased by improvements in measurements of reduced nitrogen deposition and improvements in the emissions inventories of ammonia and characterization of ammonia chemistry within the CMAQ modeling. These improvements are underway, and our

form of the standard is designed to allow for dynamic updates to reduced nitrogen deposition parameters.

9.1.5 Additional protections for ecosystems against the effects of terrestrial acidification and terrestrial and aquatic nutrient enrichment

While we are not basing the elements of this standard primarily on consideration of effects other than aquatic acidification, our approach recognizes that some level of protection against effects of acidification in terrestrial ecosystems and effects of nutrient enrichment in terrestrial and aquatic ecosystems is likely to be realized through changes in air quality to meet the AAPI standard. We recognize that an annual standard focused on aquatic acidification cannot be expected to offer protection against all of the welfare effects from NO_y and SO2+SO4, especially in areas that are sensitive to nutrient enrichment but are not acid sensitive. However, based on the information available in the ISA and REA, we conclude that the available information is not sufficient to set a complementary standard to provide protection against additional effects of NO_y through nutrient enrichment, and that additional research is necessary to support the setting of such a standard, especially in the areas of identifying the specific impacts of decreases in atmospheric nitrogen deposition (see chapter 7). CASAC has noted that our current framework, with appropriate modifications, should be applicable to developing standards to provide protection against acidification effects in sensitive terrestrial ecosystems. However, staff has concluded that the current data is not sufficient to develop a separate terrestrial acidification based standard at this time. A primary limitation is the identification of specific levels of harm associated with the BC/Al ecological indicator.

Sensitive terrestrial ecosystems that are located in watersheds with acid sensitive water bodies are likely to receive the most protection under an aquatic acidification targeted standard. Terrestrial ecosystems outside of these watersheds are likely to see some level of protection, but will not realize targeted changes in ambient NO_y and SO2+SO4 (Chapter 6).

Chapter 6 evaluated the relative protection for terrestrial ecosystems in areas from meeting a target ANC of 50 µeq/L compared to meeting a target Bc:Al ratio of 10. Critical loads for N and S were compared to determine which of the targets would result in a more

stringent critical load. Over half of the watersheds had a lower critical load to meet the ANC target compared to the critical load to meet the Bc:Al ratio target. As a result, those watersheds are likely to be protected from both terrestrial and aquatic impacts when the ANC target is met. When the water bodies are more sensitive to deposition ("highly sensitive" or "moderately sensitive"), the aquatic critical acid loads generally provide a greater level of protection against acidifying nitrogen and sulfur deposition in the watershed.

The tradeoff curves for NO_y and SO2+SO4 that are associated with protection against aquatic acidification also provide bounding conditions for nitrogen that can be compared against benchmarks of effects associated with nitrogen deposition in sensitive terrestrial and aquatic ecosystems. Achieving an ANC level of 50 µeq/L for 90 percent of lakes and streams nationwide would provide some protection against leaching in northeast forests, but would need to be lower to protect California coastal sage scrub, lichens in mixed conifer forests, alpine lake communities, and Minnesota grasslands (Section 6.2). In the case of aquatic nutrient enrichment, comparison of maximum allowable NO_X levels on the tradeoff curves with deposition requirements to meet the Chesapeake Bay TMDL shows that without further restrictions on NO_y concentrations, standards set to protect against aquatic acidification will not be protective against effects of aquatic nutrient enrichment in the Chesapeake Bay.

9.1.6 Summary of options

To facilitate evaluation of the elements of the standard and staff conclusions regarding those elements, we have constructed a summary table showing the elements of the AAPI, options for each element, and staff conclusions where appropriate.

[Table 9-1 to be provided]

9.2 CONCLUSIONS

The following secondary NAAQS conclusions encompass the breadth of policy-relevant considerations described in this policy assessment. We note that staff conclusions to be presented in the final PA will consider input received from CASAC and the public on this second draft PA. 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 assumptions that underlie the quantitative risk assessment. In identifying these alternative secondary standards and ranges of levels for consideration, we are mindful that the Clean Air Act requires standards to be set that are requisite to protect public from known or anticipated adverse effects, such that the standards are to be neither more nor less stringent than necessary. Thus, the Act does not require that the NAAQS be set at no effect levels, but rather at levels that avoid adverse effects on public welfare:

(1) Based on the policy-relevant findings from the ISA described in Chapter 2, and while recognizing that important uncertainties and research questions remain, staff conclude that great progress has been made since the last reviews of the secondary standards for NO_X and SO_X. We generally find support in the available effects-based evidence for consideration of NOx and SOx standards that are at least as protective as the current standard and do not find support for consideration of NO_X and SO_X standards that are less protective than the current standard. The staff also concludes that consideration of joint standards for NO_X and SO_X is appropriate given the common atmospheric processes governing the deposition of NO_X and SO_X to sensitive ecosystems, and given the combined effects of N and S deposition on acidification of soil and water.

(2) Staff concludes that ambient NO_X is a significant component of atmospheric nitrogen deposition, even in areas with relatively high rates of deposition of reduced nitrogen. Staff make this conclusion based on the analysis in Chapter 3 of the REA, which provides a thorough assessment of the contribution of NO_X to nitrogen deposition throughout the U.S., and the relative contributions of ambient NO_X and reduced forms of nitrogen.

(3) Staff concludes based on the case study results provided in the REA, that current levels of NO_X and SO_X are associated with deposition that leads to ANC values below benchmark values that cause ecological harm and losses in ecosystem services. Staff concludes that the evidence and risk assessment support strongly a relationship between atmospheric deposition of NO_X and SO_X and ANC, and that ANC is an excellent indicator of aquatic acidification. Staff also concludes that at levels of deposition associated with NO_X and SO_X 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, which is associated with reductions in recreational fishing services. Although there are many other

ecosystem services potentially affected by reductions in ANC, including subsistence fishing, natural habitat provision, and biological control, confidence in the specific translation of ANC values to these additional ecosystem services is much lower.

(4) Losses in aquatic resources associated with ANC levels below 50 µeq/L are clearly associated with significant losses in economic value. Based on the best available data, just in New York., increasing ANC levels to 50 in the Adirondacks is estimated to result in $300 to $800 million in annual benefits in 2006 dollars. This estimate represents only a fraction of the total economic value of ecosystem damages as many impacted resources are not amenable to economic valuation methods. In addition, economic damages are also likely to occur in other areas affected by acidification, including New England, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), and the Upper Midwest. Staff concludes that reducing acidifying deposition of NO_X and SO_X will result in improvements in public welfare by increasing the quantity and quality of ecosystem services, including recreational fishing and other services associated with improved water quality.

(5) Staff initially concludes based on the case study results that current levels of ambient NOx and SOx are associated with deposition that leads to Bc:Al values below benchmark values that cause ecological harm and losses in ecosystem services. Staff concludes that the evidence and risk assessment support strongly 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. Staff also concludes that 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 losses in tree health and growth, which are associated with reductions in timber production. While there are many other ecosystem services, including maple syrup production, natural habitat provision, and regulation of water, climate, and erosion, potentially affected by reductions in Bc:Al, confidence in the specific translation of Bc:Al values to these additional ecosystem services is much lower.

(6) On the basis of the acidification and nutrient enrichment effects that have been observed to still occur under current ambient conditions and those predicted to occur under the scenario of just meeting the current secondary NAAQS, staff concludes that the current secondary NAAQS are inadequate to protect the public welfare from known and anticipated adverse welfare effects from aquatic and terrestrial acidification associated with deposition of

NO_X and SO_X.. As discussed above, this conclusion derives from several lines of evidence. Staff also concludes that the current NO_X and SO_X secondary standards are adequate to protect against direct gas-phase effects on vegetation, and as such, should be retained to preserve protection against these welfare effects.

(7) Staff has concluded, based on the completeness of the available evidence and quantitative risk information, that effects due to aquatic acidification are most suitable for defining additional secondary standards for NO_X and SO_X. Staff notes that in developing a standard designed to protect against the effects of aquatic acidification due to deposition of NO_X and SO_X, the resulting standards may not provide protection against known effects associated with terrestrial acidification and with nutrient enrichment in sensitive aquatic and terrestrial ecosystems.

(8) It is appropriate to consider using indicators other than NO_2 and SO_2 as the indicators for an additional standard that is intended to address the ecological effects associated with deposition of NO_X and SO_X to sensitive ecosystems. Given the reasons discussed in Chapters 2, 4, and 5 of this policy assessment, staff concludes that NO_X (oxides of nitrogen, the definition in section 302 (v) of the CAA), is best represented by the atmospheric indicator NO_y, defined as NO_2 + NO + HNO_3 + PAN +$2N_2O_5$ + HONO+ NO_3 + organic nitrates + particulate NO_3 is the more appropriate indicator of oxides of nitrogen, and that SO2+SO4 is the more appropriate indicator of oxides of sulfur for purposes of a secondary standard addressing aquatic acidification.

(9) It is appropriate to use multi-year averages of concentrations of NO_y and SO2+SO4 as the averaging times for the secondary standards, based on the chronic nature of acidification, and the protection against episodic acidification provided by a standard based on annual average concentrations. Averaging periods in the range of 3 to 5 years are most appropriate.

(10) It is appropriate to consider adding a new standard with a different form for NO_y and SO2+SO4 as the current form does not take into account the linkages between NOx and SOx in the causation of effects associated with acidification of aquatic ecosystems. Based on the causal linkages between NO_X and SO_X, deposition of N and S, and the indicator of acidification, ANC, staff concludes that a standard with a form specified as an atmospheric acidification protection index (AAPI) should be added. A standard with this form would reflect the important

roles of underlying ecosystem characteristics, determinants of deposition, and deposition of reduced nitrogen in determining the potential effects from deposition of NO_X and SO_X.

(11) Staff has concluded, based on the evidence and risk based information, and consideration of information related to definitions of adversity, that

a) a target level of ANC of 20 µeq/L will protect against significant losses in fish mortality in many sensitive lakes, but will place less weight on protection against losses in aquatic biodiversity, and will be less protective against potential acidification episodes,

b) a target level of ANC of 50 µeq/L will protect against significant mortality in aquatic organisms and loss of fish health and biodiversity in sensitive lakes and streams, and will give weight to considerations of uncertainties in the time to recovery of aquatic ecosystems,

c) target levels of ANC above 50 µeq/L may provide additional protection against declines in fitness of sensitive species (e.g., brook trout, zooplankton), however, overall health of aquatic communities may not be impacted.

9.3 REFERENCES

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CASAC (2010). Review of the Policy Assessment for the Review of the Secondary National Ambient Air Quality Standards for NOx and SOx: First Draft (March 2010). EPA-CASAC-10-014. June 22.

US EPA (2008) U.S. EPA. Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur Ecological Criteria (Final Report). U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-08/082F

US EPA (2009) Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur-Main Content - Final Report. U.S. Environmental Protection Agency, Washington, D.C., EPA-452/R-09-008a

APPENDIX A
ADDITIONAL INFORMATION FOR CHAPTER 5

A.1Conceptual Design of the Standard

This is supplemental information to support the discussion of the conceptual design of the standard that is presented in Chapter 5 of the Policy Assessment Document. The aquatic acidification analyses developed in the REA used a number of different models and calculation techniques that are important for the development of the standard. The goal of this Appendix is to summarize information from the REA analysis that is most relevant to the Policy Assessment. A brief summary of the REA analyses are presented in section A.1.1. In section A.1.2 there is a general summary and technical discussion of the critical loads modeling approaches that were used in the REA, followed by a brief description of MAGIC model data requirements.

A.1.1 Technical summary of methods used in the REA Aquatic Acidification analysis

The aquatic acidification analysis is presented in Chapter 4 and Appendix 4 of the REA. The analysis uses multiple techniques to show the relationship between ANC and NOx and SOx deposition, as well as determine the current level of risk to water bodies that occur in sensitive areas. A brief summary of the techniques and objectives of the REA analysis is given in Table **A-**1.

Table A-1. Brief summary of objects and methods used in the REA Aquatic Acidification analysis.

Technique	**Objectives**	
Time-series graphs of current conditions	1	Data from monitoring networks collected from 1990 to 2006 were plotted to show trends in concentrations of pollutants, deposition and acidification for each case study site. The data included surface water concentration of nitrate, sulfate and ANC; deposition of sulfate and nitrate; as well as air concentration of SOx, NOx and NH4
MAGIC	1	Used to estimate the relationship between ANC values and anthropogenic NOx and SOx emission from the past (preacidification ~1860), present (2002 and 2006) and projected into the future (2020 and 2050). Analysis included 44 lakes from Adirondacks and 60 streams from Shenandoah.
	2	Used to develop input parameters for critical loads modeling (i.e. weathering rates)
	3	Used for uncertainty analysis
Critical Loads modeling	1	SSWC and FAB models used to calculate critical loads for critical limits of ANC = 0, 20, 50, 100

Table A-1. Brief summary of objects and methods used in the REA Aquatic Acidification analysis.		
	2	Critical loads for ANC critical limits calculated for 169 lakes in the Adirondacks and 60 streams in the Shenandoah using water quality data from monitoring sites collected in 2006
	3	Critical loads exceedences calculated by comparing the critical loads that were calculated by SSWC with deposition data from NADP for wet deposition and CMAQ for dry deposition, both for the year 2002
Regional Extrapolation	1	117 of the critical loads calculated for the Adirondacks were extrapolated to lakes defined by the New England EMAP probability survey, representing 1842 lakes, to infer the # of lakes that exceeded their critical load
	2	69 of the critical loads calculated for the Shenandoah were extrapolated to 330 streams based on bed rock geology classification.

A.1.2 Technical summary of critical loads modeling in the REA

The critical load of acidity for lakes or streams was derived from present-day water chemistry using a combination of steady-state models. Both the Steady-State Water Chemistry (SSWC) model and First-order Acidity Balance model (FAB) is based on the principle that excess base-cation production within a catchment area should be equal to or greater than the acid anion input, thereby maintaining the ANC above a preselected level (Reynolds and Norris, 2001; Posch et al. 1997). These models assume steady-state conditions and assume that all SO_4^{2-} in runoff originates from sea salt spray and anthropogenic deposition. Given a critical ANC protection level, the critical load of acidity is simply the input flux of acid anions from atmospheric deposition (i.e., natural and anthropogenic) subtracted from the natural (i.e., preindustrial) inputs of base cations in the surface water. Final Risk and Exposure Assessment September 2009 Appendix 4, Attachment A – 15 *Aquatic Acidification Case Study* Atmospheric deposition of NOx and SOx contributes to acidification in aquatic ecosystems through the input of acid anions, such as NO3- and SO_4^{2-} The acid balance of headwater lakes and streams is controlled by the level of this acidifying deposition of NO_3- and SO_4^{2-} and a series of biogeochemical processes that produce and consume acidity in watersheds. The biotic integrity of freshwater ecosystems is then a function of the acid-base balance, and the resulting acidity-related stress on the biota that occupy the water. The calculated ANC of the surface waters is a measure of the acid-base balance:

ANC = [BC]* - [AN]* (1)

where [BC]* and [AN]* are the sum of base cations and acid anions (NO_3- and SO_4^{2-}), respectively. Equation (1) forms the basis of the linkage between deposition and surface water acidic condition and the modeling approach used. Given some "target" ANC concentration [ANClimit]) that protects biological integrity, the amount of deposition of acid anions (AN) or depositional load of acidity CL(A) is simply the input flux of acid anions from atmospheric deposition that result in a surface water ANC concentration equal to the [ANClimit] when balanced by the sustainable flux of base cations input and the sinks of nitrogen and sulfur in the lake and watershed catchment.

Critical loads for nitrogen and sulfur (CL(N) + CL(S)) or critical load of acidity CL(A) were calculated for each waterbody from the principle that the acid load should not exceed the nonmarine, nonanthropogenic base cation input and sources and sinks in the catchment minus a neutralizing to protect selected biota from being damaged:

CL(N) + CL(S) or CL(A) = BC*dep + BCw – Bcu – AN - ANClimit (2)

Where,

BC*dep = (BC*=Ca*+Mg*+K*+Na*), nonanthropogenic deposition flux of base cations

BCw = the average weathering flux, producing base cations

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

AN = the net long-term average uptake, denitrification, and immobilization of nitrogen anions (e.g. NO^{3-}) and uptake of SO_4^{2-}

ANClimit = the lowest ANC-flux that protects the biological communities.

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

networks, that include Adirondack Longterm Monitoring (ALTM), Virginia Trout Stream Sensitivity Study (VTSSS), and the Shenandoah Watershed Study (SWAS), and Environmental Monitoring and Assessment Program (EMAP) (see Section 4.1.2.1 of Chapter 4).

The preacidification nonmarine flux of base cations for each lake or stream, BC*0, is

$$BC^*0 = BC^*dep + BCw - Bcu \quad (3)$$

Thus, critical load for acidity can be rewritten as

$$CL(N) + CL(S) = BC^*0 - AN - ANClimit = Q.([BC^*]0 - [AN] - [ANC]limit), \quad (4)$$

where the second identity expresses the critical load for acidity in terms of catchment runoff (Q) m/yr and concentration ([x] = X/Q). The sink of nitrogen in the watershed is equal to the uptake (Nupt), immobilization (Nimm), and denitrification (Nden) of nitrogen in the catchment. Thus, critical load for acidity can be rewritten as

$$CL(N) + CL(S) = \{fNupt + (1 - r)(Nimm + Nden)\} + ([BC]0^* - [ANClimit])Q \quad (5)$$

where f and r are dimensionless parameters that define the fraction of forest cover in the catchment and the lake/catchment ratio. The in-lake retention of nitrogen and sulfur was assumed to be negligible. Equation 5 described the FAB model that was applied when sufficient data was available to estimate the uptake, immobilization, and denitrification of nitrogen and the neutralization of acid anions (e.g. NO3-) in the catchment. In the case were data was not available, the contribution of nitrogen anions to acidification was assumed to be equal to the nitrogen leaching rate (Nleach) into the surface water. The flux of acid anions in the surface water is assumed to represent the amount of nitrogen that is not retained by the catchment, which is determined from the sum of measured concentration of NO3- and ammonia in the stream chemistry. This case describes the SSWC model and the critical load for acidity is

$$CL(A) = Q.([BC^*]0 - [ANC]limit) \quad (6)$$

where the contribution of acid anions is considered as part of the exceedances calculation (see Section 1.2.5, below). For the assessment of current condition in both case study

areas, the critical load calculation described in Equation 6 was used for most lakes and streams. The lack of sufficient data for quantifying nitrogen denitrification and immobilization prohibited the wide use of the FAB model. In addition, given the uncertainty in quantifying nitrogen denitrification and immobilization, the flux of nitrogen anions in the surface water was assumed to more accurately reflect the contribution of NO3- to acidification. Several major assumptions are made: (1) steady-state conditions exist, (2) the effect of nutrient cycling between plants and soil is negligible, (3) there are no significant nitrogen inputs from sources other than atmospheric deposition, (4) ammonium leaching is negligible because any inputs are either taken up by biota or adsorbed onto soils or nitrate compounds, and (5) longterm sinks of sulfate in the catchment soils are negligible.

A.1.2.1 Preindustrial Base Cation Concentration

Present-day surface water concentrations of base cations are elevated above their steadystate preindustrial concentrations because of base cation leaching through ion exchange in the soil due to anthropogenic inputs of SO_4^{2-} to the watershed. For this reason, present-day surface water base cation concentrations are higher than natural or preindustrial levels, which, if not corrected for, would result in critical load values not in steady-state condition. To estimate the preacidification flux of base cations, the present flux of base cations was estimated,

BC*t, given by BC*t = BC*dep + BCw – Bcu +BCexc, (7)

Where BCexc = the release of base cations due to ion-exchange processes. Assuming that deposition, weathering rate, and net uptake have not changed over time, BCexc can be obtained by subtracting Equation 5 from Equation 7:

BCexc = BC*t – BC*0 (8)

This present-day excess production of base cations in the catchment was related to the long-term changes in inputs of nonmarine acid anions (ΔSO*2 + ΔNO3) by the F-factor (see below):

$$BCexc = F (\Delta SO^*2 + \Delta NO3) \quad (9)$$

For the preacidification base cation flux, solving Equation 5 for BC*0 and then substituting Equation 8 for BCexc and explicitly describing the long-term changes in nonmarine acid ion inputs:

$$BC^*0 = BC^*t – F (SO^*4,t - SO^*4,0 + NO^*3,t - NO^*3,0) \quad (10)$$

The preacidification NO3- concentration, NO*3,0, was assumed to be zero.

A.1.2.2 F-factor

An F-factor was used to correct the concentrations and estimate preindustrial base concentrations for lakes in the Adirondack Case Study Area. In the case of streams in the Shenandoah Case Study Area, the preindustrial base concentrations were derived from the MAGIC model as the base cation supply in 1860 (hindcast) because the F-factor approach is untested in this region. An F-factor is a ratio of the change in nonmarine base cation concentration due to changes in strong acid anion concentrations (Henriksen, 1984; Brakke et al., 1990):

$$F =([BC^*]t - [BC^*]0)/([SO4^*]t - [SO4^*]0 + [NO3^*]t - [NO3^*]0), \quad (12)$$

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

$$F = \sin (\pi/2\ Q[BC^*]t/[S]) \quad (13)$$

where

Q = the annual runoff (m/yr). [S] = the base cation concentration at which F=1; and for [BC*]t>[S] F is set to 1. For Norway [S] has been set to 400 milliequivalents per cubic meter (meq/m3)(circa.8 mg Ca/L) (Brakke et al., 1990). The preacidification SO42- concentration in lakes, [SO4*]0, is assumed to consist of a constant atmospheric contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al., 1989). The preacidification SO42- concentration in lakes, [SO4*]0 was estimated from the relationship between [SO42-]o* and [BC]t* based on work completed by Henriksen et al., 2002 as described by the following equation:

[SO42-]o* = 15 + 0.16 * [BC]t* (14)

Table A-2 Illustrates SSWC Approach – Environmental Variables $CL(A) = BC^*_{dep} + BC_w - Bc_u - ANC_{limit}$ $CL(A) = Q\cdot([BC^*]_0 - [ANC]_{limit})$			
	Variable Code	**Description**	**Source**
1	BC^*_{dep}	Sum (Ca*+Mg*+K*+Na*), nonanthropogenic deposition flux of base cations	Wet NADP and Dry CASTNET
2	BC_w	Average weathering flux of base cations	Calculated (5-17)
3	Bc_u	Sum (Ca+Mg+K), the net long-term average uptake flux of base cations in the biomass	USFS-FIA data
4	ANC_{limit}	Lowest ANC-flux that protects the biological communities	Set
5	Ca^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Ca – (CL × 0.0213))	Water quality data
6	Mg^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Mg – (CL × 0.0669))	Water quality data
7	Na^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Na – (CL × 0.557))	Water quality data
8	K^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (K – (CL × 0.0.0206))	Water quality data
9	SO_4^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (SO_4 – (CL × 0.14))	Water quality data
10	CL	Surface water concentration (μeq/L) growing season average.	Water quality data
11	SO_4^*	Surface water concentration (μeq/L) growing season average.	Water quality data
12	NO_3^*	Surface water concentration (μeq/L) growing season average.	Water quality data
13	Q	The annual runoff (m/yr)	USGS
14	$[BC^*]_0$	Preindustrial flux of base cations in surface water, corrected for sea salts	Calculated from water quality data
15	$[SO_4^*]_0$	Preindustrial flux of sulfate in surface water, corrected for sea salts	Estimated
16	$[NO_3^*]_0$	Preindustrial flux of nitrate, corrected for sea salts	Equal to 0
17	F	Calculated factor	Fix values

Table A-2 FAB Approach – Environmental Variables $DL(N) + DL(S) = \{fN_{upt} + (1 - r)(N_{imm} + N_{den}) + (N_{ret} + S_{ret})\} + ([BC]_0^* - [ANC_{limit}])Q$			
	Variable Code	**Description**	**Source**
1	Ndepo	Total N deposition	NADP/CMAQ
2	ANClimit	Lowest ANC-flux that protects the biological communities	Set
3	$[BC^*]_0$	Preindustrial flux of base cations in surface water, corrected for sea salt	Calculated from water quality data
4	Ca^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Ca – (CL × 0.0213))	Water quality data
5	Mg^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Mg – (CL × 0.0669))	Water quality data
6	Na^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (Na – (CL × 0.557))	Water quality data
7	K^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (K – (CL × 0.0.0206))	Water quality data
8	SO_4^*	Sea Salt corrected Surface water concentration (μeq/L) growing season average. (SO_4 – (CL × 0.14))	Water quality data
9	CL	Surface water concentration (μeq/L) growing season average.	Water quality data
10	SO_4^*	Surface water concentration (μeq/L) growing season average.	Water quality data
11	NO_3^*	Surface water concentration (μeq/L) growing season average.	Water quality data
12	Q	The annual runoff (m/yr)	USGS
13	f	f is a dimensionless parameter that define the fraction of forest cover in the catchment	
14	r	r is a dimensionless parameter that define the lake/catchment ratio	
14	N_{ret}	The in-lake retention of nitrogen	Estimated
15	S_{ret}	The in-lake retention of sulfur	Estimated
16	N_{upt}	The net long-term average uptake flux of N in the biomass	USFS-FIA data
17	N_{imm}	Immobilization of N in the soils	Estimated fix value
18	N_{den}	Denitrification	Estimated fix value
19	Lake Size	Lake size (ha)	DLMs
20	WSH	Watershed area (ha)	Calculated

Data requirements for MAGIC

The MAGIC model (Cosby et al., 1985a; 1985b; 1985c) is a mathematical model (a lumped-parameter model) of soil and surface water acidification in response to atmospheric deposition based on process-level information about acidification. A process model, such as MAGIC, 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.

There are numerous input data required to run MAGIC making it rather data intensive. Atmospheric deposition fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. The volume discharge for the catchment must also be provided to the model. In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual simulations, i.e., mean annual deposition, precipitation and lake discharge are used to drive the model. Values for soil and surface water temperature, partial pressure of carbon dioxide and organic acid concentrations must also be provided at the appropriate temporal resolution.

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibrations are based on volume weighted mean annual or seasonal fluxes for a given period of observation. The length of the period of observation used for calibration is not arbitrary. Model output will be more reliable if the annual flux estimates used in calibration are

based on a number of years rather than just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an "outlier" year (very dry, etc.) is used to specify the primary data on which model forecasts are based. On the other hand, averaging over too long a period may remove important trends in the data that need to be simulated by the model.

The calibration procedure requires that stream water quality, soil chemical and physical characteristics, and atmospheric deposition data be available for each catchment. The water quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg, Na, and K) and acid anions (Cl, SO_4^{2-}, and NO_3^-) and the pH. The soil data used in the model include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be estimates of total deposition, not just wet deposition. In some instances, direct measurements of either atmospheric deposition or soil properties may not be available for a given site with stream water data. In these cases, the required data can often be estimated by: (a) assigning soil properties based on some landscape classification of the catchment; and (b) assigning deposition using model extrapolations from some national or regional atmospheric deposition monitoring network. Soil data for model calibration are usually derived as aerially averaged values of soil parameters within a catchment. If soils data for a given location are vertically stratified, the soils data for the individual soil horizons at that sampling site can be aggregated based on horizon, depth, and bulk density to obtain single vertically aggregated values for the site, or the stratified data can be used directly in the model.

A.1.3 Example of the two ways to calculate N_{ECO} from the first draft NOx and SOx secondary NAAQS Policy Assessment Document

The steady-state critical load model suggest for use in the NAAQS by the PA could be constrained by a quantity of N which would be taken up, immobilized or denitrified by ecosystems and used to adjust the quantity of deposition required to meet a specified critical load. This term is abbreviated by N_{eco}, and could be derived multiple

ways. The first is by taking the mean value calculated to represent the long-term amount of N an ecosystem can immobilize and denitrify before leaching (i.e. N saturation) that is derived from the FAB model. This approach requires the input of multiple ecosystem parameters. Its components are expressed by eq 1.

$$N_{eco} = fNupt + N_{ret} + (1-r)(N_{imm} + N_{den}) \quad (1)$$

Where,

N_{upt}= nitirogen uptake by the catchment

N_{imm}= nitrogen immobilization by the catchment soil

N_{den}=denitrification of nitrogen in the catchment,

N_{ret} = in-lake retention of nitrogen

f =forest cover in the catchment (dimensionless parameter)

r = fraction lake/catchment ratio (dimensionless parameter)

The second approach for estimating N_{eco} is to take the difference between N deposition and measured N leaching in a catchment as expressed by eq 2.

$$N_{eco} = DL(N) - N_{leach} \quad (2)$$

The site specific values of critical loads can be used to derive such a deposition loading, here called the deposition metric, which represents a group or percentage of water bodies that reach a specified ANC (or higher) in a given spatial area. For example, if it is desired that all water bodies reach a specified ANC, the allowable amount of deposition for all water bodies is equal to the lowest critical load the population of water bodies. Because the deposition metric represents a percentage of individual catchments from a population of water bodies, and not an individual catchment, the deposition metric is noted by the follow abbreviation $DL_{\%ECO}$.

As an example of the above approach, we evaluated the population of 169 waterbodies in the Adirondacks used in the REA analysis. For each individual waterbody in the population the critical load at ANC_{lim} = 50 μeq/L was calculated using the two equations for deriving the N_{ECO} term (eq 2 and 3). The distribution of deposition loads

for the population was assessed and Table **A.1.3**-1 shows example for the percentage of protection. The mean value for $DL_{\%ECO}$ for the 169 water bodies is presented, as well as the values for which 50, 75, 85, 95 and 100% of the water bodies in the population will not exceed their critical load at ANC = 50 μeq/L. Note, only 32% of water bodies would not exceed their critical load at ANC = 50 μeq/L for the mean value $DL_{\%ECO}$ because variability is high in the data set, therefore the mean can be problematic for areas with high variability.

Table **A.1.3**-1. Example calculations for determining the percent of water bodies achieving target ANC levels. This example is based the population of DL_{ANClim} for and ANC=50 for 169 catchments in the Adirondacks. These catchments occur across three categories of geologic sensitivity. We could separate the DL_{ANClim} values into sensitivity categories (if info is available) and do the analysis for each category or calculate one DL_{ANClim} for combined geologic categories. Units are in $meq/m^2/yr$.

	NHx dep	Neco (eq2)	$DL_{\%ECO}$ (S+N) +Neco (eq 2)	Neco (eq3)	$DL_{\%ECO}$ (S+N) +Neco (eq 3)	% of lakes within the population that have ANC ≥ 50μeq/L
Mean	20.40	19.19	162.36	63.95	207.55	31.7%
St dev	3.22	3.03	162.92	11.15	165.42	
St er	0.25	0.23	13.04	0.86	13.24	
Rank						
%tile						
50%			99.33		139.22	50%
75%			65.62		110.37	75%
85%			54.89		95.53	85%
95%			45.12		83.99	95%
100%			30.22		59.07	100%

The values for the maximum deposition N and S based on $DL_{\%ECO}$ at ANC=50 using the two approaches for N_{ECO} and protective of 95 and 50% of the population of water bodies, are given in Table **A.1.3**-2.

Table A-3 Values for N and S deposition tradeoff curves for ANC = 50, protecting 95 and 50% of the population, in Adirondacks case study area as illustrated on Fig 5.1 and Fig 5.2. Units are in meq/m2/yr unless noted otherwise.

% protection		NHxdep	Neco	$DL_{\%ECO}$ (max N)	$DL_{\%ECO}$ (max S)	$DL_{\%ECO}$ (max NOY)
95	Eq 2	20.4	19.19	45.12	25.93	141.96
50	Eq 2	20.4	19.19	99.33	80.14	78.9.3
95	Eq 3	20.4	63.75	83.99	20.04	63.59
50	Eq 3	20.4	63.75	139.22	75.27	118.82

A.1.4 Additional Analysis of Bedrock Geology as a basis for defining acid-sensitivity classes across the landscape

APPROACH

This analysis applied a methodology developed by Sullivan et al. (2007) for their exercise to test the hypotheses on watershed sensitivity to acidic deposition. Sullivan et al.'s exercise focused on streams in the Southern Appalachian Mountains region. The classification scheme was based on lithologic maps and the stream chemistry for more than 900 sites. Using logistic regression to model the presence of acid-sensitive waterbodies (expressed as ANC) with respect to lithology class, the authors found "four variables were highly significant in predicting the probability of occurrence of acid-sensitive sites (defined for this analysis as having ANC $\leq$ 20 μeq/L) in the Southern Appalachians using logistic regressions: % siliceous bedrock in watershed, % forested watershed, elevation, and watershed area". (Sullivan et al., 2007)

Using stream and lake ANC data from the Shenandoah Mountains and the Adirondack Mountains, along with lithologic classifications, linked forested area, elevation and watershed area, this NOx SOx exercise used logistic regression to determine if a correlation exists between lithology and ANC that is similar to the correlation found by Sullivan et al. in the Southern Appalachians. If similar to Sullivan et al.'s findings, then the findings of this NOx SOx exercise will be extrapolated spatially to identify areas of the U.S. potentially sensitive to aquatic acidification.

Phase I of this analysis applied the Sullivan et al. methodology separately to the two 2009 NOx-SOx Risk and Exposure Assessment (Shenandoah Mountains and the Adirondack Mountains Case Study Areas) and consists of 4 steps:

1. Site selection (i.e., lakes and streams)
2. Stream chemistry data acquisition and conversion to a spatial data layer
3. Data acquisition for % lithology classification of watershed (e.g., % siliceous bedrock), elevation, % forested area of watershed, and watershed area
4. Logistic regression modeling.

The modeling results are compared to Sullivan's SAMI analysis and, if consistent, will be extrapolated to the region surrounding the case study area (Phase II) and to other regions of the U.S. (Phase III) upon EPA directive.

The output desired for this Phase I exercise was a set of constants and coefficients that predict the probability that the acid-sensitive watersheds (having stream ANC either < 0 μeq/L or between 0 and 20 μeq/L) in the selected study areas based upon the input variables (percent lithology classification in watershed, elevation, watershed size, and percent forest cover in watershed).

PHASE I

Step 1 – Site Selection: Streams and lakes to be assessed

The Adirondack Case Study Area and the Shenandoah Case Study Area provide ideal areas to assess the risk to aquatic ecosystems from NOx and SOx acidifying deposition. Four main reasons support the selection of these two areas. First, both regions fall within the areas of the United States known to be sensitive to acidifying deposition because of a host of environmental factors that make these regions predisposed to acidification. Second, these areas are representative of other areas sensitive to acidification. Third, these regions have in the past and continue to experience substantial exposure to NOx and SOx air pollution. Fourth, these

areas have been extensively studied … over the last 3 decades (see Section 4 of the ISA Report (US EPA 2008). (US EPA, 2009, REA, Appendix 4, Section 3.1)

Freshwater surveys and monitoring in the eastern United States have been conducted by many programs since the mid-1980s, including the National Lake/Stream Surveys (NSWS), EPA's Environmental Monitoring and Assessment Program (EMAP), the Temporally Integrated Monitoring of Ecosystems (TIME) monitoring program (Stoddard, 1990), and Long-Term Monitoring (LTM) project (Ford et al., 1993; Stoddard et al, 1998). The purpose of these programs is to determine the current state and document the trends over time in surface water chemistry for regional populations of lakes or streams impacted by acidifying deposition. Based on extensive surveys and surface water data from these programs, it was determined that the most sensitive lakes and streams (i.e., ANC less than about 50 μeq/l) in the eastern US are found in New England, the Adirondack Mountains, the Appalachian Mountains (northern Appalachian Plateau and Ridge/Blue Ridge region), northern Florida, and the Upper Midwest. These areas are estimated to contain 95% of the lakes and 84% of the streams in the United States that have been anthropogenically acidified through deposition (see Annex 4.3.3.2 of the ISA, US EPA 2008). (US EPA, 2009, REA, Appendix 4, Section 3.1)

ANC in surface water from 50 lakes in the Adirondack Case Study Area were monitored through the Adirondack LTM program and 38 lakes from the TIME program **(Figure A.1.4-3).**

For the Adirondack Case Study Area, the regional EMAP probability survey of 117 lakes (i.e., weighting factors) were used to infer the number of lakes and percentage of lakes that receive acidifying deposition above their critical load of a target population of 1,842 lakes. The 117 lakes…represent a subset of 344 sampled lakes throughout New England from 1991 through 1994. (ME, NH, VT, RI, MA, CT, NY, NJ). (U.S. EPA, 2009, Appendix 4, Section 4.3.1.1)

Shenandoah Case Study Area ANC monitoring occurred as part of the Shenandoah National Park Surface Water Acidification Study (SWAS), Virginia Trout Stream Sensitivity Survey (VTSSS), and LTM programs. There are a significant number of the 67 streams in SWAS-VTSSS and LTM programs that currently have ANC of

about 50 µeq/L based on the observed annual average ANC concentrations **(Figure A.1.4-4)**.

The total number of brook trout streams represented by the SWAS-VTSSS LTM quarterly monitored sites is approximately 310 out of 440 mountain headwater streams known to support reproducing brook trout in the Shenandoah Case study Area. … The SWAS-VTSSS LTM programs began in Spring 1987, when water samples were collected form 440 streams known to have brook trout. Following the 1987 survey , a representative subset of 69 streams was selected for long-term quarterly monitoring of water quality, mostly located on National Forest lands or within the Shenandoah National Park Case Study Areas (14 SWAS and 55 VTSSS streams). (U.S. EPA, Appendix 4, Section 4.3.1.2).

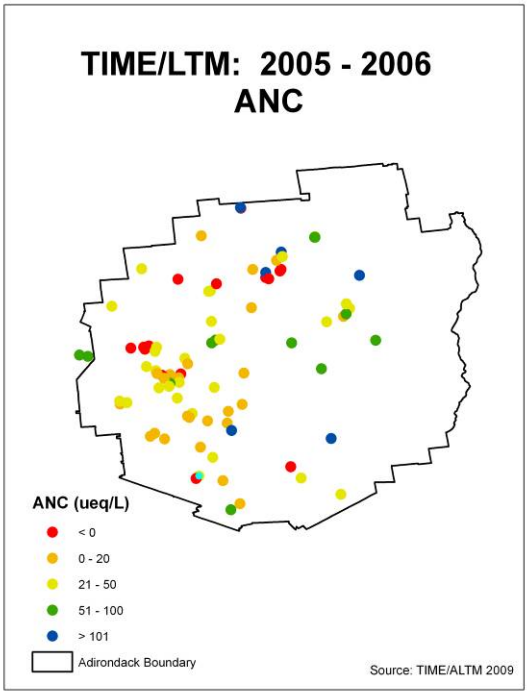


Figure A.1.4-**3.** Current yearly average for 2005 to 2006 ANC (µeq/L) in surface waters from 88 monitored lakes in the Temporally Integrated Monitoring of Ecosystems (38 Lakes) and Adirondacks Long-Term Monitoring (50 Lakes) networks in the Adirondack Case Study Area. (U.S. EPA, 2009)

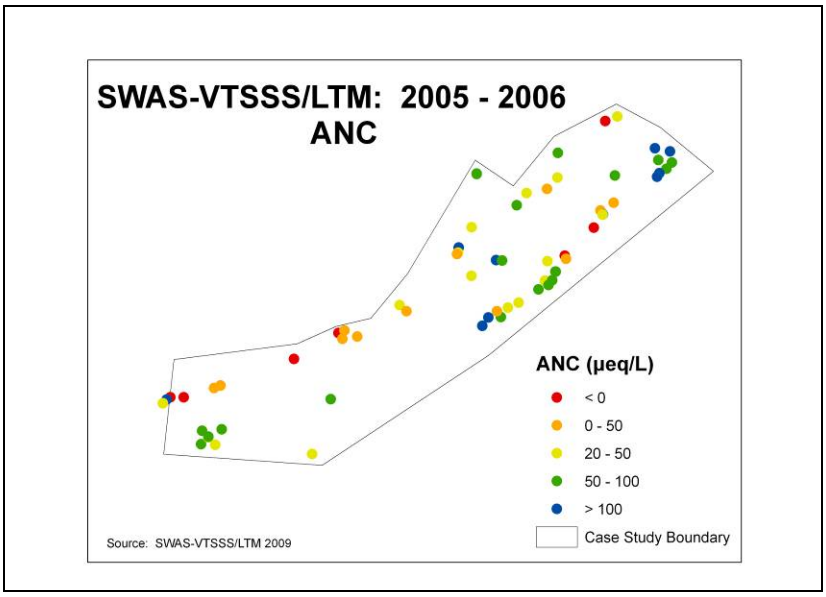


Figure A.1.4-**4.** Current yearly average for 2005 to 2006 ANC (µeq/L) in surface waters from 67 monitored streams in the Surface Water Acidification Study, Virginia Trout Stream Sensitivity, and Long-Term Monitoring network in the Shenandoah Case Study Area.

[In Phase I, efforts focused on the Shenandoah and Adirondack Mountains case study areas.]

Step 2: Stream Chemistry Data Acquisition - Water chemistry for those streams and lakes

There are numerous chemical constituents in surface water that can be use to indicate the acidification condition of lakes and streams and to assess the effects of acidifying deposition on ecosystem components. These include surface water pH and concentrations of SO_4^{2-}, NO_3^-, Al_3^+, and Ca_2^+; the sum of base cations; the recently developed base cation surplus; and the acid neutralizing capacity (ANC). Each of these chemical indicators provides direct links to the health of individual biota and the overall health and integrity of aquatic ecosystems as a result of surface water acidification.

Although ANC does not directly affect the health of biotic communities, it is calculated (or measured) based on the concentrations of chemical constituents that directly contribute to or ameliorate acidity-related stress, in particular, pH, Ca_2^+, and dissolved inorganic aluminum. Furthermore, numerical models of surface water acidification can more accurately estimate ANC than all of the individual constituents that comprise it. Consequently, for the purpose of the performing the case studies reported in the Risk and Exposure Assessment (US EPA, 2009),

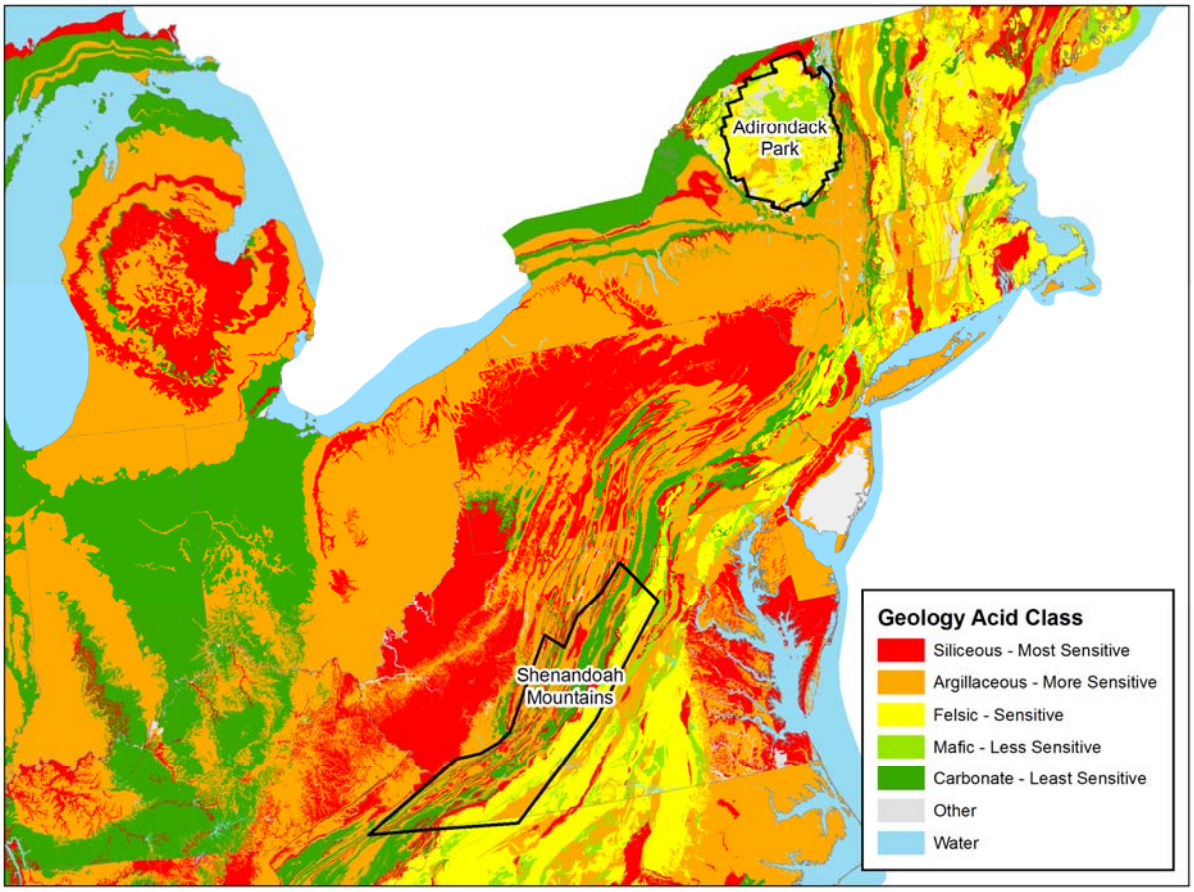
annual average ANC of surface waters was used as the primary metric to quantify the current acidic conditions and biological impacts for a subset of waterbodies in the study areas. (U.S. EPA, 2009 (REA, Appendix 4, Section 2.2)).

All lake and stream monitoring data within the Adirondack and Shenandoah study areas were used.. Although Sullivan et al. used only Spring data because those values represented the time of year when ANC is at its lowest, and is also a time when sensitive life stages (eggs and young) are present for many fish species (Kaufman, Herlihy, Mitch, Messer,& Overton, 1991) this study used data throughout the calendar year. This was done because of the considerable variation within and between the study areas in terms of the time of lowest seasonal ANC, and the life cycles of the dependent biota. ANC values were then averaged by sampling station. Those stations in the Adirondacks and Shenandoah regions that fell within a 12 digit HUC that crossed into either of the study area boundarieswere extracted to separate GIS data layers. These two collections of 12 digit HUCs were then used to extract and average the other data parameters.

Step 3: Data acquisition for percent lithology classification, elevation, percent forested area of watershed, and watershed size

Bedrock and surficial lithology **–** Information on lithology for the eastern United States was been acquired from the states' Geologic Surveys (USGS) and processed by EPA. This information was needed to determine if Sullivan et al.'s geologic classification system for the Southern Appalachian Mountains as applied to the eastern United States is a significant predictor of acid sensitivity in the Shenandoah Mountains and the Adirondack Mountains. Determining which acid class a given rock lithology falls into can be a somewhat subjective process. Upon initial inspection of the data, it appeared that there were some differences found between adjacent states **(Figure** A.-1**)**. Following discussion with EPA, it was determined that the Adirondack data would benefit from re-evaluation of the classifications assigned. The acid sensitivity classes were reviewed for consistency and correctness and found to be accurate in all but a handful of cases. These exceptions were modified to match their lithologic descriptions. The Shenandoah class assignments were deemed acceptable. The percent of each of the five classes of acid sensitivity (siliceous, argillaceous, felsic, mafic, and carbonate) were tabulated over each of the 12 digit HUCs that fell within the study areas.

Figure A.1 Distribution of geology acid classes in the eastern United States and the location of the ELSDS4 sample locations.



Elevation, feet (30m Digital Elevation Maps) The water quality sample locations for the Adirondack and Shenandoah Mountains were extracted to a single shapefile, which was then overlaid with a national 30 meter digital elevation model (DEM). The elevation was determined at each location and extracted as an attribute.

Watershed area, km^2 (HUC12) The HUC 12 identifier was extracted using GIS in a manner similar to the extraction of elevation information for each acid-sensitive sample location. The area (km^2) of the HUC 12 watershed was extracted to the water sampling location shapefile as an attribute.

Percent forested area by watershed has been estimated using 1992 US Forest Service vegetative databases and the Advanced Very High Resolution Radiometer (AVHRR) satellite

data (1,000 m cell size) to produce a raster forest type image with a 250 m cell size. This forest type image was processed using ArcGIS's Spatial Analyst by HUC 12 to determine the number of forested versus non-forested cells in each watershed. The results of this analysis were then used to calculate the percent of forested area in each watershed.

Step 4: Logistic Regression Modeling

Following Sullivan et al. (2007) a logistic regression approach with stepwise variable selection procedure was used to model binary variables derived from ANC. A significance level of α= 0.20 was used as the criterion for variable entry, and α= 0.25 was selected as the criterion for remaining in the model (Hosmer and Lemeshow (1989), p.108). The following continuous predictor variables were considered in this modeling exercise : Elevation (ft), Area (km^2), % Felsic, %_Carbonate, %Mafic, %_Siliceous, % Argillaceous, and %_FOREST. SAS PROC Logistic (SAS (version 9.2)) was used to determine the best model.

Three binary responses were considered in the logistic modeling:
1-. ANC<=20 then outcome=1; else outcome=0
2- ANC<=50 then outcome=1; else outcome=0
3- ANC<=100 then outcome=1; else outcome=0.

ADDITIONAL INFORMATION ABOUT THE METHODOLOGY

The model was run for all sites' elevations and then followed by subsequent model runs that eliminate sites below a selected elevation and above a selected elevation to discern any improvement in correlation sensitive to elevation. The lower and upper elevations were selected based on the distribution of locations provided in Step 1.

EXTRAPOLATION – PHASES II AND III

The overall goal of this exercise was to develop constants and coefficients that predict the acid-sensitivity of watersheds with a high degree of probability. A different set of coefficients were developed for each distinct geographic region for which there is

water quality monitoring data. In Phase II, the acid-sensitivity probability was calculated and mapped using GIS for all watersheds within each distinct geographic region of the case study areas, using the coefficients developed within the region.

In Phase III, the acid-sensitive probability for watersheds in other regions outside the sampled regions would be calculated and mapped using GIS by applying the set of coefficients from the sampled region which is most similar, and for which all 4 types of input data are available (i.e., percent lithology classification of watershed, percent forested watershed, elevation, and watershed area). Classified lithology data are currently only compiled for the eastern half of the United States, so extrapolation will only be possible for this portion of the country at this time.

RESULTS

GIS Mapping of Geologic Classifications and Measured ANC

Figures **A-2**andA-3 show the distribution of water sample locations in the Adirondack and Shenandoah Mountains, respectively. The average ANC values are symbolized using 20, 50, and 100 microequilavlents/litre as the break points. The five geology acid classes are also shown.

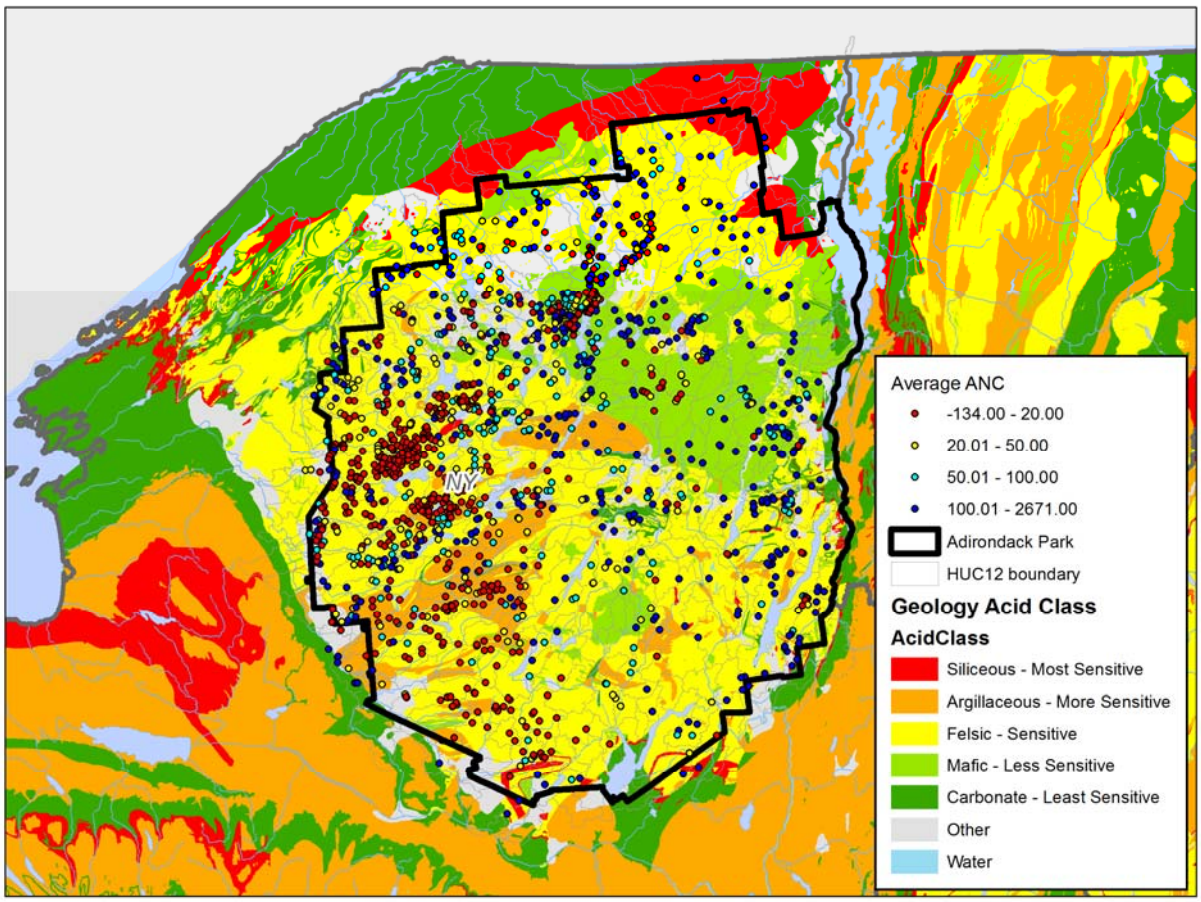


Figure A-2. Average ANC and Geology Classification: Adirondack Region

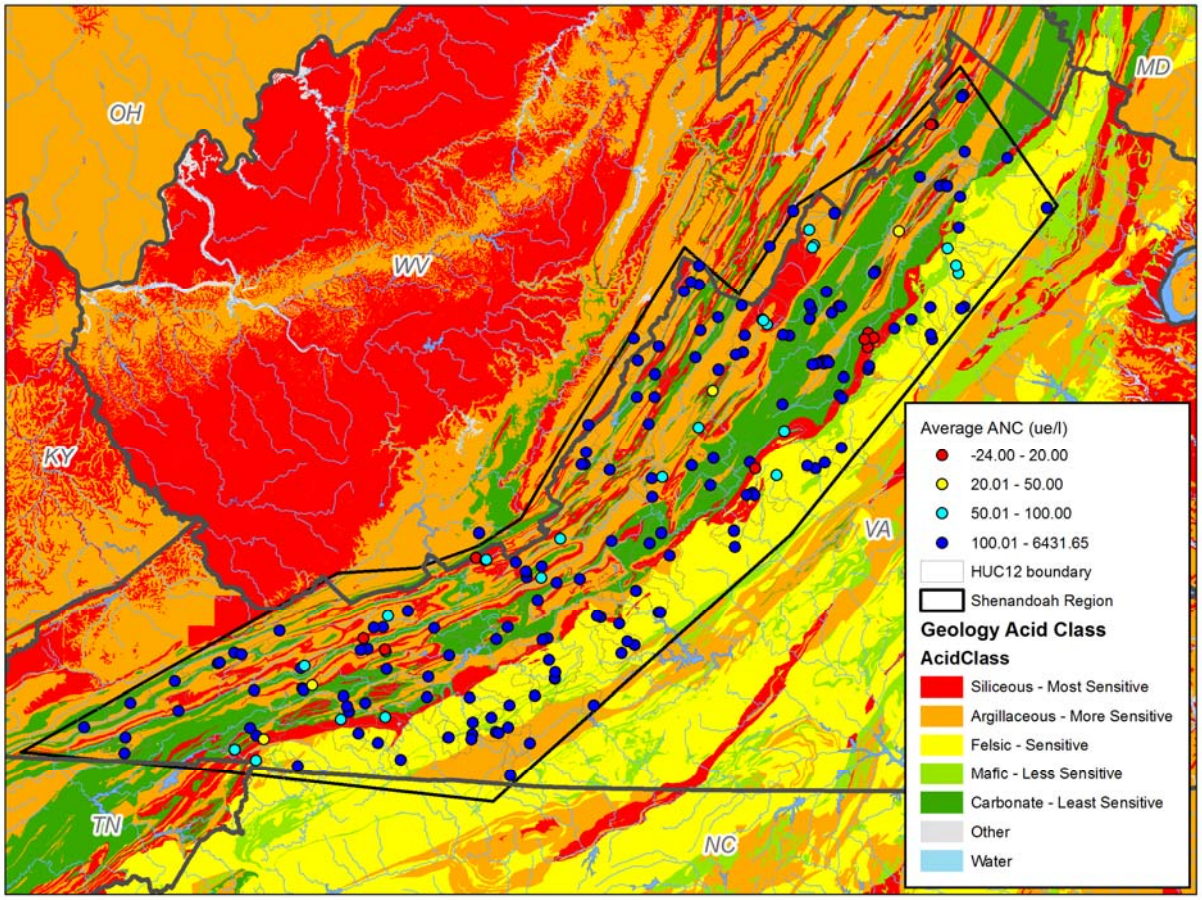


Figure A-3. Average ANC and Geology Classification: Shenandoah Region

Logistic Regression Analysis Results

Before running any modeling technique, the correlation between the predictors and ANC was explored (See Figure **A.-4**) A cell in the interception of a row and column represents the correlation between the variables at the end of the row and column. The correlation coefficient, R^2 , ranges from -70 to 30%, suggesting a low to moderate correlation between predictors and outcome. Negative correlations indicate that as the predictor value increases, the value of ANC decreases. Positive correlations suggest that as the value of the predictor increases so does the value of ANC. The correlation matrix also serves to explore the multi-co-linearity issue (presence of highly correlated predictors).

In the Adirondacks region, Elevation is the variable with higher correlation (-30% to -50%), suggesting that this variable will likely be included as a predictor in the model.

In the Shenandoah region, % Carbonate (R^2 between 40% and 70%) and % Forest (R^2 between -40% to -70%) show a modest to high correlation with ANC. (See Figure **A-5**.) Also, % Forest is moderately correlated with % Siliceous (R^2 between 40% to 70%) and

% Carbonate (R^2 between -40% to -70%), suggesting that it is likely that one of these three variables will be in the model. Similarly, % Felsic is moderately correlated with % Carbonate and % Argillaceous (R^2 between -40% to -70%) suggesting that if one of these variables is in the model, then the other two won't be in the model.

Figure A-.4. Correlation matrix for Adirondacks Region.

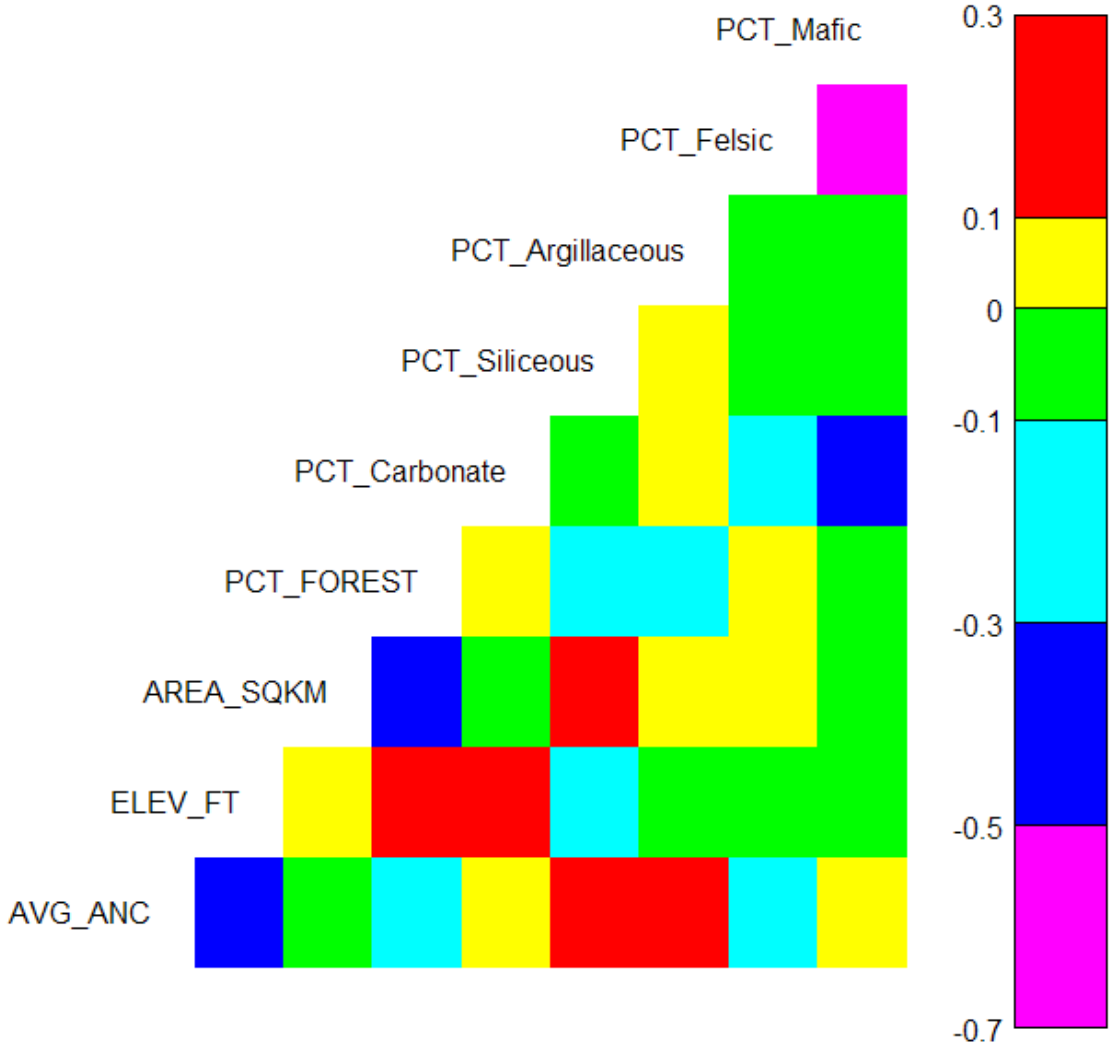
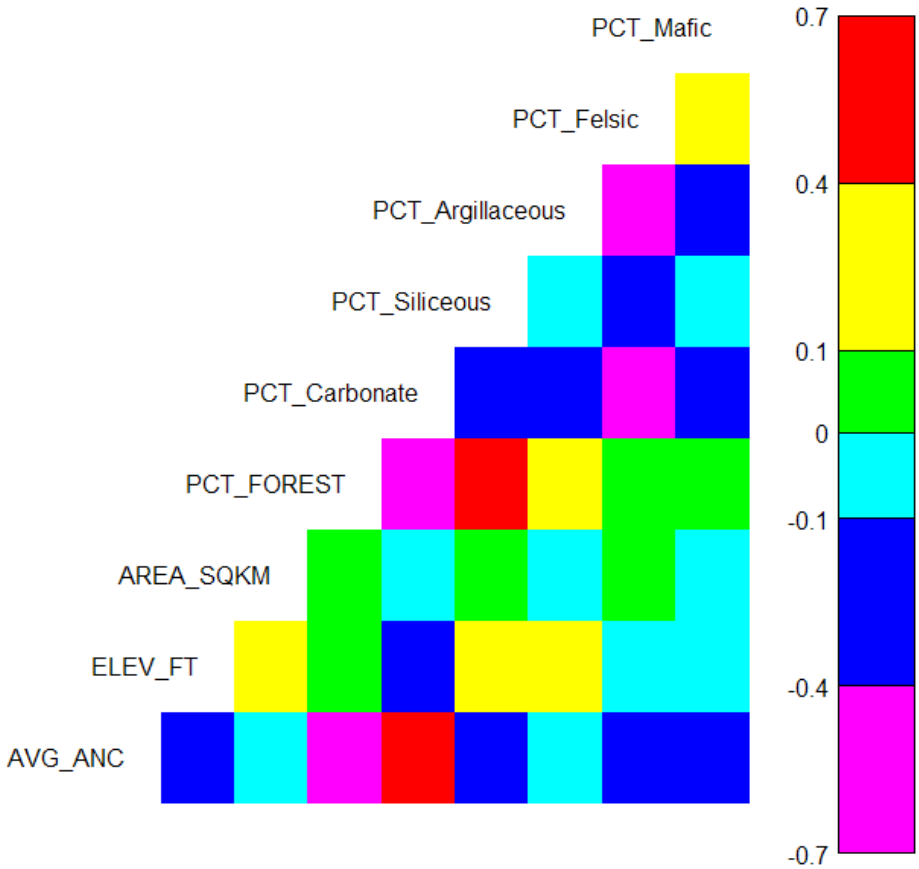


Figure A-5. Correlation matrix for Shenandoah Region.



Among the measurements of model assessment considered were C statistic (a C value of 0.5 means the model predictions are equivalent to a random guess; >0.7 denotes worthwhile to the model); the Akaike information Criteria (AIC) (Hosmer and Lemeshow (1989), p.184); and the Schwarz information criterion (SC) (Kass, R. E. & Wasserman, L. (1995)); and the -2*maximized log-likelihood (-2ML). Smaller values of all three statistics suggest a better model. To evaluate the goodness of fit of the model, the Hosmer and Lemeshow goodness of fit test (Hosmer and Lemeshow (1989)) was used (larger p-values suggest no difference between observed and model-predicted values, implying that the model's estimates fit the data at an acceptable level).

The final model for the Adirondacks Region binary variables is the following:

For the binary variable $Y_{20} = \begin{cases} 1 & ANC \le 20 \\ 0 & ANC > 20 \end{cases}$

the logistic model is the following:

$$\text{logit}(p) = -3.3933 + 0.00305 \times \text{Elevation} - 0.0142 \times (\%\text{Forest}) - 0.0216 \times (\%\text{Carbonate}) - 0.0366 \times (\%\text{Siliceous}) - 0.0172 \times (\%\text{Mafic})$$

For the binary variable $Y_{50} = \begin{cases} 1 & ANC \le 50 \\ 0 & ANC > 50 \end{cases}$

the logistic model is the following:

$$\text{logit}(p) = -4.2271 + 0.00306\text{Elevation} - 0.0197(\%\text{Carbonate}) - 0.0463(\%\text{Siliceous}) - 0.0155(\%\text{Mafic})$$

For the binary variable $Y_{100} = \begin{cases} 1 & ANC \le 100 \\ 0 & ANC > 100 \end{cases}$

the logistic model is the following:

The final model for the Shenandoah region binary variables is the following:

For the binary variable $Y_{20} = \begin{cases} 1 & ANC \le 20 \\ 0 & ANC > 20 \end{cases}$

the logistic model is the following:

$$\text{logit}(p) = -5.8725 + 0.0358(\%\text{Carbonate}) + 0.0632(\%\text{Siliceous})$$

For the binary variable $Y_{50} = \begin{cases} 1 & ANC \le 50 \\ 0 & ANC > 50 \end{cases}$

the logistic model is the following:

$$\text{logit}(p) = -6.0745 + 0.0233(\%\text{Carbonate}) + 0.0750(\%\text{Siliceous})$$

For the binary variable $Y_{100} = \begin{cases} 1 & ANC \le 100 \\ 0 & ANC > 100 \end{cases}$

the logistic model is the following:

$$\text{logit}(p) = -3.9068 + 0.000699(\%\text{Carbonate}) + 0.047(\%\text{Siliceous})$$

Betas, standard error for betas, odds ratio and relevant statistics can be found in Appendix 2.

Weibull modeling using Proc Reliability (SAS) was also used to model ANC. LCL and UCL denote the lower and upper confidence limits at 95% confidence level. If the value 0 is contained between the confidence limits then the parameter is not statistically significant at 5% level.

For the Adirondacks Region, the final predictors and estimates are shown below:

Parameter	Estimate	SE	95% LCL	95%UCL
Intercept	7.9493	0.3694	7.2254	8.6733
ELEV_FT	-0.0015	0.0001	-0.0016	-0.0013
PCT_FOREST	-0.0085	0.0039	-0.0162	-0.0008
PCT_Carbonate	0.0021	0.0012	-0.0003	0.0045
PCT_Argillaceous	0.0533	0.0208	0.0125	0.0941

According to this model, ANC decreases with each unit increase in Elevation and Forest (negative estimates) and increases with each unit increase in % Carbonate and % Argillaceous (positive estimates).

Model assessment statistics (R2, AIC, etc.) were not found in the documentation. It is possible to calculate them to evaluate the model fit to the data.

For the Shenandoah Region, the final predictors and estimates are shown below:

Intercept	7.3437	0.1585	7.0330	7.6543
ELEV_FT	-0.0015	0.0001	-0.0016	-0.0013
PCT_Siliceous	0.0167	0.0054	0.0061	0.0273
PCT_Argillaceous	0.0564	0.0209	0.0154	0.0973
PCT_Felsic	-0.0041	0.0011	-0.0062	-0.0020

According to this model, ANC decreases with each unit increase in Elevation and % Felsic (negative estimates) and increases with each unit increase in % Siliceous and % Argillaceous (positive estimates).

Appendix 2 shows the odds ratio for each predictor. The larger the Odds ratio, the higher the chances that ANC <=20 for every change in unit of the predictor.

For the Adirondacks region and ANC<=20

When elevation increases one unit, the odds that ANC<=20 increase by a factor of 1.03, when other variables are controlled (meaning the same level of % Fforest, % Carbonate, % Siliceous and % Mafic). When % Forest increases one unit, then the odds that ANC<=20 decreases by a factor of 0.972 when other predictors are held constant. Similar interpretations exist for the rest of the models.

For the Shenandoah region and ANC<=20:

When % Carbonate increases one unit, the odds that ANC<=20 increases by a factor of 1.036 when other predictors are held constant. Similarly,when % Siliceous increases one unit, the odds that ANC<=20 increases by a factor of 1.065 when other variables are held constant.

UNCERTAINTIES

Lithology classification assignments. RTI received a geodatabase of geology data from EPA to be used in the ANC GIS comparative analysis. The geodatabase includes a list of lithologies from the most recent USGS (Eastern Mineral Resources Team) national geologic map data for the continental United States. Each lithology polygon from the USGS map data set is defined by two lithology types labeled'ROCKTYPE1' and 'ROCKTYPE2'. According to the metadata for the geologic map cover, ROCKTYPE1 characterizes more than 50% of the area in the associated polygon. EPA has categorized each lithology record into one of five geologic sensitivity classes (i.e., Siliceous, Argillaceous, Felsic, Mafic, and Carbonate), after Sullivan, et al (2006). The geologic sensitivity classification is included for each lithology record of the geodatabase in a field indentified as 'AcidClassDesc'.

A cursory review was performed on EPA's assigned classifications suggesting--

- Not all rock types in the geodatabase are included in Sullivan (Table 1), but in most instances (except where noted) there was agreement between Sullivan's classification and the EPA assigned classes for rock types included in both the technical document and the geodatabase;

- Potential discrepancies in class assignments were identified such as those associated with non-descriptive lithogic description (e.g., sedimentary rock), others with typical rock chemistry and GSC (e.g., Carbonate GSC was assigned to beach sand), also classification assigned to sedimentary environments (e.g., olistostrome), or terms describing non-mineralogy specific rock texture (e.g., hornfel). The majority of these fell outside the Adirondack or Shenandoah study areas.

After discussion with EPA and a more detailed review, only a few revisions were required in the Adirondack datasets and those revisions were assigned less acid-sensitive classes. No revisions were required in the Shenandoah dataset.

A.1.5 Additional techniques explored for which to base subdivision of the U.S. based based on acid sensitivity.

Alkalinity

We also considered dividing the U.S. based on the Alkalinity from the 1984 Omernick Alkalinity map. We do not recommend using alkalinity because it includes more ecoregions as sensitive than the ANC approach, which causes the deposition loads for sensitive and less-sensitive areas to be more similar.

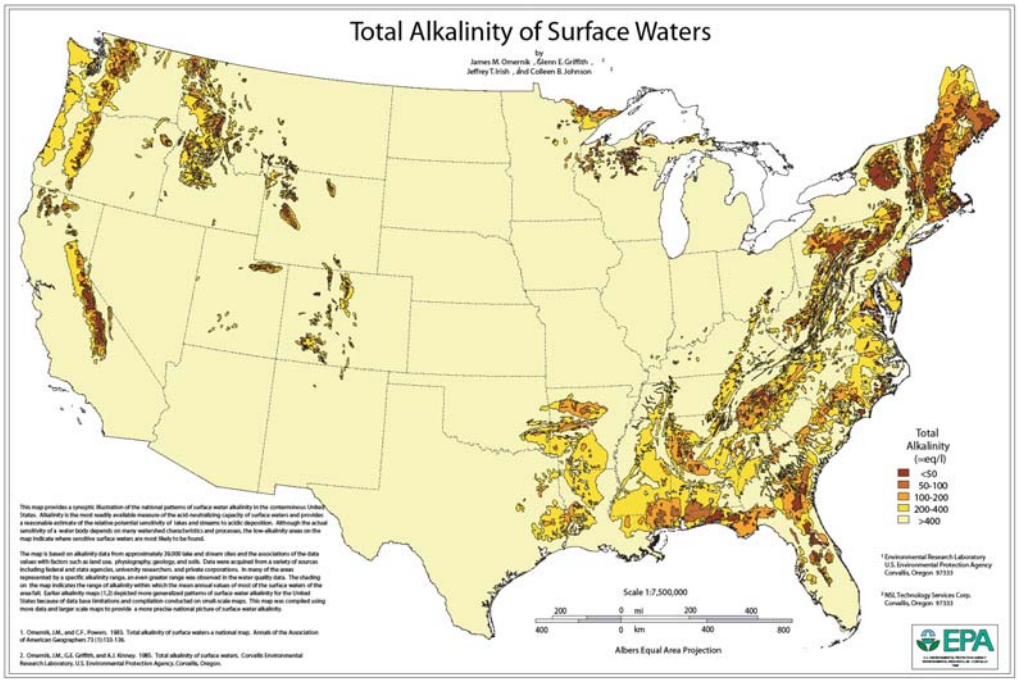


Fig A.1.5-1**. Omernick's alkalinity map (Omernick 1984)**

Table A.1.5-1. Descriptive statistics of the CL populations that result when the U.S. is divided into two categories, sensitive and non-sensitive based on Alk

Omernick sensitivity classification

CL for ANC =	Sensitivity class	CL in class n=	Mean Neco	Neco Ster	CL mean (meq/m2/yr)	CL Ster	Example deposition metrics		
							DL %90 (meq/m^2/yr)	DL %75 (meq/m^2/yr)	DL %50 (meq/m^2/yr)
50	sensitive	5446	48	0.4	274	5	28	57	123
50	Non-sensitive	346	37	1	343	15	50	109	265

Cluster Analysis

This approach uses ANC, ALK, DOC and soil BCw to categorize the acid-sensitivity of ecoregions based on a quantitative cluster analysis. The ANC dataset is described in Chapter 5, the ALK dataset is described in the previous section, and the DOC and soil BC weathering datasets are described prior to the explanation of the cluster analysis

DOC

Water chemistry data on DOC was collected from several national monitoring networks. The data sources are the same as those for ANC and summarized in Chapter 5and include approximately 11,000 observations.

Bed rock geology

Bedrock geology is the parent material to soils and can be related to acid-sensitivity. In the first draft PA the EPA staff proposed using bedrock geology to inform acid sensitivity categorization of the landscape. This approach entailed defining categories of ecosystem sensitivity to acidification based on bedrock geology/ lithology. The approach is supported by conclusions from the ISA in which geology is determined to be the governing factor that drives ecosystem sensitivity to acidification (**ISA 3.2.4.1**). A map was developed in this policy assessment to capture the heterogeneity of geologic bedrock that occurs across the eastern U.S. and link it to ecosystem acid-sensitivity (Fig A.1.5-2). The method is based on Sullivan et al. (2007) in which 70+ primary lithologies

are grouped into 5 categories of acid-sensitivity, using ANC as the ecosystem indicator upon which acid-sensitivity is based. Sullivan et al. (2007) evaluated multiple features of the landscape and found that geology is the landscape parameter that governs ecosystem sensitivity to acidic deposition. The analysis in Sullivan et al. 2007 was conducted in the Southern Appalachian Mountains region, which included sites from the states of GA, TN, NC, KT, VA and WV. EPA conducted additional analyses to further test the concept that lithology correlates to acid sensitivity based on ANC, using data from the Adirondacks and Shenandoahs. Results from this analysis indicated that North of the glaciation line, bedrock geology was not a good predictor of acid sensitivity. For example, the Adirondacks which are known to be one of the most sensitive areas to acidification is dominated by types of bedrock geology that are considered moderately to less sensitive in areas South of the glaciation line.

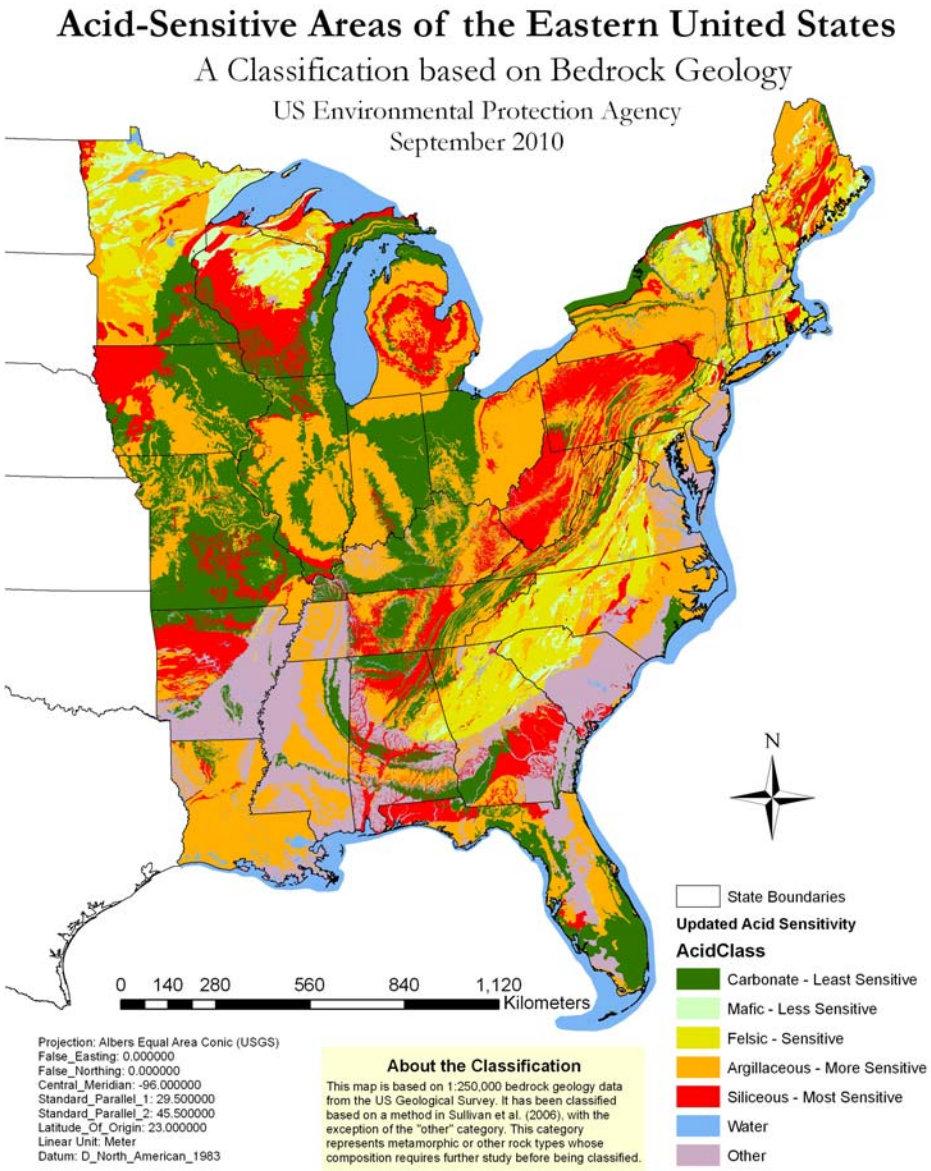


Fig A.1.5-2**. A map of acid sensitive areas of the Eastern U.S. developed from a lithology-based five-unit geologic classification system after methods in Sullivan et al. (2007).**

Soil base-cation weathering

As previously noted, the use of bedrock geology for the classification of acid sensitive catchments is problematic in areas north of the glaciation line because glacial activity has caused the surface till to become spatially disconnected from the parent geologic material. Surficial geology is therefore important to the evaluation of the spatial variability of acid-

sensitivity. For that reason a national map for soil base-cation weathering (McNulty et al. 2007) was considered in the analysis of acid-sensitivity (Fig A.1.5-3).

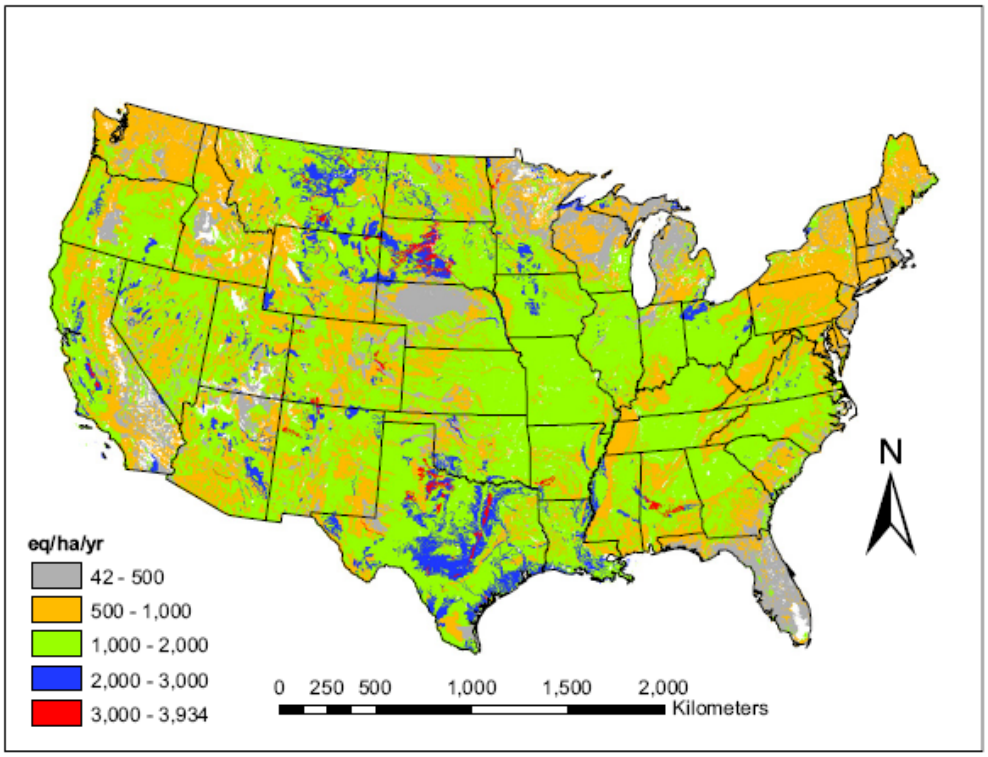


Fig A.1.5-3**.** A map of average annual forest soil base cation weathering expressed in eq ha^{-1} yr^{-1} for the conterminous US for the years 1994 to 2000 at a 1-km^2 spatial resolution from McNulty et al.

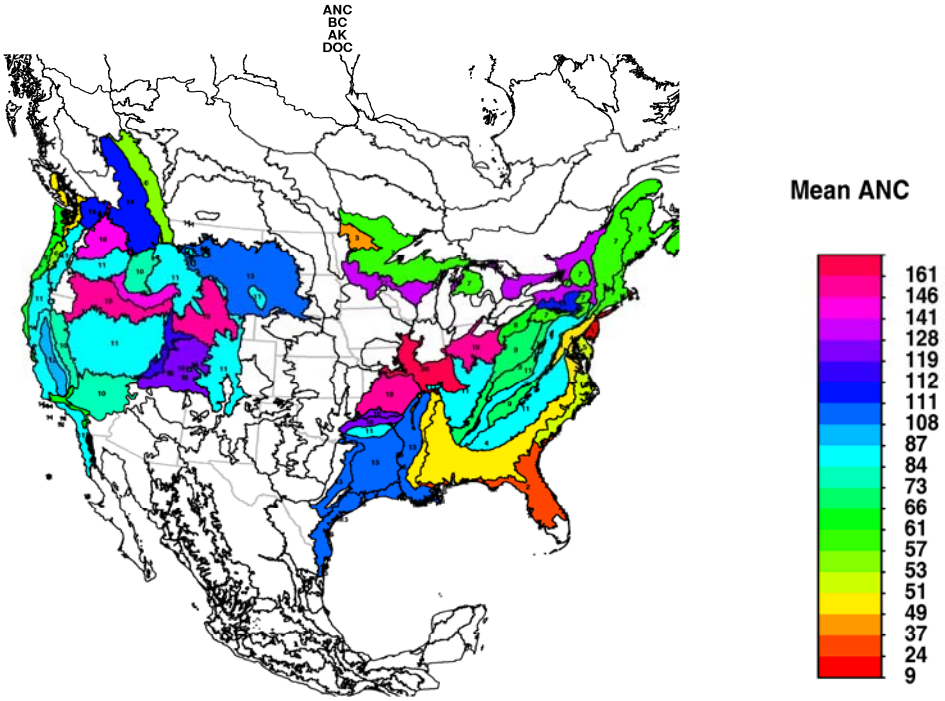
McNulty et al. 2007 estimated the base cation weathering rate using the clay correlation-substrate method (Sverdrup et al., 1990). This method used a combination of parent material and clay percent to determine the weathering rate. Base cation weathering rate (eq ha^{-1} yr^{-1}). A temperature correction can be applied to this method, but this correction is more suitable for northern climates and was not used in the model. Clay fraction was derived from a weighted average of soil fraction per map unit.

Table A.1.5-3. Data input to the U.S. national soil base cation weathering map developed by McNulty et al. 2007	
Data source	*Description of dataset*
State Soil Geographic Data Base (STATSGO)	Compilation by the Natural Resource Conservation Service (NRCS) of geology, topography, vegetation, climate, Landsat Thematic Mapper (TM) satellite imagery, and detailed, county level soil survey data. Each soil map unit in STATSGO includes multiple components and data layers (USDA NRCS, 1995). STATSGO is organized by state and consists of one geospatial vector representing the soil map units for that state and 15 tables describing characteristics of those map units. Multiple soil layers are associated with each map unit. Soil layer sampling depth is not consistent within a state or between states
CONUS-SOIL developed by the Earth System Science Center (ESSC) at Pennsylvania State University	This is a 1-km^2 multi-layer soil data set based on the STATSGO. ESSC converted the vector map unit layer in STATSGO to a 1-km^2 grid, remapped many of the original STATSGO attribute layers, and defined 11 standard soil layers (Miller and White, 1998). These data layers and tables linked the standardized data set to the original STATSGO data set distributed by ESSC as 1-km^2 soil map unit grids for the conterminous US. The CONUS-SOIL was much better suited for national-scale modeling than the original STATSGO attribute layers and was therefore used McNulty et al. 2007. Key soil data inputs included CONUS-SOIL map units and clay fraction (Miller and White, 1998).
forest soil percent organic matter (OM) layer	Was created by McNulty et al. 2007 by first averaging the maximum and minimum recorded values for OM were averaged for each layer in the STATSGO data set. Second, the average OM layers were remapped into the 11 standard CONUS-SOIL layers using a weighted average to redistribute the average OM STATSGO layers into the CONUS-SOIL layers. If a STATSGO layer was completely contained in a CONUS-SOIL layer, then the average OM was multiplied by the component percent to determine the average OM contribution to the standard layer. If the STATSGO layer overlapped more than one CONUS-SOIL layer, then the proportion of overlap was multiplied by the average OM and the component percent, where the component percent was the proportion of the soil map unit comprised of that soil component. Once the conversion from STATSGO to CONUS-SOIL layer was complete, the 11 standard layers were summed by layer and divided by the sum of component percent. Finally, the weighted average was calculated according to equation 8.
parent material class	was derived from the STATSGO map unit component (comp) and taxonomic (tax) classification tables (USDA NRCS, 1995). The dominant mineralogy for each soil map unit was determined from the comp and tax tables. Each unit was classified into parent material class based on the mineralogical description (USDA NRCS, 2006)
Soil depth	in meters was obtained from the CONUS-SOIL depth to bedrock layer. This layer identified map units with bedrock less than 1.52 m below the soil surface (i.e., map units coded with a depth of 1.52 m did not encounter bedrock) (Miller and White, 1998).

Results

This approach uses ANC, ALK, DOC and soil BCw to categorize the acid-sensitivity of ecoregions based on a quantitative cluster analysis. Cluster analysis is a method to sort a set of observations (in this case CL from watersheds) into subgroups so that the degree of association between observations is maximal if they belong to the same group and

minimal otherwise. The similarity of each site was determined using ANC, ALK, DOC and BCw. In the cluster analysis, the *k*-means algorithm assigned each point to the cluster whose center (also called centroid) is nearest. The center is the average of all the points in the cluster — that is, its coordinates are the arithmetic mean for each dimension separately over all the points in the cluster. The ecoregions was then assigned membership to a cluster. The weakness of this approach is that each of the datesets for the criteria (ANC, soilBCw, Alk and DOC), have varying levels of national coverage. If not all four criteria are available for the analysis the ecoregions drops out and is not assigned a cluster identification. The majority of ecoregions in the U.S. were not represented in the datasets for all four criteria and were not assigned a cluster identification (Fig A.1.5-4). Therefore the ulitility of this approach is limited.



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APPENDIX B

Analysis of Critical Loads, Comparing Aquatic and Terrestrial Acidification

Background

Critical load is defined as, "a quantitative estimate of ecosystem exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge" (McNulty et al., 2007), and critical loads can be estimated for aquatic and terrestrial ecosystems. Within the *Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Sulfur* (hereafter referred to as REA Report) (US EPA, 2009), critical loads of acidification for aquatic systems were determined by relating specific amounts of acidifying nitrogen and sulfur deposition to selected Acid Neutralizing Capacities (ANC) within freshwater lakes or streams. The presence and abundance of fish species served as the biological indicator of the impacts of the exceedance of critical acid loads by nitrogen and sulfur deposition. Estimation of critical acid loads for terrestrial systems within the REA Report (US EPA, 2009) related acidifying nitrogen and sulfur deposition to the base cation to aluminum (Bc/Al) ratio in the soil solution, and the health of sugar maple and red spruce in forest ecosystems served as the biological indicator of the impacts of critical acid load exceedance. A main distinction between these two critical loads is that aquatic critical loads are largely an integrated function of the chemistry of run-off waters that feed the lake or stream within a watershed, while terrestrial critical acid loads are determined by the rooting zone section of the soil profile in a forest ecosystem. Therefore, it is possible to have different critical load values for aquatic and terrestrial ecosystems within the same watershed.

The goal of this Task was to determine the relative degree of protection offered by aquatic versus terrestrial critical acid loads within a landscape. Critical acid loads for lakes and streams within watersheds of the Adirondacks and Shenandoah Valley were compared against terrestrial critical loads calculated for same watersheds to determine which estimate had the lowest, most protective critical load for acidifying nitrogen and sulfur deposition.

Methods

For the REA Report (US EPA, 2009), critical acid loads were determined for 169 lakes and 60 streams in the Adirondacks and Shenandoah Case Study Areas, respectively. These critical loads were calculated using four different ANCs, 0, 20, 50 and 100 µeq/L, that ranged in the level of protection offered to fish species abundance and diversity, and the resulting critical acid loads were classified into four "current condition of acidity and sensitivity to acidification" categories. "Highly Sensitive" water bodies had critical loads less than or equal to 50 $meq/m^2/yr$, "Moderately Sensitive" systems had critical loads ranging from 51 to 100 $meq/m^2/yr$, "Low Sensitivity" lakes and streams had critical loads that ranged from 101 to 200 $meq/m^2/yr$, and "Not Sensitive" systems had critical acid loads greater than 201 $meq/m^2/yr$.

For the purposes of this Task, aquatic critical acid loads corresponding to an ANC of 50 $meq/m^2/yr$ were selected, and the locations of the lakes and streams in the Adirondacks and Shenandoah Case Study Areas were mapped by HUC12 watersheds. Availability of data for terrestrial acidification estimates was determined for each HUC, and only HUCs that had sufficient data were mapped. Data from the U.S. Department of Agriculture- Natural Resources Conservation Service (USDA-NRCS) SSURGO soils database (USDA-NRCS, 2008) had the poorest coverage. This data restriction limited the number of water bodies that could be included in the analysis to 62 and 35 for the Adirondacks and Shenandoah Case Study Areas, respectively.

To examine a representative selection of water bodies in each Case Study Area, four watersheds containing lakes or streams from each of the four "current condition of acidity and sensitivity to acidification" categories were randomly selected. Therefore, a total of 16 watersheds were chosen for each Case Study Area. All four "current condition of acidity and sensitivity to acidification" categories were evenly represented for the Adirondacks Case Study Area (four watersheds for each of the four categories). However, due to the limited number of watersheds in the Shenandoah Area and a lower proportion of lakes with low sensitivities to acidifying nitrogen and sulfur deposition ("Low Sensitivity" and "Not Sensitive"), it was not possible to have equal representation of all "current condition of acidity and sensitivity to acidification" categories. Therefore, there was a larger representation of streams that were more sensitive to acidification ("Highly Sensitive" and "Moderately Sensitive"). All water bodies that

were located in each of the selected HUCs were included in the analyses. In many cases, these water bodies ranged in sensitivity to acidification. In total, 29 lakes and 20 streams were analyzed in the Adirondacks and Shenandoah Case Study Areas, respectively (**Table 1** and **2**).

Table 1. Watersheds (HUC 12) and fresh water lakes in the Adirondacks Case Study Area that were used in the comparison of aquatic and terrestrial critical acid loads. Lake IDs and associated aquatic critical acid loads (CL) in meq/m^2/yr, based on an ANC of 50 µeq/L, are indicated in each cell and are from the REA REPORT (US EPA, 2009).

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
020100010103				NY534L (CL = 1043)
020100040203			1A2-028O (CL = 106) NY310L (CL = 147)	NY308L (CL = 485)
020100080304				NY312L (CL = 588) NY313L (CL = 598)
020100081602				NY500L (CL = 610)
020200020101		NY013L (CL = 64)		
020200020704		NY536L (CL = 69)		
020200040805	1A2-078O (CL = 33)		NY292L (CL = 117)	
041501011001	NY029L (CL = 39)			
041503020801				NY783L (CL = 455)
041503040102	NY284L (CL = 23) NY285L (CL = 42)			
041503040204		NY278L (CL = 57)		
041503050103	1A1-089O (CL = 43)	050215AO (CL = 74) NY793L (CL = 97)		
041503050104	NY290L (CL = 30) NY289L (CL = 50)			

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
041503050302			NY008L (CL = 146) NY007L (CL = 165)	
041503050407		NY767L (CL = 51) NY529L (CL = 73) NY528L (CL = 82) NY769L (CL = 99)	NY768L (CL = 114)	
041503050601			NY004L (CL = 168)	

Table 2. Watersheds (HUC 12) and streams in the Shenandoah Case Study Area that were used in the comparison of aquatic and terrestrial critical acid loads. Stream IDs and associated aquatic critical acid loads (CL) in meq/m^2/yr, based on an ANC of 50 µeq/L, are indicated in each cell and are from the REA REPORT (US EPA, 2009).

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
020700050401	VT37 (CL = 26)			
020700050502	VT57 (CL = 39)			
020700050703	VT40 (CL = 13)			
020700050705	VT35 (CL = 37) VT36 (CL = 24)			
020700050801	DR01 (CL = 33) WOR1 (CL = 43)			
020700050803	VT53 (CL = 40)			
020700060101		VT54 (CL = 69)		
020801030301			VT60 (CL = 198)	VT61 (CL = 231)
020801030402		VT62 (CL = 68)		
020802010702	VT10 (CL = 15)			
020802010703	VT11 (CL = 14)	VT12 (C = 75)		
020802010801	VT14 (CL = 14) VT15 (CL = 13)			
020802010803	VT16 (CL = 20)			
020802020102		VT38 (CL = 66)		
020802020401	VT41 (CL = 15)			
020802030601		VT46 (CL = 52)		

Terrestrial critical acid loads were calculated for each of the 16 watersheds using the simple mass balance method (UNECE, 2004) and data sources outlined in the REA Report (US EPA, 2009), and Bc/Al soil solution indicator values of 1.2 and 10.0. Briefly, average values for base cation deposition (calcium, potassium, magnesium and sodium), chloride deposition, and annual runoff (m^3/ha/yr) were determined for each watershed (**Table 3**). The Kgibb constant (m^6eq^2) was determined by the average percent organic matter in the soil (**Table 4**), and N immobilization in the soil was set to the constant value of 42.86 eq/ha/yr (McNulty et al., 2007). It was assumed that active harvesting did not occur in each of the watersheds. Therefore base cation (calcium, magnesium and potassium) and nitrogen uptake were 0 eq/ha/yr (UNECE, 2004). Similarly, it was assumed that the majority of each watershed consisted of upland sites. Therefore, denitrification losses were assumed to be 0 eq/ha/yr (McNulty et al., 2007). Base cation weathering was estimated using the clay substrate model (equations 1-3) (McNulty et al., 2007).

$$\text{Acid Substrate: } BC_e = (56.7 \times \%\text{clay}) - \left(0.32 \times (\%\text{clay})^2\right) \quad (1)$$

$$\text{Intermediate Substrate: } BC_e = 500 + (53.6 \times \%\text{clay}) - \left(0.18 \times (\%\text{clay})^2\right) \quad (2)$$

$$\text{Basic Substrate: } BC_e = 500 + (59.2 \times \%\text{clay}) \quad (3)$$

where

BC_e = empirical soil base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$) weathering rate (eq/ha/yr)

% clay = the percentage of clay within the top 50cm of the soil.

The U.S. Department of Agriculture- Natural Resources Conservation Service (USDA-NRCS) SSURGO soils database (USDA-NRCS, 2008)) and state-level geology (U.S. Geological Survey (USGS) state-level integrated map database for the United States (USGS, 2009)) were used to determine parent material acidity classification. Parent material acidity was determined for each SSURGO polygon within each watershed using the criteria outlined in the REA Report (US EPA, 2009), and the contributions of base cations from the weathering of acid, intermediate and basic substrates (eq/ha/yr) were determined by a weighted average based on the proportion of area occupied by each parent material acidity class. Rooting depth was assumed to be 50 cm and masses of calcium, magnesium, potassium, sodium and nitrogen were converted to eq/ha/yr units

based on molar charge equivalents. Unless indicated otherwise, the units used in the calculation of critical acid loads were eq/ha/yr. The estimated terrestrial critical loads for the 16 watersheds in the Adirondacks and Shenandoah Case Study Areas are presented in **Table 5**.

Table 3. Name, type and source of data used in the simple mass balance estimates of terrestrial critical acid loads for the watersheds in the Adirondacks and Shenandoah Case Study Areas.

DATA	NAME	TYPE	SOURCE
Base cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) deposition— wet	CMAQ/ NADP	GIS datalayers	Provided by U.S. Environmental Protection Agency (EPA)/NADP, 2003a,c, d, e
Chloride (Cl^{-}) deposition— wet	NADP	GIS datalayer	NADP, 2003b
Runoff	Annual run-off (1: 7,500,000 scale)	GIS datalayer	Gebert et al., 1987
Soil horizon depth	SSURGO	GIS datalayer	USDA-NRCS, 2008
Percentage of clay by soil horizon	SSURGO	GIS datalayer	USDA-NRCS, 2008
Percentage of organic matter by soil horizon	SSURGO	GIS datalayer	USDA-NRCS, 2008
Soil parent material	SSURGO	GIS datalayer	USDA-NRCS, 2008
State-level bedrock geology	State Geological Map Compilation	GIS datalayer	USGS, 2009

Note: CMAQ = Community Multiscale Air Quality Model; NADP = National Atmospheric Deposition Program; GIS = Geographic Information System; SSURGO = Soil Survey Geographic Database

Table 4. Gibbsite equilibrium (K_{gibb}) constant determined by percentage of soil organic matter (modified from McNulty et al. 2007).

Soil Type Layer	Organic Matter %	K_{gibb} (m^6/eq^2)
Mineral soils: C layer	<5	950
Soils with low organic matter: B/C layers	5 to15	300
Soils with some organic material: A/E layers	15 to 70	100
Peaty and organic soils: organic layers	>70	9.5

Table 5. Terrestrial critical acid loads (in eq/ha/yr) for the watersheds in the Adirondacks and Shenandoah Case Study Areas.

Case Study Area	HUC12	Terrestrial Critical Acid Load (eq/ha/yr)	
		Bc/Al = 1.2	Bc/Al = 10.0
Adirondacks	020100010103	2045	1134
Adirondacks	020100040203	1316	712
Adirondacks	020100080304	1329	731
Adirondacks	020100081602	1670	922
Adirondacks	020200020101	1484	819
Adirondacks	020200020704	1707	935
Adirondacks	020200040805	1770	951
Adirondacks	041501011001	1770	955
Adirondacks	041503020801	1664	912
Adirondacks	041503040102	1627	880
Adirondacks	041503040204	1436	786
Adirondacks	041503050103	1774	957
Adirondacks	041503050104	1794	968
Adirondacks	041503050302	1754	947
Adirondacks	041503050407	1447	789
Adirondacks	041503050601	1203	656
Shenandoah	020700050401	1440	802
Shenandoah	020700050502	1560	871
Shenandoah	020700050703	1762	979
Shenandoah	020700050705	1852	1032
Shenandoah	020700050801	1799	1003
Shenandoah	020700050803	1975	1102
Shenandoah	020700060101	1638	914
Shenandoah	020801030301	1511	843
Shenandoah	020801030402	1393	776
Shenandoah	020802010702	1603	890
Shenandoah	020802010703	1642	912
Shenandoah	020802010801	1635	909
Shenandoah	020802010803	1573	876
Shenandoah	020802020102	1519	845
Shenandoah	020802020401	1264	703
Shenandoah	020802030601	1660	918

Maps were generated to compare the aquatic and terrestrial critical acid loads in each watershed to determine which estimate provided the greatest protection against acidifying nitrogen and sulfur deposition. In each watershed, the terrestrial critical load estimate was compared against each aquatic critical load, and the load with the lowest value was set to represent the most sensitive component in the watershed. All critical load estimates were converted to eq/ha/yr for the comparisons.

Results

Maps indicating and comparing the sensitivities of the terrestrial and aquatic critical loads to nitrogen and sulfur deposition in each watershed of the Adirondacks and Shenandoah Case Study Areas are presented in **Figures 1-4** and **Tables 6-9**.

In the Adirondacks Case Study Area, 7 of the 16 watersheds had terrestrial critical acid loads (based on a Bc/Al of 10.0) that were lower and therefore more sensitive to acidification than all the lakes in the watershed. However, when the terrestrial critical loads were calculated with a Bc/Al soil solution ratio of 1.2, only 5 of the 16 watersheds were protected by a terrestrial critical load that was lower than the aquatic critical loads of the lakes. Three watersheds in the Adriondacks Case Study Area had terrestrial critical loads (based on a Bc/Al of 10.0) that were lower and higher than the critical loads for the lakes in the watershed, and one watershed had a similar mixture of aquatic versus terrestrial acid load protections for terrestrial critical loads estimated with a Bc/Al of 1.2. In general, a main trend in the Adirondacks Case Study Area was that watersheds with “Highly Sensitive” and “Moderately Sensitive” lakes were more protected by aquatic than terrestrial critical acid loads, while the watersheds with “Low Sensitivity” and “Not Sensitive” lakes were more protected by terrestrial critical acid loads.

Similar trends were found in the Shenandoah Case Study Area. However, there was little distinction between terrestrial acid loads that were calculated with a Bc/Al of 10.0 versus 1.2. Terrestrial critical acid loads offered a higher level of protection than did the stream aquatic critical loads in only one watershed. The two lakes in this watershed had “Low Sensitivity” or were “Not Sensitive” to acidifying nitrogen and sulfur deposition. The 15 watersheds that had streams with aquatic critical loads lower and more protective than the terrestrial critical loads,

were all “Highly Sensitive” or “Moderately Sensitive” to acidifying nitrogen and sulfur deposition.

In summary, a comparison of the terrestrial and aquatic critical acid loads for watersheds in the Adirondacks and Shenandoah Case Study Areas indicated that, in general, the aquatic critical acid loads offered greater protection to the watersheds than did the terrestrial critical loads. In situations where the terrestrial loads were more protective, the lakes or streams in the watershed were rated as having “Low Sensitivity” or “Not Sensitive” to acidifying nitrogen and sulfur deposition. Conversely, when the water bodies were more sensitive to deposition (“Highly Sensitive” or “Moderately Sensitive”), the aquatic critical acid loads consistently provided a greater level of protection against acidifying nitrogen and sulfur deposition in the watershed.

Figure 1. Comparison of aquatic and terrestrial critical loads of acidification (in eq/ha/yr) in the 16 watersheds of the Adirondacks Case Study Area, based on an ANC of 50 eq/L for the aquatic loads and a Bc/Al of 10.0 for the terrestrial loads. Colored circles indicate the locations of the waters bodies within each watershed. Green circles indicate lakes with critical load values less than the terrestrial critical load for the same watershed. Red circles indicate a condition where the terrestrial critical load is lower than the lake critical load.

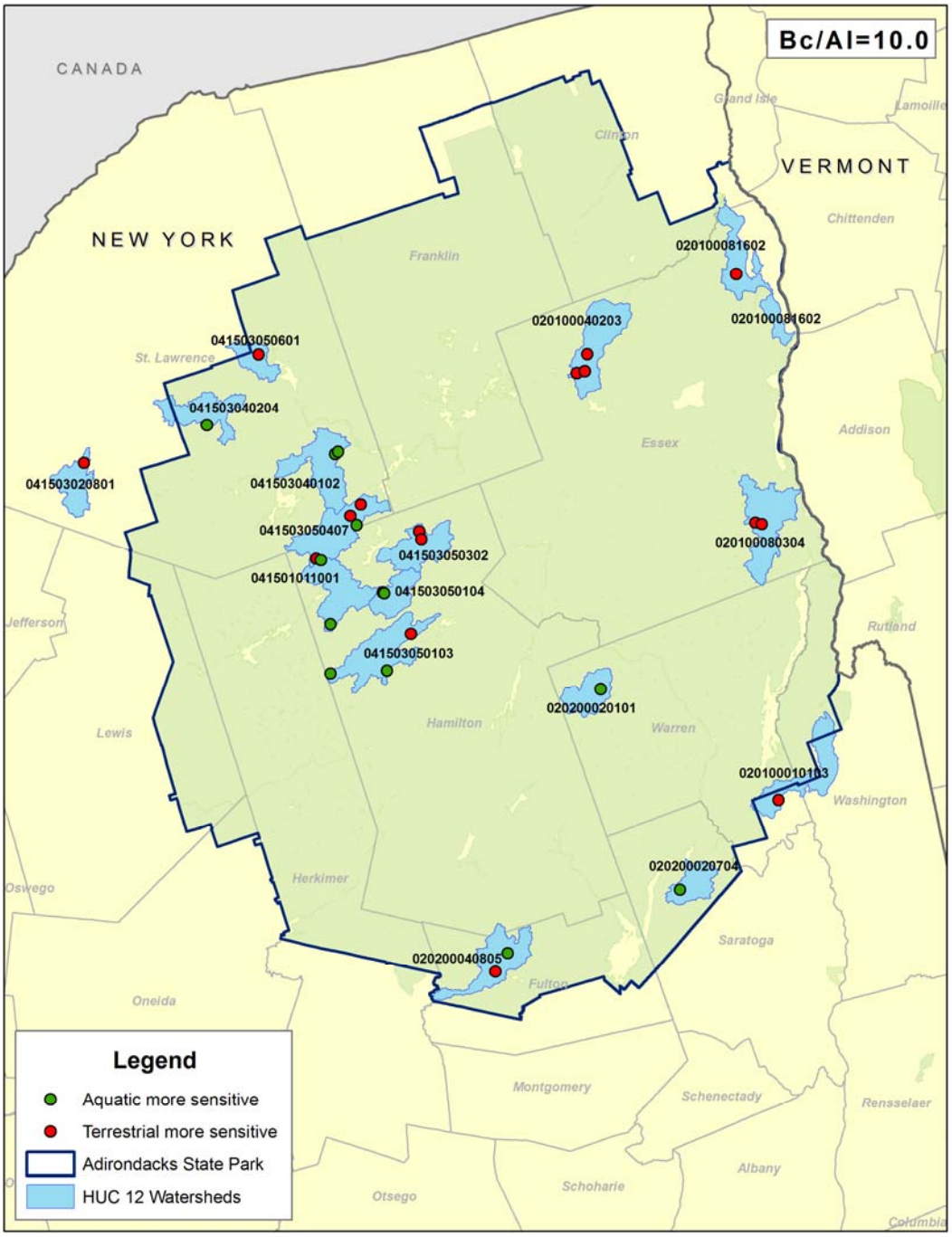

Figure 2. Comparison of aquatic and terrestrial critical loads of acidification (in eq/ha/yr) in the 16 watersheds of the Adirondacks Case Study Area, based on an ANC of 50 eq/L for the aquatic loads and a Bc/Al of 1.2 for the terrestrial loads. Colored circles indicate the locations of the waters bodies within each watershed. Green circles indicate lakes with critical load values less than the terrestrial critical load for the same watershed. Red circles indicate a condition where the terrestrial critical load is lower than the lake critical load.

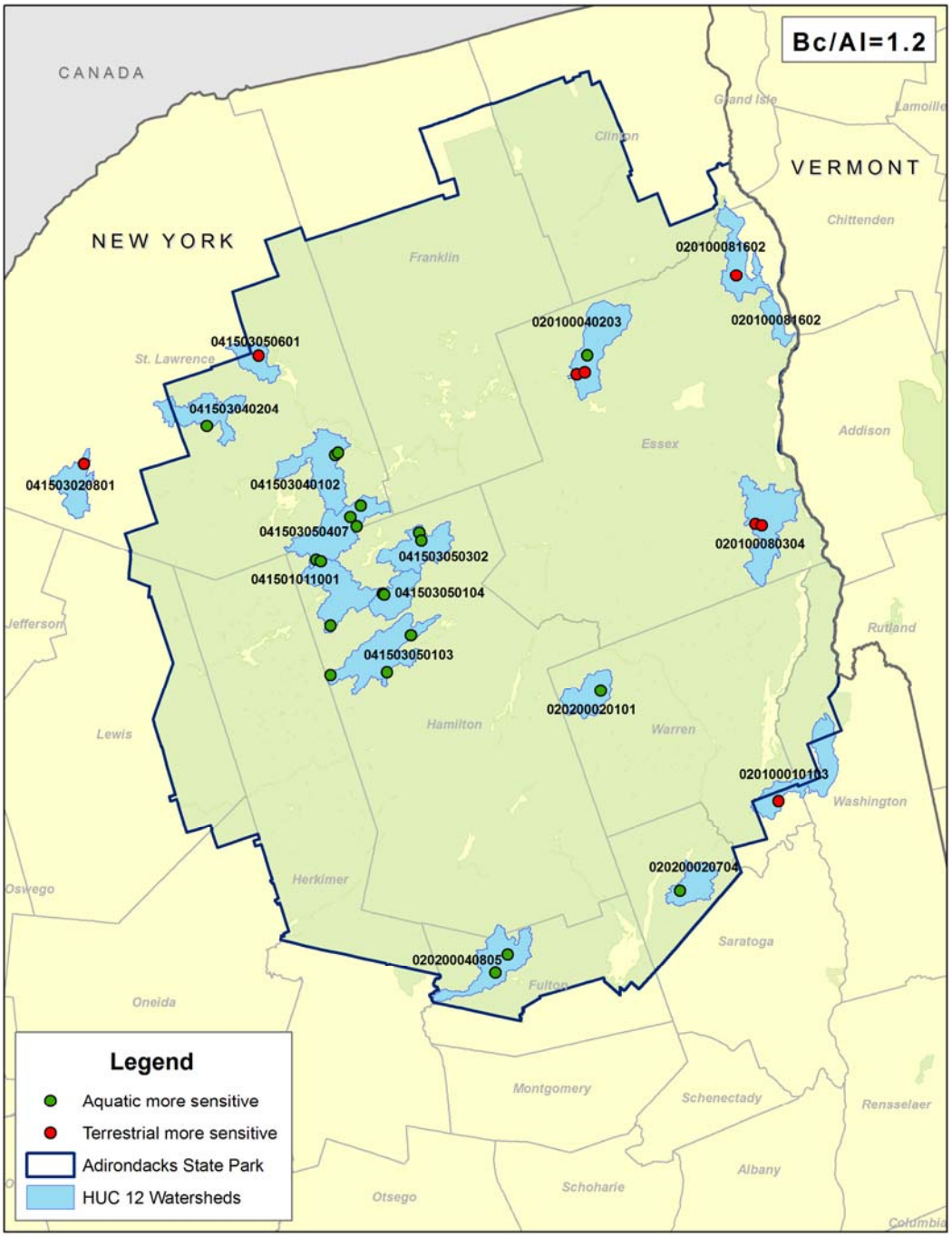

Figure 3. Comparison of aquatic and terrestrial critical loads of acidification (in eq/ha/yr) in the 16 watersheds of the Shenandoah Case Study Area, based on an ANC of 50 eq/L for the aquatic loads and a Bc/Al of 10.0 for the terrestrial loads. Colored circles indicate the locations of the waters bodies within each watershed. Green circles indicate streams with critical load values less than the terrestrial critical load for the same watershed. Red circles indicate a condition where the terrestrial critical load is lower than the stream critical load.

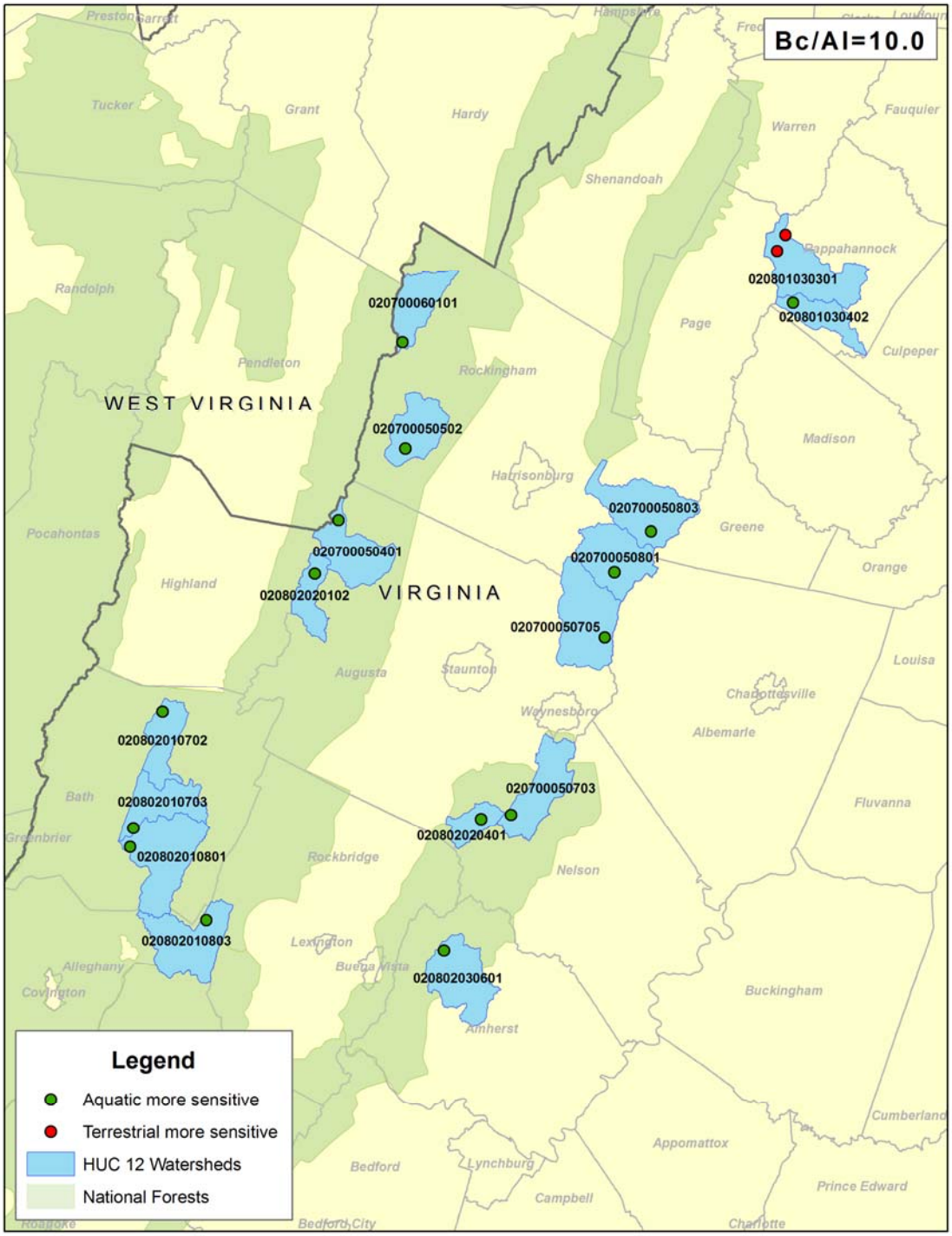

Figure 4. Comparison of aquatic and terrestrial critical loads of acidification (in eq/ha/yr) in the 16 watersheds of the Shenandoah Case Study Area, based on an ANC of 50 eq/L for the aquatic loads and a Bc/Al of 1.2 for the terrestrial loads. Colored circles indicate the locations of the waters bodies within each watershed. Green circles indicate streams with critical load values less than the terrestrial critical load for the same watershed. Red circles indicate a condition where the terrestrial critical load is lower than the stream critical load.

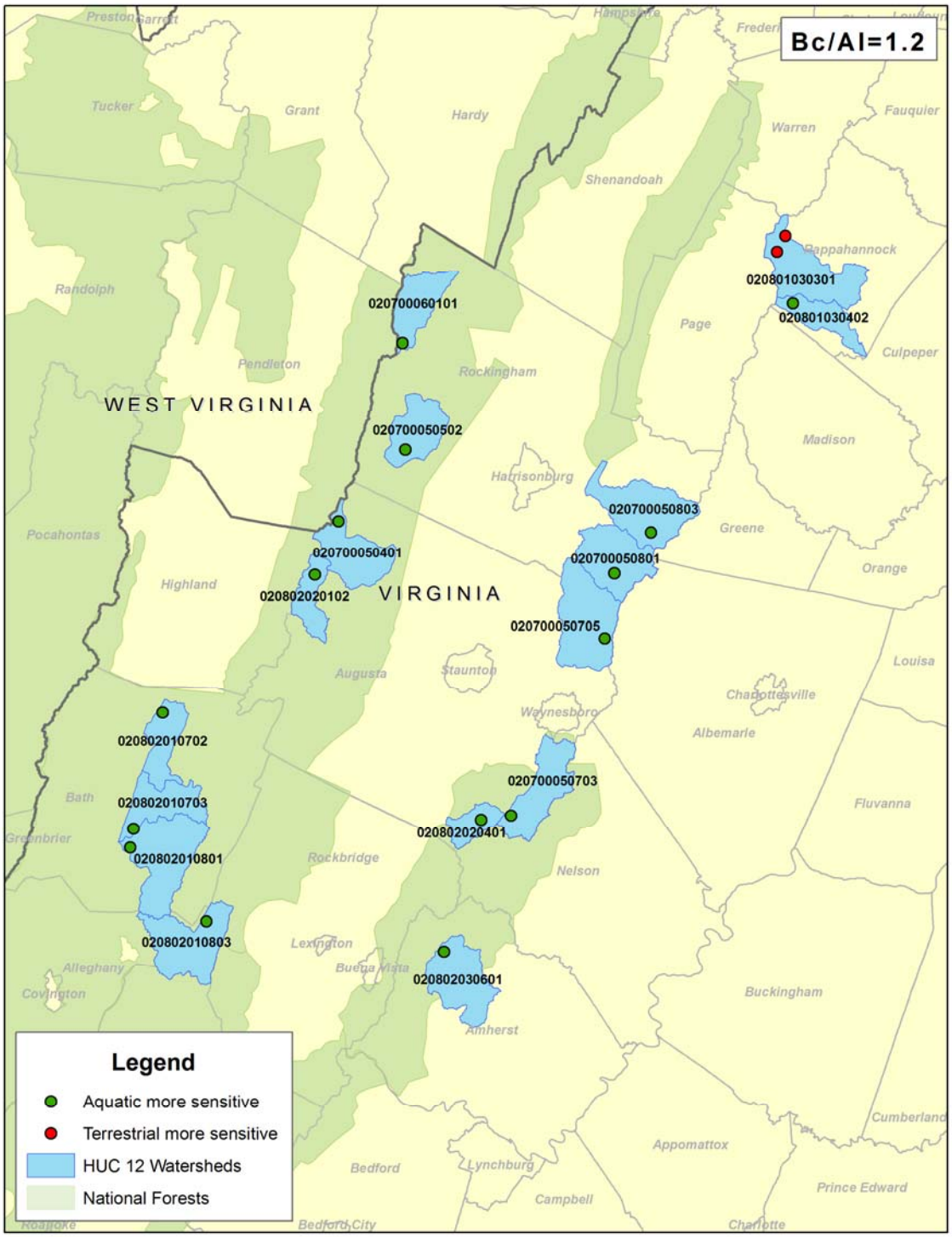

Table 6. Relative sensitivities of aquatic versus terrestrial critical loads in the 29 lakes and 16 watersheds of the Adirondack Case Study Area (based on an ANC of 50 µeq/L for the aquatic loads and a Bc/Al of 10.0 for the terrestrial critical loads and common unit of eq/ha/yr) to acidifying nitrogen and sulfur deposition. Lake IDs are indicated in each cell and are from the REA REPORT (US EPA, 2009). Green text indicates lakes where the aquatic critical load was less than the terrestrial critical load value for the watershed. Red text indicates a condition where the terrestrial critical load for the watershed was lower than the aquatic critical load for the lake within the same watershed.

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	Moderately Sensitive (CL = 51-100 meq/m^2/yr)	Low Sensitivity (CL = 101-200 meq/m^2/yr)	Not Sensitive (CL > 201 meq/m^2/yr)
020100010103				NY534L
020100040203			1A2-028O NY310L	NY308L
020100080304				NY312L NY313L
020100081602				NY500L
020200020101		NY013L		
020200020704		NY536L		
020200040805	1A2-078O		NY292L	
041501011001	NY029L			
041503020801				NY783L
041503040102	NY284L NY285L			
041503040204		NY278L		
041503050103	1A1-089O	050215AO NY793L		
041503050104	NY290L			

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
	NY289L			
041503050302			NY008L NY007L	
041503050407		NY767L NY529L NY528L NY769L	NY768L	
041503050601			NY004L	

Table 7. Relative sensitivities of aquatic versus terrestrial critical loads in the 29 lakes and 16 watersheds of the Adirondack Case Study Area (based on an ANC of 50 µeq/L for the aquatic loads and a Bc/Al of 1.2 for the terrestrial critical loads and common unit of eq/ha/yr) to acidifying nitrogen and sulfur deposition. Lake IDs are indicated in each cell and are from the REA REPORT (US EPA, 2009). Green text indicates lakes where the aquatic critical load was less than the terrestrial critical load value for the watershed. Red text indicates a condition where the terrestrial critical load for the watershed was lower than the aquatic critical load for the lake within the same watershed.

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
020100010103				NY534L
020100040203			1A2-028O NY310L	NY308L
020100080304				NY312L NY313L
020100081602				NY500L
020200020101		NY013L		
020200020704		NY536L		
020200040805	1A2-078O		NY292L	
041501011001	NY029L			
041503020801				NY783L
041503040102	NY284L NY285L			
041503040204		NY278L		
041503050103	1A1-089O	050215AO NY793L		

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	Moderately Sensitive (CL = 51-100 meq/m^2/yr)	Low Sensitivity (CL = 101-200 meq/m^2/yr)	Not Sensitive (CL > 201 meq/m^2/yr)
041503050104	NY290L NY289L			
041503050302			NY008L NY007L	
041503050407		NY767L NY529L NY528L NY769L	NY768L	
041503050601			NY004L	

Table 8. Relative sensitivities of aquatic versus terrestrial critical loads in the 20 streams and 16 watersheds of the Shenandoah Case Study Area (based on an ANC of 50 µeq/L for the aquatic loads and a Bc/Al of 10.0 for the terrestrial critical loads and common unit of eq/ha/yr) to acidifying nitrogen and sulfur deposition. Stream IDs are indicated in each cell and are from the REA REPORT (US EPA, 2009). Green text indicates streams where the aquatic critical load was less than the terrestrial critical load value for the watershed. Red text indicates a condition where the terrestrial critical load for the watershed was lower than the aquatic critical load for the stream within the same watershed.

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	Moderately Sensitive (CL = 51-100 meq/m^2/yr)	Low Sensitivity (CL = 101-200 meq/m^2/yr)	Not Sensitive (CL > 201 meq/m^2/yr)
020700050401	VT37			
020700050502	VT57			
020700050703	VT40			
020700050705	VT35 VT36			
020700050801	DR01 WOR1			
020700050803	VT53			
020700060101		VT54		
020801030301			VT60	VT61
020801030402		VT62		
020802010702	VT10			
020802010703	VT11	VT12		
020802010801	VT14 VT15			

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
020802010803	VT16			
020802020102		VT38		
020802020401	VT41			
020802030601		VT46		

Table 9. Relative sensitivities of aquatic versus terrestrial critical loads in the 20 streams and 16 watersheds of the Shenandoah Case Study Area (based on an ANC of 50 µeq/L for the aquatic loads and a Bc/Al of 1.2 for the terrestrial critical loads and common unit of eq/ha/yr) to acidifying nitrogen and sulfur deposition. Stream IDs are indicated in each cell and are from the REA REPORT (US EPA, 2009). Green text indicates streams where aquatic critical loads were less than the terrestrial critical load value for the watershed. Red text indicates a condition where the terrestrial critical load for the watershed was lower than the aquatic critical load for the stream within the same watershed.

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	Moderately Sensitive (CL = 51-100 meq/m^2/yr)	Low Sensitivity (CL = 101-200 meq/m^2/yr)	Not Sensitive (CL > 201 meq/m^2/yr)
020700050401	VT37			
020700050502	VT57			
020700050703	VT40			
020700050705	VT35 VT36			
020700050801	DR01 WOR1			
020700050803	VT53			
020700060101		VT54		
020801030301			VT60	VT61
020801030402		VT62		
020802010702	VT10			
020802010703	VT11	VT12		
020802010801	VT14 VT15			

HUC	CURRENT CONDITION OF ACIDITY AND SENSITIVITY TO ACIDIFICATION CATEGORY			
	Highly Sensitive (CL ≤ 50 meq/m^2/yr)	**Moderately Sensitive (CL = 51-100 meq/m^2/yr)**	**Low Sensitivity (CL = 101-200 meq/m^2/yr)**	**Not Sensitive (CL > 201 meq/m^2/yr)**
020802010803	VT16			
020802020102		VT38		
020802020401	VT41			
020802030601		VT46		

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APPENDIX C: Elasticity AAPI sensitivity analyses

Elasticity. One metric for determining sensitivity of the AAPI to its component parameters is elasticity. Elasticity measures the percent change in AAPI for a one percent change in the component. In general, the formula for an elasticity is:

$$E_{X_j}^{AAPI} = \frac{\partial AAPI}{\partial X_j} \cdot \frac{X_j}{AAPI}$$

Where $E_{X_j}^{AAPI}$ is the elasticity of AAPI with respect to component X_j, and j is the number of components.

So, for AAPI defined as

$$AAPI = \frac{1}{Q} N_{eco} + BC_0^* - \frac{1}{Q} NHx - \frac{1}{Q}\left[T_{NOy} \cdot NOy + T_{SOx} \cdot SOx\right]$$

The set of relevant elasticities are:

For runoff, Q:

$$E_Q^{AAPI} = -\frac{1}{Q^2}\left[N_{eco} - NHx - T_{NOy} NOy - T_{SOx} SOx\right] \times \frac{Q}{AAPI}$$, which can be rewritten as

$$E_Q^{AAPI} = -\frac{1}{Q}\left[AAPI - BC_0^*\right] \times \frac{Q}{AAPI}$$, or

$$E_Q^{AAPI} = -1 + \frac{BC_0^*}{AAPI}$$

For BC_0^*,

$$E_Q^{AAPI} = \frac{BC_0^*}{AAPI}$$

For Neco,

$$E_{N_{eco}}^{AAPI} = \frac{1}{Q} \cdot \frac{N_{eco}}{AAPI}$$

For NHx,

$$E_{NHx}^{AAPI} = -\frac{1}{Q} \cdot \frac{NHx}{AAPI}$$

For T_{NOy},

$$E_{T_{NOy}}^{AAPI} = -\frac{1}{Q} \cdot NOy \cdot \frac{T_{NOy}}{AAPI}$$

For T_{SOx},

$$E_{T_{SOx}}^{AAPI} = -\frac{1}{Q} \cdot SOx \cdot \frac{T_{SOx}}{AAPI}$$

For NOy,

$$E_{NOy}^{AAPI} = -\frac{1}{Q} \cdot T_{NOy} \cdot \frac{NOy}{AAPI}$$

For SOx,

$$E_{SOx}^{AAPI} = -\frac{1}{Q} \cdot T_{SOx} \cdot \frac{SOx}{AAPI}$$

These elasticities can be evaluated at various points along the ranges of each component, as well as along ranges of the AAPI. We evaluate the elasticities at the sample means, medians, first quartiles, and third quartiles. Elasticities are evaluated only for ecoregions that overlap the CMAQ modeling domain which provides values for reduced nitrogen and the transformation ratios (T_{NOx} and T_{SOx}). This will provide a reasonable assessment of the sensitivity of the AAPI to input components. Table 1 provides the estimated elasticities. Elasticities are summarized across ecoregions using means, medians, minimums, and maximums.

Note that elasticities can be either positive or negative. A negative elasticity means that the calculated AAPI will decrease as a component increases. The magnitude of the elasticity depends on the values of the components and the starting value of AAPI.

Based on the calculated elasticities, AAPI is most responsive to changes in Q, BC0, and Neco with some responsiveness to reduced N. Note that for some components, such as Q, the elasticities switch signs depending on the values of the variables for which the elasticity is evaluated. This suggests potentially important interactions. AAPI is not responsive to the transformation ratios, TNOx and TSOx at mean values of the AAPI components. However, when the elasticities for TNOx and TSOx are evaluated at the first quartiles of the data, some locations in the Eastern U.S. show higher responsiveness to changes in TNOx and TSOx, with elasticities as high as 2.

Table 1. Elasticity* of AAPI to Component Variables

AAPI Component	Metric for Which Elasticities are Evaluated	Mean Elasticity Across Ecoregions	Median Elasticity Across Ecoregions	Minimum Elasticity Across Ecoregions	Maximum Elasticity Across Ecoregions
Runoff (Q)	Mean	-0.1047	0.1221	-20.4572	1.6005
	Median	0.2561	0.1426	-6.2481	2.4578
	1st Quartile	-0.9283	0.1303	-135.2544	88.1063
	3rd Quartile	0.2988	0.1110	-0.1810	7.5684
Base Cation Weathering (BC0)	Mean	0.8953	1.1221	-19.4572	2.6005
	Median	1.2561	1.1426	-5.2481	3.4578
	1st Quartile	0.0717	1.1303	-134.2544	89.1063
	3rd Quartile	1.2988	1.1110	0.8190	8.5684
Neco	Mean	0.0179	0.1464	-13.8545	1.6051
	Median	0.3376	0.2563	-4.7203	2.5044
	1st Quartile	0.3543	0.2596	-115.1112	137.0526
	3rd Quartile	0.3016	0.1440	0.0137	6.5565
Reduced Nitrogen	Mean	-0.0409	-0.0702	-0.4708	3.9332
	Median	-0.1407	-0.1031	-0.7957	1.0061
	1st Quartile	-0.0308	-0.1190	-33.9063	35.3783
	3rd Quartile	-0.1128	-0.0615	-1.9167	-0.0050
NOx Transformation Ratio (T_{NOx})	Mean	0.0089	-0.0053	-0.0597	1.0598
	Median	-0.0061	-0.0064	-0.0506	0.2751
	1st Quartile	-0.0191	-0.0071	-2.7061	1.7749
	3rd Quartile	-0.0154	-0.0044	-0.5028	-0.0002

AAPI Component	Metric for Which Elasticities are Evaluated	Mean Elasticity Across Ecoregions	Median Elasticity Across Ecoregions	Minimum Elasticity Across Ecoregions	Maximum Elasticity Across Ecoregions
SOx Transformation Ratio (T_{SOx})	Mean	0.0019	-0.0024	-0.0185	0.3608
	Median	-0.0045	-0.0036	-0.0413	0.1091
	1st Quartile	0.0040	-0.0032	-1.8023	1.9860
	3rd Quartile	-0.0058	-0.0021	-0.1534	-0.0002

*Elasticity is the percent change in AAPI for a one percent change in the component variable. For example, when evaluated at the means of all component variables, the mean elasticity of AAPI to the runoff variable Q is -0.1047, which means that for each 1 percent increase in Q, the AAPI is reduced by 0.1047 percent.

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